İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

EVALUATION OF THE MECHANISM OF MULTIPLE SUBSTRATE REMOVAL BY OZONE OXIDATION

Ph.D. Thesis by

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Department : Environmental Engineering

Programme : Environmental Engineering

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OZON OKSİDASYONU İLE ÇOKLU SUBSTRAT GİDERİMİNİN MEKANİZMASININ DEĞERLENDİRİLMESİ

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PREFACE

A Ph.D thesis is simply the culmination of a few years of learning. I can simply say learning of how to think scientifically, how to be patient, how to be hard working, how to communicate, how to be silent maybe **I mean how to live**. Throughout these years, I have received much support from my family, instructors, friends and students. It would be impossible to individually acknowledge all those who merit it. However, I will try to express my gratitude to those who made this thesis possible and enriched my life in the past few years.

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EVALUATION OF THE MECHANISM OF MULTIPLE SUBSTRATE REMOVAL BY OZONE OXIDATION

SUMMARY

Increasing amount and number of resistant organics present in water and wastewaters and the increasing demand for advanced treatment have resulted in wider and increasing use of chemical treatment processes. Chemical oxidation is the most effective process for the removal of organic pollutants present in water. Chemical oxidation aims at the mineralization of the contaminants to carbon dioxide, water and inorganics or, at least, at their transformation into more environmentally friendly, i.e., more biodegradable, less resistant, and less inhibitory, products. Ozone is a very powerful oxidizing agent, which is able to participate in numerous reactions with organic and inorganic compounds. The ozone reactions are carried out in practice by purging the aqueous solution containing organic compound with gaseous ozone. The role of ozonation and its related oxidation processes in the removal of organic compounds has been studied by different researchers. However, most of these studies have been conducted on systems that include single compound. These studies also paid little attention to the gas-liquid mass transfer with chemical reaction and also the influence of intermediates formed during the oxidation reactions on oxidation mechanism and chemical kinetics.

In this respect, this study was devoted to analyze the ozone oxidation process for multiple substrate removal systems. The main objective of this study was to investigate the mechanism and process kinetics of oxidation reactions of organic compounds with molecular ozone when they exist individually or together in the aqueous medium under acidic conditions and in bubble column reactors.

The parameters monitored were, organic compound removal, intermediate formation and removal, TOC removal pattern and dissolved ozone concentration in the solution, which are required for an accurate evaluation of the kinetic behavior and the process of multiple substrate oxidation systems. The process kinetics and reaction pattern of organic compounds in the multiple substrate oxidation systems were determined to be different from those of single substrates present alone in the aqueous medium. This variation was considered to be due to the modification of reaction patterns by the interaction between the substrates during their oxidation reactions, formation and oxidation of intermediates, as well as ozone transport limitations.

Phenol and bentazone were chosen as the model compounds for the experimental studies. In addition to the measurement of phenol and bentazone, the main intermediates formed, ozone concentration in the reactor and TOC were monitored. In accordance with the aim of the study, an experimental program was adopted considering the above-mentioned aspects and experimental studies were conducted in two stages: i) single oxidation experiments for phenol and bentazone ii) mixture oxidation experiments with phenol and bentazone.

In the first stage, single phenol and bentazone oxidation experiments were run with synthetic samples for initial concentrations of 25-100 mg/l. Two different ozone dosages (approx. 3.0 and 12.0 mg/min) were applied in the experiments conducted with 25 mg/l phenol and bentazone initial concentration. The applied ozone dosages were around 3.0 mg/min in the experiments with 50, 75, and 100 mg/l initial phenol and bentazone concentrations.

In the second stage, phenol and bentazone concentrations in the synthetic mixture samples were selected similar to those in single substrate oxidation experiments and several combinations were prepared for a better comparison and evaluation of the multiple substrate oxidation systems. The experimental results evaluated and compared with the results determined from the oxidation experiments conducted on single organic compound removal systems and with the literature data.

During the oxidation experiments of single compounds and mixtures, pH was kept constant at 3.0 in order to ensure the direct reaction of phenol and bentazone with ozone. The oxidation experiments were performed at constant room temperature in a semi-batch glass reactor into which air-ozone was purged continuously.

Most of the intermediates formed during the oxidation followed and increasing pattern in time, reaching a peak value and then starting to decrease with further ozonation. The formation of a peak suggests that, the formation rate of intermediates is higher than their oxidation rate. Therefore, the intermediates accumulation occurs in a certain time period starting from the beginning of oxidation till reaching to the peak value. Cis, cis-muconic acid and hydroquinone were determined to be important intermediates formed during the ozone oxidation of phenol while cis, cis-muconic acid and phenol were the intermediates monitored during the ozone oxidation of bentazone. The peak concentrations of cis, cis-muconic acid and hydroquinone formed during the phenol oxidation increased with increasing initial phenol concentration. The peak values of cis, cis-muconic acid formed during the single phenol oxidation experiments with initial concentrations of 25-100 mg/l were between 1.58-5.22 mg/l while the observed peak concentrations were 1.6- 6.3 mg/l for hydroquinone. For single bentazone oxidation experiments with initial concentrations of 25-100 mg/l, the peak concentration of phenol was ranged between 1.21-5.70 mg/l. The peak values of cis, cis-muconic acid formed during the single bentazone oxidations for all experiments were less than 1 mg/l.

The dissolved ozone profiles were also examined during the single substrate oxidation experiments. The dissolved ozone concentrations increased with the increasing initial phenol and bentazone concentrations. This variation seemed to be reasonable considering the effect of organics on mass transfer characteristics thus changing the level of dissolved ozone in the reactor. However, the observed dissolved ozone peak concentrations for single bentazone experiments were higher than those observed for phenol oxidation experiments. The ozone concentration profile of bentazone oxidation experiments indicated that the transport of ozone could be more readily provided for bentazone with regard to phenol. The peak dissolved ozone concentrations were ranged between 3.01 and 3.67 mg/l for experiments with initial phenol concentrations of 50-100 mg/l while they were 7.64-9.75 mg/l for experiments with initial bentazone concentrations of 50-100 mg/l. During the course of the reaction, after peak ozone values reached, dissolved ozone concentrations started to decrease with further ozonation. The decrease in the dissolved ozone concentration could be attributed to the further ozonation of the

intermediates and slowly reacting end products as well as diminishing ozone transport efficiency.

The extent of organic compounds mineralization was determined by monitoring the concentration of organic carbon remaining in the solution. The mineralization of organic compounds strongly depended on the oxidation conditions, due to this dependence it was also variable. The TOC profiles during the oxidation exhibited a parallel change with the formation and oxidation of intermediates. In single phenol oxidation experiments TOC removals were between 9-19% at 3.0 mg/min ozone dosage. At the initial stage of the oxidation where cis, cis-muconic acid and hydroquinone was dominant, TOC removal was limited. TOC removals became to be significant beyond the time where peak intermediate concentrations were obtained. In single bentazone oxidation experiments TOC removals were between 16-22% at 3.0 mg/min ozone dosage. In a similar manner with single phenol experiments TOC removals in single bentazone experiments were associated with accumulated intermediates, rather than disappearance of bentazone.

The starting point of the modeling approach in this study is to search if an overall substrate removal model can be used to describe the general pattern of substrate conversion within defined intervals of the system variables. The removal model used in the study was similar to pseudo-first order kinetic expression with respect to the organic compound concentration. This expression implies a kinetic description but it is rather an overall modeling of the substrate conversion for the system employed in the study. The overall removal rate constants of single ozonation of phenol have been found ranging between 0.0133-0.0288 1/min at 3.0 mg/min ozone dosage whereas bentazone removal rates ranged between 0.044-0.0953 1/min at the same ozone dosage.

In the mixture experiments a steady removal pattern was observed for both phenol and bentazone for all concentrations studied except 25 mg/l initial concentration of both phenol and bentazone. The overall result of this study was that the rates of removal of both phenol and bentazone in mixture were less than their corresponding rates in the case of single oxidation experiments. Phenol and bentazone oxidation rates were affected in different extents in the mixture experiments. The modification of the reaction rates of phenol and bentazone in mixture experiments was explained considering the different profiles of intermediates and variation of dissolved ozone concentration through the experiments.

The peak concentrations of cis, cis-muconic acid formed during the multiple substrate oxidation experiments increased with increasing initial phenol and bentazone concentrations. The peak concentration of cis, cis-muconic acid was ranged between 2.9-9.21 mg/l for all mixture experiments. The reduction at phenol removal rate was prominent after a certain oxidation period where the cis, cis-muconic acid started to reduce. The removal of bentazone was significantly decelerated from the beginning of the mixture experiments. This deceleration was attributed to the existence of both phenol and cis, cis-muconic acid in higher concentrations with respect to single oxidation systems and their simultaneous oxidation with bentazone.

The effect of dissolved ozone concentration in the mixture experiments on the removal rate of phenol and bentazone was considered to be in a lesser extent than the effect of intermediates since in most of the cases dissolved ozone profiles of single and mixture experiments were not significantly different. The dissolved ozone

concentrations were over than 2 mg/l during the whole oxidation period for all mixture experiments. The peak dissolved ozone concentrations were ranged between 4.39-14.65 mg/l for mixture experiments at 3.0 mg/min ozone dosage.

Limited amount of mineralization was observed in all mixture experiments as indicated by the TOC removal results, which supported the existence of slowly oxidizable end products. In the case of single phenol oxidation an appreciable mineralization was not observed up to peak concentration of cis, cis-muconic acid was achieved, but following the decrease of cis, cis-muconic acid, a significant TOC removal was observed. In the case of single bentazone oxidation, TOC removal did not exhibit a lag phase but rather a parallel removal with bentazone was observed. A significant part of TOC removed as the bentazone was exhausted.

The evaluation of the results showed that the removal model used for single oxidation systems was also applicable for the oxidation of mixtures. However, the overall removal rate constants of both phenol and bentazone were found always lower than those obtained for single substrate oxidation kinetics. These changes in the overall removal rate constants were related to the accumulation of intermediates, particularly cis, cis-muconic acid for the phenol oxidation. The decrease in the overall removal rate constants, for the mixture experiments studied was in the order of 60-70% for phenol and about 50% for bentazone which indicated a significant difference.

The most important outcome of the thesis study is that in the ozone oxidation of organic matter, particularly for the analysis of multiple substrate oxidation systems, the mechanism, organic compounds removal pattern and process kinetics can be more conveniently and accurately evaluated considering the production of intermediate compounds and their oxidation characteristics and the effect of parent organic compound that are desired to be removed and also intermediates formed and removed on overall mass transfer coefficient.

OZON OKSİDASYONU İLE ÇOKLU SUBSTRAT GİDERİMİNİN MEKANİZMASININ DEĞERLENDİRİLMESİ

ÖZET

Zor ayrışabilir organik maddelerin sularda ve atık sularda gerek miktar gerek çeşit olarak giderek yükselen düzeylerde bulunması ve buna bağlı olarak artan ileri arıtma ihtiyacı, kimyasal oksidasyon proseslerinin kullanımını gerekli kılmaktadır. Kimyasal oksidasyon su içinde bulunan organik kirleticilerin gideriminde kullanılan en etkin proseslerden biridir. Kimyasal oksidasyon, kirleticilerin karbondioksit, su ve inorganik maddelere mineralizasyonunu veya en azından kirleticilerin daha çevre dostu, örneğin biyolojik olarak ayrışabilir, daha az dirençli ve daha az inhibe edici maddelere dönüşümünü amaçlamaktadır. Ozon organik ve inorganik maddelerle kolaylıkla reaksiyona girebilen güçlü bir oksidandır. Uygulamada ozon reaksiyonları, organik madde içeren sulu çözeltilerden, ozon gazının geçirilmesi ile gerçekleştirilmektedir. Ozonlamanın rolü ve buna bağlı olarak organik maddelerin gideriminde kullanımı birçok araştırmacı tarafından incelenmiştir. Fakat bu çalışmalar genel olarak tekil spesifik organik maddeler içeren sistemlerde yürütülmüştür. Ayrıca bu çalışmalarda gaz-sıvı kütle transferinin kimyasal reaksiyon ile birlikte gerçekleşmesi durumu göz ardı edilmiş ve oksidasyon reaksiyonları sırasında oluşan ara ürünlerin oksidasyon mekanizması ve kimyasal kinetik üzerine etkileri dikkate alınmamıştır.

Bu bağlamda, bu çalışmada, çoklu substrat giderim sistemlerinde ozon oksidasyon prosesinin incelenmesi hedeflenmiştir. Bu çalışmanın amacı, kabarcıklı kolon reaktörlerde, asidik koşullarda, organik maddelerin tek başına veya beraber bulunmaları durumunda, moleküler ozon ile oksidasyon reaksiyonlarının mekanizmasının ve giderim kinetiğinin incelenmesidir.

Çoklu substrat oksidasyon sistemlerinin karakteristiklerinin ve kinetik davranışlarının değerlendirilebilmesi için organik madde giderim, ara ürün oluşum ve giderim, TOK giderim mekanizması ve çözelti içindeki çözünmüş ozon konsantrasyon parametreleri izlenmiştir. Çoklu substrat oksidasyon sistemlerinde belirlenen organik madde reaksiyon mekanizmaları ve giderim kinetikleri, organik maddelerin ortamda tekil olarak bulunmaları durumuna göre farklılık göstermiştir. Bu farklılıklara, organik maddelerin oksidasyonu sırasında birbirleri ile etkileşimlerine bağlı olarak reaksiyon mekanizmasının değişimi, ara ürünlerin oluşum ve oksidasyonu ve aynı zamanda ozonun taşınımının kısıtlanmasının sebep olduğu düşünülmektedir.

Deneysel çalışmalarda örnek madde olarak fenol ve bentazon kullanılmıştır. Fenol ve bentazon ölçümlerine ek olarak, oluşan önemli ara ürünler, reaktör içindeki çözünmüş ozon konsantrasyonu ve TOK parametreleri izlenmiştir. Çalışmanın amacına uygun olarak, yukarıda sözü edilen durumlar göz önünde tutularak deneysel program planlanmıştır. Deneysel çalışmalar iki aşamada yürütülmüştür i) tekil fenol ve bentazon oksidasyon deneyleri ii) fenol ve bentazon karışım oksidasyon deneyleri

İlk aşamada deneysel çalışmalar 25-100 mg/l giriş fenol ve bentazon konsantrasyonlarına sahip sentetik numuneler üzerinde yürütülmüştür. 25 mg/l giriş fenol ve bentazon konsantrasyonu içeren sentetik numuneler üzerinde yürütülen çalışmalarda iki farklı ozon dozu (yaklaşık 3.0 ve 12.0 mg/dak) kullanılmıştır. 50, 75 ve 100 mg/l giriş konsantrasyonuna sahip numuneler için kullanılan ozon dozu 3.0 mg/dak olarak seçilmiştir.

İkinci aşamada çoklu substrat oksidasyon sistemlerinin daha iyi mukayese edilebilmesi ve değerlendirilebilmesi için, karışım numunelerinde kullanılan fenol ve bentazon konsantrasyonları tekil numunelerdekine uyumlu olarak seçilmiş ve çoklu substrat oksidasyon karakterinin daha iyi analiz edilebilmesi için uygun kombinasyonlar hazırlanmıştır. Karışım oksidasyon deneylerinden elde edilen sonuçlar, tekil oksidasyon deneysel çalışma sonuçları ve literatür verileri ile karşılaştırılmış ve değerlendirilmiştir.

pH, tekil substrat ve karışım oksidasyon deneylerinde, ozonun fenol ve bentazon ile direkt reaksiyona girmesini sağlamak için 3.0 değerinde sabit tutulmuştur. Oksidasyon deneysel çalışmaları, sabit oda sıcaklığında ve ozonun sürekli olarak beslendiği yarı-kesikli cam reaktörde yürütülmüştür.

Oksidasyon reaksiyonları sırasında oluşan birçok ara ürünün konsantrasyon profillerinin, zamanla artan, pik değerine ulaşan ve sonrasında ileri ozonlama ile azalmaya başlayan bir yapıya sahip olduğu belirlenmiştir. Pik oluşumu için, ara ürünlerin oluşum hızlarının oksidasyon hızlarından yüksek olması gerekmektedir. Bu nedenle, oksidasyon reaksiyonun başlangıcından pik değere ulaşılana dek geçen süre içerisinde, ara ürünlerin birikimi gerçekleşir. Cis, cis-mukonik asit ve hidrokinon, fenolün ozon oksidasyonu sırasında oluşan en önemli ara ürünler olarak belirlenmiş ve aynı şekilde cis, cis-mukonik asit ve fenol ise bentazonun oksidasyonu sırasında oluşan ara ürünler olarak gözlemlenmiştir. Fenol oksidasyonu sırasında oluşan Cis, cis-mukonik asit ve hidrokinonun pik konsantrasyonları artan giriş fenol konsantrasyonu ile artmaktadır. 25-100 mg/l giriş konsantrasyonlarındaki tekil fenol oksidasyon deneylerinde oluşan cis, cis-mukonik asit pik konsantrasyonları 1.58-5.22 mg/l arasında değişirken bu değerler hidrokinon için 1.6-6.3 mg/l olarak saptanmıştır. 25-100 mg/l giriş bentazone konsantrasyonuna sahip tekil oksidasyon deneylerinde, pik fenol konsantrasyonu 1.21-5.70 mg/l arasında bulunmuştur. Bentazon tekil oksidasyon deneylerinde oluşan cis, cis-mukonik asit pik değerlerinin 1 mg/l konsantrasyonunun altında olduğu bulunmuştur.

Tekil substrat oksidasyon deneysel çalışmaları sırasında çözünmüş ozon profilleri de incelenmiştir. Çözünmüş ozon konsantrasyonları fenol ve bentazon tekil oksidasyon deneylerinde artan giriş fenol ve bentazon konsantrasyonları ile yükselmiştir. Reaktör içindeki çözünmüş ozon seviyesinin değişimi, organik maddelerin kütle transfer karakteristiği üzerindeki etkileri göz önüne alındığında anlamlı kabul edilebilir. Bununla birlikte tekil bentazon oksidasyon deneylerinde gözlenen çözünmüş ozon pik konsantrasyonları, tekil fenol deneylerinde gözlenen değerlerden daha yüksek bulunmuştur. Bentazon oksidasyon deneylerindeki ozon konsantrasyon profilleri ozon taşınımının bentazon için fenole göre daha kolay gerçekleştiğini göstermiştir. Pik çözünmüş ozon konsantrasyonları, 50-100 mg/l giriş fenol konsantrasyonlarında 3.01-3.67 mg/l iken aynı giriş bentazon konsantrasyonlarında 7.64-9.75 mg/l olarak belirlenmiştir. Reaksiyon sırasında, ozon pik konsantrasyonuna ulaşıldıktan sonra, çözünmüş ozon konsantrasyonları ileri ozonlama ile düşüşe geçmiştir. Çözünmüş ozon konsantrasyonundaki bu düşüş,

yavaş reaksiyona giren son ürünlere, ara ürünlerin ileri oksidasyonuna ve ozon taşınım verimindeki azalmaya bağlanmıştır.

Organik maddelerin mineralizasyon mertebesi, çözelti içinde kalan organik karbon içeriğinin izlenmesi ile belirlenmiştir. Organik maddelerin mineralizasyonu oksidasyon koşullarına önemli derecede bağlıdır ve bu bağlılıktan ötrürü değişkendir. Oksidasyon deneyleri sırasında elde edilen TOK profilleri ara ürünlerin oluşum ve oksidasyon profilleri ile paralel bir değişim göstermiştir. Tekil fenol oksidasyon deneylerinde, 3.0 mg/dak ozon dozunda, %9-19 aralığında TOK giderimleri elde edilmiştir. Cis, cis-mukonik asit ve hidrokinonun etkin oksidasyonun başlangıç aşamasında, sınırlı TOK giderimi belirlenmiştir. Ara ürünlerin pik konsantrasyonlarının elde edildiği sürenin sonrasında TOK giderimleri önem kazanmaya başlamıştır. Tekil bentazon oksidasyon deneysel çalışmalarında, 3.0 mg/dak ozon dozunda, TOK giderimleri %16-22 aralığında elde edilmiştir. Tekil fenol deneylerine benzer olarak, tekil bentazon deneylerinde elde edilen TOK giderimleri, bentazonun azalmasından ziyade, birikmiş ara ürünler ile ilişkilendirilmiştir.

Bu çalışmada kullanılan modelleme yaklaşımının başlangıç noktası, substrat dönüşümü için mekanizmanın tanımlanmasında, genel bir substrat giderim modelinin, sistem değişkenlerinin belirlenmiş aralıklarında kullanımının araştırılmasıdır. Bu çalışmada kullanılan giderim modeli, organik madde konsantrasyonuna göre görünür 1. derece kinetik ifadesi ile benzerdir. Bu ifade bir kinetik açıklamayı belirtmekle birlikte, bu çalışmada uygulanan sistem için genel bir substrat dönüşüm modelinin tanımlanmasında kullanılmıştır. 3.0 mg/dak ozon dozunda gerçekleştirilen tekil fenol ozonlama deneysel çalışmalarından elde edilen giderim hızı katsayıları 0.0133-0.0288 1/dak iken aynı ozon dozunda tekil bentazon giderim hızları 0.044-0.0953 1/dak olarak hesaplamıştır.

Karışım deneylerinde, fenol ve bentazonun 25 mg/l giriş konsantrasyonu dışında çalışılan tüm konsantrasyonlarında kararlı bir giderim mekanizması gözlenmiştir. Bu çalışmanın genel sonucu, karışımdaki fenol ve bentazon giderim hızlarının, tekil oksidasyon deneylerinde bulunan hızlarından daha düşük olmasıdır. Karışım deneylerinde, fenol ve bentazon oksidasyon hızları, farklı derecelerde etkilenmiştir. Karışım deneylerinde fenol ve bentazonun reaksiyon hızlarının değişimi, ara ürünlerin farklı profillerini ve çözünmüş ozon konsantrasyonunun deney sırasındaki değişimi göz önünde tutularak açıklanmıştır.

Çoklu substrat oksidasyon deneyleri sırasında oluşan cis, cis-mukonik asit pik konsantrasyonları artan giriş fenol ve bentazon konsantrasyonları ile atmıştır. Tüm karışım deneylerinde cis, cis-mukonik asit pik konsantrasyonları 2.9-9.21 mg/l arasında bulunmuştur. Fenol giderim hızındaki düşüş cis, cis-mukonik asitin azalmaya başladığı, belirli bir oksidasyon süresi sonrasında belirgindir. Karışım deneylerinin başlangıcından itibaren bentazon giderimi önemli derecede yavaşlamıştır. Bu yavaşlama, fenol ve cis, cis-mukonik asitin tekil oksidasyon sistemlerine göre daha yüksek konsantrasyonlarda bulunması ve bunların bentazonla eş zamanlı oksidasyonu ile ilişkilendirilmiştir.

Karışım deneylerindeki çözünmüş ozon konsantrasyonunun fenol ve bentazon giderim hızına etkisinin, ara ürünlerin etkisinden daha az derecede olacağı düşünülmüştür. Çünkü birçok durumda tekil ve karışım deneylerinin çözünmüş ozon profilleri önemli farklılık göstermemiştir. Çözünmüş ozon konsantrasyonları oksidasyon süreci sırasında tüm karışım deneyleri için 2 mg/l değerinden yüksek

bulunmuştur. Pik ozon konsantrasyonları 3 mg/l ozon dozunda karışım deneyleri için 4.39-14.65 mg/l asında ölçülmüştür.

Karışım deneylerindeki TOK giderim sonuçlarından da görüldüğü üzere, yavaş okside olan son ürünlerin varlığını destekleyen sınırlı miktarda mineralizasyon gözlenmiştir. Tekil fenol oksidasyonunda, cis, cis-mukonik asit pik konsantrasyonuna ulaşılana kadar kayda değer bir mineralizasyon gözlenmemiş, fakat cis, cis-mukonik asitin düşüşünü takiben önemli TOK giderimi elde edilmiştir. Tekil bentazon oksidasyonunda, TOK gideriminde gecikme evresi görülmemiş bunun yanında bentazon ile birlikte paralel bir değişim göstermiştir. TOK'un önemli bir bölümü bentazon tükendiğinde giderilmiştir.

Değerlendirilen deneysel sonuçlar, tekil oksidasyon sistemlerinde kullanılan giderim modelinin, karışımların giderim kinetiği için de uygulanabilir olduğunu göstermiştir. Bununla birlikte fenol ve bentazonun hız sabitleri, tekil oksidasyon kinetik hesaplamalarından elde edilen değerlerden daha düşüktür. Hız sabitlerindeki bu değişimler, ara ürünlerin birikimine özellikle fenol oksidasyonu için cis, cis-mukonik asite bağlıdır. Çalışılan karışım deneylerinde hız sabitlerindeki düşüş fenol için %60-70, bentazon için %50 oranlarındaki değişimle önemli bir farkı göstermektedir.

Bu tez çalışmasında varılan en önemli sonuç, organik maddenin ozon oksidasyonunda, özellikle çoklu substrat oksidasyon sistemlerinin analizinde, organik madde giderim mekanizmaları ve kinetiklerinin daha uygun ve doğru değerlendirilebilmesi için, ana bileşiklerin giderimine odaklanmaktan ziyade, ara ürün bileşiklerinin oluşumu, bunların oksidasyon karakteristiklerinin ve giderimi istenen organik madde ile birlikte, oluşan ara ürünlerin genel kütle transfer katsayısı üzerindeki etkilerinin dikkate alınması gerekliliğidir.

1. INTRODUCTION

1.1 Need for the Study

The natural resources necessary to survive are for centuries under use of the mankind. In addition to the fundamental needs, new requirements arise as the population increases and technology develops. This necessitates finding new resources while imposing more pressure on the environment. The revolution of industry was fired for finding new resources and the mankind faced pollution of natural resources thereafter. Protection of the environmental resources against the wastes of the industrial activities is very important today.

The Directive 2000/60/EC defined pollutant as "any substance liable to cause pollution, in particular those listed below: "Organohalogen compounds and substances which may form such compounds in the aquatic environment, Organophosphorous compounds, Organotin compounds, Substances and preparations, or the breakdown products of such, which have been proved to possess carcinogenic or mutagenic properties or properties which may affect steroidogenic, thyroid, reproduction or other endocrine-related functions in or via the aquatic environment, Persistent hydrocarbons and persistent and bioaccumulable organic toxic substances and etc."

The effects of above-mentioned pollutants on the environmental health have led to research for applicable treatment for these pollutants. Chemical oxidation is an effective process for the removal of organic pollutants present as traces in water. Chemical oxidation aims at the mineralization of the contaminants to carbon dioxide, water and inorganics or, at least, at their transformation into harmless products. Ozone is one of the most effective oxidants that is used for oxidation processes. Ozone is a very powerful oxidizing agent, which is able to participate in a great number of reactions with organic and inorganic compounds. The basic reactions of ozone in water had been defined by various scientists. In an ozonation process two possible pathways have to be considered: the direct pathway through the reactions with molecular ozone, and the radical pathway through the reactions of hydroxyl radicals generated in the

ozone decomposition and the dissolved compounds. Much of the information about these general aspects of ozone has been reported in the literature. However, ozone oxidation process kinetics of water and wastewater has not been one of the subjects that have been fully explored. One of the missing aspects of the problem is the process kinetics when more than one substrates are involved in the reaction. In fact this is frequently the case for water and wastewater ozonation. The ozone reactions are carried out in practice by purging the aqueous solution containing organic compound with gaseous ozone. There are difficulties to evaluate the ozonation processes due to the bubble column reactor characteristics. This further complicates the problem of modeling and predicting the reaction kinetics.

In the literature the ozonation kinetics have studies mostly adopted the gas-liquid irreversible second-order reaction between ozone and the single substrate present in water with no competition from secondary direct reactions. Application of this approach requires a number of assumptions to simplify the kinetic equations. In these cases some assumptions are made to simplify the kinetic equations. As mentioned above the most common simplification is neglecting the secondary direct reactions between ozone and intermediates. This also prevents to characterize the real nature of ozonation process. In this context, the "multiple substrate oxidation" has a great importance to have an insight into the ozone oxidation as well as to provide adequate and accurate solutions to waste treatment problems.

Therefore, research efforts are needed for a thorough understanding of the molecular ozone oxidation and quantitative evaluation of the multiple substrate oxidation systems.

1.2 Scope of the Study

The main objective of this research is to understand the mechanism and process kinetics of ozonation reactions that lead to analyze the organic compounds oxidation when they are alone and in combination in the aqueous medium by molecular ozone under acidic conditions and in the bubble column reactors. For realization of the objective, the necessary works have been carried out during the thesis work are given below:

Section 2 presents a short history of ozone, its electronic structure which is responsible for ozone reactivity, its stability in water and oxidation of inorganic and organic compounds by ozone. Section 2 also focuses on the kinetics of direct ozone reactions developed for heterogeneous gas-liquid systems.

Section 3 reviews the ozone oxidation applications in water and wastewater treatment and discusses examples of kinetic works on ozonation processes, including those aspects related to the rate constant determination and kinetic regimes. Section 3 also addresses the kinetics of ozone reactions of organic compound and provides a background for planning and evaluation of thesis study.

Section 4 explains the experimental protocol and set-up used in this research. Section 4 also explains the specifications of the used materials and methods employed in the experimental study.

Section 5 discusses the experimental results determined from the oxidation experiments conducted on single and multiple substrate removal systems In this section the removal phenomena of selected substrates, intermediate formation and removal, TOC removal pattern and dissolved ozone concentration in solution both in single and multiple oxidation systems were examine. Section 5 also attempted to determine the process kinetics of the systems when organic compounds are alone or in combination in the aqueous medium.

Section 6 includes the conclusions that are formulated from the results obtained in the experimental study.

2. THEORY

2.1 Mass Transfer with Chemical Reaction for a Gas-Liquid Heterogeneous Systems

A phenomenon of mass transfer with chemical reaction takes place whenever gas and liquid phases which are not at chemical equilibrium with one another are brought into contact. Such phenomena are made up of a number of elementary steps, which may be summarized as follows (Astarita, 1967).

(i) Diffusion of one or more reactants from the bulk of gas phase to the interface between the gas and liquid phases. Physical equilibrium may be assumed to prevail at the interface; whenever the concentration of reactants at the interface is finite in one phase, it is also finite in the other.

(ii) Diffusion of the reactants from the interface towards the bulk of liquid phase

(iii) Chemical reaction within liquid phase

(iv) Diffusion of reactants initially present within liquid phase and/or of reaction products, within liquid phase, due to concentration gradients which are set up by chemical reaction.

If step (i) is rate controlling, the overall rate is not influenced by chemical reaction, and the process may be regarded as a simple mass transfer phenomenon which is not influenced by the reaction rate. Apparently, the chemical reaction may itself be the cause of an overall high mass transfer rate within liquid phase, and therefore step (i) being rate controlling.

The analysis of mass transfer with chemical reaction is of interest when the overall phenomenon resulting from steps (ii), (iii) and (iv) is rate controlling.

A number of hydrodynamic models of a gas-liquid interface have been presented in the literature. All of these are based on the hypothesis that the velocity gradient in the liquid is zero. Nevertheless, the condition of a zero velocity gradient at the gas-liquid interface is not extremely stringent as far as the applicability of chemical adsorption

theory is concerned. In fact, it can be shown that, in a majority of cases, the ratio of the rates of mass transfer in the liquid phase with and without chemical reaction does not depend on the particular hydrodynamic conditions of the liquid.

2.1.1 Film theory

Lewis and Whitman (1924) proposed that when two nonmiscible phases are in contact, the main resistance to mass transfer is located in a stationary layer of thickness δ close to the interface, called film layer. It is also assumed that mass transfer through the film is only due to diffusion and that the concentration profiles with distance to the interface are reached instantaneously.

In gas-liquid system there are two films, one for each phase. In most common situations the gas is bubbled into the liquid phase, so the interfacial surface is due to the external surface of bubbles. Concentration profiles of gas component being absorbed for both gas and liquid films are shown in Figure 2.1. The film theory assumes a plane interfacial surface when the bubble radius is much lower than the film thickness, δ, a situation that occurs in most of the gas-liquid systems (Beltran, 2004).

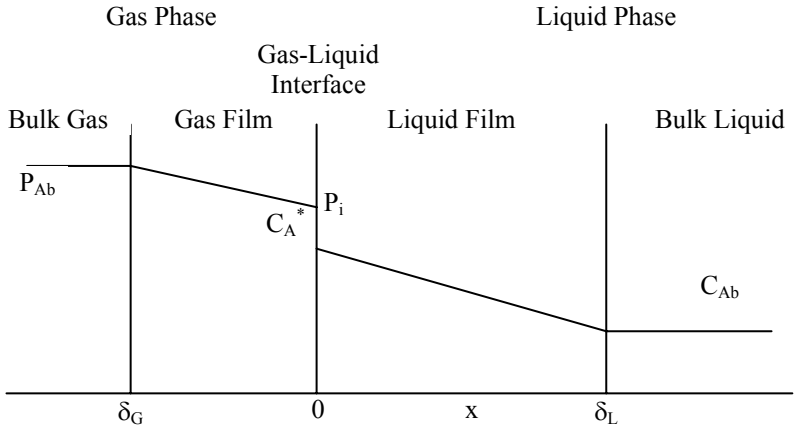


Figure 2.1: Concentration profile of a gas component A with distance to the interface during its physical absorption according to the film theory

2.1.2 Surface renewal theories

In these models, the liquid is assumed to be formed by elements of infinite width that are exposed to the interface for a given time and then are replaced by other elements from the bulk liquid. While the liquid elements are at the interface, mass transfer occurs by diffusion in a nonstationary way. The most often used surface renewal theory is that proposed by Danckwerts, which assumes a distribution function of exposition times for the liquid elements.

2.2 General Mathematical Layout

2.2.1 Diffusion-reaction differential equations

The differential equations which represent the phenomenon of simultaneous diffusion and chemical reaction in a liquid phase may be written, for each of the reacting species, in the form:

$$D_i \Delta_2 c_i = u \quad \nabla c_i \quad + \quad \frac{\partial c_i}{\partial t} \quad + \quad r \qquad \textbf{(2.1)}$$

$$Molecular \quad transport = Convection \quad + \quad Accumulation \quad + \quad \text{Re}\, action \quad Rate$$

Equation 2.1 simplifies considerably for hydrodynamic conditions such as those assumed in the film theory and in the surface renewal theory models. In fact, for both models $u = 0$, and in the case of the film theory also $\partial c_i / \partial t = 0$. Therefore Equation 2.1 can simplify to:

$$D_i \frac{\partial^2 c_i}{\partial x^2} = \frac{\partial c_i}{\partial t} \quad + \quad r \qquad \textbf{(2.2)}$$

in case of the penetration theory model; and to:

$$D_i \frac{\partial^2 c_i}{\partial x^2} = r \qquad \textbf{(2.3)}$$

in the case of the film theory model.

Even the simplified form of Equation 2.2 involves a number of analytical problems whenever r has, but the simplest relationship to the concentrations of the reactants. In general r is a function of the concentrations of more than one reactant, and therefore the mathematical problem consists of the integration of a set of differential equations such as 2.2. This general problem cannot be solved; even a set of differential equations such as 2.3 requires a number of approximations for its solution. Nevertheless, a number of asymptotic solutions can be found when very simple expressions for r are considered.

2.2.2 Boundary conditions

With the consideration of a system in which only two reactants involved, namely an absorbing component and a non-volatile liquid phase reactant in our case ozone and an organic substrate. Let b be the concentration of the latter and c the concentration of the former, at a distance x from the gas-liquid interface.

At the gas-liquid interface, the concentration of the absorbing component (ozone) is equal to its solubility under the assigned interface partial pressure:

$$x = 0 \qquad c = c'_0 \tag{2.4}$$

While the non-volatility of the other reactant imposes the condition of zero transport at the interface:

$$x = 0 \qquad \frac{\partial b}{\partial x} = 0 \tag{2.5}$$

In case of ionic species, the driving force to mass transfer is not simply the concentration gradient; in such a situation the zero transport condition may result in a finite concentration gradient at the interface.

For the penetration theory model, the concentration distribution at time zero may be written as:

$$t = 0 \qquad b = b_0 \qquad c = c_0 \tag{2.6}$$

Where b_0 and c_0 are the bulk concentrations of two reactants.

The last condition required in order to define the solution of the problem is a second condition on the space coordinate. For the film theory model, this is:

$$x = \delta \qquad c = c_0 \qquad b = b_0 \tag{2.7}$$

For the penetration theory model, the same condition should apply at $x \to \infty$. It is written in one of the two alternate forms:

$$x \to \infty \qquad c \neq \pm\infty \qquad b \neq \pm\infty \tag{2.8}$$

$$\left.\begin{array}{ll} c = c_0 & \partial c/dx = 0 \\ b = b_0 & \partial b/dx = 0 \end{array}\right\} \qquad \textbf{(2.9)}$$

Much more care should be taken in handling boundary conditions 2.8 or 2.9 whenever the bulk-liquid concentration c_0 is equal to the equilibrium concentration $c^{'}$, that is to say whenever $r = 0$ in the bulk of the liquid. This can be seen by integrating Equation 2.2 from the interface down to a distance λ where $c = c^{'}$:

$$D_1 \int_0^{\lambda} \frac{\partial^2 c}{\partial x^2} dx = \int_0^{\lambda} \frac{\partial c}{\partial t} dx \; + \; \int_0^{\lambda} r dx = D_1 \left[\left(\frac{\partial c}{\partial x} \right)_{x=\lambda} \; - \; \left(\frac{\partial c}{\partial x} \right)_{x=0} \right] \qquad \textbf{(2.10)}$$

From Equation 2.10:

$$- D_1 \left(\frac{\partial c}{\partial x} \right)_{x=\lambda} = V - \int_0^{\lambda} \frac{\partial c}{\partial t} dx \; - \; \int_0^{\lambda} r dx \qquad \textbf{(2.11)}$$

The terms appearing on the right hand side of Equation 2.11 are the instantaneous-absorption rate, the total accumulation rate of the absorbing component (ozone) and the total rate of reaction. Their algebraic sum is zero only if the value of λ does not change with time: in this case in fact the absorption rate only results in either accumulation or reaction. Hence, condition 2.9 can be applied either at steady state (when concentrations in the liquid do not change in time) or when $\lambda \to \infty$. If λ is finite value, which may happen *e.g.* if the reaction rate order is of less than one with respect to the absorbing component's concentration, a different kind of boundary condition should be employed, namely:

$$x = \lambda \qquad c = c^{'} \qquad \textbf{(2.12)}$$

Where in turn the value of λ is defined by a differential equation:

$$\frac{d\lambda}{dt} = - \left(\frac{\partial c/\partial t}{\partial c/\partial x} \right)_{x=\lambda} \qquad \textbf{(2.13)}$$

In such cases, integration of Equation 2.2 becomes a "moving boundary" problem.

2.3 Ozone Oxidation

2.3.1 Ozone chemistry

Ozone is soluble in many substances, forming either stable or metastable solutions. Under practicable conditions in water ozone is 14 times more soluble than oxygen, chlorine is 12 times more soluble than ozone. The stability is influenced by the presence of sensitizing impurities, such as heavy-metal cations and metal oxides, and by temperature and pressure. Generally an increase of the pressure or decrease of the temperature enhances the solubility of ozone in aqueous phase Table 2.1 Lists the solubility of 100% ozone in pure water, for the range of 0-60°C. Ozone concentrations used in water treatment are typically below 14 percent, which limits the mass transfer driving force of gaseous ozone into the water (EPA Guidance Manual, 1999).

Table 2.1: Solubility of Ozone in Water (Ullmann's, 1991)

Temperature (°C)	Solubility (g/l)
0	1.09
10	0.78
20	0.57
30	0.40
40	0.27
50	0.19
60	0.14

The molecular ozone reactions are extremely selective and limited to unsaturated aromatics and aliphatic compounds as well as to specific functional groups. By analysis of the electronic structure, the ozone molecule is considered to have the following resonant structure (Figure 2.2). The chemistry of ozone is largely governed by its strongly electrophilic nature.

The structure of ozone illustrates that the ozone molecule will act as a dipole, as an electrophilic agent, and as a nucleophilic agent.

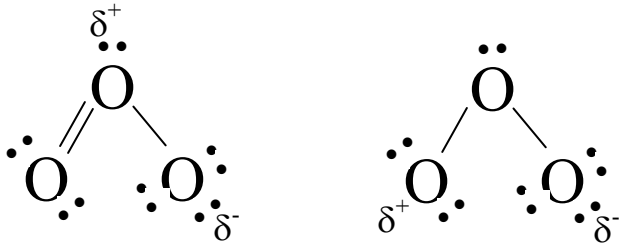


Figure 2.2: Resonant structure of ozone (Langlais *et al.,* 1991)

The high reactivity of ozone can be attributed to the electronic configuration of the molecule. Thus, the absence of electrons in one of the terminal oxygen atoms in some of the resonance structures confirms the electrophilic character of ozone. Conversely, the excess negative charge present in some other oxygen atom imparts a nucleophilic character. These properties make ozone an extremely reactive compound. Table 2.2 presents some physicochemical properties of ozone.

Table 2.2: Physico-Chemical Properties of Ozone (Perry and Green, 1997)

Property	**Value**
Melting point (°C)	-251
Boiling point (°C)	-112
Critical pressure (atm)	54.62
Critical temperature (°C)	-12.1
Specific gravity	1.658 higher than air
Critical density (kg/m3)	436
Free energy of formation (cal/mol)[a]	38860
Oxidation potential (V)[b]	2.07

[a] At 1 atm and 25°C [b] At pH = 0

2.3.2 Stability of ozone in water

Ozone is unstable in water. The decay of ozone in natural waters characterized by a fast initial decrease of ozone, followed by a second phase in which ozone decreases with first order kinetics. The mechanism and the kinetics of the elementary reactions involved in ozone decomposition have been investigated in numerous studies (Staehelin and Hoigné, 1985; Forni *et al.,* 1982; Staehelin and Hoigné, 1982; Sehested *et al.,* 1983; Bühler *et al.,* 1984; Sehested *et al.,* 1984; Staehelin *et al.,* 1984; Tomiyasu *et al.* 1985; Sehested *et al.,* 1991; Sehested *et al.,* 1998).

The stability of dissolved ozone is readily affected by pH, ultraviolet light, ozone concentration and the concentration of radical scavengers. The decomposition rate, measured in the presence of excess radical scavengers, which prevent secondary reactions, is expressed as:

$$-\frac{d[O_3]}{dt} = k\ [O_3]^m \qquad \textbf{(2.14)}$$

Where k is m^{th} order ozone decomposition reaction rate constant. By integrating and rearranging:

$$[O_3] = [O_3]_0 \exp(-kt) \qquad m = 1 \qquad \textbf{(2.15)}$$

or

$$[O_3]^{1-m} = [O_3]_0^{1-m} - kt \qquad m \neq 1 \qquad \textbf{(2.16)}$$

The decomposition rate constant k is a function of pH and hydroxyl radical scavenger concentration (Sotelo *et al.,* 1987). Staehelin and Hoigné (1985) proposed a propotionality between the ozone decomposition kinetic rate constant and the inverse of hydroxyl radical scavenger concentration. They also indicated that, k is a linear function of pH.

Benbelkacem *et al.* (2003) experimentally determined the decomposition rate constant of ozone in deionized water. They indicated that, when deionized water saturated in ozone was considered, a steady state was reached and the mass balances for gas phase and liquid phase were given by Equation 2.17 and 2.18. k was then determined by combining Equations 2.17 and 2.18 (Equation 2.19).

$$\frac{Q_g}{V_{liq}}\left([O_{3,gas}]_{in} - [O_{3,gas}]_{out} \right) = k_L a \left([O_{3,liq}]^* - [O_{3,liq}]^\infty \right) \qquad \textbf{(2.17)}$$

$$k_L a \left([O_{3,liq}]^* - [O_{3,liq}]^\infty \right) = k [O_{3,liq}]^\infty \qquad \textbf{(2.18)}$$

$$k = \frac{Q_g \left([O_{3,gas}]_{in} - [O_{3,gas}]_{out} \right)}{V_{liq} [O_{3,liq}]^\infty} \qquad \textbf{(2.19)}$$

Under the operating conditions of ozonation experiments (T=20°C, pH=7.0), k was found to equal 7.10^{-4} 1/s.

For a given pH, Sotelo and his co-workers (1989) assumed in their study that an emperical equation for the ozone decomposition kinetic rate constant consedering the ionic strenght. The equation is :

$$k = k_0 I^a \exp(-b/T) \; [Sca] \qquad \textbf{(2.20)}$$

where k_0, a and b are constants, and I, T and $[Sca]$ represents the ionic strenght, temperature and hydroxyl radical scavenger concentration. The values of k are indicated in Table 2.3.

Table 2.3: Experimental Kinetic Rate Constants for Ozone Decomposition Kinetics (l/mol s) (Sotelo *et al.*, 1989)

Salt Type		k [mol/min]	R^2
Sodium Phosphate	pH = 2	$k=4.157\times10^{7}\ \exp(-4900/T)I^{1.269}/[S]$	0.997
	pH =7	$k=7.120\times10^{10}\ \exp(-6858/T)I^{1.030}/[S]$	0.988
	pH = 8.5	$k=4.77\times10^{12}\ \exp(-8211/T)I^{0.794}/[S]$	
Sodium Phosphate and Sodium Carbonate	pH =7	$k=3.713\times10^{16}\ \exp(-10754/T)I^{0.929}/[S]$	0.997
Sodium Sulphate	pH =6, 20°C	$k=1.0114\ I^{1.22}/[S]$	0.999
Sodium Chloride	pH =6, 20°C	$k=7.47\times10^{-2}\ I^{1.01}/[S]$	0.999
Sodium Chloride and Sodium Phosphate	pH =7, 20°C	$k=0.315\ I^{0.59}/[S]$	0.999

Ozone decomposition occurs in a chain process that can be represented by the following fundamental reactions, based on the two most important models (Staehelin *et al.,* 1984; Tomiyasu *et al.,* 1985).

$$O_3 + OH^- \xrightarrow{k_1} HO_2^\bullet + O_2^{-\bullet} \qquad k_1 = 70 \ \ 1/Ms \qquad \textbf{(2.21)}$$

$$HO_2^\bullet \xrightarrow{k_2} O_2^{-\bullet} + H^+ \qquad k_2 = 10^{-4.8} \qquad \textbf{(2.22)}$$

$$O_3 + O_2^{-\bullet} \xrightarrow{k_3} O_3^{-\bullet} + O_2 \qquad k_3 = 1.6 \ \ 10^9 \ \ 1/Ms \qquad \textbf{(2.23)}$$

$$O_3 + H^+ \xleftrightarrow{k_4} HO_3^\bullet \qquad k_4 = 5.2 \ \ 10^{10} \ \ 1/Ms \ \ pK_a = 6.2 \qquad \textbf{(2.24)}$$

$$HO_3^\bullet \xrightarrow{k_5} OH^\bullet + O_2 \qquad k_5 = 1.1 \ \ 10^5 \ \ 1/s \qquad \textbf{(2.25)}$$

$$O_3 + OH^\bullet \xrightarrow{k_6} HO_4^\bullet \qquad k_6 = 2.0 \ \ 10^9 \ \ 1/Ms \qquad \textbf{(2.26)}$$

$$HO_4^\bullet \xrightarrow{k_7} HO_2^\bullet + O_2 \qquad k_7 = 2.8 \ \ 10^4 \ \ 1/s \qquad \textbf{(2.27)}$$

$$HO_4^\bullet + HO_4^\bullet \longrightarrow H_2O_2 + 2O_3 \qquad \textbf{(2.28)}$$

$$HO_4^\bullet + HO_3^\bullet \longrightarrow H_2O_2 + O_3 + O_2 \qquad \textbf{(2.29)}$$

$$OH^\bullet + CO_3^{2-} \xrightarrow{k_8} OH^- + CO_3^{\bullet-} \qquad k_8 = 4.2 \ \ 10^8 \ \ 1/Ms \qquad \textbf{(2.30)}$$

$$O_3 + CO_3^{\bullet -} \longrightarrow products \quad (CO_2 + O_2^{\bullet -} + O_2) \qquad \textbf{(2.31)}$$

$$OH^{\bullet} + HCO_3^{-} \xrightarrow{k_9} OH^{-} + HCO_3^{\bullet} \qquad k_9 = 1.5 \;\; 10^7 \;\; 1/Ms \qquad \textbf{(2.32)}$$

The overall pattern of the ozone decomposion mechanism is shown in Figure 2.3. The first fundamental element in the reaction diagram and in the rate constant values is that the free radical initiating step constitutes the rate determining step in the reaction. The second is that the regeneration of the superoxide readical ion O_2^-, or its protionic form HO_2, from the hydroxyl radical OH implies that 1 mol of ozone is consumed. As a result, all the species capable of consuming hydroxyl radicals without regenerating the superoxide radical ion will produce a stabilizing effect on the ozone molecule in water (Iglesias, 2002).

