

CATALYTIC OZONATION OF DYE SOLUTIONS IN A
SEMI-BATCH REACTOR

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ABSTRACT

CATALYTIC OZONATION OF DYE SOLUTIONS IN A SEMI-BATCH REACTOR

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Treatment of textile wastewaters containing dye materials using the conventional methods based on biological treatment is not possible. In order to overcome this problem, ozonation based on the oxidation of organic pollutants with ozone gas dissolved in aqueous phase have been studied widely. Catalytic ozonation and advanced oxidation processes (AOP) are also used in order to increase the efficiency of sole ozonation

In this work, catalytic ozonation processes in the presence of Copper Sulfide (CuS) powder and a synthesized catalyst by the impregnation of iron on alumina (Fe/Al₂O₃) were studied separately in the treatment of dye solutions, namely Remazol Brilliant Blue-R (RBBR) and Reactive Black-5 (RB-5). Besides catalytic ozonation runs, ozonation parameters and ozonation mechanism were also studied and a model was developed for the semi-batch ozonation.

Both catalysts increased the oxidation of side products measured by the decrease in the amount of total organic carbon (TOC) in the treated dye solutions. Dye removal

rates were also enhanced in the treatment of RB-5 dye solutions while no significant effect was observed on dye removal rates of RBBR solutions.

TOC removals above 90% were observed in the catalytic ozonation using CuS for both of the dye solutions at pH =10 having initial dye concentration of 100 mg/L. The most significant effect of the catalyst addition was observed at pH = 3 where the TOC removals of non-catalytic ozonation were the lowest. CuS addition increased percent TOC removal at the end of the reaction period of 80 min by 123% in the treatment of 100 mg/L RBBR solution, and by 65% in the treatment of 100 mg/L RB-5 solution at pH = 3. On the other hand, addition of Fe/Al₂O₃ catalyst increased TOC removal of 100 mg/L RB-5 solution by 52 % at pH = 3.

In addition, volumetric mass transfer coefficients (k_La) of ozone in the absence and in the presence of a chemical reaction between dye and ozone were estimated from modeling. A correlation for the enhancement factor of ozone absorbed into dye solutions in terms of initial dye concentration was obtained and reported.

Keywords: Ozonation, catalytic ozonation, iron, copper, copper sulfide, Remazol Brilliant Blue R (RBBR), Reactive Black -5 (RB-5), advanced oxidation processes (AOP)

ÖZ

BOYA ÇÖZELTİLERİNİN YARI-KESİKLİ BİR REAKTÖRDE KATALİTİK OZONLANMASI

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Boya maddeleri içeren tekstil atıksularının arıtımı biyolojik arıtmaya dayalı geleneksel yöntemlerle mümkün olmamaktadır. Bu problemin üstesinden gelebilmek için sudaki organik maddelerin suda çözünmüş ozon gazı ile yükseltgenmesine dayanan ozonlama ile arıtım metotları sıkça çalışılmıştır. Ozonlamanın yanısıra katalitik ozonlama ve ileri oksidasyon teknikleri (İOP) de ozonlamanın atıksuların muamele edilmesi üzerindeki etkisini arttırmak için kullanılmaktadır.

Bu çalışmada Bakır Sülfür (CuS) toz parçacıkları ve alumina parçacıklarının demir solusyonuyla ıslatılması (impregnation) suretiyle sentezlenmiş bir katalizör olan demir alumina (Fe/Al₂O₃) katalizörü, Reaktif Siyah-5 (RB-5) ve Remazol Parlak Mavisi-R (RBBR) boyalarının ayrı ayrı katalitik ozonlanmasında kullanılmıştır. Katalitik ozonlama deneyleri yanısıra, ozonlama parametreleri ve ozonlama mekanizması da çalışılmış, ayrıca yarı kesikli reaktörde ozonlama için bir model oluşturulmuştur.

Her iki katalizörün de toplam organik karbon (TOK) değerlerindeki düşüşün ölçülmesi ile gözlemlenen ozonlama yan-ürünlerinin yükseltgenmesinde artışa sebep

olduğu görülmüştür. Katalitik ozonlamanın RBBR çözeltilerinin boya giderim hızları üzerine önemli bir etkisi olmamasına karşın, RB-5 çözeltilerinin boya giderim hızlarında katalizör eklenmesi artışa sebep olmuştur.

Reaksiyon ortamında CuS kullanılmasıyla, 100 mg/L başlangıç boya konsantrasyonuna sahip pH = 10'daki boya çözeltilerinin her iki boya için de TOK giderim değerlerinin %90' ın üzerinde olduğu gözlemlenmiştir. Katalitik ozonlamanın en kayda değer etkisi, katalizörsüz ozonlamada TOK giderimlerinin en düşük olduğu pH = 3'de görülmüştür. CuS eklenmesi reaksiyon süresi olan 80 dak sonundaki yüzde TOK giderim değerini 100 mg/L başlangıç konsantrasyonuna sahip pH = 3'teki RBBR çözeltilerinde %123, RB-5 çözeltilerinde %65 arttırmıştır. Öte yandan Fe/Al₂O₃ katalizörünün ortama eklenmesi 100 mg/L başlangıç konsantrasyonuna sahip pH = 3'teki RB-5 çözeltisinin ozonlanmasında TOK giderim değerini %52 arttırmıştır.

İlave olarak, ozonun hacimsel kütle transfer katsayısı (k_La) boyanın ortamda bulunduğu (boya-ozon reaksiyonunun olduğu) ve bulunmadığı durumlarda matematiksel modelleme ile yaklaşık olarak tespit edilmiştir. Tespit edilen değerler kullanılarak başlangıç boya derişimi ve boya-ozon reaksiyonunun ozonun fiziksel absorpsiyon hızını artırma katsayısı (E) arasında bir korelasyon bulunmuştur.

Anahtar Kelimeler: Ozonlama, katalitik ozonlama, Demir, Bakır, Bakır sulfur (CuS), Remazol Parlak Mavisi-R (RBBR), Reaktif Mavi-5 (RB-5), ileri oksidasyon prosesi (İOP)

To my family...

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LIST OF SYMBOLS

$C_{O_3}^*$	Dissolved ozone concentration at equilibrium (mg/L)
C_{O_3}	Bulk phase concentration of ozone (mg/L)
k	Second order reaction rate constant (1/min)
k_d	Decomposition rate constant (1/min)
C_d	Liquid phase dye concentration (mg/L)
k_La	Volumetric mass transfer coefficient (1/min)
H_A	Henry's law constant (L/atm.mol)
D	Diffusivity (m ² /s)
$p_{x,i}$	partial pressure of any component at the interface (atm)
$(k_La)_E$	Enhanced volumetric mass transfer coefficient (1/min)
k_{obs}	Observed reaction rate constant (1/min)
k'	Pseudo first order observed reaction rate constant (1/min)
C_{cat}	Catalyst dosage (g/L)
C_d	Dye concentration (mg/L)
$C_{d,i}$	Initial dye concentration (mg/L)

CHAPTER 1

INTRODUCTION

Treatment of dyed wastewaters has always been a problem. The main source of this type of wastewaters is the textile industry. There are many different types of dyes which are used for the different necessities in the textile industry and considerable amounts of dyes used in the dyeing processes remain in water and are discharged with the waste stream [1-6]. It is reported in the literature that up to 50% of reactive dyes, 8-20% of disperse dyes and 1% of the pigments used may be discharged with the wastewater streams [2].

Among the other organic wastes, dyes bring additional problems for environment when they participate in the natural waters. Dye wastewaters may overload self purification mechanisms, prevent or reduce photosynthetic processes and they can have toxic or carcinogenic effects on the environment [3]. These additional problems necessitate the removal and de-colorization of dyes in these wastewaters. However it is very hard to treat the organic compounds having complicated structures by conventional biological treatment methods [4, 7, 8].

The conventional methods include a primary treatment which removes suspended solids of higher dimensions, oils and fats, followed by a secondary treatment of organic materials by activated sludge process most commonly at this step. Even after the second step dye materials cannot be treated as mentioned before, therefore a tertiary chemical method for the treatment of the wastewater is used to remove color detergents, organics and/or salinity. The methods used in the industry can be listed as oxidation with ozone, Fenton's reagent, UV oxidation, membranes filtration

processes, activated carbon adsorption, ion exchange resins, coagulation/flocculation or coagulation/flotation and electrochemical methods [1].

Among all the oxidation methods ozonation is one of the most promising methods for the color removal of the textile wastewaters. In the case of wastewater treatment with ozone (ozonation), ozone molecules rapidly and selectively attack unsaturated bonds of chromophores resulting in a rapid removal of color [1,4]. The oxidation of dye molecules yields ozonation by-products which cannot be oxidized by ozone molecules easily, such as organic acids, aldehydes and ketons. Therefore, mineralization that can be measured in terms of chemical oxygen demand (COD) and total organic carbon (TOC) reduction cannot be achieved efficiently [1,9-12].

Resistance of ozonation side products to further oxidation by ozone, low solubility and stability of ozone in water and high cost of ozone production arose the need for an advanced oxidation technology to overcome the mineralization problem and reduce the COD and TOC amounts in the wastewaters more efficiently. In order to overcome this difficulty, methods of advanced oxidation processes (AOP) based on the generation of hydroxyl radicals being more powerful than ozone and catalytic ozonation were investigated widely [2-5,10-12]. Some of the main types of AOPs can be listed as combination of some chemicals and ozone or combination of UV radiation and some chemicals as; O_3/H_2O_2 , H_2O_2/Fe^{2+} (Fenton's reagent), O_3/UV , H_2O_2/UV , $O_3/H_2O_2/UV$ and catalytic ozonation. Even though generation of more powerful species seems to be the solution for the oxidation of the species which are resistant against ozone, the non-selective hydroxyl radicals can be scavenged by other species that can be found in the wastewater; this may decrease the selectivity of the oxidation reaction against the target pollutant species. Because of this disadvantage of the AOPs, some researchers also worked on ozonation systems that increase the dissolution and stability of the molecular ozone in the reaction medium [12].

In this study, the objective was to investigate the oxidation efficiency of aqueous dye solutions by heterogeneous catalytic ozonation using copper sulfide powders as catalyst in terms of dye removal and mineralization of dye organics. Reaction pathway and kinetics of the catalytic reaction were also investigated. In addition another heterogeneous catalytic ozonation process, with the addition of iron impregnated on alumina ($\text{Fe}/\text{Al}_2\text{O}_3$) catalyst was investigated both in terms of catalytic efficiency and catalytic reaction mechanism.

CHAPTER 2

BACKGROUND

2.1 Ozone

Ozone is an unstable gas having a pungent, characteristic odor. It is a blue colored gas at ordinary temperatures but it is not possible to observe this color at low concentrations generated for water treatment uses. Some physical properties are given in Appendix-1. Ozone decomposes back to oxygen very rapidly in aqueous medium depending on the contaminants in the medium.

Ozone structure described in the literature as a resonance hybrid of the four canonical forms [13] is represented in Figure 2.1. Also the general representation of ozone molecule is given in Figure 2.2

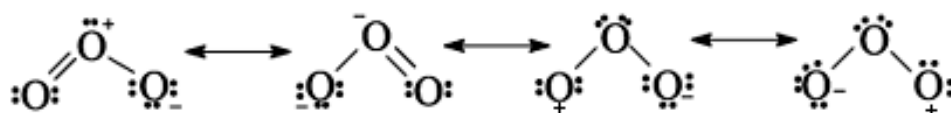


Figure 2.1 Four canonical forms of ozone

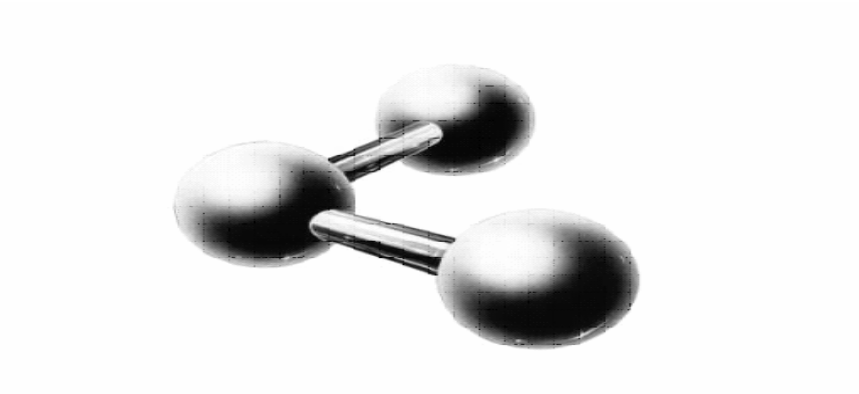


Figure 2.2 Ozone molecule

2.1.1 History of Ozone

The odor of ozone has been the reason of its first observations and then became the inspiration for its name. The odor of ozone was noticed by some scientists since 1785 but it was Schonbein who announced the discovery of ozone first at 1840. He gave the name ozone from the Greek word “ozein” which means “to smell”. Schonbein also found that ozone attacks potassium iodide in aqueous solutions to form free iodine ions. This property of ozone is still used in the determination of ozone amount in the gas phase by passing the gas through a gas washing bottle containing potassium iodide solution.

Ozone technology was advanced greatly by the invention of first ozone generator in 1857 by von Siemens. After that time, numerous studies have been done on ozone thermodynamics decomposition and dissolution in water to have a better understanding of ozone’s characteristics and uses on different areas [13]. Experimental work including this one still continue to be conducted by several researchers all over the world to obtain more useful and effective ways to use ozone.

2.1.2 Applications of Ozone

Ozonation has been applied in very different and wide areas in the industry. Its oxidative properties have been known and used for disinfection purposes for a century. Besides disinfection because of its oxidation potential ozone can be used in very different and interesting areas in the industry from disinfection of swimming pools to drinking water treatment applications of ozone technology numerously. Some applications can be listed as [14]:

- a) Drinking Water Purification
- b) Air Purification
- c) Wastewater Treatment
- d) Odour Removal
- e) Sterilization
- f) Removal of Pesticides
- g) Color Removal
- h) Food Industry
- i) Aquaculture

As an example to show the advantages of using ozone as a disinfectant (the best known and most frequently used area of ozone) a comparison between ozone and chlorine in water disinfection between is given below in Table 2.1^{*}.

^{*} Adapted from aurozon water and air treatment consultants web page [10]: <http://www.aurozon.com/students/ozone.htm>

Table 2.1 Comparison between ozone and chlorine in water disinfection

OZONE	CHLORINE
Actively kills bacteria and viruses. 3,125 times faster than chlorine.	Does not attack some viruses. Takes more time to kill bacteria.
Toxic only above 100 ppb in air (for daily 8 hours breathing continuously)	Highly poisonous, even at low concentration.
Produces H_2O , O_2 , CO_2 as by-products. So, it is environmentally friendly.	Creates dangerous carcinogenic by-products, which contaminate the water.e.g., chloromides, chloroform, trihalomethane.
Excellent deodorizer for many substances (putrefactions, hydrogen sulfide, urine, smoke, cooking smells, paint, etc.,)	It is not a deodorizing agent.
Effective against mustiness, mildew, and fungus.	Does not have such an effect.
Generated on the premises. No transport. No storage.	Stored in high pressure containers on the premises and can be dangerous.
Long term overall cost of using ozone will be low only a little power. (Typical pay back time 18 months).	Cost is increasing and has become quite prohibitive. Dependence on middle man.
Used in therapeutic pools and baths for the treatment of skin infections and burns.	No such benefits are availed when chlorine is used, on the opposite (caranogenic).
Does not affect pH.	Needs pH control (7.0-7.4 pH).

2.1.3 Mass Transfer of Ozone into Aqueous Medium

Mass transfer of ozone from gas phase to the liquid phase is one of the main concerns of the ozonation processes. Reactions of ozone and organic materials especially dyes in this case, can be considered as fast reactions so it is the mass transfer step controlling the rate of the ozonation reactions for the systems that ozone

is fed continuously. Mass transfer or the absorption of a gas from gaseous phase to liquid phase can be explained by Lewis and Whitman's two film theory which is demonstrated in Figure 2.3. According to this theory, there are two resistances in series that gas must penetrate through to reach the liquid phase. These resistances are liquid film and the gas film [13,15].

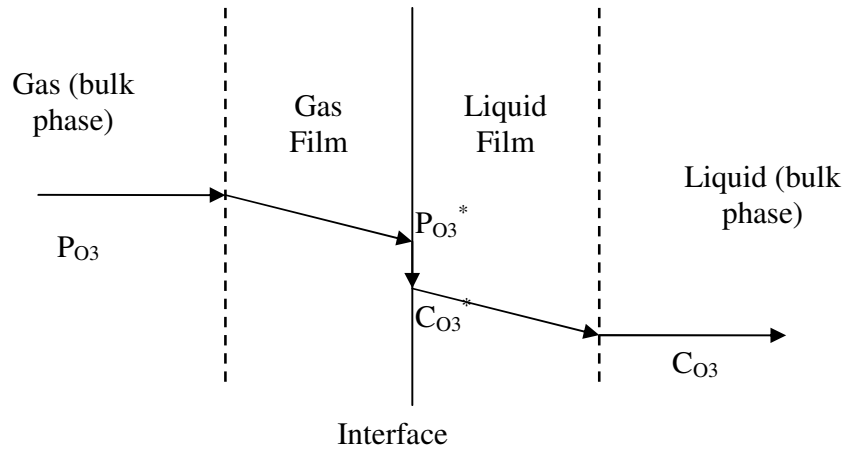


Figure 2.3 Mass transfer between phases. P_{O_3} is partial pressure of ozone, $P_{O_3}^*$ is partial pressure of ozone at the gas liquid interface and $C_{O_3}^*$ and C_{O_3} are concentrations of ozone at the interface and in the bulk liquid respectively.

Assuming equilibrium at the interface, a relationship between concentration and partial pressure can be written by using Henry's Law as below [15,16]:

$$P_{O_3}^* = H \cdot C_{O_3}^* \quad (2.1)$$

where, H is the Henry's law constant and for the ozone - water system given in the literature as [16]:

$$H = 3.84 \times 10^7 [OH^-]^{0.035} \exp\left(\frac{-2428}{T}\right) \quad (2.2)$$

where, $[\text{OH}^-]$ is the hydroxide ion concentration in terms of mol/L (reflecting the effect of pH on the dissolution and amount of ozone in the liquid phase) and T is the temperature of water in Kelvin.

The resistance in the gas film is neglected for the ozone-water case [13,16-18] so that ozone concentration in a semi-batch reactor can be expressed as:

$$\frac{dC_{O_3}}{dt} = k_L a (C_{O_3}^* - C_{O_3}) \quad (2.3a)$$

Ozone concentration in the liquid phase was also affected by the self decomposition of ozone; therefore ozone self decomposition rate expression should also be added to the Eqn (2.3a); as a result, the change of ozone concentration in the liquid phase without reaction can be expressed as follows:

$$\frac{dC_{O_3}}{dt} = k_L a (C_{O_3}^* - C_{O_3}) - k_d C_{O_3}^m \quad (2.3b)$$

where, k_d is the ozone self decomposition rate constant, m is the order of decomposition reaction rate, which is commonly taken as one but in some researches it was also found to be 2 [18]. k_L is the mass transfer coefficient of the liquid film ($\text{m}^3 \text{ liquid} / \text{m}^2 \text{ surface.s}$) and a is interfacial bubble surface area ($\text{m}^2 \text{ surface area} / \text{m}^3 \text{ contactor}$). Volumetric mass transfer coefficient ($k_L a$) usually is taken as one term in terms of $\text{m}^3 \text{ liquid} / \text{m}^3 \text{ contactor.s}$ or $1/\text{s}$.

2.1.3.1 Factors Affecting Mass Transfer

Factors that affect mass transfer of a solute gas into a liquid phase can be listed as physicochemical and hydrodynamic effects. Hydrodynamic behaviour can be defined by the movement of the molecules. Turbulent flow increases the mass transfer by increasing the contact between phases. This is reflected by the mass transfer area per unit volume which was defined as “ a ” ($\text{m}^2 \text{ surface area} / \text{m}^3$

contactor); for example, bubbles rising slowly (high contact time) in the column results a lower interfacial area, therefore the mass transfer is limited in this case; increase in the mixing rate of the system or addition of mixing to the system results smaller bubbles and higher interfacial area also with the high contact time. In these systems it is expected to have higher mass transfer rates.

Physicochemical properties can be listed as temperature, pressure, and chemical composition of the system. For example, ionic properties of the solution may affect the diffusion. Temperature and pressure both affect diffusivity and solubility [13].

Ozone decomposition must also be taken into account in ozone systems since ozone decomposes in aqueous systems.

2.1.5 Mass Transfer with Chemical Reactions

Ozone decomposition and oxidation reactions go on at the same time in aqueous ozonation systems. Because of the mass transfer limitation, process is controlled by the mass transfer step.

Ozone decomposition is an irreversible reaction being defined as first, second or one and a half order reaction by several researchers [16, 18].

Ozone decomposition term is:

$$k_d \cdot C_{O_3} \text{ (most commonly first order)} \quad (2.4)$$

In such gas-liquid systems, chemical reactions may occur at the liquid film or in the liquid bulk. Reactions at the interface occur by diffusion of the reactants from bulk to the film between interface and liquid bulk, and then products diffuse back to the liquid bulk or gas bulk if they are volatile. Reactions in the bulk also occur by the diffusion of ozone from the interface to the liquid bulk.

In such systems it will be wrong to use the mass transfer coefficient for the physical absorption cases so in order to define the difference between physical absorption case and the absorption with a chemical reaction case, an “enhancement factor” is used which can be defined as:

$$E = (k_L a)_E / k_L a \quad (2.5)$$

where $(k_L a)_E$ is the chemical absorption mass transfer coefficient and $k_L a$ is the physical absorption mass transfer coefficient.

Enhancement factor should always be greater than or equal to one. Enhancement factor can be evaluated by using two parameters Hatta Number (M_H) and instantaneous enhancement factor (E_i) with the help of the diagram obtained by van Krevelens and Hoftijzer (Figure 2.4) [15].

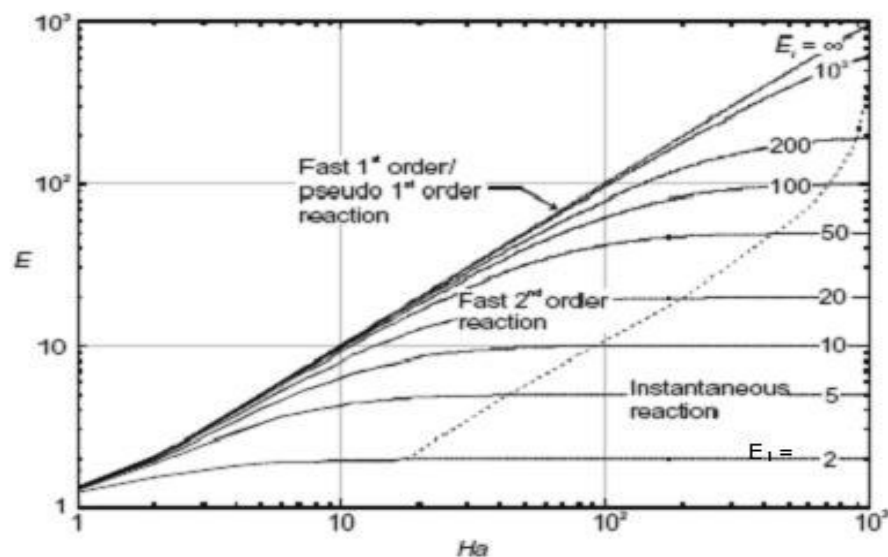


Figure 2.4* Enhancement Factor for Second Order Reactions

* adapted from the web page of Dr. C.Tizaoui linked to the site of the University of Bradford
<http://www.staff.brad.ac.uk/ctizaoui/OzonationProcesses.html#toppage>

E_i and M_H can be defined in Eqns (2.6) and (2.7);

$$E_i = 1 + \frac{D_B C_B H_A}{b D_A p_{Ai}} \quad (2.6)$$

$$M_H = \frac{\sqrt{D_A k C_B}}{k_{Al}} \quad (2.7)$$

where:

D_B = Diffusivity of reactant B (reactant in the liquid phase, dye or organic compound in ozonation processes.)

C_B = Concentration of reactant B

H_A = Henry's law constant

b = stoichiometric coefficient

D_A = Diffusivity of reactant A (reactant that transfer from gas phase, ozone in ozonation reactions.)

k = reaction rate constant

p_{Ai} = partial pressure of reactant A at the interface (since gas film resistance is neglected in ozonation reactions, partial pressure of ozone in the gas feed can be used.)

k_{La} = mass transfer coefficient of reactant A through liquid film

2.1.5.1 Meaning of Hatta Number

Hatta number which gives the comparison of maximum conversion through the film with maximum transport through the film is generally used to determine whether reaction occurs in the film or in the bulk phase. If $M_H \gg 1$, all reaction occurs in the film so the surface area of the contactor is the most important factor controlling the rate. On the other hand if $M_H \ll 1$, it means that reaction occurs in the liquid bulk so the bulk volume is the controlling factor in the reaction [15].

2. 2 Advanced Oxidation Processes (AOPs) and Catalytic Ozonation

Advanced oxidation processes arose because of the need for the improvement of the ozonation process. Ozonation includes oxidation of non-biodegradable substances with ozone molecules. Ozonation is a widely used technology for water treatment, color removal, taste and odor removals. Ozonation is especially very effective on color removal. However it has some disadvantages:

- high cost of producing ozone
- some organic compounds cannot be fully oxidized by ozonation (that arises need of biological treatment)(organics such as inactivated aromatics)
- low solubility and stability in water

At this point catalytic ozonation and advanced oxidation processes can be used to overcome these disadvantages by promoting the oxidation ability of ozone. Especially the organic acids with small molecular weights cannot be completely oxidized by conventional ozonation process. Sole ozonation can be insufficient in COD and TOC removals.

AOPs can be combinations of Ozone, UV, hydrogen peroxide and catalysts, to treat water containing organic compounds that cannot be degraded by biological methods. These methods can be used separately as well as combined together. The main idea behind the advanced oxidation processes is to produce hydroxyl radicals that are more powerful oxidants than ozone molecules. By that way oxidation rate of organics can be increased yielding the higher efficiencies in organic matter removal in terms of TOC and COD removals. Main AOP methods can be listed as [12]:

- Homogeneous systems without irradiation: $\text{O}_3/\text{H}_2\text{O}_2$, O_3/OH^- , $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ (Fenton's reagent),
- Homogeneous systems with irradiation: O_3/UV , $\text{H}_2\text{O}_2/\text{UV}$, $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$, photo Fenton, electron beam, ultrasound, vacuum-UV

- Heterogeneous systems with irradiation: $\text{TiO}_2/\text{O}_2/\text{UV}$
- Heterogeneous systems without irradiation: electro-Fenton.

2.2.1 Peroxone Process

Main aim of oxidation processes is to obtain hydroxyl radicals which are one of the most powerful oxidizers (having an oxidation potential of about 3V). By adding hydrogen peroxide, the net production of hydroxyl free radicals is 1.0 mole hydroxyl radical per mole ozone. Main difference between peroxone process and ozone process is that the ozone process is based on direct oxidation by aqueous molecular ozone while peroxone process is based on oxidation with hydroxyl radicals. Oxidation is more reactive in peroxone process. Besides decomposition rate of ozone is higher than that in ozonation carried out at high pH values which is another way to decompose ozone to obtain hydroxyl radicals. In peroxone process both direct ozonation by molecular ozone and indirect oxidation by hydroxyl radicals occur. These two reactions compete with each other in the oxidation of organics. Although hydroxyl radicals are very reactive, they exist only at smaller concentrations and they have much less stability with respect to ozone. Main event in peroxone process is hydroxyl radical oxidation since hydroxyl radicals are very powerful, but non-selective.

Oxidation potentials of hydroxyl radical and ozone are given as follows:



2.2.1.1 Some Reactions Related to Ozonation and Peroxone Processes:

There are some initiators, promoters and inhibitors for chain reactions of hydroxyl radical formation. Those compounds may be present in water or as done in peroxone process can be added. These compounds can be listed as the initiators (OH^\cdot , $\text{H}_2\text{O}_2/\text{HO}_2^\cdot$, Fe^{2+} , formate, humic substances (HS)) which are capable of inducing the formation of superoxide ion $\text{O}_2^{\cdot-}$, promoters ($\text{R}_2\text{-CH-OH}$, aryl-(R), formate, humic substances, O_3) which are responsible for the regeneration of $\text{O}_2^{\cdot-}$ ions from hydroxyl radicals and inhibitors ($\text{CH}_3\text{-COO}^-$, alkyl-(R), $\text{HCO}_3^-/\text{CO}_3^{2-}$, humic substances) that can react with hydroxyl radicals without regeneration of superoxide ion.

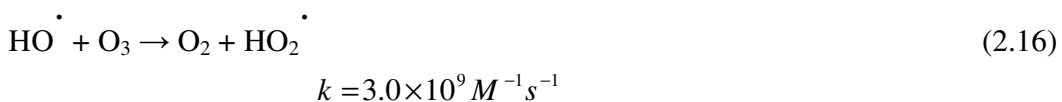
Hydroxyl formation in presence of hydrogen peroxide (during peroxone process) can be given as [19,20,4]:

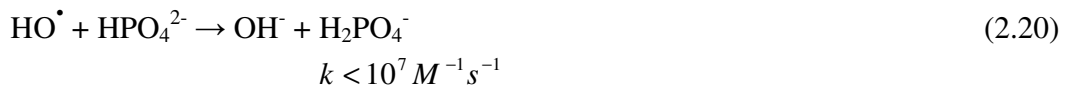
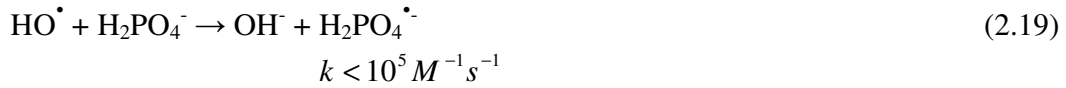
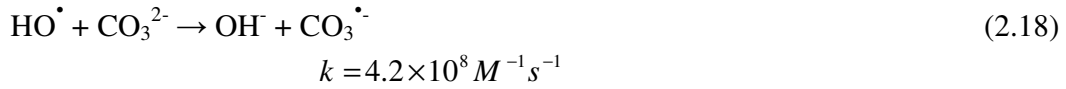
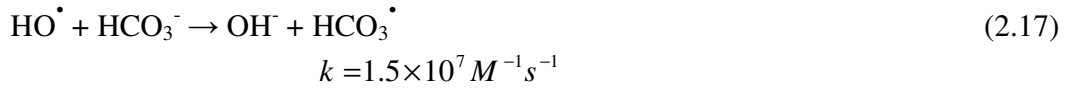


Formation of hydroxyl radical in the presence of hydrogen peroxide (HO_2^\cdot ion) can be given by chain reactions as follows [4]:



Some possible reactions of hydroxyl radicals in water can be given as follows [12]:





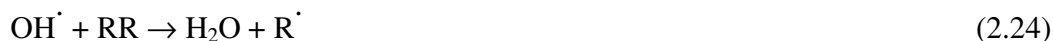
As seen from Eqn (2.16), the reaction between ozone and hydroxyl radical can significantly reduce the ozone decomposition to hydroxyl radical. It is also seen that reactions of hydroxyl radical with other organic compounds also have high reaction constants. That is the main disadvantage of hydroxyl based oxidation reactions. Hydroxyl radicals can react with other scavengers in water that can cause inhibition of free radical chain reaction [8]; that property is used for lowering the decomposition of ozone in sole ozonation process where direct oxidation by molecular ozone is needed.

Also a series of chain reactions occurs besides the reactions given above [4]:



From the above given reactions it can be observed that while working with excess hydrogen peroxide, hydrogen peroxide can act as a scavenger consuming the hydroxyl radical generated in the solution medium.

A common pathway for oxidation of organic materials is described by Carey (1990) is as follows [20]:



2.2.1.2 Effect of pH on Peroxone Process

Solution pH can be the most important parameter for the peroxone process. At basic pH values, formation of hydroxyl radicals occurs more rapidly. Therefore it is expected that at the higher pH values, effectiveness of the peroxone process will be higher. But at those pH values water may also contain radical scavengers such as carbonates which inhibit the radical chain reactions of hydroxyl ions, (“at pH values greater than 9, bicarbonate ions are converted to carbonate ions that are scavengers for hydroxyl radicals slowing down the kinetic rate of oxidation reaction”[20]).

Kurniawan et al. [20] in their studies of reviewing the technical applicability of AOP's on treatment of landfill leachate, indicated that at a pH higher than 7.0, H_2O_2 dissociates into HO_2^- as its conjugate base. In basic conditions, both OH^- and HO_2^- initiate the ozone decomposition more rapidly and more effectively into OH^\cdot radicals than the OH^- alone. Therefore, to enhance the effectiveness of the $\text{O}_3/\text{H}_2\text{O}_2$ performance for leachate treatment, the pH should vary ranging from 8 to 9. They also referred to other studies where it was reported that the basic conditions were preferable for $\text{O}_3/\text{H}_2\text{O}_2$ to degrade organic compounds.

Espulas et al. [21] compared AOP's including O_3 , O_3/H_2O_2 , UV, UV/ O_3 , UV/ H_2O_2 , O_3 /UV/ H_2O_2 , Fe^{2+}/H_2O_2 and photocatalysis on phenol degradation. They obtained the best phenol degradation for peroxone process at neutral pH. They studied at different pH and initial H_2O_2 concentrations. The experiments performed at three different pH values. The achieved degradations of phenol were: 80.6 %, 93.4 % and 92.5% at free pH (3.4-5), pH 6.8 and pH 9.3 respectively.

Catalkaya et al. [19], treated pulp mill effluent by different AOP's (hydrogen peroxide, Fenton's reagent (H_2O_2/Fe^{2+}), UV, UV/ H_2O_2 , photo-Fenton (UV/ H_2O_2/Fe^{2+}), ozonation and peroxone (ozone/ H_2O_2). During their studies on (ozone/ H_2O_2) method they worked at pH 3, 7 and 11 for 30 minutes of reaction time. They observed color removal of 95% at pH of 3 and this value was observed about 90% at pH 7, and color removal decreased to 73.4% at pH 11. They also referred to their observations about using only hydrogen peroxide and indicated the importance of using ozone along with hydrogen peroxide. Beside color removal, they also observed percent TOC removals in their studies and gave the results as 14%, 14.3% and 16 % for pH 3, 7 and 11, respectively.

2.2.2 Fenton Reagent (Fe^{2+}/H_2O_2)

This is a process using hydrogen peroxide with iron ions to generate hydroxyl radicals where ozone is not included. Besides there are some studies on a process called 'fentozone' that ozone is also included. Some of the areas where Fenton process applied can be listed as below:

- Organic pollutant destruction
- Toxicity reduction
- Biodegradability improvement
- BOD/COD removal
- Odor and color removal

Fenton process involves reactions below:



These reactions describe how OH radicals are produced by using hydrogen peroxide and iron atoms. Also chain reactions taking place with hydroxyl radicals and organic compounds exist in the system.

2.2.2.1 Parameters Involved in Fenton Process

Parameters can be listed as; temperature, amount of iron and peroxide (ratios of iron hydrogen peroxide and substrate), reaction time and pH of the medium. The most common parameters investigated in the literature are pH, concentrations of iron and hydrogen peroxide ions. It is observed from literature survey (experimental procedures used) that pH and concentration parameters are independent from each other.

(i) Temperature: It is expected that efficiency of the process increases with increasing temperature, until 40-50⁰C, after that any further increase in the temperature may affect the reaction negatively. Because of this, most of the Fenton processes were carried out at room temperature. Temperature increase is expected when higher doses of reactants are applied (10-20 g/L H₂O₂) and temperature of the system must be moderated in such operations by introducing hydrogen peroxide to the system slowly.

Torrades et al. [22] conducted experiments at different temperatures in their work which was done to make an experimental design for treating cellulose bleaching effluents with Fenton and photo Fenton processes. They indicated that temperature was a particularly significant factor for TOC removal in their system when the system was operated under low reagent load or inadequate reagent ratios. They also indicated that temperature became a key parameter when it was desired to reduce

reagent consumption or high amounts of iron were not allowed into the treated wastewaters.

(ii) Effect of pH on Fenton Process: Optimum pH for the Fenton process varies between 3 and 6; at the higher pH values hydrogen peroxide might be decomposed to oxygen which might yield a hazardous situation. During oxidation process a decrease in pH is expected; this decrease in pH occurs first as FeSO_4 is introduced to the system because of the residual H_2SO_4 in the FeSO_4 solution. After the addition of hydrogen peroxide a more pronounced reduction in pH is observed due to organic acids yield from oxidation process [23-25].

Sevimli [23] conducted experiments at pH values between 2 and 7 in order to investigate the effectiveness of oxidation processes for treating pulp and paper industry effluents. In this work pH values were changed between 2 and 7 while iron and hydrogen peroxide amounts were held constant. After those experiments optimum pH was found as 4 (other parameters were tested according to the optimum pH).

Azbar et al. [24] made a comparison between oxidation processes for treatment of polyester and acetate fiber dyeing effluents. They conducted experiments between pH 2 and 7. Optimum pH was determined by holding iron and hydrogen peroxide amounts constant and changing pH values. They found optimum pH for treating that effluent as 5 (other parameters were tested according to the optimum pH).

Torrades et al. [22] worked at pH 3 making an experimental design for treating cellulose bleaching effluents with Fenton and photo Fenton processes. They indicated that pH of 3 was the optimum pH value they found in literature for Fenton process.

H-J.Sing et al. [25] conducted experiments to investigate the performances of oxidation processes on treating Acid Orange 6 solution. They conducted experiments

by holding hydrogen peroxide and iron concentrations constant and changing pH between 2 and 7 in order to find optimum pH (other parameters tested according to optimum pH). They found optimum pH for this system as 3.

(iii) Amount of Reagents: Ratio of iron to H₂O₂: substrate is very important for the amount effect on Fenton process. Also in literature it is observed for some cases that there are amount limitations for the process.

Effect of Iron

- Minimum 3-15 mg/L iron concentration needed for reasonable reaction times regardless of the concentration of organic material.
- Ratio of iron to substrate generally given as; 1part Fe: 10-50 part substrate and Fe to H₂O₂ can be given as 1:5-25 (wt/wt).
- Properties of medium are also important; if there are chelants such as phosphates, EDTA, formaldehyde, and citric/oxalic acids or radical scavengers, iron is inhibited.
- After a certain iron amount, iron addition may be detrimental according to the reaction below:



(iv) Effect of iron type: Iron can be introduced to the system as Fe³⁺ or Fe²⁺, if H₂O₂ and organic material are in abundance, catalytic cycle can easily be started by Fe³⁺ ions but in general it is preferred to use Fe²⁺ ions as catalyst. To obtain iron ions, chloride or sulfate salts can be used; but at high dosages of chlorine the former is not preferred, therefore sulfate salts are preferred.

(v) Effect of H₂O₂: Increase in H₂O₂ concentration increases the efficiency of the system but in some cases it has been observed that excess H₂O₂ can be inhibitory according to the following reaction:



Torrades et al. [22] worked at pH 3 in their work which they made an experimental design for treating cellulose bleaching effluents with Fenton and photo Fenton processes. They indicated that the most important aspect that needs to be considered in Fenton process is the choice of right ratios of Fenton reagents. They also indicated that non-optimal initial conditions of Fenton reagent were found to be detrimental.

Sevimli [23] conducted experiments holding one of the reagents (Fe and H_2O_2) constant and changing the other to find optimum values in treating paper industry effluents where several advanced oxidation processes were compared. It was found that the optimum ratio of Fe: H_2O_2 was 1: 2 (wt:wt)

Azbar et al. [24] made a comparison between oxidation processes for treatment of polyester and acetate fiber dyeing effluents. In their work they found optimum concentrations for Fenton process as 300 mg/L H_2O_2 : 500 mg/L FeSO_4 which corresponded to a ratio of Fe: H_2O_2 , 184 mg/L : 300 mg/L (ratio = 0.6)

H-J.Sing et al. [25] conducted experiments to investigate the performance of oxidation process on treating Acid Orange 6 solution. They conducted experiments by holding iron concentration constant and changing hydrogen peroxide concentration. They found optimum H_2O_2 : Fe molar ratio as 6.58. They also indicated that added hydrogen peroxide was controlling the system and the de-colorization of the dye decreased after a maximum dosage addition of hydrogen peroxide. They explained the reason of reducing de-colorization by the scavenging effect of hydrogen peroxide on hydroxyl radicals.

2.3 Heterogeneous Catalytic Ozonation

Improvements in ozonation can also be obtained by using heterogeneous catalysts. Metal-oxides are frequently used catalysts for ozonation [26-28]. But it is not possible to say that there is a good catalyst for all kinds of water to be treated. There are several catalysts that were found effective in the literature for different kinds of

wastewaters. Catalytic ozonation may improve ozonation by enhancing the generation of hydroxyl radicals or generating other oxidizing species such as bound ozone that are more powerful oxidants than ozone molecules. Catalytic ozonation has two main advantages: (i) reducing ozone consumption: catalytic ozonation increases the rate of oxidation so it decreases the ozonation time and ozone consumption; in other words, catalytic ozonation increases the ozonation yield. Catalytic ozonation process decreases the high operating cost of producing ozone molecules due to less ozone consumption. Ozone molecules are generated by using a generator (electricity) from dry air or pure oxygen, (ii) increasing TOC and COD removals: ozone is a powerful oxidant and it is very effective especially in color removal but as mentioned before it is not sufficient in COD and TOC removals. Catalytic ozonation studies proved that ozonation in the presence of an appropriate catalyst improves the COD and TOC removals [29, 30].

2.3.1 Modelling of a Three Phase Semi-Batch Reactor

Catalytic ozonation reactors are multiphase reactors. Multiphase reactors include several rate determining steps according to the diffusion of the materials between phases and in the phases. Figure 2.1 shows a diagram of mass transfer regions.

In the ozonation process gas film mass transfer is negligible. Controlling step in ozonation is the liquid film mass transfer step. Material balances for ozone and dye molecules (treated wastewater is a dye wastewater) can be written as:

$$\frac{dC_{O_3}}{dt} = k_L a (C_L^* - C_{O_3}) - k_d C_{O_3} - k_{obs} C_{O_3}^x \cdot C_{dye}^y \quad (2.32)$$

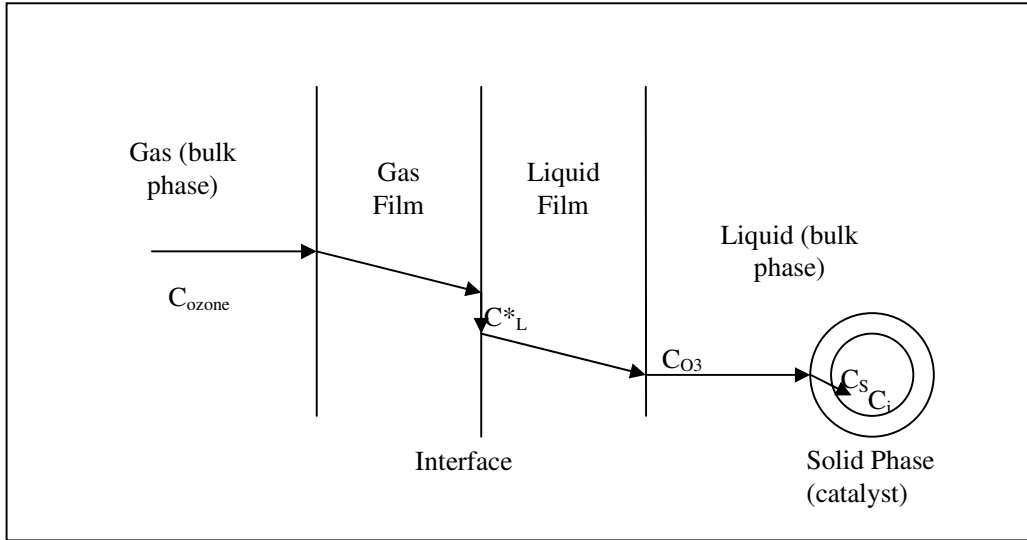


Figure 2.1 Ozone Transfer from Gas Phase to Liquid Phase

where:

C^*_L = Equilibrium concentration of ozone in liquid

C_{O_3} = Bulk phase ozone concentration

C_s = Ozone concentration at the surface of the catalyst particle

C_i = ozone concentration inside of the particle

$k_L a$ = convectonal mass transfer coefficient

k_d = ozone self decomposition rate constant

Dye mass balance as:

$$\frac{dC_{\text{dye}}}{dt} = -k_{\text{obs}} C_{O_3}^x \cdot C_{\text{dye}}^y \quad (2.33)$$

k_{obs} = is the observed reaction rate constant used to define all reactions taking place in the system to make an easy estimation for the reaction rate. This kind of approach had been used to define reaction rate constant in the literature [30].

2.3.2 Catalytic Ozonation Applications on Dye Wastewater

Yong et al. [30] used CuS as a catalyst in their work where they compared and selected CuS as the catalyst that was the only catalyst improving color removal when compared with TiO_2 , ZnO , NiO , Al_2O_3 , Cr_2O_3 , and CuO on reactive dye; C.I Reactive Blue 5. By using CuS they obtained a significant decrease in ozonation time and ozone consumption which was very important from economical point of view. They also indicated that adsorption of the dye by CuS was negligible. Catalyst load was explored for 1g/L of dye and 64.8 mg/L.min of ozone dose; they found that ozonation efficiency increased until 0.4 g of CuS addition, then ozonation was not further affected by the catalyst load. They considered 0.4 g CuS addition, as the optimal catalyst load. Reaction order of ozonation was found as first order for ozonation without catalyst and second order for the case with catalyst. They also indicated that the reaction rate expression given for the catalytic ozonation was the observed reaction rate expression, it was not the real reaction rate expression. They proposed a reaction pathway in which reaction was carried out by ozone molecules instead of hydroxyl radicals; because they did not observe any change in ozonation of the dye by increasing the pH, and also the presence of scavengers did not affect the ozonation efficiency.

Dong et al. [31] Investigated the catalytic effect of natural brucite comprised mainly MgO on ozonation of an azo dye, namely Active Brilliant Red X 30. In their work they treated 50 mL of 500 mg/L dye solution with and without catalyst at an ozone dose of 0.30 mg/min. They used 0.5 g of brucite in their runs including catalyst. They reported significant effect on dye removal and increase in chemical oxygen demand (COD) removal values. They indicated that the color removal after 15 min of oxidation is 47% with ozonation only while it is increased to 89% with the catalytic ozonation. Also COD removals increased from 9% to 32.5% with the use of catalyst. They observed that the effect of adsorption without reaction on dye degradation and COD removals was negligible.

Arslan [32] compared the processes of ferrous sulphate coagulation, ozonation and Fe^{2+} ions by ozonating a simulated dyed wastewater having an absorbance of 814 m^{-1} at 566 nm, initial COD value of 3784 mg/L, TOC value of 670 mg/L and BOD_5 value of 58 mg/L. Ozonation experiments carried out for 10 minutes with an ozonation rate of 3.5 g/h were reported corresponding to 0.62 g O_3 per initial COD, Fe^{2+} dose between 0.09 – 0.36 mM and pH range 3-11. In ferrous iron coagulation experiments, 97% color removal and 54 % COD removal were achieved at pH = 11 while in ozonation only experiments 11.4% COD removal and 77% color removal were achieved at pH = 3, and in ozonation with ferrous ions 94.6% color removal and 47.8 COD removal were achieved. It was reported that using ozonation with ferrous irons was more advantageous rather than using coagulation because of the difference in the iron doses. Also it would be practical to combine two systems by using ozonation only at neutral pH after that adding iron sulphate, by this way the amount of the iron sulphate added was decreased by a factor of 2-3. In this work there is no significant TOC reduction observed for ozonation or ozonation combined by ferrous ions with in a short ozonation interval.

Gul et al. [33] investigated the effect of granulated activated carbon (GAC) on ozonation of reactive yellow 145 (RY145) and reactive red (RR 194). They treated 100 mg/L dye solutions with an ozone dose of 28 mg O_3 /min at free pH (6.3 for RR 194 and 5.9 for RY 145). They conducted experiments to find optimum GAC concentration in those runs; they added 10, 20 and 30 g/L GAC to the dye solution. They indicated that GAC did not show an effect of color removal more than ozonation alone but the OH^\cdot radicals formed on the surface of the GAC improved the TOC removal from 25% to about 50% by the use of 10 g/L GAC. They also reported that ozone consumption was decreased by the use of 10 g/L GAC in the ozonation of RR 194 while such an effect was not observed for the RY 145. They also observed slight improvements on COD removal by adding 10 g/L for RR 194. Adding 10 g of GAC did not improve the COD removal in RY 145 solutions. They concluded that adding optimum amount of GAC could be useful for ozonation by catalyzing and enhancing the hydroxyl radical formation; however an increase in the

amount of GAC had a negative effect on de-colorization and TOC removal caused by the adsorption of the organic species on the GAC surface. Information about the chemical structures of the dyes were also given by the help of anion analysis.

Hassan et al. [34] conducted experiments in a semi-continuous mode bubble column reactor to investigate the effect of Ferral catalyst on the ozonation. They studied various dyes and operation parameters such as optimum pH and catalyst concentration. They indicated that Ferral increased the color removal and color removal rate for the dyes except chromium complex acid dye. The negative effect of chromium showed itself as a decrease in decolorization with time. They reported a color removal of 59% for Everacid Milling Yellow MR (EYMR) in 1 min of ozonation alone while in the presence of Ferral color removal increased to about 91% at pH 3.01 with initial dye concentration of 120 mg/L and Ferral dose of 0.25 mL/L. They also tested a combined method by using a two step procedure first ozonation only and then coagulation by adding Ferral in jar test apparatus. They reported that two step treatments increased the color removal of C.I. Reactive Orange from 16 to 51% while ozonation with Ferral increased ozonation efficiency to 92%. They investigated the effect of pH by conducting experiments between pH 3 and 9 and indicated that the best color removal was observed at pH 3. They also investigated the catalyst concentration by changing Ferral concentration between 0 and 487.5 mg/L. They observed that color removal rate increased sharply by increase in Ferral concentration up to a certain value, then increase continued more slowly. The COD reduction also increased with the increasing amount of Ferral. They reported COD reduction by 7% with ozonation only while the reduction increased to 76% with the addition of 488 mg/L Ferral. They concluded that Ferral showed a catalytic activity on color removal and excellent effect in the COD reduction; but its use was suitable at low pH values, therefore, for the alkaline effluents it was not useful.

Hassan et al. [10] worked on de-colorization of dye solutions in a bubble column using various catalysts such as; hydrated alumina, silica-supported ferric oxide and

activated carbon. They conducted experiments to obtain optimum conditions for catalysts such as; pH range (between pH 4 and pH 10) and optimum catalyst dose. Various dye solutions were investigated including; CI Reactive Red 45, CI Reactive Red 120,1;2 Chromium complex of CI Acid Black 60, CI Reactive Black 5, CI Reactive Red 180, CI Reactive Blue 19 (Remazol Blue R). CI Reactive Red 45 and CI Reactive Red 120 were ozonated at pH 4 with the presence of all of the catalysts (separately) at a color concentration of 120 mg/dm³ and the catalyst dose of 60 mg/L. Optimum pH investigated by ozonating Chromium complex of CI Acid Black 60 of concentration 120 mg/L in the presence of 75 mg/L Al(OH)₃, CI Reactive Black 5 of 80 mg/L concentration with the presence of 20 mg/L Carbon -C and Carbon -D and CI Reactive Red 180 of concentration 120 mg/L with the presence of 60 mg/L iron catalyst. The optimization experiments for catalyst dose were also conducted by using different dyes. The optimization of Carbon-C and Carbon-D was studied by ozonating Remazol Blue R of concentration 120 mg/L at pH 4 with different catalyst concentrations. They indicated that Carbon C did not improve the color removal with respect to ozonation alone. They also reported that all the other catalysts improved ozonation while the highest improvement resulted when hydrated alumina was added. Color removal at 80th second was given as 79% for ozonation alone where it was given as 89% for the case that hydrated alumina particles were added. Catalyst effectiveness was listed as Al(OH)₃ > Fe₂O₃-SiO₂ > Carbon-D for the ozonation of CI Reactive Red 45 and Al(OH)₃ > Carbon-D > Fe₂O₃-SiO₂ for the ozonation of CI Reactive Red 120. In pH experiments, it was observed that Carbon D showed a good color removal in both acidic and alkaline conditions while hydrated alumina yielded the best color removal at pH 4. The color removal for hydrated was lowered as pH approached to 7; then it increased after pH = 7, but it was reported that at pH =10 it was still lower than the efficiency obtained at pH 4. They also indicated that as the amount of catalyst added increased the efficiency also increased up to a certain point which were 100 mg/L for hydrated alumina, 80 mg/L for Carbon-D and Fe₂O₃-SiO₂ for the dyes observed. They also discussed the reaction mechanism of Carbon-D, they observed that the presence of even a little amount of Carbon in the ozonation medium could start radical chain

reactions by producing hydroxyl radicals. They also conducted de-sorption experiments to test whether color removal occurred by adsorption or reaction and they reported that no colored molecules were observed in the de-sorption medium.

Hassan et al [2] studied various dyes and a dye house effluent by using potassium permanganate, hydrogen peroxide and Ferral in a bubble column reactor. They investigated the improvement in ozonation by catalyst addition, pH effect on ozonation, and the effect of Ferral amount. Remazol Brilliant Red F-3B was treated to compare the effects of catalysts; it was observed that Ferral was the most effective one, while hydrogen peroxide did not show any effect. After a period ozonation alone and ozonation in the presence of potassium permanganate and hydrogen peroxide's efficiencies became the same while feral still had better removal efficiency, at 120th second color removal of ozonation alone, hydrogen peroxide added, potassium permanganate added and Ferral added samples were 69%, 68%, 71% and 78% respectively. De-colorization efficiency increased as pH increased for the ozone + hydrogen peroxide case while for the ozonation in the presence of potassium permanganate, the efficiency decreased as the pH increased up to pH = 8, then it did not change, highest efficiency observed being at pH = 4 and 5 for the potassium permanganate added ozonation case. They suggested the reason for the decrease of efficiency by the increasing pH due to the manganese species in the potassium permanganate which consumed hydroxyl radicals generated at high alkali conditions. For the Ferral case de-colorization was observed highest at pH 3 and it decreased with the increasing pH. The efficiency decreased until pH 8 then it increased after that pH, between pH 8 and pH 11; but the efficiency reported at pH 11 was much less than the efficiency at pH 3. They also conducted experiments to determine the optimum catalyst dose. They observed a sharp decrease in de-colorization up to 260 mg/L Ferral concentration then de-colorization increased more slowly. They calculated kinetic rate constants for reactions considering all cases as pseudo first order reactions. They also conducted two step experiments including coagulation with Ferral following ozonation. They indicated that ozonation with Ferral was more effective than the two step process; they concluded

that the result of the two step experiment could be considered as a proof that Ferral acted as a catalyst in the reaction instead of complex formation of Ferral with dyes.

Beltran et al. [35] worked on catalytic ozonation of oxalic acid. Two different iron catalysts have been investigated in this study. These catalysts were Fe^{3+} and $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$. Fe^{3+} catalyst was added into the reaction medium by dissolving the metal using its nitrate. $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst was obtained by impregnation method and calcined at 800°C . Prepared catalyst was characterized by nitrogen adsorption (BET), helium and mercury porosimetry and X-Ray characterization methods. Ozonation experiments were conducted in a 1 L reactor vessel at semi-batch conditions. Ozonation runs were conducted at $\text{pH} = 2.5$ for three hours. No significant effect of sole ozonation was observed during the tests conducted. On the other hand, addition of Fe^{3+} and $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalysts showed an oxidation degree of 6% and 28%, respectively. The adsorption of oxalic acid on solid catalyst also caused 7% removal of the oxalic acid present in the medium. They also reported iron leaching from the solid catalyst prepared proportionally to the iron concentration on the catalyst, during the reaction period. Heterogeneous catalytic ozonation mechanism was observed. They stated that the effect of tert-butanol addition as a scavenger did not affect the ozonation results indicating that hydroxyl radicals did not participate in the catalytic ozonation of oxalic acid. They explained the increase in the oxalic acid removal with heterogeneous catalytic ozonation in the use of $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst instead of an AOP. Beltran et al. [35] proposed a heterogeneous catalytic mechanism that oxalic acid adsorbed on the surface formed some kind of iron oxalate complex which later reacted with ozone. They also reported the activation energy and pseudo first order reaction rate constants for the catalytic ozonation process.

Pecchi et al. [36] worked on the preparation, characterization and the test of iron catalysts prepared on both TiO_2 and Al_2O_3 supports. They compared the methods of synthesis of these catalysts. They compared catalysts prepared by Sol-Gel method with catalysts prepared by conventional impregnation method. Catalysts were

prepared and characterized by measuring specific area (S_{BET}), temperature programmed reduction (TPR), infrared spectroscopy (FTIR), electrophoretic migration (IP) and X-ray diffraction (XRD). Catalysts were prepared to provide the presence of 10% iron by weight. As a result of characterization experiments, they indicated that iron oxide molecules were highly dispersed in catalysts prepared by Sol-Gel method while dispersion was poor in the catalysts prepared with impregnation method. They also pointed out that even the characteristic iron oxide peak was not observed in the XRD measurements which could be a result of a very high dispersion or iron loading lower than 10%. The highest COD removal was reported for the iron impregnated catalyst. They concluded that a higher surface coverage with iron resulted more active sites than the catalysts prepared by Sol-Gel method would have.

CHAPTER 3

EXPERIMENTAL

3.1 Remazol Brilliant Blue-R and Reactive Black 5

Two different textile dyes; Remazol Brilliant Blue-R (RBBR) and Reactive Black-5 (RB-5) were chosen in order to simulate textile dye effluents. Dye solutions to be treated in the experiments were prepared by dissolving desired amounts of these dyes in de-ionized water. Chemical structures of the dyes treated are given in Figure 3.1

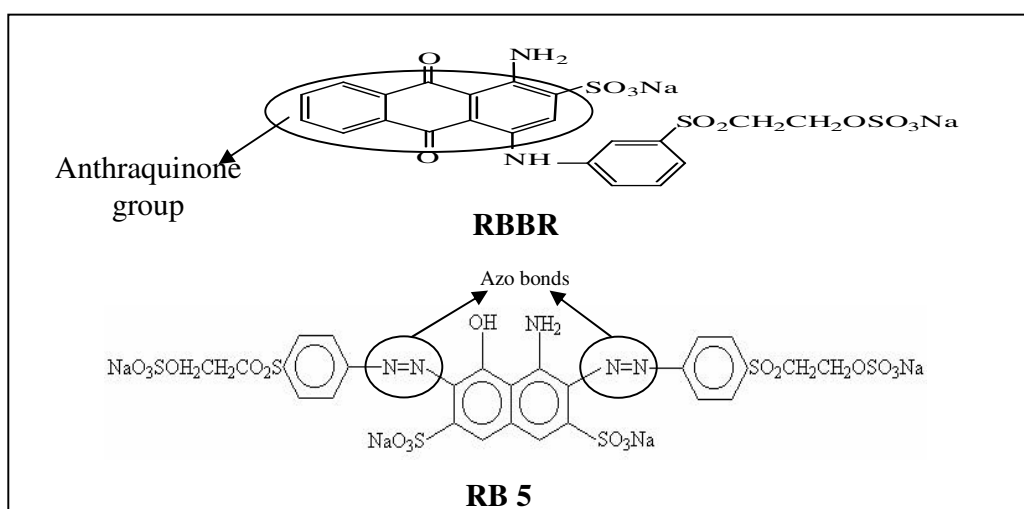


Figure 3.1 Structures of RBBR and RB-5

Both of the dyes used were reactive dyes having different chemical structures. RBBR is an anthraquinone dye having an anthraquinone group in its molecular structure and RB-5 is a diazo dye having two nitrogen to nitrogen double bonded groups in its structure.

3.2 Experimental Apparatus

Ozonation and catalytic ozonation experiments were carried out in a 1 L semi-batch reactor containing prepared dye solution at different concentrations into which ozone gas mixture was fed continuously. Samples were taken during the ozonation period in order to measure the, total organic carbon (TOC) and chemical oxygen demand (COD) values, the dye and dissolved ozone concentrations during the reactions (all of these measurements were not conducted for each run, more detailed explanations about the analyses conducted for each single run will be given later). Samples were taken into 1 mL of 0.25 M thiosulfate solutions in order to prevent further ozonation with the dissolved ozone present in the samples taken. Simultaneously, samples were also taken into Indigo solution for dissolved ozone measurement according to the Indigo method [39-41]

Ozone was generated by using Ozomax OZO 2 VTTL ozone generator from oxygen. Applied ozone dose was measured by using potassium iodide (KI) method [13] based on feeding ozone gas inlet into KI solutions for a certain time and titration of those solutions with sodium thiosulfate. Applied ozone dose used in the reactions was measured before the experiments to be sure that the ozone dose remained constant for different runs. Average applied ozone dose was measured as 115 mg/min.L with an error of $\pm 5\%$ giving the amount of ozone gas fed into one liter of solution in a minute(Appendix 1). A photograph of samples taken during an experimental run and the schematic presentation of the experimental apparatus are given in Figure 3.2 and Figure 3.3, respectively.



Figure 3.2 Samples that were taken from the reactor during an experimental run. (ozonation of Remazol brilliant blue R).

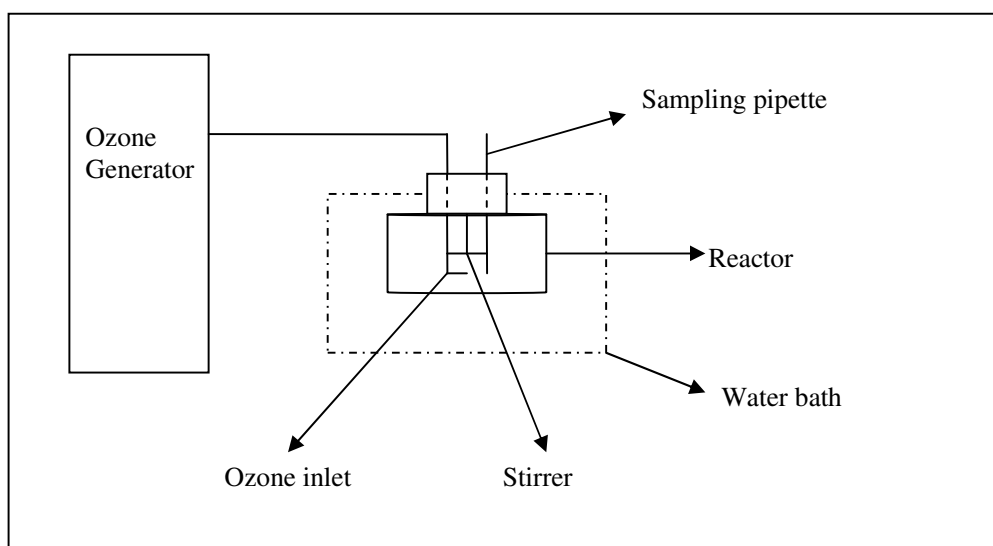


Figure 3.3 Schematic presentation of the system used.

3.3 Experimental Parameters

There are several parameters affecting the ozonation reactions. Reactant species and the ozone mass transfer are the main important parameters affecting the ozonation reactions. Talking about the reactant species it is very important whether the target polluting organic material undergoes reaction by direct ozonation with molecular

ozone or by indirect ozonation with hydroxyl radicals. On the other hand mass transfer is related with the amount of ozone fed into the system and the hydrodynamic characteristics of the system. For example in a semi-batch reactor ozone dosage and stirring speed can be effective on mass transfer while added catalyst material can be effective on the mechanism of the reactions between ozone and reactant species. Solution pH can be given as an example of a parameter that affects both of these factors.

Experimental parameters that could be effective on the ozonation process in this study can be listed as:

- Initial dye concentration
- Catalyst dosage (copper sulfide or iron supported on alumina)
- Temperature
- Ozone dosage
- pH of the dye solution to be treated
- Stirrer speed

Experimental variables selected during this study can be listed as:

- Initial dye concentration
- pH of the dye solution to be treated
- Addition and dosage of the CuS added to the reaction medium
- Addition of iron impregnated catalyst to the reaction medium

Initial dye concentration has been found effective on reaction rates of ozonation reactions [30]. The effect of initial dye concentration was studied in non-catalytic and catalytic ozonation processes, for RBBR and RB-5 solutions.

pH is one of the most important parameters in the ozonation process since it affects the ozone and hydroxyl radical concentrations in the reaction medium [1,4]. Solution pH values were investigated as 3, 7 and 10 which were adjusted by using phosphate

buffers ($\text{KH}_2\text{PO}_4/\text{HCl}$, $\text{KH}_2\text{PO}_4/\text{NaOH}$ and $\text{K}_2\text{HPO}_4/\text{NaOH}$). Solution pHs were monitored with a WTW pH 330 i pH meter and adjusted by adding 0.1M NaOH during the reaction when it was necessary. For the runs conducted at $\text{pH} = 10$, addition of NaOH during the reaction was required.

Catalytic runs were also conducted in order to investigate the effects of the catalysts used on the ozonation of each dye solution. As mentioned in Section 2.3.2, there are several works on catalytic ozonation increasing the ozonation efficiency by increasing the oxidation potential of the reaction medium.

3.4 Experimental Strategy

Experiments conducted can be divided into four parts. In the first part effects of the parameters on sole ozonation which are initial dye concentration and solution pH were investigated. In the second part, effect of CuS addition and effect of CuS dosage on ozonation of either RBBR or RB-5 dye solutions having different initial dye concentrations and solution pHs were investigated. Third part comprised synthesis of another catalyst to be tested and its application in the ozonation of RB-5 solutions having different solution pHs. The last part of the work includes the ozone absorption – decomposition experiments with mathematical modeling of the system.

3.4.1 Investigation of Effects of the Experimental Variables on Ozonation

This set of experiments was both conducted with RBBR and RB-5 solutions:

Investigated Parameters

- Initial dye concentrations: 100, 400 and 800 mg/L
- pH of the solutions to be treated: 3, 7, 10

Ozonation conditions

- Applied ozone dose: 115 mg/min.L
- Catalyst dosage: no catalyst

- Reaction time: 80 min of ozonation

Analyses conducted

- TOC
- Dye concentration
- Dissolved ozone concentration

3.4.2 Investigations of Effects of the CuS Addition on Ozonation

This set of experiments was both conducted with RBBR and RB-5 solutions:

Investigated Parameters

- Initial dye concentrations: 100, 400 and 800 mg/L
- pH of the solutions to be treated: 3, 7, 10
- CuS addition

Ozonation conditions

- Applied ozone dose: 115 mg/min.L
- Catalyst dosage: indicated in the results section for each specific run conducted for examining the effect of the catalyst dosage.
- Reaction time: 80 min of ozonation

Analyses conducted

- TOC
- Dye concentration
- Dissolved ozone concentration
- Copper concentration in the treated water (for some experiments)

3.4.3 Preparation and Test of Fe/Al₂O₃ Catalyst on Ozonation

This set of experiments was conducted with only RB-5 solutions to test the applicability of the catalyst synthesized. These experiments can be divided into two namely preparation and characterization of the catalyst, and the application of the prepared catalyst in the dye ozonation.

Preparation and Characterization of the Catalyst

Impregnation of Iron on γ -Alumina:

The supported catalyst FeO/Al₂O₃ was prepared by the impregnation method with an aqueous solution of iron chloride on γ -alumina bought from DamLa Kimya. Alumina particles were bought as pellets but became powder during the stirring and impregnation step. Preparation steps can be listed as;

- Drying of fresh Al₂O₃ at 120°C in order to evaporate water
- Cooling in a desicator to room temperature
- Weighting the Al₂O₃ (20 g)
- Adding the Al₂O₃ to 100 mL de-ionized water and mixing for 3 h
- Calculating the FeCl₃.6H₂O amount that will correspond to 15 % (w/w) Fe in alumina, and preparing a solution that will be added into the solution of Al₂O₃ (342 g/L FeCl₃.6H₂O)
- Adding 50 mL of the prepared solution of FeCl₃.6H₂O to Al₂O₃ dropwise while mixing
- Mixing of the solution for 48 h
- Evaporating the solution at 60°C on hot plate
- Calcination in static air at 450°C for 8 h

Characterization of Fe/Al₂O₃

In order to observe the catalyst's components, surface area and structure following analyses were conducted:

- X-ray diffraction (XRD)
- Energy dispersive spectroscopy (EDS)
- BET Surface area analysis

Ozonation Tests

Investigated Parameters

- pH of the solutions to be treated: 3, 7, 10
- Catalyst addition

Ozonation conditions

- Applied ozone dose: 115 mg/min.L
- Catalyst dosage: 1 g/L
- Reaction time: 80 min of ozonation
- Initial dye concentration: 100 mg/L

Analyses conducted

- TOC
- Dye concentration
- Dissolved ozone concentration
- Iron concentration in the treated water

3.4.4 Absorption - Decomposition Experiments and Modeling of the Ozonation Reactions

In the experimental part of this section ozone was fed into water and increase in the amount of the dissolved ozone was monitored by indigo method in order to estimate the mass transfer coefficient; after equilibrium was reached, ozone feed was stopped and self decomposition of the dissolved ozone in the water was monitored in order to estimate the decomposition rate constant of ozone.

Investigated Parameters

- pH of the solutions to be treated: 3, 7, 10

Ozonation conditions

- Applied ozone dose: 115 mg/min.L
- Catalyst dosage: no catalyst
- Reaction time: indicated in the Results Section
- Initial dye concentration: no dye

Analyses conducted

- Dissolved ozone concentration

3.5 Analytical Methods

Indigo colorimetric method [39-41] was used to determine the residual ozone concentrations in the liquid phase by using a Hitachi U-3010 spectrometer at a wavelength of $\lambda = 600$ nm. Dye concentrations were also measured by using the same spectrometer at the wavelengths of $\lambda = 590$ nm and $\lambda = 595$ nm by the help of calibration curves obtained using the standard solutions of the dyes RBBR and RB-5, respectively. TOC measurements of the collected samples were done by using a Shimadzu TOC-V_{CPH/CPN} total organic carbon analyzer. COD analyses were conducted by using a WTW Cr-3000 thermoreactor and a Hach DR-2010

spectrophotometer. COD values measured are given in the Appendix A.4 and used for the comparison with some of the TOC values measured in Appendix B.2. Inlet ozone concentration of the gas phase was also measured by trapping ozone in KI solutions. Measured inlet ozone concentrations are given in Appendix A.1, Table A.1.

CHAPTER 4

RESULTS

4.1 Brief Information about Reaction Rate Analysis

Ozonation kinetics was investigated by assuming a constant ozone concentration due to the excess ozone in the solution. Ozonation rate expression was written by taking the ozone concentration term as constant and including it in the reaction rate constant expression as below:

$$\frac{dC_{dye}}{dt} = k' C_{dye}^n \quad (4.1)$$

where: $k' = k.C_{ozone}$

Assuming $n = 1$ as reported frequently in the literature [22] for the ozonation experiments and by integrating Eqn (4.1), Eqn 4.2 can be obtained:

$$\ln\left(\frac{C_d}{C_{d,i}}\right) = k't \quad (4.2)$$

according to Eqn (4.2), a plot of $\ln\left(\frac{C_d}{C_{d,i}}\right)$ vs. time should give a line having a slope of k' , this will prove that the reaction is pseudo first order.

Both non-catalytic ozonation data fitted well to the pseudo first order kinetics. Plots giving the percent dye removals or pseudo first order reaction rate analyses which

are plots of $\ln (C_d/C_{d,i})$ vs. time are presented in the proceeding sections. Determined pseudo first order reaction rate constants (apparent rate constants) are also tabulated for each case presented in the results section. Figure 4.20 can be given as an example for this analysis. Percent dye removals are given in the part (a) and the linear plot of $\ln (C_d/C_{d,i})$ vs. time is given in the part (b). Besides this mentioned figure, the dye removals are presented as either percent dye removals or linear presentations of $\ln (C_d/C_{d,i})$ vs. time plots.

4.2 Effect of Experimental Variables on Ozonation of Model Dyes

4.2.1 Effect of Initial Dye Concentration

It was found in the literature that an increase in the initial dye concentration decreased the reaction rate [30, 42]. In this work the same result was also observed. The effect of the initial dye concentration on ozonation depending on the dye used was investigated. The effect of initial dye concentration on the dye and TOC removals were determined for the ozonation of RBBR and RB-5 dye solutions. Percent dye removals measured in the runs conducted with RBBR dye solutions are given in Figures 4.1-4.3 where estimated pseudo first order reaction rate constants are given in the Table 4.1.

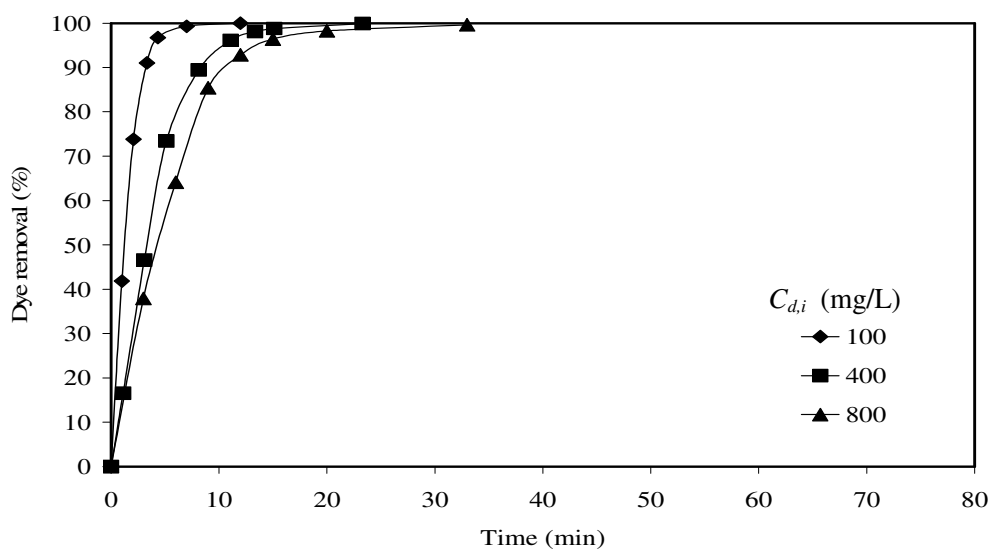


Figure 4.1 Effect of initial dye concentration on percent dye removal. pH = 3, dye = RBBR, ozone dose = 115 mg/L.min, $[\text{PO}_4^{3-}] = 20 \text{ mM}$

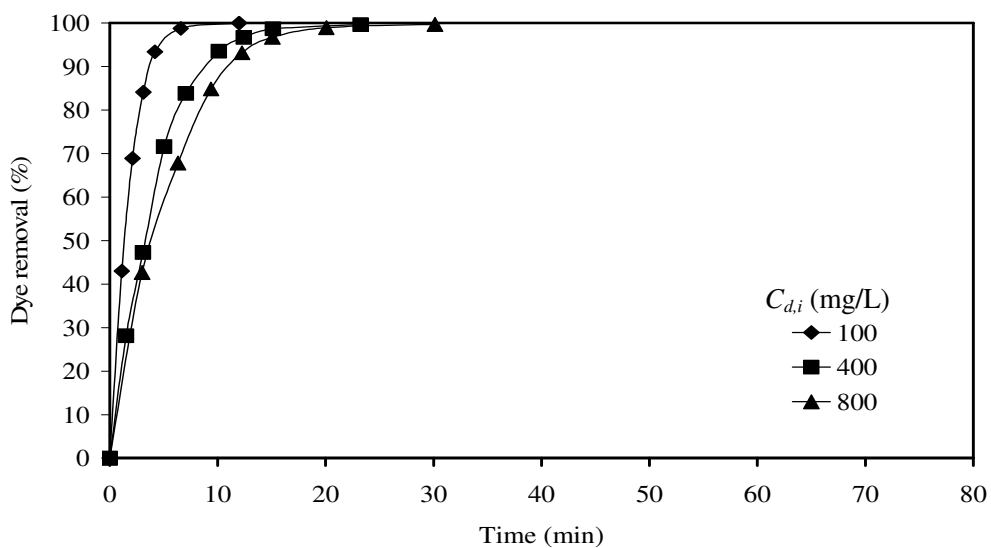


Figure 4.2 Effect of initial dye concentration on percent dye removal. pH = 7, dye = RBBR, ozone dose = 115 mg/L.min, $[\text{PO}_4^{3-}] = 20 \text{ mM}$.

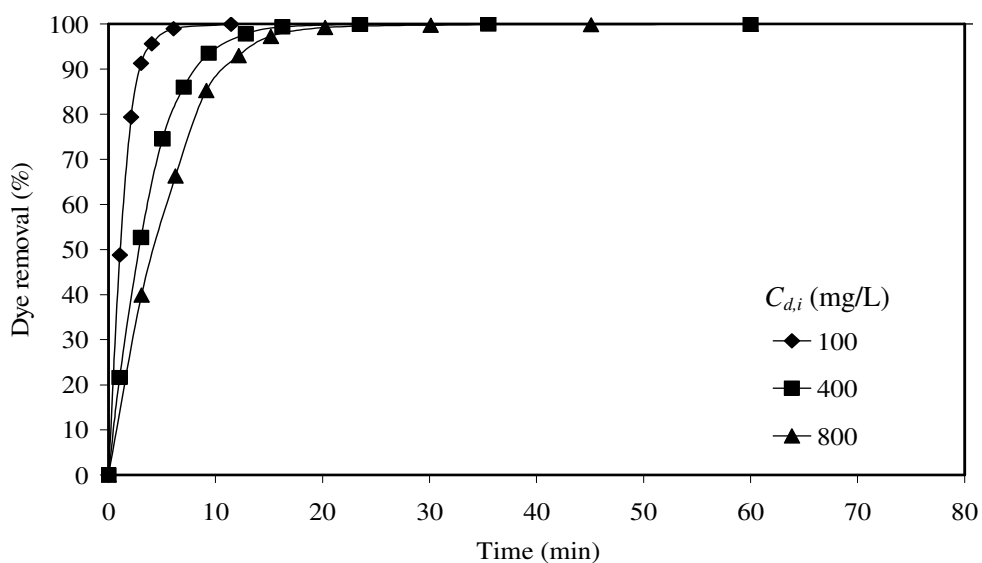


Figure 4.3 Effect of initial dye concentration on percent dye removal. pH = 10, dye = RBBR, ozone dose = 115 g/L.min, $[\text{PO}_4^{3-}] = 20 \text{ mM}$

Table 4.1 Pseudo first order rate constants and regression constants (R^2) for RBBR solutions at different $C_{d,i}$ and pH values

pH	$C_{d,i}(\text{mg/L})$	$k'(\text{min}^{-1})$	R^2
3	100	0.72	0.99
	400	0.27	0.99
	800	0.21	0.99
7	100	0.64	0.99
	400	0.27	0.99
	800	0.22	0.99
10	100	0.77	0.99
	400	0.29	0.99
	800	0.22	0.99

It was observed that the reaction rates decreased logarithmically as the initial dye concentration increased at all the studied pH. Same kind of behavior was also reported in the literature [42]. Changes in the pseudo first order reaction rates with changing initial dye concentrations are given in Figures 4.4 to 4.6. The relation

between pseudo first order reaction rates and initial dye concentrations are also given in Table 4.2. Figures 4.4-4.6 give the relation between initial dye concentration and apparent reaction rate constant.

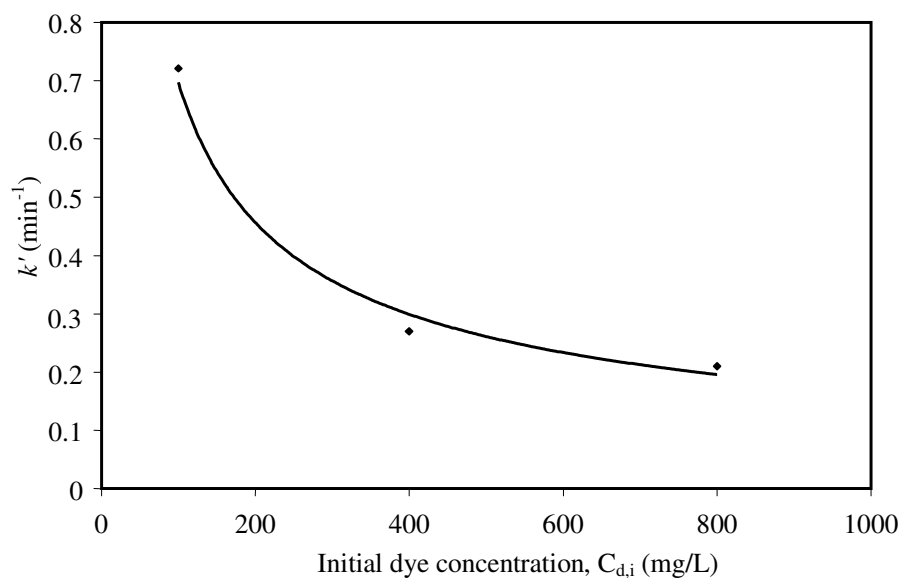


Figure 4.4 Changes in pseudo first order reaction rate constant due to changing initial dye concentration. pH = 10, dye =RBBR, $[\text{PO}_4^{3-}] = 20 \text{ mM}$.

Table 4.2 *Equations obtained for the changes in pseudo first order reaction rate constants due to the change in initial dye concentrations.

pH	Equation	R^2
3	$k' = 11.5 C_{d,i}^{-0.60}$	0.98
7	$k' = 7.1 C_{d,i}^{-0.53}$	0.98
10	$k' = 12.8 C_{d,i}^{-0.62}$	0.99

* Equations obtained by using MS Excel program based on least squares method.

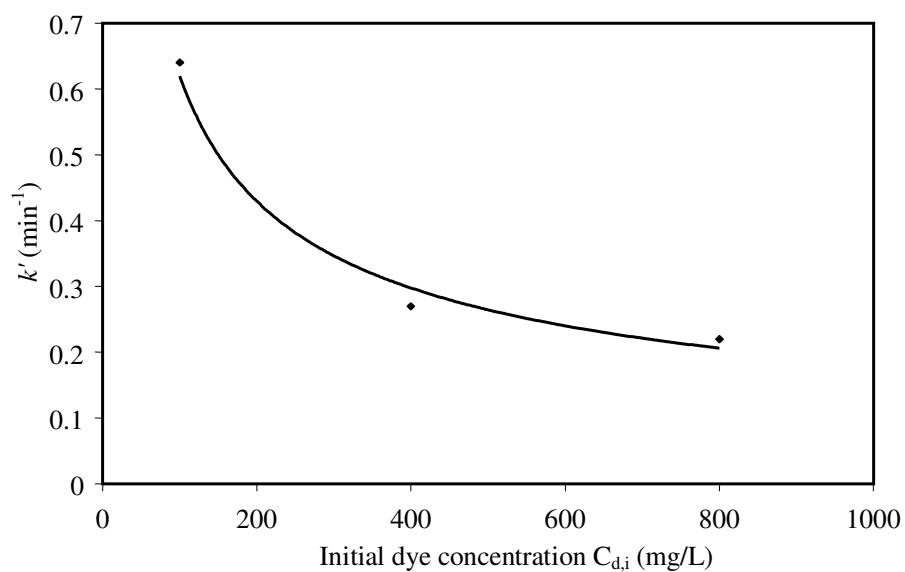


Figure 4.5 Changes in pseudo first order reaction rate constant due to changing initial dye concentration. pH = 7, dye =RBBR, $[\text{PO}_4^{3-}] = 20 \text{ mM}$.

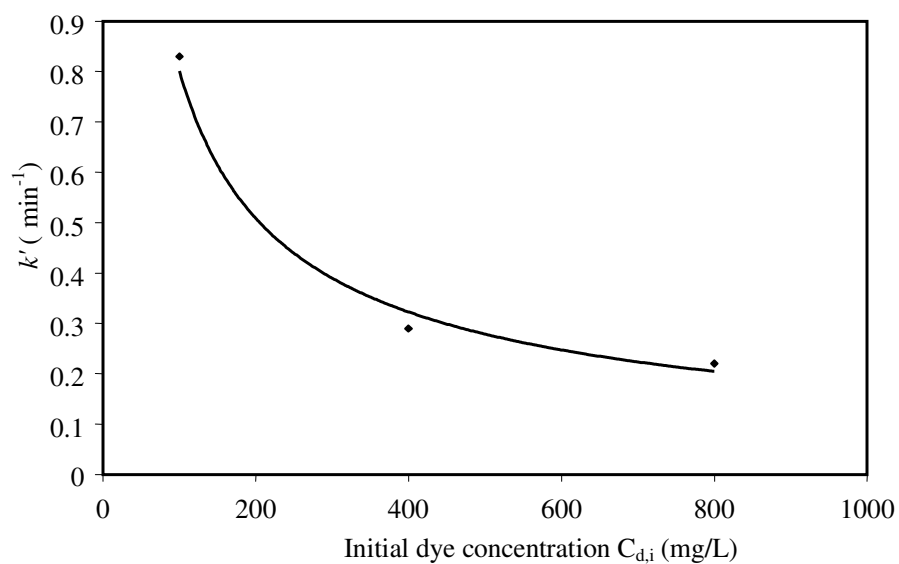


Figure 4.6 Changes in pseudo first order reaction rate constant due to changing initial dye concentration. pH = 3, dye =RBBR, $[\text{PO}_4^{3-}] = 20 \text{ mM}$.

The effect of initial dye concentration on pseudo first order reaction rate constants (or apparent rate constants) was found similar to those in the literature [42] and these rate constants were found to decrease logarithmically with the increasing initial dye concentration as given in Table 4.2. Considering the Arrhenius equation, reaction rate constant is a function of temperature only. This kind of a relationship as seen in Table 4.2 might be explained by the indirect effect of dissolved ozone concentration on k' with the increasing initial dye concentration. Also the difference in the reaction rates were explained by the help of two film theory in some researches, as the reaction between dye and ozone molecules occurs more rapidly in the liquid film during ozonation of the dye solutions having lower initial dye concentrations. On the other hand, the ozonation reaction of dye solutions having higher initial dye concentrations occurs both within the liquid film and also in the bulk liquid [43, 44]. Besides the reaction rate constants estimated in these runs were apparent rate constants which are based on the absorbance measured at a wavelength. Thinking about the reaction medium, too many side reactions besides dye ozonation occur, where the types and the rate of occurrence of the side reactions might be effective on the apparent de-colorization rates changing with the increasing initial dye concentration. In addition to the dye removals, also TOC removals were measured for the above explained runs and presented in Figures 4.7-4.9.

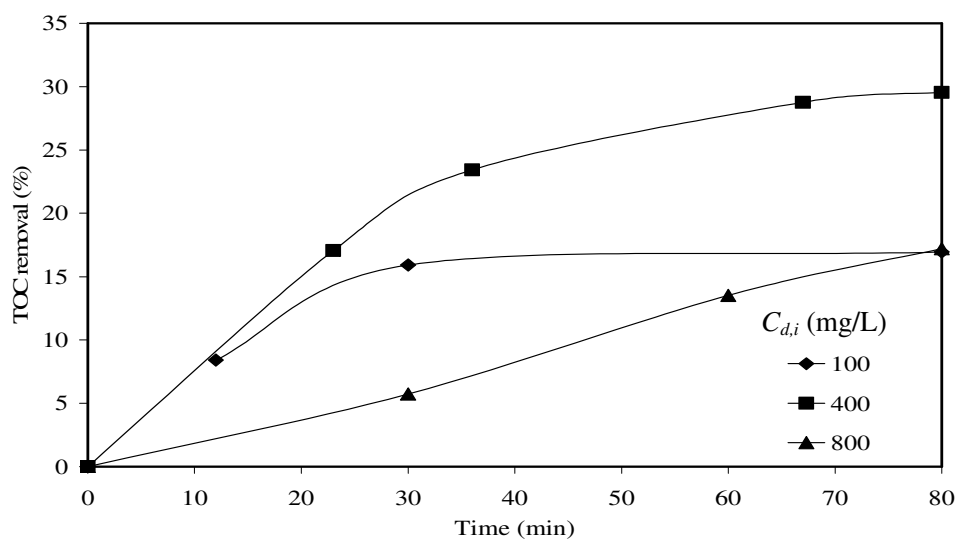


Figure 4.7 Effect of initial dye concentration on percent TOC removal. pH = 3, dye = RBBR, ozone dose = 115 mg/L.min, $[\text{PO}_4^{3-}] = 20$ mM.

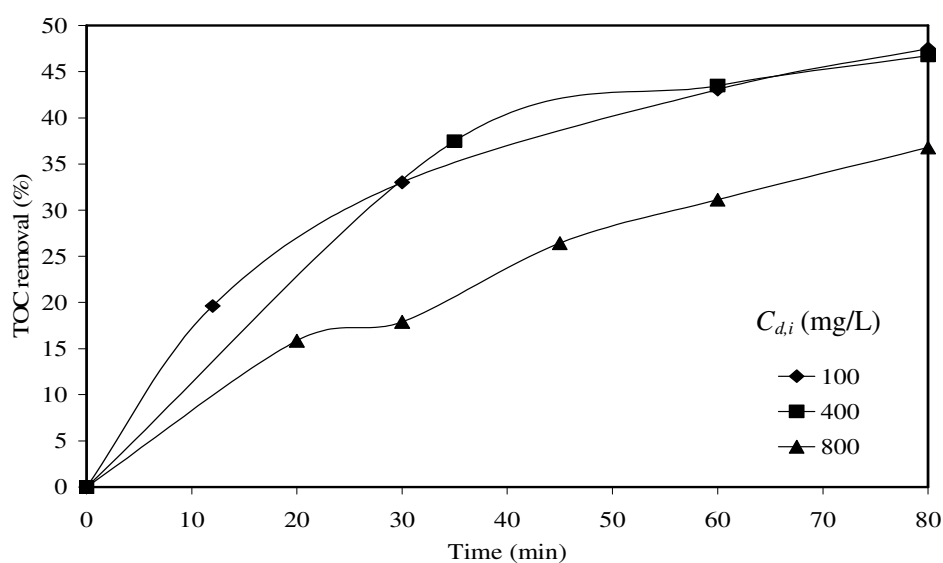


Figure 4.8 Effect of initial dye concentration on percent TOC removal. pH = 7, dye = RBBR, ozone dose = 115 mg/L.min, $[\text{PO}_4^{3-}] = 20$ mM.

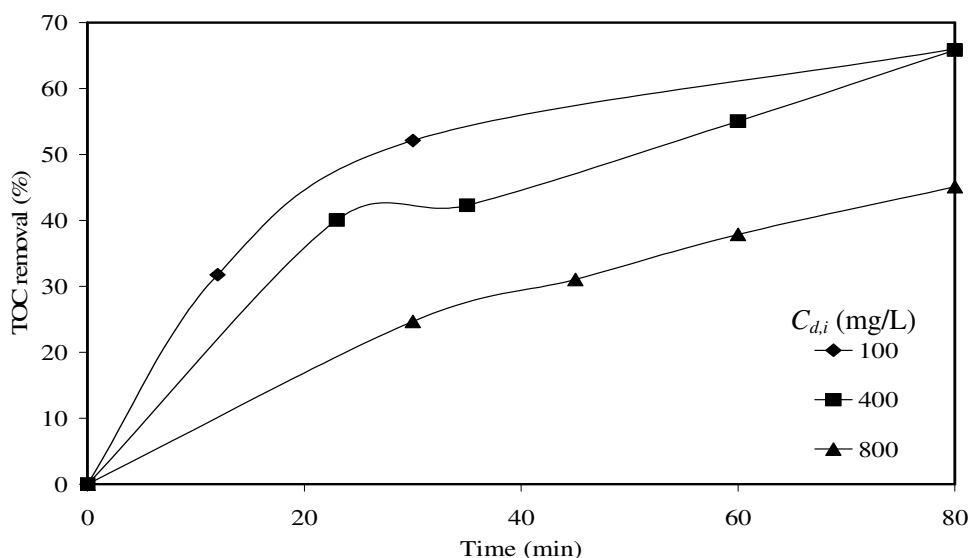


Figure 4.9 Effect of initial dye concentration on percent TOC removal. pH = 10, dye = RBBR, ozone dose = 115 mg/L.min, $[\text{PO}_4^{3-}] = 20$ mM.

Effect of initial dye concentration on TOC removal was observed only for the runs conducted with an initial dye concentration of 800 mg/L for RBBR solutions. For the runs conducted with initial dye concentrations of 100 and 400 mg/L, final TOC removals were found as same which indicated that reaction time of 80 min was enough to complete the ozonation reactions. For the runs conducted at 800 mg/L in all cases the TOC removals were found to be lower at the end of the reaction time (80 min.). This can be explained with the incomplete oxidation of side products by ozone. From Figures 4.7 to 4.9 it can be seen that TOC reduction rate became very slow for the runs conducted at the initial dye concentrations of 100 and 400 mg/L after reaction time of about 30 minutes while for the runs conducted at 800 mg/L TOC reduction still had an increasing trend. Therefore, it might be concluded that almost the same TOC removals could be obtained for different initial dye concentrations after a sufficient reaction time. For the runs conducted with 100 and 400 mg/L initial dye concentrations similar, TOC removals were obtained after almost 40 min of reaction time. TOC removals can be related with dye removal rates

TOC removals were observed to increase after the completion of color removal. A more detailed discussion is made with the help of Figures 4.17 to 4.19.