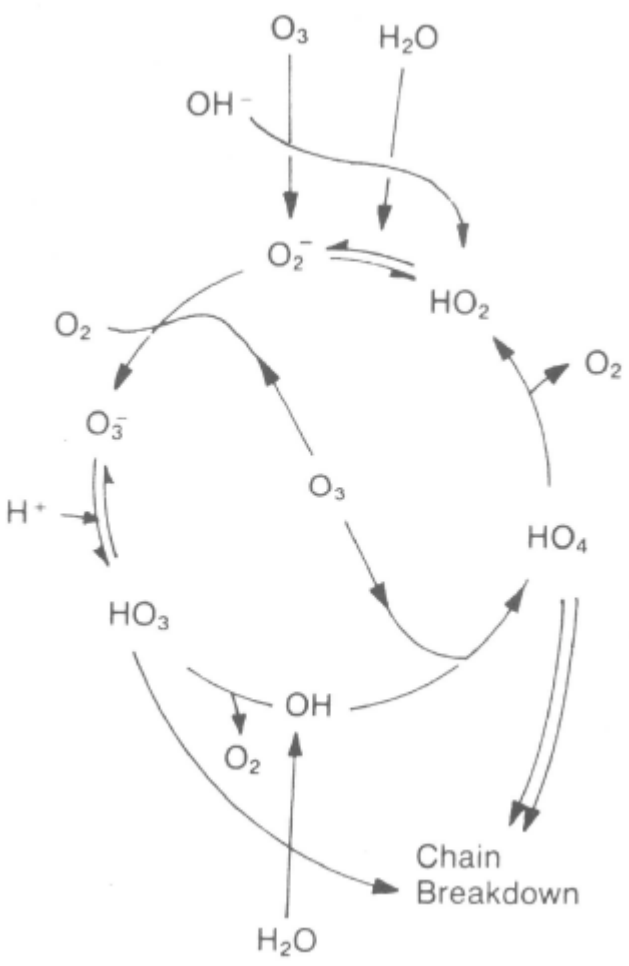


Figure 2.3: Ozone decomposition mechanism (Langlais *et al.,* 1991)

2.3.3 Oxidation of inorganic and organic compounds by ozone

Ozone may oxidize inorganic and organic compounds in the following two ways (Hoigné and Bader, 1976, 1977a, 1977b, 1978):

- by direct reaction with the molecular ozone
- by in direct reaction with the radical species that are formed when ozone decomposes in water.

The two basic reactions of ozone in water are illustrated in Figure 2.4

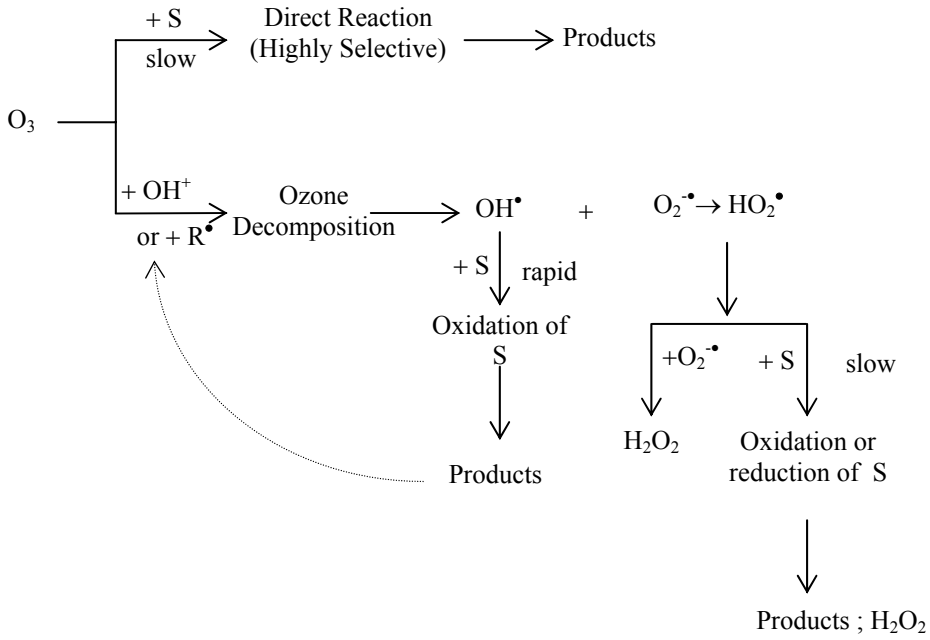


Figure 2.4: Ozone oxidation mechanism (Hoigné and Bader, 1976)

A general reaction pathway of reaction of ozone with organic and inorganic compounds is shown in Figure 2.5. An electrophilic addition of ozone to the compound S leads to an intermediate adduct $(S-O_3)$ which then decomposes by formation of primary products. It can be seen from the Figure 2.5 that there is a wide spectrum of reactions such as oxygen atom transfer to anionic, uncharged and cationic species (1), electron transfer (2), formation of an oxyl radical (3), ozone insertion (4) and ring formation (5).

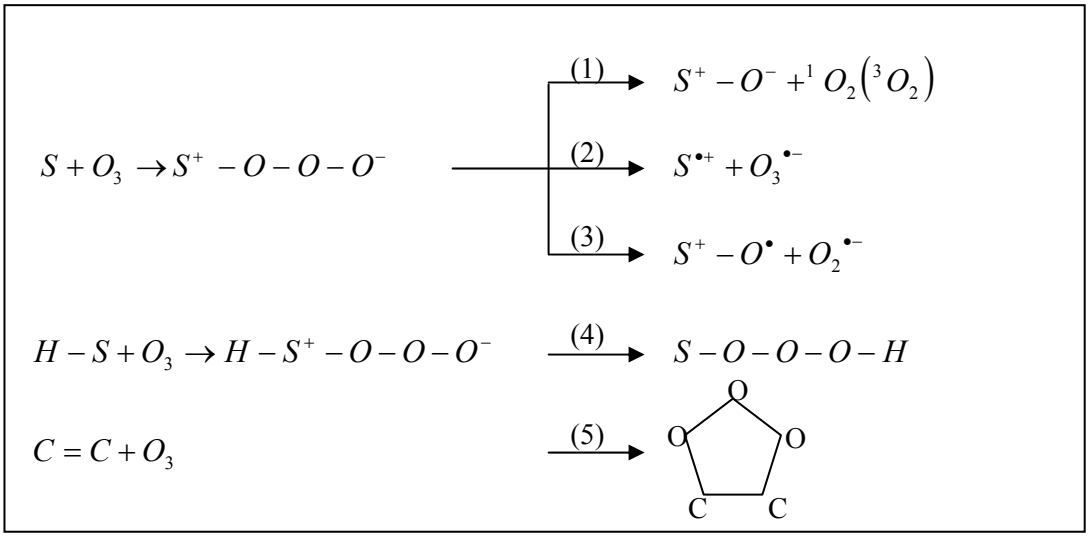


Figure 2.5: Primary reaction of ozone with a compound S (Von Gunten, 2003)

The main mechanism for the molecular ozone oxidation of inorganic compounds is the apparent transfer of an oxygen atom from ozone to the inorganic compound, according to the Figure 2.5 (Reaction 1) The transfer of an oxygen atom from ozone to the oxidizable species is formally a two-electron oxidation of this compound (Von Gunten, 2003).The corresponding two-electron reduction potential for ozone, which is connected to an oxygen transfer, can be assumed to be approximately 0.8V. A two-electron reduction potential for ozone of 2.08V is given in the literature (Weast and Astle, 1993-1994). The significance of this is limited for these non-reversible oxygen transfer reactions. One-electron transfer reactions of inorganic anions to ozone are rare and not well documented. The superoxide radical is frequently cited as a possible electro transfer reaction (Hoigné, 1998). However, an oxygen transfer from ozone to $O_2^{\bullet-}$ is also possible (Von Gunten, 2003). For slower processes, OH radicals play an important role. However, this indirect pathway leads to a substantial loss of oxidation capacity in the system due to the fast scavenging of OH radicals by many compounds.

Cyclo addition (Criegee mechanism): As a result of it dipolar structure, the ozone molecule may lead to 1-3 dipolar cyclo addition on unsaturated bonds, with the formation of primary ozonide (I) corresponding to the following reaction (Figure 2.6).

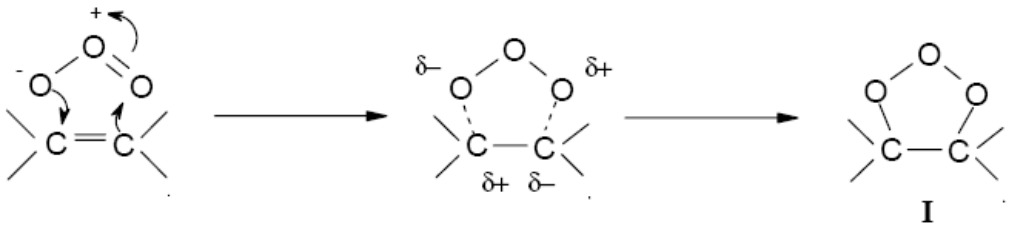


Figure 2.6: Dipolar cyclo addition of ozone on unsaturated bonds

In water, this primary ozonide decomposes into a carbonyl compound (aldehyde or ketone) and zwitterion (II) that quickly leads to a hydroxy-hydroperoxide (III) stage that, in turn, decomposes into a carbonyl compound and hydrogen peroxide (Figure 2.7).

Electrophilic reaction: The electrophilic reaction is restricted to molecular sites with a strong electronic density and, in particular, certain aromatic compounds. Aromatics substituted with electron donor groups (OH, NH_2 and similar compounds) show high electronic densities on carbons located in the ortho and para positions, and so are highly reactive with ozone at these positions. On the contrary, the aromatics substituted with electron-withdrawing groups (-COOH, $-NO_2$) are weakly ozone reactive. In this case, the initial attack of the ozone molecule takes place mainly on the least deactivated meta position.

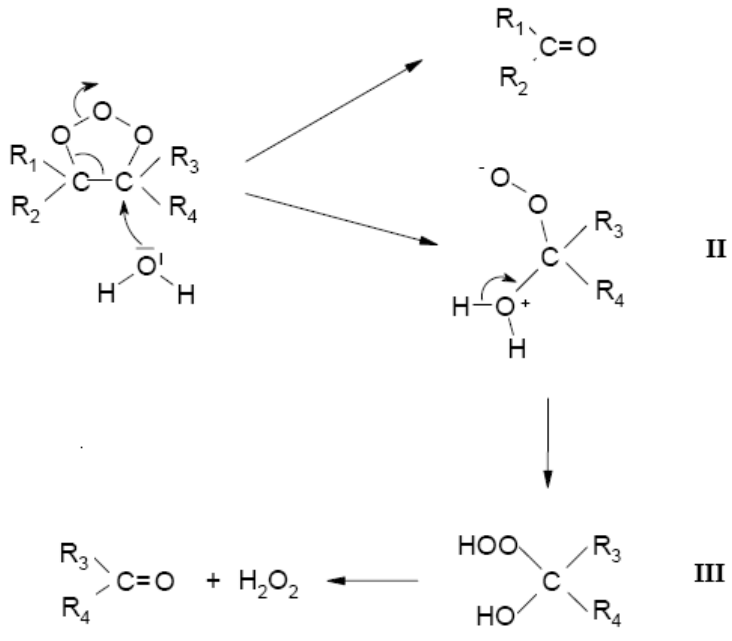


Figure 2.7: Criegee mechanism

The result of this reactivity is that the aromatic compounds bearing the electron donor groups D (for example phenol and aniline) react quickly with the ozone. The reaction is schematically represented in Figure 2.8.

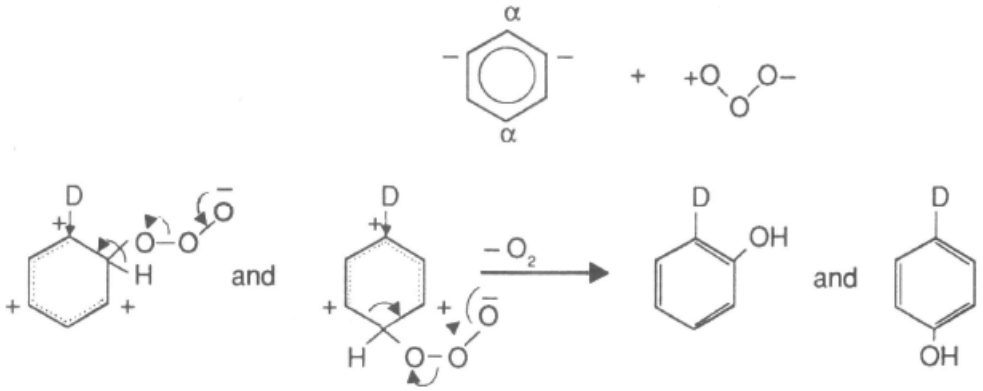


Figure 2.8: Electrophilic reaction of ozone with aromatic compounds (Langlais *et al.,* 1991)

The aromatic attack of the ozone molecule leads first to the formation of ortho- and para-hydroxylated by-products. These hydroxylated compounds are highly susceptile to furher ozonation. The compounds lead to the formation of quinoid and, due to the opening of the aromatic cycle, to the formation of aliphatic products with carbonyl and carboxyl functions. In Figure 2.9 the general reaction of ozonation of aromatics is given.

Nucleophilic reaction: The nucleophilic reaction is found locally on molecular sites showing an electronic deficit and, more frequently, on carbons carrying electron-withdrawing groups.

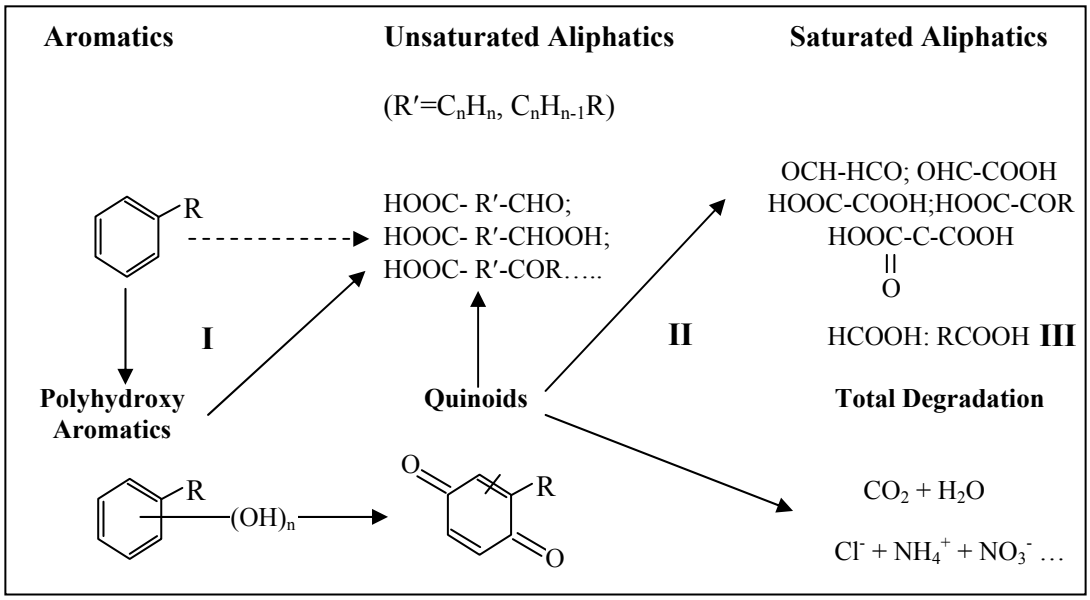


Figure 2.9: Scheme of ozonation of aromatic compounds (Langlais *et al.,* 1991)

2.4 Kinetics of the Direct Ozone Reactions

Ozone reactions in water and wastewater are heterogeneous parallel-series gas liquid reactions in which a gas component (ozone) transfers from the gas phase (oxygen or air) to the water phase where it simultaneously reacts with other substances (pollutants) while diffusing. The main aim of the kinetic study is to determine the rate constant of the reactions and mass transfer coefficients. This is achieved by establishing the corresponding kinetic law. In contrast to chemical equilibrium, kinetic laws are empirical and must be determined from experiments. The fist approach is based on experimental results of homogeneous ozonation reactions. This is the case where ozone and any compound are dissolved in water and than mixed and their concentrations with time are observed. The kinetic law, in this case, relates the chemical reaction rate to the concentration of reactants (and products, in the case of reversible reactions). Thus, for any general irreversible ozone direct reaction with a compound S,

$$z_{O3}O_3 + z_S S \rightarrow z_P P \qquad \textbf{(2.33)}$$

and z_{O3}, z_S and z_P are stoichiometric coefficients of ozone, S, and P, respectively. The kinetic law corresponding to the ozone or S, chemical reaction rates are

$$r_{O3} = z_{O3} k C^n{}_{O3} C^m{}_S \qquad \textbf{(2.34)}$$

and

$$r_B = z_B k C^n{}_{O3} C^m{}_S \qquad \textbf{(2.35)}$$

where k, n and m are the reaction rate constant and reaction orders of ozone and S, respectively. Note that z_{O3} and z_S have negative values due to convention. Both equations are related by the stoichiometric coefficients

$$r_{O3} = \frac{z_{O3}}{z_S} r_S = \frac{1}{z} r_S \qquad \textbf{(2.36)}$$

In most of the studies, however the ratio between coefficients, $z_S / z_{O3} = z$, is considered, so that Reaction 2.33 becomes

$$O_3 + zS \rightarrow z'P \quad \textbf{(2.37)}$$

where z has a negative value when used in the rate law.

The second possibility is the study of ozonation kinetics as a heterogonous process, that is, as it develops in practice. In this case, the adsorption rate of ozone or ozonation rate, N_{O3}, represents the kinetic law of the heterogeneous process, The stoichiometric equation is now

$$O_3(g) \xrightarrow{k_L a} O_3(l) \quad \textbf{(2.38)}$$

Reaction 2.38 represents the mass transfer of ozone from the gas to water phase, and $k_L a$ is the volumetric mass transfer coefficient.

The kinetic law equation is, in many cases, a complex expression that is deduced from transport phenomena studies, and it depends not only on the concentrations, chemical rate constants, and reaction orders as in the homogeneous case, but also on physical properties (diffusivities), equilibrium data (ozone solubility) and mass transfer coefficients (Beltrán, 2004).

2.4.1 Homogeneous ozonation kinetics

When a homogeneous reaction is studied, the rate law is exclusively a function of the concentration of reactants, rate constant of the reaction, and reaction orders.

The ozone reaction is carried out with one of the reactants (ozone or S) in excess so that the process behaves as a pseudo-nth order reaction. For example, if it is assumed that compound S is in excess, then its concentration remains constant with time while ozone diminishes. Application of the material balance of ozone in a batch reactor once the contribution of the hydroxyl free radical reaction has been neglected leads to

$$\frac{dC_{O3}}{dt} = -k'_D C_{O3}^n \quad \textbf{(2.39)}$$

where k'_D is the pseudo-nth order rate constant for ozone and the minus sign indicates the negative value of stoichiometric coefficient of ozone.

$$k'_D = k_D C_S^m \quad \textbf{(2.40)}$$

With k_D and m being the actual rate constant of Reaction (2.37) and reaction order for S, respectively.

Integration of Equation 2.39 leads to

- For $n = 1$:

$$\ln \frac{C_{O3}}{C_{O30}} = -k'_D t \qquad \textbf{(2.41)}$$

and

- For $n \neq 1$:

$$\frac{C_{O3}^{1-n}}{1-n} = \frac{C_{O3}^{1-n}}{1-n} - k'_D t \qquad \textbf{(2.42)}$$

Where C_{O30} is the concentration of ozone at $t = 0$. In most ozone reactions, Equation 2.41 has been confirmed from experimental data so that reactions are first order for ozone. If this procedure is applied to experiments where the concentration of S has been changed, different value of k'_D are obtained. This procedure can also be applied to experiments where the ozone concentration is in excess and the concentration does not change with time during the reaction period. Examples of these procedures can be found in the literature for inorganic and organic compound ozone direct reactions (Hoigné and Bader, 1983a; Hoigné and Bader, 1983b; Hoigné *et al.,* 1985; Yao and Haag, 1991).

Another possible approach involves ozone experiments where the aqueous solution initially contains the target compound S and another compound called reference compound R, of known ozone kinetics, that is, with known rate constant and stoichiometry. This is called relative rate constants method. Both mass-balance equations of S and R applied to the batch reacting systems are dividing by each other to yield the following equation:

$$\frac{dC_S}{dC_R} = z_{rel} k_{rel} \frac{C_S}{C_R} \qquad \textbf{(2.43)}$$

where z_{rel} is the ratio of stoichiometric coefficients of the ozone-S and ozone-R reactions and k_{rel} the ratio of their corresponding reaction rate constants. After variable separation and integration, Equation 2.43 leads to

$$\ln\frac{C_S}{C_{S0}} = z_{rel}k_{rel}\ln\frac{C_R}{C_{R0}} \qquad \textbf{(2.44)}$$

Which indicates that a plot of the logarithm of the left side against the logarithm of the ratio between the concentration of R at any time and at the start of the ozonation leads to a straight line of slope $z_{rel}k_{rel}$. Knowing z_{rel} and the rate constants of the ozone-R reaction, the target rate constant is obtained from the slope of the plotted straight line. The method has the advantage that there is no need for ozone concentration to be known. However, the reference compound should have a reactivity toward ozone similar to that of the target compound B, and the accuracy of the rate constant determined will depend on that of the rate constant of ozone-R reaction (Beltrán, 2004).

2.4.2 Heterogeneous ozonation kinetics

When ozone reactions are carried out in practice, that is, by feeding air or oxygen containing ozone into the aqueous solution of the target compound S, the process is heterogeneous and kinetic equations usually express the amount of ozone absorbed per unit time and volume. These equations not only involve chemical reaction parameters (i.e., the chemical reaction rate constant) but also transport coefficient (i.e., the mass transfer coefficient). Thus, the heterogeneous study allows the relative importance of chemical and physical steps that develop simultaneously to be established. In this sense, ozonation kinetics can be classified as fast, moderate or slow reactions, and any one of these situations leads to different rate laws (Beltrán, 2004).

2.4.2.1 Fast kinetic regime

For the fast kinetic regime the reaction develops in a zone close to the gas-water interface (Figures 2.10a and b). In this kinetic regime reaction is in a zone in the film layer. The condition for this kinetic regime is that $Ha > 3$. The general equation for the adsorption rate law is

$$N_{O3} = k_L a \frac{Ha}{\tanh Ha} \tag{2.45}$$

However, this equation gives results difficult to use in kinetic determination. A simplification comes from the possibility that the concentration profile of B through the film layer should be constant and the same as in the bulk concentration $C_S = C_{Sb}$ (Figure 2.10b). If this case holds, it is said that the kinetic regime is of fast pseudo first order. For an ozonation reaction of this type, the absorption rate law is

$$N_{O3}a = aC_{O3}^{*}\sqrt{kC_{Sb}D_{O3}} \tag{2.46}$$

For this kinetic regime, the molar balance of S is introduced for a batch system and related to the ozone adsorption rate Equation 2.47 is obtained:

$$\frac{dC_{Sb}}{dt} = zaC_{O3}^{*}\sqrt{kC_{Sb}D_{O3}} \tag{2.47}$$

Integration of Equation 2.47 between the limits

$$\begin{aligned} t &= 0 \qquad C_{Sb} = C_{Sb0} \\ t &= t \qquad C_{Sb} = C_{Sb} \end{aligned} \tag{2.48}$$

leads to the calculation of k.

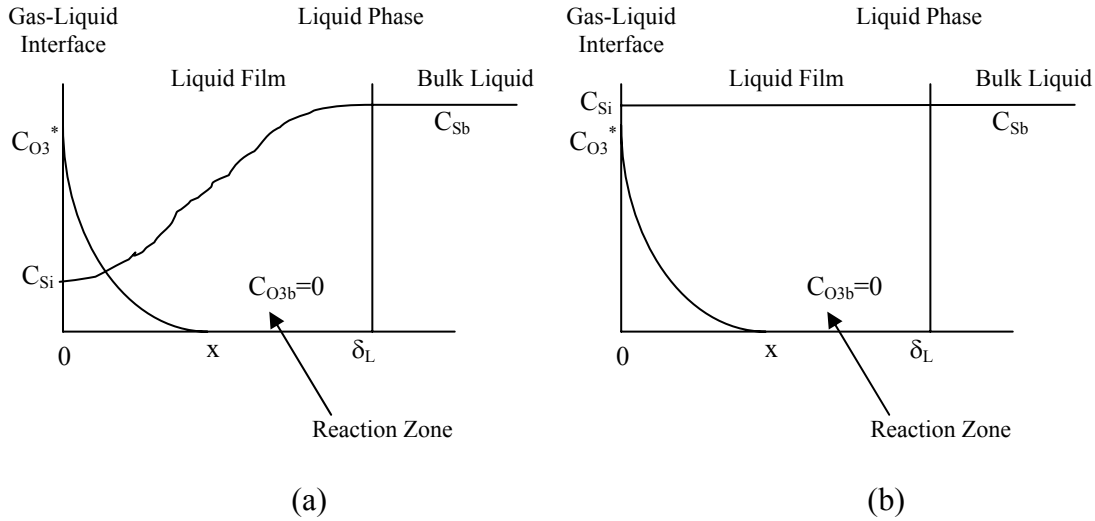


Figure 2.10: Film theory: fast kinetic regime. Concentration profiles of ozone and S with the distance to the interface (a) general; (b) fast pseudo first-order

Another possbility to apply the fast pseudo first-order kinetic regime is the use of the competitive kinetic method that is also describe in Subsection 2.4.1. With this method the ozonation of the target compound is carried out in the presence of another compound, or reference compound, R, of known ozonation kinetics (Beltrán, 2004).

2.4.2.2 Moderate (Intermediate) kinetic regime

When the reaction between ozone and target compound S is either in the film layer or in the bulk liquid the regime called moderate (intermediate) (Figure 2.11). The condition to be fulfilled is that the Hatta number must be between 0.3 and 3. Due to the complexity of the kinetic equation, it is this kinetic regime is not recommended. Nonetheless, there are two cases where the experimental data obtained at this kinetic regime can be used for this purpose. In one of these cases there is no dissolved ozone and the rate law equation can be simplified to Equation 2.45, which also applies for the fast kinetic regime. In the second case, the concentration of S can be considered constant through the film layer and the regime can be called moderate pseudo first-order (Beltrán, 2004).

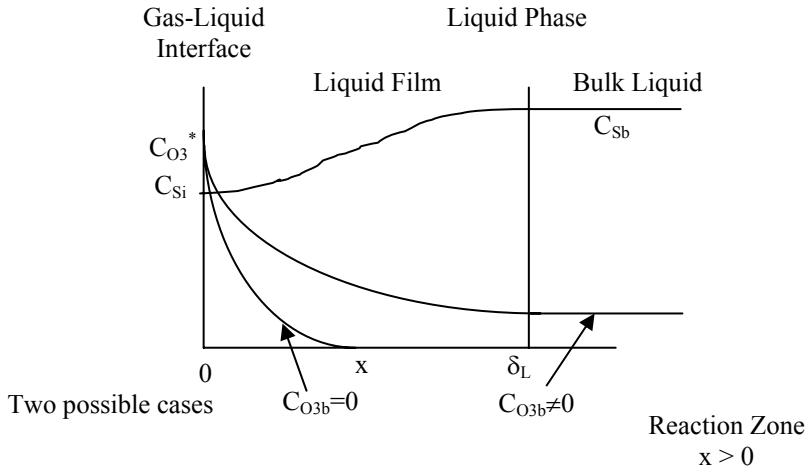


Figure 2.11: Film theory: moderate kinetic regime. Concentration profiles of ozone and S with the distance to the interface

2.4.2.3 Slow kinetic regime

The presence of dissolved ozone is the sign of slow reaction in water. In these cases Hatta number is lower than 0.3. The process presents two steps in series, with the diffusion rate of ozone through the film layer equal to the chemical reaction rate in

the bulk liquid. Figure 2.12 represents the general situation for the concentration profiles of ozone and S, the target compound.

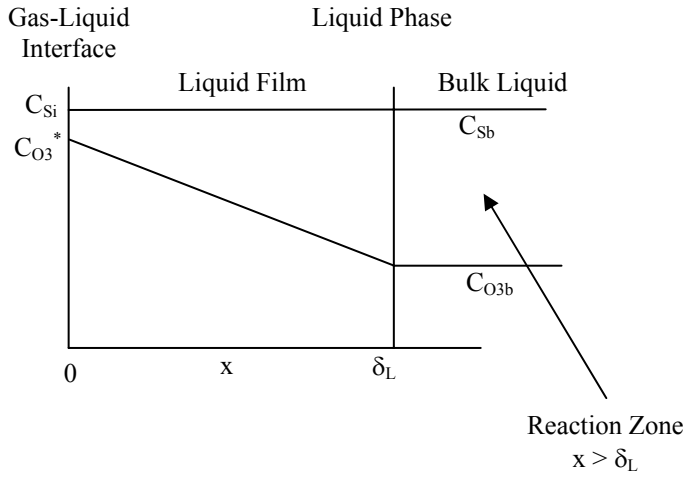


Figure 2.12: Film theory: slow kinetic regime. Concentration profiles of ozone and S with the distance to the interface

The rate constant of the direct reaction ozone-S compound can be obtained directly from the mass balance of S in the batch reactor for slow kinetic regime as follows:

$$r_B = -\frac{dC_{Sb}}{dt} = zkC_{O3b}C_{Sb} \qquad \textbf{(2.49)}$$

Equation 2.49 can be used if concentrations of B and ozone are known with time. The recommended method is the use of an analytical procedure, that is integrating the Equation 2.49. This can only be done in the absence of secondary reactions that consume ozone since, in that case, concentrations of ozone and S are functions of the conversion of S. However, this is rather difficult in ozonation reactions where ozone is also consumed in unknown direct secondary reactions. In this case, a differential method should be applied. With this method, a plot of $-r_S$ with product of concentrations of S and ozone would lead to a straight line, according to the Equation 2.49. The slope of this line is the rate constant regardless of the presence of secondary reactions. The disappearance rates of compound S, $-r_S$, can be obtained from the experimental curve of the concentration of S with time.

The other possibility of determining the rate constant is the use of competitive method explained in Subsection 2.4.1. Note that in slow reactions the concentration of S is constant through the film layer and as a consequence, the competitive kinetic method can be applied (Beltrán, 2004).

2.4.2.4 Very slow kinetic regime

For rate constant determination, the main problem associated with the methods presented above is the need to know the disappearance rate of S, either at any time or exclusively at the start of the process. For this reason the very slow kinetic regime of absorption is the most appropriated one to determine the rate constant of ozone-S direct reaction. In this case, the ozone absorption rate equals to the maximum chemical reaction rate because the process is chemically controlled. The absorption rate is related to the disappearance rate of S, so that, in a batch system the following equation is obtained:

$$r_S = -\frac{dC_{Sb}}{dt} = zN_{O3}a = z\beta kC^*_{O3}C_{Sb} \qquad \textbf{(2.50)}$$

The integration of Equation 2.50 is carried out with the initial conditions

$$t = t_i \qquad C_{Sb} = C_{Sb} \qquad \textbf{(2.51)}$$

Where β is the liquid holdup, t_i is the time needed to reach the steady-state concentration of ozone and C_{Sb} is the corresponding concentration of S at that time. Integration of Equation 2.50 leads to:

$$\ln\frac{C_{Sb}}{C_{Bbs}} = -z\beta C_{O3s}(t - t_i) \qquad \textbf{(2.52)}$$

According to the Equation 2.52, a plot on the left side against $(t - t_i)$ should lead to a straight line. The slope of this line is the product of the rate constant, stoichiometric ratio, liquid holdup and steady-state concentration of ozone (Beltrán, 2004).

2.5 Bubble Column Reactors and Their Characterization

Bubble column reactors belong to the general class of multiphase reactors which consist of three main categories namely, the trickle bed reactor, fluidized bed reactor and the bubble column reactor. A bubble column reactor is basically a cylindrical vessel with a gas distributor at the bottom. The gas sparged in the form of bubbles into either a liquid phase or a liquid-solid suspension (Kantarcı *et al.,* 2005). They are used especially in chemical processes involving reactions such as oxidation,

chlorination, alkylation, polymerization, hydrogenation and in biochemical processes such as fermentation and biological wastewater treatment (Shah *et al.,* 1982; Prakash *et al.,* 2001).

Bubble column reactors owe their wide application area to a number of advantages they provide both in design and operation as compared to other reactors. They have excellent heat and mass transfer characteristics. Little maintenance and low operating costs are required due to lack of moving parts and compactness (Kantarcı *et al.,* 2005).

2.5.1 Design and scale-up

The design and scale-up of bubble columns have gained considerable attention in recent years due to complex hydrodynamics and it influences on transport characteristics. Generally two types of mode of operation are valid for bubble columns, namely the semi-batch mode and continuous mode. In continuous operation, the gas and suspension flow concurrently upward into the column and suspension that leaves the column recycled to the feed tank. However, in the semi-batch mode the suspension is stationary, meaning zero liquid throughputs, and the gas is bubbled into the column (Pino *et al.,* 1992).

The design and scale-up of bubble column reactors generally depend on the quantification of three main phenomena: (i) heat and mass transfer characteristics; (ii) mixing characteristics; (iii) chemical kinetics of the reacting system.

In order to design bubble column reactors, the following hydrodynamics parameters are required: specific gas-liquid interfacial area, mean bubble diameter, axial dispersion coefficients of gas and liquid, mass transfer coefficients for all the species, gas holdups and physicochemical properties of the liquid medium(Kantarcı *et al.,* 2005).

2.5.2 Fluid dynamics and regime analysis

The fluid dynamic characterization of bubble column reactor has a significant effect on the operation and performance of bubble columns. The flow regimes in bubble columns are classified and maintained according to the superficial gas velocity employed in the column (Kantarcı *et al.,* 2005).

Three types of flow regimes are commonly observed in bubble columns which are the homogeneous (bubbly flow) regime; the heterogeneous (churn-turbulent) regime and slug flow regime (Hyndman *et al.,* 1997). Figure 2.13 illustrates the differences between the possible regimes discussed.

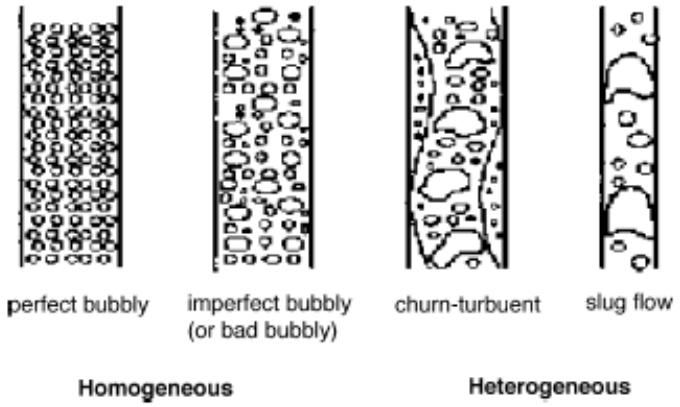


Figure 2.13: Schematic of possible flow regimes in bubble columns (Bouaifi *et al.,* 2001)

2.5.3 Gas holdup

Gas holdup is dimensionless key parameter for design purposes that characterizes transport phenomena of bubble column systems (Lua *et al.,* 1999). It is basically defined as the volume fraction of gas phase occupied by the gas bubbles. The gas holdup increases with increasing gas velocity and operating pressure; whereas it decreases with increasing liquid viscosity.

2.5.4 Bubble characteristics

Bubble populations, their holdup contributions and rise velocities have significant impact on alternating the hydrodynamics, as well as mass transfer coefficient in a bubble column. For this reason it is important to obtain information on bubble properties of the slurry.

Researches on bubble size distributions and factors affecting bubble sizes such as gas density, liquid properties, surface tension and operation conditions (pressure, temperature) are widely reported in the literature (Schafer *et al.,* 2002). The published studies discussed on bubble characteristics showed that the bubble sizes increase with increasing superficial gas velocity, liquid viscosity and surface tension.

2.5.5 Mass transfer coefficient

The overall mass transfer rate per unit volume of the dispersion in a bubble column is governed by the liquid-side mass transfer coefficient, $k_L a$ assuming that the gas side resistance is negligible. In a bubble column reactor the variation in $k_L a$ is primarily due to variations in the interfacial area (Fan *et al.,* 1985). In gas-liquid reactors, mass transfer from the gas to liquid phase is the most important goal of the process. It can be concluded that the volumetric mass transfer coefficient, $k_L a$ increases with gas velocity, gas density and pressure whereas decreases with increasing liquid viscosity. It is also concluded that the presence of surfactants increase $k_L a$, due to formation of small bubbles.

3. LITERATURE REVIEW

3.1 Organic Compounds Ozonation Studies

Phenol and phenolic substances have deserved more attention than other organics because of their toxicity and frequency of industrial processes producing wastewater contaminated by phenol as a pollutant. Moreover, phenol is considered to be an intermediate product in the oxidation pathway of higher molecular weight aromatic hydrocarbons, thus it is usually taken as a model compound for treatment systems including oxidation processes (Singer and Gurol, 1983; Gurol and Singer,1983). The ozone oxidation route of phenol has been the subject of a large number of studies. Some of these studies aimed to identify the intermediates and end products of ozone oxidation of phenol. A general shame of mechanism of phenol oxidation by molecular ozone is given in Figure 3.1 (Beltrán, 2004). As can be seen in the figure, phenol oxidation by molecular ozone, the major intermediates are hydroquinone, catechol, and cis,cis-muconic acid (Mvula and von Sonntag, 2003; Singer and Gurol,1983). Catechol and hydroquinone formed by hydroxylation pathway, cis,cis-muconic acid and other ring cleavage products formed by 1,3 cyclo addition (Gurol and Singer, 1983). Catechol and hydroquinone oxidize to dihydroxybenzenes by further ozonation. Hoigné and Bader (1979) showed that the hydroxylation pathway constitutes less than 2% of the phenol oxidation by ozone at pH 3.0 and further oxidation products such as dihydroxybenzenes species does not appear to be significant at this pH value (Singer and Gurol, 1983).

Bailey (1972) suggested that catechol is produced as an intermediate product of phenol by ozone. Both catechol and hydroquinone were identified and quantified by Singer and Gurol (1981) in concentrations as much as 30 mg/l, in the reaction mixtures of phenol and ozone at neutral and high pH values. In acidic solutions, however, the concentrations of catechol and hydroquinone were less than 1 mg/l. Gurol and Nekouinaini (1984) reported that catechol and hydroquinone respectively, 220 and 1100 times more reactive than phenol with ozone and they associated the

low concentration of these intermediates with their high reactivity with ozone in acidic conditions. Mvula and von Sonntag, (2003) indicated that at low phenol conversions, hydroquinone, catechol, and cis,cis-muconic acid yields increase nearly linearly with increasing ozone concentration.

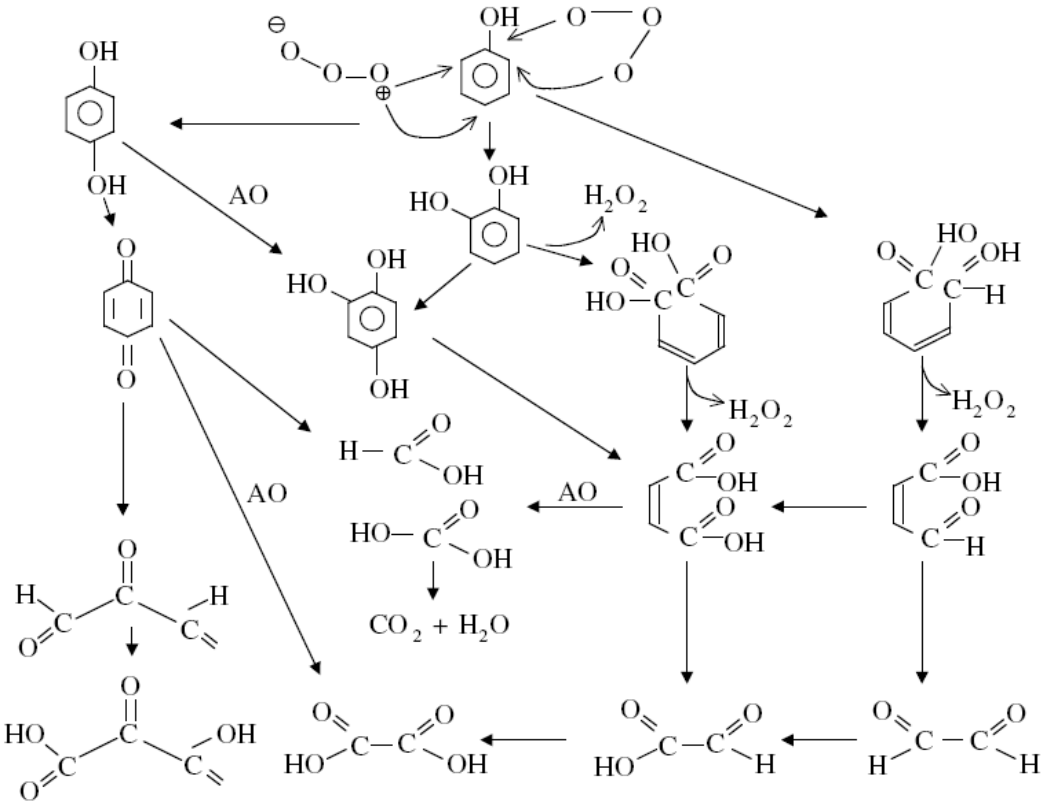


Figure 3.1: General mechanism of the ozonation of phenol
(AO : abnormal ozonolysis) (Beltrán, 2004)

Gurol and Nekouinaini (1984) aimed to derive a relation between the chemical structure of the substituted benzene ring and its reactivity with ozone. They reported that, due to the higher electron density in the aromatic ring, the hydroxylated phenols reacted faster than phenol. As for the hydroxylated phenols, hydroquinone and catechol react faster than resorcinol since the resonance effects activate the benzene ring especially at the ortho and para positions. However, the reaction is slower for catechol than for hydroquinone, probably because of the steric effects created at the ortho position by the OH substituent. They also reported that the reactivities of the CH_3-substituted phenol were in the expected order. The dimethylphenols, which reacted fastest, were followed by the mono-methylated phenols and finally by phenol.

Beltrán *et al.* (2000a) also studied the ozonation of four phenolic compounds found in wastewater effluents from food manufacturing process: Gallic and p-hydroxybenzoic

acids, catechin and tyrosol, in ultrapure water. The results of this study showed that the direct reaction between ozone and organic compounds seemed to be exclusive way of phenolic compound elimination. They conducted a series of ozonation experiments with above mentioned phenolic compounds in the presence and absence of a well-known hydroxyl radical scavenger (t-BuOH) by varying the pH of the solution from 2-12. They claimed that, radical reactions in ozonation of phenol-type substances could be discarded in all cases they studied. They explained this behavior by the presence of the hydroxyl group attached to the aromatic ring, reactions with electrophilic reagent like ozone markedly favored. They also claimed that at pH<12.0, the radical route of degradation of phenolic compounds may be neglected and these substances are degraded exclusively by direct reaction of ozone.

Andreozzi *et al.* (2000) studied N-Methyl-P-Aminophenol ozonation in aqueous solution. The ozonation of metol, one of the main constituents of photographic developers has been studied in aqueous solution in the pH range 2.0-7.0. They observed a complete disappearance of the substrate in all the cases after an ozonation time of approximately 20 min. The absence of any appreciable effect of the pH of the solution on the rate of metol disappearance suggested the intervention of diffisuonal limitation, that was due to high reactivity of the substrate with respect to ozone, the rate of metol oxidation was only determined by that of ozone diffusion from the gas bubbles to the liquid bulk. Methylamine was the main analyzed product to which nitrogen of metol was converted. They concluded that for the pH range 1.0-4.0, the kinetic constant of ozone attack to the substrate has been estimated with a good accuracy.

Le Lacheur and Glaze (1996) studied reactions of ozone and hydroxyl radicals with serine. Serine, one of the common amino acids in aquatic solution was treated with ozone in buffered aqueous solution. Reactions were conducted at pH 10.5 (adjusted with sodium hydroxide) one pH unit above the pKa of the amine functional group, with no promoter or scavenger present. For reactions of ozone with 100 μM serine solution, scavengers were used to suppress radical reactions in the study of molecular ozone processes, and a promoter was used for the study of radical reactions at pH 8.5. They concluded that, the reaction pH should be a major factor in the rate of oxidation of the byproducts, but both types of organic byproducts appear to be moderately stable to further reaction with ozone under the conditions used.

Corless *et al.* studied the reaction of pyrene with ozone in aqueous solution at low (10-200 µg/l) substrate concentration and with ozone concentrations (5 mg/l) approximating to those used in potable water treatment. Substantial destruction of pyrene was recorded within 1 min of reaction with ozone. Polyaromatic/aromatic compounds did not persist; reaction products were likely to be short chain polar aliphatic compounds.

Consequently, virtually complete destruction of pyrene has been demonstrated within 1 min of ozonation at an ozone concentration of 5 mg/l. Polyhydroxylated aromatics, quinoids, saturated and unsaturated oxygenated aliphatics was assumed to be likely products of aromatic ozonation. The implication of these results was that the oxidation ozonation of pyrene has resulted in the formation of short chain polar aliphatic compounds as the major products.

Yao *et al.* studied the ozonation of pyrene. The objective of the study was to identify the products formed from the direct reaction of ozone and to propose a pathway for the reaction of pyrene with ozone in the presence of water. They concluded that pyrene was oxidized by ozone at dosages ranging from 0.02 to 2.35 mmol of ozone. In all experiments the initial pyrene concentration was 5 mmol/l. They identified 14 products by varying the extent of reaction. Prior to the disappearance of pyrene one ring cleavage phenanthrene-type products predominated. The major product of this type was 4-carboxy-5-phenanthrene-carboxyaldehyde (4-CPA, IIIA/B). Once pyrene had completely reacted secondary ring cleavage occurred and biphenyl-type products predominated. The major product of this type was 2',6,6'-biphenyltrialdehyde-2-carboxylic acid (X). They also concluded that, the formation of H_2O_2 in the solvent mixture suggested that pyrene reacted with secondary oxidants (free radicals) formed from ozone self-decomposition in water. Even at pH 3.7 the hydroxyl free radicals appeared to be involved in the reaction. When ozone dosages ranged from 0.04 to 4.76 mol ozone / mol pyrene, they observed the stepwise ring cleavage and the oxidation of aldehydic functional groups.

Berger *et al.* (1999) studied the oxidation of glycine by ozone. They observed nitrites and nitrates as byproducts resulting from molecular ozonation of glycine. The proposed mechanism for the reaction of gylcine with molecular ozone is given in Figure 3.2

Qui *et al.* (2004) detected numerous intermediate compounds following the ozonation of 2,6-, 3,4- and 3,5-dichlorophenol isomers. For 2,6-DCP, 2,6-dichloro-1,4-benzenediol, 2,6-2,5-cyclohexadiene-1,4-dione, 2-chloro-1,4-benzenediol, 3,3′,5,5′-tetrachloro-4,4′-biphenyldiol, and ethylacetate were detected as ozonation byproducts.