It is also notable that TOC removals observed for the run conducted with an initial dye concentration of 400 mg/L were found to be higher than those obtained for the run conducted at an initial dye concentration of 100 mg/L at pH =3. This can be explained by the type and amount of the side products generated and pathway of the chain reactions occurring in the reaction due to the ratio of ozone to initial dye concentration. For example, high amounts of oxalic acid might be generated as a side product with this (ozone/initial dye) ratio. In this case the ratio is 115 mg/L ozone to 100 mg/L initial dye concentration.

The same procedure was also applied to the dye solutions of RB-5. The effect of initial dye concentrations on TOC and dye removals was investigated. Same behavior was also observed for the RB-5 dye solutions. Reaction rates logarithmically decreased with the increasing initial dye concentrations of the dye solutions ozonated. Comparing the observed reaction rates in the runs conducted for RBBR solutions with those of RB-5 solutions, the lower reaction rates were observed in the former than those in the latter conducted with RB-5 solutions. This difference also caused different behavior in the TOC removals observed for the runs conducted with the RB-5 solutions. Figures 4.10-12 represents the % dye removals while pseudo first order reaction rate constants are given in the Table 4.3. The relationships between initial dye concentrations and observed reaction rate constants are also given in the Figure 4.13 and Table 4.4.

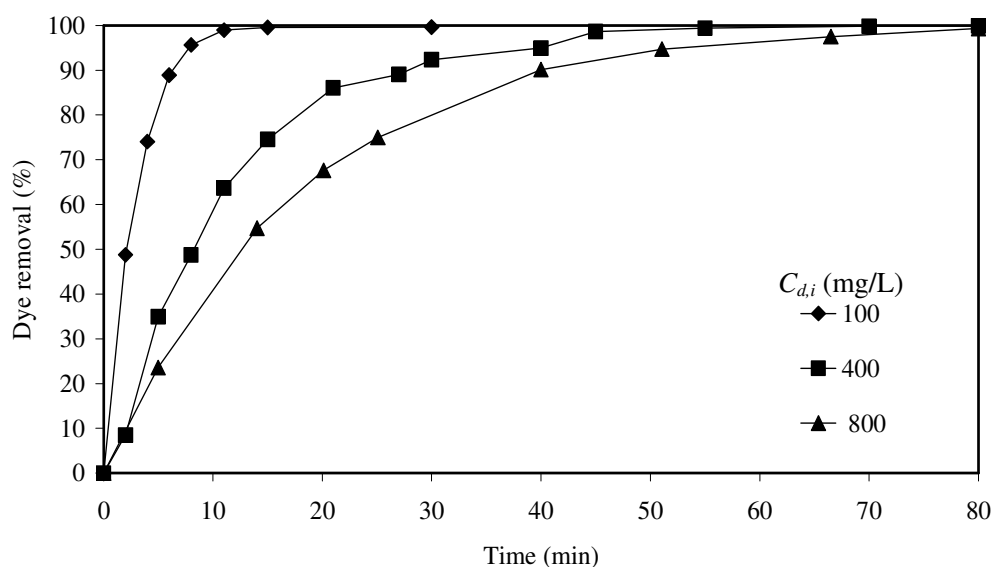


Figure 4.10 Effect of initial dye concentration on percent dye removal. pH = 3, dye= RB-5, ozone dose = 115 mg/L.min, $[\text{PO}_4^{3-}] = 20$ mM.

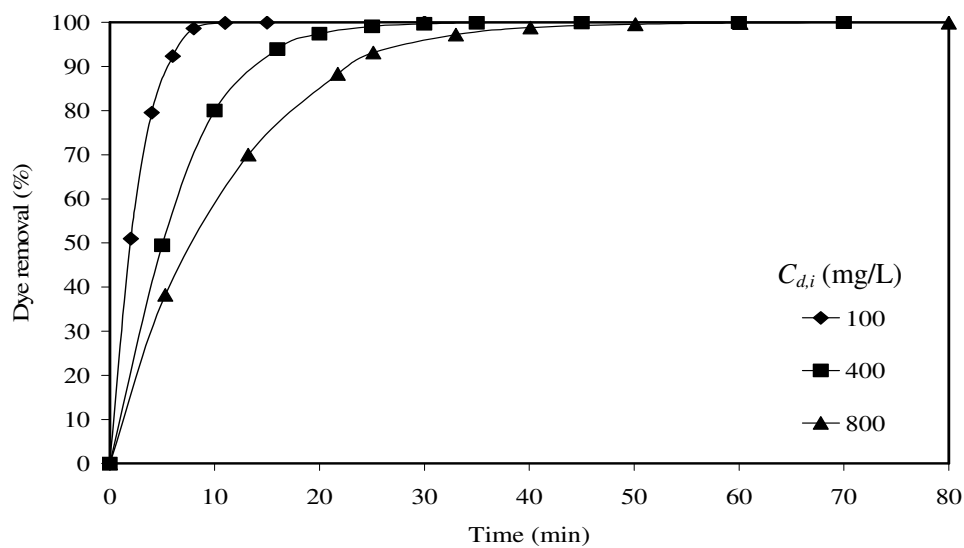


Figure 4.11 Effect of initial dye concentration on percent dye removal. pH = 7 dye= RB-5, ozone dose = 115 mg/L.min, $[\text{PO}_4^{3-}] = 20$ mM.

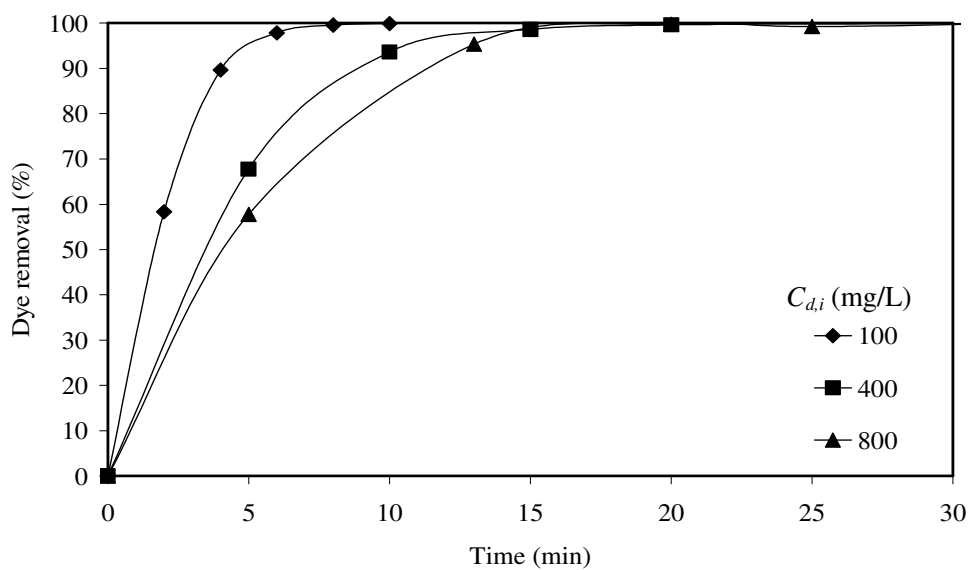


Figure 4.12 Effect of initial dye concentration on percent dye removal. pH = 10 dye= RB-5, ozone dose = 115 mg/L.min, $[\text{PO}_4^{3-}] = 20$ mM.

Table 4.3 Pseudo first order rate constants and R^2 values for RB-5

pH	$C_{d,i}$ (mg/L)	k' (min^{-1})	R^2
3	100	0.35	0.99
	400	0.09	0.99
	800	0.06	1.00
7	100	0.41	0.99
	400	0.18	0.99
	800	0.11	0.99
10	100	0.60	0.98
	400	0.27	0.99
	800	0.20	0.98

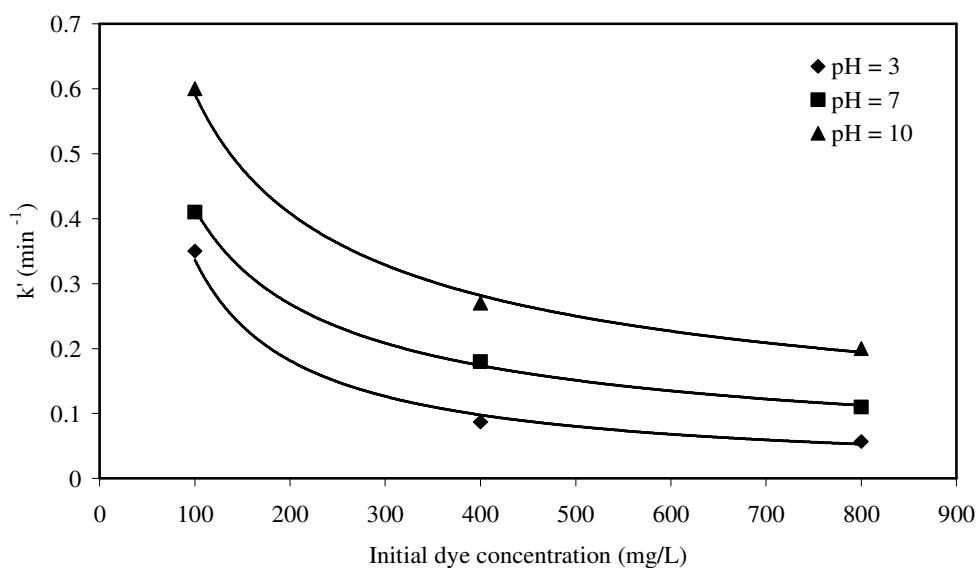


Figure 4.13 Changes in pseudo first order reaction rate constants due to changing initial dye concentrations. Dye =RB-5, $[\text{PO}_4^{3-}] = 20 \text{ mM}$.

Effect of initial dye concentration on the dye removal in the ozonation of RB-5 solutions was found similar to that of RBBR solutions as mentioned before. The fitted equations for the pseudo first order reaction rate constant changing as a function of initial dye concentration of RB-5 solutions at different pH and correlation coefficients (R^2) are given in Table 4.4.

Table 4.4 Equations obtained for the changes in pseudo first order reaction rate constants due to the change in initial dye concentration.

pH	Equation	R^2
3	$k' = 20.4 C_{d,i}^{-0.89}$	0.99
7	$k' = 7.5 C_{d,i}^{-0.63}$	1.00
10	$k' = 6.9 C_{d,i}^{-0.54}$	1.00

TOC removals measured during the runs conducted are given in Figures 4.14-4.16. It was observed that increasing the initial dye concentration decreased the TOC

removals at each initial RB-5 concentration unlike the runs conducted with RBBR solutions where only the runs conducted with an initial dye concentration of 800 mg/L yielded different behavior in terms of TOC removals.

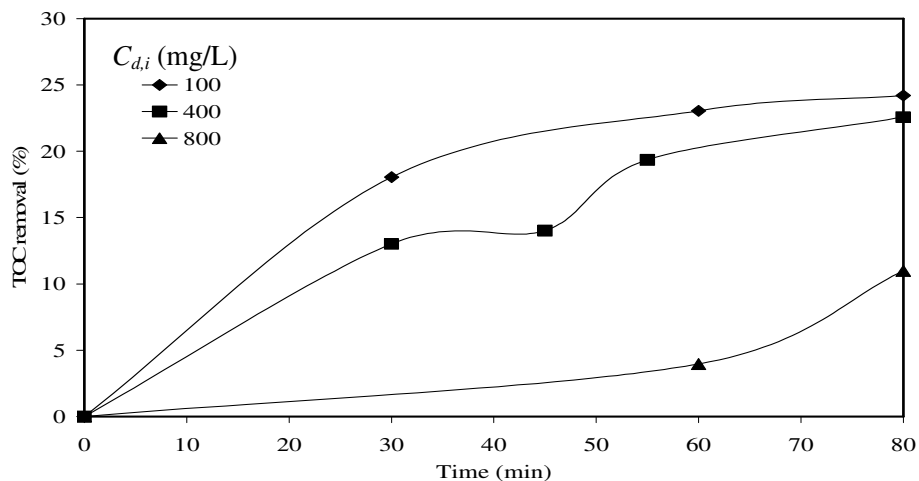


Figure 4.14 Effect of initial dye concentrations on percent TOC removals. pH = 3, dye = RB-5, ozone dose = 115 mg/L.min, $[\text{PO}_4^{3-}] = 20$ mM.

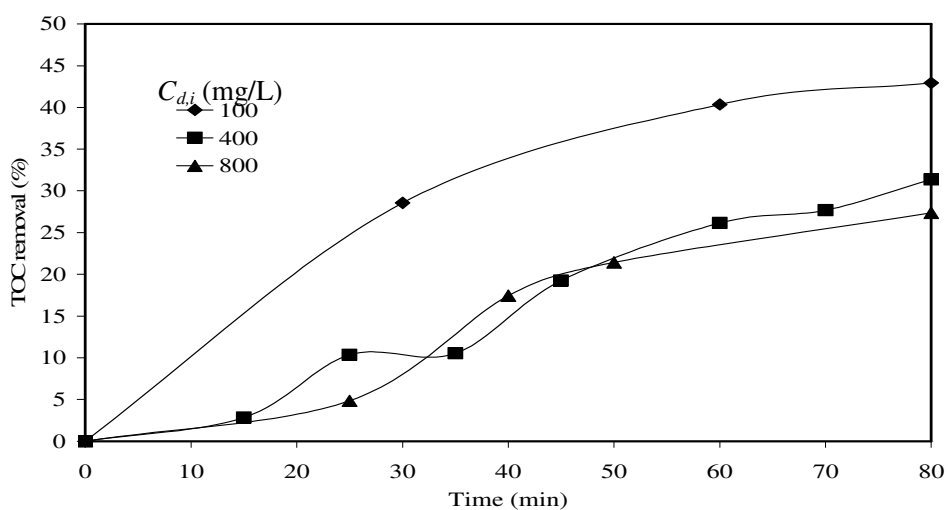


Figure 4.15 Effect of initial dye concentrations on percent TOC removals. pH = 7, dye = RB-5, ozone dose = 115 mg/L.min, $[\text{PO}_4^{3-}] = 20$ mM.

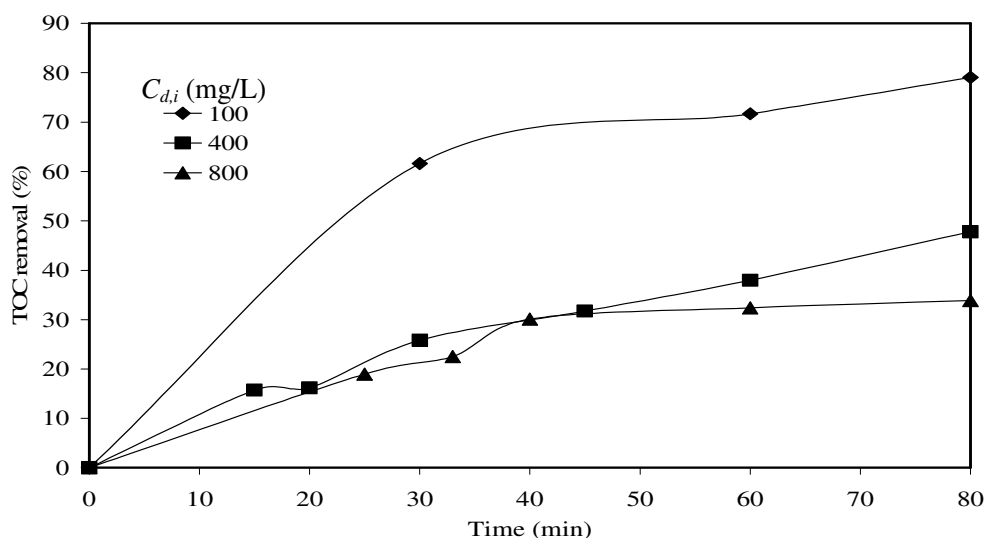


Figure 4.16 Effect of initial dye concentrations on percent TOC removals. pH = 10, dye = RB-5, ozone dose = 115 mg/L.min, $[\text{PO}_4^{3-}] = 20$ mM.

The decrease in the TOC removals can be explained by the slower reaction kinetics. Increasing the initial dye concentration resulted in the higher de-colorization time. Increased de-colorization time might result a decrease in the TOC removals due to the decreasing time period left for the oxidation of side products at a final ozonation time of 80 min.

Considering the dye and TOC removal results together it can be seen that the higher TOC removals are obtained after the de-colorization step, therefore it can be said that ozonation of dye solutions occurs in two steps. In the first step, oxidation of larger dye molecules into smaller organic molecules occurs with a limited mineralization; then in the second step, oxidation of these molecules into carbon dioxide and water occurs which results in the decrease of TOC values. Figures 4.17 to 4.19 may be useful to understand these steps.

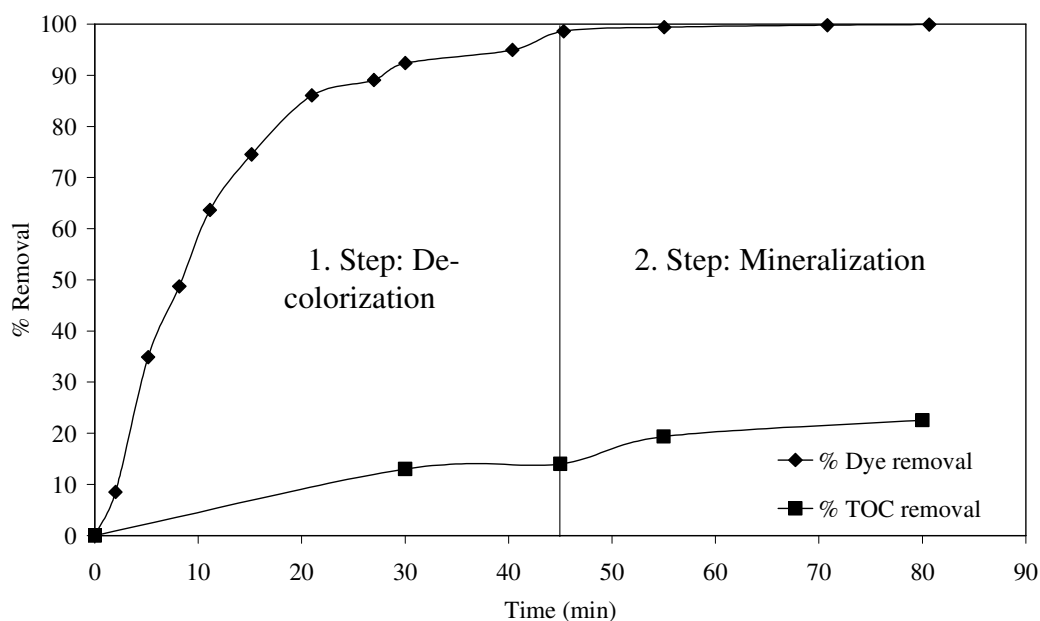


Figure 4.17 Ozonation Steps. Dye : RB-5, pH = 3, $C_{d,i} = 400$ mg/L, ozone dose = 115 mg/L.min, $[\text{PO}_4^{3-}] = 20$ mM.

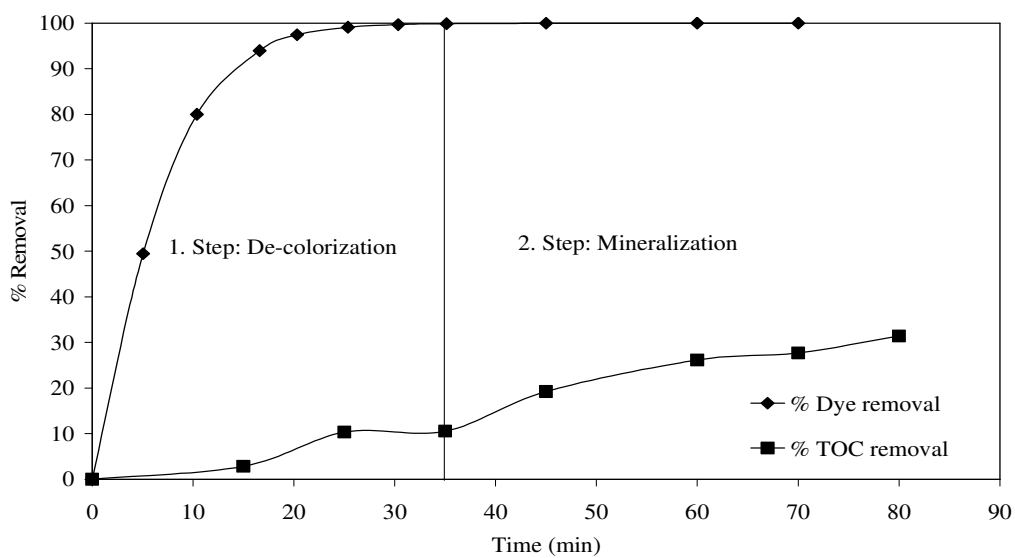


Figure 4.18 Ozonation Steps. Dye : RB-5, pH = 7, $C_{d,i} = 400$ mg/L, ozone dose = 115 mg/L.min, $[\text{PO}_4^{3-}] = 20$ mM.

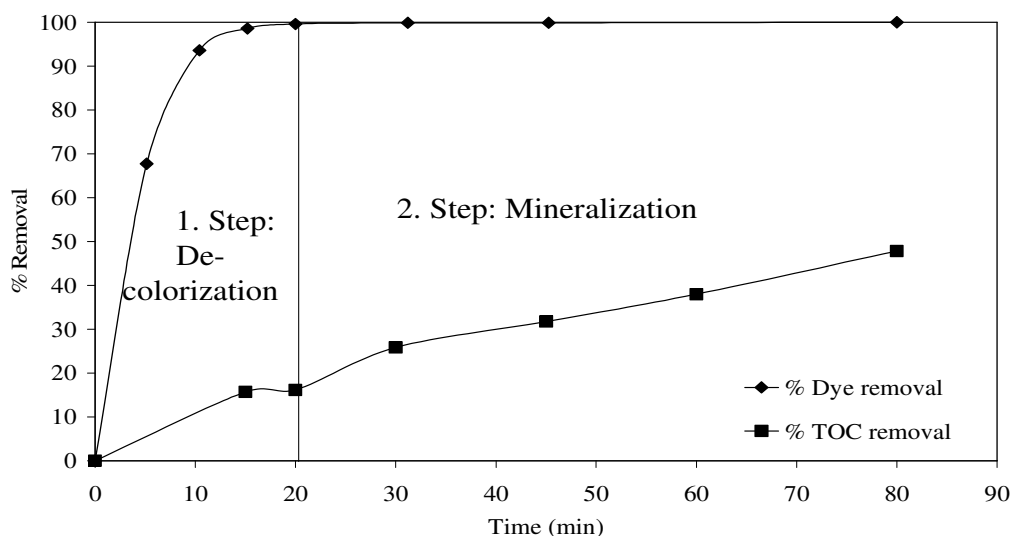


Figure 4.19 Ozonation Steps. Dye : RB-5, pH = 10, $C_{d,i} = 400$ mg/L, ozone dose = 115 mg/L.min, $[\text{PO}_4^{3-}] = 20$ mM.

As it can be seen from Figures 4.17 to 4.19, TOC removals showed an increasing trend after the dye removals reached a value close to 100 %. It can also be realized from these figures that mineralization reactions are still continuing at the time that experiments were ended. It can be seen that TOC removals are increasing with a slope proving that they have not reached an equilibrium removal value. This also explains why the TOC removals were found to be lower for the runs conducted at the initial dye concentrations of 400 and 800 mg/L. In other words, ozonation time of 80 min was not enough to oxidize all the by-products.

The runs conducted with 400 mg/L RB-5 solutions were selected to represent the discussion for the reaction steps. The de-colorization period in these runs was suitable for the observations mentioned above. It was also seen that the de-colorization time decreased and the slope of TOC removal rate increased as the pH of the treated solution increased. The effect of pH will be discussed in more details in the next section, although its effect on TOC removal rate can be seen from Figures 4.17 to 4.19.

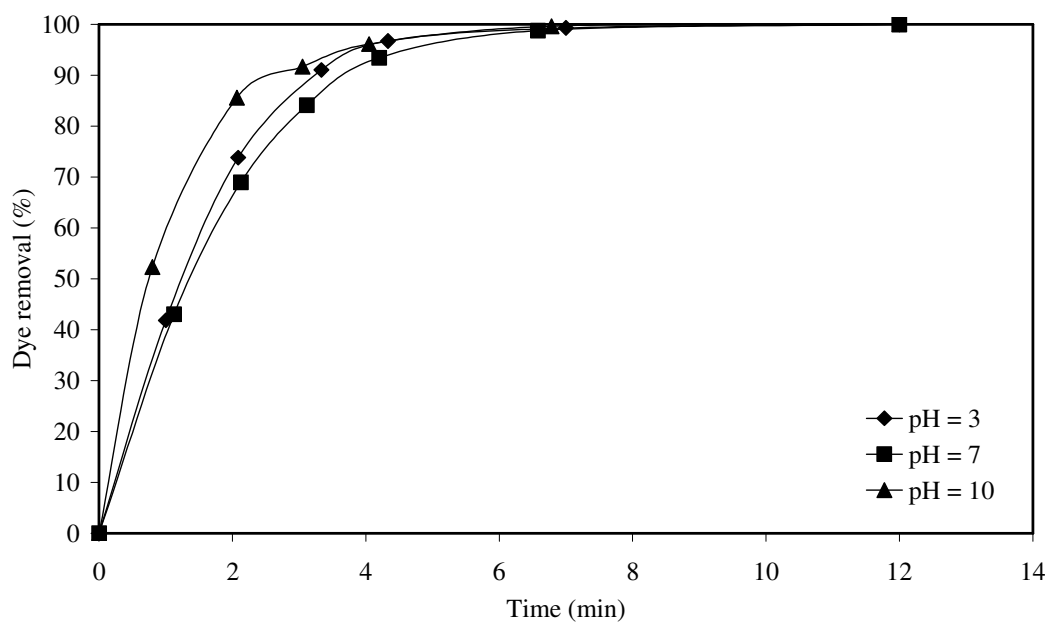
4.2.2 Effect of pH

Solution pH is one of the most important parameters in the ozonation processes. Reaction pathway is determined by solution pH especially for sole ozonation processes. Molecular ozone is the dominant species at acidic conditions in the ozonation reactions while the effect of hydroxyl radicals becomes significant at basic conditions [37]. Effect of pH on the dye removal efficiencies have been found to differ for different dyes having different chemical structures [37]. It is also known that molecular ozone is insufficient for complete mineralization of ozonation by-products [12, 30]. Therefore it is expected to have higher TOC removals as the pH increased. In this case TOC removals increased as pH increased from 3 to 7 and even higher TOC removals were measured when it was increased further to pH = 10.

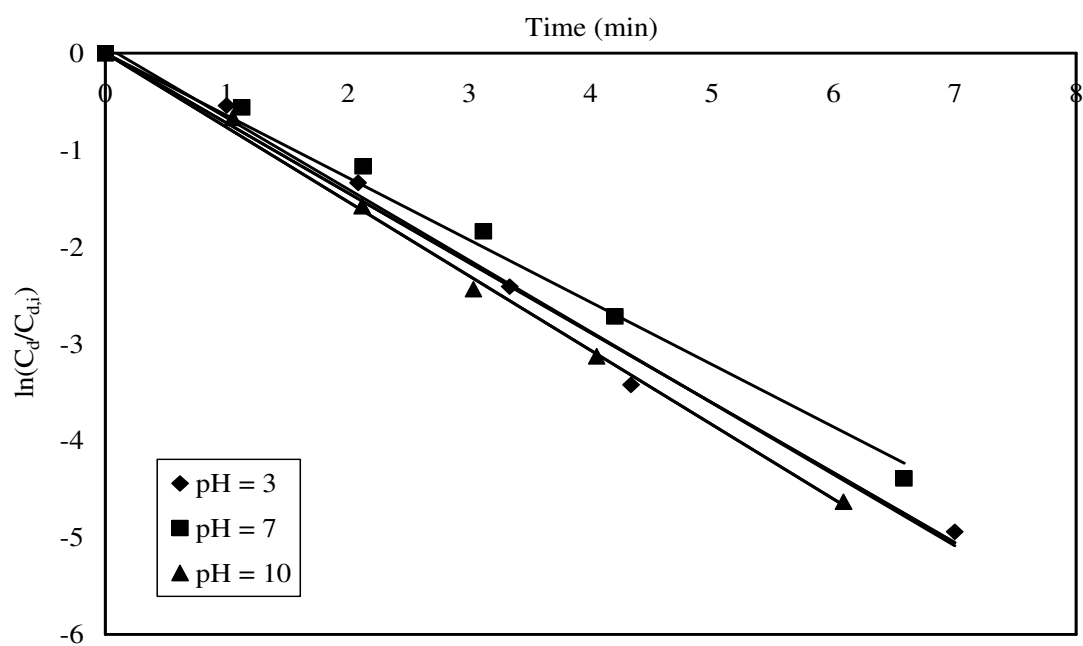
Effect of solution pH on the dye and TOC removals were investigated for the dye solutions at pH values of 3, 7 and 10. Different behavior was observed for the RBBR and RB-5 dye solutions. Solution pH was found to be effective only on TOC removals for the RBBR solutions while significant increases with the increasing pH in both the dye and TOC removals were observed in the RB-5 solutions.

The results for the dye removals are given in Figures 4.20 and 4.21, and TOC removals are shown in Figure 4.22 for the runs conducted at the initial dye concentration of 100 mg/L for both RBBR and RB-5 solutions, while the results of the other runs are listed in Table 4.5.

From Figures 4.20 and 4.21 it can be seen that only the changing solution pH had a significant effect on the ozonation of RB-5 solutions. The pseudo first order reaction rate constants for the reactions conducted are given in Table 4.5.



(a)



(b)

Figure 4.20 Effect of solution pH on dye removal. (a) percent dye removals, (b) pseudo first order reaction rate constant analysis. Dye = RBBR, $C_{d,i} = 100$ mg/L, ozone dose = 115 mg/L.min, $[\text{PO}_4^{3-}] = 20$ mM.

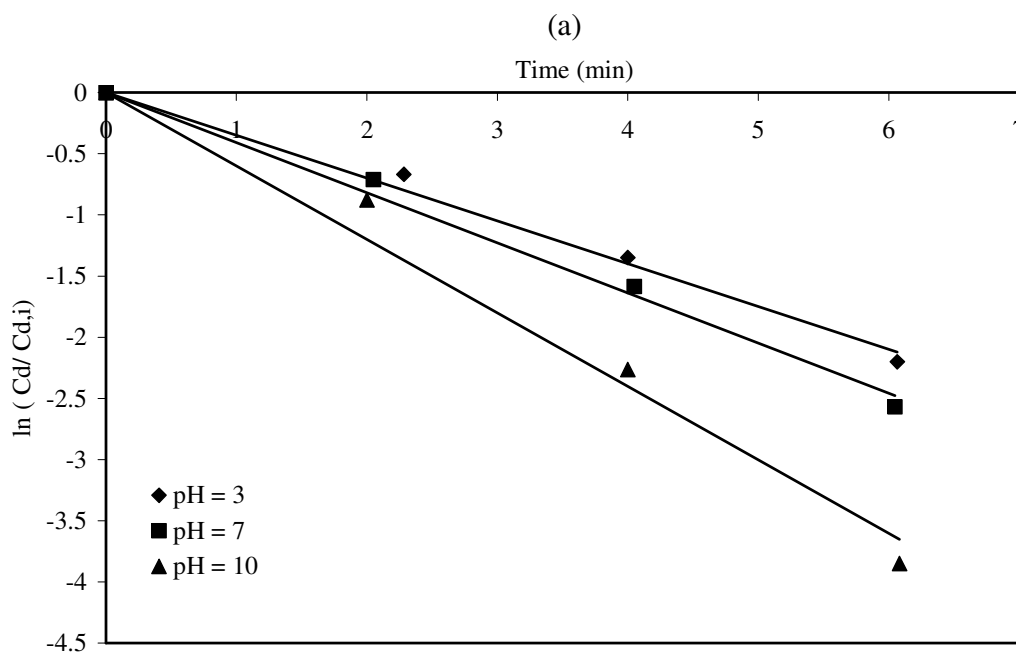
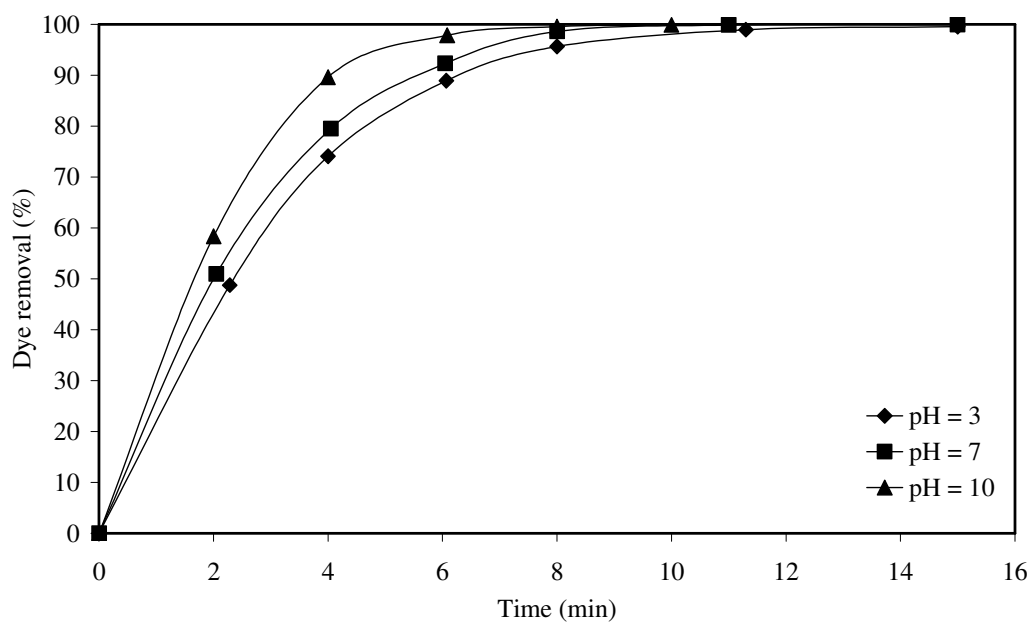


Figure 4.21 Effect of solution pH on dye removal. (a) percent dye removals, (b) pseudo first order reaction rate constant analysis. Dye = RB-5, $C_{d,i} = 100$ mg/L, ozone dose = 115 mg/L.min, $[\text{PO}_4^{3-}] = 20$ mM.

Table 4.5 Pseudo first order rate constants and R^2 values for the pseudo first order reaction rate analysis of ozonation runs conducted.

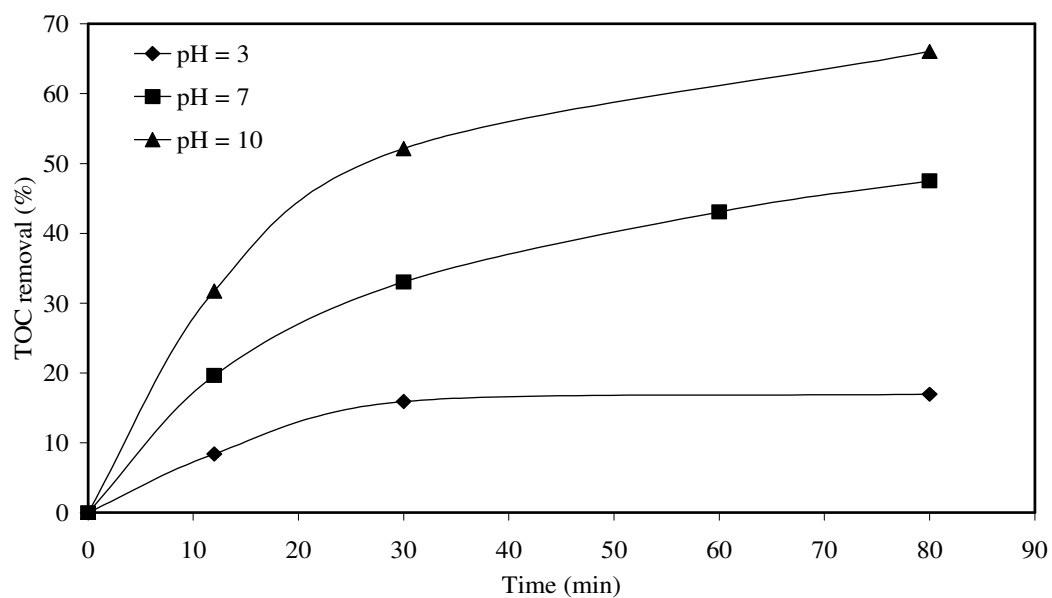
Dye	$C_{d,i}$ (mg/L)	pH	k' values (min ⁻¹)	R^2
RBBR	100	3	0.72	0.99
		7	0.64	0.99
		10	0.77	0.99
	400	3	0.27	0.99
		7	0.27	0.99
		10	0.29	0.99
	800	3	0.21	0.99
		7	0.22	0.99
		10	0.22	0.99
RB-5	100	3	0.35	0.99
		7	0.41	0.99
		10	0.60	0.98
	400	3	0.09	0.99
		7	0.18	0.99
		10	0.27	0.99
	800	3	0.06	1.00
		7	0.11	0.99
		10	0.20	0.98

Figure 4.22 shows the maximum observed TOC removals for the RBBR and RB-5 dye solutions at the conditions chosen especially for the ozone dose applied in these sets of experiments. Increasing the solution pH, increased the TOC removals. Since it is known that molecular ozone is insufficient in the oxidation of ozonation by-products it was expected to have higher TOC removals in the runs conducted at basic conditions. It can also be observed from Figure 4.22 that similar TOC removals were obtained for both the RBBR and RB-5 solutions. In order to make further comments on this situation, a detailed study of by-products produced during the ozonation of the present dye solutions, is needed.

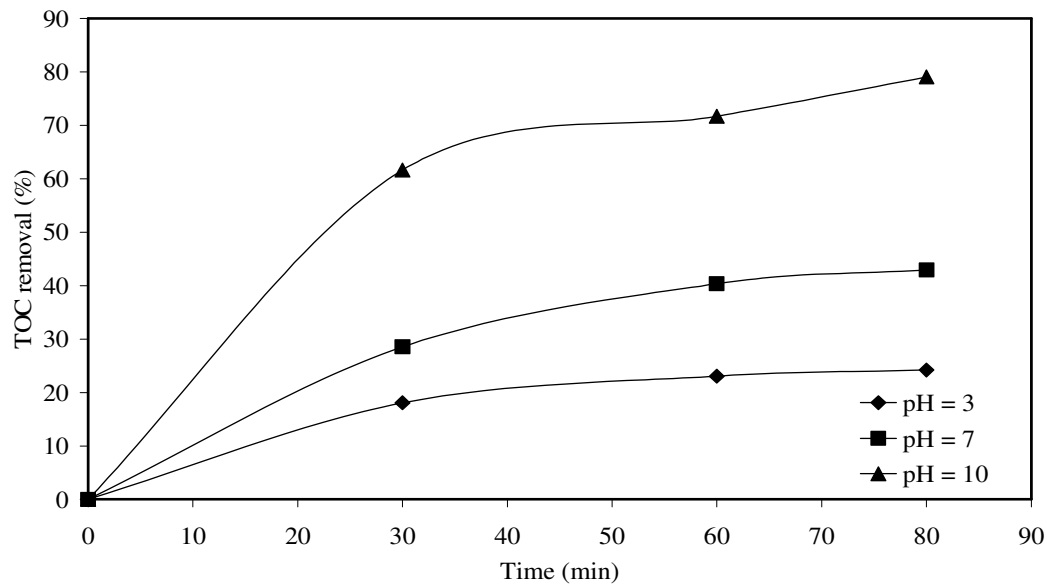
Table 4.5 can be used for summarizing the results of all non-catalytic ozonation experiments. It can be noted that the effect of solution pH on the dye removals of RBBR dye solutions is insignificant especially at the higher initial dye concentrations of 400 and 800 mg/L. This can be explained by the fast reaction between the dye and ozone molecules. Oxidation of dye molecules occurs very fast with molecular ozone [16, 22]. On the other hand ozonation alone was not sufficient for the oxidation of the RB-5 solutions. De-colorization rates were found to be higher at basic solutions where generation of hydroxyl radicals was enhanced. As seen in Table 4.5, pseudo first order reaction rates showed an increasing trend with the increasing solution pH, and the lowest reaction rates were found in the runs conducted with acidic dye solutions where molecular ozone was dominant. These kinds of differences in the ozonation of dye solutions with azo and anthraquinone structures like RB-5 and RBBR respectively were also reported in the literature by Chu et al. [37]. It was also stated that the oxidation via molecular ozone is dominant in ozonation of anthraquinone dyes while oxidation by hydroxyl radicals played an important role in the oxidation of azo dyes [37]. The effect of solution pH was more significant on the TOC removals. TOC removals observed during ozonation of the RBBR and RB-5 solutions are given in Figure 4.22.

The results obtained in this set of experiments showed that hydroxyl radicals played an important role in the oxidation of by-products generated during the ozonation of the dye solutions examined. On the other hand, increasing pH for the RBBR solutions did not improve the de-colorization rate significantly; this observation arose a question about the role of the hydroxyl radicals in the oxidation of the dye molecules. In order to test the effect of hydroxyl radicals on the dye removal of RBBR solutions, sodium carbonate was added to the reaction medium as a carbonate ion source which is known as a scavenger [12]. Sodium carbonate was also used in the literature as a scavenger to stop the radical activity in the ozonation process [37,38]. Dye removal rates were observed to investigate the effect of hydroxyl radicals on the de-colorization of the dye solutions. In order to study the scavenging effect, a RBBR solution at pH = 10 was chosen at an initial dye concentration of 400

mg/L. Basic conditions were set in order to conduct the experiments in a medium where hydroxyl radicals would be present. Results are given in Figure 4.23.

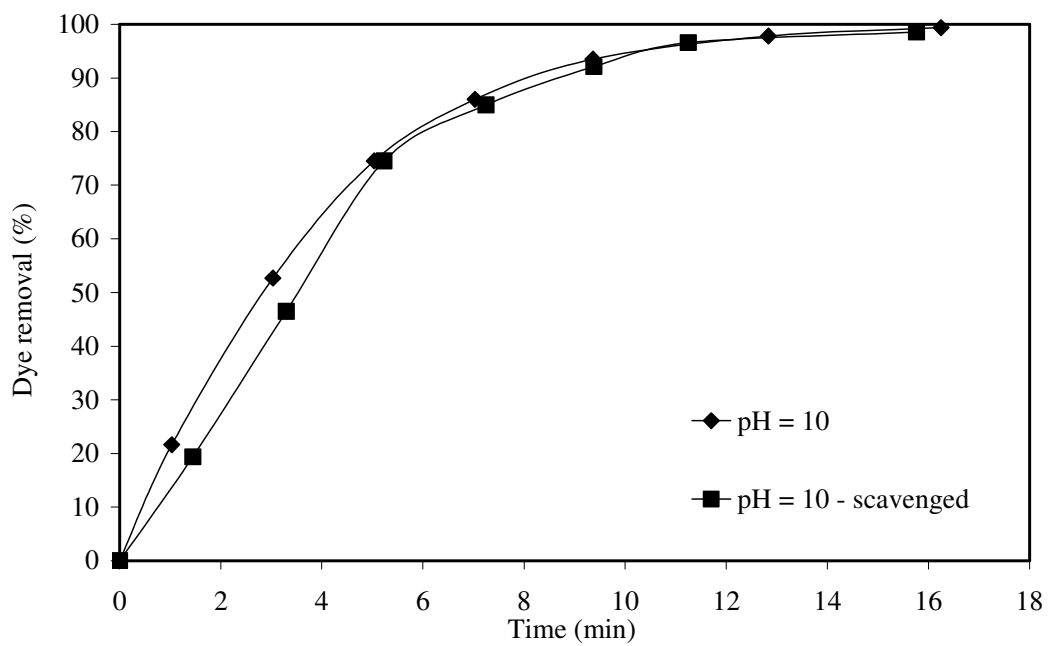


(a)

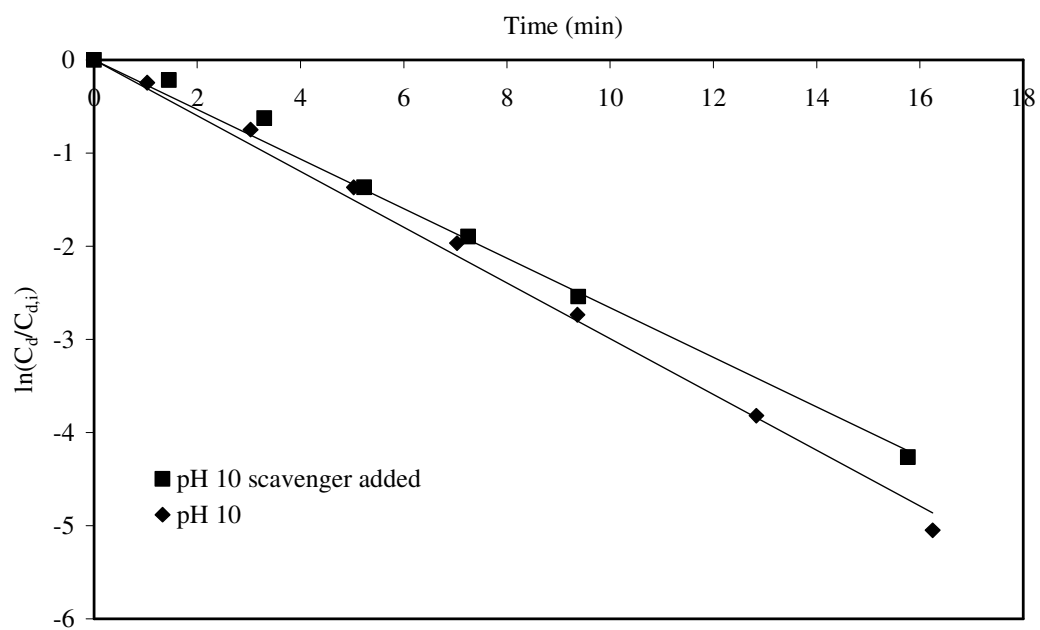


(b)

Figure 4.22 Effect of pH on TOC removals. (a) RBBR, (b) RB-5, $C_{d,i} = 100$ mg/L, ozone dose = 115 mg/L.min, $[PO_4^{3-}] = 20$ mM.



(a)



(b)

Figure 4.23 Effect of solution pH on dye removal. (a) percent dye removals, (b) pseudo first order reaction rate constant analysis. Dye = RBBR, $C_{d,i} = 400$ mg/L, solution pH = 10, ozone dose = 115 mg/L.min, $[\text{PO}_4^{3-}] = 20$ mM.

The addition of 20 g/L of sodium carbonate (Na_2CO_3) decreased the dye removal rate. This decrease in the dye removal rates can be attributed to the decrease in the level of hydroxyl radicals in the solution, since sodium carbonate decreases the amount of hydroxyl radicals [37, 38]; this result can be regarded as a proof that hydroxyl radicals are effective on the dye removals at basic conditions. It can be said that molecular ozone is responsible for the dye removal at acidic conditions while both molecular ozone and hydroxyl radicals take apart in the ozonation of the dye molecules at basic conditions. Although these results show that the role of hydroxyl radicals in dye removal rate of the RBBR solutions is significant, it is also noted in Table 4.6 that the scavenger addition reduced the pseudo first order reaction rate constant only by 10 %. Pseudo first order reaction rate constants for scavenged and non-scavenged runs are given in the Table 4.6.

Table 4.6 Pseudo first order rate constants and R^2 values for the experiments with a scavenger.

Scavenger	k' (min^{-1})	R^2
Yes	0.266	0.99
No	0.299	0.99

4.2.3 Effect of Phosphate Buffers

Since the solution pH is one of the most important factors in ozonation processes; therefore, its effect has been studied widely. In this work, pH was adjusted by phosphate buffers, it is known that using phosphate buffers may effect the ozonation results [12]. This set of experiments was conducted in order to investigate the possible scavenging effect of the phosphate ions. Ozonation runs at different phosphate concentrations were conducted. The dye and TOC removals for these runs are given below in Figures 4.24-4.25 and the pseudo first order reaction rate constants are tabulated in Table 4.7:

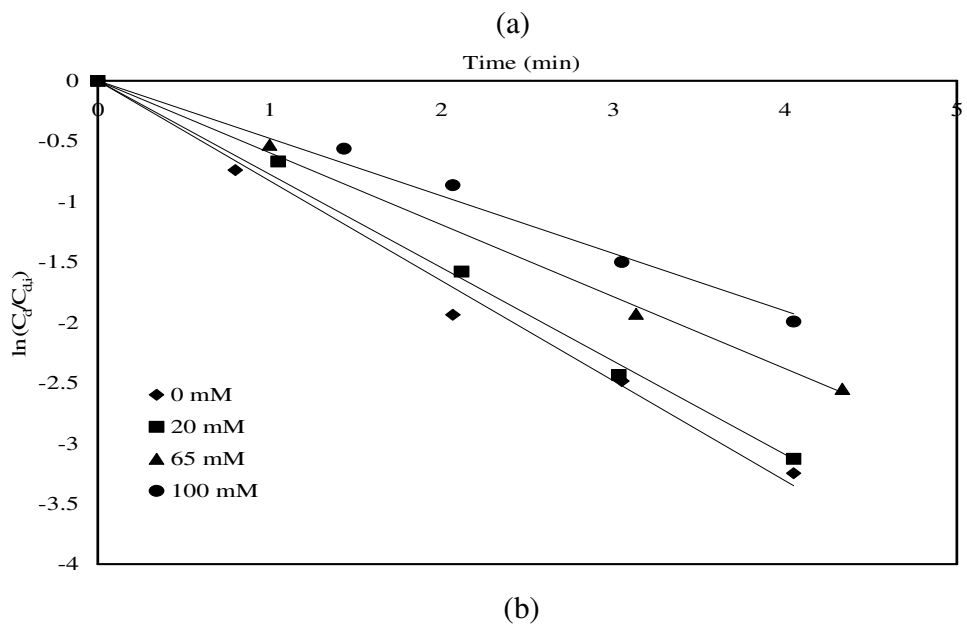
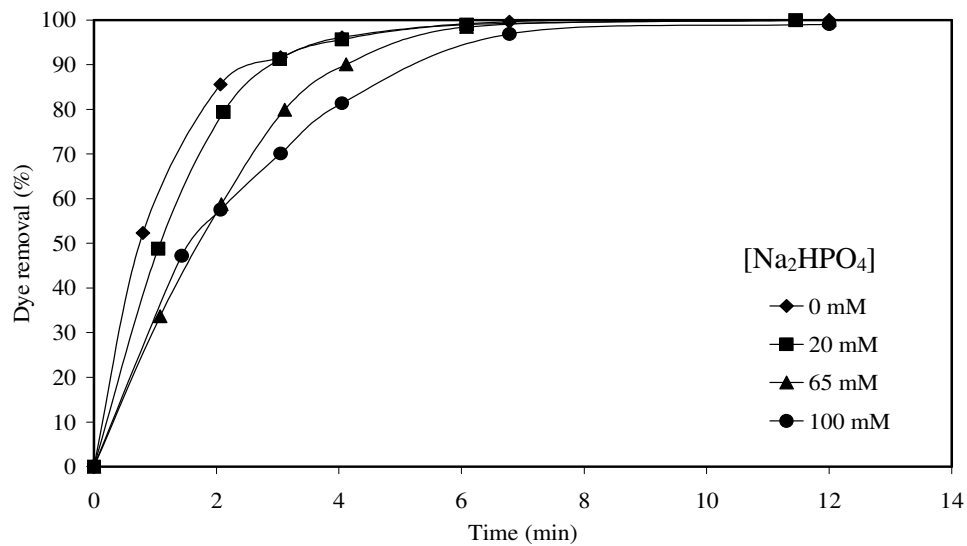


Figure 4.24 Percent dye removals obtained from the ozonation of dye solutions having different phosphate concentrations. (a) = percent dye removals, (b) = pseudo first order reaction rate constant analysis. Dye = RBBR, $C_{d,i} = 100$ mg/L, solution pH = 10

Table 4.7 Pseudo first order rate constants and R^2 values at different phosphate concentrations

[Na ₂ HPO ₄]	k' values (min ⁻¹)	R^2
0 mM	0.83	0.99
20 mM	0.77	1.00
65 mM	0.60	1.00
100 mM	0.48	0.99

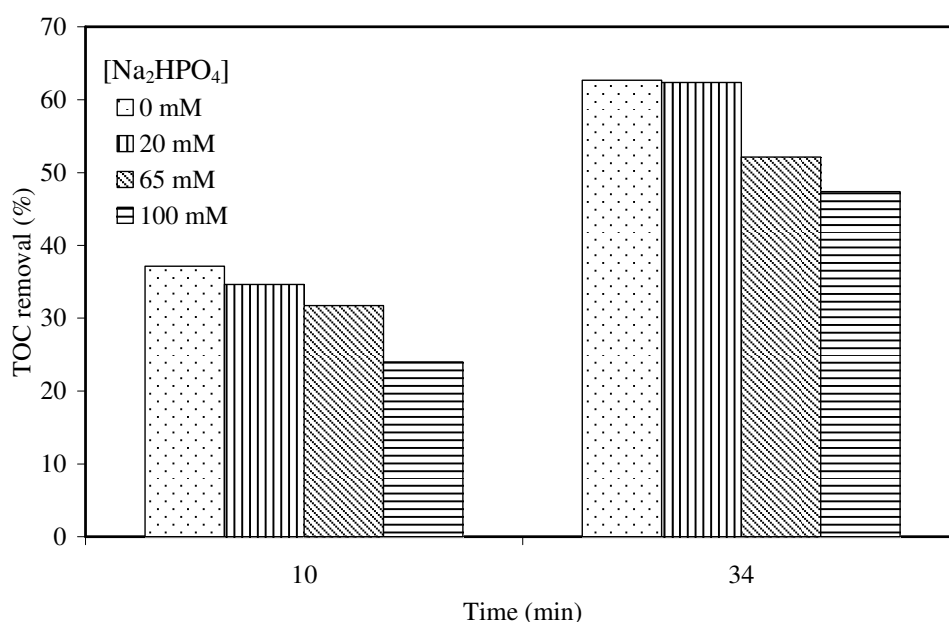


Figure 4.25 Percent TOC removals in ozonation of dye solutions having different phosphate concentrations. Dye = RBBR, $C_{d,i} = 100$ mg/L, pH = 10

As mentioned before, ozone molecules decompose into hydroxyl radicals at basic conditions; because of that ozonation mostly was carried out by hydroxyl radicals at those conditions instead of by molecular ozone. Results given in Figures 4.26 and 4.27 showed that increasing phosphate ion concentration decreased the dye removal rate and percent TOC removal which can be explained by the scavenging effect of the phosphate ions. Especially the decrease in the TOC removals can be attributed to

the consumption of hydroxyl radicals by phosphate ions. Phosphate ions were also listed as possible hydroxyl radical scavenger by B.Kasprzyk-Hodern et al. [12].

4.3 Effect of Copper Sulfide Addition as a Catalyst

Heterogeneous three phase system was obtained by the addition of CuS powder to the reaction medium. CuS addition was found effective on color removal of Reactive Blue 15 [30]. Yong et al. [30] proposed CuS as an alternative catalyst for the heterogeneous catalytic ozonation, but they did not give any further information about the TOC removals, and the mechanism of catalytic ozonation.

In this set of experiments, the effects of CuS on dye and TOC removals in the ozonation of RBBR and RB-5 solutions were observed and compared with the previous non-catalytic ozonation data at different values of pH and initial dye concentration. The effect of the catalyst dosage was also investigated.

4.3.1 Effect of CuS Addition with Changing Initial Dye Concentration

Copper sulfide (CuS) addition to the dye solutions of RBBR and RB-5 at different initial dye concentrations was investigated. The results of these investigations are given in this section. Figures 4.26-4.31 represent the percent dye removals for RBBR and RB-5 dye solutions at pH of 3, 7 and 10 with and without CuS addition for the runs conducted at different initial dye concentrations. Pseudo first order reaction rate constants are also given in Table 4.8

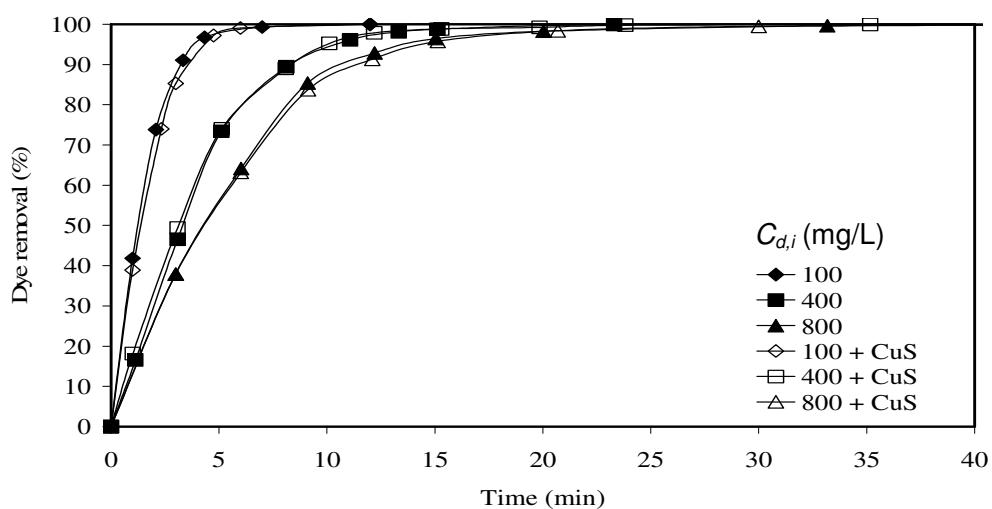


Figure 4.26 Effect of CuS on dye removals in RBBR solutions at different $C_{d,i}$. pH = 3, ozone dose = 115 mg/L.min, $[\text{PO}_4^{3-}] = 20 \text{ mM}$, $C_{cat} = 0.1 \text{ g/L}$.

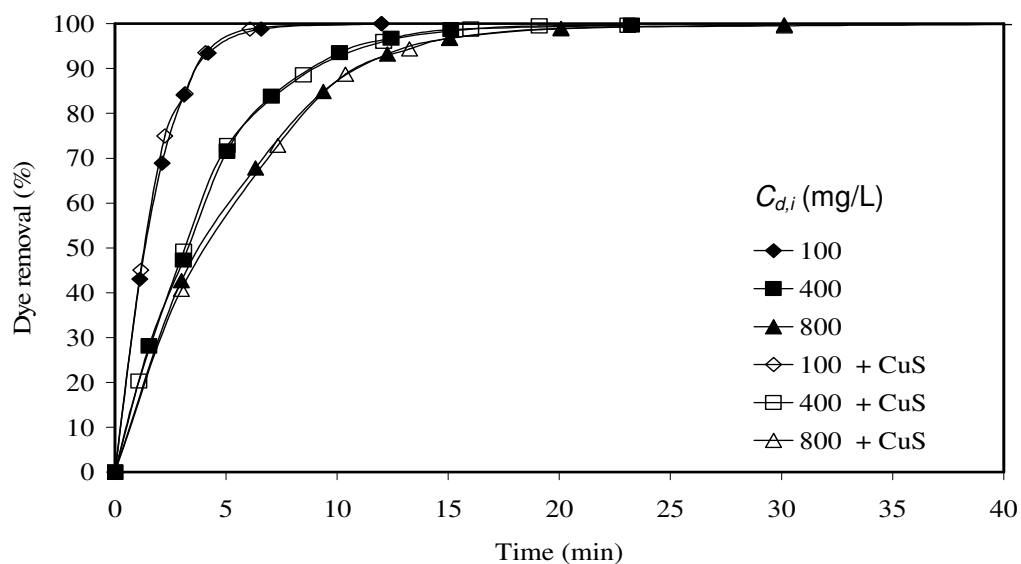


Figure 4.27 Effect of CuS on dye removals in RBBR solutions at different $C_{d,i}$. pH = 7, ozone dose = 115 mg/L.min, $[\text{PO}_4^{3-}] = 20 \text{ mM}$, $C_{cat} = 0.1 \text{ g/L}$.

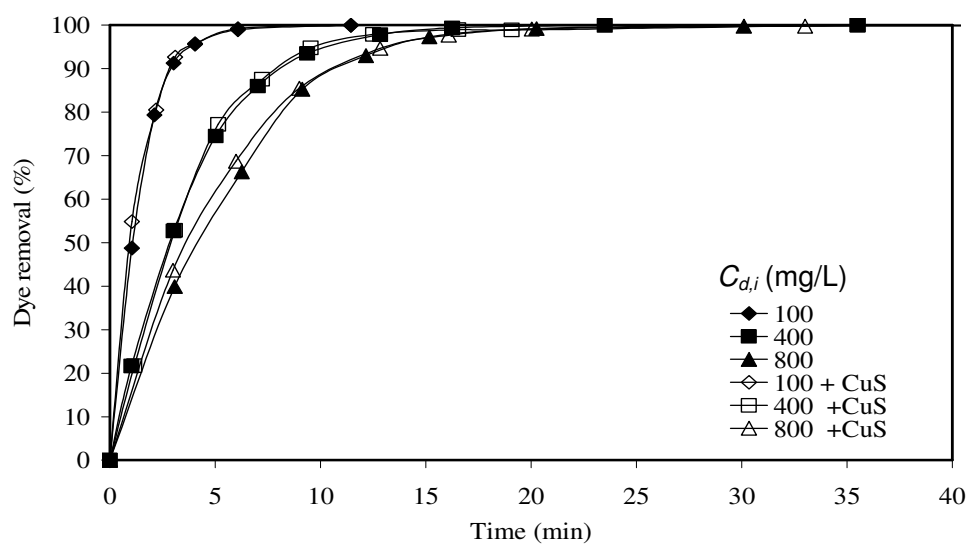


Figure 4.28 Effect of CuS on dye removals in RBBR solutions at different $C_{d,i}$. pH = 10, ozone dose = 115 mg/L.min, $[\text{PO}_4^{3-}] = 20 \text{ mM}$, $C_{cat} = 0.1 \text{ g/L}$.

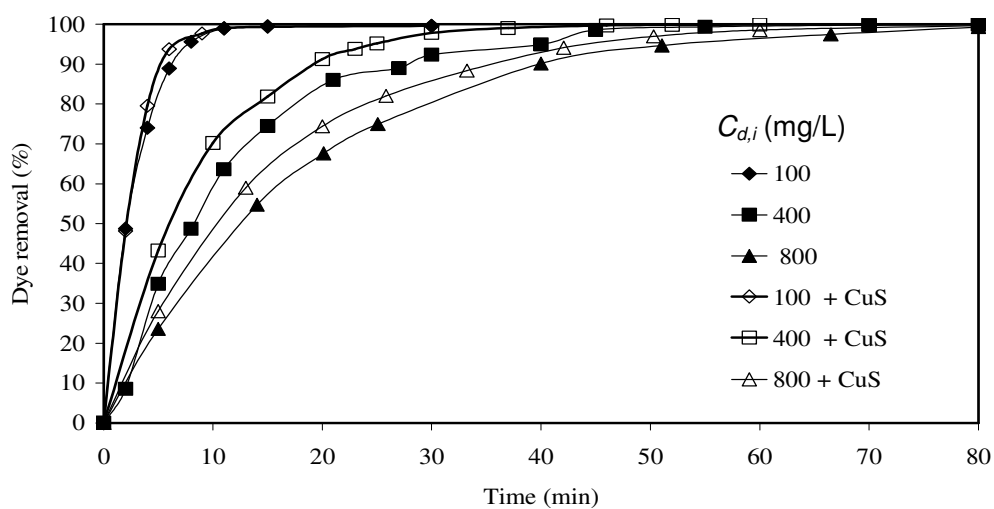


Figure 4.29 Effect of CuS on dye removals in RB-5 solutions at different $C_{d,i}$. pH = 3, ozone dose = 115 mg/L.min, $[\text{PO}_4^{3-}] = 20 \text{ mM}$, $C_{cat} = 0.1 \text{ g/L}$.

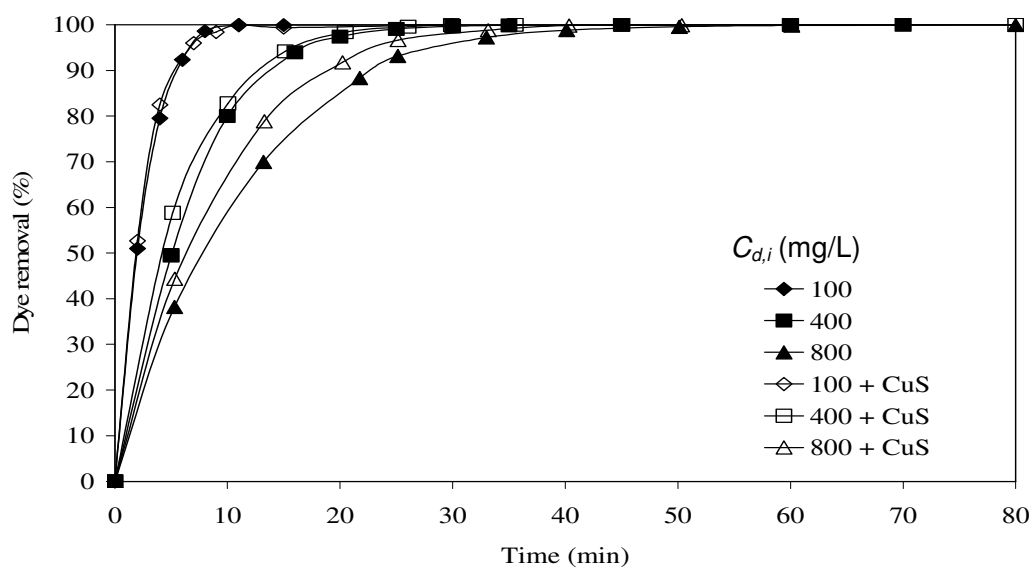


Figure 4.30 Effect of CuS on dye removals in RB-5 solutions at different $C_{d,i}$. pH = 7, ozone dose = 115 mg/L.min, $[\text{PO}_4^{3-}] = 20$ mM, $C_{cat} = 0.1$ g/L.

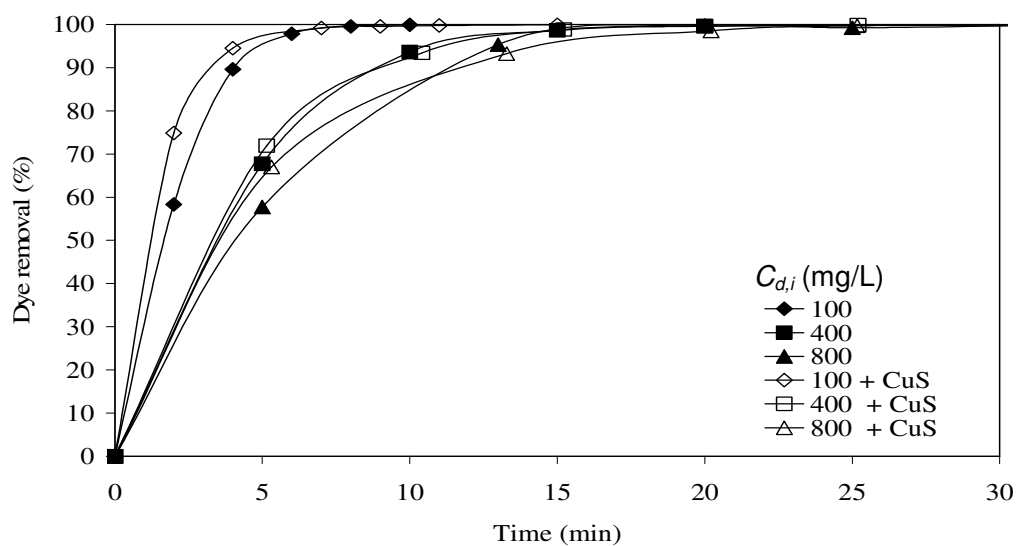


Figure 4.31 Effect of CuS on dye removals in RB-5 solutions at different $C_{d,i}$. pH = 10, ozone dose = 115 mg/L.min, $[\text{PO}_4^{3-}] = 20$ mM, $C_{cat} = 0.1$ g/L.

CuS addition did not show any significant improvement on dye removal rates in the runs conducted with the RBBR solutions. In Table 4.8, it can be seen that CuS addition had only a slight effect on the rate constants for the runs at the initial dye concentration of 100 mg/L RBBR. From these results obtained it is hard to say that CuS addition had an effect on the dye removal rate of the RBBR solutions.

Table 4.8 Pseudo first order reaction rate constants estimated. ozone dose = 115 mg/L.min, $[\text{PO}_4^{3-}] = 20 \text{ mM}$, Catalyst dosage = 0.1 g/L.

Dye	$C_{d,i}$	pH	k' values (min^{-1})		% improvement *
			Sole ozonation	Catalytic ozonation	
RBBR	100	3	0.72	0.74	2.8
	400		0.28	0.30	7.1
	800		0.21	0.22	4.8
	100	7	0.64	0.68	6.3
	400		0.27	0.26	-3.7
	800		0.22	0.22	0.0
	100	10	0.76	0.79	3.9
	400		0.30	0.29	-3.3
	800		0.22	0.23	4.5
RB-5	100	3	0.35	0.43	22.9
	400		0.09	0.12	33.3
	800		0.06	0.07	16.7
	100	7	0.41	0.45	9.8
	400		0.18	0.20	11.1
	800		0.11	0.13	18.2
	100	10	0.60	0.66	10.0
	400		0.27	0.28	3.7
	800		0.20	0.21	5.0

Catalyst addition also did not change the behavior of the reaction rate constant with the changing initial dye concentration; the pseudo first order reaction rate constants (apparent rate constants) decreased logarithmically with the increasing initial dye

* % improvement = $((k'_{\text{cat}} - k'_{\text{sole}})/k'_{\text{sole}}) \cdot 100$

concentration. Equations obtained for the catalytic runs are also given in Table 4.9 and Table 4.10.

Table 4.9 Relationship obtained between apparent rate constants (k') and $C_{d,i}$. Ozone dose = 115 mg/L.min, $[\text{PO}_4^{3-}] = 20 \text{ mM}$, Catalyst dosage = 0.1 g/L, dye = RBBR

pH	Equation	R^2
3	$k' = 13.5 C_{d,i}^{-0.63}$	1.00
7	$k' = 8.7 C_{d,i}^{-0.56}$	0.96
10	$k' = 12.7 C_{d,i}^{-0.62}$	0.98

Table 4.10 Relationship obtained between apparent rate constants (k') and $C_{d,i}$. Ozone dose = 115 mg/L.min, $[\text{PO}_4^{3-}] = 20 \text{ mM}$, Catalyst dosage = 0.1 g/L, dye = RB-5

pH	Equation	R^2
3	$k = 8.5 C_{d,i}^{-0.56}$	0.99
7	$k = 7.0 C_{d,i}^{-0.60}$	1.00
10	$k = 24.4 C_{d,i}^{-0.88}$	1.00

Low TOC removal or mineralization is one of the main disadvantages of sole ozonation [12,30]. Keeping this in mind, it is important to investigate the TOC removals when a catalyst is added to the medium. Comparison of the sole and catalytic ozonation processes in removing TOC for the runs conducted with RBBR and RB-5 dye solutions are given below in Figures 4.32-4.37:

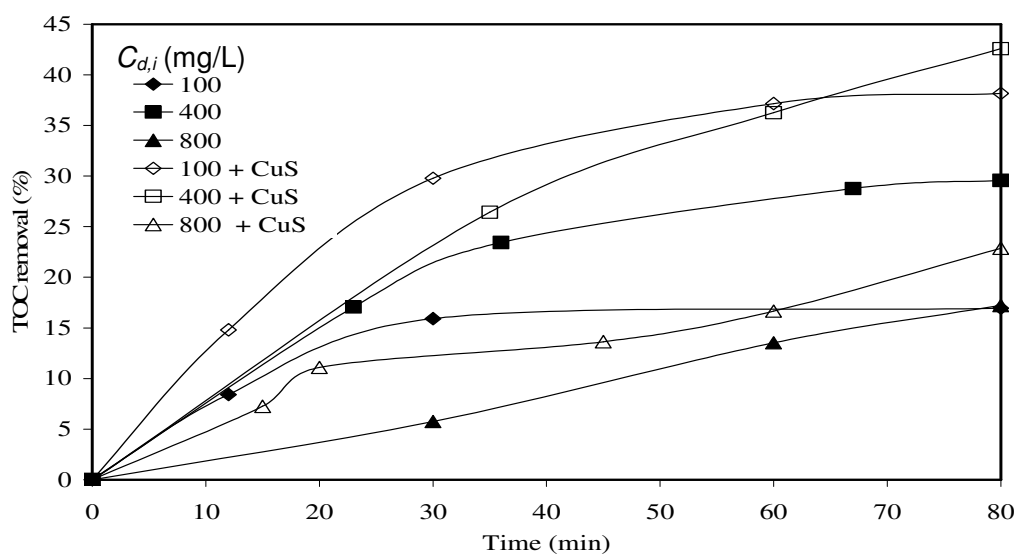


Figure 4.32 Effect of CuS on TOC removals in RBBR solutions at different $C_{d,i}$. pH = 3, ozone dose = 115 mg/L.min, $[\text{PO}_4^{3-}] = 20 \text{ mM}$, $C_{\text{cat}} = 0.1 \text{ g/L}$.

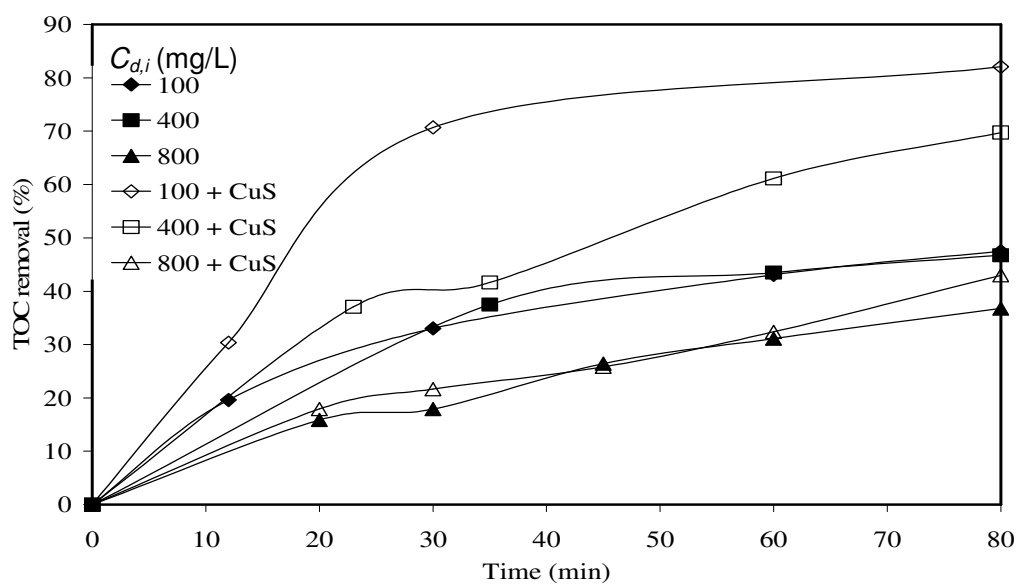


Figure 4.33 Effect of CuS on TOC removals in RBBR solutions at different $C_{d,i}$. pH = 7, ozone dose = 115 mg/L.min, $[\text{PO}_4^{3-}] = 20 \text{ mM}$, $C_{\text{cat}} = 0.1 \text{ g/L}$.

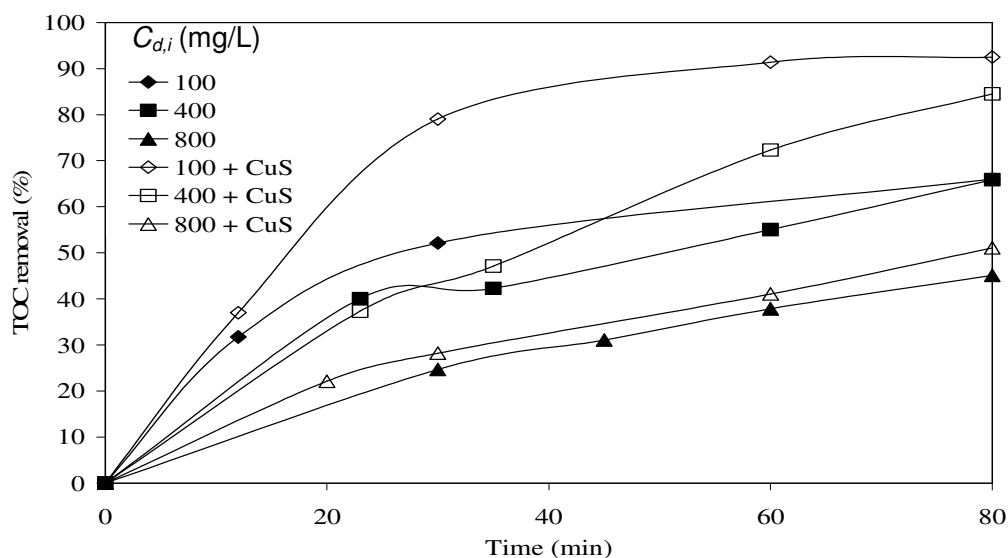


Figure 4.34 Effect of CuS on TOC removals in RBBR solutions at different $C_{d,i}$. pH = 10, ozone dose = 115 mg/L.min, $[\text{PO}_4^{3-}] = 20 \text{ mM}$, $C_{\text{cat}} = 0.1 \text{ g/L}$.

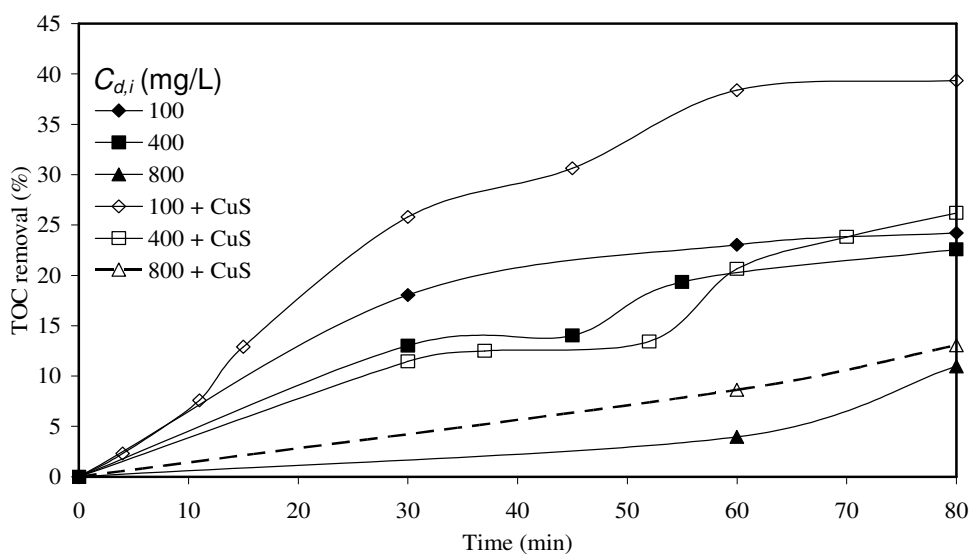


Figure 4.35 Effect of CuS on TOC removals in RB-5 solutions at different $C_{d,i}$. pH = 3, ozone dose = 115 mg/L.min, $[\text{PO}_4^{3-}] = 20 \text{ mM}$, $C_{\text{cat}} = 0.1 \text{ g/L}$.

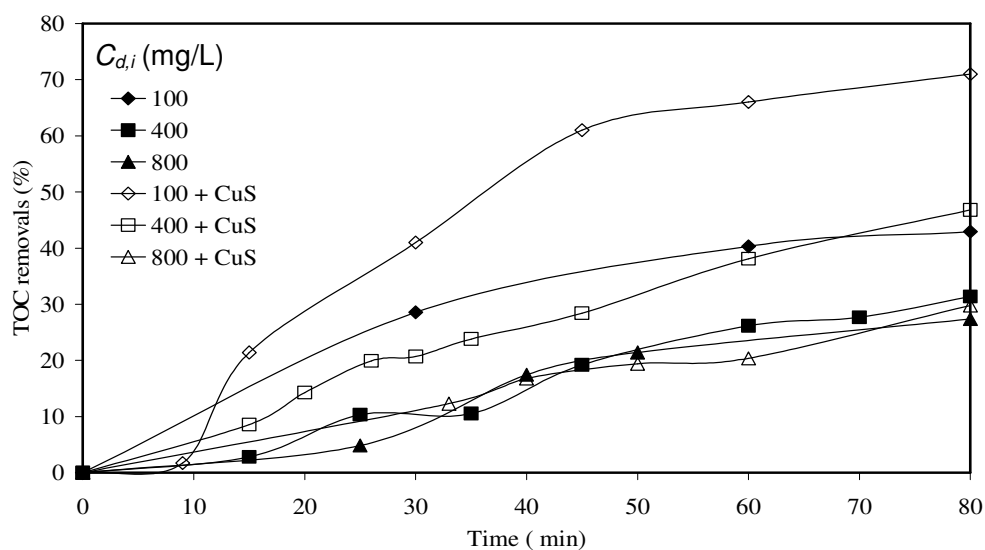


Figure 4.36 Effect of CuS on TOC removals in RB-5 solutions at different $C_{d,i}$. pH = 7, ozone dose = 115 mg/L.min, $[\text{PO}_4^{3-}]$ = 20 mM, C_{cat} = 0.1 g/L.

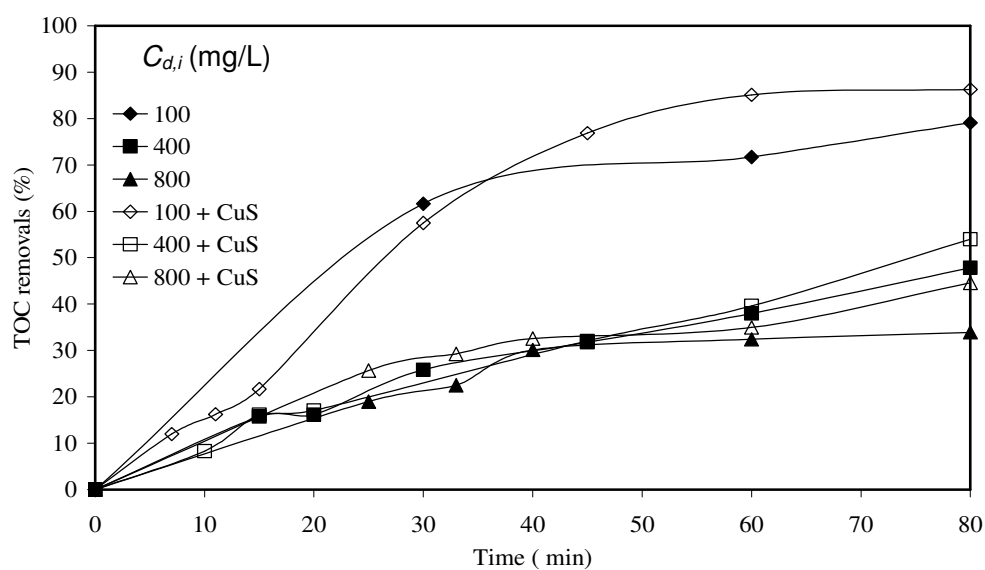


Figure 4.37 Effect of CuS on TOC removals in RB-5 solutions at different $C_{d,i}$. pH = 10, ozone dose = 115 mg/L.min, $[\text{PO}_4^{3-}]$ = 20 mM, C_{cat} = 0.1 g/L.

4.3.2 Effect of pH on Catalytic Activity of CuS

Copper Sulfide addition to the reaction medium was examined separately for both of the dye solutions at different pH values. Effect of CuS addition on the dye removal rates (on k' values) was found significant only for the runs conducted with RB-5 solutions. From Table 4.11 it can be seen that CuS was found more effective in acidic solutions rather than in basic solutions. The addition of CuS was found to be effective also on TOC removals at each condition examined. The greatest improvements in the overall TOC removals after 80 min of ozonation were observed at the acidic conditions for the catalytic ozonation. Overall TOC removals for an ozonation time of 80 min are given in Table 4.12 for both of the dyes studied individually.

Percent TOC removals for the runs conducted at acidic conditions were found to be lower for both the catalytic and non-catalytic ozonations. In order to have an idea about the effect of the CuS addition on ozonation or mineralization of the dye solutions treated, the last column of Table 4.12 can be observed. The effect of the catalyst was found to be lower at basic conditions in terms of percent improvement in the % TOC removals. It can also be observed from this table that already high TOC removals were obtained in the non-catalytic runs conducted with the basic dye solutions; therefore the improvement in TOC removals by the use of catalyst was relatively lower in basic solutions compared to those in acidic solutions. It can also be noted that in the runs conducted with RB-5 dye solutions, effect of CuS addition on TOC removals was observed more significantly at basic conditions in the runs conducted for the dye solutions having initial dye concentration of 800 mg/L. The decrease in the percent improvement in the TOC removals at acidic conditions can be explained by the incomplete oxidation of side products at high initial dye concentrations. TOC removals were lower in the case of sole ozonation at acidic solutions because of the insufficient oxidation of side products with molecular ozone which is the dominant species in the ozonation processes at acidic conditions.

Table 4.11 Comparison of pseudo first order reaction rate constants between non-catalytic and catalytic ozonations of the dyes at different $C_{d,i}$ and pH

Dye	$C_{d,i}$ (mg/L)	pH	k' values (min^{-1})		% improvement*
			Sole ozonation	Catalytic ozonation	
RBBR	100	3	0.72	0.74	2.8
	400		0.28	0.30	7.1
	800		0.21	0.22	4.8
	100	7	0.64	0.68	6.3
	400		0.27	0.26	-3.7
	800		0.22	0.22	0.0
	100	10	0.76	0.79	3.9
	400		0.30	0.29	-3.3
	800		0.22	0.23	4.5
RB-5	100	3	0.35	0.43	22.9
	400		0.09	0.12	33.3
	800		0.06	0.07	16.7
	100	7	0.41	0.45	9.8
	400		0.18	0.20	11.1
	800		0.11	0.13	18.2
	100	10	0.60	0.66	10.0
	400		0.27	0.28	3.7
	800		0.20	0.21	5.0

Table 4.12 %TOC removals obtained at the end of the ozonation period (80 min).

Dye	$C_{d,i}$ (mg/L)	pH	%TOC removals (overall)		% diff.
			Sole ozonation	Catalytic ozonation	
RBBR	100	3	17	38	123.5
	400		29	43	48.3
	800		17	23	35.3
	100	7	47	82	74.5
	400		47	70	48.9
	800		36	43	19.4

* % improvement = $((k'_{\text{cat}} - k'_{\text{sole}})/k'_{\text{sole}}) \cdot 100$

Table 4.12 Continued

Dye	$C_{d,i}$ (mg/L)	pH	%TOC removals (overall)		
			Sole ozonation	Catalytic ozonation	% diff.
RBBR	100	10	66	92	39.4
	400		66	85	28.8
	800		43	51	18.6
RB-5	100	3	24	39	62.5
	400		23	27	17.4
	800		11	13	18.2
	100	7	43	71	65.1
	400		31	47	51.6
	800		27	30	11.1
	100	10	79	86	8.9
	400		48	54	12.5
	800		34	45	32.4

4.3.3 Effect of CuS Dosage on the Ozonation of the Dye Solutions

Effect of CuS dosage used was also investigated. These experiments were performed with dye solutions of RBBR and RB-5, each having an initial dye concentration of 100 mg/L and pH of 3. The lowest initial dye concentration studied in the previous runs was selected in order to guarantee the completion of both the dye removal and the mineralization reactions. Acidic pH was chosen, because the effect of CuS was more significant for these runs as mentioned previously. Different catalyst dosages were examined for RBBR and RB-5 dye solutions. Since the effect of CuS on the dye removal rates for the RBBR solutions was not very significant therefore, higher amounts of CuS was used, while lower catalyst amounts were sufficient to observe the effect of catalyst dosage on the RB-5 solutions. Pseudo first order kinetic rate constants for these runs are given in Table 4.13 and % TOC removals are shown in Figures 4.38 and 4.39.

Table 4.13 Pseudo first order reaction rate constants. $C_{d,i} = 100$ mg/L, ozone dose = 115 mg/L min, $[\text{PO}_4^{3-}] = 20$ mM.

Dye	CuS (g/L)	k' (min^{-1})	% improvement*
RBBR	0	0.72	0
	0.1	0.74	3
	0.2	0.70	-3
	0.4	0.66	-8
	0.7	0.65	-10
RB-5	0	0.35	0
	0.002	0.39	11
	0.05	0.41	17
	0.1	0.43	23

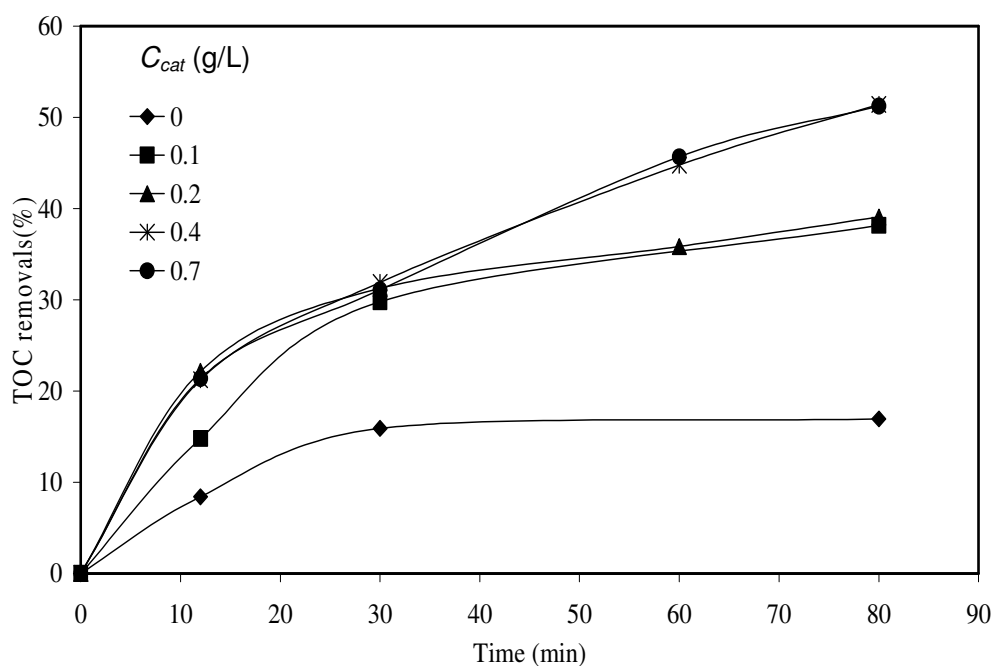


Figure 4.38 Effect of catalyst dosage. Dye = RBBR, $C_{d,i} = 100$ mg/L, ozone dose = 115 mg/L min, $[\text{PO}_4^{3-}] = 20$ mM.

* % improvement = $((k'_{\text{cat}} - k'_{\text{sole}}) / k'_{\text{sole}}) \cdot 100$

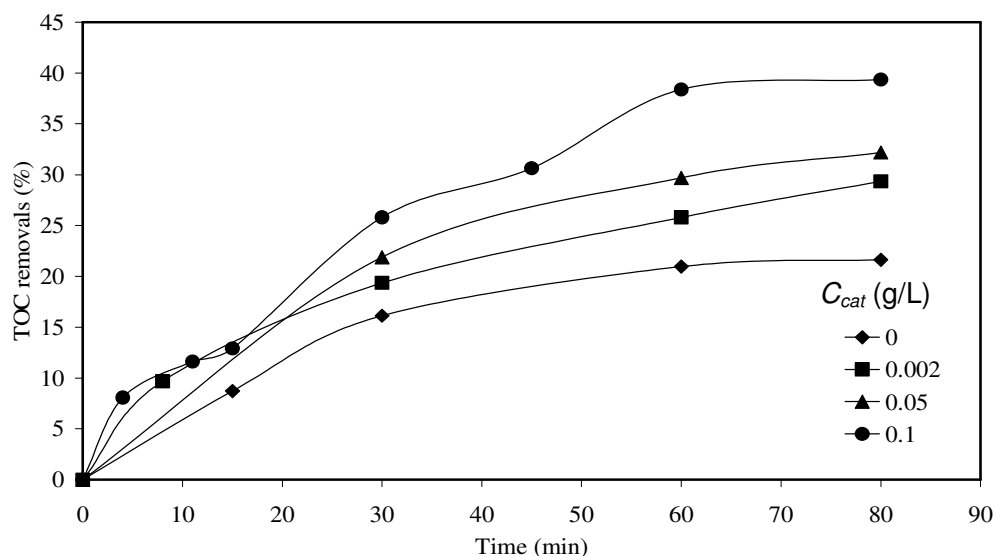


Figure 4.39 Effect of catalyst dosage. Dye = RB-5, $C_{d,i} = 100$ mg/L, ozone dose = 115 mg/L min, $[\text{PO}_4^{3-}] = 20$ mM.