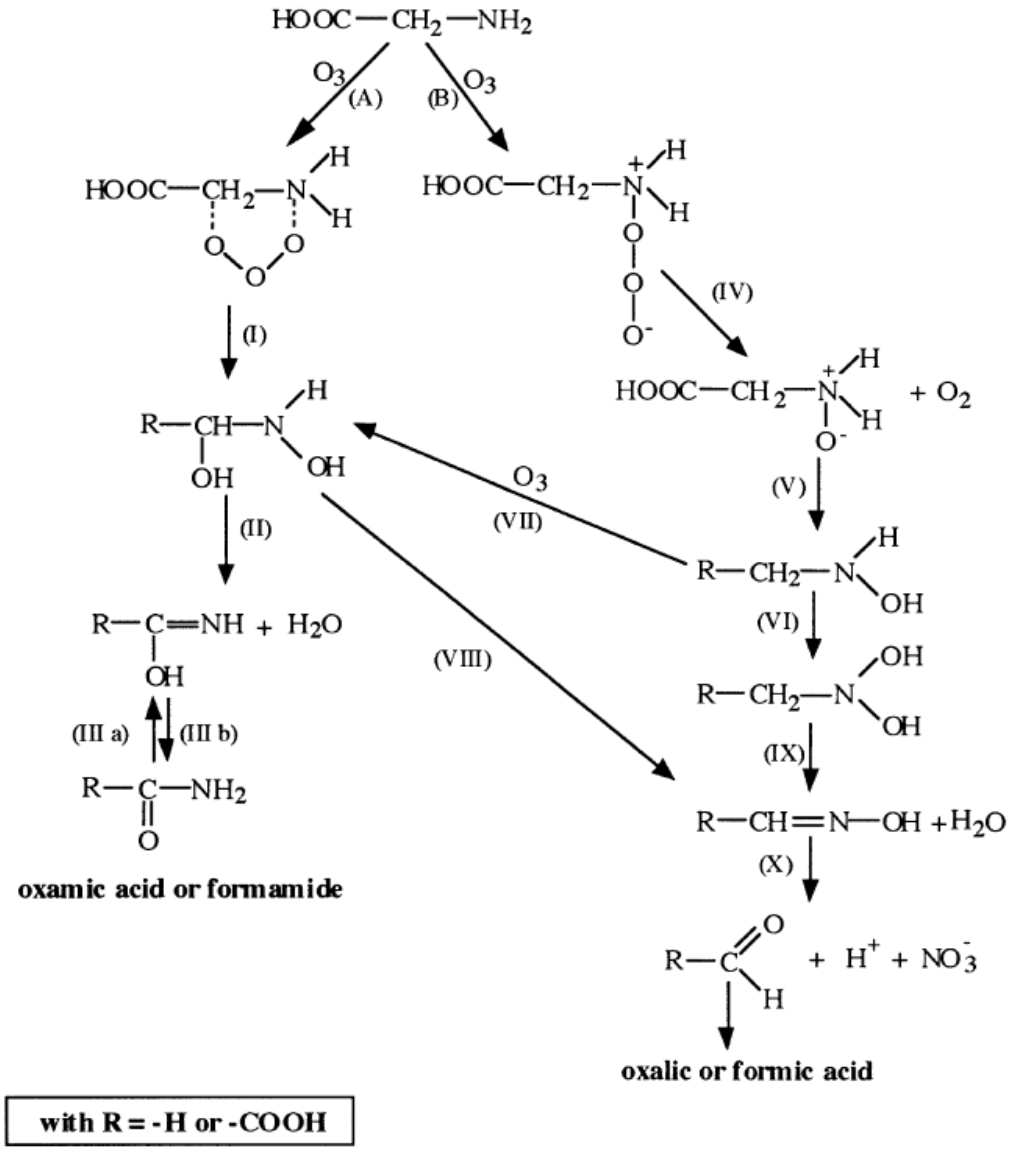


Figure 3.2: Mechanism for the reaction of gylcine with molecular ozone (Berger *et al.*,1999) (A) Ozonide form intermediates; (B) electrophilic attack on nitrogen; (I) oxidation on the carbon with or without decarboxylation; (II) dehydratation; (V) oxidation on N with or without decarboxylation; (VI) oxidation on N; (VII) oxidation on the carbon; (IX) dehydratation.

For 3,4-DCP, the following were found: 2,4-dichlorobenzenediol, 3-chlorohexadiene-1,4-dione, 2-chloro-1,4-benzenediol, and ethylacetate. Finally, identified products from 3,5-DCP ozonation were 3,5-dichloro-1,4-bezenediol, 3,5-dichloro2,5-cyclohexadiene-

1,4-dione, phenol, ethylacetate, and 3-heptone. In addition to the compounds listed, several species with molecular weights two to three times that of dichlorophenol were detected but not identified following the ozonation of 2,6-DCP and 3,4-DCP. Qui *et al.* (2004) explored possible pathways of the ozonation of 2,6-DCP molecules and 2,6-DCP anions as an example of DCPs. The initial attack of an ozone molecule was directed at the ortho position of the hydroxyl group to release a chlorine atom and produced a monochlorobenzenediol molecule. Simultaneously, the ozone molecule could also attack the para position of the hydroxyl group because of its high electron density. This resulted in the production of a dichlorobenzenediol molecule. The path for the ozonation was likely via the aromatic substitution transition state. This reaction scheme is illustrated below in Figure 3.3

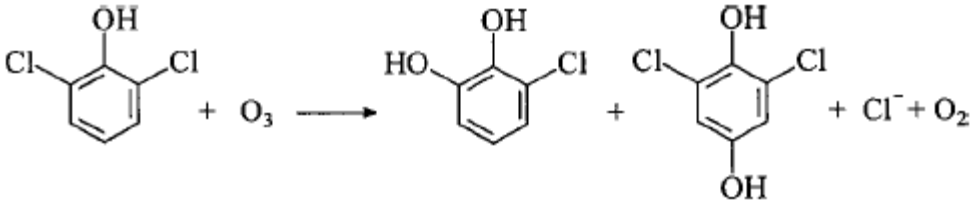


Figure 3.3: The initial attack of ozone to 2,6-Dichlorophenol molecule (Qui *et al.* 2004)

The chlorinated 1,6-benzenediol was then easily attacked by another ozone molecule to break the 1–6 C–C bond of the benzene ring; thereby, producing a chlorinated muconic acid as shown below in Figure 3.4.

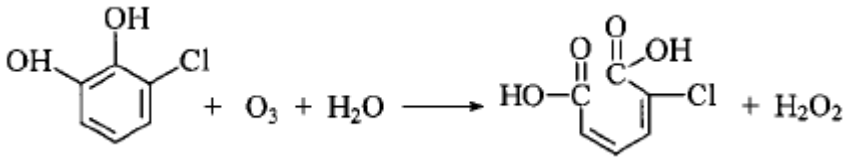


Figure 3.4: Production of chlorinated muconic acid (Qui *et al.* 2004)

The chlorinated 1,4-benzenediol was also susceptible to further oxidation to form chlorinated cyclohexadienedione (benzoquinone) as illustrated below in Figure 3.5.

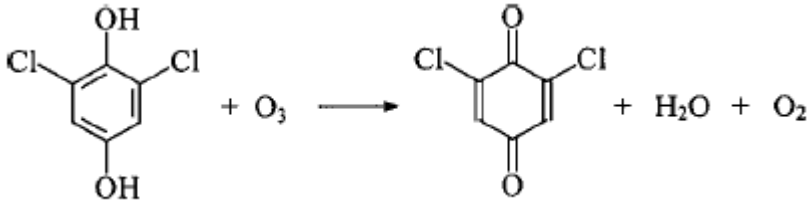


Figure 3.5: Formation of chlorinated cyclohexadienedione (benzoquinone) (Qui *et al.* 2004)

Both the chlorinated muconic acid and chlorinated benzoquinone were relative stable compared to the parent compound. If additional ozone molecules were available, both chlorinated muconic acid and benzoquinone could be oxidized further to release the chlorine atoms and yielded acetic acid, oxalic acids, and ethylacetate as the major organic oxidation products (Figure 3.6).

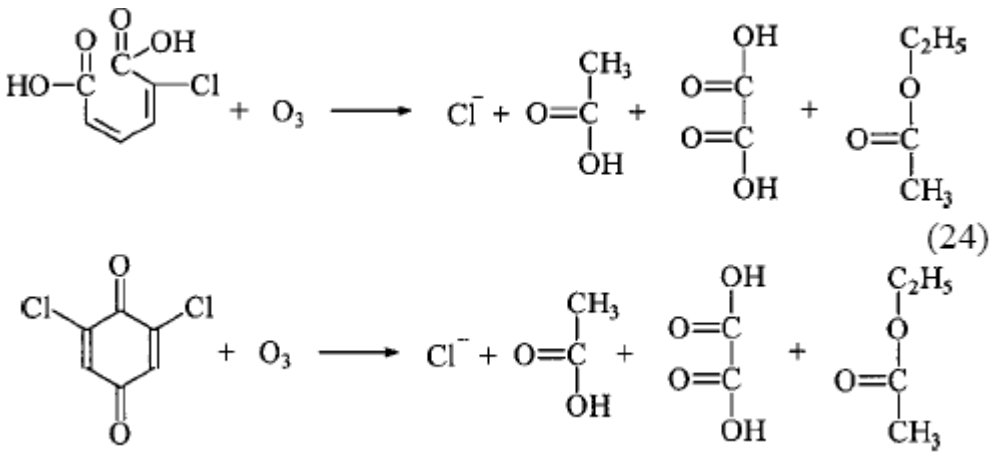


Figure 3.6: Major organic en product of 2,6-dichlorophenol ozonation (Qui *et al.,* 2004)

The much higher electron-donating effects of the negative-charged oxygen atom of a dichlorophenoxide anion may result in a faster attack of ozone molecules on the anion than on the dichlorophenol molecules. The ozonation of dichlorophenoxide anions was likely to follow a similar degradation pathway to that of the dichlorophenol molecules. The reaction path for the ozonation of 2,6-dichlorophenoxide anions could be expressed consecutively as in Figure 3.7 (Qui *et al.,* 2004).

Qui and his co-workers (2004) expected that the reactions of ozone with 3,4-DCP and 3,5-DCP followed a similar degradation pathway to that of 2,6-DCP with the initial attack of ozone molecules taking place at the ortho or para position of the hydroxyl group or the negative-charged oxygen group. Since there was a chlorine atom bonded to the para position other than the ortho position of the hydroxyl group or the negatively charged oxygen group of 3,4-DCP, the electrophilic attack of an ozone molecule to the para position released the chlorine atom producing a monochlorobenzenediol.

Utrilla-Rivera *et al.* (2002) studied the degradation of naphthalene sulfonic acid by oxidation with ozone in aqueous phase. This work analyzed the efficacy of oxidation with ozone in the treatment of waters containing naphthalene-1-sulfonic acid (NS),

naphthalene-1,5-disulfonic acid (NDS) and naphthalene-1,3,6-trisulfonic acid (NTS) and completed with determination of the oxidation products for each aromatic sulfonic acid and analysis of the reaction mechanism. They proposed that the ozone attack on aromatic sulfonic acids proceeded mostly by 1,3-dipolar cycloaddition to the carbon–carbon double bond of highest electron density.

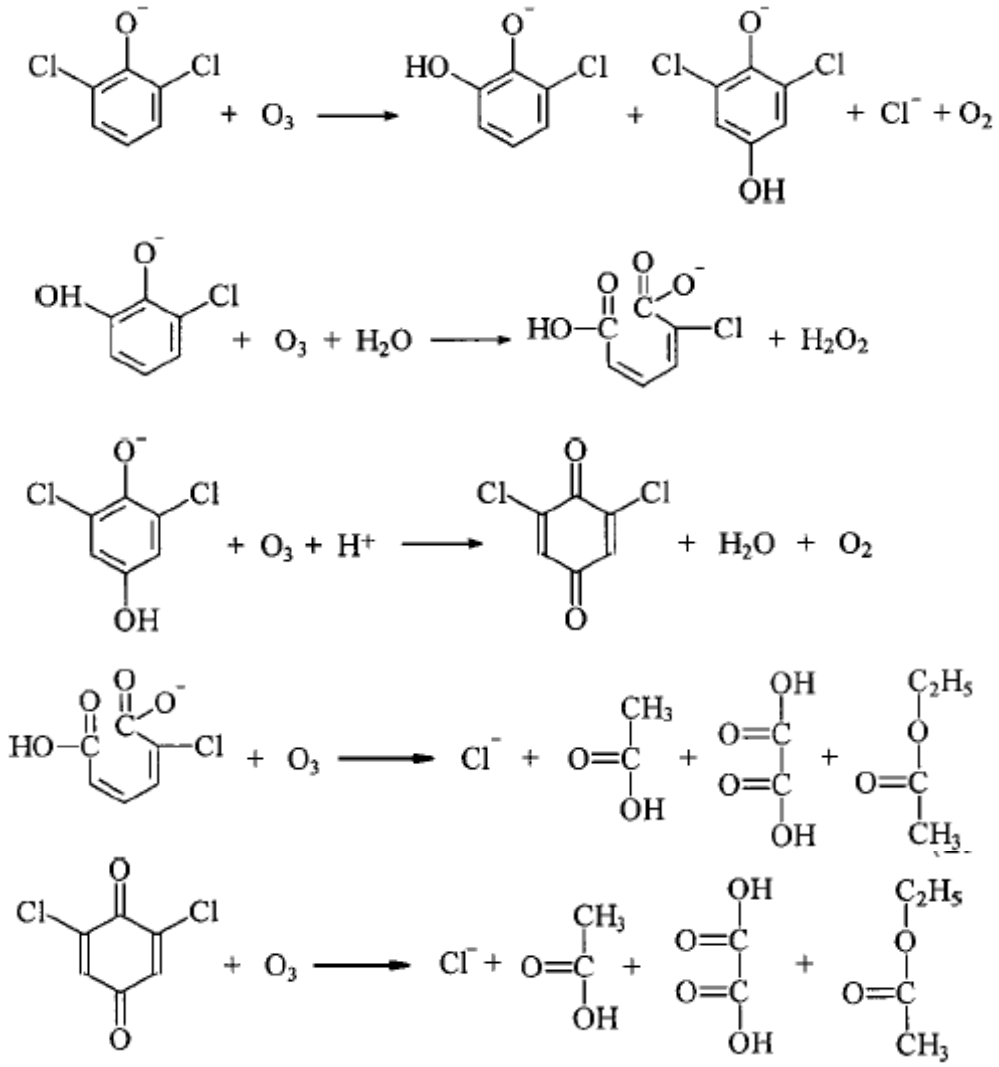


Figure 3.7: The reaction path for the ozonation of 2,6-dichlorophenoxide anions (Qui *et al.* 2004)

According to Bailey (1982), the first step was a 1,3-dipolar addition of ozone to the substrate to give the ‘‘initial’’ or ‘‘primary’’ ozonide (molozonide). This ozonide may then undergo various reactions to give the corresponding carbonyl product, which would be degraded by further oxidations (Figure 3.8).

In the oxidation of NS, Utrilla-Rivera *et al.* (2002) identified the intermediate organic compounds glyoxal and acetic acid, which appeared after 60 s of the ozone treatment and they did not detect oxalic acid. They monitored the presence of sulfate

ions in solution and detected concentrations of 0.04 M in the first seconds of the reaction. Hydrogen peroxide has generated as a secondary product of the ozonization reaction between naphthalene sulfonic acid and ozone.

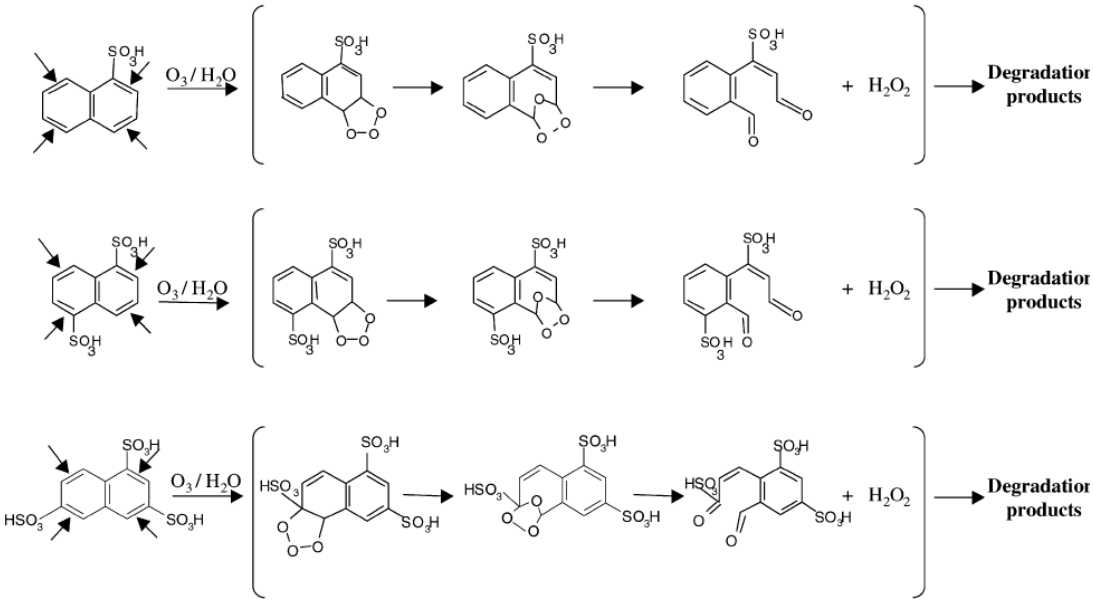


Figure 3.8: Direct ozonation reactions of naphthalene-1-sulfonic acid (NS), naphthalene-1,5-disulfonic acid (NDS) and naphthalene-1,3,6-trisulfonic acid (NTS) (Utrilla-Rivera *et al.,* 2002)

In the oxidation of NDS, Utrilla-Rivera *et al.* (2002) detected the presence of highly oxidized compounds such as oxalic acid and glyoxal after 90 s of ozone treatment. As in the case of NS, they detected sulfates after 60 s of treatment. The concentration of sulfate ions continued to increase after all of the NDS was consumed, indicating the formation of intermediate sulfonic organic compounds during the ozonation process. In the ozonation of NTS, the final products were oxalic acid and formic acid, detected after 600 s of ozone treatment. This long time period before detection of highly oxidized compounds suggested the formation of intermediate compounds that were very stable against ozonation. Unlike in the case of NS and NDS, no sulfate ions were detected after 60 s of reaction. This was explained by the much slower ozonation of the aromatic ring of NTS compared with that of NS and NDS, so that H_2O_2 was generated at a very slow rate. From the experimental study they concluded that the oxidation products of these sulfonic acids confirmed that the interaction of ozone with aromatic sulfonic acids did not proceed at the most polar bond of the molecule (carbon-sulfur) but predominantly at the carbon-carbon bond of greatest electronic density. Bailey (1982) studied the oxidation of aromatic compounds and

concluded that, when the stoichiometry was one, the main mechanism is 1,3-dipolar cycloaddition at the double bond of highest electron density. Beltrán *et al.* (1995) corroborated these results after analyzing the ozonation of polycyclic aromatic hydrocarbons. They found that the oxidation of phenanthrene, which only occurred by 1,3-dipolar cycloaddition, had a stoichiometric factor of one mole ozone consumed per one mole hydrocarbon consumed. Pryor *et al.* (1983) observed that the ozonation of alkenes with electron-withdrawing substituents took place mainly via 1,3-dipolar cycloaddition. Moreover, olefins in which the double bond was connected to electron-donating groups reacted many times faster than those in which it was connected to electron-withdrawing groups.

3.2 Kinetic Modeling of Ozonation Processes

There are many studies listed in the literature for the direct reactions of ozone. Pioneering studies for that purpose were carried out by J. Hoigné and H. Bader. By studying ozone consumption in the presence of several relatively slow reacting compounds in batch reactors and at acidic pH values, Hoigné (1982) has established that the rate in the direct reaction of ozone with a solute can usually be expressed by an equation that is first order with respect to the concentrations of both ozone and the solute.

Hoigné and Bader (1983), determined the rate constants of reactions of ozone with non-ionized solutes, such as aliphatic alcohols, olefins, chlorosubstituted ethylenes, substituted benzenes and carbohydrates from the absolute rate constants for ozone consumption and they have also tested these compounds in comparison with the relative reaction rate constants. They eliminated the interferences between the direct reactions of ozone and reactions due to its preliminary decomposition to secondary oxidants in their study. The model predictions that they used in their study were as follows:

For the direct reaction of ozone with dissolved organic substance may be written as:

$$S + O_3 \rightarrow X + (\eta - 1)O_3 \rightarrow S_{oks} \qquad \textbf{(3.1)}$$

where, η is a stoichiometric factor for the number of ozone molecules consumed per molecule S transformed to S_{oxid}. X is the primary intermediate formed by the rate determining step. In this case, the entire reaction could be written as:

$$S + \eta O_3 \rightarrow S_{oks} \quad \textbf{(3.2)}$$

For the determination of absolute rate constants for ozone consumption they reported that if the rate of direct reaction of ozone with dissolved substances is assumed to be first order with respect to ozone concentration. Than the rate law can be formulated as:

$$\frac{d[O_3]}{dt} = -k_{O_3}[O_3][S]^n \quad \textbf{(3.3)}$$

where, k_{O_3} is the rate constant for the consumption of ozone by all reactions. When S is present in large excess, reaction rate is reported to be evident 1st order. With this assumption, integrating the Equation 3.3 yields the following equation where $[O_3]_0$ and $[O_3]_t$ represent the ozone concentrations respectively at the time zero and t.

$$\ln\frac{[O_3]_t}{[O_3]_0} = k_{O_3}[S]_0^n \times t \quad \textbf{(3.4)}$$

For this equation, a τ_{O_3} parameter was defined to represent the time providing a reduction in the ozone concentration equal to a factor e.

$$\tau_{o_3} = \frac{[O_3]_t}{[O_3]_0} = e \quad \textbf{(3.5)}$$

than, the Equation 3.4 can be expressed as follows:

$$\frac{1}{\tau_{O_3}} = k[S]_0^n \quad \textbf{(3.6)}$$

The Equation 3.4 now provided with the opportunity to find k_{O_3} coefficient by means of this definition and a simpler graphical method. Using this equation, from the graph to be plotted between $\log(1/\tau_{O_3})$ and $\log[S]_0$, yields a straight line from

which k_{O_3} can be determined. This plot gives a straight line relationship if k_{O_3} (that means also the stoichiometric factor η is independent of $[S]_0$. The slope of these lines becomes 1.0 if the reaction is first order with respect to the solute concentration.

Hoigné and Bader (1983) reported that all results complied with the assumption that the rate laws for the reactions of ozone with aqueous solutes are first order with respect to both ozone and solute concentration (Equation 3.7).

$$-\frac{dO_3}{dt} = k_{O3}[O_3]^{1.0}[S]^{1.0} \qquad \textbf{(3.7)}$$

They have also observed that k_{O3} values neither changed significantly within the ranges of the ratios of $[S]_0/[O_3]_0$ used in the experiments nor with the time of ozonation. They claimed that this observation indicated the apparent stoichiometric factor did not vary during ozonation and this invariance of stoichiometric factor facilitated the evaluation of the k_{O3} values.

Gurol and Nekouinaini (1984) applied a dynamic approach which simulated the real oxidation systems to determine the relative rate constants. They analyzed the results to derive a relation between the chemical structure of the substituted benzene ring and its reactivity with ozone. They claimed that, the kinetic expression for fast reactions could not be determined by using the conventional batch method in which either the ozone consumption or the solute removal needed to be measured by taking samples from the reaction mixture at various time intervals. They adopted a dynamic approach to study the reaction rates of phenolic compounds. Ozone gas was continuously bubbled into an ozone contactor which contained aqueous solutions of phenolic compounds. They claimed that, under these conditions, the rate of change in the ozone concentration could be expressed as

$$\frac{d[O_3]}{dt} = k_L a\left([O_3]^* - [O_3]\right) - k_d[O_3]^2 - \sum Z_i k_i [O_3][S_i] \qquad \textbf{(3.8)}$$

The first and second terms represented, respectively, the rates of mass transfer and second-order decomposition of ozone (Gurol and Singer, 1982). The last term was the total consumption rate of ozone due to its direct reaction with solutes.

The rate of disappearance of solute *i* in acidic condition would be the direct reaction by ozone, as follows

$$-\frac{d[S_i]}{dt} = k_i[O_3][S_i] \qquad \textbf{(3.9)}$$

Acidic solutions of pairs of phenolic compounds, or mixtures were ozonated simultaneously in the ozone contactor. According to the equation 3.3, the ratio of the rates of removal of the compounds would be

$$\frac{d[S_1]/dt}{d[S_2]/dt} = \frac{k_1[S_1]}{k_2[S_2]} \qquad \textbf{(3.10)}$$

or, upon integration between time = 0 and time = t

$$\ln\frac{[S_1]}{[S_1]_0} = \frac{k_1}{k_2}\ln\frac{[S_2]}{[S_2]_0} \qquad \textbf{(3.11)}$$

The apparent ratio of the rate constants was obtained by plotting $\ln([S_1]/[S_1]_0)$ against $\ln([S_2]/[S_2]_0)$, according to Equation 3.11.

Gurol and Nekouinaini (1984) observed that, the simultaneous ozonation of the solutes, the removal rates increased after the fastest reacting solute was oxidized to an extent to allow more ozone to be available for the reactions of the remaining solutes. When the ozonation process was continued further, this behavior repeated for the subsequent fastest reacting compound. They reported that, nevertheless, this change in the slopes of the concentration profiles did not affect the measured relative rates significantly. This is anticipated, since the relative rates are independent of the ozone concentration. Relative rate constants that they calculated in their study are given in Table 3.1.

Gurol and Nekouinaini (1984) indicated in their study that, the reactions between solute and ozone were first order with respect to the solute and the ozone molecule, and that stoichiometric factor was 1.0. They also concluded that, the dynamic approach used in their study has proven to be a practical and reliable method for determining the rate constants of the fast-reacting compounds with ozone, with the provisions regarding the mass-transfer characteristics of the ozonation system.

Table 3.1: The Relative Oxidation Rate Constants of Substituted Phenols with Respect to Phenol (Gurol and Nekouinaini, 1984)

Compound	k_i / k_p
o-Cresol	4.4
m-Cresol	4.4
p-Cresol	11
2,6-Xylenol	15
2,3-Xylenol	19
Resorcinol	70
3,4-Xylenol	76
2,4-Xylenol	76
Catechol	220
Hydroquinone	1100

Beltrán *et al.* (2000a) studied the ozonation kinetics of gallic and p-hydroxybenzoic acids, catechin and tyrosol and they stated that due to the rapidity of the chemical reactions in the heterogeneous system, the kinetic regime was fast with the reaction developed in the film layer region. The stoichiometric coefficients were obtained following a procedure that was reported by Sotelo *et al.* (1990). The calculated stoichiometric coefficients were reported as 1 for gallic acid and catechin, 1.5 for p-hydroxybenzoic acid and 0.75 for tyrosol. In this study, they used a competitive kinetic method reported by Gurol and Nekouinaini (1984). The reference compounds in the kinetic study were resorcinol and phenol. Table 3.2 shows the rate constants obtained from this study by using the competitive kinetic method.

Table 3.2: Rate Constants Derived from the Application of Competitive Ozonation Kinetic (Beltrán *et al.,* 2000a)

Compound	pH	k_s (1/(M s))
p-Hydroxybenzoic acid	2.0	0.002
p-Hydroxybenzoic acid	6.3	1.78
Gallic acid	2.0	0.97
Gallic acid	6.3	4.60
Catechin	2.0	5.30
Catechin	6.3	10.2
Tyrosol	2.0	0.03
Tyrosol	6.3	2.11

Benitez *et al.* (2000) studied the reaction of ozone with chlorophenols in aqueous solutions. The main objective of the study was to obtain values of the rate constants for the direct reaction between ozone and each chlorophenol. They also studied the stoichiometric ratios of the individual reactions ozone-chlorophenols (CPs). The results that they obtained showed that, regardless of the CP considered, this ratio remained around 2 mol of ozone consumed per mol of each CP reacted as several

authors pointed out (Hoigné and Bader, 1983a; Hoigné and Bader, 1983b; Gurol and Nekouinaini, 1984; Yao and Haag, 1991; Trapido *et al.*, 1997)

In first stage experiments conducted by Benitez *et al.* (2000), single ozonation of 4-CP was conducted in homogeneous system, and the overall rate constants were evaluated for this reaction by varying the pH (2.0, 2.5 and 3.0) in acidic conditions. These experiments were conducted by mixing aqueous buffered solutions of known concentrations of both ozone and CP, being the latter around 10 times higher to ensure the total consumption of ozone practically at an instantaneous rate by the CP and not by the intermediates formed. Benitez and co-workers (2000) also reported that reactions of ozone with dissolved organic substrates were assumed to be first order with respect to each reactant, yielding an overall second order kinetics for homogeneous systems. The overall rate constant of 4-CP is depicted in Table 3.3 at pH 3.0 for homogeneous system.

Table 3.3: Overall Rate Constants for Ozonation of Chlorophenols (CP) (Benitez *et al.* 2000)

Compound	k_{O_3} **(l/(mol s)**
4-CP	2437
2,4-DCP	9167
2,4,6-TCP	47477
2,3,4,6-TeCP	80967
4-CGC	138211
TeCC	54110

At the second stage of the study (Benitez *et al.,* 2000), the simultaneous degradation of mixtures of 2,4-DCP, 2,4,6-TCP, 2,3,4,6-TeCP, 4-CGC and TeCC in a heterogeneous reaction system was investigated and the evaluation of the overall rate constants for the ozonation was computed by a competitive kinetic model proposed by Gurol and Nekouinaini (1984). In every mixture, one of the organic substrate was a reference compound, whose degradation rate constant was known: the remaining substrates constitute the target compound, whose rate constants are unknown. This procedure is reliable when measuring the rates of fast reactions in aqueous solutions, and is based on assuming that the reaction between the oxidant and the organic substrate follows an overall second-order kinetics, and more specifically, of first order with respect to both reactants. These values are also depicted in Table 3.3.

Qui *et al.* (2004) studied the ozonation of 2,6-, 3,4- and 3,5-dichlorophenol (DCP) isomers within aqueous solutions. They found that 2 moles of ozone were required

for the initial degradation of 1 mole of dicholorophenols. They indicated that in aqueous solution containing dissolved ozone and DCPs both dichlorophenol molecules and dichlorophenoxide ions could be oxidized by a similar mechanism at the same stoichiometric ratio, γ. The overall reaction then was expressed as:

$$\gamma O_3 + DCP_{mol} \rightarrow P_1 \quad \textbf{(3.12)}$$

$$\gamma O_3 + DCP^-_{ion} \rightarrow P_2 \quad \textbf{(3.13)}$$

where P_1 and P_2 are the reaction products.

Qui *et al.* (2004) expressed depletion rate of ozone by neglecting the ozone decomposition during the ozonation experiments as follows:

$$-\frac{dO_3}{dt} = \gamma k_{mol}\left[O_3\right]^m\left[DCP_{mol}\right]^n + \gamma k_{ion}\left[O_3\right]^m\left[DCP^-_{ion}\right]^n \quad \textbf{(3.14)}$$

where k_{mol} and k_{ion} are the ozonation rate constants for the molecular and ionic reactions, respectively. The reaction orders with respect to ozone and DCP in both molecular and ionic forms, respectively, were denoted by m and n. Qui *et al.* (2004) defined α as the degree of dissociation, then the concentrations of dichlorophenol and dichlorophenoxide ions in solution could be expressed as:

$$\left[DCP_{mol}\right] = (1-\alpha)\left[DCP\right] \quad \textbf{(3.15)}$$

$$\left[DCP^-_{ion}\right] = \alpha\left[DCP\right] \quad \textbf{(3.16)}$$

where $\left[DCP\right]$ is the total dichlorophenol concentration. By substituting Equation 3.15 and 3.16 into 3.14 the depletion rate of ozone could be rewritten as:

$$-dC_A/dt = \gamma k C_A^m C_B^n \quad \textbf{(3.17)}$$

where C_A and C_B expressed as in term of ozone and total DCP concentrations, respectively. The overall reaction rate constant, k, was defined as

$$k = k_1(1-\alpha)^n + k_2\alpha^n \quad \textbf{(3.18)}$$

Since the kinetic experiments were carried out with DCPs in large excess Equation 3.17 could be simplified to

$$-dC_A/dt = k'C_A^m \qquad \textbf{(3.19)}$$

where k/, the apparent rate constant was calculated as:

$$k' = \gamma k C_B^n \approx \gamma k C_{B0}^n \qquad \textbf{(3.20)}$$

Integration of Equation 3.19 yielded the dimensionless concentration distribution of ozone as follows:

$$C_A/C_{A0} = \exp(-k't) \qquad for \qquad m = 1 \qquad \textbf{(3.21)}$$

and

$$\left[C_A/C_{A0}\right]^{1-m} = 1 + (m-1)C_{A0}^{m-1}k't \qquad for \qquad m \neq 1 \qquad \textbf{(3.22)}$$

If the ozonation reaction was first order with respect to ozone, a straight line could be obtained on a semilogarithmic scale by plotting the dimensionless concentration of ozone against reaction time, as dictated by Equation 3.21. If the ozonation reaction was of another order with respect to ozone, a plot of the dimensionless concentration of ozone of exponent (1-m) versus reaction time yielded a straight line, as dictated by Equation 3.22. The apparent rate constant k/ could be calculated from the slope of the straight line via regression analysis. The order with respect to the concentration of dichlorophenol, n, could be determined by plotting k/ versus the initial concentration of dichloropheno on a logarithmic scale. A straight line could be obtained from such a plot as indicated by the following equation:

$$\log(k') = \log(\gamma k) + n\log(C_{B0}) \qquad \textbf{(3.23)}$$

The slope of the straight line was equal to the reaction order with respect to dichlorophenol. The overall reaction rate constant, k, could be determined by using Equation 3.23, if the stoichiometric ratio was known.

Qui *et al.* (2004) also indicated that, if ozonation reaction order with respect to dichlorophenol was unity, Equation 3.18 could be rearranged as

$$k - k_{mol} = (k_{ion} - k_{mol})\alpha \quad \textbf{(3.24)}$$

The above equation indicated that a plot of ($k-k_{mol}$) against the degree of dissociation (α) on a logarithmic scale yielded a straight line with slope of unity. The molecular reaction rate constant, k_{mol}, could be determined by trial and error method. The ionic reaction rate constant, k_{ion} could be calculated from Equation 3.24 with the known k_{mol}.

A total of 48 experiments were conducted for determination of the required DCP/ozone stoichiometry: half of these experiments were conducted under acidic conditions and other half were conducted under basic conditions. No residual ozone was detected during any of these experiments when analyzing the water samples using the iodometric method, thereby indicating complete usage of the transferred ozone. The results indicated that an average of 1.95 moles of ozone was consumed per mole of DCP consumed. The determined stoichiometric ratios of ozonation of dichlorophenols are given in Table 3.4.

Table 3.4: Stoichiometric Ratio of Ozonation of Dichlorophenol (Qui *et al.,* 2004)

pH	**2.0**			**13.0**			
Dichlorophenol	**γ**	**D_s**	**N**	**γ**	**D_s**	**N**	**Average γ**
2,6-DCP	1.89	0.70	8	2.06	0.26	8	1.92
3,4-DCP	2.00	0.70	8	1.88	0.28	8	1.92
3,5-DCP	2.02	0.69	8	1.87	0.22	8	2.00
Average	1.97			1.94			1.95

γ : stoichiometric ratio; D_s : standard deviation; N : number of experiments

The average overall rate constants at different pHs determined by Qui *et al.* (2004) are given in Table 3.5 along with the respective standard deviations, the degree of dissociation, and number of experiments performed.

The individual rate constants for the reaction with the molecular and ionic DCP forms could be determined from the overall reaction rate constant and the degree of dissociation as discussed before. Since the reaction order in dichlorophenol was first order, Equation 3.24 could be used to obtain the individual reaction rate constant. By the iteration procedure using a correctly assumed k_{mol} value, a plot of ($k-k_{mol}$) against α on the logarithmic scale yielded a straight line with a slope of unity.

Table 3.5: Overall Rate Constants for Ozonation of Dichlorophenol (Qui *et al.* 2004)

Dichlorophenol	pH	Degree of Dissociation α	Overall Rate Constant k (1/M s)	D_S (1/M s)	D_M (%)	N
2,6-DCP	2.0	$1.7\ 10^{-5}$	131000	2100	30.4	11
	3.0	$1.7\ 10^{-5}$	610000	46000	13.3	10
	4.0	$1.7\ 10^{-5}$	3360000	310000	16.2	8
3,4-DCP	2.0	$4.0\ 10^{-7}$	4120	1300	41.7	11
	3.0	$4.0\ 10^{-6}$	16600	2000	16.8	10
	4.0	$4.0\ 10^{-5}$	117000	18000	19.7	10
	5.0	$4.0\ 10^{-4}$	1020000	69000	9.1	8
	6.0	$4.0\ 10^{-3}$	11400000	2000000	27.3	8
3,5-DCP	2.0	$8.0\ 10^{-7}$	18700	3100	33.1	11
	3.0	$8.0\ 10^{-6}$	44300	8100	28.7	10
	4.0	$8.0\ 10^{-5}$	161000	28000	26.9	10
	5.0	$8.0\ 10^{-4}$	1250000	130000	14.0	8
	6.0	$8.0\ 10^{-3}$	12200000	1500000	16.6	8

D_S : standard deviation; D_M : maximum deviation; N : number of experiments

The rate constant for the ionic reaction, k_{ion} , could be calculated from Equation 3.24 with the known rate constant for the molecular reaction, k_{mol} . As presented in Table 3.6, the results showed that the rates of molecular form reactions of 3,4-DCP seemed moderately rapid (k_{mol} =2800 1/M s), but was extremely rapid with regard to 2,6-DCP and 3,5-DCP (k_{mol}= 93000 and 17000 1/M s, respectively. On the other hand, the ionic form reactions were much more rapid for all of the isomers studied; with the k_{ion} values calculated to be $2.4\ 10^9$, $2.8\ 10^9$, and $1.9\ 10^9$ for 2,6-, 3,4-, and 3,5-DCP ions, respectively (Qui *et al.,* 2004).

Table 3.6: Correlation of Overall Reaction Rate Constant and Individual Rate Constants for Ozonation of Molecular and Ionic Dichlorophenols (Qui *et al.,* 2004)

Organic	pK_a	Overall Reaction k (1/M s)	Molecular Reaction k_{mol} (1/M s)	Ionic Reaction k_{ion} (1/M s)
2,6-DCP	6.77	$1.80\ 10^{14}\ [OH^-]^{0.77}$	93000	$2.4\ 10^9$
3,4-DCP	8.40	$3.72\ 10^{13}\ [OH^-]^{0.85}$	2800	$2.8\ 10^9$
3,5-DCP	8.10	$1.34\ 10^{12}\ [OH^-]^{0.68}$	17000	$1.9\ 10^9$

Beltrán *et al.* (1990) studied the o-creosol aqueous solution ozonation of concentrations similar to those encountered in some wastewaters. They obtained the average value of stoichiometric ratio 2.03±0.10 mole of ozone consumed per mole of o-creosol consumed. They indicated that this value agreed with the two strongest nucleophilic positions in the o-creosol molecule. Beltrán *et al.* (1990) concluded from the experimental results that, the ozone o-creosol reaction corresponded to a gas absorption accompanied by fast irreversible reactions in the water. They also

concluded that the presence of the hydroxyl and methyl groups in the aromatic ring strongly enhanced the ozone absorption rate.

Beltrán *et al.* (1992) studied the degradation of p-nitrophenol with ozone at varying pH and ozone partial pressure. They indicated that at pH 2 the kinetic regime corresponded to a slow reaction regardless of the ozone partial pressure applied. At pH 6.5 the adsorption of ozone, developed in the fast kinetic regime the reaction being pseudo first-order with respect to ozone. They carried out some experiments under homogeneous conditions and pHs ranging from 2 to 8.5 to obtain the stoichiometric ratio of the reaction between ozone and p-nitrophenol. The stoichiometric ratio was found to be about 3 mol of ozone consumed per mol of p-nitrophenol consumed. Beltrán *et al.* (1992) also evaluated the p-nitrophenol conversion with time at various pHs at an average ozone partial pressure of 165Pa. They observed that an increase of pH from 2 to 8.5 led to an increase of p-nitrophenol conversion at a given time. They indicated that these results were due to the increase of the rate constant from pH 2 (100 1/(M s)) up to pH 8.5 (1.4×10^{7} 1/(M s)). Beltrán *et al.* (1992) concluded that p-nitrophenol ozonation contactors should have high interfacial areas because ozonation was mainly controlled by the mass transfer in two cases: (a) at pH 2 by diffusion of ozone alone and (b) at pH equal to or above 8.5 and at high ozone partial pressures by diffusion of both reactants

Beltrán *et al.* (1994) studied the ozonation of atrazine in water and their major aim was the determination of the rate constant of the direct reaction ozone atrazine. Ozone-oxygen mixture was fed into the reactor filled with the solution of atrazine through a porous plate situated at the bottom. They pointed out that in any case the most noticeable fact, the presence of dissolved ozone, suggests that the ozonation of atrazine, regardless of the mechanism (through direct or radical reactions), was a set of slow gas-liquid reactions. They expressed the rate of the atrazine oxidation as

$$-\frac{d[S_i]}{dt} = k_i[O_3][S_i] \qquad \textbf{(3.25)}$$

Beltrán *et al.* (1994) reported that the dissolved ozone concentration reached its stationary and maximum value in three minutes of the reaction. They also indicated that if Equation 3.25 was applied to reaction times equal to or higher than that

necessary for ozone to reach its stationary concentration, $[O_3]_s$ then the oxidation of atrazine followed pseudo first-order kinetics

For $t \geq t_s$

$$-\frac{d[S_i]}{dt} = k_i'[S_i] \qquad \textbf{(3.26)}$$

where $k_d' = k_d / z\ [O_3]_s$. Equation 3.26 can be integrated under the following boundary conditions

$t = t_s \qquad [S_i] = [S_i]_s$

$t = t \qquad [S_i] = [S_i]$

$[S_i]_s$, being the concentration of atrazine when the ozone concentration reached its stationary value, $[O_3]_s$. After integration, the resulting equation was

$$\ln\frac{[S_i]}{[S_i]_s} = -k_i' \ (t - t_s) \qquad \textbf{(3.27)}$$

According to the Equation 3.27 a plot of $\ln([S_i]/[S_i]_s)$ versus $t - t_s$ yielded a straight line whose slope was k_i'. Under these conditions, Beltrán *et al.* (1994) determined the rate constant of the direct reaction of atrazine and ozone as 4.5 1/ (M s) at 20°C.

The later studies of Beltrán and his co-workers (2000b) were conducted on the kinetic modeling of aqueous atrazine ozonation process in a continuous flow bubble contactor. The model they proposed were based on a molecular mechanism of reactions, reaction rate and mass transfer data and non-ideal flow analysis models for gas and water phases through the contactors (the tank in series model and the dispersion model). From the experimental result they concluded that atrazine conversions were observed to be highly dependent on the nature of water in which ozonation was carried out. Ozonation results of atrazine in ultrapure water and surface water were first simulated with both kinetic models derived from the application of non-ideal fluid flow analysis. An example of the results obtained from the study presented in Figure 3.9. Figure 3.9 showed the change of both experimental

and calculated (with the tanks in series model) concentrations of atrazine with time corresponding to ozonation experiments in different waters. As could be seen, depending on the water quality, oxidation rate may slow down or accelerate. This confirms the nature of the ozonation.

Benitez and his co-workers (1998) studied the kinetics of four phenolic aldehydes from ozone adsorption experiments in a semi-continuous reactor. They evaluated the stoichiometric ratios for individual reactions between ozone and each aldehyde. They also investigated the ozonation of a mixture of protocatechuic aldehyde, p-hydroxybenzaldehyde, vanillin aldhyede and stringaldehyde. The kinetic study was performed employing the competitive method that took vanillin aldhyde as reference compound.

Benitez and his co-workers (1998) indicated that, the kinetic regime of absorption was fast and pseudo first-order with respect to ozone. They concluded that the homogeneous experiments performed by mixing separate aqueous solutions of ozone and each aldhyde led to stoichiometric ratios of 2 moles of ozone consumed per mole of aldhyde reacted, at the pH between 2 and 9. They reported that, in the single ozonation of vanillin aldhyde, the operating variables (temperature, pH and ozone patial pressure) had a positive effect on the oxidation process. They deduced an overall second order reaction and the kinetic constants were evaluated and correlated by the Arrhenious-type expressions as follows:

$$k = 2.47 \times 10^{15} \exp\left(-\frac{4406}{T}\right)\left[OH^-\right]^{0.26} \qquad \textbf{(3.28)}$$

where k is the kinetic rate constant for the ozone-vanillin aldhyde reaction (l/mol s), T is temperature.

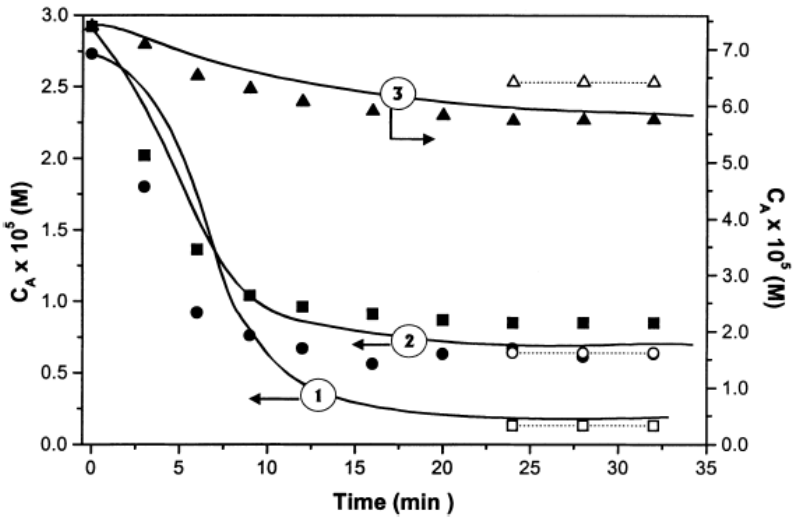


Figure 3.9: Ozonation of atrazine in natural waters. Evolution of atrazine concentration with time. (Beltrán *et al.*, 2000b) Conditions : pH : 8.5, T : 293 K, contactor (I), ozone dose : 6.65 10^{-5} M. Water type: (•, o, 1) ultrapure water; (□, ■, 2) Cordobilla reservoir water; (▲, Δ, 3) Gevora river water. Solid symbols: experimental results; solid numbered lines: tanks in series model; dotted lines plus open symbols: steady state concentrations; dispersion model.

The rate constants that they obtained from the simultaneous ozonation of mixtures of protocatechuic aldehyde, p-hydroxybenzaldehyde, and stringaldehyde by using the competitive model were 9.4×10^{-4}, 10.2×10^{-4} and 33.3×10^{-4} l/(mol s) respectively. The temperature, pH and ozone partial pressure was 20°C, 2 and 0.121 kPa respectively at this experimental study (Beltrán *et al.*, 2000b).

In another study carried out by Beltrán-Heredia *et al.* (2001), the same experimental approach as Benitez *et al.* (1998) was employed. They studied the kinetics of three phenolic acids from ozone adsorption experiments in a semi-continuous reactor. They concluded that the homogeneous experiments performed by mixing separate aqueous solutions of ozone and each acid led to stoichiometric ratios of 0.5 for ferulic acid, 1.5 for p-hydroxibenzoic acid and β resocylic acid mole of ozone consumed per mole of acid reacted. They also deduced the Arrhenious-type expression that is given below:

$$k = 3.56\times10^{15}\exp\left(-\frac{4871}{T}\right)\left[OH^-\right]^{0.31} \qquad \textbf{(3.29)}$$

where k is the kinetic rate constant for the ozone p-hydroxy-benzoic acid reaction (l/mol s), T is temperature.

The rate constants that they obtained from the simultaneous ozonation of mixtures of ferulic acid and β-resocylic acid by using the competitive model were 26×10^{-4} and 3.4×10^{-4} l/(mol s) respectively. The temperature, pH and ozone partial pressure were 20°C, 2 and 0.35 kPa respectively at this experimental study.

Ku *et al.* (1998) studied the decomposition of diazinon in aqueous solution by ozonation. They reported that ozonation has been shown to be feasible for achieving nearly complete decomposition of diazinon within 1 hour. They also reported that the surface tension of aqueous solution was found to be affected by the dissolved diazinon and influenced the oxidation mechanism of diazinon by ozonation in aqueous solution. They suggested the decomposition pathways of diazinon by ozonation as shown in Figure 3.10.