Effect of catalyst dosage was observed more significantly for the runs conducted with RB-5 solutions for both the dye and TOC removals. The effect of catalyst dosage was only significant on the TOC removals in the runs conducted with the RBBR solutions at catalyst dosages of 0.2 and 0.4 g/L (Figure 4.38). It is also notable that increasing the catalyst dosages showed a slightly negative effect on dye removals of RBBR solutions (Table 4.13). On the other hand, TOC and dye removals increased with the increased CuS dosage for the runs conducted with RB-5 solutions (Table 4.13 and Figure 4.39).

4.3.4 Catalytic Mechanism of CuS

Catalytic mechanism of CuS addition was investigated in three steps. First step is the investigation of copper presence in the liquid phase. Second step is the investigation of the effect of the liquid phase copper ions and as the third step the effect of CuS on the hydroxyl radical formation was investigated.

Step 1:

Copper concentrations in the dye solutions after ozonation with presence of CuS were measured by using Atomic Absorption Spectrometry (AAS). Copper concentrations of 27, 7 and 4 mg/L were measured for the runs conducted at pH = 3, 7 and 10, respectively (RBBR dye solutions having initial dye concentration of 100 mg/L). Keeping in mind the low solubility of CuS, the measured copper amounts in the liquid samples might be resulted due to the possible oxidation of CuS by ozone in the medium.

Step 2:

Catalytic effect was tested whether it was homogeneous or heterogeneous. Since it was given in the literature that metal ions in the liquid phase might also have a catalytic effect on ozonation processes [12], therefore the effect of liquid phase copper ions was tested. Homogeneous ozonation run was conducted in two steps. First step includes the pre-ozonation of 0.4 g/L CuS in the de-ionized water in order to obtain the same copper amount in the liquid phase with the heterogeneous run conducted with 0.4 g/L CuS. At the second step, filtrated de-ionized water including copper concentration of 39 mg/L was used to prepare 100 mg/L of RBBR solution and ozonated at the same conditions. Copper concentration of the last sample taken in the heterogeneous run was also measured 39 mg/L. TOC removal results of these runs were compared in order to investigate the homogeneous catalytic reaction.

From Figure 4.40 it can easily be said that almost no difference in terms of % TOC removals was observed between homogeneous and heterogeneous catalytic reactions. According to these results, the catalytic effect of CuS observed in the previous runs was due to the homogeneous copper present in the reaction medium

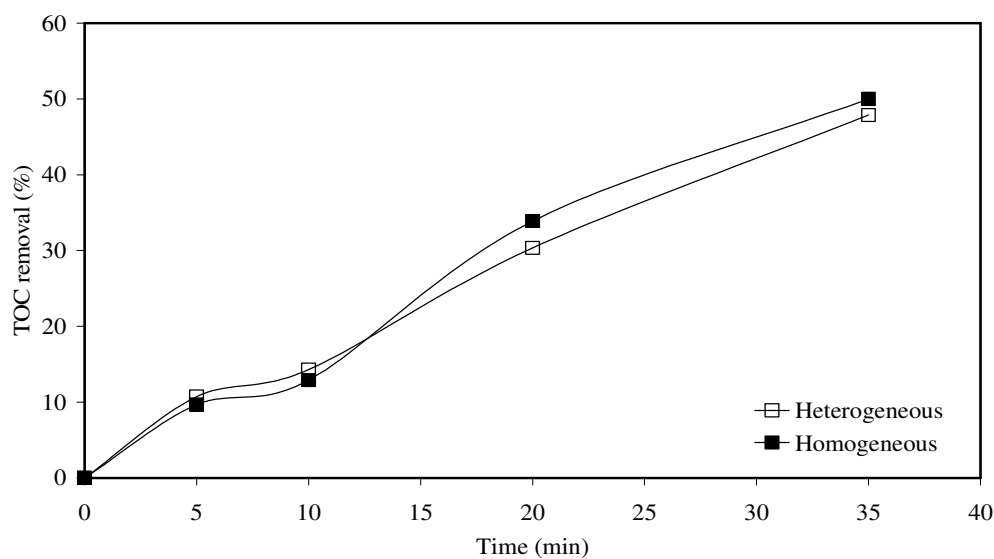


Figure 4.40 %TOC removals of heterogeneous and homogeneous catalytic ozonations. Dye = RBBR, $C_{d,i} = 100$ mg/L, ozone dose = 115 mg/Lmin, $[\text{PO}_4^{3-}] = 0$, pH = 6.7 (not set).

Step 3:

Third step includes the scavenger test. Phosphate buffer was used as the scavenger in the catalytic reaction instead of Tert-butanol which causes interference in TOC measurements in order to be able to measure the TOC removals avoiding the interference of organic scavenger Tert-butanol. The results for TOC removals in the RBBR solutions at pH = 3 using 500 mM and 20 mM phosphate buffers were compared.

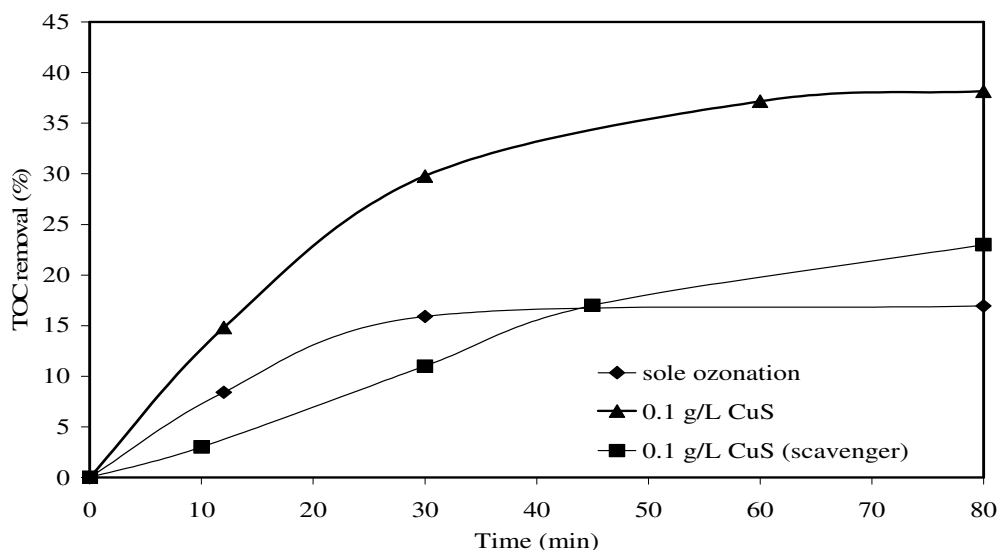


Figure 4.41 Effect of scavenger on TOC removals. Dye = RBBR, $C_{d,i} = 100$ mg/L, ozone dose = 115 mg/Lmin, $[\text{PO}_4^{3-}] = 20$ mM for the sole and catalytic ozonation runs 500 mM for the scavenged run, pH = 3

Results presented in Figure 4.41 showed the scavenging effect of phosphate ions on the catalytic reaction. This can be regarded as the proof for showing the active role of hydroxyl radicals in the catalytic reaction. Ozone decomposition rate calculations by measuring the absorption and decomposition of ozone in de-ionized water were also conducted, in order to investigate the effect of CuS on ozone decomposition. It was observed that CuS catalyst increased the ozone decomposition rate yielding higher concentrations of hydroxyl radicals in the solution [35].

The enhancing effect of the CuS on ozone decomposition can easily be seen from Figures 4.42 and 4.43. Decomposition rate constant according to a first order decomposition rate assumption of ozone, was measured from the slope of the $\ln(C_{O_3}/C_{O_{3,i}})$ vs. time graph just like the pseudo first order reaction rate analyses done in the previous sections.

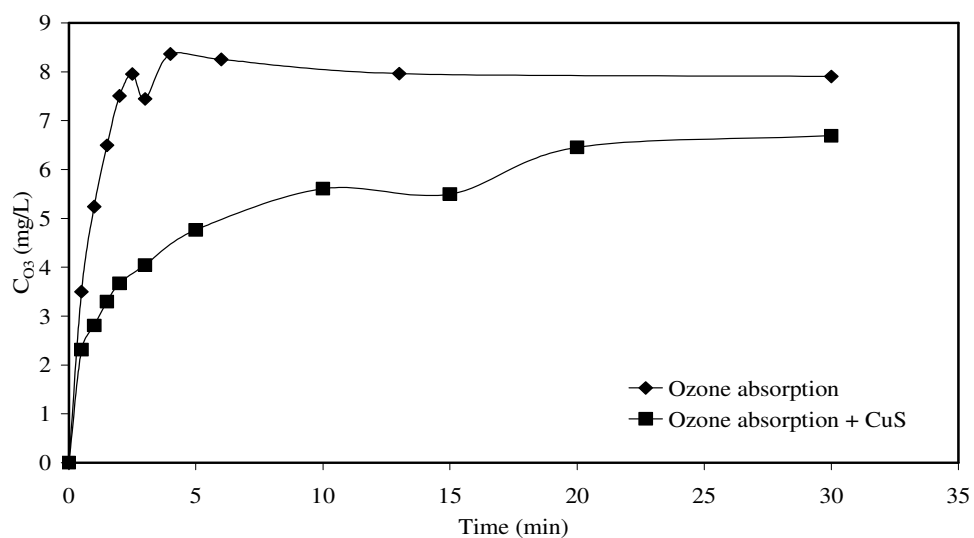


Figure 4.42 Ozone absorption data with and without CuS. pH = 3, ozone dose = 115 mg/min.L, $[\text{PO}_4^{3-}] = 20 \text{ mM}$

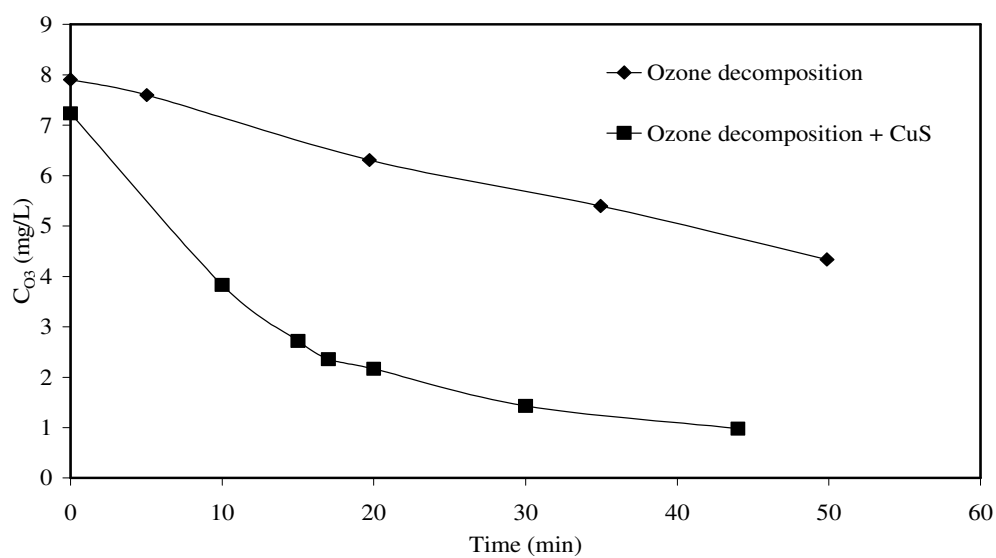


Figure 4.43 Ozone decomposition data with and without CuS. pH = 3, ozone dose = 115 mg/min.L, $[\text{PO}_4^{3-}] = 20 \text{ mM}$

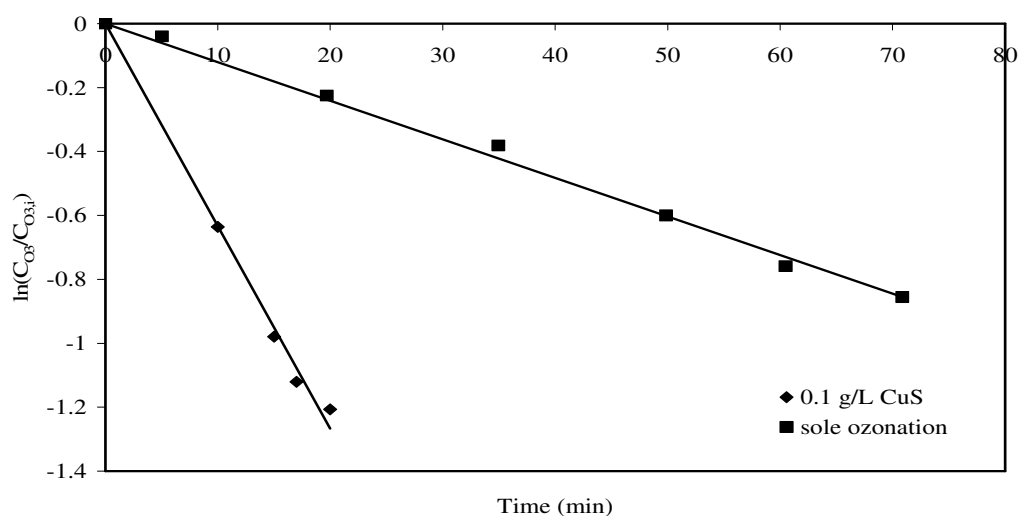


Figure 4.44 First order decomposition rate (k_d) analysis. pH = 3, ozone dose = 115 mg/minL, $[\text{PO}_4^{3-}] = 20 \text{ mM}$

Figures 4.42 to 4.43 and Table 4.14 also show that presence of CuS increased the decomposition rate of ozone probably leading to hydroxyl radical formation.

Table 4.14 First order decomposition rate analysis k_d and correlation constant values.

CuS(g/L)	$k_d(\text{min}^{-1})$	R^2
0	0.01	0.98
0.1	0.06	0.99

According to the results obtained in this section it can be said that the catalytic oxidation reactions were carried out by copper ions present in the liquid phase by enhancing the hydroxyl radical production. It was also given in the literature that copper ions had such an effect on ozonation [27,12].

In addition to these results, the changes in the molecular structure and composition of the CuS catalyst used in the reaction medium were investigated by the XRD and

EDS analyses of the fresh and used CuS particles. The results are given below in Figures 4.45-47. Copper and sulfur contents are also given in Table 4.15 :

- EDS Results

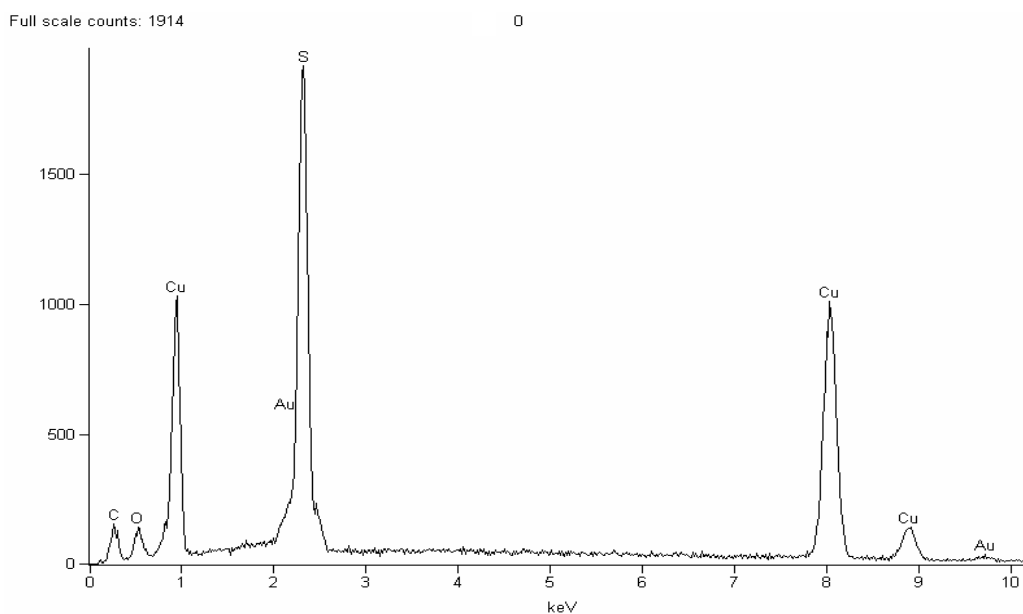


Figure 4.45 EDS output for unused CuS

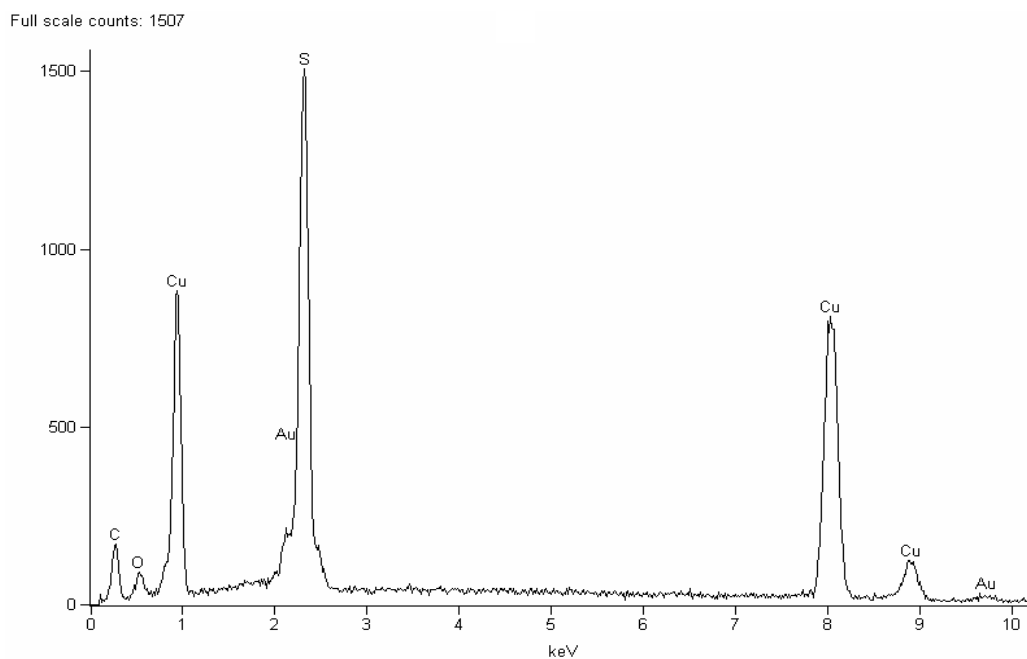


Figure 4.46 EDS output for ozonated CuS without dye

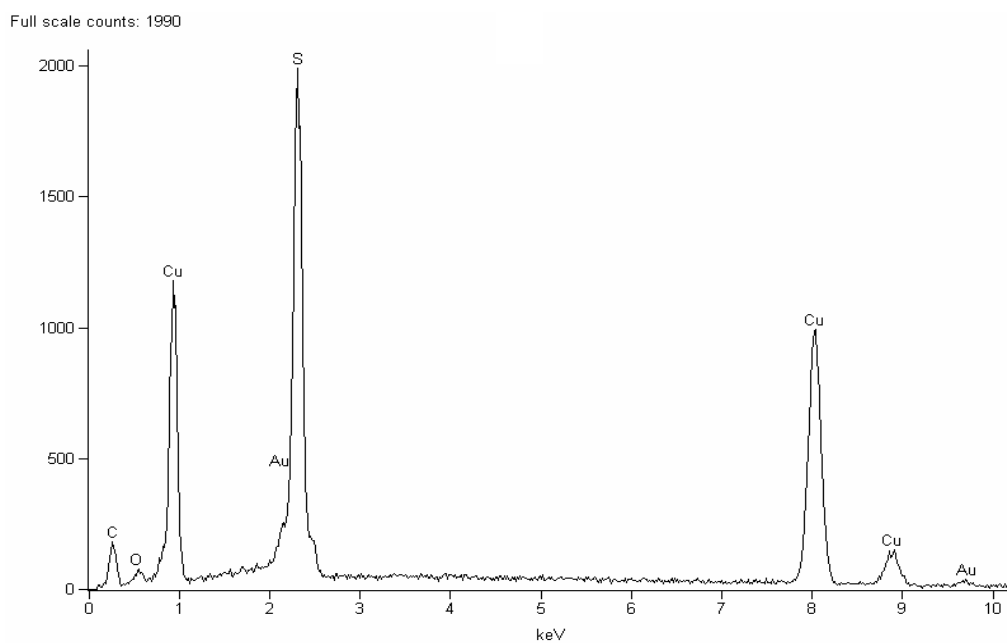


Figure 4.47 EDS output for used CuS

Table 4.15 Sulfur and copper contents of the CuS particles. Values calculated from the EDS output by EDS analyzer

	Elements	Weight %	Atom %
Unused	S	29.4	45.2
	Cu	70.6	54.8
Ozonated	S	27.0	42.4
	Cu	73.0	57.7
Used	S	29.5	45.3
	Cu	70.6	54.7

- XRD Results

XRD results are given in Figure 4.48 for unused used and ozonated CuS particles.

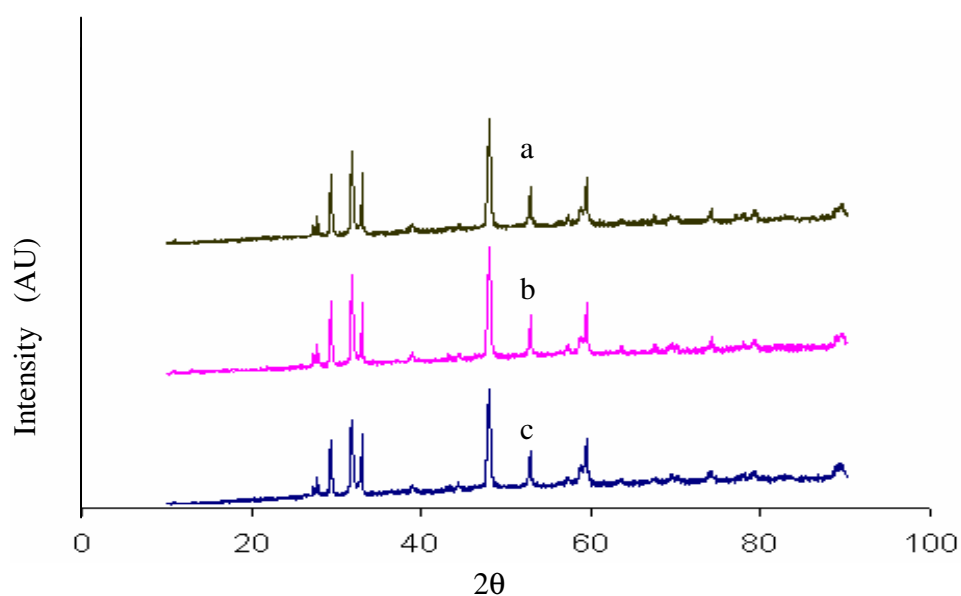


Figure 4.48 XRD results for CuS particles. a = Used in reaction, b = Ozonated without dye in the medium, c = Unused.

XRD and EDS results show that the structure and composition of the CuS particles did not change during the reaction period.

4.4 Another Catalytic Approach; Iron Impregnated on Alumina

Heterogeneous catalytic activity could not be achieved by using CuS catalyst. In search for a heterogeneous catalytic ozonation process, iron impregnated alumina catalyst was prepared, characterized and used for the catalytic ozonation process.

4.4.1 Catalyst Characterization

Characterization of the catalyst prepared was done by XRD, EDS and BET surface analyses. The results are shown in Figures 4.49 to 4.54 and Tables 4.16 to 4.19

(I) XRD Results

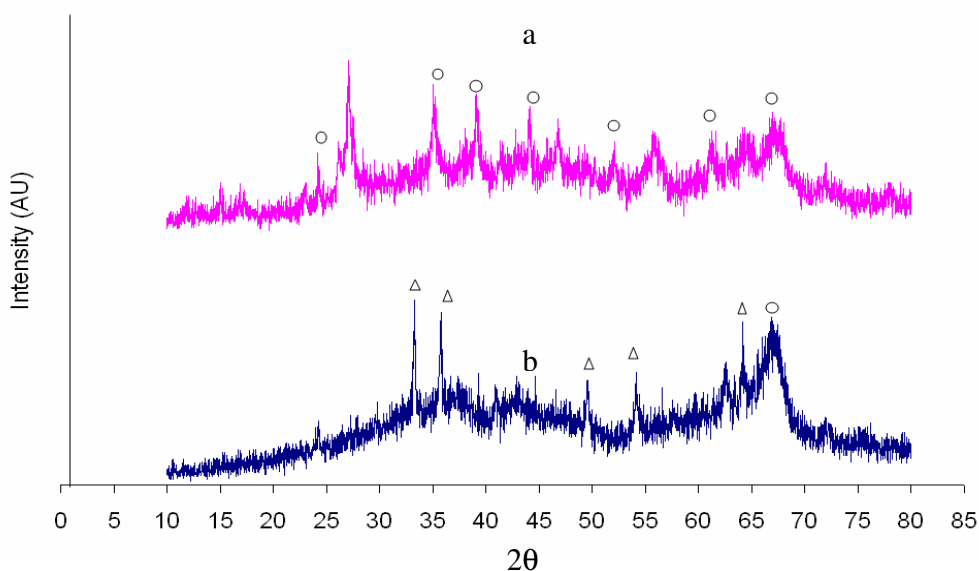


Figure 4.49 XRD results of calcined and uncalcined catalysts. a = un-calcined, b = calcined. Symbols; Δ for Fe₂O₃ and o for γ-Al₂O₃.

XRD results showed that iron ions present in the solution, used for iron impregnation, turned into iron oxide after calcination, and a material having Fe_2O_3 and $\gamma\text{-Al}_2\text{O}_3$ in its structure was obtained.

(ii) EDS Results

EDS outputs of un-calcined, calcined and used catalysts are given in Figures 4.50 to 4.54 and calculated amounts of iron, aluminium and chlorine are given in Tables 4.16 to 4.18

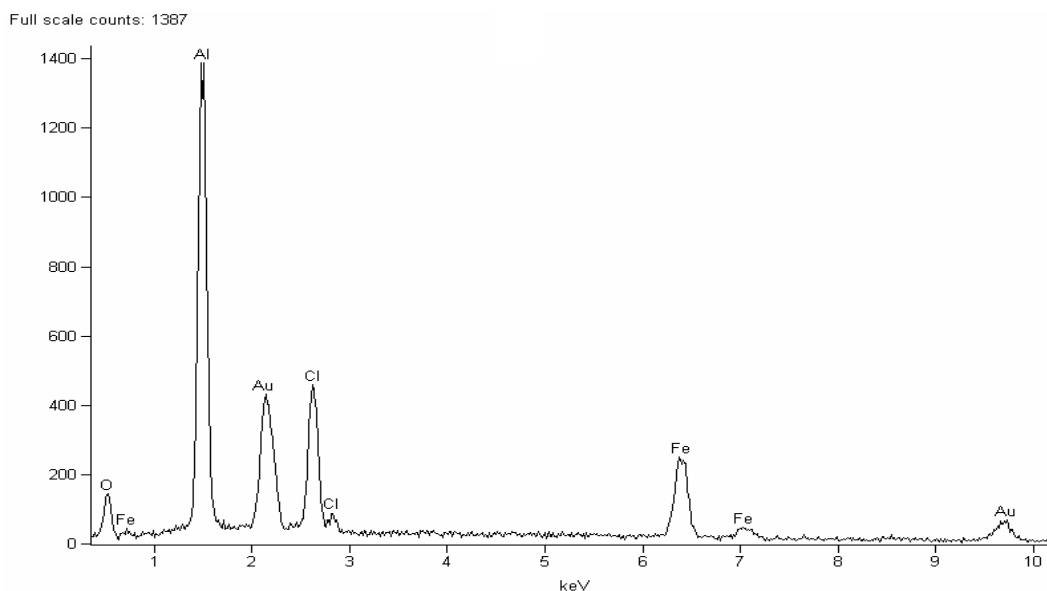


Figure 4.50 EDS output for un-calcined catalyst.

Table 4.16 Aluminium, Chlorine and Iron contents of the catalyst prepared. Values calculated from the EDS output by EDS analyzer

Elements	Weight %	Atom %
Al	49.8	62.4
Cl	20.4	19.5
Fe	29.8	18.1

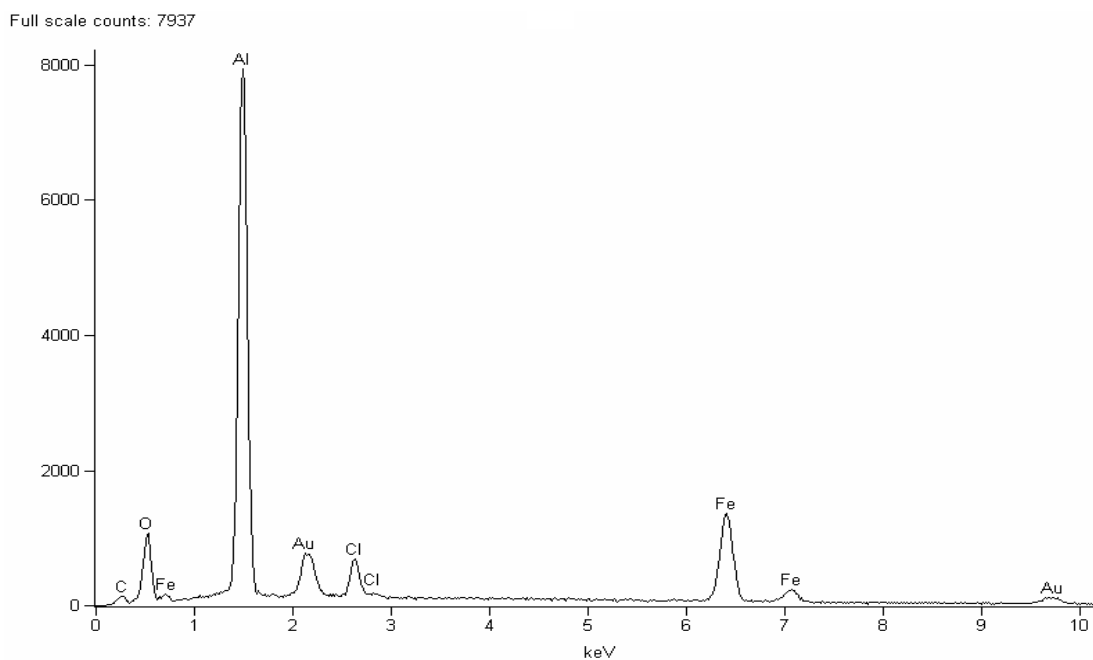


Figure 4.51 EDS output for calcined catalyst.

Table 4.17 Aluminium, Chlorine and Iron contents of the catalyst prepared after calcination. Values calculated from the EDS output by EDS analyzer

Elements	Weight %	Atom %
Al	60.7	74.7
Cl	5.6	5.3
Fe	33.7	20.4

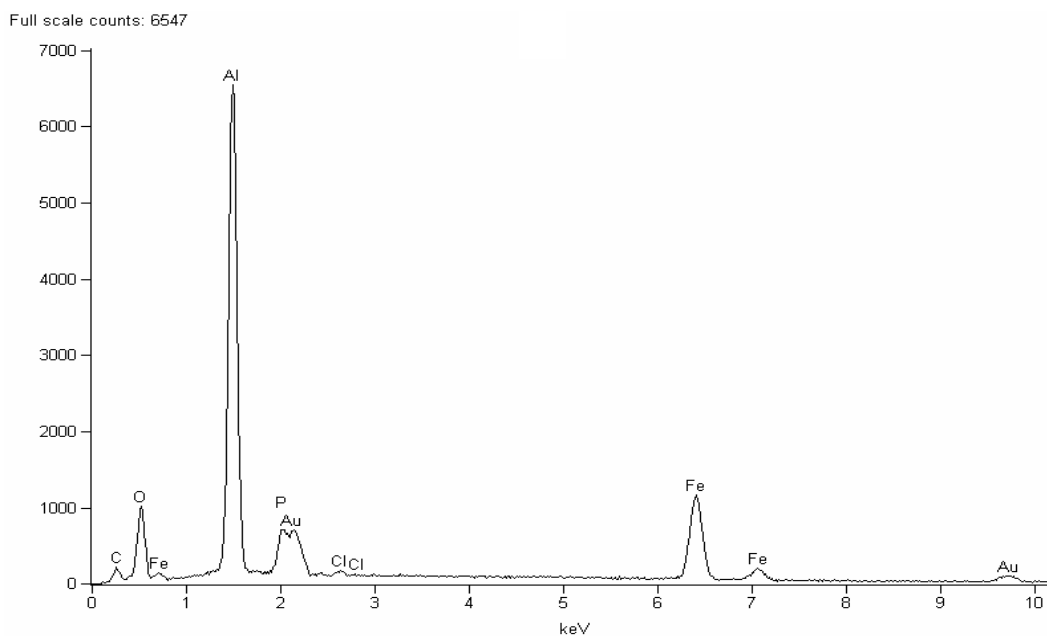


Figure 4.52 EDS output for used catalyst. Dye = RB-5, $C_{d,i}$ = 100 mg/L, ozone dose = 115 mg/L min, $[\text{PO}_4^{3-}]$ = 20 mM, pH = 3

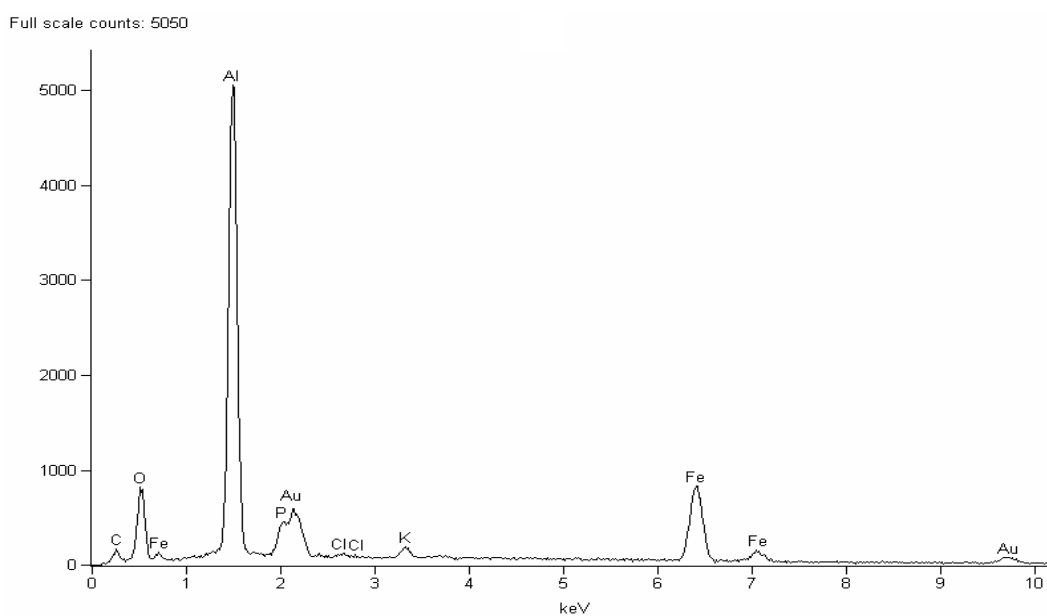


Figure 4.53 EDS output for used catalyst. Dye = RB-5, $C_{d,i}$ = 100 mg/L, ozone dose = 115 mg/L min, $[\text{PO}_4^{3-}]$ = 20 mM, pH = 7

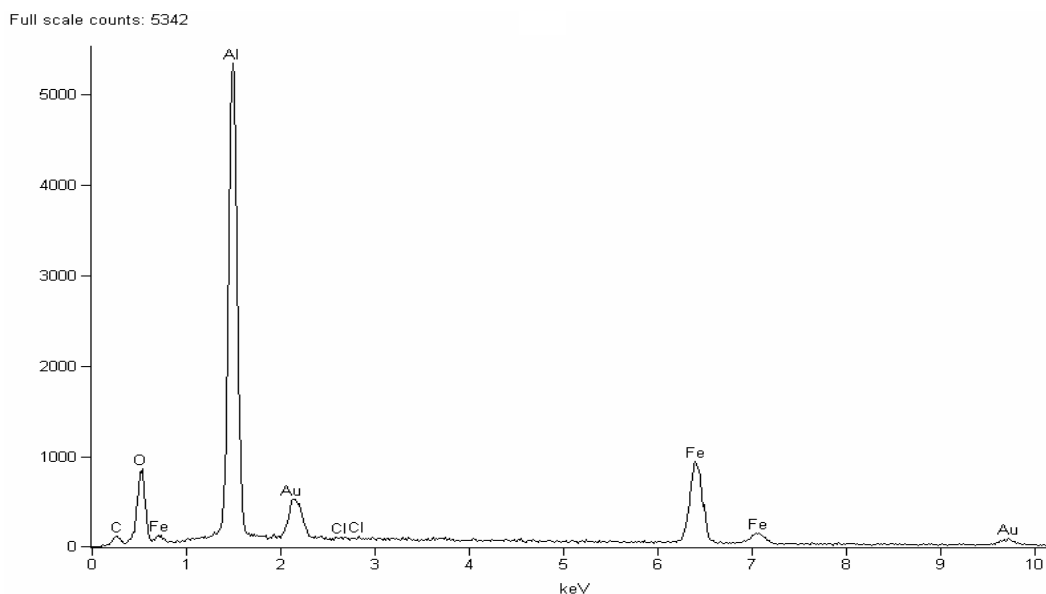


Figure 4.54 EDS output for used catalyst. Dye = RB-5, $C_{d,i} = 100$ mg/L, ozone dose = 115 mg/L min, $[\text{PO}_4^{3-}] = 20$ mM, pH = 10

Table 4.18 Aluminium, Chlorine and Iron contents of the used catalysts in ozonation of dye solutions having different pH values. Values calculated from the EDS output by EDS analyzer

pH	Elements	Weight %	Atom %
3	Al	62.8	77.6
	Cl	0.9	0.8
	Fe	36.3	21.7
7	Al	64.4	78.8
	Cl	0.7	0.6
	Fe	34.9	20.6
10	Al	63.4	78.5
	Cl	0.3	0.3
	Fe	35.8	21.2

From the EDS results, it was observed that most of the chlorine coming from the FeCl_3 precursor was removed during the calcination of the catalyst and almost all the remaining chlorine was further removed during the first use of the catalyst. It is also worth to note that phosphorus peaks are observed in the EDS results of the used catalysts in the runs at $\text{pH} = 7$ and 10. Phosphorus observed in the EDS analyses might be found on the catalyst as a result of phosphate adsorption.

(iii) BET Results

BET results are shown in Table 4.19 and Figure 4.55

Table 4.19 Summary of the BET analysis conducted for prepared catalyst and $\gamma\text{-Al}_2\text{O}_3$ used in preparation

	$A_{\text{BET}} (\text{m}^2/\text{g})$	$D_{\text{pore}} (\text{\AA})$	$V_{\text{T}} (\text{cm}^3/\text{g})$
Alumina	249	42.4	0.30
$\text{Fe}/\text{Al}_2\text{O}_3$	159	38.3	0.18

decrease in the surface area, pore size and the total pore volume of the prepared catalyst compared to those of fresh alumina resulted from the deposition of iron molecules on the catalyst surface as a result of impregnation process. Adsorption decomposition curve obtained in the BET analysis for nitrogen adsorption is given in Figure 4.55.

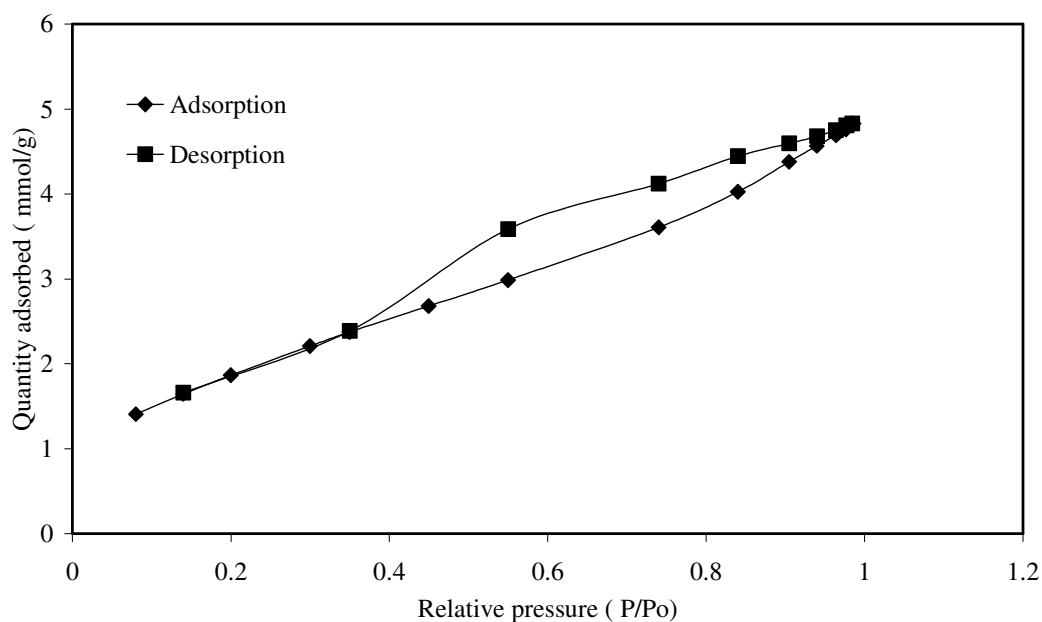


Figure 4.55 BET analysis for Fe/Al₂O₃, nitrogen adsorption - desorption curve.

4.4.2 Catalytic Ozonation Tests

Prepared catalyst was tested with RB-5 dye solutions at pHs of 3, 7 and 10 having initial dye concentration of 100 mg/L. TOC, COD and dye removals were measured in order to investigate the effectiveness of the iron-alumina catalyst on the ozonation of dye solutions.

Effect of iron catalyst was observed most significantly for the run conducted at pH =3. Dye removals and pseudo first order reaction rate analysis for this run are given in Figures 4.56 and 4.57, while estimated pseudo first order reaction rate constants for all the runs conducted are given in Table 4.20. Figure 4.58 also shows the effect of the catalyst on TOC removals at different solution pHs.

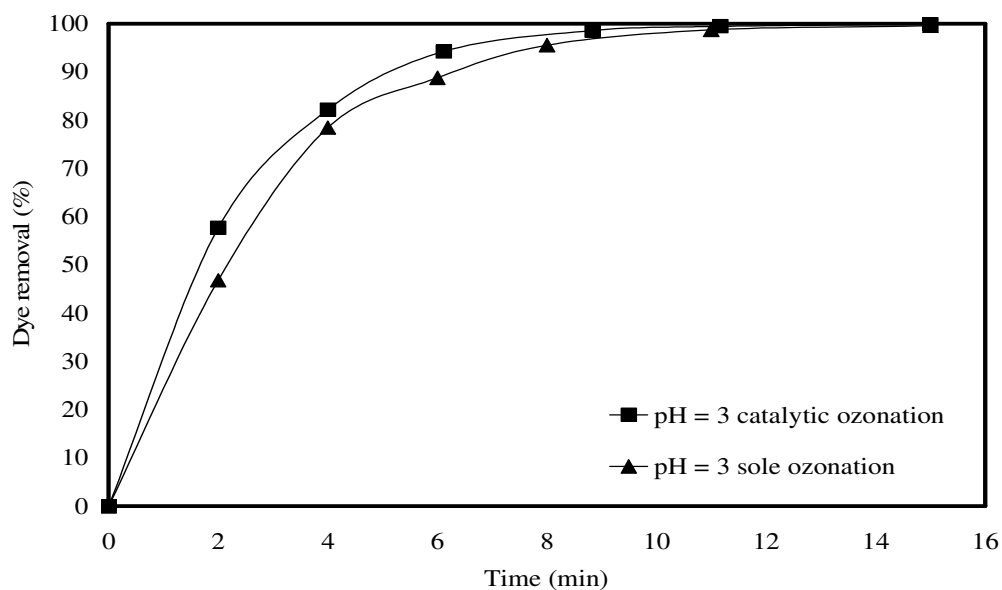


Figure 4.56 Percent dye removals for catalytic and non-catalytic ozonation of RB-5 solutions. Dye = RB-5, $C_{d,i} = 100$ mg/L, ozone dose = 115 mg/L.min, $[\text{PO}_4^{3-}] = 20$ mM.

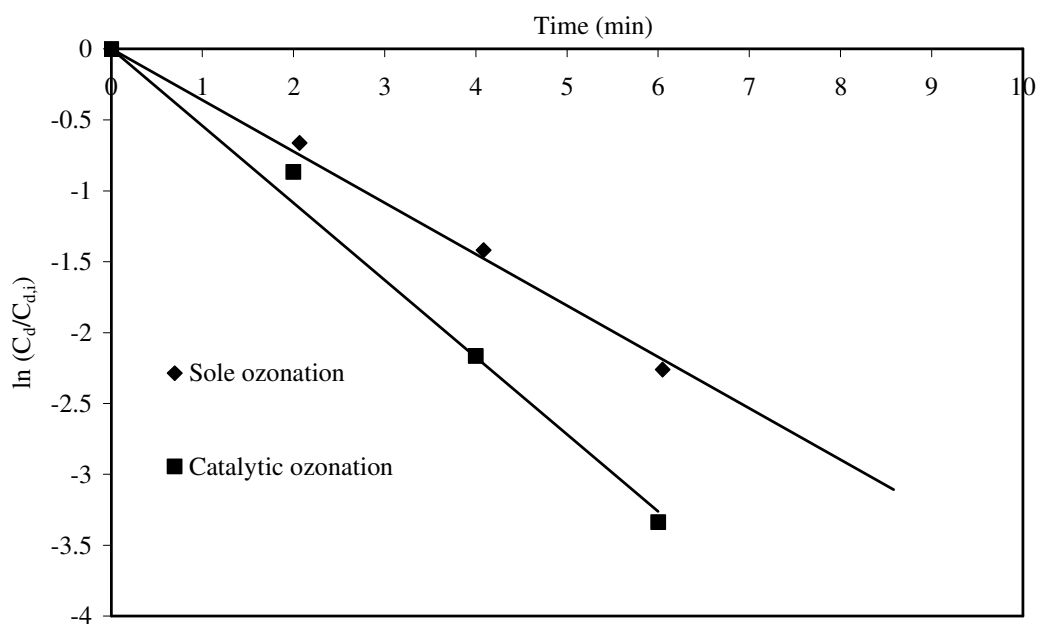


Figure 4.57 Pseudo first order reaction rate constant analysis. Dye = RB-5, $C_{d,i} = 100$ mg/L, ozone dose = 115 mg/L.min, $[\text{PO}_4^{3-}] = 20$ mM, $C_{cat} = 1$ g/L.

Table 4.20 Comparison of catalytic and non catalytic ozonations. Dye = RB-5, $C_{d,i} = 100$ mg/L, ozone dose = 115 mg/L.min, $[\text{PO}_4^{3-}] = 20$ mM, $C_{cat} = 1$ g/L.

pH	$k' (\text{min}^{-1})$		% difference
	sole ozonation	catalytic ozonation	
3	0.36	0.52	44.4
7	0.40	0.41	2.5
10	0.60	0.74	23.3

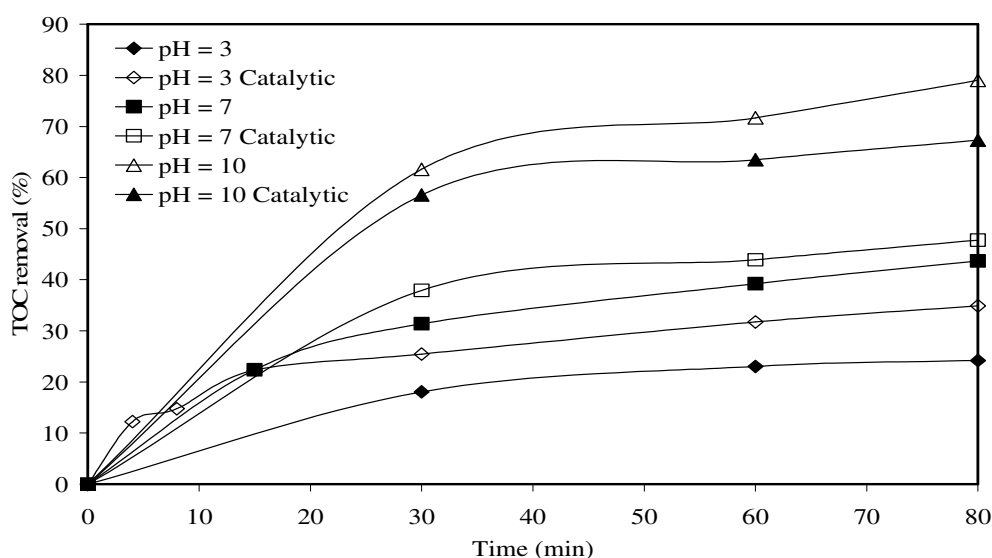


Figure 4.58 Effect of $\text{Fe}/\text{Al}_2\text{O}_3$ catalyst on TOC removals. Dye = RB-5, $C_{d,i} = 100$ mg/L, ozone dose = 115 mg/L.min, $[\text{PO}_4^{3-}] = 20$ mM, $C_{cat} = 1$ g/L.

Dye and TOC measurements both showed that iron impregnated catalyst increased the dye removal rate and %TOC removals especially in the treatment of dye solutions at low pH. This effect must be investigated to observe if it was caused by a heterogeneous reaction or because of some other reasons such as, adsorption of organic materials on the catalyst or effect of the leached metal into solution acting as a homogeneous catalyst. The discussion of catalytic mechanism is given in the Section 4.4.3.

4.4.3 Catalytic Mechanism of Iron Impregnated on Alumina

Addition of $\text{Fe}/\text{Al}_2\text{O}_3$ to the reaction medium had a positive effect on both the TOC and dye removals. The main reason for the increases in TOC and dye removals must be examined to be sure for the mechanism of heterogeneous catalytic ozonation due to the addition of the $\text{Fe}/\text{Al}_2\text{O}_3$ catalyst. The main concerns about this type of catalytic systems can be listed as, the metal leaching during the reaction period and dominating effect of homogeneous catalytic activity due to this leaching; the effect of solid particles (heterogeneous phase) on ozone decomposition causing generation of hydroxyl radicals [35].

The experiments were carried out in four steps similar to the examination of the catalytic mechanism for CuS catalyst. In the first step, iron leaching into solution; in the second step, the effect of dissolved iron in the liquid phase; in the third step the effect of physical adsorption on the catalyst was examined by desorption experiments and lastly the effect of catalyst on ozone decomposition were examined.

Step 1:

The iron concentrations in the liquid phase at the end of the ozonation period were measured by an AAS. These values at different pH are given in Table 4.21

Table 4.21 Iron concentrations in the RB-5 solution after ozonation.

pH of the solution	$[\text{Fe}^{3+}]$, (mg/L)
3	1.35
7	0.1
10	0.1

AAS measurements showed that iron leaching was not significant and a small amount of iron was found in the solution.

Step 2:

Homogeneous catalytic ozonation was tested by dissolving FeCl_3 in RB-5 solution to reach 1.4 mg/L Fe^{3+} concentration in the dye solution. The comparison of homogeneous and heterogeneous runs is given in Figure 4.59 yielding apparent rate constants for dye removals.

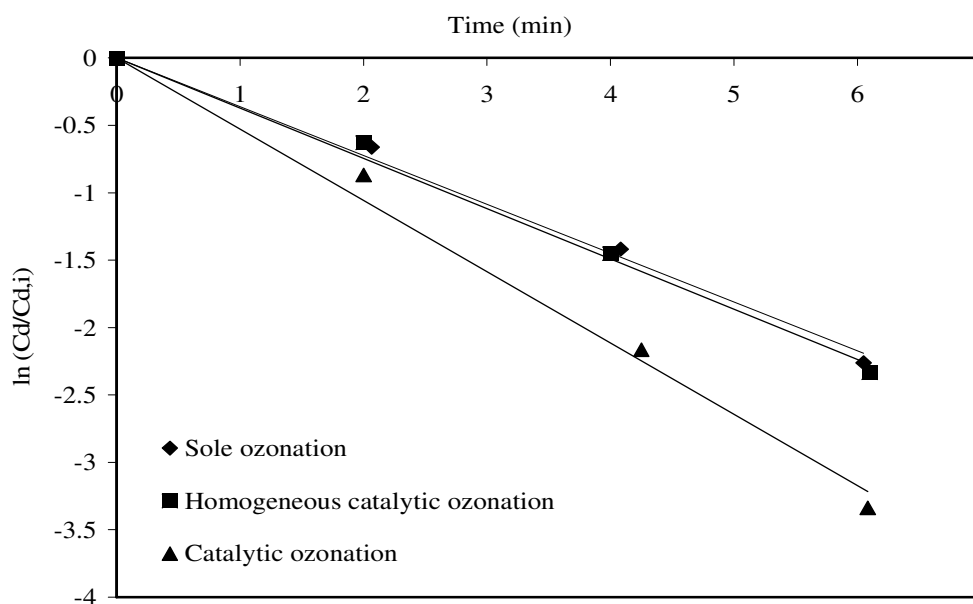


Figure 4.59 Reaction rate analyses for the comparison of the homogeneous and heterogeneous catalytic reactions. Dye = RB-5, $C_{d,i} = 100 \text{ mg/L}$, ozone dose = 115 mg/L.min , $[\text{PO}_4^{3-}] = 20 \text{ mM}$, $C_{cat} = 1 \text{ g/L}$.

Table 4.22 Comparison of homogeneous and heterogeneous catalytic reactions, pseudo first order reaction rate constants.

	k' values (min^{-1})	R^2	% Improvement
pH = 3	0.366	1.00	-
pH = 3 heterogeneous	0.526	1.00	44
pH = 3 homogeneous	0.373	0.99	2

From Figure 4.59 and Table 4.22, it can be seen that homogeneous catalytic effect is negligible. Regarding the pseudo first order reaction rate constants (apparent rate constants) homogeneous catalytic reaction increased the reaction rate by 2%, while heterogeneous catalytic reaction increased the reaction rate by 44%. These results showed that effect of dissolved iron in the solution was not significant. Heterogeneous catalytic activity was dominant in the catalytic reaction. Beltran et al. [35] also found that homogeneous catalytic activity was limited compared to the heterogeneous catalytic activity in catalytic ozonation of oxalic acid with Fe/Al₂O₃.

Step 3:

Adsorption of target organic material might also happen without any chemical reaction when porous materials, such as γ - Alumina was used. In order to investigate the effect of physical adsorption of the dye on dye removal, the catalysts used were filtered and desorption experiments were conducted [10]. Desorption experiments were conducted by stirring the used catalyst in de-ionized water overnight and heating at 50°C. As a result of de-sorption experiments, the un-reacted dye concentration in 200 mL of de-ionized water was found to be This meant that 0.24 mg dye out of 100 mg dye treated in the ozonation process was found to be physically adsorbed at the end of the reaction. Step 3 was also resulted in favor of the heterogeneous catalytic reaction mechanism, because the adsorption effect was found to be negligible.

Step 4:

This step includes the investigation of ozone decomposition caused by catalyst addition. 1 g/L of catalyst was added into de-ionized water which was ozonated for carrying out “absorption-decomposition experiments” for ozone in the liquid phase. Absorption and decomposition data showing the dissolved ozone concentrations in the liquid versus time with catalyst and without catalyst are given in Figures 4.60

and 4.61. The decomposition rate constants of ozone (k_d) with and without catalyst were obtained from Figure 4.62 and shown in Table 4.23.

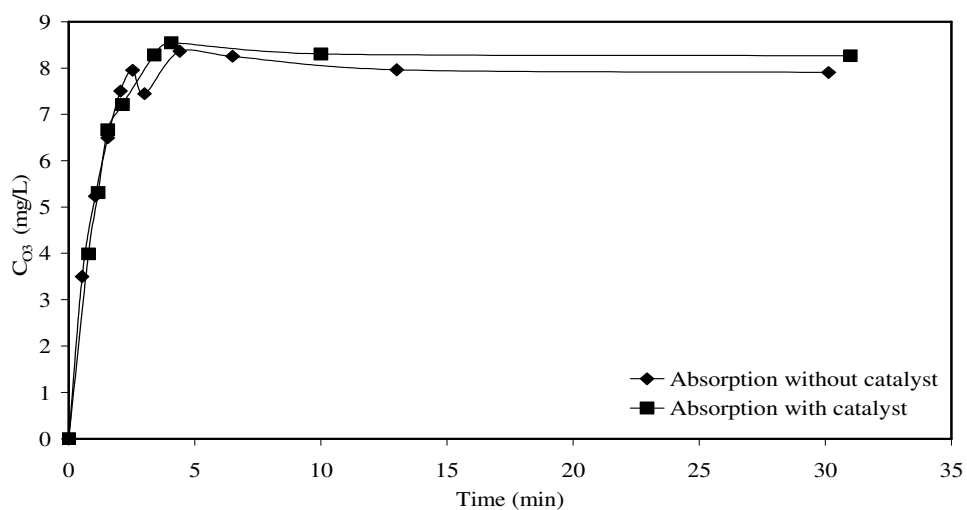


Figure 4.60 Absorption measurements with and without catalyst. pH = 3, dye = none, ozone dose = 115 mg/L.min, $[\text{PO}_4^{3-}] = 20 \text{ mM}$.

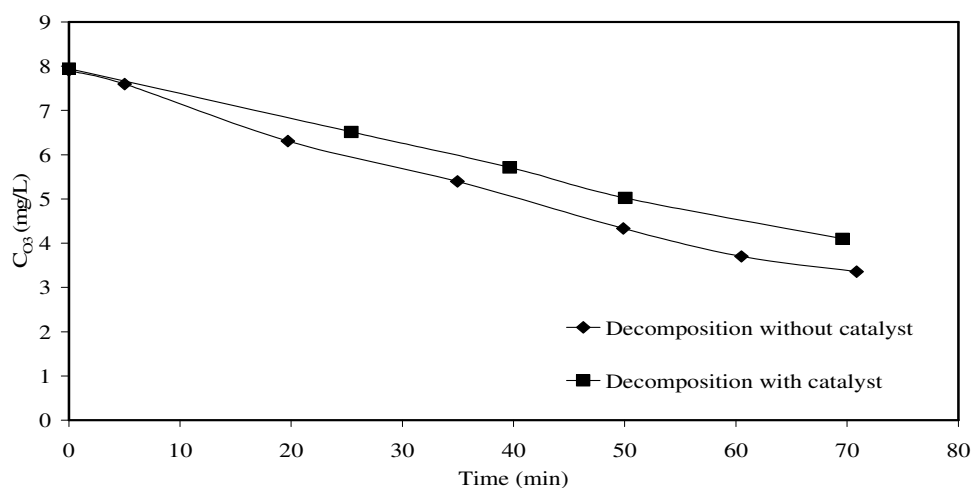


Figure 4.61 Decomposition measurements with and without catalyst. pH = 3, dye = none, ozone dose = 115 mg/Lmin, $[\text{PO}_4^{3-}] = 20 \text{ mM}$.

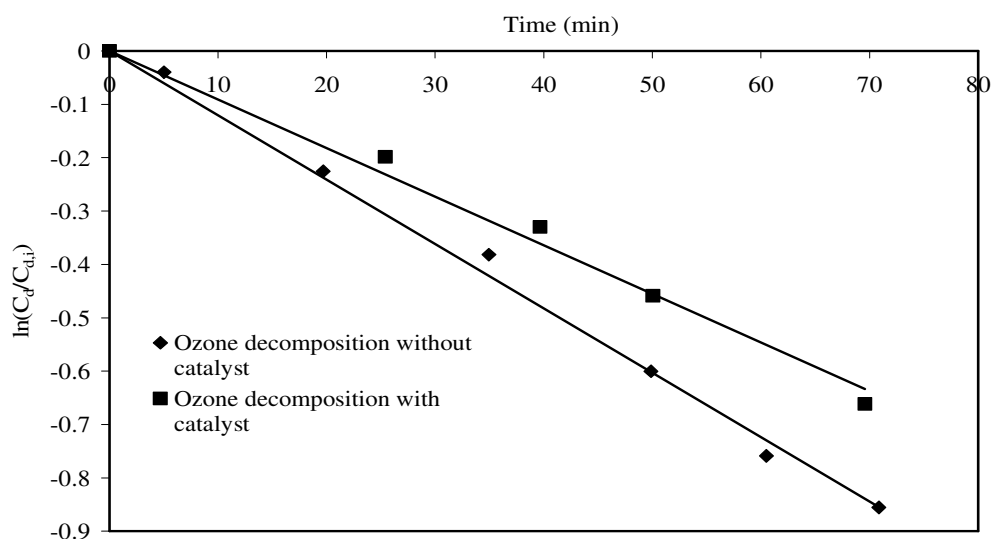


Figure 4.62 Decomposition rate analysis of decomposition measurements. pH = 3, dye = none, ozone dose = 115 mg/Lmin, [PO₄³⁻] = 20 mM.

Table 4.23 First order decomposition rate constants

	$k_d(\text{min}^{-1})$	R^2
with catalyst	0.009	0.99
without catalyst	0.012	0.98

Data obtained from the absorption - decomposition experiments showed that the addition of Fe/Al₂O₃ did not enhance the ozone decomposition rate. The catalyst particles caused a decrease in the decomposition rate of ozone instead of an enhancement in its decomposition. This can be attributed to the enhancement of ozone absorption into water by the catalyst and thus, the faster use of most dissolved molecular ozone by dye molecules occurs before its decomposition. As a result, only some ozone may decompose at a slow rate.

4.5 Absorption - Decomposition Experiments and Modeling of Semi-Batch Reactor

Absorption – decomposition experiments were conducted in order to investigate firstly the mass transfer of ozone into liquid phase and, then its decomposition in liquid phase in the absence of dye. Ozone absorption and decomposition data obtained in these runs were also used in the modeling of the semi-batch reactor.

4.5.1 Absorption – Decomposition Experiments and Estimation of Ozone Mass Transfer Coefficient, K_La

Mass transfer coefficient can be estimated from the absorption data with the aid of the mass balance for ozone. The mass balance was written by using the two film theory. The equation for the mass balance is given in Eqn 2.3(b) and Eqn (4.3). Absorption data of ozone at different pH with respect to time are shown in Figure 4.63.

$$\frac{dC_{O_3}}{dt} = k_L a (C_{O_3}^* - C_{O_3}) - k_d C_{O_3}^m \quad (4.3)$$

Neglecting the decomposition rate and taking the integral of both sides from $t = 0$ to t and from $C_{O_3} = 0$ to C_{O_3} , the mass transfer coefficient can be found from the plot of $\ln \left(\frac{C^*}{C^* - C} \right)$ vs. time

Plots obtained from the absorption data (Figure 4.63) and the k_La values estimated are given in Figure 4.64 and Table 4.24, respectively.

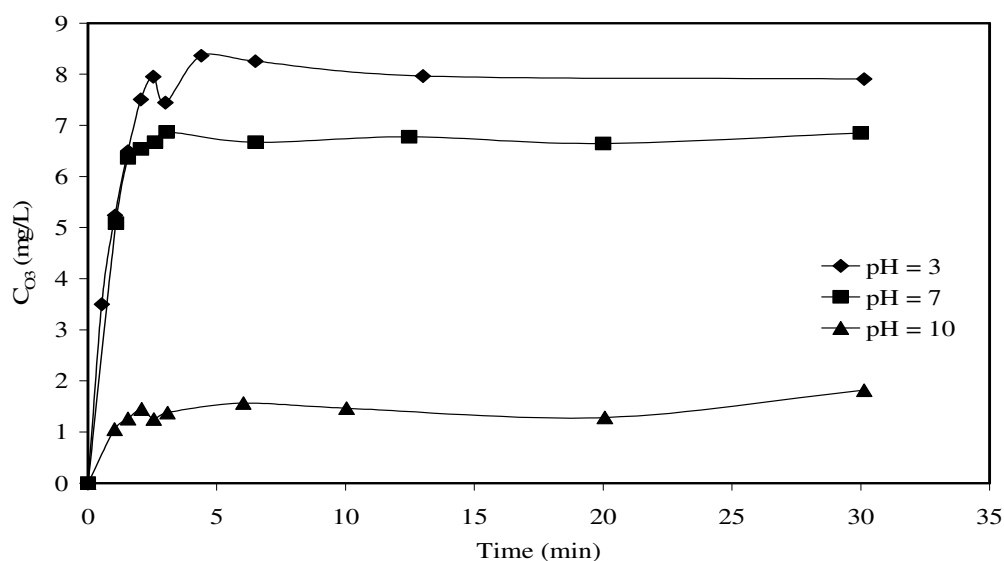


Figure 4.63 Ozone absorption into the buffer solutions having different pH values. Dye = no dye, ozone dose = 115 mg/L.min, $[\text{PO}_4^{3-}] = 20 \text{ mM}$.

Table 4.24 Estimated k_{La} values by using the absorption data.

pH	$k_{La} \text{ (min}^{-1}\text{)}$	R^2
3	1.0	0.99
7	1.4	0.97
10	1.5	0.93

Neglecting the ozone decomposition was only acceptable for the acidic conditions. It can be seen from Table 4.24 that regression coefficient (R^2) decreased as the pH of the solution increased. In order to obtain more precise k_{La} estimations, decomposition rates must be taken into account. For this reason decomposition rate constants were determined from the decomposition data obtained. The plot of decomposition rate analyses and rate constants are given in Figure 4.65 and Table 4.25, respectively.

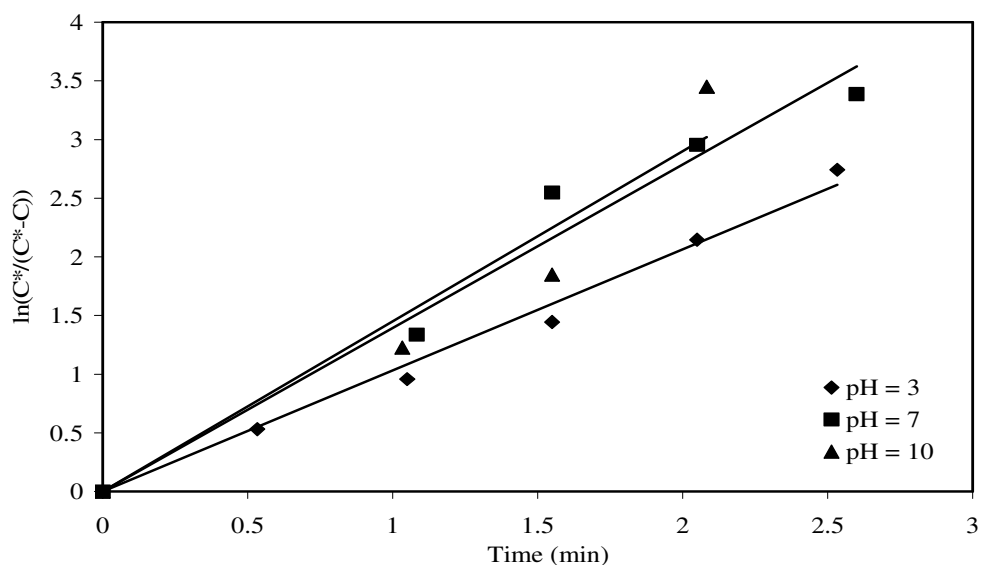


Figure 4.64 Plots to find k_La values for ozone absorption in buffered solutions at different pH values. Dye = none, ozone dose = 115 mg/Lmin, $[\text{PO}_4^{3-}] = 20$ mM.

The k_La values were re-estimated by solving the ozone mass balance in Eqn (4.3) by including the ozone decomposition term. The procedure used here was to try different k_La values in the model equation until the best fit between the experimental dissolved ozone concentrations vs. time curve and the corresponding curve from the model equation was obtained.

Table 4.25 k_d values estimated from the decomposition data.

pH	k_d (min ⁻¹)	R ²
3	0.012	0.99
7	0.040	0.99
10	0.310	0.99

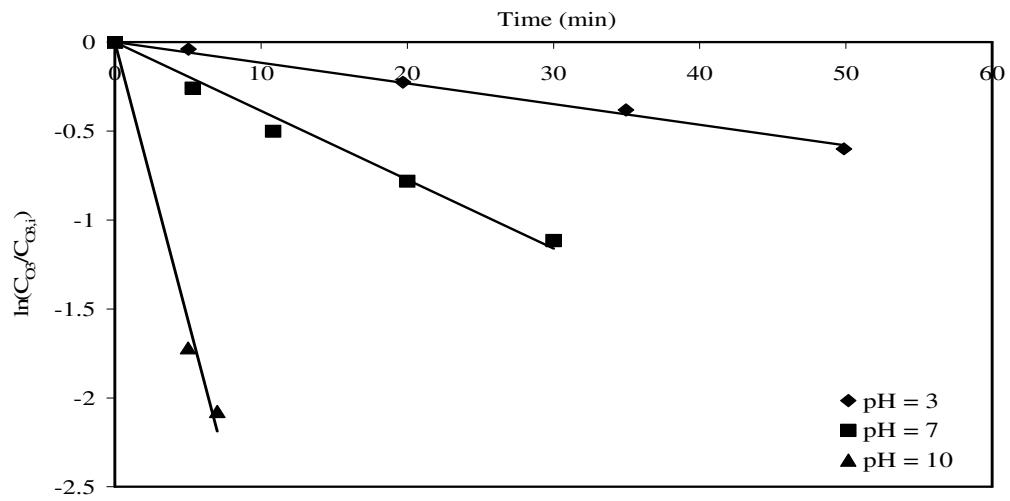


Figure 4.65 Decomposition rate analyses.

Model solutions and the experimental data measured for ozone absorption are given in Figures 4.66-4.68 for pH values of 3, 7 and 10, respectively.

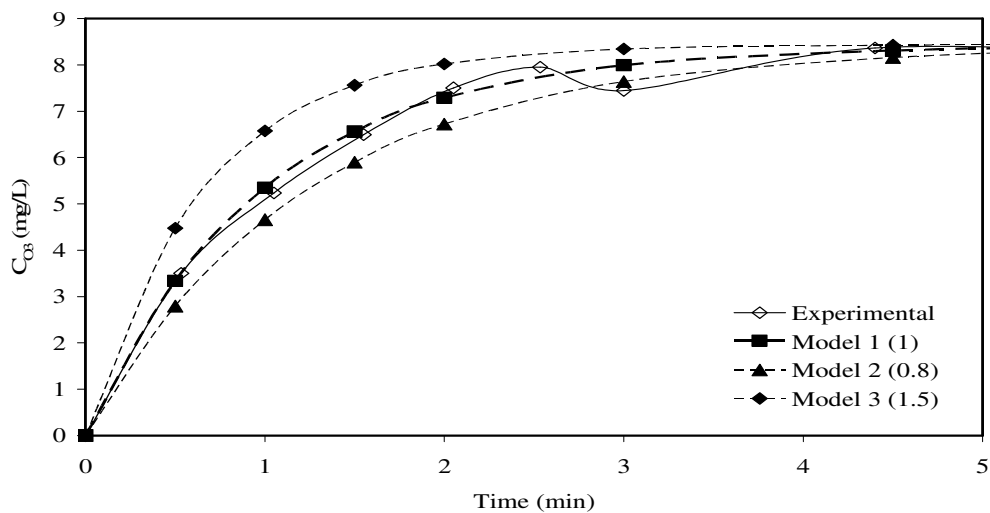


Figure 4.66 Comparison of the model and experimental data for absorption at pH = 3. Values in the brackets represent the k_{La} values used for the model solution in the unit of min^{-1}

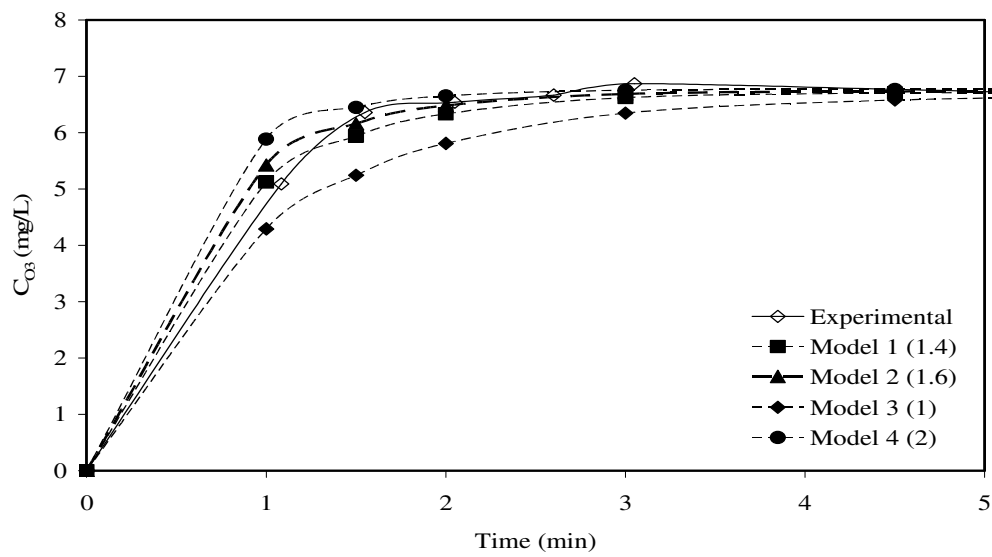


Figure 4.67 Comparison of the model and experimental data for absorption at pH = 7. Values in the brackets represent the k_La values used for the model solution in the unit of min^{-1}

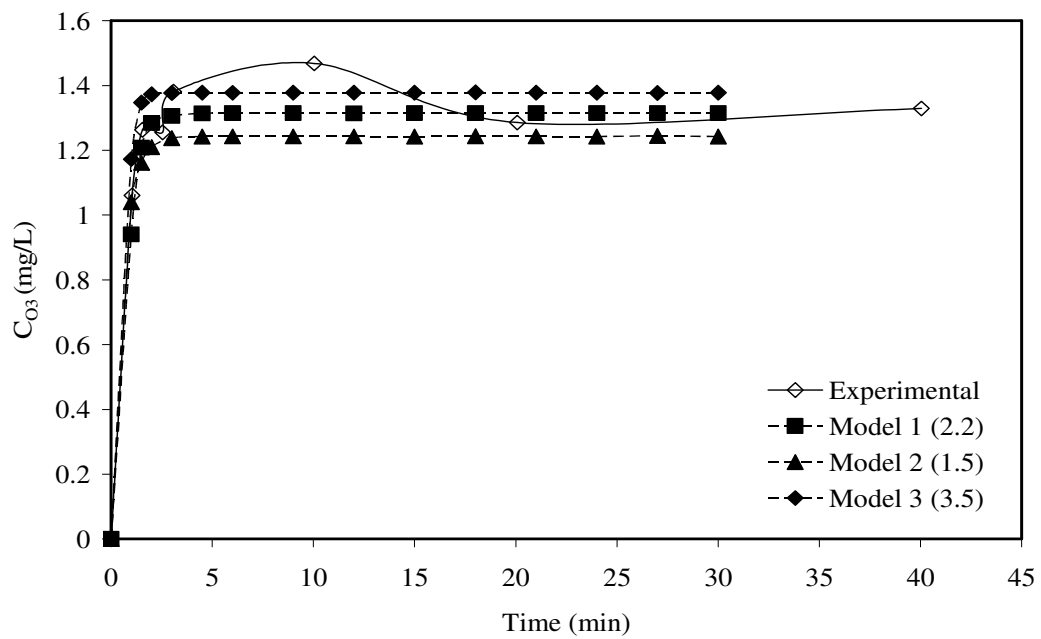


Figure 4.68 Comparison of the model and experimental data for absorption at pH = 10. Values in the brackets represent the k_La values used for the model solution in the unit of min^{-1}

The k_{La} values yielding the best agreement between the model and the experimental data (Figures 4.66-68) at each pH value are given in Table 4.26.

Table 4.26 Re-estimated k_{La} values by using the model approach.

pH	k_{La} (min ⁻¹)
3	1.0
7	1.6
10	2.2

Only the k_{La} value estimated for pH = 3 was found the same by using both of the cases, namely including and excluding the ozone decomposition term in the model equation (Eqn 4.3).

4.5.2 Semi - Batch Model

Semi-batch ozonation was also modeled and enhancement factors were estimated for the ozonation runs conducted at pH = 3. Since the model includes mass balances for the dye and ozone only, it was preferred to be applied at acidic conditions where ozone is the dominant oxidant. Solving Eqns (2.32) and (2.33) simultaneously for two phase ozone-dye reaction system, k_{La} values were estimated by assigning trial values to k_{La} and comparing the model results with the experimental data obtained. Model equations are given below:

$$\frac{dC_{O_3}}{dt} = k_{La}(C_{O_3}^* - C_{O_3}) - k.C_{O_3}C_d - k_dC_{O_3} \quad (4.3)$$

$$\frac{dC_d}{dt} = -k.C_{O_3}C_d \quad (4.4)$$

where:

$C_{O_3}^*$ = Dissolved ozone concentration at equilibrium

C_{O_3} = Bulk phase concentration of ozone

k = Reaction rate constant

k_d = Decomposition rate constant

C_d = Liquid phase dye concentration

$k_L a$ = Mass transfer coefficient

Among all these above parameters k_d was estimated from the decomposition data as explained in the previous section; ozone and dye concentrations were calculated and $k_L a$ values were estimated by comparing the calculated values with the experimental data. Also k was estimated from the found pseudo first order reaction rate constants. In order to obtain the k value, ozone concentrations in the liquid phase during the ozonation reaction must be known. Since the k value is equal to k'/C_{O_3} (Eqn 4.1) the k values are estimated accordingly using the average ozone concentration measured during the de-colorization of dye solution.

Equations (4.3) and (4.4) were solved simultaneously by using Matlab program with “ode 45 ordinary differential equation” solver. Best fits to the experimental data are given in Figures 4.69 to 4.71 as percent dye removals and dissolved ozone concentrations with respect to time.

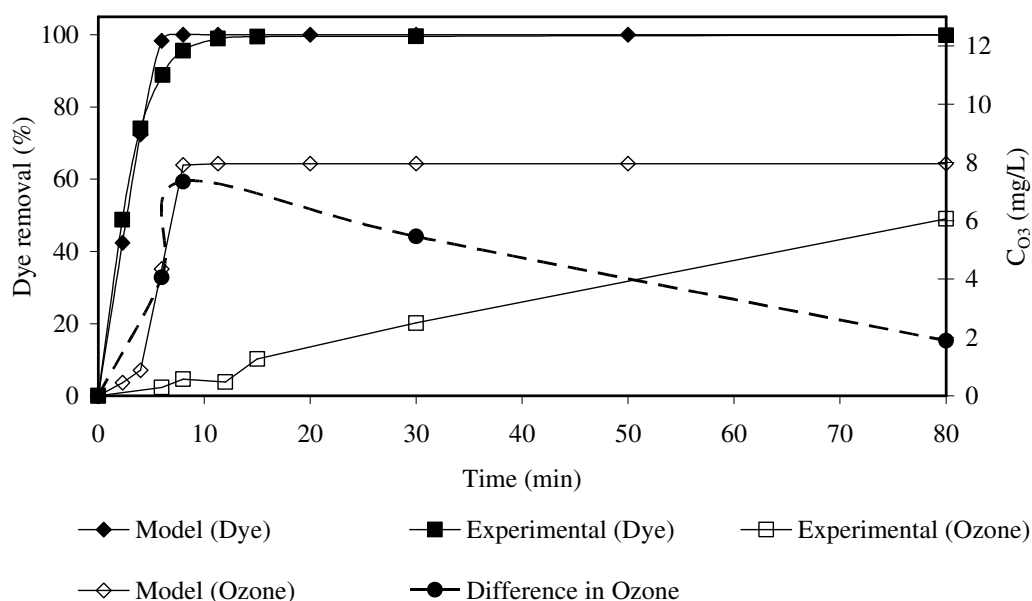


Figure 4.69 Comparison of results obtained from the model and the experiments. Dye = RB-5, pH = 3, $C_{d,i} = 100 \text{ mg/L}$, $k_{La} = 2.6 \text{ min}^{-1}$, $k = 0.7 \text{ mg.L}^{-1} \text{ min}^{-1}$, $C_{cat} = 0$.

The ozone concentration in the pseudo first order reaction rate term was taken as 0.5 mg/L according to the data given in Table 4.26. Since the de-colorization happened in the first ten min of ozonation, therefore the data measured up to 12 min was taken into account. After that time, increase in ozone concentrations was expected. On the other hand the ozone concentrations were expected to remain almost constant after the completion of the dye de-colorization. Actually model ozone concentrations were also found to follow these expectations. However the increase in the dissolved ozone concentration with time might be attributed to the resistance of by-products generated due to the oxidation by ozone. In order to emphasize this difference between model and experimental results, the differences between the calculated and measured ozone concentrations are also plotted in Figures 4.69 - 4.71. The difference curve represents the ozone concentration consumed for the oxidation of by-products and for mineralization of some organics in the medium or it can be

accepted as a relative measure of the side product oxidation taking place in the medium. Increasing difference might be regarded as increasing ozone consumption due to the reaction between side products and ozone, and decreasing difference might be regarded as decreasing ozone consumption due to the resistant by-products generated and ozone accumulation in the medium.

Table 4.27 Ozone concentrations measured. Dye = RB-5, pH = 3, $C_{d,i} = 100$ mg/L. ozone dose = 115 mg/Lmin, $[\text{PO}_4^{3-}] = 20$ mM.

Time (min)	C_{O_3} (mg/L)
0	0
6	0.29
8	0.57
12	0.48
15	1.26
30	2.50
80	6.07

Similar plots such as Figure 4.69 are given for the runs conducted at the initial dye concentrations of 400 and 800 mg/L in Figures 4.70 and 4.71; liquid phase ozone concentrations are also given in Tables 4.28 and 4.29.

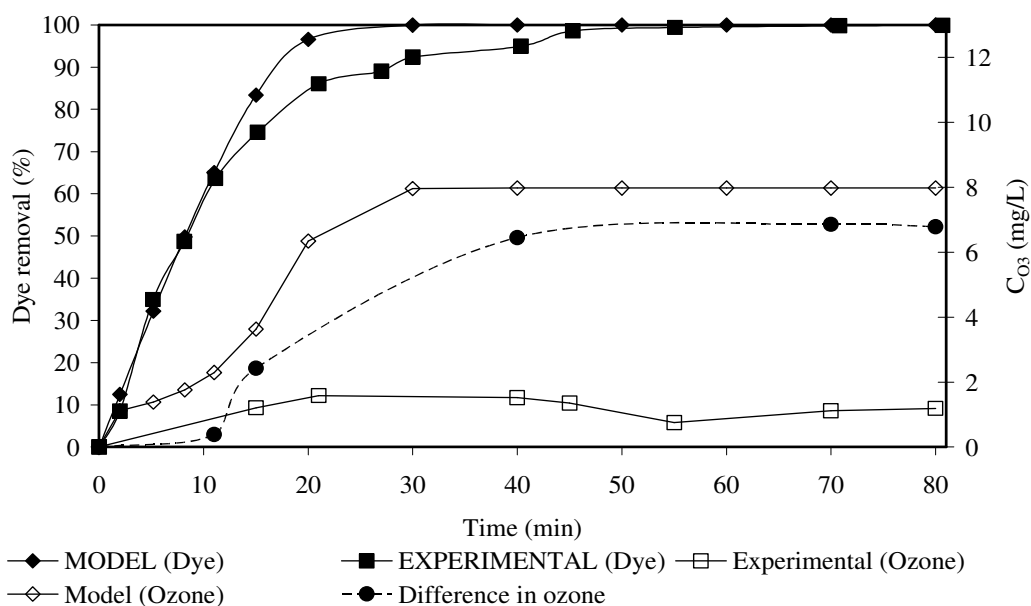


Figure 4.70 Comparison of results obtained from the model and the experiments. Dye = RB-5, pH = 3, $C_{d,i} = 400 \text{ mg/L}$, $k_{La} = 4 \text{ min}^{-1}$, $k = 0.063 \text{ mg.L}^{-1}\text{min}^{-1}$

Table 4.28 Ozone concentrations measured. Dye = RB-5, pH = 3, $C_{d,i} = 400 \text{ mg/L}$. ozone dose = 115 mg/Lmin, $[\text{PO}_4^{3-}] = 20 \text{ mM}$.

Time (min)	C_{O_3} (mg/L)
11	1.91
15	1.21
21	1.58
40	1.52
45	1.36
70	1.11
80	1.19

Average value for ozone was selected as the average of the data taken between 15th to 45th minutes as 1.4 mg/L, as seen in Table 4.28, and this value was used in Figure 4.70.

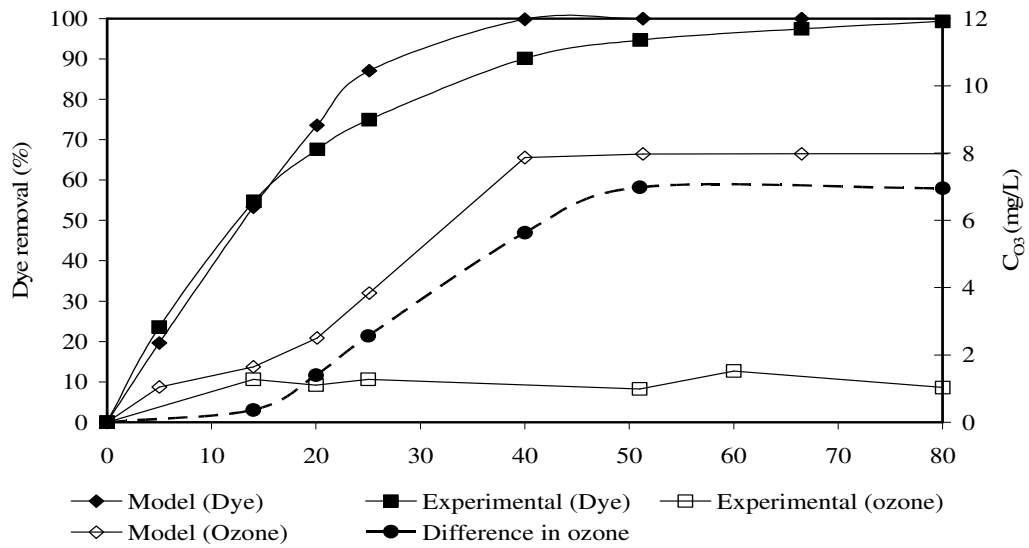


Figure 4.71 Comparison of results obtained from the model and the experiments. Dye = RB-5, pH = 3, $C_{d,i} = 800 \text{ mg/L}$, $k_{La} = 5 \text{ min}^{-1}$, $k = 0.05 \text{ mg.L}^{-1}\text{min}^{-1}$

Table 4.29 Ozone concentrations measured. Dye = RB-5, pH = 3, $C_{d,i} = 800 \text{ mg/L}$. ozone dose = 115 mg/Lmin , $[\text{PO}_4^{3-}] = 20 \text{ mM}$.

Time (min)	C_{O_3} (mg/L)
0	0.00
14	1.28
20	1.11
25	1.28
40	1.55
51	0.99
60	1.52
80	1.03

Average value for ozone was selected as the average of the data taken between 14th to 40th minutes as 1.3 mg/L , as seen in Table 4.28, and this value was used in Figure 4.70.

The first thing to be noticed in Figures 4.69 to 4.71 is the inconsistency of the ozone concentrations between the model and the experiments. It resulted from the

assumption of a single reaction between the dye and ozone while there are other side reactions carried out in the system which consume ozone. The model must be corrected including the side reactions or with a general TOC removal rate term in order to be more applicable. There are also inconsistencies between the dye removals obtained from the model and experiments which also resulted from the differences between ozone concentrations. Deviation in the experimental data was more significant, therefore the difference between the model and experimental ozone concentration values is more significant. For a better fit ozonation side products must be monitored and their oxidation rates must be included in the model equation.

The enhancement factors for the ozone absorption in the presence of oxidation reactions can be calculated from Eqn (2.5) and they are given in Table 4.30 and Figure 4.72.

Table 4.30 Enhancement factors calculated vs. initial dye concentrations. Dye = RB-5, pH = 3, ozone dose = 115 mg/Lmin, $[\text{PO}_4^{3-}] = 20 \text{ mM}$.

$C_{d,i} \text{ (mg/L)}$	E
100	2.6
400	4
800	8

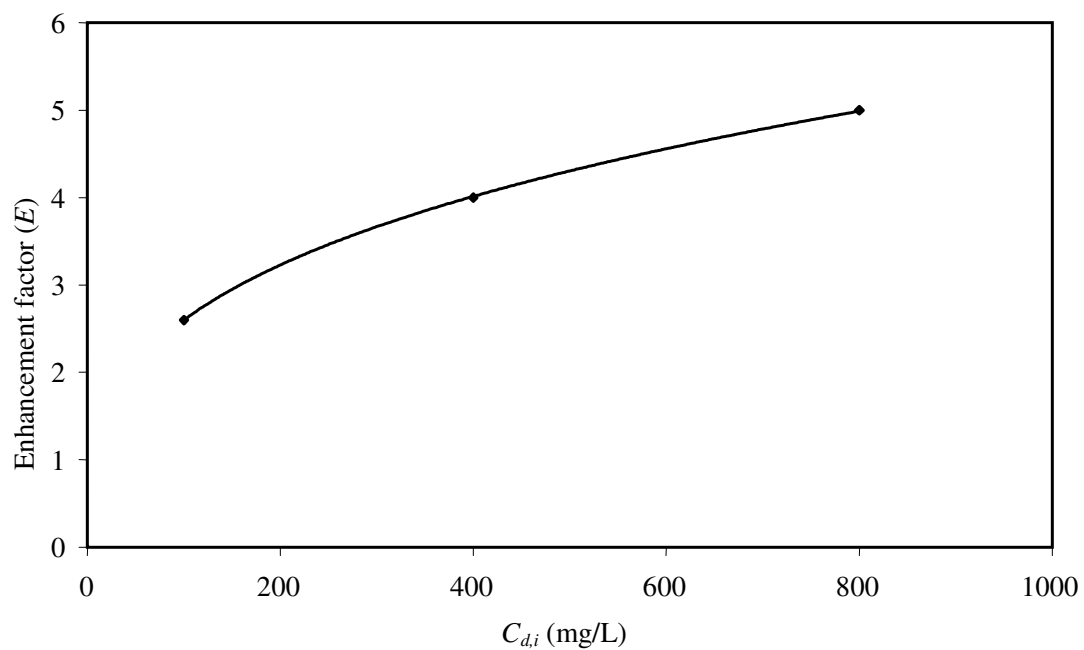


Figure 4.72 Enhancement factors calculated vs. initial dye concentrations, regression analysis. Dye = RB-5, pH = 3, ozone dose = 115 mg/Lmin, $[\text{PO}_4^{3-}] = 20$ mM.

According to the regression analysis the Enhancement factor was found to be increasing as a power function of initial dye concentration with a regression coefficient, of $R^2 = 0.999$. Equation obtained is given below:

$$E = 0.61 C_{d,i}^{0.31} \quad (4.5)$$

CHAPTER 5

CONCLUSIONS

Effects of operation parameters in sole ozonation such as initial dye concentration, solution pH, phosphate addition were investigated besides the catalytic ozonation experiments. Effect of Copper Sulfide (CuS) catalyst and the iron impregnated on alumina (Fe/Al₂O₃) catalyst were tested in the catalytic ozonation of two dyes separately.

It was found that increasing the solution pH increased the oxidation efficiency in both of the dye solutions while significant increase in the dye removal rates were only observed in the ozonation of Reactive Black-5 (RB-5) solutions. On the other hand increasing the initial dye concentration decreased the dye removal rate. Also mineralization rate decreased parallel to the dye removal rate. The scavenging effect of the buffer solutions on the ozonation was also observed in this work. Because of that acid or base additions during the reaction period with the use of a pH controller is recommended in ozonation experiments. It was observed that without any addition of buffer solutions, pH of the treated solution decreased rapidly due to the organic acid formation as a result of the oxidation of dye molecules. It was also observed that ozonation occurred in two steps. TOC removals were observed to be limited during the time that the dye removal occurred. After dye removal was completed, a higher increase in the TOC removals was observed.

In the catalytic runs, both the CuS and Fe/Al₂O₃ catalysts were found to be effective on the dye and TOC removals in the ozonation of RB-5 dye solutions. Only CuS was tested in the ozonation of RBBR dye solutions. Addition of CuS was found to be effective on the TOC removals only. It was also investigated whether these catalytic

reactions were effective through a heterogeneous catalytic mechanism or the catalytic effect was observed just due to the leaching metal ions into the aqueous medium when the catalyst particles were added.