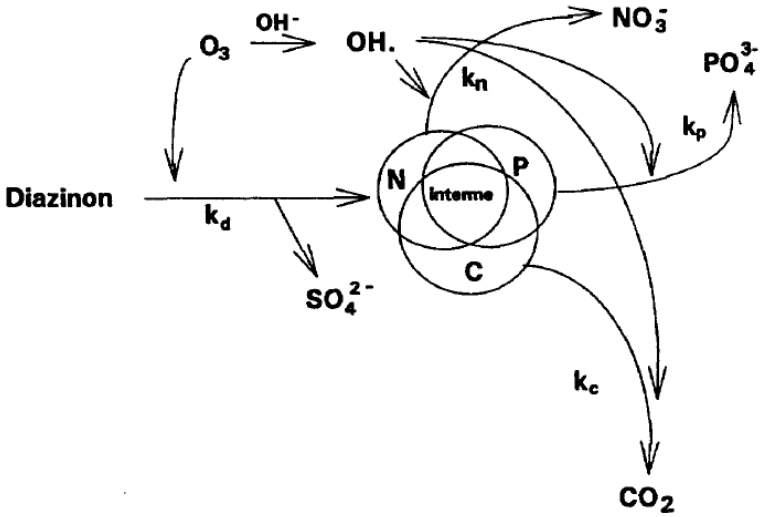


Figure 3.10: Simplified decomposition pathways of diazinon by ozonation (Ku *et al.,* 1998)

They assumed that each of the reactions based on the simplified pathway were first order and reversible. They derived the rate equations of various reacting species by establishing the elemental mass balances as follows:

$$[D]=[D]_0 e^{-k_d t} \tag{3.30}$$

$$\left[SO_4^{2-}\right]=[D]_0(1-e^{-k_d t}) \tag{3.31}$$

$$[Interme]_n=[D]_0 k_d(e^{-k_d t}-e^{-k_n t})/(k_n-k_d) \tag{3.32}$$

$$[Interme]_c=[D]_0 k_d(e^{-k_d t}-e^{-k_c t})/(k_c-k_d) \tag{3.33}$$

$$[Interme]_p = [D]_0 - [D] - [PO_4^{3-}] \quad \textbf{(3.34)}$$

$$[NO_3^-]_n = [D]_0 - [D] - [Interme]_n \quad \textbf{(3.35)}$$

$$[CO_2]_n = [D]_0 - [D] - [Interme]_c \quad \textbf{(3.36)}$$

$$[PO_4^{3-}]_n = [D] - [D]_0 / (k_p t [D]_0 + 1) \quad \textbf{(3.37)}$$

where D is the concentration of diazinon, mg/l; D_0 is the initial concentration of diazinon, mg/l; $[Interme]_c$ is the concentration of carbon-containing intermediates, mg/l; $[Interme]_n$ is the concentration of nitrogen-containing intermediates, mg/l; $[Interme]_p$ is the concentration of phosphate-containing intermediates, mg/l; k_d is the pseudo first-order decomposition rate constant of diazinon, 1/min; k_c is the pseudo first-order formation rate constant of carbonate, 1/min; k_n is the pseudo first-order formation rate constant of nitrate, 1/min; and k_p is the pseudo first-order formation rate constant of phosphate, 1/min. The pseudo first-order reaction rate constant of diazinon and various anions in aqueous solution by ozonation in various conditions determined in this study are summarized in Table 3.7. Ku *et al.* (1998) concluded that, the species distribution of dissolved ozone (molecule) and diazinon (molecule or ion) in bulk solution was not considered to be the dominate factor for ozonation of diazinon.

Table 3.7: The Pseudo First-Order Reaction Rate Constant of Diazinon and Various Anions in Aqueous Solution at Various Solution pH Values by Ozonation (Ku *et al.,* 1998)

		Rate Constants							
Effect	**Level**	**k_d (1/min)**	**r^2**	**k_p (1/min)**	**r^2**	**k_n (1/min)**	**r^2**	**k_c (1/min)**	**r^2**
pH	5	$1.27\ 10^{-1}$	0.99	=0		=0		=0	
	7	$1.06\ 10^{-1}$	0.99	$2.58\ 10^{-3}$	0.92	$4.14\ 10^{-4}$	0.75	$5.07\ 10^{-4}$	0.92
	9	$1.12\ 10^{-1}$	1.00	$1.37\ 10^{-2}$	0.95	$1.44\ 10^{-3}$	0.99	$3.59\ 10^{-3}$	0.98
	11	$1.21\ 10^{-1}$	1.00	$1.30\ 10^{-2}$	0.97	$1.69\ 10^{-3}$	0.98	$2.04\ 10^{-3}$	0.94
Alkalinity (mM HCO_3^-)	0	$1.25\ 10^{-1}$	0.99	$1.37\ 10^{-2}$	0.95	$1.44\ 10^{-3}$	0.99	$3.59\ 10^{-3}$	0.98
	1	$1.25\ 10^{-1}$	0.99	$5.66\ 10^{-3}$	0.93	$1.29\ 10^{-3}$	0.98	$1.77\ 10^{-3}$	0.92
	10	$1.13\ 10^{-1}$	1.00	$2.02\ 10^{-3}$	0.92	$1.00\ 10^{-3}$	0.98	$1.59\ 10^{-3}$	0.90
T (°C)	15	$1.11\ 10^{-1}$	1.00	$4.98\ 10^{-3}$	0.96	$8.69\ 10^{-3}$	0.97	$1.43\ 10^{-3}$	0.87
	25	$1.25\ 10^{-1}$	0.99	$1.37\ 10^{-2}$	0.95	$1.44\ 10^{-3}$	0.99	$3.59\ 10^{-3}$	0.98
	33	$1.06\ 10^{-1}$	0.99	$1.63\ 10^{-2}$	0.98	$1.70\ 10^{-3}$	0.99	$4.00\ 10^{-3}$	0.98
P (atm)	1	$1.21\ 10^{-1}$	0.89	-	-	-			
	2	$2.34\ 10^{-1}$	0.95	-	-	-			

In order to find the surface behavior of diazinon in aqueous solution, experimental studies conducted in the presence of very low concentration of diazinon. It was found that low concentration of diazinon significantly deceased the static surface tension of solution from 72 to 55 dyne/cm and the dynamic surface tension from 70 to 62 dyne/cm within 2 s and thus enhanced the accumulation of diazinon in the gas liquid interface. The surface tension of water was found to be less influenced by appearance of organic intermediates generated from the decomposition of diazinon (Ku *et al.*, 1998). The gas-liquid reaction model that Ku *et al.* (1998) proposed to describe the transfer behavior of reacting species in the system was illustrated in Figure 3.11.

In the figure, $[O_3]_{gas}$ is the concentration of ozone in the gas region; $[O_3]^*$ is the concentration of ozone in the film region; $[O_3]_{bulk}$ is the concentration of ozone in the bulk region; $[Diazinon]^*$ is the concentration of diazinon in the film region; $[Diazinon]_{bulk}$ is the concentration of diazinon in the bulk region; $[SO_4^{-2}]^*$ is the concentration of diazinon in the film region; $[SO_4^{-2}]_{bulk}$ is the concentration of diazinon in the bulk region; $[Interme]_{bulk}$ is the concentration of intermediates in the film region and $[Interme]_{bulk}$ is the concentration of intermediates in the bulk region.

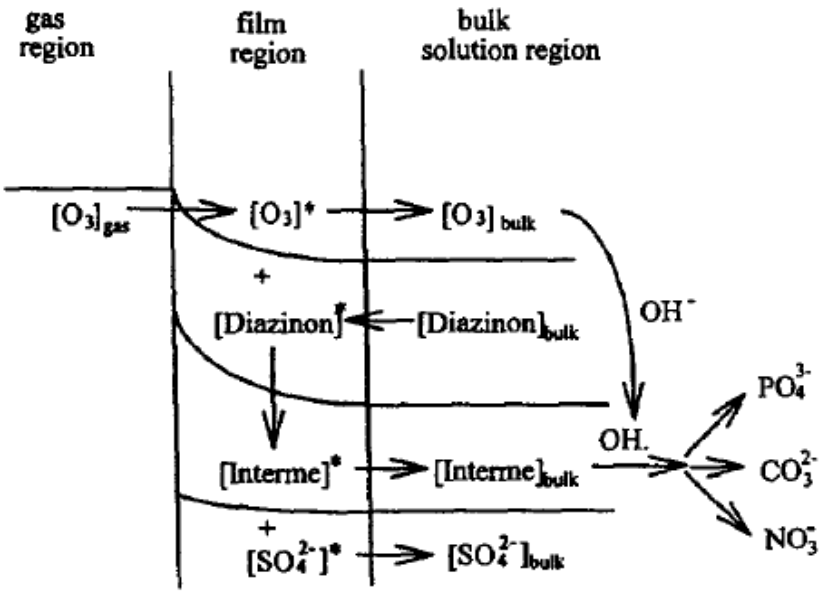


Figure 3.11: The gas-liquid reaction model for the decomposition of diazinon by ozonation (Ku *et al.*, 1998)

From a study conducted on the ozonation of metol, it was suggested that the kinetic assessment for an oxidation processes carried out in a gas-liquid reactor could be performed only in the case in which the process developed under a kinetic (slow or

fast) or a quasi-diffusive regime of absorption with reaction (Andreozzi *et al.,* 2000). Andreozzi *et al.* (2000) suggested that ozone oxidation process of metol could develop in a quasi-diffusive regime of absorption with reaction because of the phenolic nature of this compound. A simplified kinetic submodel, in which a single overall reaction was thus used to describe the ozone attack to the substrate and intermediates:

$$Metol + zO_3 \xrightarrow{k} products \qquad \textbf{(3.38)}$$

with the coefficient $z = z(t)$ accounting also for ozone consumed by the intermediates. The best estimated kinetic constants and the values of z found by Andreozzi *et al.* (2000) are reported in Table 3.8.

Table 3.8: Kinetic Parameters Obtained from Experimental Ozonation Runs at Different pH Values of Metol (Andreozzi *et al.,* 2000)

pH	k (dm^3 / mol s)	z
0.96	$5.76\ 10^3$	1.14
1.35	$7.21\ 10^3$	1.27
2.0	$1.92\ 10^4$	1.92
2.30	$2.52\ 10^4$	1.94
2.50	$8.15\ 10^4$	2.17
2.70	$9.95\ 10^4$	1.94
3.0	$1.94\ 10^5$	2.10
3.5	$7.96\ 10^5$	2.13
4.0	$2.84\ 10^6$	2.15

Benbelkacem *et al.* (2003) studied the maleic acid ozonation and presented a new model which was based on film theory. In the first part of their study the theoretical approach to which the model referred was described. In the second part, a set of experiments on maleic acid ozonation was performed and used for validation of the model. They concluded that to describe globally a gas-liquid reactor, it was necessary to write the mass balances for all the compounds. Therefore, Equations 3.39-3.41 were written.

$$Q_g C_{g,in} dt = \mathrm{Q_g} C_{g,out} dt + Ek_L S\left(\overline{C_A^*} - C_{A,bulk}\right)dt + V_{gas} d\overline{C_g} \qquad \textbf{(3.39)}$$

$$Ek_L S\left(\overline{C_A^*} - C_{A,bulk}\right)dt = \left\{\begin{matrix}[E-D]k_L S\left(\overline{C_A^*} - C_{A,bulk}\right) \\ + kC_{A,bulk} C_{B,bulk} V_{bulk}\end{matrix}\right\} dt + V_{bulk} dC_{A,bulk} \qquad \textbf{(3.40)}$$

$$v\left\{[E-D]k_L S\left(\overline{C_A^*} - C_{A,bulk}\right) + kC_{A,bulk} C_{B,bulk} V_{bulk}\right\}dt + V_{bulk} dC_{B,bulk} = 0 \qquad \textbf{(3.41)}$$

where Q_g represents the gas flow rate (m^3 /s), V_{gas} is the gas volume within the reactor (m^3), V_{bulk} is the volume of the liquid bulk within the reactor (m^3), $C_{i,bulk}$ is the concentrations within the bulk liquid (mol/m^3), C_{gin} and C_{gout} are gas concentrations at the inlet and the outlet of the column (mol/m^3), C_g is the average gas concentration in the reactor (mol/m^3), and C^*_A is the average equilibrium concentration with the gas at the concentration C_g, E is enhancement factor, which characterizes the mass transfer acceleration, caused by the chemical reaction, D is depletion factor that allows the location where the reaction takes place to be known. The experimental conditions used in this study are given in Table 3.9.

Table 3.9: Experimental Condition Used in the Study of Benbelkacem *et al.*(2003)

	Q_g (l/h)	$[O_{3,gas}]_{in}$ (g/m^3)	$[MA]^0$ (mol/m^3)
Experiment 1	200	35.3	3.81
Experiment 2	250	34.6	3.86
Experiment 3	300	34.3	3.83

Figure 3.12, showed the variation of acid concentration versus time when they reacted with ozone. The symbols represents the experimental results of muconic acid (MA), fumaric acid (FA), gallic acid (GA) and oxalic acid (OA). The set of reactions 1 to 4 were represented the balance of compounds observed during the oxidation. Following results have been obtained by Benbelkacem *et al.* (2003) as could be seen also from the Figure 3.12.

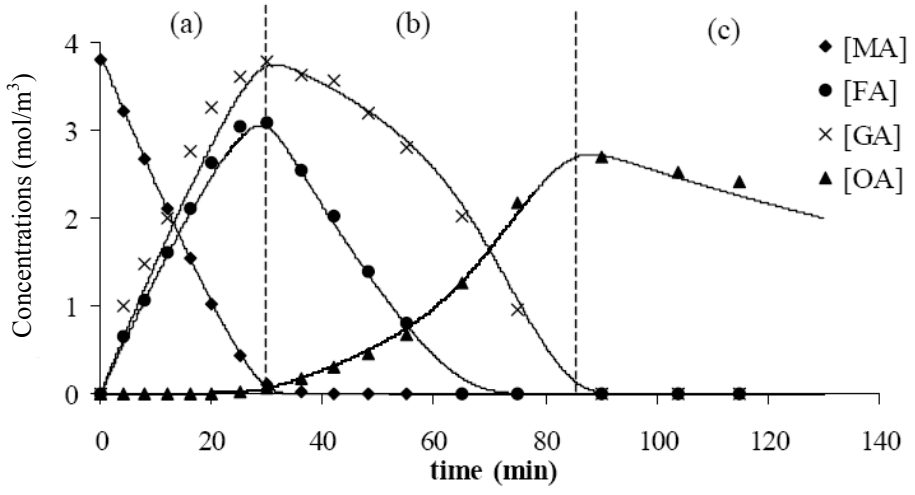


Figure 3.12: Experimental (symbols) and calculated (continuous line) kinetics of organic acids ozonation (Benbelkacem *et al.,*2003)

The first step (a) represented the maleic acid consumption, giving formic acid, glyoxylic acid and end products (reaction 1). During the second step (b), formic acid

was transformed into end products (reaction 2) and glyoxylic acid was oxidized into oxalic acid and end products (reaction 3). Finally, in a third step (c), oxalic acid reacted slowly to give end products as well (reaction 4).

The second part of this work (Benbelkacem *et al.*, 2003) consisted in modeling the gas absorption process with an irreversible chemical reaction. Because of the ozonation byproducts (reaction 2, 3 and 4), the mass balance Equations 3.39 and 3.41 had to be modified to take into account all these reactions and also the self decomposition of ozone. Consequently, the set of Equations 3.39 and 3.41 were rewritten and became the equation system 3.42 to 3.47.

$$V_{gas}\frac{d\left[O_{3,gas}\right]^0}{dt} = \left(Q_g\left(\left[O_{3,gas}\right]_{in} - \left[O_{3,gas}\right]_{out}\right) - Ek_L S\left(\left[O_{3,liq}\right]^* - \left[O_{3,liq}\right]\right)\right) \tag{3.42}$$

where $\left[O_{3,liq}\right]^* = m * \left[O_{3,gas}\right]^0$

$$\begin{aligned} V_{bulk}\frac{d\left[O_{3,liq}\right]}{dt} &= Ek_L S\left(\left[O_{3,liq}\right]^* - \left[O_{3,liq}\right]\right) \\ &- \left[(E-D)k_L S\left(\left[O_{3,liq}\right]^* - \left[O_{3,liq}\right]\right) + k_{MA}\left[MA\right]\left[O_{3,liq}\right]V_{bulk}\right] \\ &- k_{FA}\left[FA\right]\left[O_{3,liq}\right]V_{bulk} - k_{GA}\left[GA\right]\left[O_{3,liq}\right]V_{bulk} - k_{OA}\left[OA\right]\left[O_{3,liq}\right]V_{bulk} - k_c\left[O_{3,liq}\right]V_{bulk} \end{aligned} \tag{3.43}$$

$$V_{bulk}\frac{d\left[MA\right]}{dt} = -\left[(E-D)k_L S\left(\left[O_{3,liq}\right]^* - \left[O_{3,liq}\right]\right) + k_{MA}\left[MA\right]\left[O_{3,liq}\right]V_{bulk}\right] \tag{3.44}$$

$$\begin{aligned} V_{bulk}\frac{d\left[FA\right]}{dt} &= \nu_{FA}\left[(E-D)k_L S\left(\left[O_{3,liq}\right]^* - \left[O_{3,liq}\right]\right) + k_{MA}\left[MA\right]\left[O_{3,liq}\right]V_{bulk}\right] \\ &- k_{FA}\left[FA\right]\left[O_{3,liq}\right]V_{bulk} \end{aligned} \tag{3.45}$$

$$\begin{aligned} V_{bulk}\frac{d\left[GA\right]}{dt} &= \nu_{GA}\left[(E-D)k_L S\left(\left[O_{3,liq}\right]^* - \left[O_{3,liq}\right]\right) + k_{MA}\left[MA\right]\left[O_{3,liq}\right]V_{bulk}\right] \\ &- k_{GA}\left[GA\right]\left[O_{3,liq}\right]V_{bulk} \end{aligned} \tag{3.46}$$

$$\begin{aligned} V_{bulk}\frac{d\left[OA\right]}{dt} &= \nu_{FA}\left[(E-D)k_L S\left(\left[O_{3,liq}\right]^* - \left[O_{3,liq}\right]\right) + k_{MA}\left[MA\right]\left[O_{3,liq}\right]V_{bulk}\right] \\ &- k_{OA}\left[OA\right]\left[O_{3,liq}\right]V_{bulk} \end{aligned} \tag{3.47}$$

The kinetic constants determined in this study are given in Table 3.10.

Table 3.10: Kinetic Rate Constants and Global Stoichiometric Coefficients of Muconic (MA), Fumaric (FA), Gallic (GA) and Oxalic (OA) Acids (Benbelkacem *et al.*, 2003)

i	MA	FA	GA	OA
k_i (l/mol s)	$12\ 10^3$	500	90	0.7
ν_i		0.9	1	0.7

Beltrán *et al.* (1998) considered an irreversible gas-liquid reaction of global kinetic order two between ozone and the organic acid being studied. Because of the absence of dissolved ozone during the oxidation, the reactions were considered to develop in the fast kinetic regime. A trial-and-error procedure was then applied. The values of the kinetic rate constant obtained by this method are given in Table 3.11. According to the Beltrán *et al.* (1998) the film model does not have the capability to describe the mass transfer phenomenon during the ozonation of crotonic acids.

Table 3.11: Kinetics of Kinetic Rate Constants Given by Beltrán *et al.* (1998) for Ozonation of Crotonic and Cinnamic Acid in the Agitated Cell and Cosidering the Danckwerts Theory

Kinetic Rate Constant (l/mol s)	Crotonic Acid	Cinnamic Acid
pH 3.0	$65\ 10^3$	$40\ 10^3$
pH 7.0	$150\ 10^3$	$80\ 10^3$

Benbelkacem and Debelefontaine (2003) proposed a mathematical model, based on the film theory, which was developed to describe the behavior of a global gas-liquid reactor. In the first part of the model, the concentration profiles within the film of the dissolved ozone and crotonic acid were determined by solving the mass balances within this film using a finite differences method The second part of the model included the mass balance equations for a reactor closed to the liquid phase and open to the gas phase (Equations 3.48-3.51)

$$Q_g C_{g,O3} dt = \mathrm{Q_g} C_{O3,out} dt + Ek_L S\left(\overline{C^*_{O3}} - C_{O3,bulk}\right)dt + V_{gas}\, d\overline{C_{gO3}} \qquad \textbf{(3.48)}$$

$$\begin{aligned} &Ek_L S\left(\overline{C^*_{O3}} - C_{O3,bulk}\right)dt = \\ &\left\{[E-D]k_L S\left(\overline{C^*_{O3}} - C_{O3,bulk}\right) + k_2 C_{A,bulk} C_{B,bulk} V_{bulk}\right\}dt \\ &+ k_{bP} C_{O3,bulk} C_{bP,bulk} V_{bulk} dt + k_c C_{O3,bulk} C_{bP,bulk} V_{bulk} dt \\ &+ V_{bulk} dC_{O3,bulk} \end{aligned} \qquad \textbf{(3.49)}$$

$$v\left\{[E-D]k_L S\left(\overline{C^*_{O3}}-C_{O3,bulk}\right)+k_2 C_{O3,bulk}C_{B,bulk}V_{bulk}\right\}dt + V_{bulk}dC_{B,bulk}=0 \quad \textbf{(3.50)}$$

$$v_{bP}\left\{[E-D]k_L S\left(\overline{C^*_{O3}}-C_{O3,bulk}\right)+k_2 C_{O3,bulk}C_{B,bulk}V_{bulk}\right\}dt + k_{bP}C_{O3,bulk}C_{bP,bulk}V_{bulk}dt+V_{bulk}dC_{bP,bulk}=0 \quad \textbf{(3.51)}$$

where V_{gas} is the gas volume within the reactor (m^3), V_{bulk} is the volume of the liquid bulk within the reactor (m^3), k_c is the self-decomposition rate constant (1/s), k_{bP} is the by-products oxidation rate constant (m^3/mol/s), ν_{bP} is the stoichiometric coefficient of the by-products, S is the interfacial area (m^2), $C_{i,bulk}$ is the concentrations within the bulk liquid (mol/m^3), $C_{gO3,in}$ and $C_{gO3,out}$ are the gas concentrations at the inlet and the outlet of the column (mol/m^3), $\overline{C_{gO3}}$ is the average gas concentration in the reactor (mol/m^3) and $\overline{C^*_{O3}}$ is the average equilibrium concentration with the gas at the concentration, E is the enhancement factor, D is the depletion factor. The trial-and-error method was then applied to determine the kinetic rate constant of crotonic acid ozonation. The model results predicted from the study are shown in Figure 3.13. The results obtained from the study suggest that a fast or intermediate regime occurs during oxidation of crotonic acid and a mass transfer acceleration were also observed due to the variation in ozone gas concentration at the outlet of the column. Benbelkacem and Debelefontaine (2003) used the first 20 minute period of the experiment to determine the kinetic constant of 500 10^3 l/mol/s at the gas flow rates of 200 and 300 l/h as shown in Figure 3.14.

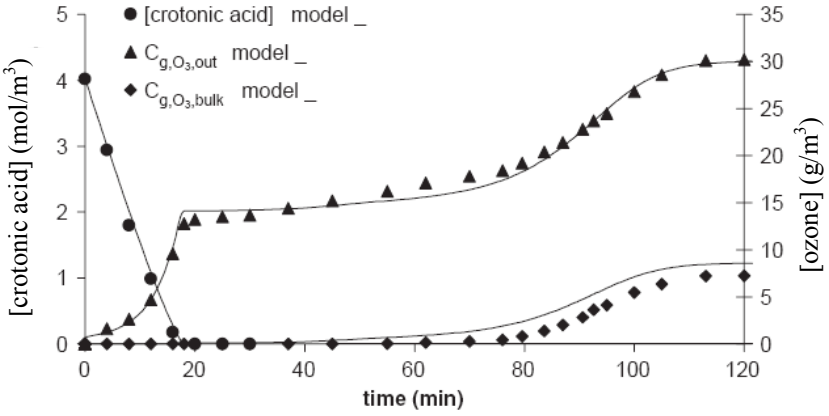


Figure 3.13: Experimental (symbols) and calculated (continuous line) crotonic acid and ozone concentrations at the outlet gas and within the liquid (Benbelkacem and Debelefontaine, 2003)

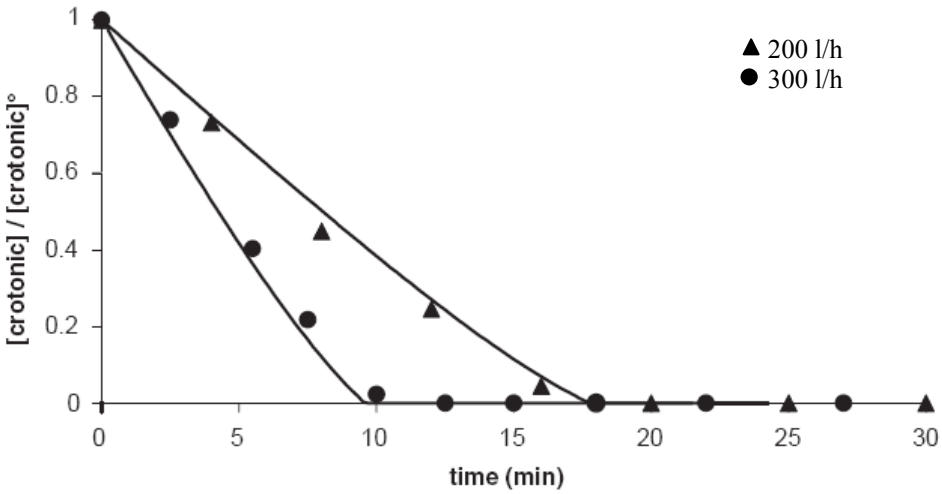


Figure 3.14: Experimental (symbols) and calculated (continuous line) results of crotonic acid ozonation for two gas flow rates in a bubble column (Benbelkacem and Debelefontaine, 2003)

In a study of Liakou *et. al.* (1997a), the Orange II-4 pigment of textile industry was found to oxidize into 2 groups of compounds, one was biologically degradable and the other was not degradable and 2 groups re-reacted with ozone. The model defined in this study could verified with measurable parameters without needing to know the intermediate products in detail. The reactions have been shown as below:

$$S_o + v_1 O_{3(l)} \rightarrow v_2 S_b + v_3 S_{nb} \qquad \textbf{(3.52)}$$

$$S_b + v_4 O_{3(l)} \rightarrow v_5 S_b + v_6 S_{nb} \quad \textbf{(3.53)}$$

$$S_{nb} + v_7 O_{3(l)} \rightarrow v_8 S_b + v_9 S_{nb} \quad \textbf{(3.54)}$$

where S_o is the dye concentration at the beginning, S_b is the organic substances that would decompose at the beginning, S_{nb} is biologically indecomposable organic substances, V_1, V_2, V_3, V_4, V_5, V_6, V_7, V_8 and V_9 are the stoichiometric coefficients, $O_{3(l)}$ is the ozone concentration in the liquid phase (mg/l).

The dye concentration (C_A) defined as parameters that have been related to COD, BOD_5, S_o, S_b, S_{nb} as follows:

$$C_A = aS_o \quad \textbf{(3.55)}$$

$$COD = S_o + S_b + S_{nb} \quad \textbf{(3.56)}$$

$$BOD_5 = bS_b \quad \textbf{(3.57)}$$

where a is the translation factor in terms of mole Orange II / equivalent COD (mg/l), while b is the BOD_5/COD ratio of the biologically decomposing substances.

The substrate removal rate equations and the ozone consumption rate equation for all these assumptions as well as reactions 3.52, 3.53 and 3.54 are given below:

$$\frac{dS_o}{dt} = -k_1 S_o C_{O_{3(l)}} \quad \textbf{(3.58)}$$

$$\frac{dS_b}{dt} = v_2 k_1 S_o C_{O_{3(l)}} + (v_5 - 1) k_2 S_b C_{O_{3(l)}} + v_8 k_3 S_{nb} C_{O_{3(l)}} \quad \textbf{(3.59)}$$

$$\frac{dS_{nb}}{dt} = v_3 k_1 S_o C_{O_{3(l)}} + v_6 k_2 S_b C_{O_{3(l)}} + (v_9 - 1) k_3 S_{nb} C_{O_{3(l)}} \quad \textbf{(3.60)}$$

$$\frac{dO_{3(l)}}{dt} = K k_{La} \Delta C_{O_3} - v_1 k_1 S_o C_{O_{3(l)}} - v_4 k_2 S_b C_{O_{3(l)}} - v_7 k_3 S_{nb} C_{O_{3(l)}} \quad \textbf{(3.61)}$$

where k_1, k_2 and k_3 are rate coefficients, K is the ozone quantity supplied to the reactor per minute, ΔC_{O3} is the difference between the ozone concentration in gaseous phase and that passing to liquid phase, k_{La} is the ozone mass transfer coefficient.

Inserting these equations in 3.55, 3.56 and 3.57

For Orange II

$$\frac{d(C_A)}{dt} = l_1(C_A)C_{O_{3(l)}} \quad \textbf{(3.62)}$$

For BOD_5

$$\frac{d(BOD_5)}{dt} = l_5 C_A C_{O_{3(l)}} + l_6(BOD_5)C_{O_{3(l)}} + l_7(COD)C_{O_{3(l)}} \quad \textbf{(3.63)}$$

For COD

$$\frac{d(COD)}{dt} = l_8 C_A C_{O_{3(l)}} + l_9(BOD_5)C_{O_{3(l)}} + l_{10}(COD)C_{O_{3(l)}} \quad \textbf{(3.64)}$$

For Ozone

$$\frac{dC_{O_{3(l)}}}{dt} = Kk_{La}\Delta C_{O_3} - l_2(C_A)C_{O_{3(l)}} - l_3(BOD_5)C_{O_{3(l)}} - l_4(COD)C_{O_{3(l)}} \quad \textbf{(3.65)}$$

were obtained. Solving the equations together, the numerical values of the l_i model parameters which are directly related to stoichiometric factor V_i, kinetic rate k_i and translation factors a, b could be obtained.

Liakau *et al.* (1997b) reviewed the same model in more detail also considering the oxidation intermediate products. In the oxidation process of the Orange II pigment with ozone, the intermediate products such as formate, oxalate and benzensulfonate were found to form. The intermediate product formate would oxidize up to CO_2 and H_2O while oxalate and benzensulfonate would not be re-reacting with ozone. With these considerations, the oxidation reactions could be expressed as

$$S_o + v_1 O_{3(l)} \rightarrow v_2 S_{bs} + v_3 S_f + v_4 S_b \quad \textbf{(3.66)}$$

$$S_f + v_5 O_{3(l)} \rightarrow CO_2 + H_2O \quad \textbf{(3.67)}$$

$$S_b + v_6 O_{3(l)} \rightarrow v_7 S_{bs} + v_8 S_{ox} \quad \textbf{(3.68)}$$

where S_o, S_{bs}, S_f, S_{ox} and S_b respectively are the biologically decomposing substance concentrations of Orange II, benzensulfonate, formate, oxalate. The kinetic rate coefficients of these reactions have been given as k_1, k_2 and k_3.

The system COD and BOD parameters could be given with the following expressions:

$$COD = S_o + S_{ox} + S_{bs} + S_f + S_b \quad \textbf{(3.69)}$$

$$BOD_5 = bS_{ox} + \frac{12{,}99.10^{-3} S_{bs}}{0{,}67.10^{-3} + S_{bs}} + \frac{38{,}28.10^{-3} S_f}{8{,}93.10^{-3} + S_f} + b_2 S_b \quad \textbf{(3.70)}$$

The system rate equations were:

For Orange II:

$$\frac{dS_o}{dt} = -k_1 S_o C_{O_{3(l)}} \quad \textbf{(3.71)}$$

For benzensulfonate

$$\frac{dS_{bs}}{dt} = v_2 k_1 S_o C_{O_{3(l)}} + v_7 k_3 S_b C_{O_{3(l)}} \quad \textbf{(3.72)}$$

For oxalate

$$\frac{dS_{ox}}{dt} = v_8 k_3 S_b C_{O_{3(l)}} \quad \textbf{(3.73)}$$

For formate

$$\frac{dS_f}{dt} = v_3 k_1 S_o C_{O_{3(l)}} - k_2 S_f C_{O_{3(l)}} \quad \textbf{(3.74)}$$

For the biologically decomposing intermediate products:

$$\frac{dS_b}{dt} = v_4 k_1 S_o C_{O_{3(l)}} + k_3 S_b C_{O_{3(l)}} \quad \textbf{(3.75)}$$

For Ozone

$$\frac{dC_{O_{3(l)}}}{dt} = Kk_{La}\Delta C_{O_3} - v_1 k_1 S_o C_{O_{3(l)}} - v_5 k_2 S_f C_{O_{3(l)}} - v_6 k_3 S_b C_{O_{3(l)}} \quad \textbf{(3.76)}$$

After solving the equations 3.69-76 the stoichiometric factors and rate coefficients could be determined.

Laari *et al.* (2000) studied the selective removal of lipophilic wood extractives (LWE) from paper mill water circulations by ozone. They proposed simple but a relatively accurate model for ozonation that could be obtained when ideal mixing was assumed in the liquid phase and plug flow in the gas phase. They derived the reaction rate equation for COD and extractives as follows:

$$r_{COD} = \frac{1}{z} V_G (c_{g,O3}^{in} - c_{g,O3}^{out}) \frac{1}{A_{cr} h_T} \quad \textbf{(3.77)}$$

$$r_{LWE} = S_{LWE} r_{COD} \frac{c_{LWE}}{COD} = \frac{S_{LWE}}{z} V_G (c_{g,O3}^{in} - c_{g,O3}^{out}) \frac{c_{LWE}}{COD} \frac{1}{A_{cr} h_T} \quad \textbf{(3.78)}$$

where, z is the stoichiometric consumption of ozone, V_G is the gas phase flow rate, (m^3/s), c_{gO3}^{in} and c_{gO3}^{out} are ozone concentrations at the inlet and the outlet (mol/m^3), A_{cr} is the cross-sectional area of reactor (m^2), h_T is the height of the column (m), S_{LWE} is the selectivity of reaction against extractives, COD is the chemical oxygen demand (mg O/l), c_{LWE} is the concentration of extractives. Then macroscopic mass balances for COD and extractives were

$$V_L (COD_{in} - COD) = r_{COD} A_{cr} h_T = \frac{1}{z} (c_{g,O3}^{in} - c_{g,O3}^{out}) \quad \textbf{(3.79)}$$

$$V_L (c_{LWE}^{in} - c_{LWE}^{out}) = r_{LWE} A_{cr} h_T = \frac{S_{LWE}}{z} V_G (c_{g,O3}^{in} - c_{g,O3}^{out}) \frac{c_{LWE}}{COD} \quad \textbf{(3.80)}$$

The model equations were iteratively solved for COD and extractives taking into account the variation of the reaction rate coefficient with respect to water composition and the extent of the reaction. The stoichiometric consumption of ozone was determined as the consumption of ozone relative to the decrease in water COD.

$$z = \frac{V_G (c_{GO3}^{in} - c_{GO3}^{out})}{dCOD/dt} \quad \textbf{(3.81)}$$

Laari *et al.* (2000) concluded that the reaction between ozone and extractives was selective. The selectivity for the reaction between ozone and different groups of compounds of wood extractives was found to be between 3 to 20, depending on the component of LWE's. The highest selectivity was shown for triglycerides. The estimated reaction rate coefficient for the reaction of ozone found to be high at the start of the reaction, diminishing as the reaction proceeded. At the start of the experiment the reaction rate coefficient had a value of about 0.8-2.0 l/mg s. They also made the simulation runs for an industrial ozonation reactor and the results showed that almost all of the ozone from the gas was consumed in the reactions. They concluded that the reaction was fast and it was limited by mass transfer of ozone from gas to liquid.

Rivera-Utrilla *et al.* (2002) investigated the degradation of naphthalenesulfonic acids (NS) by oxidation with ozone. In their study, the stoichiometry of the direct reaction between ozone and the corresponding aromatic sulfonic acid was determined by mixing 1.04 10^{-4} M saturated ozone solutions with aromatic sulfonic acid solutions at concentrations ranging from one- to eight-fold the initial ozone concentration. The experiments were carried out at pH 2 and in the presence of 0.01 M t-BuOH to avoid the contribution of the radical reaction to the oxidation process. They calculated the stoichiometry of the oxidation reaction by using the Equation 3.82.

$$z = \frac{(C_{O3})_0 - (C_{O3})_f}{(C_M)_0 - (C_M)_f} \quad \textbf{(3.82)}$$

where $(C_{O3})_0$ is the initial concentration of ozone, $(C_{O3})_f$ is the final concentration of ozone, $(C_M)_0$ is the initial concentration of sulfonic acid and $(C_M)_f$ is the final concentration of sulfonic acid. Rivera-Utrilla *et al.* (2002) determined the stoichiometric factor to be approximately one mole of ozone consumed per mole of sulphonic acid consumed.

For the kinetic study of the direct reaction of ozone against the aromatic sulfonic acids, experiments were performed at pH 2 and in the presence of 0.01 M t-BuOH, to eliminate the contribution of the radical reaction to the overall oxidation process (Rivera-Utrilla *et al.,* 2002). The reactor was operated in semi-continuous mode and

contained approximately 1.04 10^{-4} M dissolved ozone. It could be observed in Figure 3.15 that as the number of sulfonic groups in the aromatic ring increased, there was a greater resistance of the organic compound to ozonation. This resulted from a reduction in the electronic density in the aromatic ring because of the electron-withdrawing sulfonic groups in it. These functional groups withdraw electronic density from the aromatic ring, deactivating the aromatic ring against electrophilic attacks.

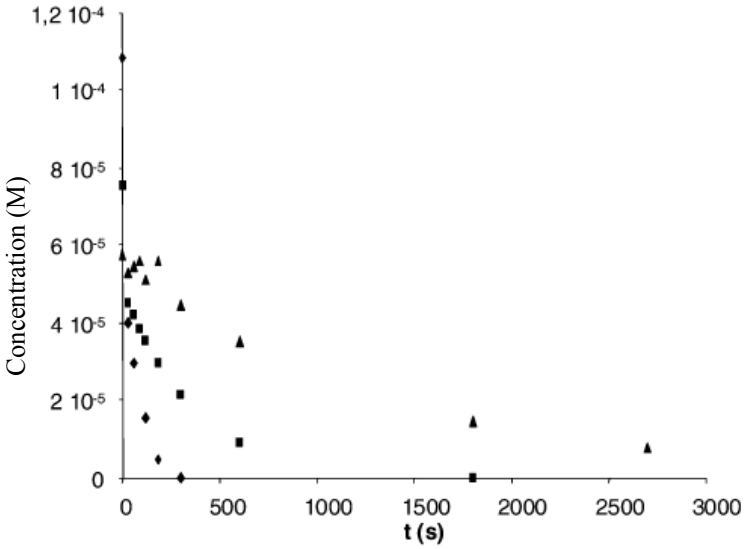


Figure 3.15: Variation of concentration of aromatic sulfonic acids with ozone treatment time (Rivera-Utrilla *et al.,* 2002). (♦) NS, (■) NDS, (▲) NTS. pH 2, T^a : 25°C, P_{O3} : 1100 Pa. [t-BuOH] : 0.01 M.

Rivera-Utrilla *et al.* (2002) represented the ozonation rate by Equation 3.83 according to the results published Hoigné (1998).

$$\frac{dC_M}{dt} = r_D = k_D C_M C_{O3} \qquad \textbf{(3.83)}$$

Integrating the Equation 3.83 gives

$$\ln\left(\frac{C_M}{C_{M0}}\right) = k_D C_{O3} t = k_{obs} t \qquad \textbf{(3.84)}$$

where r_D is the contribution of direct reaction. When $\ln(C_M/C_{M0})$ was plotted against time, in all cases, the data fitted a straight line, with a regression coefficient of 0.99; k_{obs} corresponded to the slope of this line, and from it, k_D was calculated (C_{O3} = 1.04 10^{-4} M).

Table 3.12 lists the values of the direct reaction constants for the sulfonic acids studied showing that the constant decreased considerably with the increase of the number of sulfonic groups in the aromatic ring.

Table 3.12: Rate Constants of Direct Reaction of the Naphthalenesulfonic Acids with Ozone (Rivera-Utrilla *et al.,* 2002)

Compound	k_D (1/M s)
NS	111.8±0.3
NDS	23.6±0.2
NTS	6.7±0.2

Chu and Ma (2000) aimed in their study to quantitatively determine the ratio of direct/indirect oxidation by: (1) studying the kinetics of ozonation of the purified aromatic dye materials with different assorted chromophores and different physical properties by adjusting the dye/ozone ratio; (2) determining the effect of pH on the dye's degradation. Azo dyes and anthraquinone dyes were selected for investigation (Figure 3.16).

Chu and Ma (2000) indicated that the reaction kinetics of ozonation could be determined after the O_{sat} was reached, and the resistance of the ozone transfer from gas phase to liquid phase became insignificant where the concentrations of ozone were uniform in the liquid. In this case, the ozone consumption rate was determined solely by the rate of chemical reaction in the bulk The reaction kinetics of dye ozonation, therefore, was studied under this circumstance, and the rate constants of dye decay were determined at various initial dye concentrations and pHs. The results obtained from dye ozonation at different pHs have showed that the reaction followed a pseudo first-order reaction (Figure 3.17).

Since the oxidizing ability of ozone comes from either molecular ozone or hydroxyl free radicals, the rate of dye disappearance formulated as follows:

$$-\frac{d[D]}{dt} = k_{O3}[D][O_3] + k_{OH}[D][OH] \qquad \textbf{(3.85)}$$

where [D] is the concentration of the dye in the solution, $[O_3]$ and $[OH^-]$ are the concentrations of ozone and hydroxyl radicals, and k_{O3} and k_{OH} are the respective kinetic rate constants. In their study, since the ozone was present in excess, the hydroxyl free radicals and ozone concentration in the solution were presumably close to constants (i.e. at steady state). Therefore, Equation 3.85 could be rearranged to the pseudo first-order equation in Equation 3.86, where the k is the overall or pseudo first-order rate constant.

$$-\frac{d[D]}{dt} = -\left(k_{O3}[O_3] + k_{OH}[OH] \right)[D] = -k[D] \qquad \textbf{(3.86)}$$

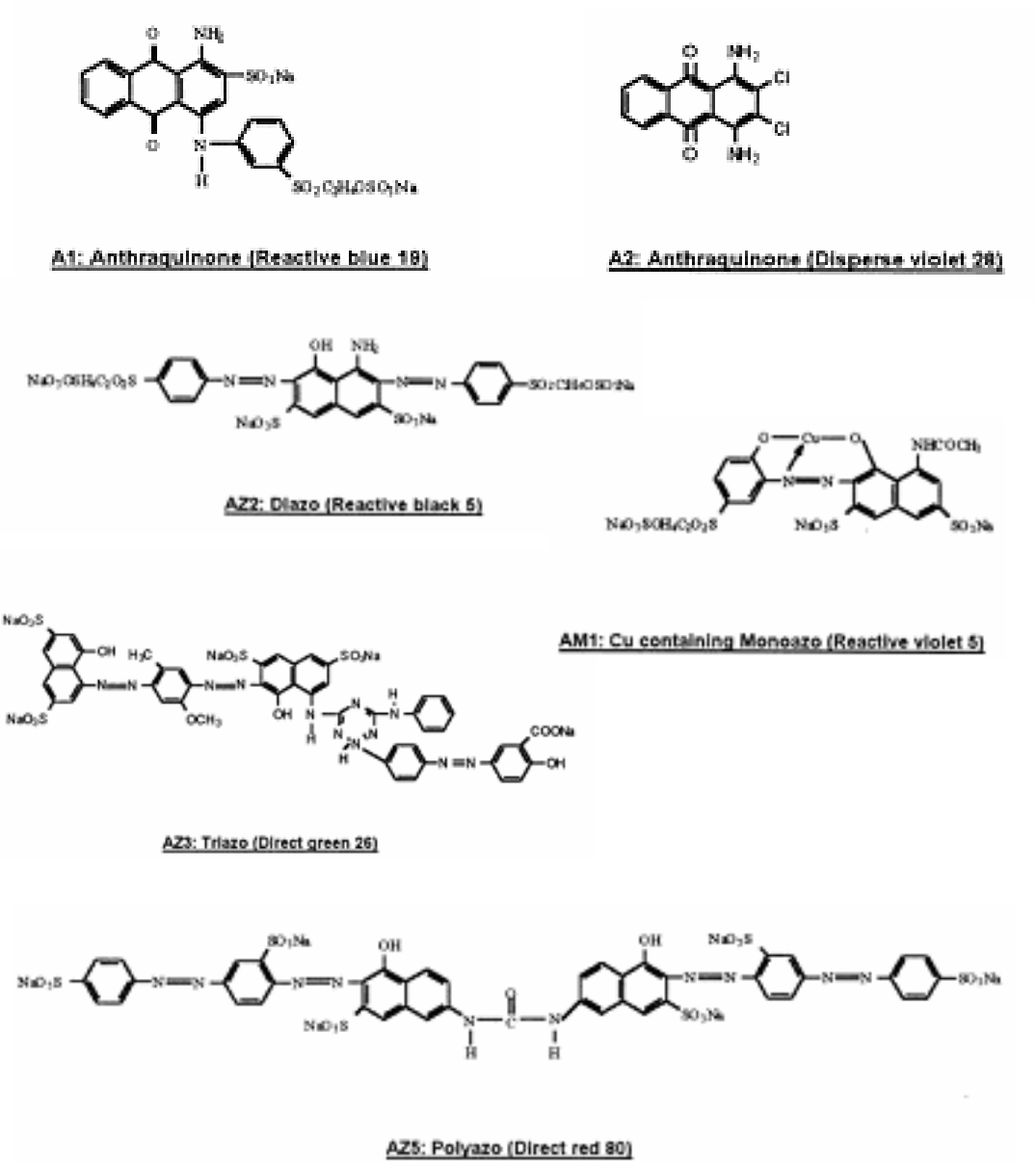


Figure 3.16: The chemical structure of dye materials (Chu and Ma, 2000)

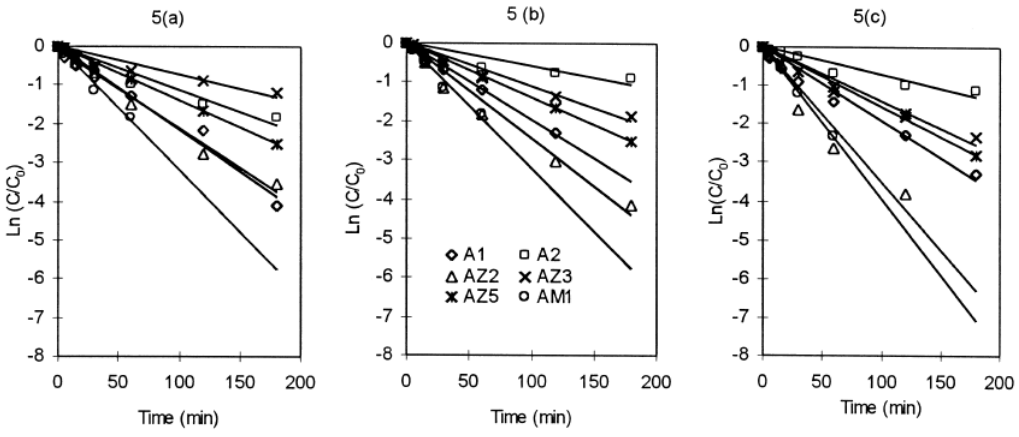


Figure 3.17: The pseudo-first-order decay rate constants of dye ozonation at different initial pHs-(a) pH 4; (b) pH 7; and (c) pH 10 under (Chu and Ma, 2000)

The ozonation of dyes at various initial pHs (4, 7and 10) was examined by Chu and Ma (2000), and was shown in Figure 3.18. The pseudo first-order rate constants of ozonation of all selected dyes varied from 5.2 10^{-4} to 1.2 10^{-4} 1/s at pH 4, 1.5 10^{-4} to 5.1 10^{-4} 1/s at pH 7, and 1.1 10^{-4} to 6.3 10^{-4} 1/s at pH 10, respectively, as shown in Figure 3.18.

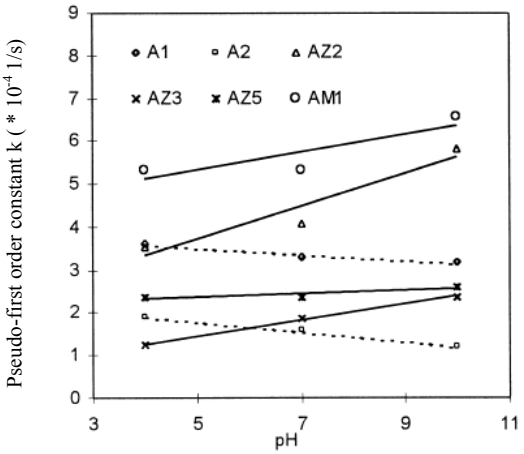


Figure 3.18: Variation of pseudo first-order rate constants at different pH (Chu and Ma, 2000)

The decay rates of azo dyes were found to increase with the increase of the pH, and the solution pH decreased during ozonation because of the higher oxidation potential of hydroxyl radical. However, Chu and Ma (2000) indicated that the increase of solution pH did not show a positive enhancement of the ozone oxidation of the two anthraquinone dyes (A1 and A2); instead, the lower the pH, the higher the reaction rate.

Chu and Ma (2000) investigated the pseudo first-order rate constants for dyes carrying various chromophores at different initial pHs as demonstrated in Figure 3.19(a), where the decay rates of azo dyes (AZ2 and AZ3) were shown to be higher than that of anthraquinone dye (A1). Equation 3.86 was further studied by changing the dye/ozone ratio. As demonstrated in Figure 3.19(b), three different dyes (A1, AZ2 and AZ3) with different initial concentrations (14.4, 7.2 and 3.6 10^{-2} mmol/l) were used to study the effect of initial dye concentration in ozonation. It was found that the pseudo first order rate constants decreased as the dye/ozone ratio increased. From the results they concluded that when the dye/ozone ratio was increased, the ozone concentration no longer had the chance, or had a lower chance, to be present in excess, resulting in the term of .($k_{O3}.[O_3]+ k_{OH} [OH^-]$) in Equation 3.86 being actually reduced.