It was observed that the addition of CuS to the reaction medium resulted in an increase in the liquid phase copper concentration during ozonation probably due to the oxidation of solid CuS by ozone. It was found that oxidation of dye solutions was enhanced by the hydroxyl radical generating effect of copper ions leached into the aqueous phase; in other words homogeneous catalytic effect of copper was significant. On the other hand, heterogeneous catalytic activity by Fe/Al₂O₃ was observed. Heterogeneous catalytic effect of iron impregnated alumina on the ozonation of oxalic acid was also reported in the literature [35].

In addition, ozonation was modeled to find the mass transfer effects in these ozonation systems. Model equations were found to be insufficient for determining the dissolved ozone concentrations during the reaction. The side reactions of the intermediates by ozone should be studied in more detail in an improved model.

CHAPTER 6

RECOMMENDATIONS

- Semi-batch runs can be conducted with the aid of a pH controller in order to avoid the side effects of phosphate buffers.
- Ozonation side products must be investigated in a more detailed way besides the TOC measurements, in order to explain the ozonation process better. For this purpose side products which are mainly organic acids and aldehydes can be investigated by HPLC analysis.
- Further investigations on copper as a catalyst can be made. Copper can be investigated as either a homogeneous or a heterogeneous catalyst in ozonation reactions. Copper salts can be used as copper source in desired amounts for homogeneous catalytic ozonation. Heterogeneous catalytic ozonation can also be investigated by copper loaded on a support such as γ -Alumina.
- Iron impregnation examined in this work can also be further studied by trying other iron loadings on alumina and catalysts dosages in reaction medium to investigate the optimum conditions for using iron impregnated on alumina ($\text{Fe}/\text{Al}_2\text{O}_3$) catalyst in a more feasible way.

- Use of a chlorine including precursor resulted chlorine impurities in the catalyst synthesized. Usage of iron nitrate as a precursor can be recommended for further works.
- A detailed study on the side reactions between ozone and the intermediates forming during the dye-ozone oxidation reactions, is recommended in a future study to achieve better results in modeling.

CHAPTER 7

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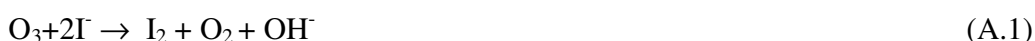
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APPENDIX A

ANALYTICAL METHODS AND DATA OBTAINED

A1. KI Method for Ozone

Potassium iodide method is used to measure gas phase ozone which is based on reaction of ozone with iodide at acidic conditions ($\text{pH} = 2$) reducing iodide to iodine then further titration of iodine with sodium thiosulfate. Measuring the iodine amount by the titration lead us to ozone amount fed into the solution by using the stoichiometry between iodine and ozone. These reactions are given below:



According to the stoichiometry two moles of thiosulfate ($\text{S}_2\text{O}_3^{2-}$) used in the titration as sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) goes into reaction with one mole of iodine. Also the stoichiometric factor between iodine and ozone is one therefore stoichiometric coefficient between ozone and thiosulfate is 1/2 (mole ozone / mole thiosulfate). Simplified equation for the determination of ozone amount is given in the procedure section.

Reagents

KI Solution: dissolve 20 g KI in a freshly boiled and cooled 1 L water store in a brown bottle avoiding the sunlight in a dark place, wait 1 day before use.

Starch Indicator: add 5 g to 800 mL boiling water with stirring dilute to 1 L then boil a few minutes and let settle overnight.

Other reagents are 1 N H_2SO_4 and 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$

Procedure:

Add 200 mL of KI solution in washing bottles feed ozone into the solution then take the KI solution into a 1 L flask add 10 mL 1N H₂SO₄, in order to set the solution pH to 2. titrate with 0.1 M Na₂S₂O₃ until the color before acid addition is re-obtained then add 4 mL of starch indicator to obtain the blue color and titrate again until blue color disappears. Continue with the blank test add 20 mL 1N H₂SO₄ and 4 mL starch if blue color obtained titrate if not titrate with 0.005 M iodine until blue color obtained then titrate with 0.05 M Na₂S₂O₃

$$\text{mg } O_3 / L = \frac{(A - B) \times M \times 24000}{\text{ml sample}} \quad (\text{A.3})$$

A = mL titrant for sample

B = mL titrant for blank

M = molarity of the Na₂S₂O₃

Ozone dose fed into the reactor was measured by KI method during the period with different time intervals. A sample calculation is given below and the the results are given in Table A.1.

A (V_{tit}) = 48 mL

B (V_{blank}) = 0.2 mL

M = 0.1 M

Sample volume = 200 mL

$$\text{mg } O_3 / L = \frac{(48 - 0.2) \times 0.1 \times 24000}{200} = 573.6 \text{ mg } O_3 / L \text{ in 200 mL solution (must be}$$

divided by the dilution factor.)

$$573.6 \frac{\text{mg } O_3}{L} \times \frac{200 \text{ ml}}{1000 \text{ ml}} \times \frac{1}{1 \text{ min}} = 114.7 \frac{\text{mg } O_3}{L / \text{min}}$$

Table A.1 Ozone dose measured during the period that experimental runs are conducted. $V_{KI} = 200$ mL and 0.1 or 0.3 M sodium thiosulfate was used as titrant.

#	O ₃ dose (mg/L _{liq} min)	% Error	Absolute % Error
1	117.4	-1.7	1.7
2	125.3	-8.5	8.5
3	104.4	9.6	9.6
4	116.6	-1.0	1.0
5	111.6	3.4	3.4
6	110.2	4.6	4.6
7	110.9	4.0	4.0
8	107.1	7.2	7.2
9	102.7	11.1	11.1
10	138.2	-19.7	19.7
11	121.4	-5.2	5.2
12	128.7	-11.4	11.4
13	110.2	4.6	4.6
14	107.3	7.1	7.1
15	128.2	-11.0	11.0
16	119.5	-3.5	3.5
17	112.3	2.7	2.7
18	119.8	-3.7	3.7
19	112.3	2.7	2.7
20	109.4	5.2	5.2
21	114.7	0.7	0.7
22	117.1	-1.4	1.4
23	107.5	6.9	6.9
24	118.1	-2.2	2.2
25	109.7	5.0	5.0
26	122.7	-6.2	6.2
27	111.2	3.7	3.7
28	109.7	5.0	5.0
29	117.9	-2.1	2.1
30	105.4	8.7	8.7
31	120.5	-4.4	4.4
32	115.1	0.3	0.3
33	109.7	5.0	5.0
34	118.4	-2.5	2.5
35	124.8	-8.1	8.1
36	116.2	-0.6	0.6
37	120.5	-4.4	4.4
Average = 115.5		ave. %error \pm = 5.3	

A2 Indigo Method

Method for dissolved ozone measurements based on the decolorization of indigo trisulfonate at acidic conditions. This method was found by H. Bader and J. Hoigné with their work “Determination of Ozone in Water by the Indigo Method” [39]. They stated that it can be assumed that one mole of ozone undergoes reaction with one mole of sulfonated indigo. They also determined a constant sensitivity factor which reflects the change in absorbance with the amount of ozone added as $\Delta A = 20\,000\text{ cm}^{-1} (\text{mol.L}^{-1})^{-1}$. They stated that the factor given does not vary with ozone concentration, small changes in temperature of reaction or with the chemical composition of the water unless pH is below 4. In this work dissolved ozone amount was measured by using the sensitivity factor given by Bader et al. [39]. UV absorbance measurements were conducted at wavelength of 600 nm.

Reagent Preparation

Stock Solution (1 L)

500 mL water + 1 mL dose Phosphoric acid + 770 mg potassium indigo phosphate + fill to mark

Indigo Reagent I (1 L)

20 mL stock + 10 g NaH_2PO_4 + 7 mL conc phosphoric acid + dilute to mark

Indigo Reagent II (1 L)

100 mL stock + 10 g NaH_2PO_4 + 7 mL conc phosphoric acid + dilute to mark

APPLICATION

10 mL Reagent II + 10 mL sample → 100 mL

read absorbance at 600 nm against the blank

Use formula to calculate the oxygen amount:

$$mg\ O_3 / L = \frac{100 \times \Delta A}{f \times b \times V} \quad (A.4)$$

ΔA = absorbance difference between the blank and the sample $f = 0.42$ (factor depends on the sensitivity factor in order to obtain a result in terms of mg/L).

b = pathway length of the cell (1)

V = sample volume (90 mL) (found value must be corrected by a correction factor according to the dilution (10 mL of sample added))

Sample Calculation:

In most of the cases that ozone was measured, it was measured in dye solutions which have maximum absorptions at 590 and 595 nm which resulted interference in measurements. That interference problem was handled by taking the difference between the calculated absorbance of the dye solution at that particular time which sample was taken in indigo solution and the absorbance of the sample taken in indigo solution. A sample calculation is given below:

Calculation of ozone concentration at the time of 13.8 min: In the ozonation of 400 mg/L RBBR dye solution at pH = 3, pseudo reaction rate constant for dye removal was found to be $0.27\ min^{-1}$ from the data obtained for dye removal. Since there is no measured absorbance of dye solution at that specific time (there is about 30 seconds of time between the sampling of dye removal tests and ozone conc tests), the possible absorbance value that dye solution has at the time of 13.8th min was calculated from the estimated k' value.

$$\ln\left(\frac{C_d}{C_{d,i}}\right) = -0.27 \times 13.8 = -3.73$$

$$C_d = e^{-3.73} \times 417\ mg / L = 10\ mg / L$$

$$C_d = Abs \times 78$$

$$Abs = \frac{C_d}{78} = \frac{10}{78} = 0.129$$

up to this point, absorbance of the dye that interfered with the absorbance value measured for the indigo sample was calculated. Keeping in mind the dilution of the indigo samples before the measurement, this absorbance value must also be multiplied by the dilution factor.

$$\text{Dilution} = \frac{V_{\text{sample}}}{V_{\text{dil.}}(100\text{ ml})} = \frac{14\text{ ml}}{100\text{ ml}} = 0.14$$

$$Abs = 0.129 \times 0.14 = 0.018$$

True absorbance of the indigo solution was found by subtracting the correction value calculated from the absorbance measured for the indigo sample.

$$Abs_{\text{measured}} = 0.19$$

$$Abs_{\text{True}} = 0.19 - 0.018 = 0.17$$

$$mg\ O_3 / L = \frac{100 \times \Delta A}{f \times b \times V}$$

$$\Delta A = Abs_{\text{blank}} - Abs_{\text{True}} = 0.217 - 0.17 = 0.05$$

Putting ΔA in the equation ozone concentration:

$$mg\ O_3 / L = \frac{100 \times 0.05}{0.42 \times 1 \times 14} = 0.77\text{ mg} / L$$

Note: The absorbance values measured for the dye solutions at 590 nm and 600 nm were found to be very close that is why the absorbance was calculated by the use of the k' value estimated at 590 nm. The linear relationship obtained by the use of absorbance values measured both at 590 and 600 nm is given the calibration curve obtained for RBBR is also given in Figure A.1 as an example.

$$0.96 \text{ Abs } 590 \text{ nm} = \text{Abs } 600 \text{ nm} (R^2 = 0.999) \quad (\text{A.5})$$

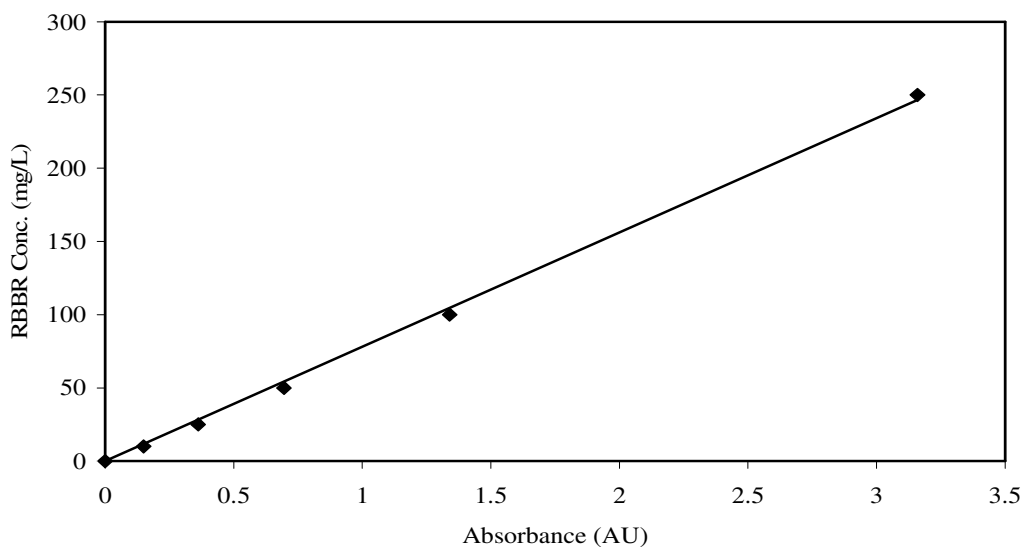


Figure A.1 Relation between absorbance values obtained at 590 and 600 nm. From the data obtained in a preliminary experiment; ozonation of 300 mg/L RBBR dye solution.

Data collected for dissolved ozone measurements and ozone concentrations measured are given in Tables A.2-A.35:

Table A.2 Ozone Concentrations. Dye = RBBR, $C_{d,i} = 400 \text{ mg/L}$, $\text{pH} = 3$, Ozone Dose = 115 mg/min.L . $C_{cat} = 0 \text{ g/L}$, $[\text{PO}_4^{3-}] = 20 \text{ mM}$

t(min)	Abs sample	V (mL) sample	O ₃ mg/L
5.6	0.3	11	0.1
8.6	0.2	10	1.2
11.6	0.2	11	0.7
13.8	0.2	14	0.7
15.5	0.2	11.5	0.8
36.4	0.1	12	1.6
60.6	0.0	10	5.0
80.3	0.0	12	4.3

Table A.3 Ozone Concentrations. Dye = RBBR, $C_{d,i} = 400$ mg/L, pH = 7, Ozone Dose = 115 mg/min.L. $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

t(min)	Abs sample	V (mL) sample	O ₃ mg/L
1.5	0.663	11	-1.51
5.5	0.353	11	-0.38
8.5	0.264	12	0.13
10.8	0.223	10	0.39
12.8	0.204	9	0.62
16.7	0.198	11	0.49
19.4	0.195	11	0.50
35.8	0.173	13	0.79
60.8	0.11	9	2.80
80.0	0.13	13.5	1.52

Table A.4 Ozone Concentrations. Dye = RBBR, $C_{d,i} = 400$ mg/L, pH = 10, Ozone Dose = 115 mg/min.L. $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

t(min)	Abs sample	V (mL) sample	O ₃ mg/L
5.5	0.299	10	-0.04
8.9	0.223	10	0.38
12.5	0.184	9	0.80
16.6	0.179	10.5	0.64
23.8	0.182	8	0.64
36.0	0.182	12.5	0.40
60.0	0.19	9	0.34
80.0	0.158	14	0.77

Table A.5 Ozone Concentrations. Dye = RBBR, $C_{d,i} = 400$ mg/L, pH = 3, Ozone Dose = 115 mg/min.L. $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

t(min)	Abs sample	V(mL) sample	O ₃ mg/L
3.3	0.442	10	-0.25
5.6	0.371	12	-0.29
8.5	0.26	11	0.37
10.3	0.229	11	0.57
12.8	0.207	10	0.74

Table A.5 Continued

t(min)	Abs sample	V(mL) sample	O ₃ mg/L
15.5	0.191	10	0.93
20.3	0.181	10	1.04
35.5	0.18	10	1.02
60.7	0.172	9	1.35
80.8	0.13	14	1.64

Table A.6 Ozone Concentrations. Dye = RBBR, $C_{d,i} = 400$ mg/L, pH = 7, Ozone Dose = 115 mg/min.L. $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

t(min)	Abs sample	V(mL) sample	O ₃ mg/L
5.5	0.357	12	0.07
8.5	0.24	10	0.62
12.5	0.203	11	0.58
16.8	0.19	11.8	0.51
19.8	0.193	10	0.41
23.7	0.184	10	0.57
35.4	0.184	12	0.46
60.8	0.188	10	0.45
80.8	0.13	11	1.67

Table A.7 Ozone Concentrations. Dye = RBBR, $C_{d,i} = 400$ mg/L, pH = 10, Ozone Dose = 115 mg/min.L. $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

t(min)	Abs sample	V(mL) sample	O ₃ (mg/L)
7.8	0.25	9	0.36
9.9	0.229	11	0.44
11.6	0.218	12	0.46
16.2	0.214	12	0.28
24.1	0.217	12	0.13
35.7	0.201	12	0.44
62.0	0.189	12	0.67
80.3	0.118	12	2.08

Table A.8 Ozone Concentrations. Dye = RBBR, $C_{d,i} = 800$ mg/L, pH = 3, Ozone Dose = 115 mg/min.L. $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

t(min)	Abs sample	V(mL) sample	O ₃ mg/L
6.8	0.6	14	-1.61
9.9	0.3	11	0.34
12.6	0.2	13	0.52
16.2	0.1	8	1.28
21.1	0.1	12	0.99
30.7	0.1	12	1.25
47.0	0.1	14	1.31
80.3	0.1	10	2.26

Table A.9 Ozone Concentrations. Dye = RBBR, $C_{d,i} = 800$ mg/L, pH = 7, Ozone Dose = 115 mg/min.L. $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

t(min)	Abs sample	V(mL) sample	O ₃ mg/L
6.7	0.490	12	-0.40
9.5	0.296	10	0.02
12.7	0.210	11	0.48
15.3	0.162	12	0.81
20.3	0.138	12	0.65
30.4	0.114	10	0.99
45.4	0.113	11	0.89
80.3	0.050	12	2.06

Table A.10 Ozone Concentrations. Dye = RBBR, $C_{d,i} = 800$ mg/L, pH = 10, Ozone Dose = 115 mg/min.L. $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

t(min)	Abs sample	V (mL) sample	O ₃ mg/L
6.4	0.452	11	-0.99
9.4	0.290	11	-0.12
12.6	0.208	12	0.33
15.4	0.175	9	0.19
20.5	0.152	10	0.29
30.4	0.138	11	0.37
45.4	0.136	14	0.31
80.4	0.135	9	0.50

Table A.11 Ozone Concentrations. Dye = RBBR, $C_{d,i} = 800$ mg/L, pH = 3, Ozone Dose = 115 mg/min.L. $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

t(min)	Abs sample	V(mL) sample	O ₃ mg/L
6.3	0.542	11	-0.37
9.4	0.336	9	0.07
12.5	0.276	13	0.55
15.4	0.204	12	0.92
21.0	0.166	11	0.91
30.3	0.151	11	0.90
45.4	0.139	10	1.22
80.3	0.138	10	1.24

Table A.12 Ozone Concentrations. Dye = RBBR, $C_{d,i} = 800$ mg/L, pH = 7, Ozone Dose = 115 mg/min.L. $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

t(min)	Abs sample	V (mL) sample	O ₃ mg/L
7.3	0.439	12	-0.29
10.4	0.250	10	0.51
13.3	0.188	11	0.74
15.3	0.159	10	0.84
20.4	0.140	11	0.63
30.8	0.135	10.5	0.47
45.3	0.130	11	0.52
80.4	0.098	11	1.21

Table A.13 Ozone Concentrations. Dye = RBBR, $C_{d,i} = 800$ mg/L, pH = 10, Ozone Dose = 115 mg/min.L. $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

t(min)	Abs sample	V(mL) sample	O ₃ mg/L
6.4	0.393	9.5	-0.79
9.4	0.291	11	-0.34
12.6	0.178	10.5	0.69
15.4	0.162	11	0.43
20.5	0.138	11	0.48
30.4	0.129	11	0.48
45.4	0.143	11	0.15
80.4	0.142	10	0.19

Table A.14 Ozone Concentrations. Dye = RBBR, $C_{d,i} = 100$ mg/L, pH = 3, Ozone Dose = 115 mg/min.L. $C_{cat} = 0.2$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

t (min)	Abs sample	V(mL) sample	O ₃ mg/L
1.5	0.3	11	-0.01
2.4	0.2	12	0.15
3.4	0.2	12	0.57
4.4	0.2	9	0.91
6.6	0.2	12	1.12

Table A.15 Ozone Concentrations. Dye = RBBR, $C_{d,i} = 100$ mg/L, pH = 3, Ozone Dose = 115 mg/min.L. $C_{cat} = 0.4$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

t(min)	Abs sample	V(mL) sample	O ₃ mg/L
1.4	0.261	12	0.32
2.4	0.223	12	0.49
3.5	0.199	10	0.71
4.8	0.185	12	0.74
6.7	0.171	14	0.80

Table A.16 Ozone Concentrations. Dye = RBBR, $C_{d,i} = 100$ mg/L, pH = 3, Ozone Dose = 115 mg/min.L. $C_{cat} = 0.7$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

t(min)	Abs sample	V (mL) sample	O ₃ mg/L
1.5	0.255	8	0.11
2.7	0.241	13	0.12
3.6	0.217	12	0.33
4.6	0.201	12	0.49
7.1	0.192	12	0.53

Table A.17 Ozone Concentrations. Dye = RBBR, $C_{d,i} = 400$ mg/L, pH = 10, Ozone Dose = 115 mg/min.L. $C_{cat} = 0$ g/L, $[\text{CO}_3^{2-}] = 20$ g/L

t(min)	Abs sample	V(mL) sample	O ₃ mg/L
7.8	0.3	13	-0.28
9.9	0.2	10	0.27
11.6	0.2	12	-0.06
16.2	0.2	10	0.41
24.1	0.2	10	0.44
35.7	0.2	10	0.50
62.0	0.2	11	0.24

Table A.18 Ozone Concentrations. Dye = RB-5, $C_{d,i} = 100$ mg/L, pH = 3, Ozone Dose = 115 mg/min.L. $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

t(min)	Abs sample	V (mL) sample	O ₃ mg/L
6.4	0.22	12	0.42
9.1	0.17	13	0.65
12.8	0.17	12	0.51
15.5	0.13	12	1.27
30.5	0.10	8	2.50
80.3	0.05	10	6.07

Table A.19 Ozone Concentrations. Dye = RB-5, $C_{d,i} = 100$ mg/L, pH = 7, Ozone Dose = 115 mg/min.L. $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

t(min)	Abs sample	V(mL) sample	O ₃ mg/L
4.6	0.255	10	0.23
6.5	0.225	13	0.26
8.7	0.194	13	0.44
11.7	0.179	10	0.65
15.5	0.19	12	0.27
30.5	0.15	11	3.25
80.5	0.038	12	5.20

Table A.20 Ozone Concentrations. Dye = RB-5, $C_{d,i} = 100$ mg/L, pH = 10 , Ozone Dose = 115 mg/min.L. $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

t(min)	Abs sample	V(mL) sample	O ₃ mg/L
4.8	0.212	15	0.45
7.5	0.185	11	0.51
9.4	0.186	11	0.40
11.5	0.187	11	0.36
15.6	0.171	12	0.64
45.8	0.223	11	1.67
80.3	0.220	11	1.74

Table A.21 Ozone Concentrations. Dye = RB-5, $C_{d,i} = 100$ mg/L, pH = 3 , Ozone Dose = 115 mg/min.L. $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

t(min)	Abs sample	V (mL) sample	O ₃ mg/L
4.3	0.24	10	0.41
6.3	0.20	9	0.37
9.3	0.16	8.5	0.74
11.8	0.17	10	0.49
15.4	0.15	12	0.75
30.7	0.09	12	1.94
45.7	0.06	9.5	3.21
80.5	0.03	9	4.07

Table A.22 Ozone Concentrations. Dye = RB-5, $C_{d,i} = 100$ mg/L, pH = 7 , Ozone Dose = 115 mg/min.L. $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

t(min)	Abs sample	V(mL) sample	O ₃ mg/L
4.5	0.215	11	0.21
7.4	0.161	11	0.36
9.4	0.166	12	0.04
11.7	0.149	11	0.29
16.0	0.149	10	0.27
45.4	0.03	10	3.10
80.4	0.042	6.5	4.32

Table A.23 Ozone Concentrations. Dye = RB-5, $C_{d,i} = 100$ mg/L, pH = 10 , Ozone Dose = 115 mg/min.L. $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

t(min)	Abs sample	V (mL) sample	O ₃ mg/L
4.8	0.166	13	0.29
7.5	0.157	11	0.13
9.4	0.158	11	0.06
11.5	0.155	11	0.11
15.6	0.155	13	0.09
45.8	0.127	7	1.12
80.3	0.081	13	1.45

Table A.24 Ozone Concentrations. Dye = RB-5, $C_{d,i} = 400$ mg/L, pH = 3 , Ozone Dose = 115 mg/min.L. $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

t(min)	A sample	V (mL) sample	O ₃ mg/L
8.4	1.00	12	2.68
11.3	0.79	11	1.41
15.3	0.61	11	0.83
21.8	0.36	10	1.19
40.4	0.15	12	1.37
45.7	0.14	12	1.25
55.7	0.14	10	0.70
70.5	0.11	13	1.09
80.5	0.11	10	1.18

Table A.25 Ozone Concentrations. Dye = RB-5, $C_{d,i} = 400$ mg/L, pH = 7 , Ozone Dose = 115 mg/min.L. $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

t(min)	Abs sample	V(mL) sample	O ₃ mg/L
5.4	0.901	10	-1.10
10.7	0.475	11	-0.41
16.8	0.224	11	0.73
20.6	0.163	12	1.02
25.8	0.133	11	1.01
30.7	0.113	10	1.29
35.5	0.111	10	1.24

Table A.26 Ozone Concentrations. Dye = RB-5, $C_{d,i} = 400$ mg/L, pH = 10 , Ozone Dose = 115 mg/min.L. $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

t(min)	Abs sample	V (mL) sample	O ₃ mg/L
5.5	0.535	10	0.16
10.3	0.154	11	2.46
15.4	0.140	11	0.91
20.7	0.141	12	0.39
25.4	0.138	12	0.34
30.6	0.137	11	0.36
45.8	0.135	18	0.24
80.4	0.138	13	0.28

Table A.27 Ozone Concentrations. Dye = RB-5, $C_{d,i} = 400$ mg/L, pH = 3 , Ozone Dose = 115 mg/min.L. $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

t(min)	Abs sample	V(mL) sample	O ₃ mg/L
5.3	1.12	11	0.29
11.3	0.69	13	0.65
15.3	0.35	8	0.57
21.0	0.28	11	0.54
25.4	0.21	11	0.70
31.1	0.16	9	0.92
60.7	0.12	10	0.72
80.6	0.11	10	0.98

Table A.28 Ozone Concentrations. Dye = RB-5, $C_{d,i} = 400$ mg/L, pH = 7 , Ozone Dose = 115 mg/min.L. $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

t(min)	Abs sample	V(mL) sample	O ₃ mg/L
15.4	0.207	9	0.43
20.7	0.158	11	0.54
26.8	0.142	11	0.43
30.6	0.134	12	0.47
35.8	0.134	13	0.38
45.7	0.129	12	0.48
60.5	0.131	12	0.44

Table A.29 Ozone Concentrations. Dye = RB-5, $C_{d,i} = 400$ mg/L, pH = 10 , Ozone Dose = 115 mg/min.L. $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

t(min)	Abs sample	V(mL) sample	O ₃ mg/L
10.7	0.208	10	0.95
15.8	0.154	9	0.66
20.4	0.140	11	0.57
31.8	0.141	10	0.46
45.5	0.138	11	0.48
60.4	0.137	13	0.42
80.3	0.135	10	0.60

Table A.30 Ozone Concentrations. Dye = RB-5, $C_{d,i} = 800$ mg/L, pH = 3 , Ozone Dose = 115 mg/min.L. $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

t(min)	Abs sample	V(mL) sample	O ₃ mg/L
14.4	1.67	11	1.58
20.4	1.35	12	0.77
25.5	1.04	12	0.74
40.7	0.46	11	1.34
51.5	0.30	10	0.84
60.5	0.21	10	1.17
80.4	0.15	14	0.92

Table A.31 Ozone Concentrations. Dye = RB-5, $C_{d,i} = 800$ mg/L, pH = 7 , Ozone Dose = 115 mg/min.L. $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

t(min)	Abs sample	V(mL) sample	O ₃ mg/L
13.3	0.867	9	0.64
22.0	0.482	11	0.62
33.3	0.171	9	1.63
40.4	0.128	10	1.46
50.4	0.110	11	1.06
60.6	0.119	11	0.60
80.3	0.119	12	0.43

Table A.32 Ozone Concentrations. Dye = RB-5, $C_{d,i} = 800$ mg/L, pH = 10 , Ozone Dose = 115 mg/min.L. $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

t(min)	Abs sample	V(mL) sample	O ₃ mg/L
13.4	0.379	10	-0.18
20.5	0.183	12	0.53
25.3	0.149	12	0.42
33.3	0.133	10	0.40
40.3	0.128	13	0.35
60.4	0.131	12	0.30
80.4	0.126	12	0.40

Table A.33 Ozone Concentrations. Dye = RB-5, $C_{d,i} = 800$ mg/L, pH = 3 , Ozone Dose = 115 mg/min.L. $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

t(min)	Abs sample	V(mL) sample	O ₃ mg/L
13.4	1.74	12	1.7
20.4	1.00	10	0.9
26.2	0.93	14	1.1
33.6	0.48	10	1.1
42.4	0.31	10	1.4
60.4	0.16	10	1.4
80.8	0.14	13	0.8

Table A.34 Ozone Concentrations. Dye = RB-5, $C_{d,i} = 800$ mg/L, pH = 7 , Ozone Dose = 115 mg/min.L. $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

t(min)	Abs sample	V(mL) sample	O ₃ mg/L
13.3	0.84	11	-0.27
20.9	0.383	13	1.08
26.3	0.222	11	1.05
34.2	0.144	12	1.00
42.6	0.126	12	0.72
60.4	0.130	11	0.38
80.4	0.129	12	0.34

Table A.35 Ozone Concentrations. Dye = RB-5, $C_{d,i} = 800$ mg/L, pH = 10, Ozone Dose = 115 mg/min.L. $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

t(min)	Abs sample	V(mL) sample	O ₃ mg/L
13.6	0.365	11	0.14
20.6	0.159	11	0.91
25.5	0.131	10	0.84
33.5	0.121	10	0.76
40.7	0.12	14	0.53
50.6	0.116	8	1.01
60.2	0.122	10	0.67

A3. TOC Measurements

Dissolved organic carbon content in the samples collected was measured by Shimadzu TOC-V_{CPH/CPN} TOC analyzer as Total Carbon / Inorganic Carbon (TC/IC) analysis. For the samples collected at pH = 3 and 7 only TC measurements were done, while for the samples collected at pH = 10 both TC and IC analyses were performed to measure the inorganic carbon which came from the carbon dioxide dissolved in water at basic conditions and TOC was calculated from the difference between TC and IC.

Principles of Total Carbon (TC) analysis

TC analysis is based on combustion of the sample presented in the analyzer by its injector. Sample is presented in a combustion tube which was filled with a Pt/Al₂O₃ combustion catalyst. Combustion tube is heated to 680°C before the analysis begins by the heating chamber that it is placed in. TC components in the sample are turned into carbon dioxide as the result of combustion and carbon dioxide is carried by the carrier gas (dry air) which flows with a rate of 150 mL/min. Combustion products are carried with the carrier gas in an electronic dehumidifier where the gas is cooled

and dehydrated. The sample then is carried into a halogen scrubber where chlorine and other halogens produced in the combustion are removed and finally carbon dioxide is delivered to the cell of a non-dispersive infrared (NDIR) gas analyzer, where the carbon dioxide is detected. The NDIR outputs an analog detection signal that is received as a peak by the software (TOC-Control V software) of the analyzer where area is calculated in terms of carbon concentration according to the calibration curve obtained [46].

The peak area generated is proportional to the TC concentration of the sample. In order to measure the TC in the solution a calibration curve that mathematically expresses the relation between the peak area and TC concentration was generated by using a potassium acid phthalate solution which was purchased commercially from Hach Lange.

Principles of IC Analysis

Inorganic carbon found in carbonates and carbon dioxide dissolved in water. In this work, IC content measured in the samples was resulted from carbon dioxide dissolved in water at pH = 10. IC analysis is based on acidifying the solution to a pH less than 3 with hydrochloric acid where all carbonates turn into carbon dioxide. Then dissolved carbon dioxide in the sample is volatilized by bubbling the sample in the syringe with the carrier gas (dry air). The carbon dioxide gas again is carried through dehumidifier and halogen scrubber to the NDIR and detected as carbon dioxide peaks. Calibration curve was generated by using reagent grade sodium hydrogen carbonate and sodium carbonate according to the manual Section 4.1.14.

TOC results measured in the experiments are given in Tables A.36-A.77:

Table A.36 TOC results measured. Dye =RBBR, $C_{d,i} = 100$ mg/L, pH = 3, Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	TOC (mg/L)
0	29.9
12	27.4
30	25.1
80	24.8

Table A.37 TOC results measured. Dye =RBBR, $C_{d,i} = 100$ mg/L, pH = 7, Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	TOC (mg/L)
0	30
12	24.0
30	20.0
60	17.0
80	15.7

Table A.38 TOC results measured. Dye =RBBR, $C_{d,i} = 100$ mg/L, pH = 10, Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	TOC (mg/L)
0	27.3
12	18.7
30	13.1
80	9.3

Table A.39 TOC results measured. Dye =RBBR, $C_{d,i} = 100$ mg/L, pH = 3, Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	TOC (mg/L)
0	29.9
12	25.5
30	21.0
60	18.8
80	18.5

Table A.40 TOC results measured. Dye =RBBR, $C_{d,i} = 100$ mg/L, pH = 7, Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	TOC (mg/L)
0	30.1
12	21.0
30	8.8
80	5.4

Table A.41 TOC results measured. Dye =RBBR, $C_{d,i} = 100$ mg/L, pH = 10, Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	TOC (mg/L)
0	28.5
12	17.9
30	6.0
60	2.5
80	2.1

Table A.42 TOC results measured. Dye =RBBR, $C_{d,i} = 100$ mg/L, pH = 3, Ozone Dose = 115 mg/min.L, $C_{cat} = 0.2$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	TOC (mg/L)
0	28.9
12	22.5
30	19.9
60	18.5
80	17.6

Table A.43 TOC results measured. Dye =RBBR, $C_{d,i} = 100$ mg/L, pH = 3, Ozone Dose = 115 mg/min.L, $C_{cat} = 0.4$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	TOC (mg/L)
0	24.5
12	19.3
30	16.7
60	13.5
80	11.9

Table A.44 TOC results measured. Dye =RBBR, $C_{d,i} = 100$ mg/L, pH = 3, Ozone Dose = 115 mg/min.L, $C_{cat} = 0.7$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	TOC (mg/L)
0	31.5
12	24.8
30	21.7
60	17.1
80	15.4

Table A.45 TOC results measured. Dye =RBBR, $C_{d,i} = 400$ mg/L, pH = 3, Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	TOC (mg/L)
0	126.4
23	104.8
36	96.8
67	90.0
80	89.0

Table A.46 TOC results measured. Dye =RBBR, $C_{d,i} = 400$ mg/L, pH = 7, Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	TOC (mg/L)
0	129.7
23	88.4
35	73.8
60	69.5
80	64.0

Table A.47 TOC results measured. Dye =RBBR, $C_{d,i} = 400$ mg/L, pH = 10, Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	TOC (mg/L)
23	70.9
35	68.3
60	53.2
80	40.4

Table A.48 TOC results measured. Dye =RBBR, $C_{d,i} = 400$ mg/L, pH = 3, Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	TOC (mg/L)
0	114.9
35	84.6
60	73.2
80	66.0

Table A.49 TOC results measured. Dye =RBBR, $C_{d,i} = 400$ mg/L, pH = 7, Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	TOC (mg/L)
0	118.1
23	74.3
35	68.9
60	45.9
80	35.7

Table A.50 TOC results measured. Dye =RBBR, $C_{d,i} = 400$ mg/L, pH = 10, Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	TOC (mg/L)
0	118.2
23	74.1
35	62.5
60	32.7
80	18.3

Table A.51 TOC results measured. Dye =RBBR, $C_{d,i} = 800$ mg/L, pH = 3, Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	TOC (mg/L)
0	244.0
30	230.0
60	211.0
80	202.0

Table A.52 TOC results measured. Dye =RBBR, $C_{d,i} = 800$ mg/L, pH = 7, Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	TOC (mg/L)
0	246.0
20	207.0
30	202.0
45	181.0
60	169.4
80	155.5

Table A.53 TOC results measured. Dye =RBBR, $C_{d,i} = 800$ mg/L, pH = 10, Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	TOC (mg/L)
0	235.0
30	177.0
45	162.0
60	146.0
80	129.0

Table A.54 TOC results measured. Dye =RBBR, $C_{d,i} = 800$ mg/L, pH = 3, Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	TOC (mg/L)
0	248.0
15	230.0
20	220.5
45	214.2
60	206.7
80	191.3

Table A.55 TOC results measured. Dye =RBBR, $C_{d,i} = 800$ mg/L, pH = 7, Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	TOC (mg/L)
0	240.0
20	197.0
30	188.0
45	178.0
60	162.3
80	136.8

Table A.56 TOC results measured. Dye =RBBR, $C_{d,i} = 800$ mg/L, pH = 10, Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	TOC (mg/L)
0	235.0
20	183.0
30	168.7
60	138.5
80	115.0

Table A.57 TOC results measured. Dye =RB-5, $C_{d,i} = 100$ mg/L, pH = 3, Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	TOC (mg/L)
0	31.8
30	26.1
60	24.5
80	24.1

Table A.58 TOC results measured. Dye =RB-5, $C_{d,i} = 100$ mg/L, pH = 7, Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	TOC (mg/L)
0	32.0
30	22.9
60	19.1
80	18.3

Table A.59 TOC results measured. Dye =RB-5, $C_{d,i} = 100$ mg/L, pH = 10 , Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	TOC (mg/L)
0	32.7
30	12.6
60	9.3
80	6.9

Table A.60 TOC results measured. Dye =RB-5, $C_{d,i} = 100$ mg/L, pH = 3 , Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	TOC (mg/L)
0	31.0
4	30.3
11	28.6
15	27.0
30	23.0
45	21.5
60	19.1
80	18.8

Table A.61 TOC results measured. Dye =RB-5, $C_{d,i} = 100$ mg/L, pH = 7 , Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	TOC (mg/L)
0	30.0
9	29.5
15	23.6
30	17.7
45	11.7
60	10.2
80	8.7

Table A.62 TOC results measured. Dye =RB-5, $C_{d,i} = 100$ mg/L, pH = 10 , Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	TOC (mg/L)
0	31.0
7	27.3
11	26.0
15	24.3
30	13.2
45	7.2
60	4.6
80	4.3

Table A.63 TOC results measured. Dye =RB-5, $C_{d,i} = 400$ mg/L, pH = 3 , Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	TOC (mg/L)
0	124.0
30	107.9
45	106.6
55	100.0
80	96.0

Table A.64 TOC results measured. Dye =RB-5, $C_{d,i} = 400$ mg/L, pH = 7 , Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	TOC (mg/L)
0	130.0
15	126.3
25	116.6
35	116.3
45	105.0
60	96.0
70	94.0
80	89.2

Table A.65 TOC results measured. Dye =RB-5, $C_{d,i} = 400$ mg/L, pH = 10 , Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	TOC (mg/L)
0	125.0
15	105.4
20	104.8
30	92.7
45	85.3
60	77.5
80	65.2

Table A.66 TOC results measured. Dye =RB-5, $C_{d,i} = 400$ mg/L, pH = 3 , Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	TOC (mg/L)
0	126.0
30	111.6
37	110.3
52	109.1
60	100.0
70	96.0
80	93.0

Table A.67 TOC results measured. Dye =RB-5, $C_{d,i} = 400$ mg/L, pH = 7 , Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	TOC (mg/L)
0	126.0
15	115.2
20	108.0
26	100.9
30	99.9
35	96.0
45	90.2
60	78.0
80	67.0

Table A.68 TOC results measured. Dye =RB-5, $C_{d,i} = 400$ mg/L, pH = 10 , Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	TOC (mg/L)
0	126.0
10	115.5
15	105.7
20	104.5
45	85.6
60	76.1
80	58.0

Table A.69 TOC results measured. Dye =RB-5, $C_{d,i} = 800$ mg/L, pH = 3 , Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	TOC (mg/L)
0	255.0
60	244.9
80	227.0

Table A.70 TOC results measured. Dye =RB-5, $C_{d,i} = 800$ mg/L, pH = 7 , Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	TOC (mg/L)
0	252.0
25	239.8
40	208.0
50	198.0
80	183.0

Table A.71 TOC results measured. Dye =RB-5, $C_{d,i} = 800$ mg/L, pH = 10 , Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	TOC (mg/L)
0	258.0
25	209.0
33	199.9
40	180.3
60	174.4
80	170.6

Table A.72 TOC results measured. Dye =RB-5, $C_{d,i} = 800$ mg/L, pH = 3 , Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	TOC (mg/L)
0	254.0
60	232.1
80	220.8

Table A.73 TOC results measured. Dye =RB-5, $C_{d,i} = 800$ mg/L, pH = 7 , Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	TOC (mg/L)
0	260.0
33	228.0
40	216.3
50	209.6
60	207.0
80	182.6

Table A.74 TOC results measured. Dye =RB-5, $C_{d,i} = 800$ mg/L, pH = 10 , Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	TOC (mg/L)
0	258.0
25	191.8
33	182.5
40	174.0
60	167.9
80	143.0

Table A.75 TOC results measured. Dye =RB-5, $C_{d,i} = 100$ mg/L, pH = 3 , Ozone Dose = 115 mg/min.L, $C_{cat} = 1$ g/L Fe/Al₂O₃, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	TOC (mg/L)
0	31.8
4	27.9
8	27.1
15	24.7
30	23.7
60	21.7
80	20.7

Table A.76 TOC results measured. Dye =RB-5, $C_{d,i} = 100$ mg/L, pH = 7 , Ozone Dose = 115 mg/min.L, $C_{cat} = 1$ g/L Fe/Al₂O₃, [PO₄³⁻] = 20 mM

Time (min)	TOC (mg/L)
0	31.5
9	24.1
30	21.2
60	17.9
80	17.0

Table A.77 TOC results measured. Dye =RB-5, $C_{d,i} = 100$ mg/L, pH = 10 , Ozone Dose = 115 mg/min.L, $C_{cat} = 1$ g/L Fe/Al₂O₃, [PO₄³⁻] = 20 mM

Time (min)	TOC (mg/L)
0	34.2
4	23.5
30	13.6
60	11.0
80	9.0

A4. Chemical Oxygen Demand (COD) Analysis

COD is another important parameter in determining the wastewater characteristics. COD measurements were conducted in order to check its relation to the TOC measurements and also report how this important parameter behaves in ozonation reactions.

COD measurements were conducted according to the dichromate method. The measurements conducted by adding the samples into digestion solutions purchased from Hach Lange and after 120 minutes of reaction time at 150°C in a WTW-CR 3000 thermo reactor, the COD values were measured using a DR / 2010 Hach portable spectrophotometer.