Gurol and Singer (1983) developed an explicit mathematical model which described the rate of change in the concentration of phenol and ozone in an ozone contactor at low pH where the rate of ozone decomposition and ionization of phenol were insignificant and they verified the predicted model by using the experimental observations presented in their previous study (Singer and Gurol, 1983).

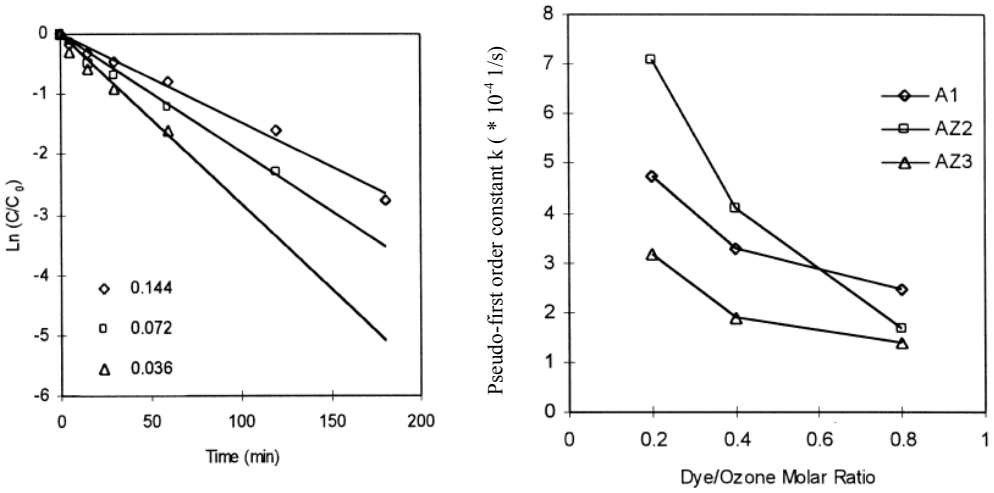


Figure 3.19: (Left) Pseudo first-order decay of A1 at different initial dye concentrations (mmol/l); (Right) Ozonation of three different dyes at various dye/ozone ratios (Chu and Ma, 2000)

Gurol and Singer (1983) reported that, in an acidic solution it was expected that the direct oxidation of phenol would be the major oxidation pathway. In a semi-batch reactor into which ozone was continuously bubbled to react with phenol at pH 3.0, the rate of change in the concentrations of phenol and ozone could be expressed as:

$$-\frac{d[P]}{dt} = k_P[P]\ [O_3] \qquad \textbf{(3.87)}$$

and

$$-\frac{d[O_3]}{dt} = k_L a\left([O_3]^* - [O_3]\right) - \sum z_i k_i [O_3] S_i \qquad \textbf{(3.88)}$$

Where $[P]$ is the concentration of phenol in bulk solution, $[O_3]$ is the concentration of dissolved ozone in water, $k_L a$ is the liquid-side overall mass-transfer coefficient, $[O_3]^*$ is the saturation concentration of ozone as determined by Henry's Law, k_P is the rate constant for oxidation phenol, $[S_i]$ is the concentration of solute "i" in bulk

solution, k_i is the the rate constant for oxidation solute "i". In order to able to write an equation for the rate of change of phenol and ozone concentrations in solution as in Equation 3.87 and 3.88, it was assumed that the extent of the reactions between ozone and various substrates, including phenol, was insignificant in the diffuse film. The diffuse film was defined as the liquid region near the gas-liquid interface where mass-transfer of ozone occurred by molecular diffusion.

Gurol and Singer (1983) indicated that to predict the profiles of phenol and ozone as a function of time, according to Equations 3.87 and 3.88, it was necessary to know the nature and kinetics of the reactions between molecular ozone and daughter products of the phenol oxidation reaction, and the kinetics of mass-transfer of ozone. For the oxidation of the phenol, the relevant chemical reactions which were assumed to be significant in the acidic system were indicated as follows:

$$P + O_3 \xrightarrow{k_1} C \quad \textbf{(3.89)}$$

$$P + O_3 \xrightarrow{k_2} H \quad \textbf{(3.90)}$$

$$P + O_3 \xrightarrow{k_3} MA \quad \textbf{(3.91)}$$

$$P + 3O_3 \xrightarrow{k_4} Stable \quad products \quad \textbf{(3.92)}$$

$$C + 3O_3 \xrightarrow{k_c} Stable \quad products \quad \textbf{(3.93)}$$

$$H + 3O_3 \xrightarrow{k_H} Stable \quad products \quad \textbf{(3.94)}$$

$$MA + 2O_3 \xrightarrow{k_{MA}} Stable \quad products \quad \textbf{(3.95)}$$

where C, H and MA stood for catechol, hydroquinone, and muconic acid respectively, k_1, k_2, k_3 and k_4 are the rate constants for formation of catechol, hydroquinone, muconic acid and other ring cleavage product from phenol, k_C, k_H and k_{MA} are the rate constants for oxidation of catechol, hydroquinone and muconic acid, respectively. According to the reactions listed in equations 3.89-3.95, the reaction rates of phenol, ozone and intermediates were written as:

$$\frac{d[P]}{dt} = -k_1[P]\ [O_3] - k_2[P]\ [O_3] - k_3[P]\ [O_3] - k_4[P]\ [O_3] = k_p[P]\ [O_3] \qquad \textbf{(3.96)}$$

where $k_P = k_1 + k_2 + k_3 + k_4$

$$\frac{d[C]}{dt} = k_1[P]\ [O_3] - k_C[C]\ [O_3] \qquad \textbf{(3.97)}$$

$$\frac{d[H]}{dt} = k_2[P]\ [O_3] - k_H[H]\ [O_3] \qquad \textbf{(3.98)}$$

$$\frac{d[MA]}{dt} = k_3[P]\ [O_3] - k_{MA}[MA]\ [O_3] \qquad \textbf{(3.99)}$$

$$\frac{d[O_3]}{dt} = k_L a\left([O_3]^* - [O_3]\right) - k_1[P]\ [O_3] - k_2[P]\ [O_3] - k_3[P]\ [O_3] - 3k_4[P]\ [O_3] - 3k_C[C]\ [O_3] - 3k_H[H]\ [O_3] - 2k_{MA}[MA]\ [O_3] \qquad \textbf{(3.100)}$$

Equations 3.96-3.100 were solved numerically for the concentrations of phenol, catechol, hydroquinone, muconic acid and ozone as a function of time. Gurol and Singer (1983) assumed for the simplicity of the model that $k_1 = k_2 = k_3$, $k_4 = 0$ and $k_C = k_H = k_{MA}$. Further k_C, k_H and k_{MA} were assumed to be equal 4 k_P since the rates of ozonation of hydroxylated phenols and muconic acid were expected to be faster than that of phenol. According to the predictions of the model, they concluded that the system was mass-tranfer limited as long as phenol was present in solution, i.e. the ozone concentration in the bulk solution would be very small until phenol essentially disappeared. Thereafter, the ozone concentration would increase and approach its saturation value. The model predicted the same concentration profiles for catechol, hydroquinone and muconic acid since for illustrative purpose, the reaction rate constants for these compounds were assumed equal to each other.

In the study of Gurol and Singer (1983) the reaction rate constants for the direct oxidation of catechol, hydroquinone and muconic acid by ozone were measured at pH 3.0 by the relative rate method proposed by Hoigné and Bader (1976). The following equations expressed the rate of oxidation of phenol and catechol

$$-\frac{d[P]}{dt} = k_p[P]\ [O_3] \qquad \textbf{(3.101)}$$

and

$$-\frac{d[C]}{dt} = k_C[C]\ [O_3] \quad \textbf{(3.102)}$$

The initial concentrations of catechol, $[C]_0$, in the mixture were selected to be several times greater than that of phenol, $[P]_0$, in order to keep the amount of catechol formed from the oxidation of phenol small. Dividing Equation 3.101 by Equation 3.102 and integrating yielded

$$\frac{\ln([C]/[C]_0)}{n([P]/[P]_0)} = \frac{k_C}{k_P} \quad \textbf{(3.103)}$$

$\ln([C]/[C]_0)$ and $\ln([P]/[P]_0)$ were calculated for several sets of data with different $[C]_0$ and $[P]_0$. These terms were plotted against each other. k_C/k_P , which was equal to the slope of the straight line according to the Equation 3.103 was found to be 2.5. The same analysis for hydroquinone and muconic acid showed that k_H/k_P and k_{MA}/k_P were respectively, 1.8 and 5.5. Since k_P was reported to be 400 l/mol s, the absolute reaction rate constants, k_C, k_H and k_{MA} would be 1000, 720 and 2200 l/mol s, respectively at pH 3.0.

Gurol and Singer (1983) assumed that the rate of formation of intermediates (k_1, k_2, k_3 and k_4) was equal to their rate of removal, the rate of change in their concentration , in accordance with Equations 3.97-3.99, became zero and the concentration profiles reached their peak. For example for catechol, this expressed as:

$$k_1[P]^*[O_3] = k_C[C]^*[O_3] \quad \textbf{(3.104)}$$

and

$$k_1 = k_C\frac{[C]^*}{[P]^*} \quad \textbf{(3.105)}$$

where $[P]^*$ and $[C]^*$ are the concentrations of phenol and catechol at the point where $d[C]/dt = 0$. Hence, applying Equation 3.105 the formation rate constant of the intermediates from phenol k_1, k_2, k_3 and k_4 calculated to be 0.8, 6, 88 and 350 l/mol s, respectively. Then the oxidation rate constants of intermediates obtained by using

the relative rate technique, the results were 1000, 720 and 2200 for catechol, hydroquinone and muconic acid respectively.

Gurol and Singer (1983) concluded that the agreement between the experimental observations and the predictions of the model for the concentration of phenol was almost perfect. The maximum concentrations of catechol and hydroquinone were predicted to be less than 1 mg/l. They indicated that this was close agreement with the observed concentrations. The model adequately predicted the maximum concentrations of muconic acid produced, however, the predicted profiles shifted. They indicated that this suggested that in addition to direct ring-cleavage of phenol, other mechanisms, such as the oxidation of intermediate muconaldehyde, were contributing significantly to the formation of muconic acid. They also indicated that the mathematical model did not include direct reactions of non-olefinic ring-cleavage products with ozone, e.g. glyoxal, glyoxalic acid. It had been assumed, based upon Hoigné's (1982) results, that the direct reaction rates of these compounds with ozone would be slow enough so as not to compete with the reaction of phenol. The proposed model predicted small but measurable ozone concentration until the complete disappearance of phenol. After phenol was completely eliminated, the model predicted a faster approach of the ozone concentration to its saturation value. They concluded that these observations might all be attributed to the ozone demand of slowly reacting reaction products which were not included in the model. Alternatively, it might also be possible that the decomposition of ozone was catalyzed by one or more of the products of the reaction.

4. MATERIALS AND METHODS

4.1 Experimental Protocol

The role of ozonation and its related oxidation processes in the removal of organic compounds has been studied by different investigators. However, most of these studies conducted on systems that included single compound. These studies also paid little attention to the gas-liquid mass transfer with chemical reaction, the influence of intermediates formed to the oxidation pathway and chemical kinetics. Therefore, this study was devoted to analyze the mechanism of ozonation reactions that lead evaluation of organic compounds oxidation by molecular ozone under acidic conditions.

In natural waters and wastewaters organic compounds cannot be found alone in the medium. Therefore for better understanding and underlying the ozone oxidation process the removal pattern of organics compounds should be analyzed alone and in combination in the aqueous medium.

Phenol and phenolic substances are abundantly present in wastewaters from agro-industries. Natural organic matter may contain phenolic groups. Because of their toxicity, refractory character and high stability in aqueous medium phenolics deserve attention. Also, phenol is considered to be an intermediate product in the oxidation pathway of higher molecular weight aromatic hydrocarbons. Thus it is usually taken as a model compound for treatment systems including oxidation processes to improve treatment techniques and removal efficiencies. In the literature there are numerous studies performed to investigate the ozone oxidation characteristics of phenol. In these studies the chemical kinetics data, the kinetic regime of reaction were determined for the reaction between ozone and phenol. However, there are missing aspects in these studies to define the oxidation systems in detail. These studies also paid little attention to the influence of intermediates formed to the chemical kinetics. For the fundamental characteristics of phenol that was written

previously, to complete the missing points of phenol oxidation and also for the purpose of this study, it was selected as one of the model compounds.

For the selection of the other model compound and better evaluation of the system the intermediates formed during the course of the reaction should be taken into account. For these purpose pre-experiments were conducted on different organic matters to analyze their removal pattern, oxidation characteristics and the intermediates formed. The results of pre-oxidation experiments conducted using bentazone herbicide showed that phenol was one of the main intermediate formed during the course of the molecular ozone oxidation of bentazone. This characteristic of bentazone oxidation was considered as an advantage for the evaluation of the multiple oxidation systems. The selection of the bentazone as the other model compound understanding of the multiple oxidation system that was also taking into account the intermediates formed was considered to be facilitated. The advantages of the selection of bentazone could be pointed out as follows:

The single oxidation of bentazone could also be considered as a mixture of selected model compounds due to the phenol formation.

For these ozonation characteristics of the bentazone herbicide, it was selected as the other model compound for the experimental study.

Bentazone formulations are used as post-emergence herbicides for the control of broad-leaved weeds and Cyperaceae in a range of crops. Bentazone has a contact action on the leaves and to a lesser extent an action via the soil. The active ingredient is principally absorbed by the green parts of plants and acts as a photosynthesis inhibitor (Food and Agricultural Organization (FAO), 1992). The 1991 Joint Meeting of Pesticide Residues reported that bentazone has a relatively low acute toxicity in rats, guinea pigs and rabbits (World Health Organization, 1992). World Health Organization (WHO) has classified bentazone as slightly hazardous. Bentazone was not degraded after 120 days in either distilled water or WHO Standard Hard Water in the dark at pH levels of 5.0, 7.0 or 9.0 (FAO, 1992).Thus, chemical oxidation could be a potential treatment method for the removal of bentazone however there has been no research conducted ozone oxidation of bentazone. Bentazone is a commonly used herbicide all over the world so to investigate the ozone oxidation of bentazone could be an advantage for its control. The chemical structure of bentazone is given in

Figure 4.1. The molecular formula and molecular mass of bentazone are $C_{10}H_{12}N_2O_3S$ and 240g.

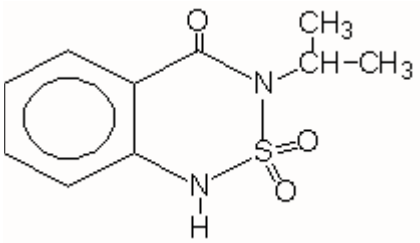


Figure 4.1: Chemical structure of bentazone

For concentration selection of model compounds to be studied, the ozone oxidation application characteristics and the existence level of model compounds in wastewater streams were taken into account. The selected concentrations were also adequate for the analysis and evaluation of the model compounds removal during the all oxidation periods and the selected concentrations were also relevant for monitoring the concentrations of intermediates formed.

Ozone reacts with organic compounds in two different ways: by a direct attack of molecular ozone and through free radicals, especially hydroxyl radicals. Hydroxyl radicals resulting from the decomposition of ozone serve as the oxidants which is favored when the pH increases. At acid pH values the oxidation reaction takes place only through the direct attack, in which molecular ozone reacts at electron-rich sites of the solutes. At the same time in acidic conditions, the rate of decomposition of ozone and the rate of hydroxyl radical formation are negligible. Therefore, in an acidic solution (at pH 3.0) it is expected that direct reaction of phenol and bentazone will be the major oxidation pathway.

It is necessary to use semi-batch reactor systems in water and wastewater treatment, in order to maintain dissolved ozone concentrations at desired levels. In batch systems the initial ozone concentration would have to be very high due to the high ozone demand of organic compounds. Therefore, the experiments were performed in constant temperature room by a semi-batch glass reactor into which ozone is continuously bubbled to react with organic compounds. The mass ozone in the gas entering the reactor per minute was described as ozone dosage and measured at the beginning of all experiments in the study.

The volumetric mass transfer coefficient of the ozone reactor was determined during a set of preliminary experiments. Equation 4.1 was used for the determination of $(k_L a)_{O3}$ when the reactor operated in a semi-batch mode and the experiments which were conducted with ultrapure water at pH 3.0. Due to the acidic pH studied the ozone decomposition was neglected at the equation.

$$\frac{d[O_3]}{dt} = (k_L a)_{O3} \quad \left(\left[O_3^*\right] - [O_3] \right) \tag{4.1}$$

where $(k_L a)_{O3}$ is the volumetric mass transfer coefficient of ozone in water (1/s), $\left[O_3^*\right]$ is the saturation concentration of ozone (mg/l) and $[O_3]$ is the ozone concentration in the bulk liquid (mg/l). The differential equation 4.1 can be obtainable by MAPLE 8.0 software and equation 4.2 was derived.

$$[O_3] = \left[O_3^*\right] - \left[O_3^*\right] \; e^{(k_L a * t)} \tag{4.2}$$

Volumetric mass transfer coefficients were determined using equation 4.2 by Origin 7.5 software with non-linear curve fitting method. The experimental conditions employed in this study and estimated values of $(k_L a)_{O3}$ are given in Table 4.1. Ozone was continuously bubbled into the ultrapure water at pH 3.0 at a flow rate of 0.6 Nl/h.

Table 4.1: Experimental Conditions Employed in This Study and Estimated values of Volumetric Mass Transfer Coefficient

	Experiment I	**Experiment II**	**Experiment III**
Ozone Dosage (mg/min)	3.52	3.76	4.0
Ionic Strenght (M)	$1.1\ 10^{-2}$	$1.0\ 10^{-3}$	$2.2\ 10^{-3}$
$(k_L a)_{O3}$(1/s)	0.243 ± 0.05	0.240 ± 0.03	0.409 ± 0.05

Benbelkacem *et. al.* (2004) determined the volumetric mass transfer coefficient in pure water and they reported that the values were between $1.2\ 10^{-2}$ and $1.7\ 10^{-2}$ 1/s for gas flow rates ranging between 200 and 300 l/h at 20°C and 1 atm. They also indicated that the volumetric mass transfer coefficient could increase because of the surfactant properties of organic mater oxidized and the calculated volumetric mass transfer coefficients for ozonation of crotonic acid was between $1.8\ 10^{-2}$ and $2.5\ 10^{-2}$ 1/s at the same gas flow rates. Benbelkacem *et. al.* (2003) studied the maleic acid ozonation and they reported the volumetric mass transfer coefficients as $1.14\ 10^{-2}$

and 1.69 10^{-2} 1/s for gas flow rates ranging between 200 and 300 l/h. The reported volumetric mass transfer coefficients for the ozonation of fumaric acid were 2.4 10^{-2} and 3.2 10^{-2} 1/s for the gas flow rates of 200 and 300 l/h (Benbelkacem and Debellefontaine, 2003). Gurol and Singer (1983) reported the values of volumetric mass transfer coefficients as 0.55 10^{-2}, 0.83 10^{-2} and 1.39 10^{-2} 1/s for gas flow rates of 20, 30 and 50 l/h respectively. The values of volumetric mass transfer coefficient obtained in this study were in accordance with the literature data.

4.2 Experimental Set-up

The experimental set-up used in this study is shown in Figure 4.2. The set-up includes an ozone generator and a reaction vessel. Ozone was provided using Erwin Sander Elektroapparatebau brand Laborozonisator 301.7 Model ozone generator that was fed with dry air. Ozone gas concentration in the influent and effluent gas was measured by the Potassium Iodide Method (APHA Standard Methods, 1998). Influent and effluent ozone gas were trapped using three serially connected gas-washing bottles containing 2% KI solution. The flow rate of the ozone gas was controlled by a gas flowmeter.

Figure 4.2: Experimental set-up

The experiments were performed in a semi-batch reactor. The ozonation reactor was made of Pyrex glass which had openings for ozone inlet and outlet and also for liquid sampling. The ozone-air mixture was fed through the sintered glass diffuser placed at the bottom of the reactor. All connections in the experimental set-up were made using Teflon and stainless steel fittings.

The sample volume was taken as one liter in all experiments. Samples were taken at time intervals to analyze; dissolved ozone concentration, phenol, bentazone, intermediate concentrations and TOC.

4.3 Materials

Phenol (≥ 99.5%) was obtained from Fluka Chemical Company. Bentazone was extracted as active material from Basagran Herbicide agricultural chemical purchased from BASF Corp. Chemical Division. For extraction of bentazone active material, sublimation technique was used (Green, 2005).

The purity of bentazone active material was tested by melting point determination and mass spectroscopy. Cis, cis-muconic acid and hydroquinone were obtained from Sigma-Aldrich chemical company. For HPLC measurements HPLC-grade acetonitrile was purchased from MERCK.

Standard solutions, for HPLC calibration curves, were prepared by making dilutions from stock solutions.

All aqueous solutions were prepared with distilled water. Sartorius Ultra Pure Water System has a unique carbon-resin combination with ultrafilter and UV lamp to produce ultrapure water with a resistivity up to 18.2 MΩ × cm, with Total Organic Carbon (TOC) levels as low as < 1 ppb.

4.4 Experimental Methods

Ozone gas concentration at influent and effluent gas was measured by Potassium Iodide Method (APHA Standard Methods, 1998). This method is based on dissolution of ozone gas in 2% KI solution and titration of formed iodine with standardized sodium thiosulphate solution under acidic conditions. Indigo Method was used to determine the liquid phase ozone concentration. This method is based on the decolorization of potassium indigo trisulfonate upon its reaction with ozone

below pH 4.0. The decolorization of potassium indigo trisulfonate was monitored with a spectrophotometer at a wavelength of 600 nm at which potassium indigo trisulfonate absorbs light.

Phenol, bentazone and intermediate concentrations were monirored by using HPLC equipped ECOM SPOL. S R.O. LCP4100 pump and ECOM SPOL. S R.O. LCD2084 UV detector. Inertsil ODS2 column was used for the measurement. The reverse phase C-18 column was packed silica particles of 5µm in diameter. The length and diameter of the column was 250×4.6 mm. It has a guard column with dimensions 40×4.6mm. The mobile phase was selected as 60/40 (v/v) Acetonitrile/Water and 0.1 % H_3PO_4. The solvent flow rate was maintained at 1.7 ml/min.

TOC measurements were made by Shimadzu TOC-5000A Total Organic Carbon Analyzer.

5. RESULTS AND DISCUSSION

5.1 Introduction

The main objective of this research is to understand the mechanism and process kinetics of ozonation reactions that lead evaluation of organic compounds oxidation by molecular ozone under acidic conditions. For this purpose in the following subsections, the evaluation of organic compound oxidation by ozone was investigated experimentally in terms of organic compound removal phenomena, intermediate formation and removal, TOC removal pattern and dissolved ozone concentration in solution. The experimental results evaluated and compared with literature data.

5.2 Phenol Experiments

5.2.1 Phenol removal

Phenol and phenolic substances have attracted more attention because of their toxicity and frequency of use in industrial processes producing wastewater contaminated by phenol as a pollutant. Natural organic matter may contain phenolic groups although phenol is considered to be an intermediate product in the oxidation reactions of higher molecular weight aromatic hydrocarbons. Thus it is usually taken as a model compound for treatment systems including oxidation processes to improve treatment techniques and removal efficiencies (Singer and Gurol, 1983; Gurol and Singer, 1983).

This part of the study was devoted to the investigation of the removal pattern of phenol by molecular ozone under acidic conditions for examining ozone oxidation processes. In the study, phenol removal pattern monitored with time and several parameters of importance were also measured. The initial concentrations were selected as concentrations that can be met in the industrial wastewaters.

The removal of phenol by ozone oxidation was investigated in synthetic solutions containing phenol concentrations of 25 (Experiment P-1a and P-1b), 50 (Experiment P-2), 75 (Experiment P-3) and 100 (Experiment P-4) mg/l and at pH 3.0. Ozone was continuously bubbled into the solution at a flow rate of 0.6 Nl/h.

The removal of phenol in the solution containing 25 mg/l phenol by ozone at two different ozone dosages is given in Figure 5.1 (P-1a and P-1b). The results of the experiments showed that ozonation provided a considerable amount of phenol removal with increasing ozone dosage. The ozone dosages were 3.4 and 13.8 mg/min for P-1a and P-1b experiments respectively. For experiment P-1a the complete phenol removal observed at 60^{th} minute, increasing the ozone dosage approximately 4 times, reduced the complete oxidation time to 30^{th} minute. For a better understanding of the system, the $C*t$ parameter can also be evaluated where C is the applied ozone dosage (mg/min) and t is the reaction time where phenol removed completely (min). For experiment P-1a, the $C*t$ value was calculated as 197 mg and 396 mg for experiment P-1b. As can be seen from the results, increasing the applied ozone dosage approximately 4 times doubled the $C*t$ values. Further studies are needed to be done for the evaluation of the relationship between the applied ozone dosage and the reaction time.

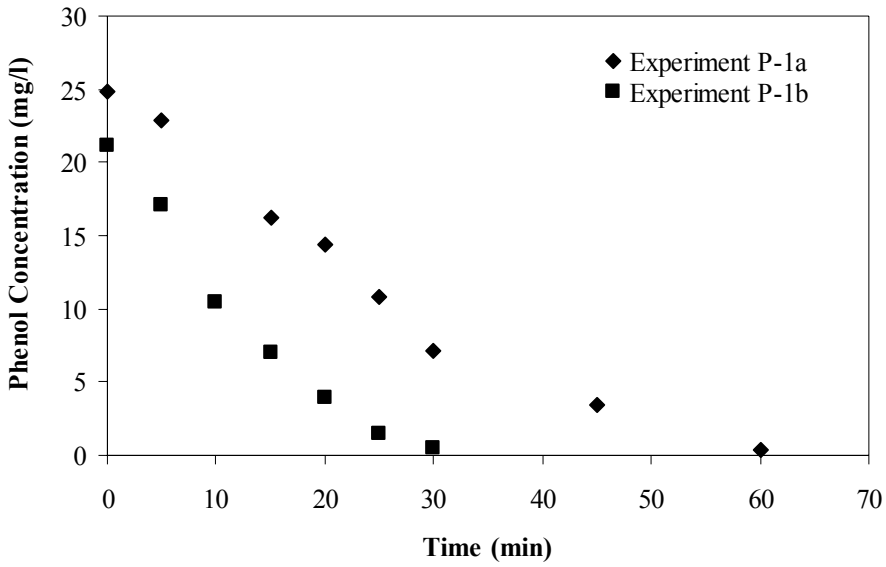


Figure 5.1: Removal of phenol by ozonation at different ozone dosages

Figure 5.2 shows the results of P-2, P-3 and P-4 experiments, for ozone dosages 3.1, 3.8 and 3.6 mg/min respectively. As seen from the figure 50% phenol removal efficiency was achieved in 60 minutes for all initial concentrations. Although, at the end of the oxidation period of 150 minute the removal efficiencies were over 90%. These rates are comparable with that of experiment P-1a.

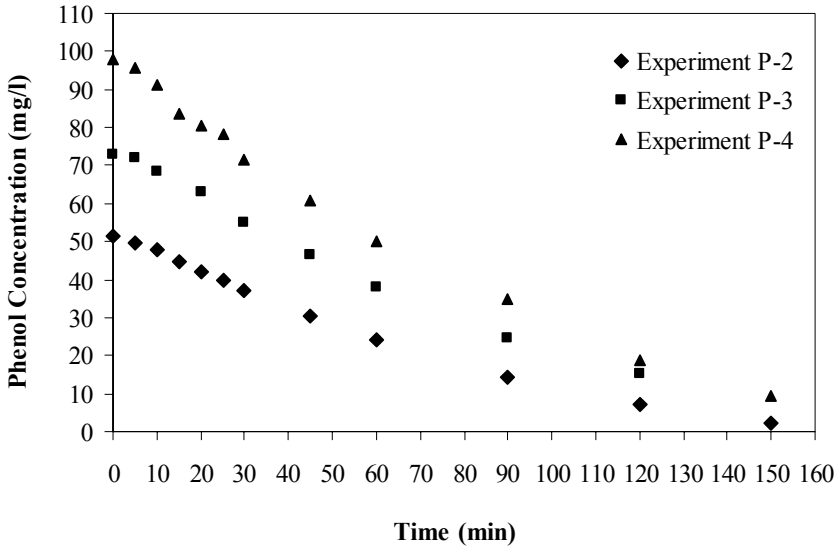


Figure 5.2: Removal of phenol by ozonation at different initial phenol concentrations

These experimental results are in agreement with the results reported by other investigators who have also observed comparable oxidation level of phenol by ozonation. Singer and Gurol (1983) studied dynamics of ozonation of phenol under acidic conditions. They reported that the complete removal was achieved at 15 and 23 minutes for 9 mg/l and 7 mg/l ozone saturation concentrations for 140 mg/l phenol initial concentration. For these experiments mass-transfer coefficients were 60 1/hr and 43 1/hr respectively. Beltrán *et al.* (1990) studied ozonation of o-creosol in aqueous solutions. They reported that for an initial o-creosol concentration of 10^{-3} M during the first 20 minutes of ozonation, 11.7 mg of ozone per minute permitted to obtain conversions of 70%.

5.2.2 Intermediate formation

As discussed in detail in Section 3, the organic pollutants initially present in natural waters and wastewaters are not oxidized directly to CO_2. During the oxidation route many organic intermediates may form. For the design of an oxidation process to treat

natural waters and wastewaters it is quite helpful to understand and consider the oxidation mechanism of organic compounds.

Oxidation of organic compounds by ozone has been examined by different investigators (Dore *et al.*, 1978; Hoigné, 1982; Beltrán *et al.*, 1990; Andreozzi *et al.*, 1992). However, most of these works paid little attention to reveal the oxidation mechanism, taking into account the intermediates, their affects to the removal pattern and reaction kinetics. Therefore, to understand the true mechanism of phenol oxidation and to evaluate the kinetics, the formation of intermediates should be evaluated.

Most of the intermediates formed during the oxidation have a pattern that the concentrations increase with time, reach a peak value and then start to decrease upon further ozonation. The formation of a peak suggests, the formation rate of intermediates is higher than their oxidation rate. Therefore, the accumulation of intermediates occurs in a certain time period following the beginning of oxidation.

For the oxidation of phenol by molecular ozone, Bailey (1972) proposed that the electrophilic attack of ozone to phenol molecule leads to formation of hydroxylated products, catechol and hydroquinone, as major intermediates. On the other hand, 1,3 dipolar cyclo addition of ozone causes direct ring-cleavage of phenol to produce cis, cis-muconic acid or muconaldehyde (Figure 3.1). Cis, cis-muconic acid can be also produced from the ring cleavage of catechol and also from the oxidation of muconaldehyde which is itself another ring-cleavage product. However, the contribution through catechol oxidation is expected to be insignificant due to the negligible production of catechol. Also neglecting the oxidation of muconaldehyde, an approximate figure of 22% was calculated for the percentage of phenol undergoing ring-cleavage to form cis, cis-muconic acid (Gurol and Singer, 1983). The experimental results showed that cis, cis-muconic acid and hydroquinone were produced in relatively large amounts during the oxidation of phenol (Singer and Gurol, 1983; Mvula and von Sonntag, 2003). Hoigné and Bader (1979) showed that the hydroxylation pathway constitutes less than 2% of the phenol oxidation by ozone at pH 3.0 and further oxidation products such as dihydroxybenzene species do not appear to be significant at this pH value. At the higher pH values significant amount of catechol and hydroquinone was found to form by ozonation of phenol (Singer and Gurol, 1983).The maximum concentrations of catechol, hydroquinone and muconic

acid formed by ozone oxidation at different pH values were given in Table 5.1. As can be seen from the table direct ring cleavage of phenol is the major mechanism in acidic solutions. Significant amounts of catechol and hydroquinone formed upon ozonation of phenol at the higher pH values. The ratio of maximum muconic acid concentration to initial phenol concentration was 3% (mg/mg) in these experiments. For hydroquinone this ratio was relatively small as compared to muconic acid ratio.

Table 5.1: Maximum Concentrations of Intermediates Formed By Ozonation of 141 mg/l Phenol at Various pH Values (Singer and Gurol, 1983)

pH	3.0	4.5	6.0	8.9
Catechol (mg/l)	0.1	10.5	30.0	12.5
Hydroquinone (mg/l)	0.3	1.4	10.5	0
Muconic Acid (mg/l)	4.4	16.0	11.2	10.6

Mvula and von Sonntag (2003) studied ozonolysis of phenols in aqueous solution. They reported products and their yields in % of ozone consumed at 2.5×10^{-4} M phenol concentration below pH 3.0. These percentages were found to be 1.6 for hydroquinone, 1.8 for catechol and 4.8 for cis, cis-muconic acid.

This part of the study devoted to a better understanding of oxidation pathway of phenol by molecular ozone by taking into account of formed intermediates. For this purpose due to their importance for the understanding of the oxidation pathway of phenol under acidic conditions, to evaluate the oxidation mechanism and oxidation rate of phenol with molecular ozone, it is important to follow up the concentrations of hydroquinone and cis, cis-muconic acid.

Gurol and Singer (1983) indicated that 0.2% of the initial phenol is oxidized by the way of catechol and 1.5% of the initial phenol is oxidized by way of hydroquinone. Hence, the total hydroxylation pathway constitutes less than 2% of the total oxidation at pH 3.0. The remaining 98% phenol is apparently oxidized by the ring cleavage pathway.

With these intentions four different initial phenol concentrations were chosen to monitor the formation and removal mechanism of these two intermediates over the course of time. During the ozone oxidation of phenol, the maximum concentrations of formed intermediates and their ratios to initial phenol concentration (mg/mg) were followed and evaluated in detail.

The intermediate formation during phenol oxidation at different ozone dosages for synthetic solution containing 25 mg/l phenol is presented in Figures 5.3 and 5.4 (P-1a

and P-1b). As seen from these figures for the experiment conducted with 3.4 mg/min ozone dosage, peak value of cis, cis-muconic acid concentration was reached at 20th minute. The ratio of cis, cis-muconic acid concentration in mg/l to the initial phenol concentration in mg/l was approximately 6%. The removal efficiency of phenol was 42% at 20th minute. However the peak value of hydroquinone was reached at 45th minute and its ratio to initial phenol concentration was 10% (mg/mg).

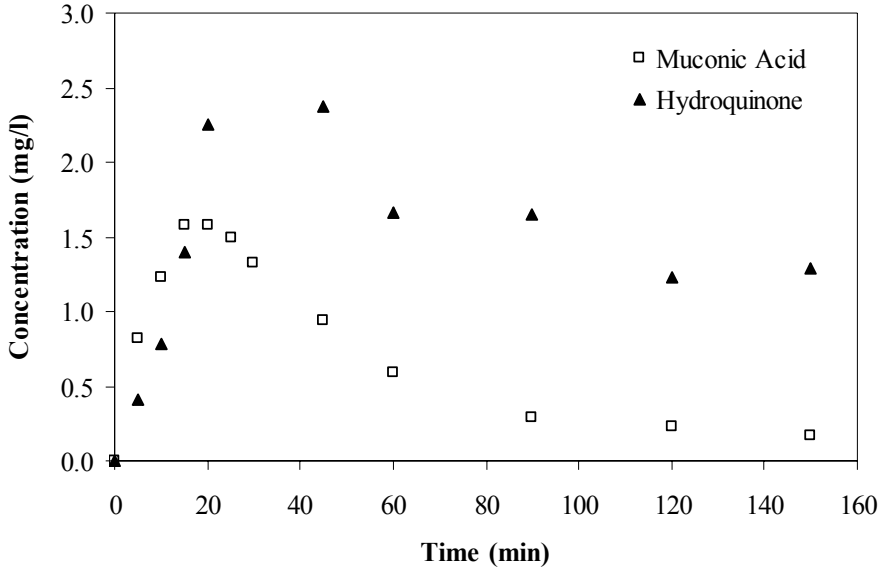


Figure 5.3: Intermediate formation during the phenol oxidation at 3.4 mg/min ozone dosage for P-1a experiment

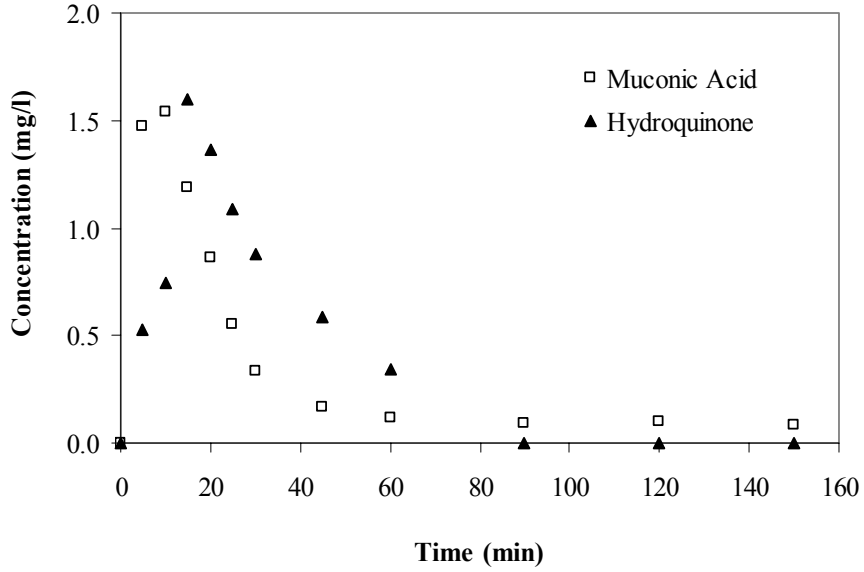


Figure 5.4: Intermediate formation during the phenol oxidation at 13.2 mg/min ozone dosage for P-1b experiment

The removal efficiency of phenol at this time was 81%. The removal efficiency of phenol, when the peak value of hydroquinone reached was higher than the cis, cis-muconic acid reached its peak value. At the end of the 150 minute reaction period this ratios were 0.7% for cis, cis-muconic acid and 5% for hydroquinone.

It should be also necessary to state that the ratios of cis, cis-muconic acid and hydroquinone concentrations to initial phenol concentration, the ratio for hydroquinone should be higher than cis, cis-muconic acid because of the molecular stoichiometry. These higher ratios can be seen more clearly at the peak values reached during the course of oxidation reaction.

The results illustrated in Figure 5.4 for P-1b, peak value of cis, cis-muconic acid concentration was reached at around 10^{th} minutes with the ratio of 7%. For hydroquinone these values are 15^{th} minute and 7.5%. Although, the concentration levels of cis, cis-muconic acid and hydroquinone, during oxidation time and at the end of the experiment, were lower than the experiments conducted on 3.4 mg/min ozone dosage. During the oxidation period at 60^{th} minute the cis, cis-muconic acid concentration was 0.6 mg/l for 3.4 mg/min and 0.1 mg/l for 13.2 mg/min ozone dosage. At the end of the oxidation period at 3.4 mg/min ozone dosage (P-1a) cis, cis-muconic acid concentration was 1.7 mg/l while it was completely oxidized at 13.2 mg/min ozone dosage (P-1b). The same profile could be also seen for hydroquinone. At 60^{th} minute the hydroquinone concentration was 1.7 mg/l for 3.4 mg/min and 0.3 mg/l for 13.2 mg/min ozone dosage. At the end of the oxidation period at 3.4 mg/min ozone dosage hydroquinone concentration was 1.3 mg/l while it was completely oxidized at 13.2 mg/min ozone dosage.

The determination of intermediate formation by ozonation experiments conducted on P-2, P-3 and P-4 experiments are given in Table 5.2. The ozone dosages were 3.1 for P-2, 3.8 and 3.6 mg/min for P-3 and P-4 respectively. As seen from the table, for higher initial phenol concentrations the intermediate formation profile was the same as the solution containing 25 mg/l phenol. Although, the concentration levels of cis, cis-muconic acid and hydroquinone were changed due to the initial concentration of phenol. The higher initial concentration of phenol the higher concentration of intermediates achieved.

Table 5.2: Concentrations of Intermediates During Phenol Oxidation Experiments

Time (min)	Experiment P-2		Experiment P-3		Experiment P-4	
	Cis, cis-Muconic Acid (mg/l)	Hydroquinone (mg/l)	Cis, cis-Muconic Acid (mg/l)	Hydroquinone (mg/l)	Cis, cis-Muconic Acid (mg/l)	Hydroquinone (mg/l)
Initial	-	-	-	-	-	-
5	0.83	-	1.23	0.89	1.42	0.93
10	1.46	-	2.13	1.90	2.53	1.32
15	1.84	-	2.63	1.50	3.30	1.49
20	2.07	-	3.32	3.04	3.93	2.09
25	2.60	-	3.22	2.15	4.51	2.73
30	2.28	-	3.71	3.87	4.68	2.67
45	2.27	1.02	3.92	-	5.22	4.25
60	2.02	1.69	3.74	4.82	5.02	4.92
90	1.64	2.36	3.02	5.34	4.25	5.72
120	1.26	2.74	2.36	5.51	3.10	6.27
150	0.96	3.16	1.18	4.87	2.25	5.92

The peak values reached for cis, cis-muconic acid were at 45th minute for 75 (P-3) and 100 mg/l (P-4) initial phenol concentrations and the ratio of cis, cis-muconic acid to the initial phenol concentration was approximately 5% for each experiment. Similar to 25 mg/l initial phenol concentration, at these initial concentrations, hydroquinone needed longer time (120th minute) to achieve its peak value. The ratio of hydroquinone concentrations to initial phenol concentrations at this time were 7.5 and 6.4% respectively. Summarized results of concentration of cis, cis-muconic acid and hydroquinone, their maximum concentrations to initial phenol concentration and the time reached to maximum concentrations were given in Table 5.3 and 5.4. The results of the experiment conducted at 13.2 mg/min ozone dosage on solution containing 25 mg/l initial phenol (P-1b) was given in the tables for the evaluation of the effect of higher ozone concentration to oxidation reactions.

Table 5.3: Formation Profiles of Cis, cis-Muconic Acid at pH 3.0

Experiment	Initial Phenol Concentration (mg/l)	Maximum Concentration (mg/l)	Ratio to Initial Phenol Concentration (%)	Time achieved (min)
P-1a	25[1]	1.58	6.0	20
P-1b	25[2]	1.54	7.0	10
P-2	50	2.60	5.0	25
P-3	75	3.92	5.0	45
P-4	100	5.22	5.0	45

[1] Ozone Dose : 3.4 mg/min
[2] Ozone Dose : 13.2 mg/min

Table 5.4: Formation Profiles of Hydroquinone at pH 3.0

Experiment	Initial Phenol Concentration (mg/l)	Maximum Concentration (mg/l)	Ratio to Initial Phenol Concentration (%)	Time achieved (min)
P-1a	25[1]	2.37	10	45
P-1b	25[2]	1.60	7.5	15
P-2	50	3.16	6.2	150
P-3	75	5.51	7.5	120
P-4	100	6.27	6.4	120

[1] Ozone Dose : 3.4 mg/min
[2] Ozone Dose : 13.2 mg/min

As seen from the Table 5.2 and 5.3 for the cis, cis muconic acid, the ratio to initial phenol concentration was decreasing. However after 50 mg/l initial phenol concentration the ratio remained at the same degree. From the results, it could be concluded that the reaction time to reach cis, cis-muconic acid peak value was increasing with the increasing initial phenol concentration but after a certain initial phenol concentration the time needed for reaching the peak value was remained at 45 minutes.

The results that can be seen from the Table 5.3 and 5.4 indicate that increasing the initial phenol concentration resulted a decrease in the ratio of peak concentration to initial phenol concentration. The ratio decreased from 10% to 6.4% for 25 mg/l and 100 mg/l initial phenol concentrations. For the reaction to reach hydroquinone peak value the same conclusion can be made as cis, cis-muconic acid. After a certain initial phenol concentration the time needed for reaching the peak value for hydroquinone was remained at 120 minutes.

5.2.3 TOC removal

The extent of phenol mineralization was determined by monitoring the concentration of organic carbon remaining in solution as phenol was oxidized to CO_2 and H_2O. The mineralization of organic compounds strongly depend on the oxidation conditions, due to this dependence it is also variable. The glyoxal and glyoxylic acid are believed to be major end products of phenol oxidation by ozone and are relatively stable in the presence of ozone (Gould and Weber, 1976; Bailey, 1978; Yamamoto *et al.,* 1979). Continued ozonation of these compounds leads to formation of oxalic acid that is a stable end product and not efficiently oxidized with molecular ozone. According to the TOC measurements during the oxidation experiments and calculated theoretical TOC of phenol and intermediates, a portion of TOC which is attributed to unidentified intermediates and products, increases with ozonation time. Singer and Gurol (1983) studied dynamics of the ozonation of phenol and explained that most of this unresolved TOC consists of products such as formic, glyoxalic and oxalic acids which are assumed to react with ozone at such slow rates at pH 3.0 that will not affect the kinetics of phenol reaction.

Singer and Gurol (1983) claimed that at 140 mg/l initial phenol concentration and at 9 mg/l ozone saturation concentrations, in 16 minutes all of the phenol is oxidized but only 21% of the initial TOC has been removed. They concluded that the remaining 79% of the initial TOC is in the form of intermediates and products such as glyoxal. They also reported that at the end of 2 hr ozonation period, only 50% of TOC was removed at pH 3.0 (ozone saturation concentration : 7 mg/l; mass-transfer coefficient : 43 1/hr).

In this part of the study, mineralization pathway of phenol by ozone oxidation under acidic conditions was studied. For this purpose the theoretical TOC levels of selected initial phenol concentrations were considered as an important parameter.

The TOC removal results of P-1a and P-1b experiments are given in Table 5.5. As seen from the table, For 3.4 mg/min ozone dosage (P-1a) the TOC removal efficiencies were under 5% for the first 30 minutes. In this oxidation period the mineralization cannot be seen through the high formation rate of intermediates. The removal efficiency was 7.4% at 45th minute and this can be attributed to oxidation of cis, cis-muconic acid. After the complete removal of phenol and the hydroquinone peak concentration was past, further ozonation caused an increase of approximately 19% at 150 min. This increase can be associated by the oxidation of the intermediates and slow mineralization of end products.

For experiment P-1b, for the first 20 minutes the TOC removal efficiencies were under 10%. After the complete removal of phenol, which was achieved at 30th minute (Figure 5.1), TOC removals were started to increase likely due to the oxidation of intermediates. At the end of the 150 minute reaction period the TOC removal efficiency was around 40% which represent a significant degree of mineralization. At the end of the oxidation period cis, cis-muconic acid and hydroquinone were oxidized completely and more stable products remained in the system. For further ozonation longer than 150 minutes, TOC removal and removal rate is expected to be at a lesser degree.

Table 5.5: TOC Removal at Different Ozone Dosages for 25 mg/l Initial Phenol Concentration

Time (min)	Experiment P-1a TOC Concentration (mg/l) (Ozone Dosage : 3.4 mg/min)	Experiment P-1b TOC Concentration (mg/l) (Ozone Dosage : 13.2 mg/min)
Initial	16.93	16.14
5	16.67	15.65
10	16.69	15.38
15	16.52	15.37
20	16.29	14.70
25	16.15	14.21
30	16.11	13.36
45	15.67	12.89
60	15.18	11.84
90	13.72	10.37
120	13.13	9.86
150	12.4	9.71

Table 5.6 shows the TOC measurements during the oxidation experiments of synthetic phenol solutions containing 50, 75 and 100 mg/l initial phenol. The ozone dosages were 3.1 for P-2, 3.8 and 3.6 mg/min for P-3 and P-4 respectively. The TOC removals for these systems were around 10% at the end of the reaction time of 150 minute.

For 50 mg/l initial phenol concentration at the 30th minute oxidation time the TOC removal efficiency was 2% where the cis, cis-muconic acid reached its peak concentration. For further ozonation the TOC removals increased presumably due to the mineralization of cis, cis-muconic acid oxidation products. This observation was also in agreement with the TOC profiles of P-3 and P-4 experiments. The time for cis, cis-muconic acid to reach its peak concentration was 45 minutes for these experiments. However, like 50 mg/l initial phenol concentration experiment (P-2) the TOC removal efficiencies were only 2% and removals started to increase after 45 minutes oxidation period that can be related to the cis, cis-muconic acid oxidation. As can be seen from the Table 5.2 the time to reach hydroquinone peak values for 50, 75 and 100 mg/l initial phenol concentrations was around 120 minutes. For the oxidation of hydroquinone and its products and as a consequence to achieve higher TOC removals, the oxidation duration should be longer than 150 minutes.

Table 5.6: Results of TOC Measurements at Different Initial Phenol Concentrations

Time (min)	Experiment P-2	Experiment P-3	Experiment P-4
	TOC (mg/l)	TOC (mg/l)	TOC (mg/l)
Initial	39.66	55.56	73.99
5	40.25	55.41	73.95
10	39.97	55.15	73.75
15	39.61	55.27	73.64
20	39.46	55.08	73.74
25	39.53	55.04	73.46
30	39.37	55.16	73.28
45	38.65	54.5	72.72
60	38.33	53.98	71.94
90	37.42	52.87	70.36
120	36.17	51.24	68.43
150	35.3	50.83	66.30

As an overall conclusion the intermediates formed by the oxidation processes although the mineralization could be an indication of the intermediates removal. While the removal rate of intermediates increased as a consequence the mineralization yields increase.

The calculated specific ozone consumption values were 0.022 and 0.006 mg TOC removed / mg O_3 consumed for experiments P-1a and P-1b. For experiments P-2, P-3 and P-4 the calculated values were 0.024, 0.012 and 0.024 mg TOC removed / mg O_3 consumed respectively. Specific ozone consumption rate was highly dependent on ozone dosage. For approximately the same ozone dosages, the values were close to each other. However since the TOC removals were limited the specific ozone consumption values can not be obtained in an accurate way. A detailed evaluation of consumption values can be obtained if all substrates and intermediates are measured against ozone consumption for each reaction period.

5.2.4 Ozone concentration in solution

In order to be able to analyze the nature and the kinetics of the oxidation systems, the reactions between organic compounds and dissolved ozone should be assessed. According to the determination of the rate constants of the molecular ozone-organic compound and the predictions for kinetic modeling of the oxidation systems it was necessary to determine experimentally the organic compound, intermediates and ozone profiles. Legube *et al.* (1987), proposed a molecular mechanism indicating the importance of contact time, pH and dissolved ozone concentration on the rate of reactions. With these intentions this part of the study id devoted to analyze the dissolved ozone concentration profiles during the course of oxidation reaction.

Gurol and Singer (1983) investigated dynamic of the ozonation of phenol and developed an explicit mathematical model which described the rate of change in the concentration of phenol and ozone in an ozone contactor at a low pH. They concluded that, according to the predictions of model, the system is mass-transfer limited as long as phenol is present in the solution, and the ozone concentration in the bulk solution would be very small until the phenol essentially disappeared. Thereafter they concluded that dissolved ozone concentration would increase and approach its saturation value.

Beltrán *et al.* (1994) studied advanced oxidation of atrazine in water. They stated that the concentration of dissolved ozone increases with time, only for a few minutes, until reaching a stationary value. They also indicated that in any case the most noticeable fact, the presence of dissolved ozone, suggests that the ozonation of atrazine, regardless the mechanism is a set of slow gas-liquid reactions.

Singer and Gurol (1983), investigated dynamics of the ozonation of phenol and they concluded that dissolved ozone concentration should begin to increase when phenol, muconic acid and the other unidentified reactive intermediates were completely oxidized. They also indicated that, the observed appearance of dissolved ozone after 15 minutes for their experimental study was in accordance with this expectation.

In this study in order to analyze the nature and the kinetics of the oxidation reaction between molecular ozone and phenol and to establish a kinetic modeling, dissolved ozone profile was determined experimentally.

Dissolved ozone concentration profiles of P-1a and P-1b experiments at 3.4 and 13.2 mg/min ozone dosages are given in Figure 5.5. Dissolved ozone profiles of 25 mg/l initial phenol concentration should be analyzed individually because of the difference in the course of the reaction mechanism of the system. As seen from the figure, concentration of dissolved ozone began to increase from the beginning of oxidation reaction. It has a peak value at a certain time which could be attributed to the profile of phenol and intermediate concentration during the course of the reaction. Peak values of dissolved ozone concentrations were at the time that phenol was completely oxidized for both ozone dosages and than started to decrease for further oxidation periods. For 3.4 mg/min ozone dosage the peak value of dissolved ozone was reached at 90^{th} minute. At this oxidation time phenol was removed completely. For 13.2 mg/min ozone dosage the peak value of dissolved ozone was reached at 45^{th} minute and like 3.4 mg/min phenol was oxidized completely at this oxidation time. The peak value of dissolved ozone reached at ozone dosage 13.2 mg/min was approximately two times higher than that of 3.4 mg/min ozone dosage. It should be also stated that the cis, cis-muconic acid and hydroquinone were considerably removed than the concentrations that they had at their peak value.

Figure 5.6 shows the dissolved ozone measurements during the oxidation experiments of P-2, P-3 and P-4. The ozone dosages were 3.1 for P-2, 3.8 and 3.6 mg/min for P-3 and P-4 experiments respectively. As depicted in figure, peak values were at the time of 45 minute and the phenol removal efficiencies were between 35-40%. At this oxidation time it should be stated that the cis, cis-muconic acid was started to oxidize at this oxidation period during the course of the reaction but the hydroquinone was still forming through the reaction between molecular ozone and phenol for all initial phenol concentrations.

Dissolved ozone concentrations increase with the increasing initial phenol concentration (Figure5.6). For experiment P-2 the peak value of dissolved ozone concentration was 3.01 mg/l. For P-3 and P-4 experiments peak values were 3.34 and 3.67 mg/l, respectively. During the course of the reaction, after peak values reached, dissolved ozone concentrations started to decrease upon further ozonation and reached a stationary concentration at around 2.0 mg/l. The phenol concentrations were under 10 mg/l for each experiment at the end of 150 minute reaction time.

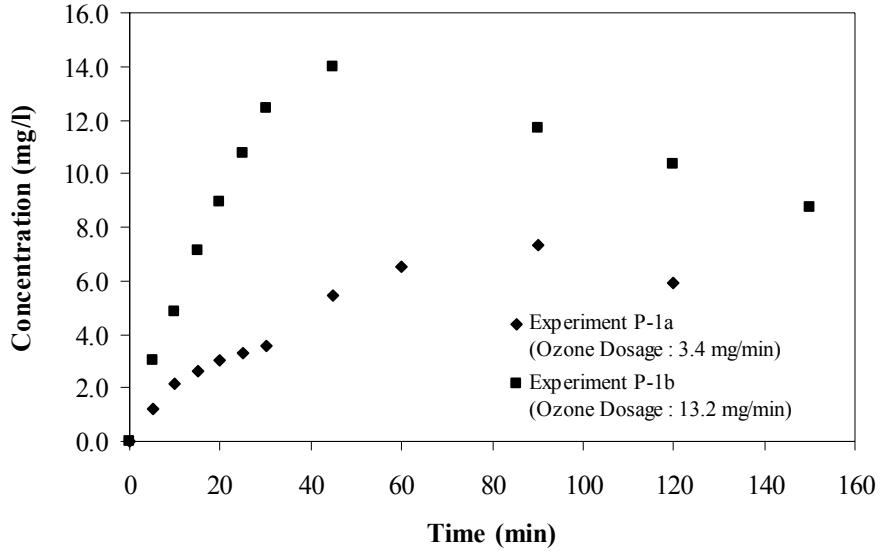


Figure 5.5: Dissolved ozone profile experiment P-1a and P-1b

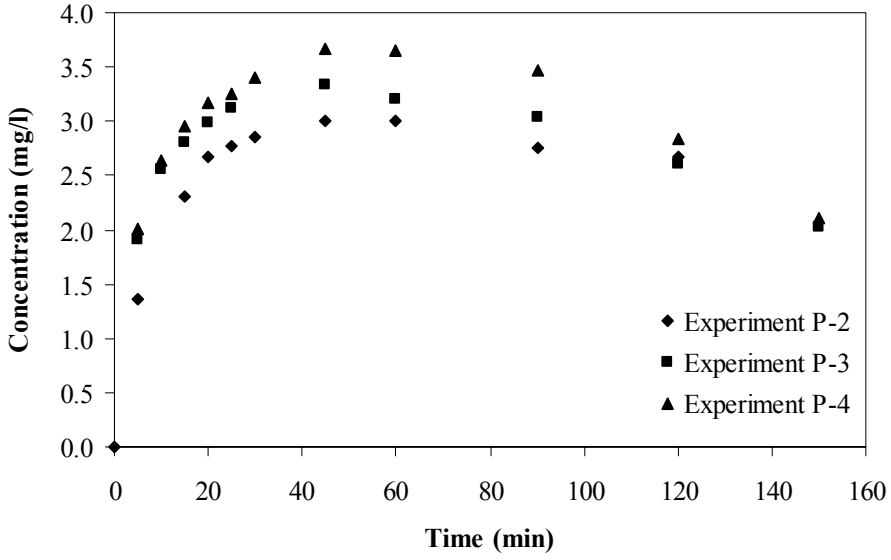


Figure 5.6: Dissolved ozone profile for different concentrations of initial phenol

5.3 Bentazone Experiments

5.3.1 Bentazone removal

Ozone has an ability to oxidize various organic contaminants in water. It is very effective for the oxidation of polyaromatic hydrocarbons such as naphthalene, anthracine and hydroxylated aromatics (Hoigné and Bader, 1983a). Investigation conducted on bentazone ozonation in aqueous solution can help to elucidate the chemical mechanisms involved in the oxidation by ozone, N and S containing heterocyclic compounds. In this subsection the bentazone ozonation process characterized from the chemical point of view. This could disclose new opportunities of water pollution research, which also include the treatment of nitrogen and sulphur containing pesticides and herbicides.

Oxidation experiments of bentazone were conducted on synthetic solutions containing 4 different initial bentazone concentrations at pH 3.0 to investigate the oxidation of bentazone by molecular ozone. The experiment conducted on the solutions containing 25, 50, 75 and 100 mg/l initial bentazone concentrations, named as B-1a and b, B-2, B-3 and B-4 respectively. Ozone was continuously bubbled into the reactor. Samples were taken at time intervals to analyze the removal pattern of bentazone under acidic conditions (pH:3.0).

The removal pattern of solution containing 25 mg/l initial bentazone by molecular ozone at two different levels of applied ozone dosages is presented in Figure 5.7 (B-1a and B-1b). The ozone dosages used for experiments B-1a and B-1b were 3.8 and 13.0 mg/min respectively. The results of the experiments revealed that ozonation provided complete bentazone oxidation for both ozone dosages. For 3.8 mg/min ozone dosage the complete bentazone removal observed at 30th minute, increasing the ozone dosage decrease the complete oxidation time to 10th minute. The calculated $C*t$ values were 113 and 129 mg for experiments B-1a and B-1b respectively. As can be seen from the results, increasing the applied ozone dosage did not significantly affect the $C*t$ values. Further studies are needed to be done for the evaluation of the relationship between the applied ozone dosage and the reaction time.

The effect of initial bentazone concentration on oxidation reaction is represented in Figure 5.8. The ozone dosages were 3.3 mg/min for experiment B-2, 3.9 and 4.3 mg/min for experiments B-3 and B-4. As seen from the figure at first 20 minutes

removal efficiencies were over 50%. The complete removal was achieved at the of the 60 minutes reaction time. A remarkable reactivity of bentazone toward ozone is observed in the light of these experiments.

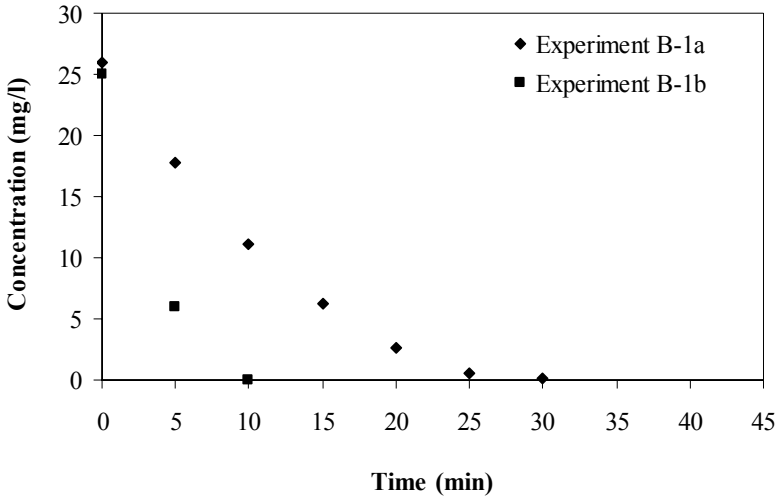


Figure 5.7: Removal of bentazone by ozonation at different ozone dosages

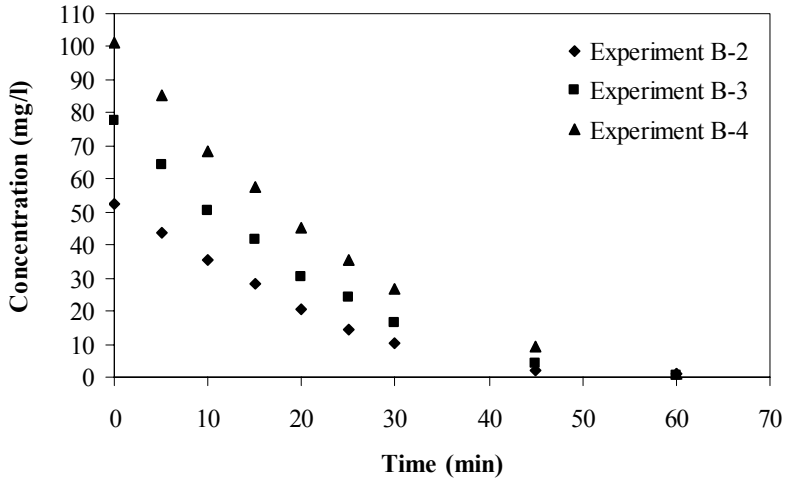


Figure 5.8: Removal of bentazone by ozonation at different initial bentazone concentrations

These experimental results are in agreement with the results reported by other investigators who have also observed comparable oxidation level of nitrogen containing heterocyclic organic compounds. Andreozzi *et al.* (1992) investigated quinoline ozonation in aqueous solution. They reported that the complete oxidation of quinoline was reached in 125 minutes with an initial concentration of 775 mg/l and at pH 1.8. The ozonation of metol (*N*-Methyl-*P*-Aminophenol) containing

solution has been studied by Andreozzi *et al.* (2000). They pointed out that a complete disappearance of the substrate was observed in all the cases, they studied, after an ozonation time approximately 20 minutes.

5.3.2 Intermediate formation

Ozonation is able to oxidize inorganics and organics to their oxidation states, depending on the molecular selectivity and decay rates (Hung, 1994) and it rarely produces complete mineralization to CO_2 and H_2O, but leads to partial oxidation products such as organic acids, aldehydes and ketones where oxygen is introduced into many of the carbonaceous sites within the product molecules (Gerald, 1994).

As also discussed in Section 3 and Subsection 5.2.2 to reveal the true oxidation mechanism of organic compounds, intermediates and their affects to the removal pattern and reaction kinetics should be taken into account. Therefore, to understand the true mechanism of bentazone oxidation and to evaluate the process kinetics, the formation of intermediates should be evaluated.

The purpose of this subsection was to understand the main oxidation pathway and to evaluate the oxidation mechanism and oxidation rate of bentazone with molecular ozone under acidic conditions. Therefore during course of the oxidation the intermediate formation should be taken into account.

Analyses of the reaction mixture by HPLC indicated that a group of intermediates are produced during the oxidation reaction between bentazone and molecular ozone. The HPLC results showed that phenol and cis, cis-muconic acid were some of the intermediates produced during the oxidation reaction. The suggested oxidation pathway by ozone is given in Figure 5.9. This scheme has been developed based on measured components which were indicated in the figure in bold letters as well as basic information on the ozone reactions of organic compounds.

The phenol and cis, cis-muconic acid formation during bentazone oxidation at different ozone dosages for synthetic solution containing 25 mg/l bentazone are presented in Figures 5.10 and 5.11. For experiment B-1a, phenol peak value reached at 10^{th} minute and its concentration was 1.27 mg/l at 3.8 mg/min ozone dosage. For 13.0 mg/min ozone dosage (B-1b) the phenol peak value reached at 5^{th} minute and its concentration was 1.21 mg/l. The ratio of maximum phenol concentrations reached to initial bentazone concentration was 5% for both experiments. The ozone dosage

affects the oxidation time to reach the peak value of phenol; the reached concentrations were approximately same for both ozone dosages.

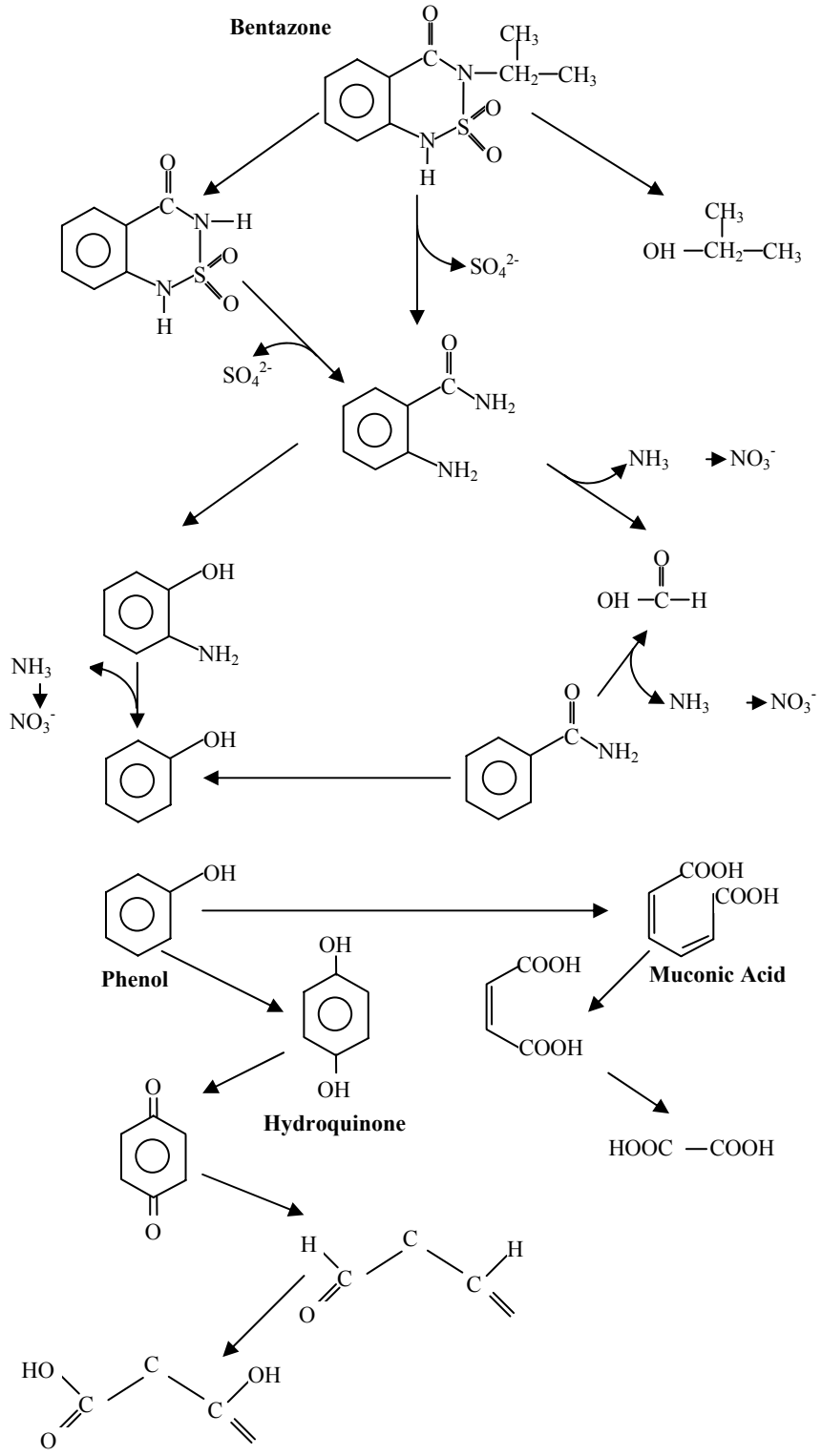


Figure 5.9: The suggested oxidation pathway of bentazone by ozone

For cis, cis-muconic acid, the formation profile is given in Figure 5.11. For experiment B-1a at 3.8 mg/min ozone dosage cis, cis-muconic acid started to form after 15 minutes and after 5 minutes at 13.0 mg/min ozone dosage. The peak values were also different for the applied ozone dosage. The peak concentrations are 0.28 and 0.49 mg/l for 3.8 and 13.0 mg/min ozone dosage. As seen from the figure, increasing the ozone dosage causes an increase in peak concentration and a decrease in time to reach this peak concentration.

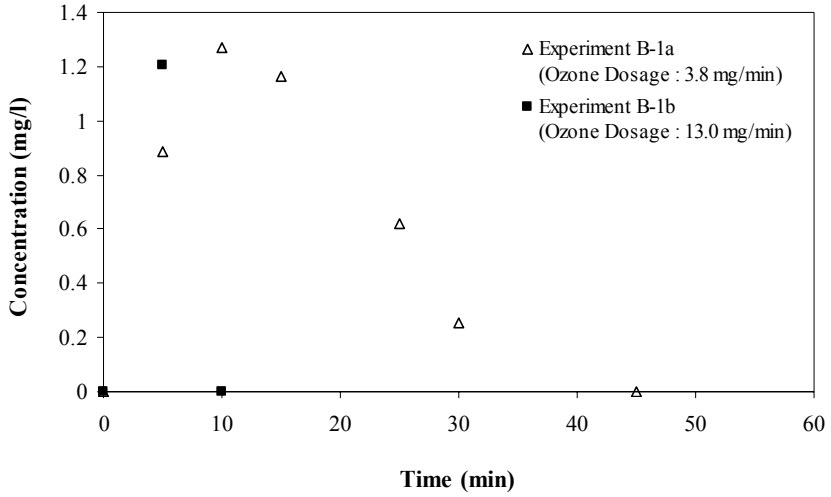


Figure 5.10: Phenol formation during the oxidation of solution containing 25 mg/l bentazone

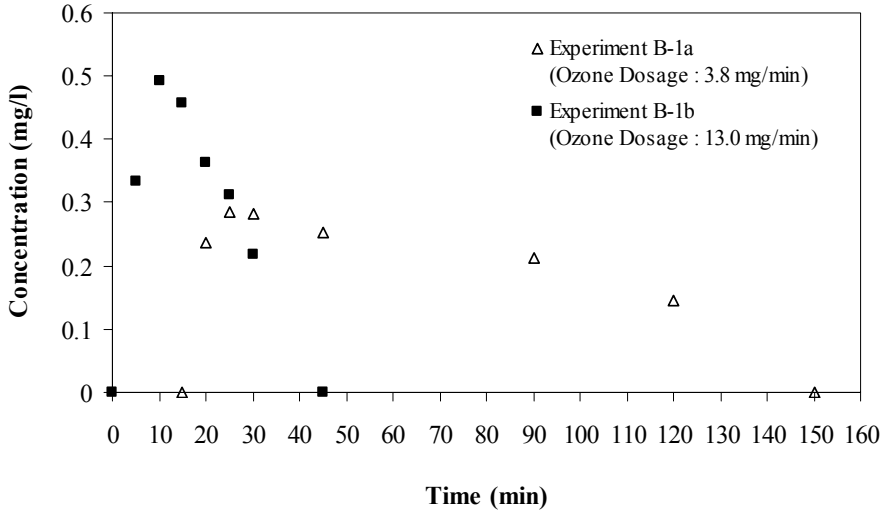


Figure 5.11: Cis, cis-muconic acid formation during the oxidation of solution containing 25 mg/l bentazone

For higher initial bentazone concentrations intermediate concentration profiles can be seen more clearly. It should be also evaluated the removal pattern of phenol during oxidation reaction of bentazone with ozone. The complete removal was achieved 45 minutes at this ozone dosage while it was 10 minutes for 13.0 mg/min. For cis, cis-muconic acid the complete removal was at the end of the 150 minutes oxidation period for 3.8 mg/min while it was 45 minutes at 13.0 mg/min ozone dosage. It could be also said as a conclusion to increase the ozone dosage at the oxidation of bentazone by ozone the formed intermediates needed longer times for the complete removal.

Figure 5.12 illustrated the phenol formation during the bentazone oxidation by ozone for experiments B-2, B-3 and B-4. The results presented in this figure indicated that phenol was one of the important intermediates that measured in the reaction mixture and its formation and removal should be considered for kinetic evaluation. As seen from the figure, for higher initial bentazone concentrations the phenol formation profile was similar to the solution containing 25 mg/l initial bentazone, although, the concentration level of phenol was changed due to the initial concentration of bentazone. The higher initial concentration of bentazone the higher concentration of phenol achieved as an intermediate.

The peak values reached for phenol were between 20-30 minutes for 50, 75 and 100 mg/l initial bentazone concentrations and the ratio of phenol to the initial bentazone concentration was 1.7% for 50 mg/l, 5.1 and 5.6% for 75 and 100 mg/l initial bentazone concentration. The time needed for the complete removal of phenol increased as the initial bentazone concentration was increased.

Ozonation causes changes in the structures of organic compounds. As the structure of organic compound changes, the nature of the reaction that occurs between organic compound, in this situation bentazone, and ozone changes as well. Therefore the formation mechanism of cis, cis-muconic acid in this reaction system needs to be considered accurately. Cis, cis-muconic acid could be formed from the oxidation of phenol, unidentified intermediates and/or bentazone itself. The concentration profile of cis, cis-muconic acid at different initial bentazone concentrations are given in Figure 5.13.

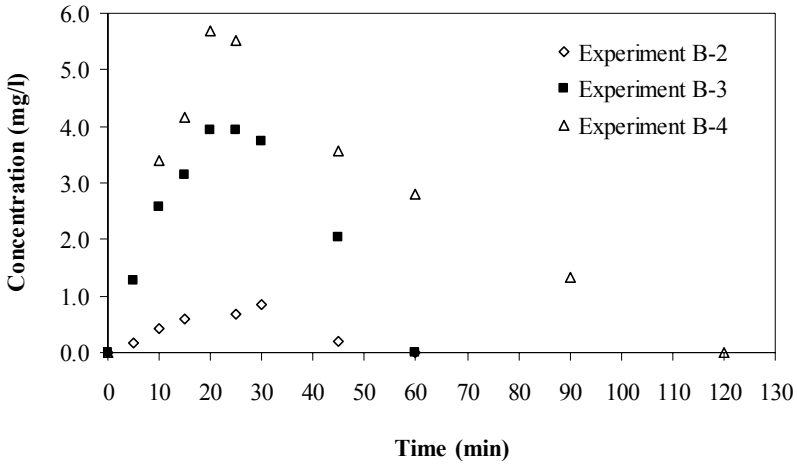


Figure 5.12: Phenol formation during the bentazone oxidation at different initial bentazone concentrations

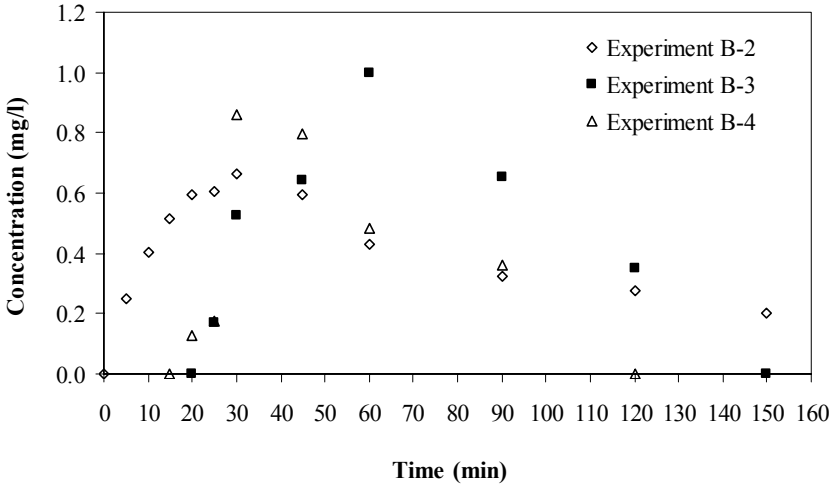


Figure 5.13: Cis, cis-muconic Acid formation during the bentazone oxidation at different initial bentazone concentrations

The measured intermediate concentrations during the bentazone oxidation at each reaction period are given in Table 5.7. Summarized results of concentration of phenol and cis, cis-muconic acid, their maximum concentrations to initial bentazone concentration and the time reached to maximum concentrations were given in Table 5.8 and 5.9. The results of the experiments conducted on solution containing 25 mg/l initial bentazone at 13.0 mg/min ozone dosage were given in the tables for the evaluation of the affect of higher ozone concentration to formation of intermediates.

Table 5.7: Concentrations of Intermediates During Bentazone Oxidation Experiments

Time (min)	Experiment B-2		Experiment B-3		Experiment B-4	
	Cis, cis-Muconic Acid (mg/l)	Phenol (mg/l)	Cis, cis-Muconic Acid (mg/l)	Phenol (mg/l)	Cis, cis-Muconic Acid (mg/l)	Phenol (mg/l)
Initial	0	0		0		
5	0.25	0.17		1.28		0
10	0.40	0.43		2.58		3.39
15	0.51	0.59		3.13	0	4.17
20	0.59	-	0	3.94	0.13	5.70
25	0.60	0.68	0.17	3.95	0.18	5.51
30	0.66	0.86	0.52	3.75	0.86	5.51
45	0.59	0.20	0.64	2.03	0.80	3.56
60	0.43	0	1.0	0	0.48	2.81
90	0.32		0.65		0.36	1.33
120	0.28		0.35		0	0
150	0.20		0			

Table 5.8: Formation Profiles of Phenol at pH 3.0

Experiment	Initial Bentazone Concentration (mg/l)	Maximum Concentration (mg/l)	Ratio to Initial Bentazone Concentration (%)	Time achieved (min)
B-1a[1]	25	1.27	4.8	10
B-1b[2]	25	1.21	4.8	5
B-2	50	0.86	1.7	30
B-3	75	3.95	5.1	25
B-4	100	5.70	5.6	20

[1] Ozone Dose : 3.8 mg/min
[2] Ozone Dose : 13.0 mg/min

Table 5.9: Formation Profiles of Cis, cis-Muconic Acid at pH 3.0

Experiment	Initial Bentazone Concentration (mg/l)	Maximum Concentration (mg/l)	Ratio to Initial Bentazone Concentration (%)	Time Achieved (min)
B-1a[1]	25	0.28	1.1	25
B-1b[2]	25	0.49	1.9	10
B-2	50	0.66	1.2	30
B-3	75	0.99	1.3	60
B-4	100	0.86	1.0	30

[1] Ozone Dose : 3.8 mg/min
[2] Ozone Dose : 13.0 mg/min

5.3.3 TOC removal

In this part of the study, mineralization pathway of bentazone by ozone oxidation under acidic conditions was studied. For this purpose the theoretical TOC levels of selected initial bentazone concentrations were considered an important parameter.

Similar to phenol oxidation, TOC measurements during the oxidation experiments and calculated theoretical TOC of bentazone and intermediates, the portion of TOC which is attributed to unidentified intermediates and products, increases with ozonation time. At the end of the 120 minute the TOC removal efficiencies for 3.8 and 13.0 mg/min applied ozone dosages, for experiments B-1a and B-1b, were 22 and 27% respectively (Table 5.10).

As seen from the table, for 3.8 mg/min ozone dosage the TOC removal efficiency was 12% for the 30^{th} minute where the complete removal of bentazone achieved. The removal efficiency was 22% at 120^{th} minute and this can be attributed to oxidation of phenol, cis, cis-muconic acid and other unidentified intermediates.

For 13.0 mg/min ozone dosage, after the complete removal of bentazone, which was achieved at 10^{th} minute the TOC removal efficiency was 13%. For further ozonation periods TOC removals were started to increase likely due to the oxidation of intermediates. At the end of the 120 minute reaction period the TOC removal

efficiency was 27%. At the end of the oxidation period cis, cis-muconic acid and phenol were oxidized completely and more stable products remained in the system.

The TOC concentration during the ozonation experiments conducted on 50, 75 and 100 mg/l initial bentazone concentrations (B-2, B-3 and B-4) are presented in Table 5.11. The ozone dosages were 3.3 mg/min for experiment B-2, 3.9 and 4.3 mg/min for experiment B-3 and B-4 respectively.

Table 5.10: TOC Removal at Different Ozone Dosages for 25 mg/l Initial Bentazone Concentration

Time (min)	Experiment B-1a TOC Concentration (mg/l) (Ozone Dosage : 3.8 mg/min)	Experiment B-1b TOC Concentration (mg/l) (Ozone Dosage : 13.0 mg/min)
Initial	10.67	10.90
5	10.11	10.15
10	10.06	9.51
15	9.85	9.15
20	9.76	9.08
25	9.72	8.91
30	9.43	8.88
45	9.32	8.63
60	8.93	8.41
90	8.72	8.26
120	8.36	7.98

Similar to experiments conducted on 25 mg/l initial bentazone concentration, TOC removals were around 12% after the complete removal of bentazone achieved at 60th minute. For further ozonation TOC removals were started to increase likely due to the oxidation of intermediates. The TOC removals for these systems were 17% for experiment B-2, 18% for experiment B-3 and 16% for experiment B-4 at the end of the reaction time of 120 minute.

Table 5.11: Results of TOC Measurements at Different Initial Bentazone Concentrations

Time (min)	Experiment B-2	Experiment B-3	Experiment B-4
	TOC (mg/l)	TOC (mg/l)	TOC (mg/l)
Initial	27.54	36.05	49.74
5	27.07	35.61	48.25
10	26.81	35.20	48.03
15	26.38	34.92	47.06
20	26.34	34.55	46.93
25	25.61	34.26	46.44
30	25.22	33.58	45.65
45	24.45	32.80	44.43
60	23.98	31.74	43.09
90	23.39	31.14	42.88
120	22.96	29.59	41.88

The calculated specific ozone consumption values for single oxidation of bentazone were 0.011 and 0.003 mg TOC removed / mg O_3 consumed for experiments B-1a and B-1b. For experiments B-2, B-3 and B-4 the calculated values were 0.024, 0.025 and 0.022 mg TOC removed / mg O_3 consumed, respectively. Similar to single phenol experiments as can be seen from the results the specific ozone consumption rate was highly dependent on ozone dosage. For approximately the same ozone dosages, the values were similar. However since the TOC removals were limited the specific ozone consumption values can not be obtained in an accurate way. For an accurate determination of specific ozone consumption rates all substrates and intermediates could be measured against ozone consumption for each reaction period.

5.3.4 Ozone concentration in solution

In order to be able to analyze the nature and the kinetics of the oxidation systems, it was necessary to determine experimentally the organic compound, intermediates and ozone profiles. With these intentions this part of the study is devoted to analyze the nature and the kinetics of the oxidation reaction between molecular ozone and bentazone and to establish a kinetic modeling, dissolved ozone profile was determined experimentally during the course of oxidation reaction.

Dissolved ozone concentration profiles of 25 mg/l bentazone solution at 3.8 and 13.0 mg/min ozone dosages are given in Figure 5.14. Dissolved ozone profiles should be analyzed individually because of the difference in the course of the reaction mechanism of the system for 25 mg/l initial bentazone concentration. As seen from the figure, concentration of dissolved ozone began to increase from the beginning of oxidation reaction. It has a peak value at a certain time and than started to decrease for further oxidation periods.

For 3.8 mg/min ozone dosage the peak value of dissolved ozone was reached at 45^{th} minute. At this oxidation time bentazone was removed completely. For this ozone dosage phenol was reached its peak value at 10^{th} minute, for further ozonation it started to oxidize by dissolved ozone and completely removed at 45^{th} minute (Figure 5.10). However cis, cis muconic acid started to form at 15^{th} minute and reached its peak value at 25^{th} minute. During the oxidation period cis, cis-muconic acid consumed dissolved ozone for further oxidation (Figure 5.11).

For 13.2 mg/min ozone dosage the peak value of dissolved ozone was reached at 30th minute. Bentazone was oxidized completely at 10th minute oxidation time. Phenol was reached its peak value at 5th minute and completely removed at 10th minute for this ozone dosage. However cis, cis-muconic acid started to form from the beginning of the oxidation period. Its peak value was reached at 10th minute and completely removed at 45th minute. The peak value of dissolved ozone reached at ozone dosage 13.0 mg/min was approximately two times higher than that of 3.8 mg/min ozone dosage.

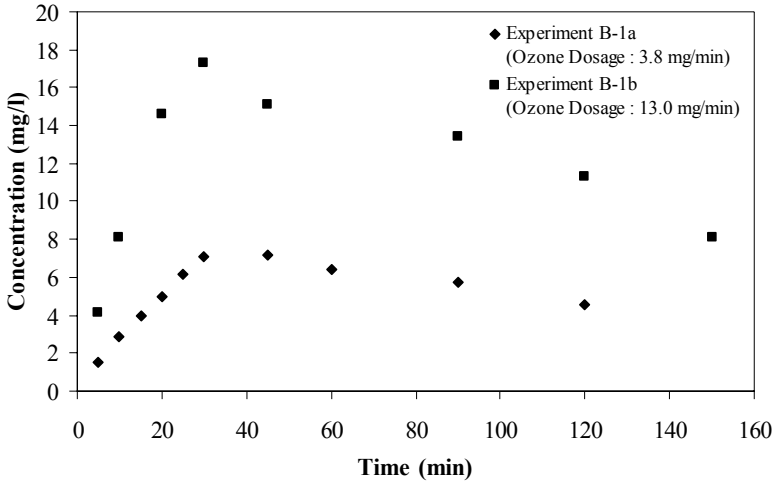


Figure 5.14: Dissolved ozone profile during the bentazone oxidation at two different ozone dosage for 25 mg/l initial bentazone concentration

Figure 5.15 shows the dissolved ozone measurements during the oxidation experiments of B-2, B-3 and B-4. The ozone dosages were 3.3 mg/min for experiment B-2, 3.9 and 4.3 mg/min for experiments B-3 and B-4 respectively.

As delineated in the figure, dissolved ozone peak value for 50 mg/l initial bentazone concentration (B-2) was at the time of 45 minute. Bentazone was removed completely at this oxidation period. It should be also stated that phenol was started to oxidize at 30th minute and removed completely at 60th minute. At the same time, cis, cis-muconic acid was started to oxidize at 30th minute oxidation period.

For experiment B-3 (75 mg/l) dissolved ozone peak concentration was reached at 60th minute. Phenol was removed completely at this oxidation time while cis, cis-muconic acid achieved its peak value. After this oxidation time it should be stated that the cis, cis-muconic acid was started to oxidize during the course of the reaction (Figure 5.12, 5.13).

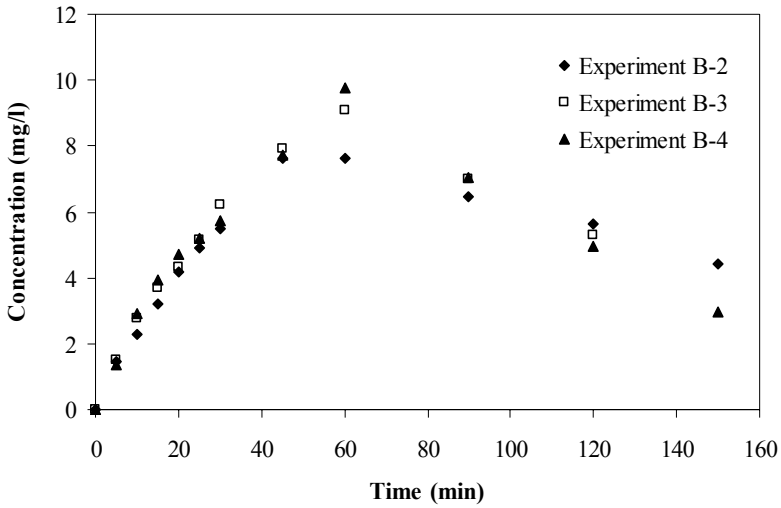


Figure 5.15: Dissolved ozone profile for different concentrations of initial bentazone

For 100 mg/l initial bentazone concentration (B-4) dissolved ozone maximum concentration was achieved at 60th minute. It should be indicated that phenol and cis, cis-muconic acid were consuming dissolved ozone during the oxidation reactions.

Dissolved ozone concentrations increase with the increasing initial bentazone concentration (Figure 5.15). For experiment B-2 the peak value of dissolved ozone concentration was 7.64 mg/l. For experiments B-3 and B-4 peak values were 9.08 and 9.75 mg/l, respectively. During the course of the reaction, after peak values reached, dissolved ozone concentrations started to decrease upon further ozonation. The decrease in the dissolved ozone concentration can be attributed to the further ozonation of the unidentified intermediates and slowly reacting end products.

5.4 Mixture Experiments

For a better understanding of ozone oxidation process and process kinetics of organic compounds oxidation by molecular ozone under acidic conditions the process needs to be analyzed when they are alone and in combination in the aqueous medium. For this purpose in the following subsections, the evaluation of organic compounds oxidation by ozone was investigated experimentally as they exist in mixture in the aqueous medium. For analyzing the mechanism of multiple substrate oxidation systems, organic compound removal, intermediate formation and removal, TOC removal pattern and dissolved ozone concentration in the solution were investigated experimentally.

The experimental results evaluated and compared with the results determined from the oxidation experiments conducted on single organic compound removal systems and with the literature data. For a better comparison and evaluation of the system, phenol and bentazone concentrations in the mixture samples were selected similar to single oxidation systems and several combinations were prepared to analyze better the system behavior. The selected initial phenol - bentazone concentrations and TOC levels of the mixture samples are given in Table 5.12.

Table 5.12: Initial concentrations and theoretical TOC levels of mixture samples

Experiment	Initial Phenol Concentration (mg/l)	Initial Bentazone Concentration (mg/l)	TOC Concentration (mg/l)
M-1	75	75	95
M-2	75	25	70
M-3	50	50	63
M-4	50	25	51
M-5	25	75	57
M-6	25	50	44
M-7a[1]	25	25	31
M-7b[2]	25	25	31

[1] Ozone dosage : 3.4 mg/min
[2] Ozone dosage : 12.6 mg/min

5.4.1 Results of experiment M-1

In Subsection 5.2.1 phenol removal in single oxidation systems was investigated and reported in detail for 75 mg/l initial concentration (Experiment P-3). For the experiment M-1, the initial phenol and bentazone concentrations were selected as 75 mg/l and applied ozone dosage was 3.4 mg/min. The removal of phenol and bentazone are represented in Figure 5.16.

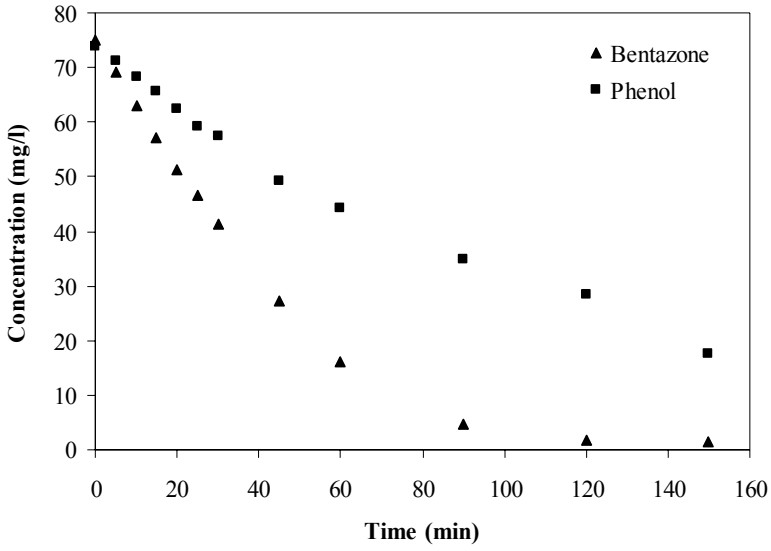


Figure 5.16: Removal of phenol and bentazone at M-1 experiment by ozonation

In this set of the experiment a steady removal pattern was observed for both phenol and bentazone. First 45 minutes of oxidation process, the phenol removal rate was similar to experiment P-3. The removals were 33% for M-1 and 36% for P-3 experiments. However, after 45 minutes, phenol removal rate decreased as compared to single oxidation of phenol. At 60^{th} minute oxidation time phenol concentrations were 49.3 for experiment M-1 and 37.9 for experiment P-3. At the end of the oxidation period of 120 minutes, remaining phenol concentrations were 28.4 and 15 mg/l for experiments M-1 and P-3 respectively.

As shown in Figure 5.16 the bentazone oxidation occurred in parallel to phenol oxidation. The comparison can be made between the bentazone concentrations during the course of the M-1 oxidation and single oxidation of the 75 mg/l initial bentazone oxidation (B-3) experiments. The basic profile was the clear decrease in the removal rate of bentazone in M-1 experiment. The removal rate of bentazone slowed down with a smooth pattern during the oxidation period of M-1. 50% removal efficiency was observed between 30-45 minutes for M-1 while it was between 15-20 minutes for experiment B-3. The complete removal was achieved at 60 minutes for experiment B-3 however, 79% removal was observed for experiment M-1 at 60^{th} minute

It is necessary to clarify the decrease at removal rates of phenol and bentazone in mixture systems. As it was also stated in literature, solution pH, dissolved ozone concentration and intermediate formation have influence on removal rates of organic compounds. pH has an important effect on removal rate of organic compounds, to avoid this influence at the mixture experiments the pH was kept constant and equal with those of single oxidation systems during the oxidation reactions. In this context, the dissolved ozone in solution and intermediate concentration profiles are analyzed to examine the nature and the kinetics of the bentazone and phenol oxidation in mixture systems.

The decreases at bentazone and phenol removal rates can be explained as follows.

As discussed in Subsections 5.2.4 and 5.3.4 dissolved ozone concentration has a great importance on the rate of reactions between molecular ozone and organic compounds. The measured concentrations of dissolved ozone in mixture systems evaluated and compared with single bentazone and phenol oxidation results.

The dissolved ozone concentration profile for M-1 experiment is given in Figure 5.17. As seen from the figure the dissolved ozone concentrations were over than 2 mg/l during the whole oxidation period. The dissolved ozone concentration was adequate during the oxidation period.

The dissolved ozone concentrations for experiment M-1 were higher than that measured for the same initial bentazone and phenol concentrations at single oxidation experiments (B-3 and P-3). The maximum dissolved ozone concentration was reached at 60th minute and its level was 8.8 mg/l. For experiments P-3 and B-3 these values were 45 minutes, 3.3 mg/l and 60 minutes, 9.1 mg/l respectively. The same level or an increase in the dissolved ozone concentration can affect the removal rates, as acceleration. However, the removal rates of both phenol and bentazone were decelerated. From the comparison of measured dissolved ozone concentrations in the solution for single and mixture experiments, it can be concluded that the decrease in bentazone and phenol removal rates cannot be attributed to the dissolved ozone concentrations in solution.

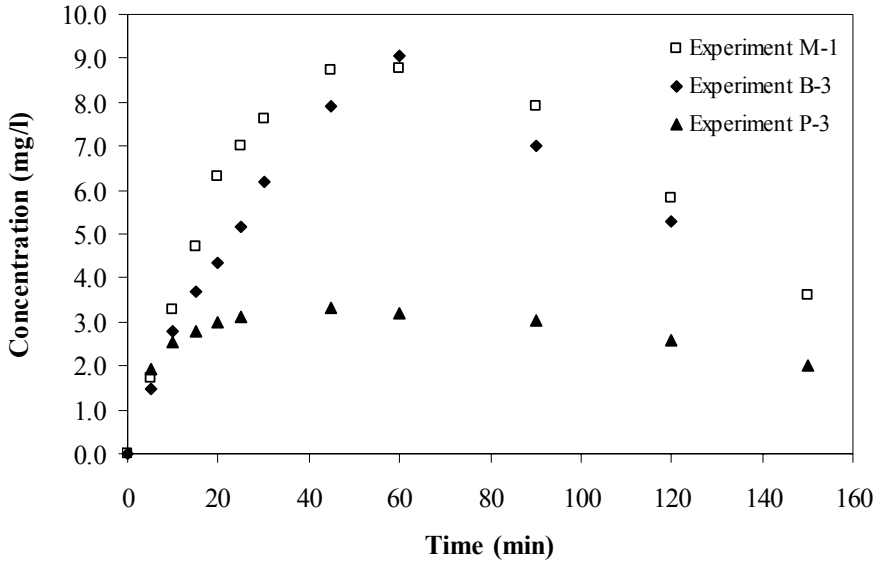


Figure 5.17: Dissolved ozone profile during the mixture and single oxidation experiments

As discussed in detail in Subsections 5.2.2 and Subsection 5.2.3 for the design of an oxidation process and to reveal the true oxidation mechanism of organic compounds alone and in combination it is quite helpful to monitor the formation and removal of intermediates during the course of the reaction.