COD amounts measured during the experiments are given in Tables A.78-A.101:

Table A.78 COD amounts measured. Dye =RB-5, $C_{d,i} = 100$ mg/L, pH = 3, Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	COD (mg/L)
0	99
60	55
80	52

Table A.79 COD amounts measured. Dye =RB-5, $C_{d,i} = 100$ mg/L, pH = 7, Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	COD (mg/L)
0	100
30	28
60	23
80	26

Table A.80 COD amounts measured. Dye =RB-5, $C_{d,i} = 100$ mg/L, pH = 10, Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	COD (mg/L)
0	100
30	34
60	28
80	14

Table A.81 COD amounts measured Dye =RB-5, $C_{d,i} = 100$ mg/L, pH = 3, Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	COD (mg/L)
0	99
30	46
60	43
80	41

Table A.82 COD amounts measured. Dye =RB-5, $C_{d,i} = 100$ mg/L, pH = 7, Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	COD (mg/L)
0	103
30	24
60	20
80	18

Table A.83 COD amounts measured. Dye =RB-5, $C_{d,i} = 100$ mg/L, pH = 10, Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	COD (mg/L)
0	100
30	14
60	10
80	6

Table A.84 COD amounts measured. Dye =RB-5, $C_{d,i} = 400$ mg/L, pH = 3, Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	COD (mg/L)
0	430
80	228

Table A.85 COD amounts measured. Dye =RB-5, $C_{d,i} = 400$ mg/L, pH = 7, Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	COD (mg/L)
0	420
80	158

Table A.86 COD amounts measured. Dye =RB-5, $C_{d,i} = 400$ mg/L, pH = 10, Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	COD (mg/L)
0	439
80	89

Table A.87 COD amounts measured. Dye =RB-5, $C_{d,i} = 400$ mg/L, pH = 3, Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	COD (mg/L)
0	433
80	223

Table A.88 COD amounts measured. Dye =RB-5, $C_{d,i} = 400$ mg/L, pH = 7, Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	COD (mg/L)
0	410
80	121

Table A.89 COD amounts measured. Dye =RB-5, $C_{d,i} = 400$ mg/L, pH = 10, Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	COD (mg/L)
0	433
80	105

Table A.90 COD amounts measured. Dye =RB-5, $C_{d,i} = 800$ mg/L, pH = 3, Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	COD (mg/L)
0	852
80	735

Table A.91 COD amounts measured. Dye =RB-5, $C_{d,i} = 800$ mg/L, pH = 7, Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	COD (mg/L)
0	840
80	385

Table A.92 COD amounts measured. Dye =RB-5, $C_{d,i} = 800$ mg/L, pH = 10 , Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	COD (mg/L)
0	860
80	245

Table A.93 COD amounts measured. Dye =RB-5, $C_{d,i} = 800$ mg/L, pH = 3 , Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	COD (mg/L)
0	825
80	679

Table A.94 COD amounts measured. Dye =RB-5, $C_{d,i} = 800$ mg/L, pH = 7, Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	COD (mg/L)
0	838
80	350

Table A.95 COD amounts measured. Table A TOC results measured. Dye =RB-5, $C_{d,i} = 800$ mg/L, pH = 10, Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	COD (mg/L)
0	870
80	224

Table A.96 COD amounts measured. Dye =RB-5, $C_{d,i} = 800$ mg/L, pH = 3, Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	COD (mg/L)
0	870
80	524

Table A.97 COD amounts measured. Dye =RB-5, $C_{d,i} = 800$ mg/L, pH = 7, Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	COD (mg/L)
0	870
80	250

Table A.98 COD amounts measured. Dye =RBBR, $C_{d,i} = 800$ mg/L, pH = 10, Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	COD (mg/L)
0	870
80	223

Table A.99 COD amounts measured. Table A TOC results measured. Dye =RBBR, $C_{d,i} = 800$ mg/L, pH = 3 , Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	COD (mg/L)
0	860
80	380

Table A.100 COD amounts measured. Dye =RBBR, $C_{d,i} = 800$ mg/L, pH = 7, Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	COD (mg/L)
0	880
80	240

Table A.101 COD amounts measured. Dye =RBBR, $C_{d,i} = 800$ mg/L, pH = 10, Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	COD (mg/L)
0	870
80	175

A5. Dye Removal

To measure dye removals, the dye concentrations in liquid samples are needed at specific times during reaction. The dye concentrations were determined by measuring absorbance values and using a calibration curve as absorbance versus concentration. Calibration curves were generated by using prepared standard dye solutions. Samples were taken into Erlenmeyer containing 1 mL of sodium thiosulfate solutions; because of that sample volumes were also measured and absorbance values were multiplied by the dilution factor arising from thiosulfate addition. Calibration curves and dye removal data are given in Tables A.102 - A.142:

Table A.102 Dye removal data Dye = RBBR, $C_{d,i} = 100$ mg/L, pH = 3 , Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	Abs	V (mL)	C_d (mg/L)
0.0	1.26	10	98.4
1.0	0.73	11	57.2
2.1	0.33	13	25.8
3.3	0.11	9	8.8
4.3	0.04	10	3.2
7.0	0.01	12	0.7
12.0	0.00	10	0.0

Table A.103 Dye removal data Dye = RBBR, $C_{d,i} = 100$ mg/L, pH = 7, Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	Abs	V (mL)	C_d (mg/L)
0.0	1.29	10	100.7
1.1	0.74	11	57.4
2.1	0.40	13	31.3
3.1	0.21	9	16.0
4.2	0.09	10	6.6
6.6	0.02	12	1.2
12.0	0.00	10	0.0

Table A.104 Dye removal data Dye = RBBR, $C_{d,i} = 100$ mg/L, pH = 3, Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	Abs	V (mL)	C_d (mg/L)
0.0	1.30	11	101.5
1.0	0.79	12	62.0
2.3	0.34	10	26.4
3.0	0.19	10	14.9
4.8	0.04	11	2.8
6.0	0.01	11	0.9
12.0	0.00	12	0.0

Table A.105 Dye removal data Dye = RBBR, $C_{d,i} = 100$ mg/L, pH = 7, Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	Abs	V (mL)	C_d (mg/L)
0.0	1.25	10	97.6
1.2	0.69	11	53.6
2.3	0.31	13	24.4
3.2	0.20	9	15.2
4.1	0.08	10	6.3
6.1	0.02	12	1.2
12.0	0.00	10	0.0

Table A.106 Dye removal data Dye = RBBR, $C_{d,i} = 400$ mg/L, pH = 3, Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	Abs	V (mL)	C_d (mg/L)	dilution
0.0	1.07	0	417.3	5
1.1	0.79	8	348.4	5
3.1	0.53	12	223.1	5
5.1	1.28	9	110.9	1
8.1	0.53	14	44.0	1
11.1	0.19	12	16.2	1
13.3	0.09	11	7.9	1
15.1	0.06	13	5.0	1
23.3	0.01	13	0.4	1

Table A.107 Dye removal data Dye = RBBR, $C_{d,i} = 400$ mg/L, pH = 7, Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	Abs	V (mL)	C_d (mg/L)	dilution
0.0	1.06	0	413.4	5
1.0	0.96	15	320.2	4
3.1	0.59	8	208.5	4
5.2	1.29	18	106.2	1
8.1	0.50	16	41.7	1
10.5	0.22	23	17.6	1
12.1	0.09	13	7.6	1
16.2	0.01	15	1.0	1
19.3	0.02	22	1.5	1
23.0	0.00	22	0.0	1
35.0	0.00	20	0.0	1

Table A.108 Dye removal data Dye = RBBR, $C_{d,i} = 400$ mg/L, pH = 10 , Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	Abs	V (mL)	C_d (mg/L)	dilution
0.0	0.94	0	365.4	5
1.0	0.82	15	272.9	4
3.3	0.50	8	174.8	4
5.1	1.06	18	87.3	1
8.4	0.41	16	34.0	1
12.1	0.11	23	8.6	1
16.2	0.03	13	2.7	1
23.2	0.01	15	1.0	1
35.3	0.00	22	0.0	1
60.0	0.00	22	0.0	1
80.0	0.00	20	0.0	1

Table A.109 Dye removal data Dye = RBBR, $C_{d,i} = 400$ mg/L, pH = 3, Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	Abs	V (mL)	C_d (mg/L)	dilution
0.0	1.06	0	413.4	5
1.0	0.99	12	338.3	4
3.1	0.63	11	209.3	4
5.1	1.29	14	107.3	1
8.1	0.55	15	45.5	1
10.1	0.25	16	19.7	1
12.2	0.11	15	8.7	1
15.3	0.06	15	4.8	1
19.9	0.04	13	3.3	1
23.8	0.01	15	0.9	1
35.2	0.00	20	0.2	1

Table A.110 Dye removal data Dye = RBBR, $C_{d,i} = 400$ mg/L, pH = 7, Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	Abs	V (mL)	C_d (mg/L)	dilution
0.0	1.07	0	417.3	5
1.1	1.01	18	332.6	4
3.1	0.64	18	211.8	4
5.1	1.37	16	113.5	1
8.5	0.56	11	47.8	1
12.1	0.20	15	16.6	1
16.0	0.06	20	5.2	1
19.1	0.03	12	2.1	1
23.1	0.02	13	1.5	1
35.0	0.00	13	0.0	1
60.0	0.00	10	0.0	1

Table A.111 Dye removal data Dye = RBBR, $C_{d,i} = 400$ mg/L, pH = 10, Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	Abs	V (mL)	C_d (mg/L)	dilution
0.0	0.87	0	337.4	5
1.2	0.62	14	260.9	5.02
3.1	0.38	19	157.2	5
5.2	0.92	17	76.0	1
7.2	0.50	18	41.5	1
9.5	0.21	20	17.4	1
12.5	0.09	18	7.1	1
16.6	0.04	17	3.3	1
19.1	0.05	20	3.7	1
35.5	0.00	14	0.0	1
60.0	0.00	20	0.0	1

Table A.112 Dye removal data Dye = RBBR, $C_{d,i} = 800$ mg/L, pH = 3, Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	Abs	V (mL)	C_d (mg/L)	dilution
0.0	1.11	0	865.8	10
3.0	0.64	14	537.4	10
6.0	0.38	19	310.4	10
9.1	1.53	17	126.4	1
12.2	0.75	18	61.8	1
15.0	0.38	20	31.0	1
20.0	0.19	18	15.2	1
33.2	0.04	17	3.2	1
46.7	0.01	20	0.9	1
60.0	0.01	14	0.5	1
80.0	0.00	20	0.0	1

Table A.113 Dye removal data Dye = RBBR, $C_{d,i} = 800$ mg/L, pH = 7, Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	Abs	V (mL)	C_d (mg/L)	dilution
0.0	1.11	0	865.8	10
3.0	0.63	10	496.3	10
6.3	0.34	12	278.5	10
9.4	1.60	13	130.7	1
12.3	0.72	14	58.9	1
15.1	0.35	15	28.3	1
20.1	0.11	18	8.8	1
30.1	0.03	11	2.5	1
45.1	0.01	12	0.7	1
60.1	0.00	11	0.2	1
80.1	0.00	13	0.0	1

Table A.114 Dye removal data Dye = RBBR, $C_{d,i} = 800$ mg/L, pH = 10, Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	Abs	V (mL)	C_d (mg/L)	dilution
0.0	0.95	0	741.0	10
3.1	0.57	100	445.1	10
6.3	0.30	19	249.6	10
9.1	1.32	17	109.0	1
12.2	0.63	18	51.9	1
15.2	0.24	20	20.0	1
20.3	0.07	18	5.8	1
30.1	0.02	17	1.7	1
45.1	0.02	20	1.2	1
60.0	0.00	14	0.3	1
80.0	0.00	20	0.0	1

Table A.115 Dye removal data Dye = RBBR, $C_{d,i} = 800$ mg/L, pH = 3, Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	Abs	V (mL)	C_d (mg/L)	dilution
0.0	1.08	0	842.4	10
3.0	0.64	23	523.3	10
6.0	0.37	13	310.0	10
9.1	1.67	19	137.1	1
12.1	0.89	18	73.3	1
15.1	0.43	19	35.6	1
20.7	0.16	19	13.5	1
30.0	0.06	100	4.5	1
45.0	0.02	100	1.5	1
60.0	0.00	100	0.2	1
80.0	0.00	100	0.0	1

Table A.116 Dye removal data Dye = RBBR, $C_{d,i} = 800$ mg/L, pH = 7, Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	Abs	V (mL)	C_d (mg/L)	dilution
0.0	1.09	0	850.2	10
3.0	0.61	19	503.3	10
7.3	0.28	19	230.7	10
10.4	1.17	19	96.1	1
13.3	0.58	14	48.1	1
15.1	0.33	11	28.1	1
20.1	0.12	19	9.9	1
30.1	0.05	20	4.3	1
45.1	0.01	15	1.1	1
60.1	0.01	15	0.4	1
80.1	0.00	13	0.0	1

Table A.117 Dye removal data Dye = RBBR, $C_{d,i} = 800$ mg/L, pH = 10, Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	Abs	V (mL)	C_d (mg/L)	dilution
0.0	0.95	0	741.0	10
3.0	0.50	18	417.4	10.2
6.0	0.28	13	231.8	10
9.0	1.26	11	107.2	1
12.8	0.46	9	39.5	1
16.1	0.21	15	17.1	1
20.0	0.08	20	6.6	1
33.0	0.02	14	1.6	1
45.1	0.01	14	0.8	1
60.0	0.00	14	0.2	1
80.0	0.00	15	0.0	1

Table A.118 Dye removal data Dye = RBBR, $C_{d,i} = 100$ mg/L, pH = 3, Ozone Dose = 115 mg/min.L, $C_{cat} = 0.2$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	Abs	V (mL)	C_d (mg/L)
0.0	1.25	0	97.7
1.0	0.70	11	59.7
2.1	0.41	13	34.5
3.0	0.17	20	14.3
4.0	0.06	12	5.1
6.4	0.01	20	0.7
12.0	0.00	0	0.0

Table A.119 Dye removal data Dye = RBBR, $C_{d,i} = 100$ mg/L, pH = 3, Ozone Dose = 115 mg/min.L, $C_{cat} = 0.4$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	Abs	V (mL)	C_d (mg/L)
0.0	1.28	0	99.7
1.0	0.79	26	63.9
2.0	0.42	12	35.5
3.1	0.19	14	15.7
4.2	0.07	17	6.0
6.3	0.02	18	1.2
12.0	0.00	0	0.0

Table A.120 Dye removal data Dye = RBBR, $C_{d,i} = 100$ mg/L, pH = 3, Ozone Dose = 115 mg/min.L, $C_{cat} = 0.7$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	Abs	V (mL)	C_d (mg/L)
0.0	1.28	0	100.1
1.0	0.80	26	64.6
2.1	0.42	12	35.7
3.3	0.15	14	12.5
4.3	0.04	17	3.0
6.2	0.02	18	1.9
12.0	0.00	0	0.0

Table A.121 Dye removal data Dye = RBBR, $C_{d,i} = 400$ mg/L, pH = 10, Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{CO}_3^{2-}] = 20$ g/L

Time (min)	Abs	V (mL)	C_d (mg/L)	dilution
0.0	0.87	0	337.4	5
1.5	0.66	19	272.0	5
3.3	0.44	20	180.6	5
5.2	1.05	20	86.0	1
7.3	0.62	19	50.7	1
9.4	0.33	20	26.6	1
11.3	0.14	21	11.6	1
15.8	0.06	15	4.7	1
23.6	0.05	20	3.7	1
35.5	0.00	14	0.0	1
60.0	0.00	20	0.0	1

Table A.122 Dye removal data Dye = RB-5, $C_{d,i} = 100$ mg/L, pH = 3, Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	Abs	V (mL)	C_d (mg/L)	dilution
0.0	0.41	0	107.1	10
2.3	0.20	14	54.9	10
4.0	0.99	15	27.8	1
6.1	0.41	15	11.9	1
8.0	0.15	15	4.7	1
11.3	0.03	18	1.1	1
15.0	0.00	25	0.5	1
30.0	0.00	21	0.4	1

Table A.123 Dye removal data Dye = RB-5, $C_{d,i} = 100$ mg/L, pH = 7, Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	Abs	V (mL)	C_d (mg/L)	dilution
0.0	0.40	0	104.5	10
2.1	0.18	14	51.3	10
4.1	0.79	22	21.4	1
6.1	0.29	21	8.0	1
8.0	0.05	16	1.5	1
11.0	0.01	15	0.1	1
15.0	0.00	25	0.1	1
30.0	0.00	21	0.0	1

Table A.124 Dye removal data Dye = RB-5, $C_{d,i} = 100$ mg/L, pH = 10, Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	Abs	V (mL)	C_d (mg/L)	Dilution
0.0	0.43	0	111.8	10
2.0	0.16	9	46.6	10.2
4.0	0.43	23	11.6	1
6.1	0.09	24	2.4	1
8.0	0.02	26	0.5	1
10.0	0.00	15	0.1	1

Table A.125 Dye removal data Dye = RB-5, $C_{d,i} = 100$ mg/L, pH = 3, Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	Abs	V (mL)	C_d (mg/L)	dilution
0.0	0.42	0	110.2	10
2.0	0.20	13	57.1	10
4.1	0.80	16	22.5	1
6.1	0.23	14	6.9	1
9.1	0.08	16	2.5	1
11.5	0.03	22	1.1	1
15.0	0.01	30	0.7	1
30.0	0.00	21	0.4	1

Table A.126 Dye removal data Dye = RB-5, $C_{d,i} = 100$ mg/L, pH = 7 , Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	Abs	V (mL)	C_d (mg/L)	dilution
0.0	0.43	0	111.3	10
2.1	0.19	14	52.7	10
4.1	0.72	22	19.5	1
7.1	0.16	21	4.5	1
9.0	0.07	16	1.8	1
11.0	0.00	15	0.0	1
15.0	0.03	25	0.7	1
30.0	0.00	21	0.0	1

Table A.127 Dye removal data Dye = RB-5, $C_{d,i} = 100$ mg/L, pH = 10 , Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	Abs	V (mL)	C_d (mg/L)	dilution
0.0	0.38	0	100.1	10.1
2.2	0.09	9	25.1	10
4.4	0.20	23	5.5	1
7.2	0.03	24	0.9	1
9.0	0.02	26	0.5	1
11.2	0.01	15	0.2	1
15.3	0.00	16	0.1	2

Table A.128 Dye removal data Dye = RB-5, $C_{d,i} = 400$ mg/L, pH = 3 , Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	Abs	V (mL)	C_d (mg/L)	dilution
0	0.84	0	437.3	20
2	0.68	8	400.1	20
5.2	0.52	19	284.6	20
8.2	0.81	14	224.3	10
11.1	0.57	13	159	10
15.2	0.41	20	111.4	10
21	2.21	16	61.1	1
27	1.72	14	47.9	1

Table A.128 Continued

Time (min)	Abs	V (mL)	C_d (mg/L)	dilution
30	1.24	27	33.4	1
40.4	0.81	18	22.1	1
45.3	0.22	13	6.1	1
55.1	0.1	18	2.6	1
70.8	0.03	16	0.9	1
80.7	0.01	17	0.4	1

Table A.129 Dye removal data Dye = RB-5, $C_{d,i} = 400$ mg/L, pH = 7 , Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	Abs	V (mL)	C_d (mg/L)	dilution
0.0	0.92	0	478.9	20
5.1	0.44	18	242.1	20
10.4	0.17	12	95.8	20
16.6	1.06	19	29.0	1
20.3	0.44	11	12.4	1
25.4	0.16	16	4.4	1
30.3	0.06	15	1.6	1
35.1	0.02	13	0.6	1
45.0	0.01	50	0.2	1
60.0	0.00	0	0.0	1
70.0	0.00	0	0.0	1

Table A.130 Dye removal data Dye = RB-5, $C_{d,i} = 400$ mg/L, pH = 10 , Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	Abs	V (mL)	C_d (mg/L)	dilution
0.0	0.85	0	440.4	20
5.2	0.25	9	142.1	20
10.4	0.05	23	28.2	20
15.2	0.23	24	6.3	1
20.0	0.07	26	1.8	1
31.2	0.02	15	0.5	1
45.3	0.02	16	0.6	1

Table A.131 Dye removal data Dye = RB-5, $C_{d,i} = 400$ mg/L, pH = 3 , Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	Abs	V (mL)	C_d (mg/L)	dilution
0.0	0.84	0	436.8	20
5.0	0.46	23	248.0	20
10.2	0.23	10	129.8	20
15.2	0.28	12	79.1	10
20.1	1.37	15	38.0	1
23.2	0.99	19	27.1	1
25.0	0.76	19	20.9	1
30.0	0.34	20	9.4	1
37.0	0.14	14	4.0	1
46.4	0.05	17	1.3	1
52.3	0.02	30	0.6	1
60.1	0.02	30	0.4	1
70.8	0.01	30	0.2	1
80.7	0.00	30	0.1	1

Table A.132 Dye removal data Dye = RB-5, $C_{d,i} = 400$ mg/L, pH = 7 , Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	Abs	V (mL)	C_d (mg/L)	dilution
0.0	0.85	0	442.0	20
5.1	0.34	22	182.1	20
10.1	0.14	13	76.2	20
15.1	0.93	15	25.7	1
20.5	0.26	17	7.2	1
26.1	0.07	25	1.9	1
29.9	0.01	21	0.3	1
35.6	0.01	50	0.1	1
45.0	0.01	50	0.2	1
60.0	0.00	50	0.0	1
80.0	0.00	50	0.0	1

Table A.133 Dye removal data Dye = RB-5, $C_{d,i} = 400$ mg/L, pH = 10 , Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	Abs	V (mL)	C_d (mg/L)	dilution
0.0	0.87	0	452.4	20
5.2	0.22	9	127.1	20
10.4	0.11	23	29.8	10
15.2	0.20	24	5.4	1
20.0	0.07	26	1.9	1
25.2	0.03	15	0.9	1
30.3	0.01	16	0.1	1

Table A.134 Dye removal data Dye = RB-5, $C_{d,i} = 800$ mg/L, pH = 3 , Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	Abs	V (mL)	C_d (mg/L)	dilution
0.0	1.03	0	892.7	33.3
5.0	0.74	15	682.2	33.3
14.1	0.43	13	404.1	33.3
20.1	0.32	18	289.1	33.3
25.1	0.24	18	223.2	33.3
40.0	0.32	21	88.0	10
51.1	1.69	13	47.3	1
66.5	0.82	18	22.5	1
80.0	0.23	40	6.1	1

Table A.135 Dye removal data Dye = RB-5, $C_{d,i} = 800$ mg/L, pH = 7 , Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	Abs	V (mL)	C_d (mg/L)	dilution
0.0	1.01	0	875.3	33.3
5.3	0.59	19	541.0	33.3
13.2	0.28	15	262.5	33.3
21.8	0.19	16	102.2	20
25.1	2.19	20	59.8	1
33.0	0.90	24	24.5	1
40.1	0.38	23	10.4	1
50.1	0.14	17	3.8	1
60.1	0.05	24	1.4	1
80.0	0.02	40	0.6	1

Table A.136 Dye removal data Dye = RB-5, $C_{d,i} = 800$ mg/L, pH = 10 , Ozone Dose = 115 mg/min.L, $C_{cat} = 0$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	Abs	V (mL)	C_d (mg/L)	dilution
0.0	1.01	0	875.3	33.3
5.0	0.40	15	369.8	33.3
13.1	0.12	22	40.8	12.5
20.1	0.08	17	2.2	1
25.1	0.25	20	6.8	1
33.0	0.04	22	1.1	1
40.1	0.01	30	0.3	1
51.5	0.01	40	0.2	1
60.0	0.00	40	0.0	1

Table A.137 Dye removal data Dye = RB-5, $C_{d,i} = 800$ mg/L, pH = 3 , Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	Abs	V (mL)	C_d (mg/L)	dilution
0.0	1.01	0	875.3	33.3
5.0	0.69	20	629.7	33.3
13.0	0.39	16	359.1	33.3
20.0	0.24	13	224.0	33.3
25.8	0.17	18	157.3	33.3
33.2	0.11	21	101.7	33.3
42.1	0.15	19	51.3	12.5
50.3	0.97	20	26.4	1
60.0	0.46	20	12.6	1

Table A.138 Dye removal data Dye = RB-5, $C_{d,i} = 800$ mg/L, pH = 7 , Ozone Dose = 115 mg/min.L, $C_{cat} = 0.1$ g/L, $[\text{PO}_4^{3-}] = 20$ mM

Time (min)	Abs	V (mL)	C_d (mg/L)	dilution
0	1.05	0	910	33.3
5.3	0.56	20	506	33.3
13.3	0.21	14	192.2	33.3
20.2	0.23	50	74.9	12.5
25.2	1.13	22	30.7	1

Table A.138 Continued

Time (min)	Abs	V (mL)	C_d (mg/L)	dilution
33.2	0.4	19	10.9	1
40.3	0.06	22	1.5	1
50.3	0.04	40	1.1	1
60.1	0.02	40	0.5	1
80.2	0	40	0.1	1

Table A.139 Dye removal data Dye = RB-5, $C_{d,i}$ = 800 mg/L, pH = 10 , Ozone Dose = 115 mg/min.L, C_{cat} = 0.1 g/L, $[\text{PO}_4^{3-}]$ = 20 mM

Time (min)	Abs	V (mL)	C_d (mg/L)	dilution
0.0	1.05	0	910.0	33.3
5.3	0.33	20	300.3	33.3
13.3	0.11	14	61.3	20
20.2	0.50	20	13.7	1
25.2	0.11	22	3.0	1
33.2	0.04	19	1.1	1
40.3	0.04	22	1.1	1
50.3	0.02	40	0.5	1
60.1	0.01	40	0.3	1

Table A.140 Dye removal data Dye = RB-5, $C_{d,i}$ = 100 mg/L, pH = 3, Ozone Dose = 115 mg/min.L, C_{cat} = 1 g/L Fe/Al₂O₃, $[\text{PO}_4^{3-}]$ = 20 mM

Time (min)	Abs	V (mL)	C_d (mg/L)	dilution
0.0	0.42	0	110.2	10
2.0	0.17	19	46.3	10
4.3	0.47	24	12.6	1
6.1	0.14	22	3.9	1
8.2	0.05	24	1.3	1
12.3	0.01	22	0.3	1
15.7	0.01	18	0.2	1
35.0	0.00	27	0.0	1

Table A.141 Dye removal data Dye = RB-5, $C_{d,i} = 100$ mg/L, pH = 7, Ozone Dose = 115 mg/min.L, $C_{cat} = 1$ g/L Fe/Al₂O₃, [PO₄³⁻] = 20 mM

Time (min)	Abs	V (mL)	C_d (mg/L)	dilution
0.0	0.42	0	110.0	10
2.0	0.17	19	47.3	10
4.0	0.72	24	19.5	1
7.3	0.13	22	3.6	1
9.5	0.02	24	0.6	1
12.2	0.01	22	0.2	1
16.5	0.00	18	0.1	1
35.0	0.00	27	0.0	1

Table A.142 Dye removal data Dye = RB-5, $C_{d,i} = 100$ mg/L, pH = 10, Ozone Dose = 115 mg/min.L, $C_{cat} = 1$ g/L Fe/Al₂O₃, [PO₄³⁻] = 20 mM

Time (min)	Abs	V (mL)	C_d (mg/L)	dilution
0.0	0.43	0	112.6	10
2.0	0.11	19	28.7	10
4.1	0.16	24	4.3	1
6.6	0.03	22	0.7	1
8.2	0.01	24	0.3	1
12.1	0.01	22	0.2	1
15.0	0.00	18	0.1	1

APPENDIX B

ACCURACY OF TOC RESULTS

Dissolved organic carbon content of the samples measured was measured by a TOC- $V_{CPH/CPN}$ TOC analyzer. In order to test the consistency of the results obtained by this method, COD tests and an analytical method developed by our research group in order to test the carbon content from the released carbon dioxide were applied.

B1. Determination of Carbon Amount in the Carbon Dioxide Released in Ozonation

Carbon dioxide amount was determined by using $Ba(OH)_2$ solutions connected to the reactor in series. Reactor selected was a gas washing bottle having a volume of 500 mL, where 300 mL of 100 mg/L RBBR dye solution was treated with an ozone dose of 81.4 mg O_3 /L.min. $Ba(OH)_2$ solutions were also connected to the reactor in series. Two gas washing bottles were used for that purpose having volumes of 500 mL and 250 mL including 350 mL and 150 mL of $Ba(OH)_2$ solutions (10 g/L), respectively. $Ba(OH)_2$ solutions were filtered before they were connected to the reactor in order to eliminate the impurities coming from the non-dissolved $Ba(OH)_2$.

Carbon dioxide amount was measured by filtering the $Ba(OH)_2$ solutions at the end of the ozonation period (30 min). After drying the filtrate, it was weighted as $BaCO_3$; also a blank run was conducted without dye solution by feeding ozone to de-ionized water connected to the washing bottles containing $Ba(OH)_2$ solutions. Thus any interference due to precipitation that was not caused by the CO_2 generation during the reaction was eliminated. Amount of Carbon dioxide was measured according to the Equation (B.1):



TOC measurement was also conducted parallel to these measurements in order to compare the amount of carbon dioxide measured by using these two methods. TOC amounts in the solution before and after the ozonation were measured in order to calculate the carbon dioxide released from the difference of the carbon amounts in the solutions (Δ carbon will be equal to the amount of carbon in the carbon dioxide released).

Results are given on the basis of carbon amount reduced in terms of milli grams, both for TOC results and BaCO_3 precipitation results. In Tables B.1-B.3.

Table B.1. TOC results for ozonation of 100 mg/L RBBR solutions.

#	TOC _i (mg/L)	TOC _f (mg/L)	Reactor Volume(L)	M _{carbon,i} (mg)	M _{carbon,f} (mg)	Carbon (mg)
1	31	24	0.3	9.3	7.2	2.1
2	30.4	21	0.3	9.12	6.3	2.82
3	30.4	21.6	0.3	9.12	6.48	2.64

Table B.2. CO₂ and carbon amounts measured by using Ba(OH)₂ precipitation for ozonation of 100 mg/L RBBR solutions

#	BaCO ₃	CO ₂ (mg)	Carbon (mg)
1	31.1	6.95	1.89
2	43.1	9.63	2.63
3	38.2	8.53	2.33

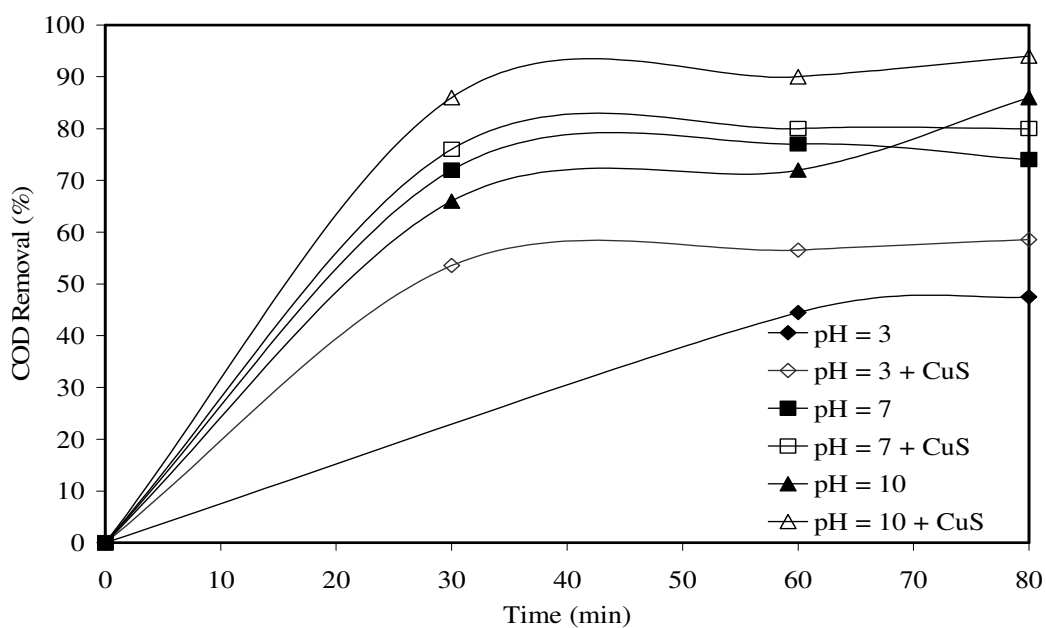
Table B.3 Percent error between the two methods

#	% Error
1	9.8
2	6.9
3	11.9

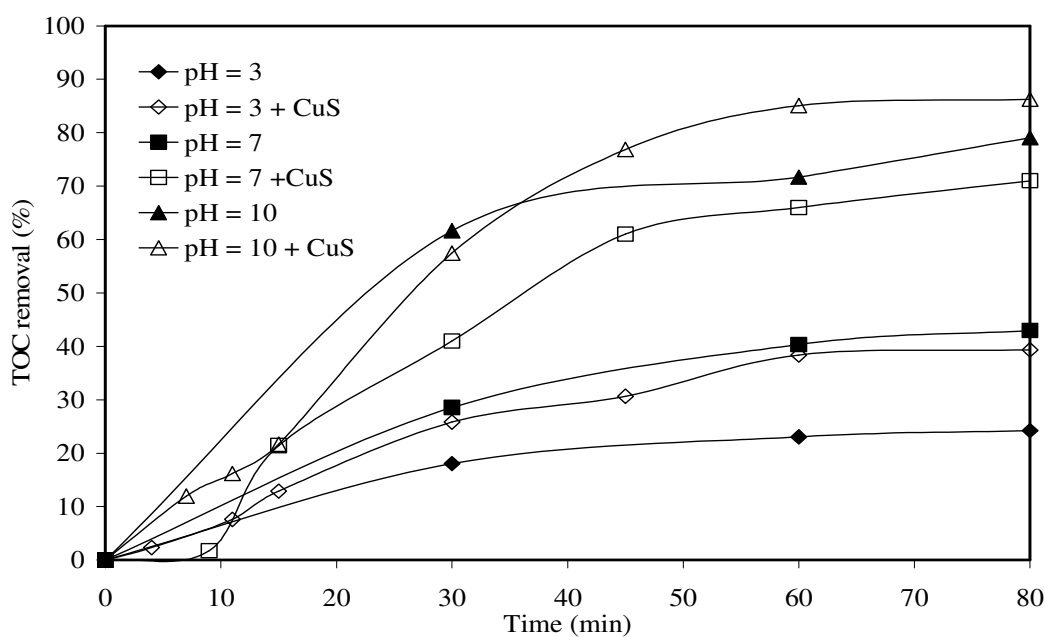
B2. Comparison of TOC and COD results

The results obtained for COD and TOC removals were not expected to be the same, but the behavior was found to be similar between two methods [Figures (B.1-a) and B.1-b)]. CuS addition was found to be effective in terms of increasing both TOC and COD removals. COD removals were found to be higher for the runs conducted at pH = 3 and 7 than the TOC removals. TOC and COD removals over 90% were obtained in the catalytic ozonation of RB-5 solutions at pH =10.

The COD results and the results obtained for the released carbon dioxide (showing the extent of mineralization) emission tests were found to be parallel with the TOC results proving the accuracy of the methods.



(a)



(b)

Figure B.1 Comparison between %TOC and COD removals. (a) = percent COD removals, (b) = percent TOC removals, Dye =RB-5, $C_{d,i} = 100$ mg/L, Ozone dose = 115 mg/L.min

APPENDIX C

REPRODUCIBILITY OF EXPERIMENTAL RUNS

Dye removal results were chosen to check the consistency (reproducibility) between the experimental runs, because it was observed that most of the inconsistency between the runs came from the dye removal results.

Since it is too hard to take the samples at the same time (order of seconds) for each experimental run, therefore the calculated pseudo first order reaction rate constants were used as the comparison parameter. In dealing with such fast reactions, taking samples, for example at 3.1th min and 3.5th min of the reaction time yields considerable differences in the absorbance values measured for the samples besides the experimental error coming from other sources. Figures C.1-C.6, and Tables C.1-C.6 show the work related to the percent errors occurring between the repeated runs conducted at identical conditions, for each of the pH values of 3, 7 and 10.

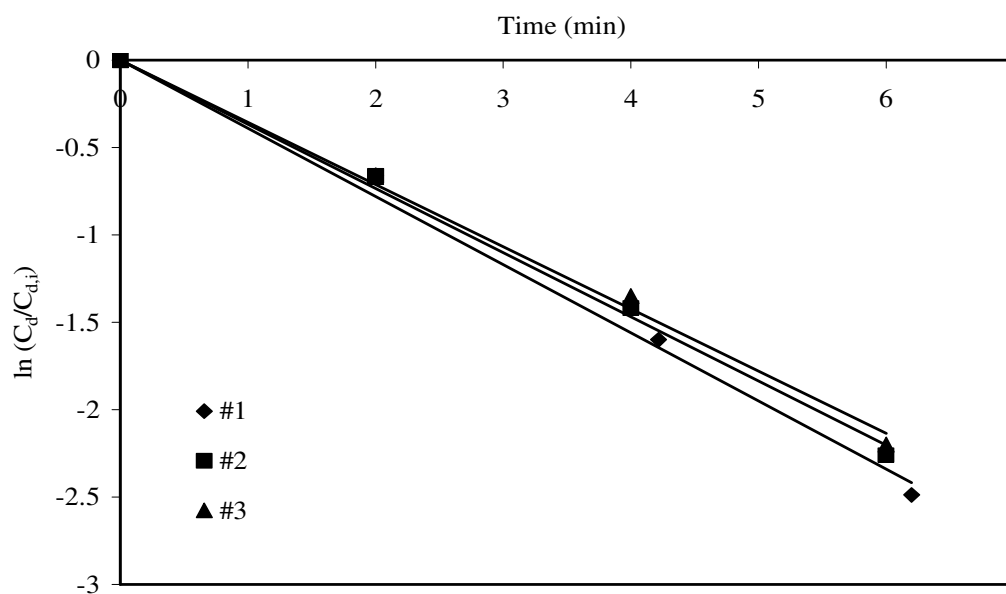


Figure C.1 Three identical experimental runs conducted for RB-5 solution at pH = 3, having an initial dye concentration of 100 mg/L. Ozone dose = 115 mg/min.L

Table C.1 comparison of the k' values obtained from Figure C.1; % error was calculated according to the average

#	k' (min ⁻¹)	% error
1	0.39	5.4
2	0.37	0
3	0.36	2.7
Ave.= 0.37 min ⁻¹		

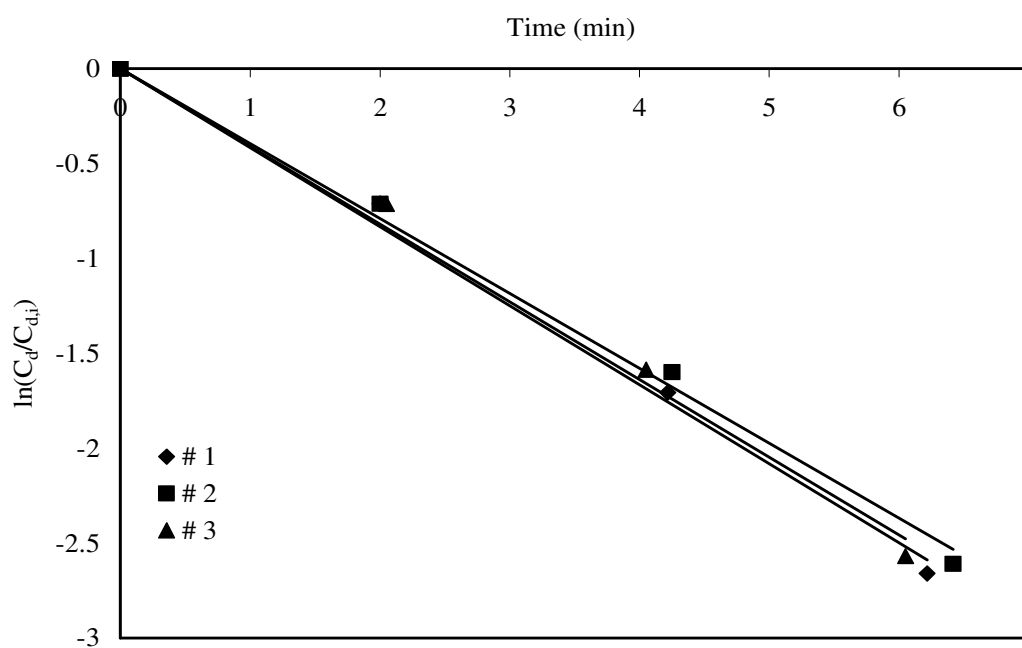


Figure C.2 Three identical experimental runs conducted for RB-5 solution at pH = 7, having an initial dye concentration of 100 mg/L. Ozone dose = 115 mg/min.L

Table C.2 Comparison of the k' values obtained from Figure C.2; % error was calculated according to the average

#	k' (min ⁻¹)	% error
1	0.41	0
2	0.40	2.4
3	0.42	4.9
Ave.= 0.41		

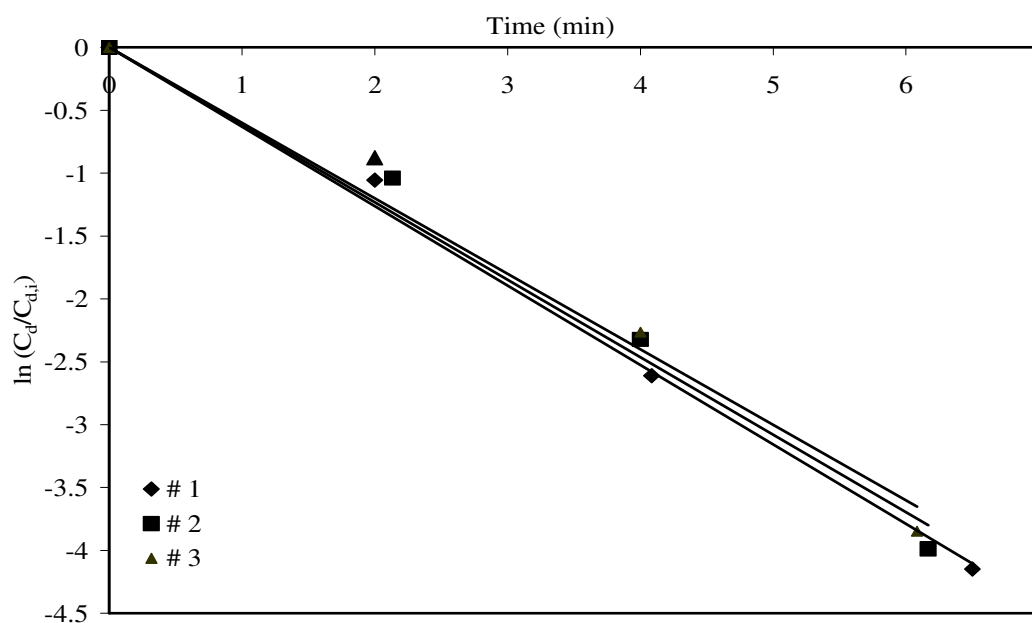


Figure C.3 Three identical experimental runs conducted for RB-5 solution at pH = 10, having an initial dye concentration of 100 mg/L. Ozone dose = 115 mg/min.L

Table C.3 comparison of the k' values obtained from Figure C.3; % error was calculated according to the average

#	k' (min ⁻¹)	% error
1	0.63	2.2
2	0.62	0.5
3	0.60	4.8
Ave.= 0.62		

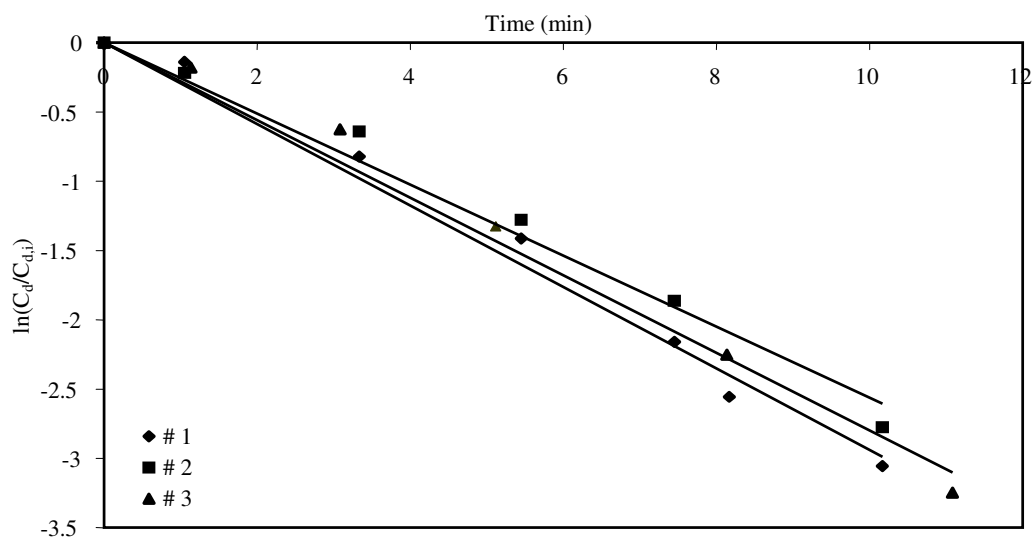


Figure C.4 Three identical experimental runs conducted for RBBR solution at pH = 3 having an initial dye concentration of 400 mg/L. Ozone dose = 115 mg/min.L

Table C.4 comparison of the k' values obtained from Figure C.4; % error was calculated according to the average

#	k' (min ⁻¹)	% error
1	0.29	4.8
2	0.26	- 6.0
3	0.28	1.2
Ave. = 0.276		

Table C.5 comparison of the k' values obtained from Figure C.5; % error was calculated with respect to each other

#	k' (min ⁻¹)	% error
1	0.261	-10.3
2	0.288	10.3

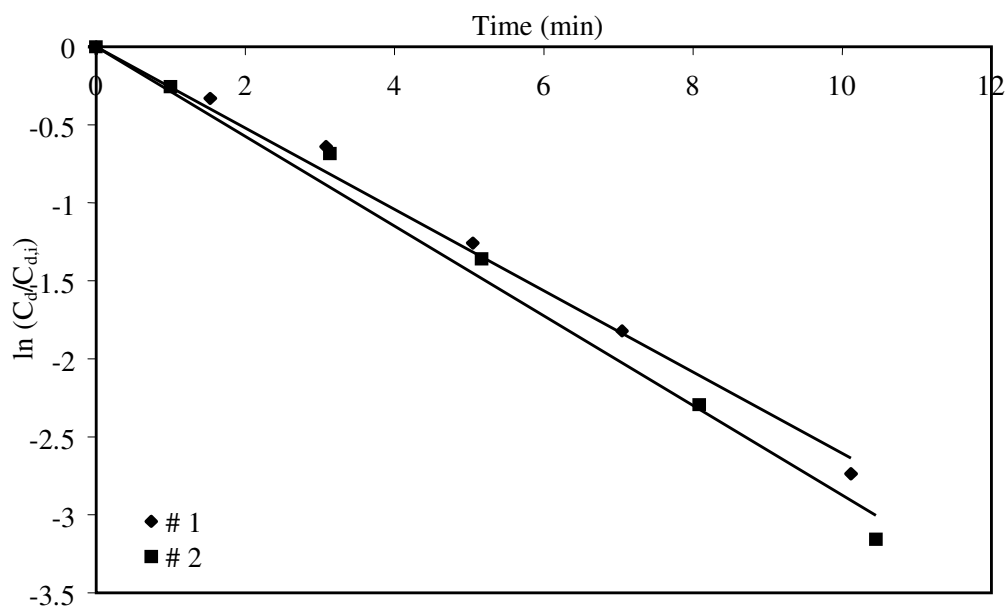


Figure C.5 Two identical experimental runs conducted for RBBR solution at pH = 7, having an initial dye concentration of 400 mg/L. Ozone dose = 115 mg/min.L

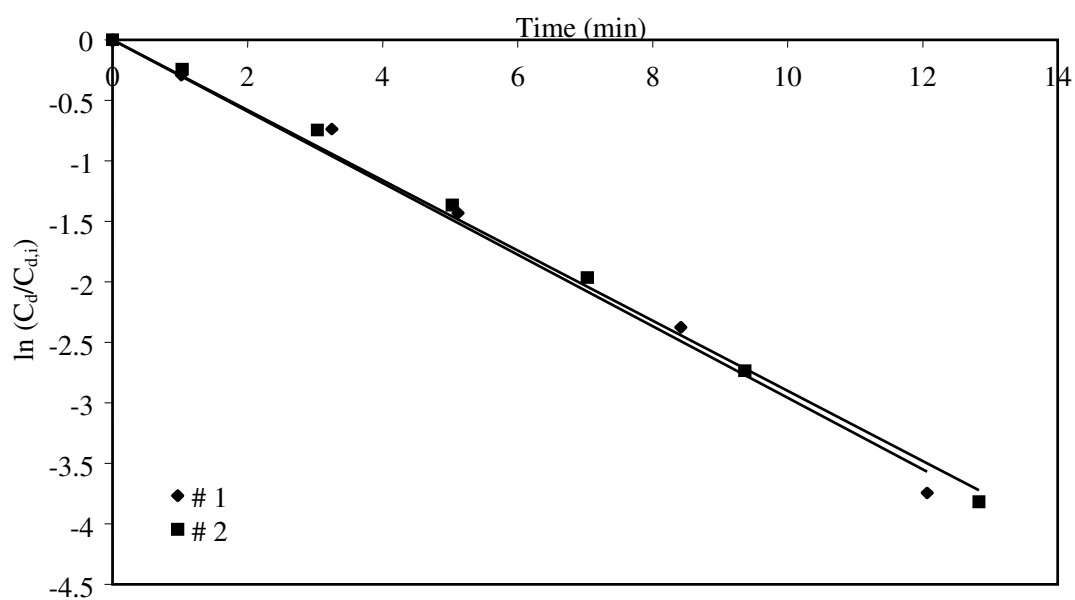


Figure C.6 Two identical experimental runs conducted for RBBR solution at pH = 10 having an initial dye concentration of 400 mg/L. Ozone dose = 115 mg/L

Table C.6 comparison of the k' values obtained from Figure C.6; percent error was calculated with respect to each other

#	$k'(\text{min}^{-1})$	% error
1	0.296	2.0
2	0.290	-2.0

From the results listed above it can be seen that the maximum difference among the k' values for the experiments conducted is at most 10%. Keeping this fact in mind, it can be said that any difference over 10% between the results of the catalytic and non-catalytic ozonation experiments can be regarded as a significant improvement by catalysis.