For the oxidation of phenol by molecular ozone, Bailey (1972) proposed that the electrophilic attack of ozone to phenol molecule leads to formation of hydroxylated products, catechol and hydroquinone, as major intermediates. On the other hand, 1,3 dipolar cyclo addition of ozone causes direct ring-cleavage of phenol to produce cis, cis-muconic acid or muconaldehyde Most of the authors reported that cis, cis-muconic acid and hydroquinone were produced in relatively large amounts during the oxidation of phenol (Singer and Gurol, 1983; Mvula and von Sonntag, 2003).

From analyses of the reaction mixture by HPLC showed that a group of intermediates are produced between the reaction of bentazone by molecular ozone at acidic conditions (pH 3.0). The HPLC results showed that phenol and cis, cis-muconic acid were two important intermediates produced during the oxidation reaction.

With these conclusions, hydroquinone and cis, cis-muconic acid, were chosen to be monitored over the course of the mixture experiments. During the ozone oxidation at mixture experiments, the maximum concentrations of the intermediates formed and their ratios to initial phenol and bentazone concentrations (mg/mg) were measured and evaluated.

The concentration profiles of cis, cis-muconic acid and hydroquinone at 75 mg/l initial bentazone and phenol concentration (M-1) are given in Figure 5.18.

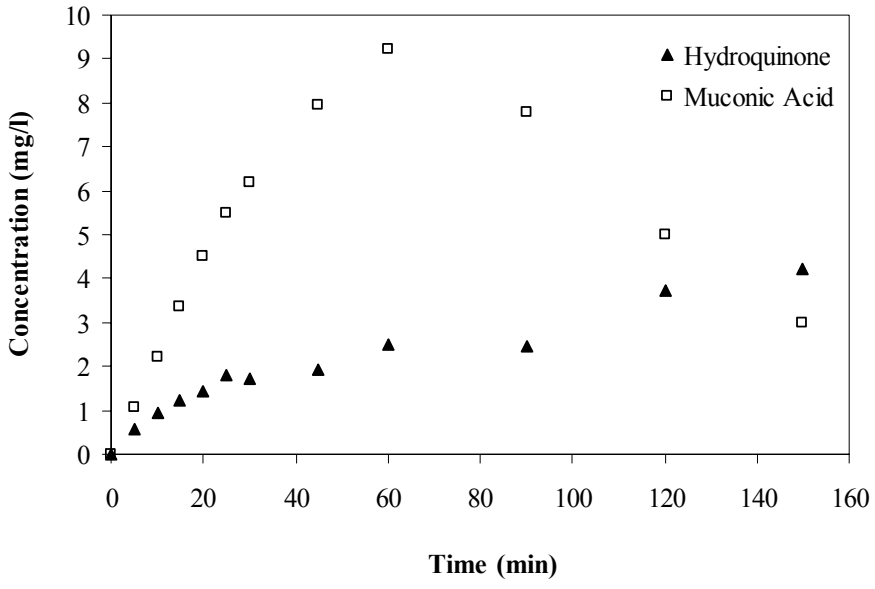


Figure 5.18: Concentration profiles of formed intermediates (M-1)

The peak value reached for cis, cis-muconic acid was at 60th minute and the concentration was 9.2 mg/l for M-1 experiment. The ratio of cis, cis-muconic acid to the initial phenol concentration was approximately 12%. The concentration profile of cis, cis muconic acid at the same initial phenol concentration at single oxidation experiment (P-3) was given previously in Table 5.2. The cis, cis-muconic acid peak value observed at 45th minute at the concentration of 3.9 mg/l and the ratio of cis, cis-muconic acid to the initial phenol concentration was approximately 5% for experiment P-3.

A significant increase was observed in the peak concentration of cis, cis muconic acid. The cis, cis-muconic acid peak concentration observed for experiment B-3 was around 1 mg/l at 60th minute. As seen from the results this concentration increase cannot be due to formation of cis, cis-muconic acid from the bentazone oxidation in the M-1 experiment.

As noted previously, the phenol removal rate was similar to the experiment P-3 for first 45 minutes. After 45 minutes, phenol removal rate was decreased compared to single oxidation of phenol. This decrease cannot be explained by the influence of the bentazone oxidation to the phenol removal rate. The bentazone concentrations were 27 mg/l for 45 minute, 16 and 4.5 mg/l for 60 and 90 minutes respectively and the bentazone concentrations were not at high level to cause this decrease in phenol removal rate. At the same time the removal rate of bentazone slowed down with a smooth pattern during the oxidation period of M-1.

Therefore, the explanation of the decrease in phenol removal rate can be made by considering the effect of accumulation of intermediates. In mixture experiments M-1, it was observed that the difference between the formation rate and the oxidation rate of intermediates are different from that of experiment P-3. Thus, the peak concentration of the cis, cis-muconic acid in experiment M-1 was higher than observed for single oxidation experiment of phenol at the same initial concentration. This accumulation of cis, cis-muconic acid was assumed to affect the reduction rate of phenol. For the mixture experiment M-1, this reduction was prominent for phenol after 45th minute. As seen from the Figure 5.18, cis, cis-muconic acid started to reduce after 60 minutes and this pattern had an effect at the oxidation system to decrease the phenol removal rate. As noted before, bentazone reduction was decelerated from the beginning of the experiment M-1. This deceleration can be

explained by the parallel oxidation of phenol and cis, cis-muconic acid oxidation. The concentration of cis, cis-muconic acid was over 2 mg/l at the 10th minute oxidation period and did not decrease under this point at the whole oxidation period for experiment M-1. The concentration of cis, cis-muconic acid was around 1 mg/l for the same initial bentazone concentration at single oxidation experiment (B-3). This high level of cis, cis-muconic acid concentration during the oxidation period had a retarding effect on bentazone removal rate in the experiment M-1 due to the parallel oxidation of cis, cis-muconic acid.

As an overall conclusion, the main reason of decreasing the oxidation rate of phenol was figured out as the accumulation and the preferential oxidation of cis, cis-muconic acid. The decrease at removal rate of bentazone can also be attributed to the high concentration of cis, cis-muconic acid from the beginning of the oxidation reaction and the parallel oxidation of phenol and cis, cis-muconic acid.

In this part of the study, for evaluation of multiple substrate oxidation systems by ozone under acidic conditions, mineralization pattern of mixture solutions was studied.

As noted before, the mineralization of organic compounds strongly depends on the oxidation conditions; due to this dependence it is also variable. The glyoxal and glyoxylic acid are believed to be major end products of phenol oxidation by ozone and are relatively stable in the presence of ozone (Gould and Weber, 1976; Bailey, 1978; Yamamoto *et al.*, 1979).

Singer and Gurol (1983) claimed that at 140 mg/l initial phenol concentration and at 9 mg/l ozone saturation concentrations, in 16 minutes all of the phenol is oxidized but only 21% of the initial TOC has been removed. They concluded that the remaining 79% of the initial TOC is in the form of intermediates and products such as glyoxal.

Table 5.13 shows the TOC measurements during the experiment M-1. The ozone dosage was 3.4 mg/min. The TOC removal for this system was around 12% at the end of the reaction time of 150 minute.

The removed TOC concentration was 10.65 mg/l at the end of the oxidation period of 120 minutes of experiment M-1 and this amount of TOC removal can be accepted as a significant level of mineralization. At the end of the 120 minutes for experiment M-1 the amount of removed TOC was approximately the same as the sum of P-3 and B-3 at 120 minutes. However in the 45th minute TOC removal in experiment M-1 was

higher than the sum of TOC removals of experiments P-3 and B-3. The calculated specific ozone consumption value for experiment M-1 was 0.034 mg TOC removed / mg O_3 consumed. The calculated specific ozone consumption value was approximately the same as the sum of P-3 and B-3.

Table 5.13: Results of TOC Measurements at Experiment M-1

Time (min)	Experiment M-1
	TOC (mg/l)
Initial	94.23
5	93.15
10	93.00
15	92.51
20	92.14
25	92.07
30	90.17
45	88.99
60	85.58
90	84.53
120	83.58
150	82.91

5.4.2 Results of experiment M-2

For the experiment M-2 the initial phenol and bentazone concentrations were selected as 75 and 25 mg/l respectively. The applied ozone dosage was 3.8 mg/min for the experiment. The removals of phenol and bentazone are illustrated in Figure 5.19.

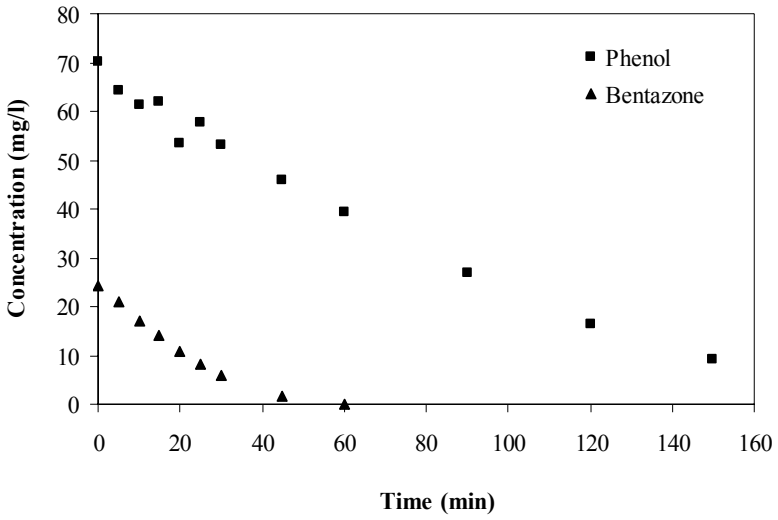


Figure 5.19: Removal of phenol and bentazone at M-2 experiment by ozonation

In a similar manner to M-1, in this set of mixture experiment, for first 45 minutes a parallel pattern was seen between M-2 and single phenol oxidation experiment of the same initial concentration (P-3). The phenol removal was 34% for M-2 and 36% for experiment P-3. After 45 minutes a slight slowing down of the rate of phenol oxidation

can be seen. For further ozonation at 60th minute oxidation time the phenol concentrations were 39.3 for M-2 and 37.9 for single oxidation experiment. At the end of the oxidation period of 120 minutes, remaining phenol concentration for M-2 was 16.3 and it was 15 mg/l for experiment P-3. A similar decrease can also be seen in the removal rate of bentazone in experiment M-2. The complete bentazone removal was observed at 20th minute for single oxidation of bentazone of 25 mg/l initial concentration (B-1a). However, in experiment M-2, the time needed for complete removal increased to 60 minutes. 50% removal efficiency was observed between 15-20 minutes for M-2 while it was between 5-10 minutes for experiment B-1a.

In Figure 5.20 the dissolved ozone concentration profile for M-2 experiment is given. As seen from the figure, after 5 minutes the dissolved ozone concentration reached 2 mg/l and remained over 2 mg/l during the whole oxidation period. As a result of dissolved ozone profile of experiment M-2, the decrease in removal rates cannot be related to the limitation of dissolved ozone concentrations in the solution.

As can bee seen from the figure, the dissolved ozone concentrations for experiment M-2 were higher than that measured for the same initial bentazone and phenol concentrations at single oxidation experiments. The maximum dissolved ozone concentration for experiment M-2 was reached at 30th minute and its level was 8.2 mg/l. For single oxidation experiment for phenol and bentazone these values were 45 minutes, 3.3 mg/l and 45 minutes, 7.2 mg/l respectively.

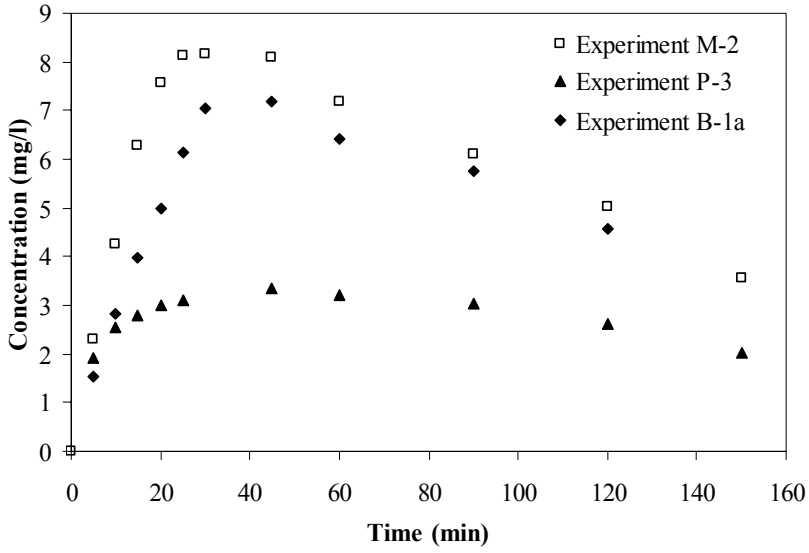


Figure 5.20: Dissolved ozone profile during the experiment M-2 and single oxidation experiments

The same hypothesis as with M-1 can be made for experiment M-2 from the results of measured dissolved ozone concentrations in the solution. For mixture oxidation experiment of M-2, the decreases in removal rates of phenol and bentazone cannot be attributed to the dissolved ozone concentrations in the solution

The concentration profiles of cis, cis-muconic acid and hydroquinone at 75 mg/l initial phenol and 25 mg/ initial bentazone concentration (M-2) are given in Figure 5.21.

The peak value reached for cis, cis-muconic acid was at 45th minute and the concentration was 4.9 mg/l for M-2 experiment. The ratio of cis, cis-muconic acid to the initial phenol concentration was approximately 7%. The concentration profile of cis, cis muconic acid at the same initial phenol concentration at single oxidation experiment (P-3) was given previously in Table 5.2. The cis, cis-muconic acid peak value observed at 45th minute at the concentration of 3.9 mg/l and the ratio of cis, cis-muconic acid to the initial phenol concentration was approximately 5%.

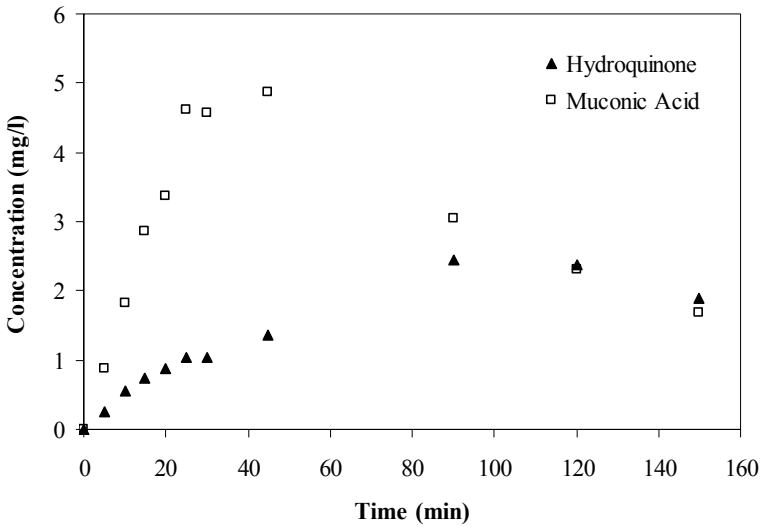


Figure 5.21: Concentration profiles of formed intermediates (M-2)

The cis, cis-muconic acid peak concentration observed for single oxidation of 25 mg/l initial bentazone experiment (B-1a) was less than 0.5 mg/l during the oxidation period. As seen from the results, the cis, cis-muconic acid concentration increase in mixture experiment of M-2 cannot be attributed to the formation of cis, cis-muconic acid from the bentazone oxidation.

At this point a comparison of M-1 and M-2 would be useful. The general characteristics of the oxidation of phenol and bentazone are quite similar in the

experiments M-1 and M-2. In experiment M-2 variation of the measured phenol concentrations were consistent with the experiment P-3 for first 45 minutes. This consistency cannot be seen in experiment M-1 where the differences between mixture and single oxidation rates were more pronounced for first 45 minutes. After 45 minutes, phenol removal rate decreased as compared to single oxidation of phenol. Although, this decrease was not as high as that was observed for experiment M-1. The remained phenol concentrations at the end of the 150 minutes reaction period for experiments M-1 and M-2 were 17.5 and 9.2 mg/l respectively. As seen from the results, this can be associated with lower bentazone concentration.

In mixture experiment M-2, the difference between the formation rate and the oxidation rate of intermediates was less redundant than with the comparison to M-1 experiment. The reason for this was low concentration of bentazone in experiment M-2. Thus the peak concentration and the accumulation of the cis, cis-muconic acid in experiment M-2 was less than observed for experiment M-1.Concurrently bentazone removal rate was also decreased due to the high level of cis, cis-muconic acid concentration. In experiment M-2 2 mg/l cis, cis muconic acid concentration was reached at 10^{th} minute oxidation period and it was over this concentration during the time that bentazone removed completely. Similar with experiment M-1, it can be concluded that the bentazone removal rate was decreased as a result of the parallel oxidation of phenol and cis, cis-muconic acid.

Table 5.14 shows the TOC measurements during the experiment M-2. The TOC removal for this system was around 18% at the end of the reaction time of 150^{th} minute.

For experiment M-2, the removed TOC was 8.45 mg/l at the end of the oxidation period of 120 minutes while the same oxidation duration, the sum of removed TOC of single oxidation experiments of P-3 and B-1a was 6.63 mg/l. The level of removed TOC in experiment M-2 was almost equal to the sum of removed TOC level of experiments P-3 and B-1a at 45^{th} minute. After 45^{th} minute the removed TOC was started to increase in comparison with single oxidation experiments. The calculated specific ozone consumption value was 0.035 mg TOC removed / mg O_3 consumed for experiment M-2 while they were 0.012 and 0.011 mg TOC removed / mg O_3 consumed for experiments P-3 and B-1a respectively.

Table 5.14: Results of TOC Measurements at Experiment M-2

Time (min)	Experiment M-2
	TOC (mg/l)
Initial	70.10
5	70.06
10	69.40
15	69.30
20	68.07
25	67.90
30	-
45	67.70
60	66.50
90	63.30
120	61.65
150	57.31

5.4.3 Results of experiment M-3

For the experiment M-3 the initial phenol and bentazone concentrations were selected as 50 mg/l and the applied ozone dosage was 4.0 mg/min. The removals of phenol and bentazone are given in Figure 5.22.

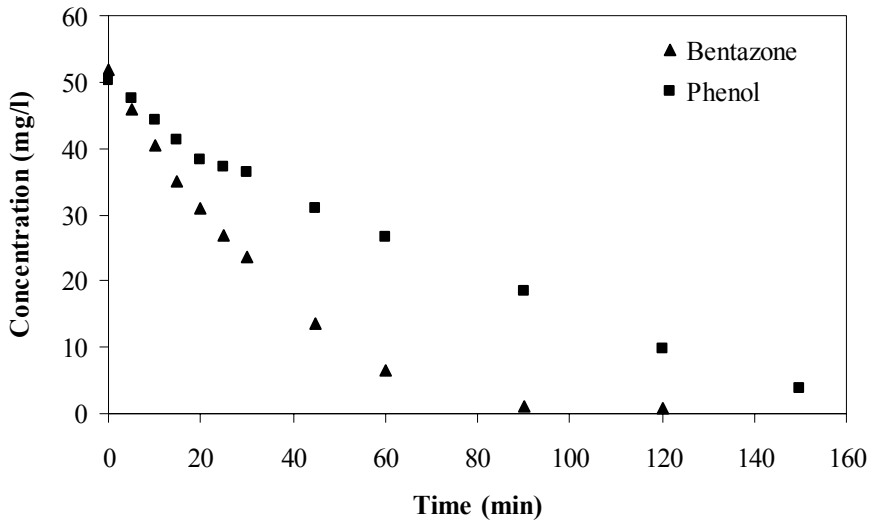


Figure 5.22: Removal of phenol and bentazone at M-3 experiment by ozonation

In this set of mixture experiment, for first 45 minute a slight increase in the phenol oxidation followed by slowing down the rate of oxidation in a quite similar manner to those of M-1 and M-2. The phenol removals at 45th minute were 38% and 41% for experiment M-3 and experiment P-2 (50 mg/l initial phenol) respectively. For further ozonation at 60th minute oxidation time the phenol concentrations were 26.7 for M-3 and 24.2 for experiment P-2. At the end of the oxidation period of 150 minutes,

remained phenol concentrations were 3.9 and 2.1 mg/l for experiment M-3 and experiment P-2, respectively.

The complete bentazone removal was observed at 60th minute for single oxidation of bentazone at 50 mg/l initial concentration (B-2). However, in experiment M-3, the time needed for complete removal increased to 90 minutes. A similar time difference in mixture and corresponding single substrate experiment has also been observed for M-1 and M-2. This difference can be attributed to the initial concentration of phenol and also to intermediate formation.

The dissolved ozone concentration profile of M-3 experiment is delineated in Figure 5.23. The profile had a different pattern with compared to experiments M-1 and M-2. In this set of mixture experiment the measured dissolved ozone concentrations were lower than those measured for single bentazone oxidation experiment. The measured dissolved ozone concentrations in experiment M-3 would affect the removal rates of phenol and bentazone. However the dissolved ozone concentrations were over 2 mg/l during the whole oxidation period. The peak concentration reached at 45th minute and its value was 4.4 mg/l.

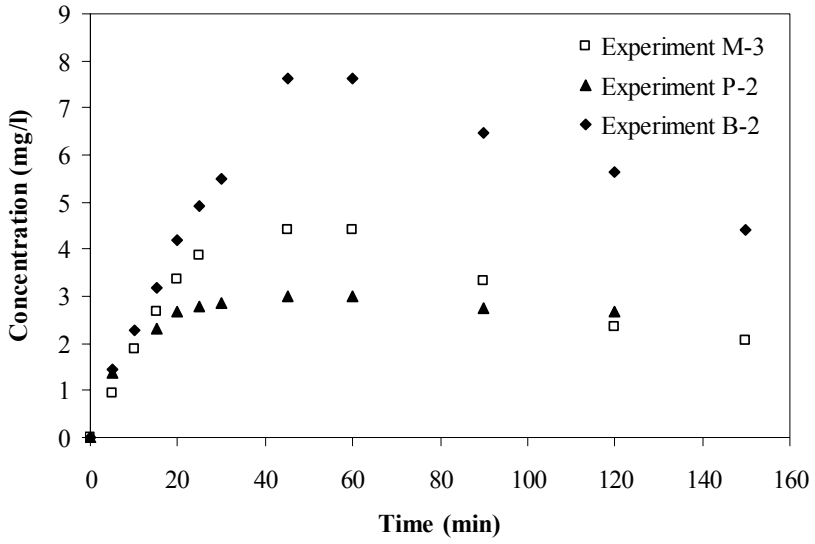


Figure 5.23: Dissolved ozone profile during the experiment M-3 and single oxidation experiments

The concentration profiles of cis, cis-muconic acid and hydroquinone at 50 mg/l initial phenol and 50 mg/ initial bentazone concentration (M-3) are given in Figure 5.24.

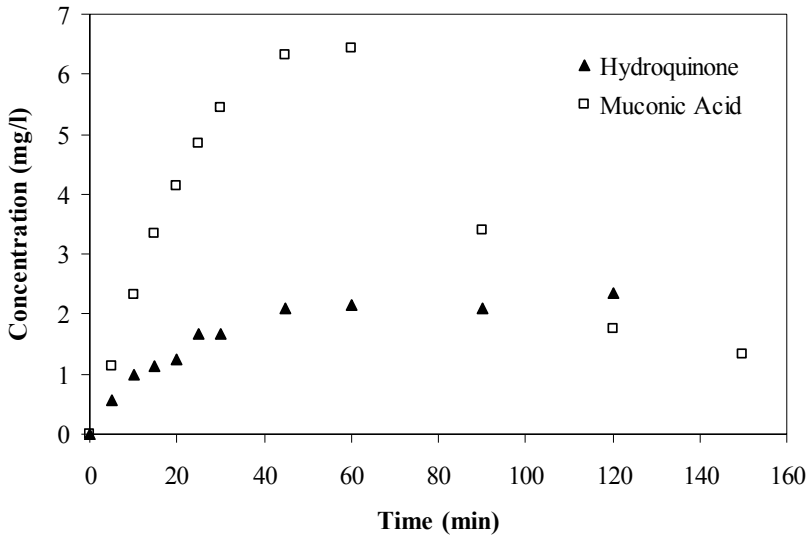


Figure 5.24: Concentration profiles of formed intermediates (M-3)

The peak value reached for cis, cis-muconic acid was at 60th minute and the concentration was 6.4 mg/l for M-3 experiment. The ratio of cis, cis-muconic acid to the initial phenol concentration was approximately 13%. The time reached its peak value and the ratio were similar to experiment M-1. However the peak concentration of cis, cis- muconic acid was lower than that detected for experiment M-1 due to the lower concentration of phenol. The cis, cis-muconic acid peak value observed for experiment P-2 was 2.6 mg/l and the ratio of cis, cis-muconic acid to the initial phenol concentration was approximately 5% at 25th minute (Table 2).

The cis, cis-muconic acid peak concentration observed for experiment M-3 was approximately 2.5 times higher than that observed for experiment P-2. The cis, cis-muconic acid concentration increase in mixture experiment of M-3 cannot be attributed to the formation of cis, cis-muconic acid from the bentazone oxidation because its concentration was less than 0.7 mg/l during the oxidation period at experiment B-2.

An evaluation of experimental results of M-1, M-2 and M-3 can be made as follows; in a quite similar manner to those of M-1 and M-2 the phenol removal rate decreased after 45 minutes. The explanation of this tendency can be made using the hypothesis applied for the cases of M-1 and M-2. However, the reduction in phenol oxidation rate following 45 minutes is less pronounced due to the fact that lower initial concentration of phenol with respect to M-1 and M-2 so having lower concentration of intermediates. The remaining phenol concentration at the end of the 150 minutes

was 3.9 mg/l for experiment M-3 while it was 9.2 mg/l for experiment M-2. This remaining phenol concentration difference between experiment M-2 and M-3 can be attributed to the lower concentration of phenol and as well as the lower accumulation of intermediates that decreases the removal rate of phenol oxidation.

Table 5.15 shows the TOC measurements during the experiment M-3. The TOC removal for this system was about 12% at the end of the reaction time of 150 minute.

Table 5.15: Results of TOC Measurements at Experiment M-3

Time (min)	Experiment M-3
	TOC (mg/l)
Initial	66.87
5	66.33
10	65.57
15	65.46
20	65.12
25	64.86
30	64.81
45	63.47
60	62.64
90	60.24
120	59.50
150	58.83

For experiment of M-3 the removed TOC concentration was 3.4 mg/l at the 45^{th} minute. At this time the sum of removed TOC of the single oxidation experiments of P-2 and B-2 was 4.1 mg/l. Similar character was also observed for 120^{th} minutes, the removed TOC concentration was 7.37 mg/l at the 120^{th} minute for experiment M-3 while the sum of removed TOC was 8.07 mg/l for experiments P-2 and B-2. The calculated specific ozone consumption value was 0.026 mg TOC removed / mg O_3 consumed for experiment M-3 and it was close to values which were calculated for single oxidation experiments of P-2 and B-2.

5.4.4 Results of experiment M-4

For the experiment M-4 the initial phenol and bentazone concentrations were selected as 50 and 25 mg/l respectively. The applied ozone dosage was 4.0 mg/min. The removals of phenol and bentazone are given in Figure 5.25.

For first 45^{th} minute the same compatibility was detected for experiment M-4 and P-2. The phenol removals at 45^{th} minute were 38% and 41% for experiment M-4 and experiment P-2 (50 mg/l initial phenol) respectively. From the results of further oxidation, it can be said that the reduction in the phenol oxidation was insignificant

than those observed in experiments M-1 and M-2. At the end of the oxidation period of 150 minutes, the remaining phenol concentrations were 2.3 and 2.1 mg/l for experiment M-4 and experiment P-2. As can be seen from the remaining phenol concentrations, the initial bentazone concentration of 25 mg/l did not affect the phenol oxidation in the experiment M-4.

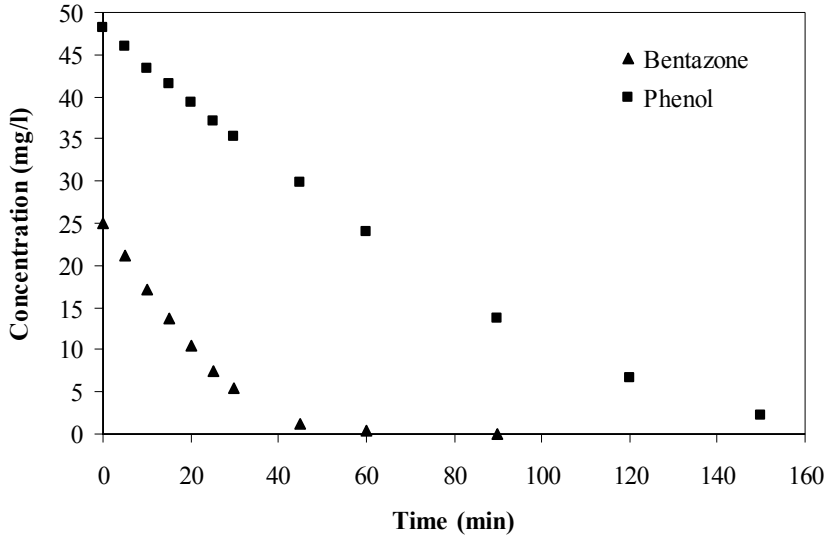


Figure 5.25: Removal of phenol and bentazone at M-4 experiment by ozonation

In this set of the mixture experiment the bentazone oxidation pattern was similar to experiment M-2. The initial bentazone concentrations were 25 mg/l for each experiment. The decrease at initial phenol concentration from 75 mg/l to 50 mg/l did not affect the removal rate of bentazone in the mixture solution. The same decrease in bentazone removal rate was also seen in experiment M-4. The complete bentazone removal was seen at 20th minute for experiment B-1a while it was increased up to 60 minutes for experiment M-4 which was also similar to experiment M-2.

The dissolved ozone concentration profile of M-4 experiment is represented in Figure 5.26. The profile had a similar pattern to experiment M-3. Similar to experiment M-3, the measured dissolved ozone concentrations in experiment M-4 were lower than that measured for experiment B1-a. The same conclusion can be made similar to experiment M-3, this lower dissolved ozone concentrations would decrease the removal rates of phenol and bentazone in mixture experiment of M-4. The measured peak concentration of dissolved ozone was 4.5 mg/l and it was reached at 30th minute. However, 2 mg/l dissolved ozone concentration was observed at 10th minute and it remained over this concentration during the whole oxidation period.

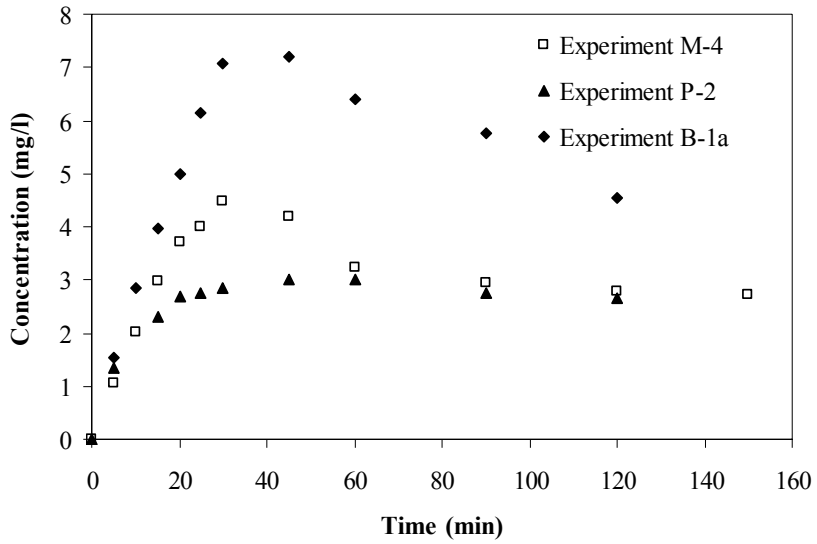


Figure 5.26: Dissolved ozone profile during the experiment M-4 and single oxidation experiments

The intermediate formation during the M-4 experiment is given in Figure 5.27. In the experiment M-4, the peak value observed for cis, cis-muconic acid was at 30th minute and the concentration was 4.8 mg/l. The ratio of cis, cis-muconic acid to the initial phenol concentration was approximately 10%. The observed peak value was similar to experiment M-2. It can be said that reducing the phenol concentration down to 50 mg/l did not affect the cis, cis-muconic acid peak concentration. The measured peak value of cis, cis-muconic acid was observed as 2.6 mg/l for experiment P-2 was and the ratio of cis, cis-muconic acid to the initial phenol concentration was approximately 5% at 25th minute (Table 2).

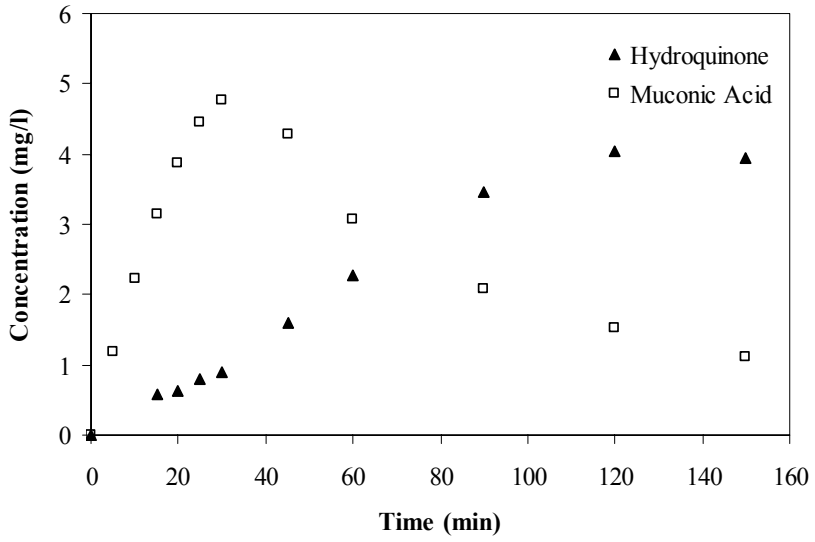


Figure 5.27: Concentration profiles of formed intermediates (M-4)

The cis, cis-muconic acid concentration formed from the bentazone oxidation in experiment B-1a was less than 0.3 mg/l during the oxidation period. This high level cis, cis muconic acid concentration cannot be originating from bentazone oxidation.

Table 5.16 shows the TOC measurements during the experiment M-4. The TOC removal for this system was around 11% at the end of the reaction time of 150 minute.

Table 5.16: Results of TOC Measurements at Experiment M-4

Time (min)	Experiment M-4
	TOC (mg/l)
Initial	53.79
5	54.07
10	53.42
15	52.97
20	53.13
25	52.52
30	51.86
45	51.39
60	50.64
90	49.51
120	47.87
150	47.86

The removed TOC concentrations obtained for experiment M-4 and single oxidation experiments of P-2 and B-1a were similar (2.4 mg/l) at the 45^{th} minute. The same character was also observed for 120^{th} minutes, the removed TOC concentration was 5.92 mg/l at the 120^{th} minute for experiment M-4 while the sum of removed TOC was 5.8 mg/l for the single oxidation experiments. The calculated specific ozone consumption value for experiment M-4 was 0.015 mg TOC removed / mg O_3 consumed and while they were 0.024 and 0.011 for experiments P-2 and B-1a respectively.

5.4.5 Results of experiment M-5

For the experiment M-5 the initial phenol and bentazone concentrations were selected as 25 and 75 mg/l respectively. The applied ozone dosage was 3.4 mg/min. The removals of phenol and bentazone are given in Figure 5.28.

For experiment M-5 the complete phenol removal was observed at 90^{th} minute. For the single oxidation experiment of 25 mg/l initial phenol concentration (P-1a) the time needed for complete oxidation for phenol was 60 minutes. The same deceleration effect for the removal rate of phenol can be seen for the experiment M-5. However, due to the low concentration of initial phenol concentration it was inconvenient to see the decrease at the removal rate of phenol.

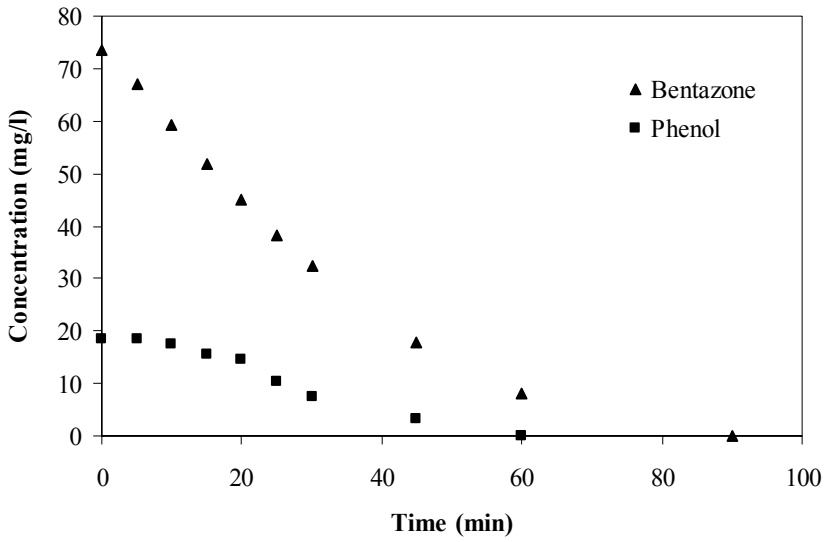


Figure 5.28: Removal of phenol and bentazone at M-5 experiment by ozonation

In this set of the mixture experiment the same retarding affect can be seen in the reduction of bentazone. As illustrated in Figure 5.28 the bentazone oxidation occurred in parallel to phenol oxidation. The comparison can be made between the bentazone concentrations during the course of the experiment M-5 and the single oxidation experiment of bentazone (B-3). The basic profile was the obvious decrease in the removal rate of bentazone in the experiment M-5. The removal rate of bentazone slowed down with a smooth pattern during the oxidation period of M-5. The complete removal of bentazone observed at 90^{th} minute for experiment M-5 while it was 60^{th} minute for experiment B-3. It would be also useful to make a comparison between experiments M-1 and M-5 to evaluate the effect of initial phenol concentration to the removal pattern of bentazone. As noted before the initial concentration of phenol was 75 mg/l for experiment M-1 and the time needed to complete removal of bentazone was 150 minutes. As can be seen from the results increasing the phenol initial concentration, extended the time needed for complete removal of bentazone in mixture experiment of M-5.

The dissolved ozone concentration profile of M-5 experiment is represented in Figure 5.29. As can bee seen from the figure, the dissolved ozone concentrations for experiment M-5 were higher than those measured for the same initial bentazone and phenol concentrations at single oxidation experiments. The maximum dissolved ozone concentration for experiment M-5 was reached at 90^{th} minute and its level was 14.6 mg/l. For single oxidation experiment for phenol (P-1a) and bentazone (B-3)

these values were 90 minutes, 7.3 mg/l and 60 minutes, 9.1 mg/l respectively. The same hypothesis as with M-1 and M-2 can be made for experiment M-5 from the results of measured dissolved ozone concentrations in the solution. For single and mixture oxidation experiments, the decreases in removal rates of phenol and bentazone cannot be attributed to the dissolved ozone concentrations in the solution.

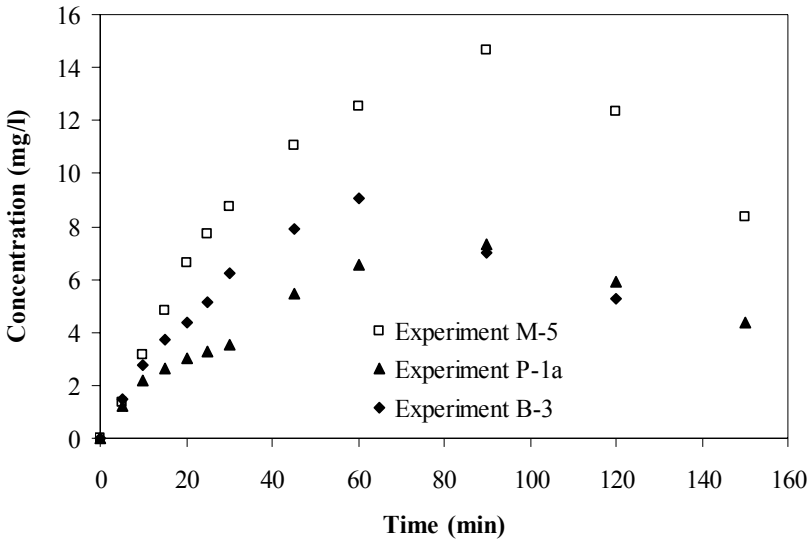


Figure 5.29: Dissolved ozone profile during the experiment M-5 and single oxidation experiments

The intermediate formation during the experiment M-5 is given in Figure 5.30. The peak value reached for cis, cis-muconic acid was at 45th minute and the concentration was 4.4 mg/l for M-5 experiment. The ratio of cis, cis-muconic acid to the initial phenol concentration was approximately 22%. The concentration profile of cis, cis muconic acid at the same initial phenol concentration at single oxidation experiment (P-1a) was noted previously. The cis, cis-muconic acid peak value observed at 20th minute at the concentration of 1.6 mg/l and the ratio of cis, cis-muconic acid to the initial phenol concentration was approximately 6%.

At this point a comparison of M-1 and M-5 would be useful. As noted before due to the low concentration of initial phenol concentration it was inconvenient to see the decrease at the removal rate of phenol and consistence of concentrations between experiments M-5 and P-1a.

In mixture experiment M-5, the difference between the formation rate and the oxidation rate of intermediates was less redundant than with the comparison to M-1 experiment. The reason for this was low concentration of initial phenol concentration

in experiment M-5. Thus the peak concentration and the accumulation of the cis, cis-muconic acid in experiment M-5 was less than observed for experiment M-1.

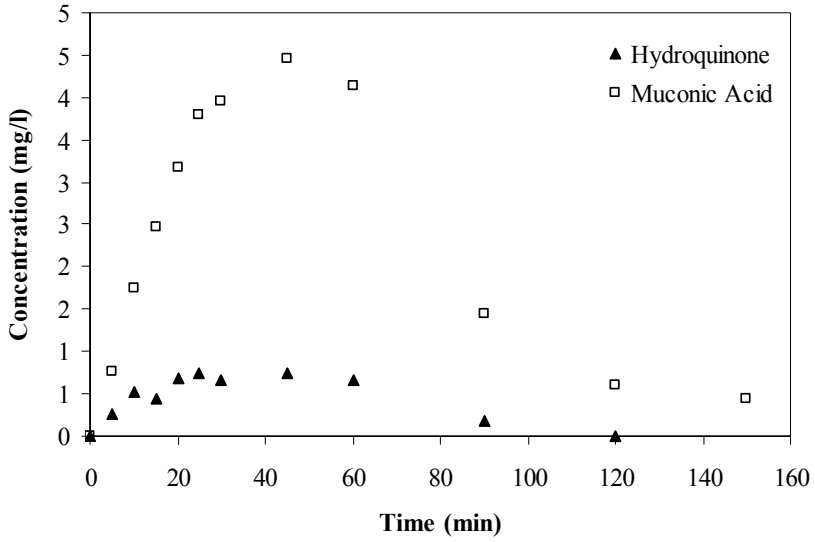


Figure 5.30: Concentration profiles of formed intermediates (M-5)

The peak values of cis, cis-muconic acid observed in experiments M-5 and M-1 were 4.4 mg/l and 9.2 mg/l respectively. The main reason of decreasing the oxidation rate of phenol was figured out as the accumulation and the preferential oxidation of cis, cis-muconic acid at the same time the removal rate of bentazone slowed down with a smooth pattern during the oxidation period of M-5. This decrease can be due to the high level of cis, cis-muconic acid concentration. Similar to other mixture experiments in experiment M-5 2 mg/l cis, cis muconic acid concentration was reached between 10-15 minutes oxidation period and it was over this concentration during the time that bentazone removed completely. Similar to other mixture experiments, it can be concluded that the bentazone removal rate was decreased as a result of high level concentration of cis, cis-muconic acid from the beginning of the experiment.

Table 5.17 shows the TOC measurements during the experiment M-5. The TOC removal for this system was around 16% at the end of the reaction time of 150 minute.

The sum of removed TOC of single oxidation experiments of P-1a and B-3 was 4.51 mg/l at 45^{th} minute oxidation period while it was 2.4 for experiment M-5. At the end of the 120 minutes the amount of removed TOC increased up to 10.26 mg/l for experiment M-5. In this experiment TOC removal was seen to be accelerated with respect to TOC removal of single oxidation experiments P-1a and B-3 at the end of 120 minutes. The calculated specific ozone consumption value for experiment M-5 was 0.031 mg TOC

removed / mg O_3 consumed and while they were 0.022 and 0.025 for experiments P-1a and B-3 respectively.

Table 5.17: Results of TOC Measurements at Experiment M-5

Time (min)	Experiment M-5
	TOC (mg/l)
Initial	58.51
5	58.36
10	58.32
15	58.19
20	57.80
25	57.61
30	56.86
45	56.11
60	55.21
90	53.24
120	51.52
150	49.25

5.4.6 Results of experiment M-6

For the experiment M-6 the initial phenol and bentazone concentrations were selected as 25 and 50 mg/l respectively. The applied ozone dosage was 3.8 mg/min. The removals of phenol and bentazone are given in Figure 5.31.

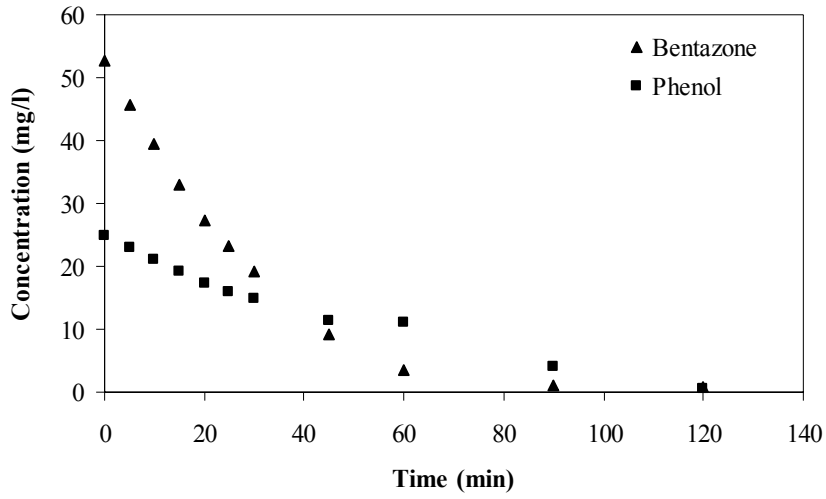


Figure 5.31: Removal of phenol and bentazone at M-6 experiment by ozonation

As can be seen from the figure the complete phenol removal was observed at 120th minute oxidation period. For the single oxidation experiment of 25 mg/l initial phenol concentration (P-1a) the time needed for complete removal was 60 minutes. From the comparison of the results of experiments M-6 and P-1a it can be said that the decrease in phenol removal rate was similar to other mixture experiments. The

50% removal efficiency was achieved between 20-25 minutes for experiment P-1a while it was between 30-45 minutes for experiment M-6. A deceleration between 25-60 minutes was also seen for the experiment M-6. However, a rapid decrease in phenol concentration was observed after 60 minutes.

As illustrated in the Figure 5.31 bentazone reduction has a clear decrease during the whole oxidation period. The removal rate of bentazone slowed down with a smooth pattern during the oxidation period of M-6 as compared to experiment B-2. The complete removal of bentazone observed at 120^{th} minute for experiment M-6 while it was 60^{th} minute for experiment B-2. 50% removal efficiency was observed between 15-20 minutes for single experiment of bentazone, while the same efficiency was between 20-25 minutes for experiment M-6.

An evaluation of experimental results of M-3, M-5 and M-6 can be made as follows; in a quite similar manner to those of M-3 the phenol removal rate decreased with compared to single oxidation experiment of phenol (P-1a). However, a sagnation between 25-60 minutes followed by a rapid decrease in phenol concentration was seen for the experiment M-6. This sagnation in phenol oxidation after 60 minutes is less pronounced than experiment M-5 due to the fact that higher initial concentration of bentazone with respect to M-6. In the experiment M-3 the initial concentration of bentazone was 50 mg/l similar to experiment M-6. The complete removal of bentazone was observed at 120 minutes for the experiment M-3 similar to experiment M-6. It can be said that decreasing the phenol concentration from 50 mg/l down to 25 mg/l did not change the time needed for complete removal of bentazone.

In Figure 5.32 the dissolved ozone concentration profile of the experiment M-6 is delineated. The dissolved ozone concentrations for experiment M-6 were lower than those measured for the same initial bentazone and phenol concentrations at single oxidation experiments. The maximum dissolved ozone concentration for experiment M-6 was reached at 60^{th} minute and its level was 5.92 mg/l.

The same conclusion can be made similar to experiment M-3, this lower dissolved ozone concentrations would decrease the removal rates of phenol and bentazone in mixture experiment of M-6. However, 2 mg/l dissolved ozone concentration was observed 10-15 minutes and it remained over this concentration during the whole oxidation period of experiment M-6.

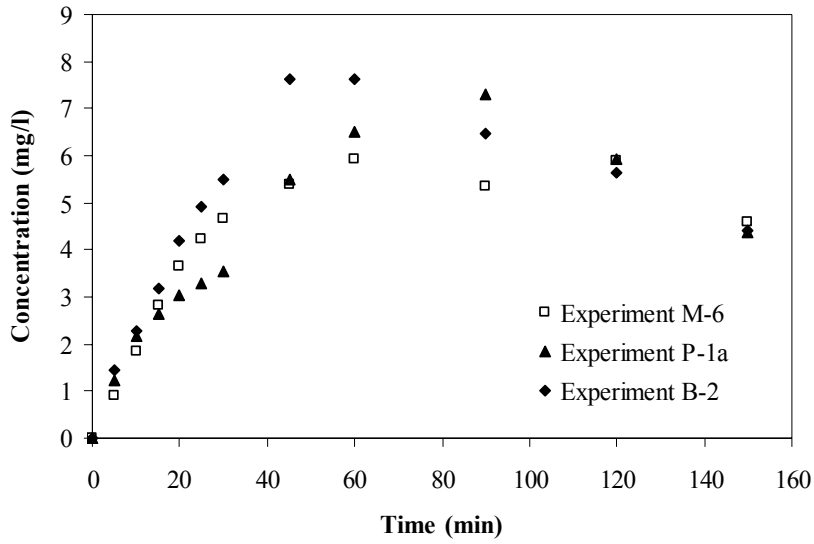


Figure 5.32: Dissolved ozone profile during the experiment M-6 and single oxidation experiments

The intermediate concentrations formed during the experiment M-6 is given in Figure 5.33. The ratio of peak concentration of cis, cis-muconic acid formed during the experiment M-6 to the initial phenol concentration was approximately 19%. The peak value reached for cis, cis-muconic acid was at 45th minute and the concentration was 4.8 mg/l for M-6 experiment. For experiment P-1a, the cis, cis-muconic acid peak value observed at 20th minute at the concentration of 1.6 mg/l and the ratio of cis, cis-muconic acid to the initial phenol concentration was approximately 6%.

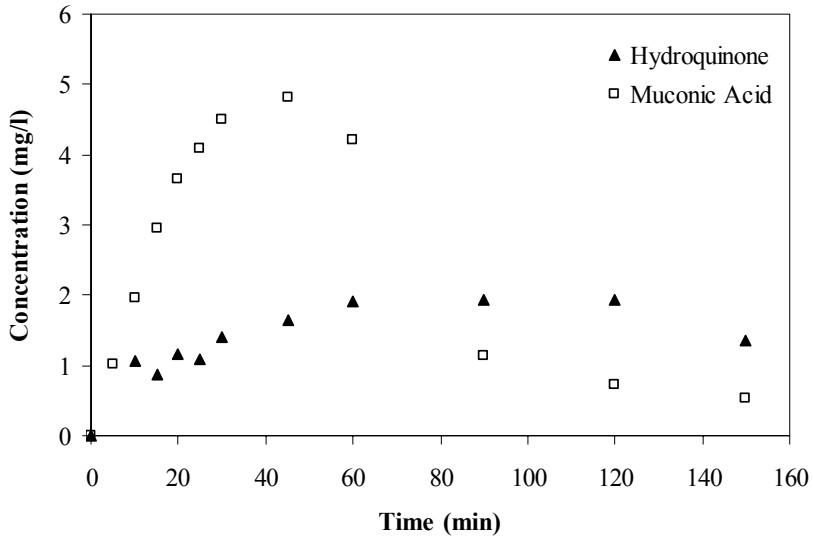


Figure 5.33: Concentration profiles of formed intermediates (M-6)

The cis, cis-muconic acid peak concentration observed for single oxidation of 50 mg/l initial bentazone experiment (B-2) was less than 0.7 mg/l during the whole oxidation period. Therefore, the formation of cis, cis-muconic acid seemed to be mainly associated with phenol oxidation but preferential oxidation of bentazone gives rise to accumulation of cis, cis-muconic acid in mixture experiments

In mixture experiment M-6, the difference between the formation rate and the oxidation rate of intermediates was close to one another. The peak values of cis, cis-muconic acid observed in experiments M-5 and M-6 were 4.4 mg/l and 4.9 mg/l respectively. As also noted before, the main reason of decreasing the oxidation rate of phenol compared with single oxidation experiments, was figured out as the accumulation and the preferential oxidation of cis, cis-muconic acid. The reduction in removal rate of bentazone can be attributed to phenol and produced cis, cis-muconic acid oxidation in parallel with bentazone. 2 mg/l cis, cis muconic acid concentration was reached at 10^{th} minute and it remained over this concentration till 90 minutes where 98% bentazone removal achieved.

Table 5.18 shows the TOC measurements during the experiment M-6. The TOC removal for this system was around 20% at the end of the reaction time of 150 minute.

Table 5.18: Results of TOC Measurements at Experiment M-6

Time (min)	Experiment M-6
	TOC (mg/l)
Initial	47.55
5	46.87
10	47.14
15	46.62
20	46.73
25	46.30
30	45.84
45	45.62
60	46.24
90	42.44
120	41.05
150	37.95

The removed TOC concentrations were 1.93 and 6.5 mg/l at 45^{th} and 120^{th} minutes respectively. The sum of the removed TOC for single oxidation experiments P-1a and B-2 was 4.35 mg/l at 45^{th} minute and 8.38 pp at 120^{th} minute all being higher than those of M-6 experiments. The calculated specific ozone consumption value for experiment M-6 was 0.045 mg TOC removed / mg O_3 consumed.

5.4.7 Results of experiment M-7a and M-7b

For the experiment M-7a and M-7b the initial phenol and bentazone concentrations were selected as 25 mg/l. The applied ozone dosages were 3.4 and 12.6 mg/min respectively. The removals of phenol and bentazone for these two experiments are given in Figure 5.34.

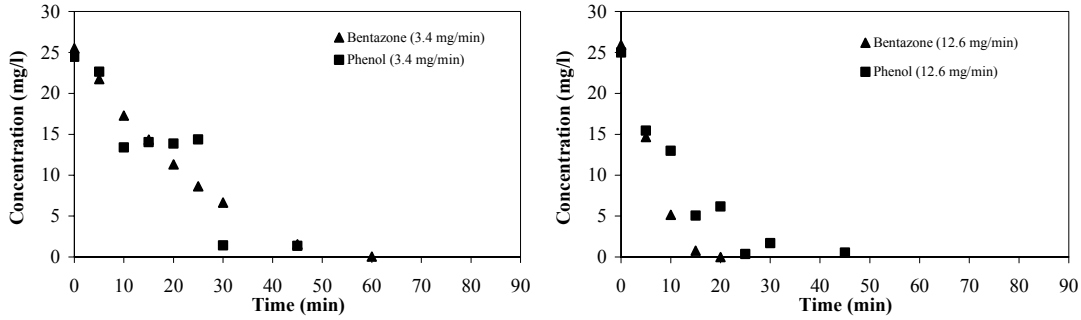


Figure 5.34: Removal of phenol and bentazone at M-7a and M-7b experiments by ozonation

As illustrated in the figure remaining phenol concentration was 1.3 mg/l at 45th minute for experiment M-7a while it was completely removed at this time for experiment M-7b. For the single oxidation experiment of 25 mg/l initial phenol concentration (P-1a) the time needed for complete removal 60 minutes for the same ozone dosage that applied for experiment M-7a. As can be seen from the figure for experiment M-7a a sustained phenol concentration between 10-25 minutes was observed. Another peculiarity in this case was a rapid removal of phenol between 25-30 minutes. However, this observed pattern in multiple oxidation systems was not seen for experiment M-7b due to the higher applied ozone dosage. For experiment P-1b phenol removal had a smooth removal during the whole oxidation period. The complete removal was observed at 30th minutes while the time was extended to 45 minutes for experiment M-7b.

As illustrated in the Figure 5.34 bentazone reduction has a clear decrease during whole oxidation periods of experiments M-7a and M-7b. The removal rate of bentazone slowed down with a smooth pattern during the oxidation period of M-7a as compared to experiment B-1a. The complete removal of bentazone observed at 45th minute for experiment M-7a while it was 20th minute for experiment B-1a. For experiment M-7b the complete removal of bentazone was observed at the first 15 minutes while it was 10 minute for experiment B-1b.

In Figure 5.35 the dissolved ozone concentration profile of the experiments M-7a and M-7b are delineated. The dissolved ozone concentrations for experiment M-7a were lower than that measured for the single oxidation experiment of same initial bentazone concentrations for first 45 minutes. However after first 45 minutes the dissolved ozone concentrations were higher than those observed for single oxidation experiments of P-1a and B-1a. Similar to experiment M-7a the observed dissolved ozone concentrations for M-7b were lower than that of single oxidation experiment of B-1b for first 25 minutes. After this oxidation period the dissolved ozone concentrations were smaller than those observed for experiments P-1b and B-1b. The maximum dissolved ozone concentration for experiments M-7a and M-7b were reached at 120th and 45th minute and concentrations were 7.28 and 14.73 mg/l respectively. For each case, during whole oxidation period the dissolved ozone concentrations remained over 2 mg/l.

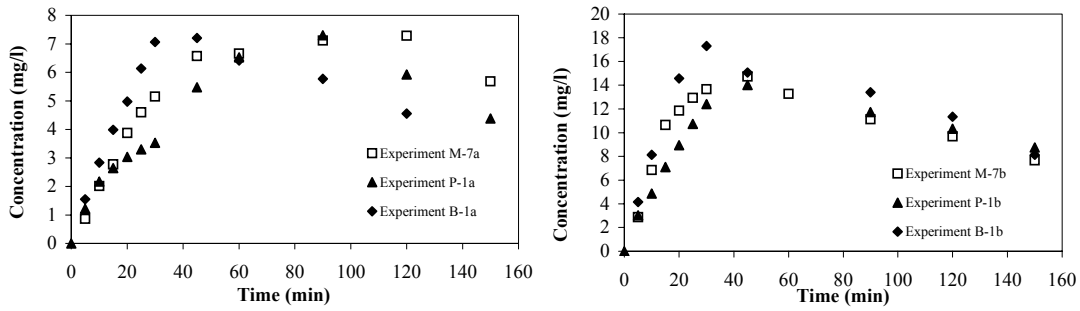
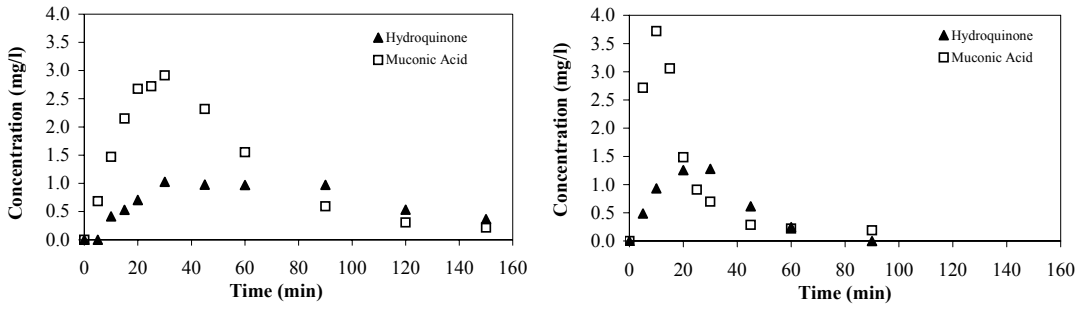


Figure 5.35: Dissolved ozone profile during the experiments M-7a, M-7b and single oxidation experiments

The intermediate concentrations formed during the experiments M-7a and M-7b are illustrated in Figure 5.36. The ratio of peak concentration of cis, cis-muconic acid formed during the experiment M-7a was at 30th minute the concentration was 2.91 mg/l. The ratio to the initial phenol concentration was approximately 12%. For experiment M-7b these values observed as 10th minute and 3.72 mg/l respectively. The ratio to the initial phenol concentration was approximately 15% for experiment M-7b. The observed differences between the peak concentrations of cis, cis-muconic acid and the time needed to reach the peak values may occur due to the differences in dissolved ozone concentrations in those cases. Although the level of formed cis, cis muconic acid was higher than those observed for experiments P-1a and P-1b due to the effect of parallel oxidation of bentazone. The observed cis, cis-muconic acid peak values were at 20th and 10th minute at the concentration of 1.58 and 1.54 mg/l respectively for experiments P-1a and P-1b.



M-7a M-7b

Figure 5.36: Concentration profiles of formed intermediates (M-7a and M-7b)

Table 5.19 shows the TOC measurements during the experiment M-7a and M-7b. The TOC removals for these systems were 16% and 31% at the end of the reaction time of 150 minute for experiments M-7a and M-7b respectively.

Table 5.19: Results of TOC Measurements at Experiment M-7a and M-7b

Time (min)	Experiment M-7a TOC Concentration (mg/l) (Ozone Dosage : 3.4 mg/min)	Experiment M-7b TOC Concentration (mg/l) (Ozone Dosage : 12.6 mg/min)
Initial	30.10	32.12
5	30.02	30.43
10	29.85	30.04
15	29.53	29.13
20	29.36	28.46
25	29.27	28.09
30	29.01	27.09
45	28.73	26.44
60	27.82	25.29
90	27.32	23.6
120	25.78	23.19
150	25.11	22.22

The removed TOC concentrations in experiment M-7a at 45th and 120th minute were 1.37 and 4.32 mg/l respectively. These values were lower than sum of P-1a and B-1a TOC removals. The difference, however, decreased with increasing oxidation time. On the other hand the difference between the mixture experiment of M-7b and the sum of TOC removals P-1b and B-1b became very low as a result of increasing ozone dosage. The calculated specific ozone consumption values were 0.018 and 0.009 mg TOC removed / mg O_3 consumed for experiments M-7a and M-7b. As can be seen from the calculated values the specific ozone consumption rate was highly dependent on ozone dosage.

5.5 Evaluation of Modeling Approach

As noted in detail in Subsection 2.3.4 ozone oxidation of organic compounds and kinetics of this process were investigated by various scientists. In these research papers, the ozonation kinetics had been studied mostly adopting the gas-liquid irreversible second-order reaction between ozone and the single substrate present in water with no competition from secondary direct reactions. Application of this approach requires a number of assumptions to simplify the kinetic equations. The common approach is to use pseudo first-order reaction kinetics. The general principle is, when ozone is present in excess and ozone concentration in the solution is stable at a certain level during the oxidation reaction, the reaction rate conforms to pseudo first-order. However, these assumptions may not be valid for every case due to the bubble column operating characteristics, substrate specifications and substrate decomposition rate. Especially for the transport limiting case, ozone supply controls the system instead of kinetic limitations. In this situation the kinetics may be expressed independent of substrate concentration. The other most common simplification is neglecting the secondary direct reactions between ozone and intermediates. However, this also prevents to characterize the real nature of ozonation process. In this context, the concept of "multiple substrate oxidation" has a great importance to have an insight into the ozone oxidation. Therefore, research efforts are needed for a thorough understanding of the molecular ozone oxidation and quantitative evaluation of the multiple substrate oxidation systems.

In the model applications, the substrate concentrations were expressed in terms of specific matter concentration, as phenol or bentazone, rather than the collective parameter TOC measured during experimental studies, which was not accurate for evaluation due to the limited extent of removal.

For better understanding and evaluation of the ozonation process, existing models for direct ozone reactions with and without considering the reactor characteristics for single and multiple substrates were tested. These models were used in most of the studies concerning ozone oxidation processes. In these studies a number of assumptions have been made and also some model parameters assumed to be constant for the application of the models. Within this context, the applied models could not describe the system characteristics in detail and represented rather overall removal of a substrate. The models were also tested for the investigation and evaluation of the

substrate removal in the multiple substrate oxidation systems and also for the applicability and accuracy of the common assumptions that have been made in the literature. The reactions that have been used for the models and also the related differential equations were given below, assuming stoichiometric coefficients are all unity. The end products that mentioned in the reactions could be described as relatively slow reacting organic compounds with ozone such as glyoxal for the ozone oxidation of phenol.

Ozone direct reactions with a single substrate without considering the reactor characteristics: In this system only one substrate reacts with ozone to form end products with the rate coefficient of k_1.

$$S_1 + O_3 \xrightarrow{k1} End \quad products \tag{5.1}$$

$$\frac{d[S_1]}{dt} = -k_1[O_3]\ [S_1] \tag{5.2}$$

when ozone is present in excess and ozone concentration in the solution is stable at a certain level during the oxidation reaction, the reaction rate conforms to pseudo first-order

$$\frac{d[S_1]}{dt} = -k'[S_1] \tag{5.3}$$

where $k' = k_1[O_3]$ and

$$\frac{d[O_3]}{dt} = -k'[O_3] = -k'[S_1] \tag{5.4}$$

Ozone direct reactions with multiple substrates without considering the reactor characteristics: In this system more than one substrate reacts with ozone to form end products. For two substrates with the rate coefficients of k_1 and k_2 for S_1 and S_2 respectively;

$$S_1 + O_3 \xrightarrow{k1} End \quad products \tag{5.5}$$

$$S_2 + O_3 \xrightarrow{k2} End \quad products \tag{5.6}$$

$$\frac{d[S_1]}{dt} = -k_1[S_1]\ [O_3] \quad \textbf{(5.7)}$$

$$\frac{d[S_2]}{dt} = -k_2[S_2]\ [O_3] \quad \textbf{(5.8)}$$

$$\frac{d[O_3]}{dt} = -k_1[S_1]\ [O_3] - k_2[S_2]\ [O_3] \quad \textbf{(5.9)}$$

The pseudo first order kinetic approach could be also used for this system.

Ozone direct reactions incorporating intermediates without considering the reactor characteristics: In this system the organic compound (S_1) reacts with ozone to form an intermediate (P_1), and this intermediate is than oxidized to end products. The second substrate (S_2) is directly oxidized to end products. k_1, k_2 and k_3 are the rate coefficients of S_1, P_1 and S_2 respectively.

$$S_1 + O_3 \xrightarrow{k1} P_1 \quad \textbf{(5.10)}$$

$$P_1 + O_3 \xrightarrow{k2} End \quad products \quad \textbf{(5.11)}$$

$$S_2 + O_3 \xrightarrow{k3} End \quad products \quad \textbf{(5.12)}$$

$$\frac{d[S_1]}{dt} = -k_1[S_1]\ [O_3] \quad \textbf{(5.13)}$$

$$\frac{d[P_1]}{dt} = -k_2[P_1]\ [O_3] + k_1[S_1]\ [O_3] \quad \textbf{(5.14)}$$

$$\frac{d[S_2]}{dt} = -k_3[S_2]\ [O_3] \quad \textbf{(5.15)}$$

$$\frac{d[O_3]}{dt} = -k_1[S_1]\ [O_3] - k_2[P_1]\ [O_3] - k_3[S_2]\ [O_3] \quad \textbf{(5.16)}$$

Ozone direct reactions with a single substrate considering the reactor characteristics: In this system the ozone mass transfer is also included in the

differential equations. $k_L a$ is the ozone mass transfer coefficient and $[O_3]^*$ is the ozone saturation concentration.

$$S_1 + O_3 \xrightarrow{k1} End \quad products \tag{5.17}$$

$$\frac{d[S_1]}{dt} = -k_1[O_3]\ [S_1] \tag{5.18}$$

$$\frac{d[O_3]}{dt} = k_L a\left([O_3]^* - [O_3]\right) - k_1[O_3]\ [S] \tag{5.19}$$

Ozone direct reactions with multiple substrates considering the reactor characteristics:

$$S_1 + O_3 \xrightarrow{k1} End \quad products \tag{5.20}$$

$$S_2 + O_3 \xrightarrow{k2} End \quad products \tag{5.21}$$

$$\frac{d[S_1]}{dt} = -k_1[S_1]\ [O_3] \tag{5.22}$$

$$\frac{d[S_2]}{dt} = -k_2[S_2]\ [O_3] \tag{5.23}$$

$$\frac{d[O_3]}{dt} = k_L a\left([O_3]^* - [O_3]\right) - k_1[O_3]\ [S_1] - k_2[O_3]\ [S_2] \tag{5.24}$$

For z number of substrates general equation for ozone is

$$\frac{d[O_3]}{dt} = k_L a\left([O_3]^* - [O_3]\right) - \sum z_i k_i[O_3]\ [S_i] \tag{5.25}$$

Ozone direct reactions incorporating intermediates considering the reactor characteristics

$$S_1 + O_3 \xrightarrow{k1} P_1 \tag{5.26}$$

$$P_1 + O_3 \xrightarrow{k2} End \quad products \tag{5.27}$$

$$S_2 + O_3 \xrightarrow{k3} End \quad products \tag{5.28}$$

$$\frac{d[S_1]}{dt} = -k_1[S_1]\ [O_3] \tag{5.29}$$

$$\frac{d[P_1]}{dt} = -k_2[P_1]\ [O_3] + k_1[S_1]\ [O_3] \tag{5.30}$$

$$\frac{d[S_2]}{dt} = -k_3[S_2]\ [O_3] \tag{5.31}$$

$$\frac{d[O_3]}{dt} = k_L a\left([O_3]^* - [O_3]\right) - k_1[O_3]\ [S_1] - k_2[O_3]\ [P_1] - k_3[O_3]\ [S_2] \tag{5.32}$$

The above mentioned models have been tested using the data obtained from the experimental studies conducted in this thesis by making appropriate assumptions which were commonly applied the literature. However no consistent results obtained for all the models, particularly the ones incorporating reactor characteristics. The reasons could be the difficulties in the determination of boundary conditions of the models particularly for the ones involving diffusion transport and also there were problems in defining the mass transfer characteristics or in other words reactor characteristics. As also emphasized in the previous subsections the bubble characteristics in the reactor have changed during the course of the oxidation reaction due to the effect of organic compounds. (Figure 5.37).

At the beginning of the experiment | In the middle of the experiment | At the end of the experiment

Figure 5.37: The change in bubble character in the reactor during the course of the oxidation reaction

The model compounds that used in the thesis study and also the organic compound desired to be removed in the actual conditions by ozone oxidation have surface active character that affects the bubble characteristics in the reactor. The changes in the

bubble diameters directly influenced the interfacial area and as discussed in the subsection 2.5.5 the variations in the interfacial area cause variations in overall mass transfer coefficient ($k_L a$) in a bubble column reactor (Fan *et al.*, 1985).

As can be seen from the figure the effect of organic compounds on mass transfer was very important at the beginning of the reaction. And also during the oxidation period the removal of the initial compound also changes the $k_L a$ value of the system. As a consequence the mass transfer characteristics also became different at each oxidation period. Another important point that should be considered was the effect of intermediates formed during the course of the oxidation reaction on the mass transfer characteristics. So the $k_L a$ value should also express as a function of not only any initial substrate but also a multitude of intermediates and substrates depending on reaction characteristics.

For the evaluation of the ozonation process, kinetic regimes (fast, moderate or slow reactions) should be determined and any one of these situations leads to different rate laws. The kinetic regime of the system could be assessed by the calculation of the Hatta number of the system. The Hatta number is directly related to the mass transfer. The changes at $k_L a$ value directly influence the Hatta number of the systems and the kinetic regime. So the derived equations for the ozonation process need to be modified for each oxidation period during the course of the reactions. However, the expression of $k_L a$ value by differential equation is very difficult and the physical aspects did not described yet. Therefore, no consistent results could be obtained with the use of known $k_L a$ values.

The starting point of the modeling approach in this study is to search if an overall substrate removal model can be used to describe the general pattern of substrate conversion within defined intervals of the system variables. Within this framework several models have been tested considering the process as a black box. The predicted data from the model was in a good fit with the use of the expression of,

$$\frac{d[S_1]}{dt} = -k[S_1] \qquad \textbf{(5.33)}$$

at certain boundary conditions. The above given removal model used in the study was similar to pseudo-first order kinetic expression. This expression implies a kinetic

description but it is rather an overall modeling of the substrate conversion for the system employed in the study.

5.6 Kinetic Evaluation of Single Phenol Experiments

As noted in detail in Subsection 2.3.4 ozone oxidation of organic compounds and kinetics of this process were investigated by various scientists. The common approach is to use pseudo first-order reaction kinetics. The general principle is, when ozone is present in excess and ozone concentration in the solution is stable at a certain level during the oxidation reaction, the reaction rate conforms to pseudo first-order. However, these assumptions may not be valid for every case due to the bubble column operating characteristics, substrate specifications and substrate decomposition rate. Especially for the transport limiting case, ozone supply controls the system instead of kinetic limitations. In this situation the kinetics may be expressed independent of substrate concentration. In this subsection kinetic evaluation of phenol oxidation by ozone was made considering the above-mentioned physical framework of the system.

In order to examine the reaction kinetics the solution characteristics should be analyzed in detail. For this purpose the dissolved ozone concentration and time needed to achieve its peak concentration, the observed peak value, formation of intermediates and remaining phenol concentration for the analyzed periods of reaction kinetics are given in Table 5.20 for experiments P-2, P-3 and P-4. Experiments P-1a and P-1b need to be analyzed separately because of the dissimilarity in the course of the reaction mechanism of the system.

Table 5.20: Solution Characteristics of Experiments P-2, P-3 and P-4

		Experiment		
		P-2	**P-3**	**P-4**
Dissolved O_3	Peak value (mg/l)	3.01	3.34	3.67
	Observed Time (min)	45	45	45
Cis, cis Muconic Acid	Peak value (mg/l)	2.60	3.92	5.22
	Observed Time	25	45	45
Remaining Phenol concentration (mg/l)	90^{th} minute	14.5	24.41	34.88
	120^{th} minute	7.05	15.12	18.72

As can be seen from the table, increasing initial phenol concentration increases the dissolved ozone peak concentration. This variation seems to be reasonable considering the effect of organics on mass transfer characteristics thus changing the level of dissolved ozone in the reactor. Ozone concentration reached around 2.0 mg/l for first 10 minutes for all experiments and stayed over this concentration during the whole oxidation period. This picture indicates that there was no limitation of dissolved ozone during the whole reaction period. As discussed in Subsection 5.2.4 in detail, for the experiments P-1a and P-1b the concentration of dissolved ozone began to increase from the beginning of oxidation reaction. Peak values of dissolved ozone concentrations were obtained where phenol was completely oxidized, for both ozone dosages and than ozone concentration started to decrease for further oxidation periods. For experiments P-1a and P-1b the peak values of dissolved ozone were reached at 90^{th} and 45^{th} minute respectively. Similar to experiments P-2, P-3 and P-4, the observed ozone concentrations were over 2.0 mg/l for first 5 minutes and stayed over this concentration during the whole oxidation period.

Cis, cis muconic acid started to form from the beginning of the phenol oxidation by ozone. The peak value was reached at 20, 10, 25 and 45 minutes for experiments P-1a and P-1b, P-2, P-3 and P-4 respectively. The concentration level of cis, cis-muconic acid was changed due to the initial concentration of phenol. The higher initial concentration of phenol the higher concentration of cis, cis-muconic acid achieved. It should be also noted that, the concentration level of cis, cis muconic acid was over 1 mg/l for all experiments. The effect of cis, cis-muconic acid on reaction kinetics may affect the reaction rate due to varying cis, cis-muconic acid profiles.

The above discussion indicates the applicability of removal model similar to pseudo first-order kinetics expression. Graphical representations of removal kinetics for experiments P-1a and P-1b are depicted in Figure 5.38.

As illustrated in figure, a good fit for removal was observed for experiments P-1a and P-1b for first 20 minutes. The overall removal rate constant of experiment P-1b was approximately 3 times higher than that observed for experiment P-1a due to the higher ozone dosage.

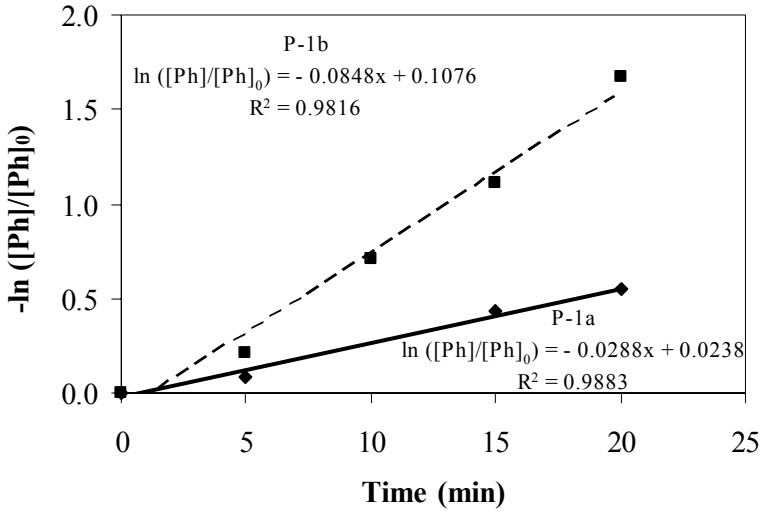


Figure 5.38: Evaluation of removal kinetics for experiments P-1a and P-1b (♦ P-1a; ■ P-1b)

Graphical representations of removal kinetics for experiments P-2, P-3 and P-4 were depicted in Figures 5.39, 5.40 and 5.41 respectively.

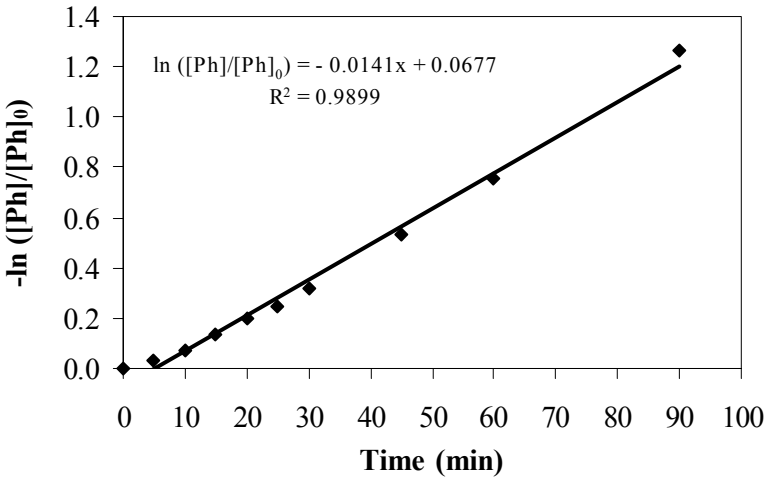


Figure 5.39: Evaluation of removal kinetics for experiment P-2

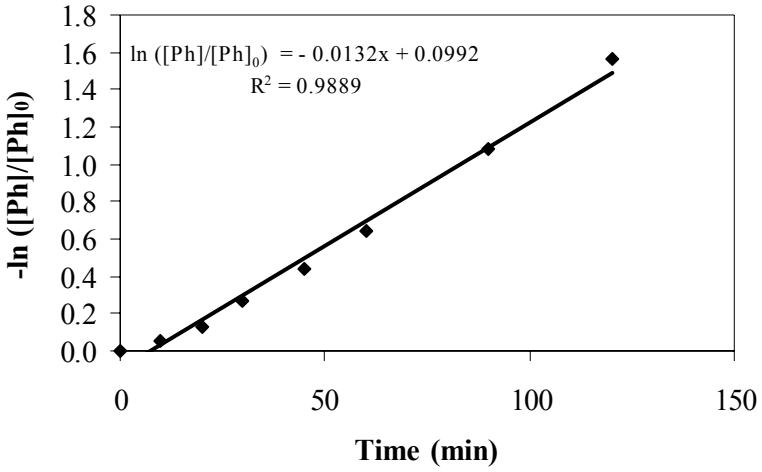


Figure 5.40: Evaluation of removal kinetics for experiment P-3

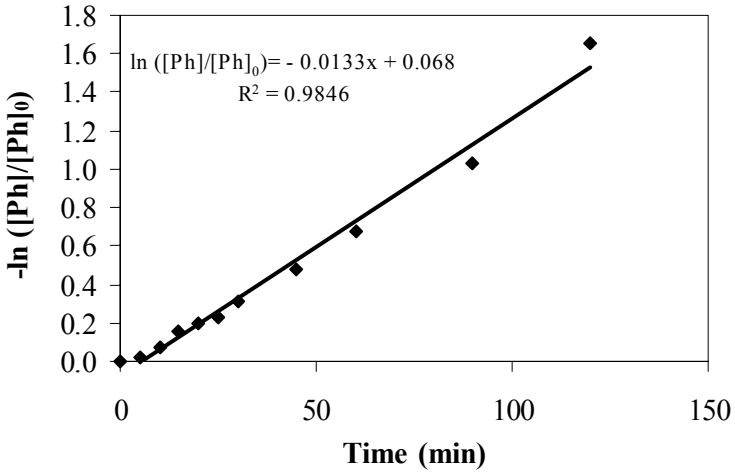


Figure 5.41: Evaluation of removal kinetics for experiment P-4

As can be seen from the figures, a good fit for removal model was observed for experiments P-2, P-3 and P-4. The overall removal rate constants were compatible to each other and the correlation coefficients were high enough for the experiments. The level of ozone concentration in solution affected the rate constant as can be seen by comparing the rate constants of P-1a and P-2 experiments. The observed peak ozone concentration of P-1a was 7.30 mg/l while it was 3.01 mg/l for experiment P-2 and the value of the constants exhibited almost a proportional variation. However in case of a small difference in dissolved ozone profiles, the overall removal rate constants did not change significantly as seen from comparable k values obtained from P-2, P-3 and P-4 experiments. In a similar manner the different cis, cis-muconic acid profiles did not seem to affect the rate of reactions observed for P-2, P-3 and P-4 experiments.

On the other hand, zero-order kinetics was also evaluated for all experiments. The accordance to zero-order kinetics of experiments P-1a and P-1b were delineated in Figure 5.42.

As can be seen from the figure, a high accordance was observed for zero-order kinetics with a high correlation coefficient for experiments P-1a and P-1b. A similar fit was also obtained for experiments P-2, P-3 and P-4. However, the calculated rate constants for zero-order kinetics were different from each other for all experiments. The rate constants increased with increasing initial phenol concentration and as also can be seen from Figure 5.42 with increasing ozone dosage. This implies the requirement of close control and assessment of transportation as well as reaction conditions for generalized application for zero order kinetics.

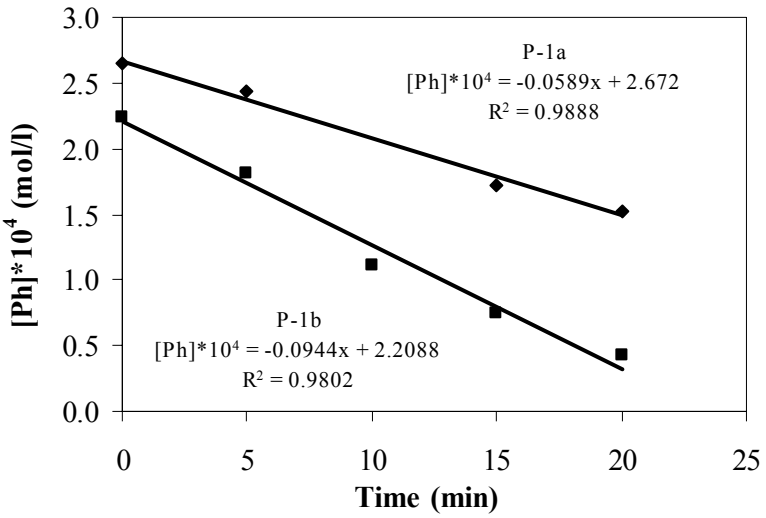


Figure 5.42: Zero-order kinetic evaluation for experiment P-1a and P-1b (♦ P-1a; ■ P-1b)

5.7 Kinetic Evaluation of Single Bentazone Experiments

In order to examine the reaction kinetics of bentazone oxidation by ozone the oxidation characteristics should be assessed. The most important parameters are given in Table 5.21 for experiments B-2, B-3 and B-4. Experiments B-1a and B-1b should be analyzed separately because of the difference in the course of the reaction mechanism of the system.

Table 5.21: Solution Characteristics of Experiments B-2, B-3 and B-4

		Experiment		
		B-2	**B-3**	**B-4**
Dissolved O_3	Peak Value (mg/l)	7.64	9.07	9.75
	Observed Time (min)	45	60	60
Phenol	Peak Value (mg/l)	0.86	3.95	5.70
	Observed Time (min)	30	25	20
Remaining Bentazone Concentration (mg/l)	30^{th} minute	10.05	16.53	26.75
	45^{th} minute	2.04	3.91	9.07

As can be seen from the table, the same tendency for dissolved ozone profile like phenol experiments was observed for bentazone oxidation experiments. Increasing the initial bentazone concentration increases the dissolved ozone peak concentration. The ozone concentration profile indicated that the transport of ozone could be more readily provided for bentazone with regard to phenol. The dissolved ozone concentration levels reached above 2.0 mg/l for first 10 minutes and above 4.0 mg/l for first 20 minutes for all experiments and stayed over 4.0 mg/l for further oxidation periods. Therefore, similar to phenol, dissolved ozone did not seem to be limiting during the whole oxidation period of bentazone ozonation. For experiments B-1a and B-1b the peak values of dissolved ozone was reached at 45^{th} and 30^{th} minute. For experiment B-1a bentazone was removed completely at 45^{th} minute while it was 10^{th} minute for experiment B-1b.

As also discussed in Subsection 5.3.2 the intermediates formed during the bentazone oxidation were phenol and cis, cis-muconic acid. Cis, cis-muconic acid concentration levels were under 1 mg/l for all bentazone experiments. The peak value of phenol increased with increasing initial bentazone concentration. The highest peak concentration was observed for experiment B-4 and its value was 5.70 mg/l. It can be assumed that, cis, cis-muconic acid did not affect the reaction kinetics due to the lower concentrations during the whole oxidation period. However, phenol can affect the reaction kinetics through parallel oxidation as well as ozone consumption.

Graphical representation of removal kinetics for experiment B-1a was illustrated in Figure 5.43. For experiment B-1b it the reaction kinetics did not worked due to the fast oxidation of bentazone for higher ozone dosage.

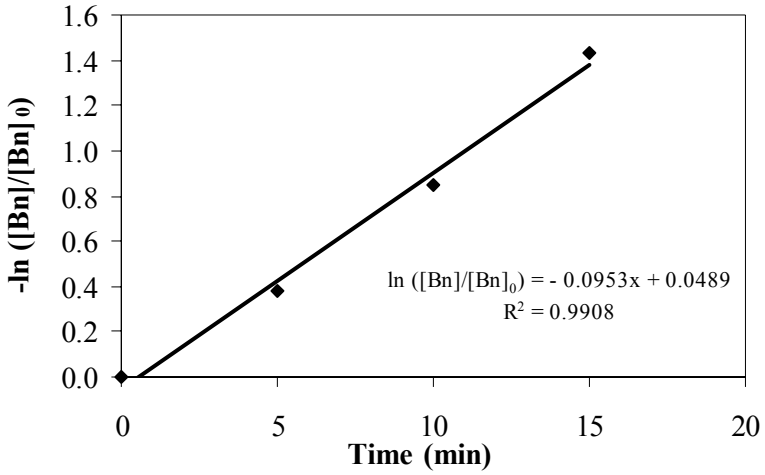


Figure 5.43: Evaluation of removal kinetics for experiment B-1a

Graphical representations of removal kinetics for experiments B-2, B-3 and B-4 were given in Figures 5.44, 5.45 and 5.46 respectively.

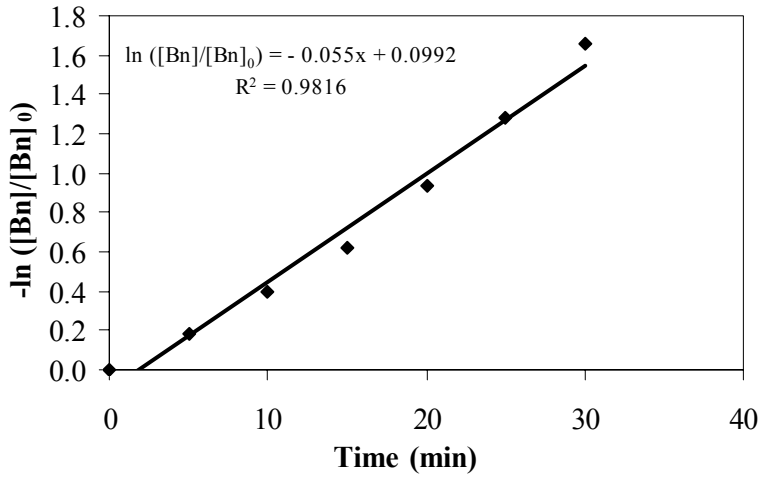


Figure 5.44: Evaluation of removal kinetics for experiment B-2

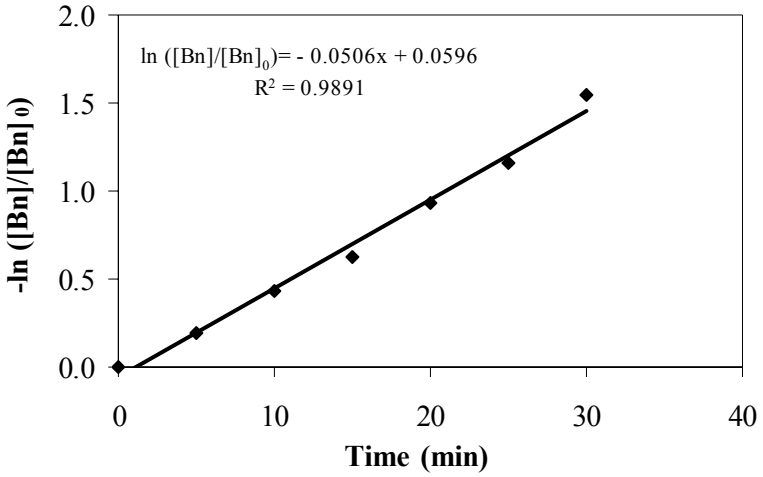


Figure 5.45: Evaluation of removal kinetics for experiment B-3

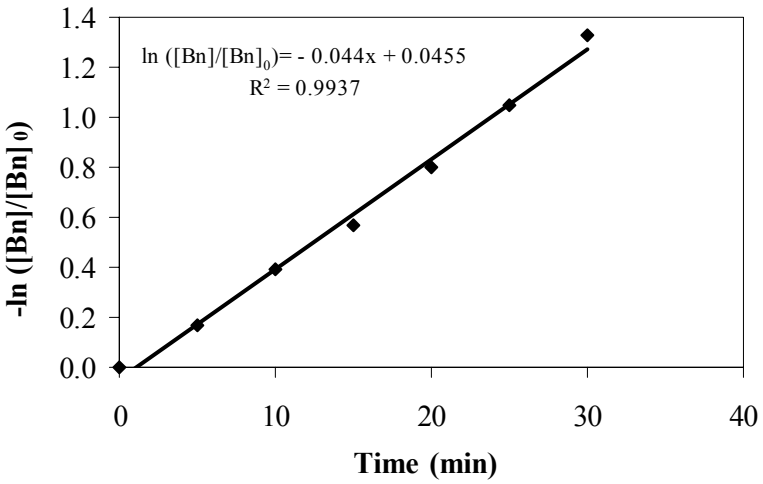


Figure 5.46: Evaluation of removal kinetics for experiment B-4

As can be seen from the figures, removal kinetics was applied for first 30 minutes for experiments B-2, B-3 and B-4. As given in Table 5.21 for further ozonation period of 45 minutes, remaining bentazone concentrations were under 10 mg/l and did not seem to be represented by a regular kinetic expression.

All reactions provided good fits to removal kinetics. The overall removal rate constants obtained for B-3 and B-2 experiments are close to one another and lower constant of B-4 may be explained by the high concentration of phenol produced during this experiment as compared to that of B-3 since the dissolved ozone profiles of the two experiments were similar. The slope of the equation obtained for B-2 and B-3 are closer to one another while the produced phenol concentrations are different. The reason for that may be the difference between dissolved ozone concentration

profiles of the two experiments. In that while increasing phenol concentration tend to reduce the reaction rate, increasing ozone concentration exerts an accelerating effect on the reaction rate.

Zero-order kinetics was also evaluated for bentazone oxidation experiments. The fit of zero-order kinetics of experiments B-1a was delineated in Figure 5.47.

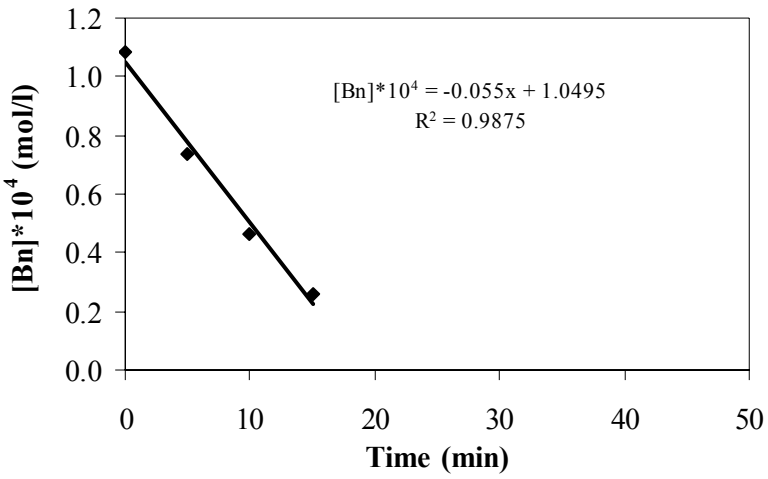


Figure 5.47: Zero-order kinetic evaluation for experiment B-1a

As can be seen from the Figure 5.47, a good fit was observed for zero-order kinetics with a correlation coefficient of 0.9875 for experiments B-1a. The same high level of fit was also observed for experiments B-2, B-3 and B-4 for zero-order kinetics. However, the calculated rate constants for zero-order kinetics were different from each other for all bentazone oxidation experiments like that those calculated for phenol oxidation experiments.

5.8 Kinetic Evaluation of Mixture Experiments

As discussed in Subsection 2.3.4 ozone oxidation of organic compounds when they are in combination in the aqueous medium, the common approach is to find out the relative rate constants of the two compounds reacting with ozone. With this assumption, in every mixture, one of the organic substrate is a reference compound, whose degradation rate constant is known: the remaining substrate constitutes the target compound, whose rate constant is unknown. This procedure is reliable when measuring the rates of fast reactions in aqueous solutions, and is based on the assumption that the reaction between the oxidant and the organic substrate follows an

overall second-order kinetics, and more specially, of first order with respect to both reactants.

In the following subsection, the kinetic evaluation of ozone oxidation of organic compounds oxidation by ozone was made as they exist in mixture in the aqueous medium. A detailed analysis was made in Subsection 5.4 for all mixture experiments to evaluate the multiple oxidation systems considering the organic compound removal, intermediate formation and removal and dissolved ozone concentration in the solution.

The overall removal rate constants of phenol and bentazone mixtures were evaluated and compared with the overall removal rate constants determined from the oxidation experiments conducted on single organic compound removal systems. For a better kinetic evaluation of the multiple oxidation system, the solution characteristics should be analyzed in detail when phenol and bentazone exist in combination in aqueous medium. The solution characteristics for mixture experiments are given in Table 5.22.

Table 5.22: Solution Characteristics of Mixture Experiments

		Experiment							
		M-1	**M-2**	**M-3**	**M-4**	**M-5**	**M-6**	**M-7a**	**M-7b**
Dissolved O_3	Peak Value (mg/l)	8.76	8.18	4.39	4.48	14.65	5.93	7.28	14.73
	Observed Time (min)	60	30	60	30	90	60	120	45
Cis, cis-muconic acid	Peak Value (mg/l)	9.21	4.87	6.45	4.78	4.45	4.82	2.9	3.7
	Observed Time (min)	60	45	60	30	45	45	30	10

Graphical representations of removal kinetics for experiment M-1 for both phenol and bentazone are given in Figure 5.48.

From previous discussions, two important parameters affecting the rate of oxidation, are dissolved ozone concentration in solution and accumulation of cis, cis-muconic acid in experiments. The dissolved ozone concentration was 8.8 mg/l while it was 3.34 mg/l for experiment P-3. This variation seems to be reasonable considering the effect of bentazone on mass transfer characteristics thus changing the level of dissolved ozone in the reactor. The dissolved ozone concentration level was 9.1 mg/l for experiment B-3.

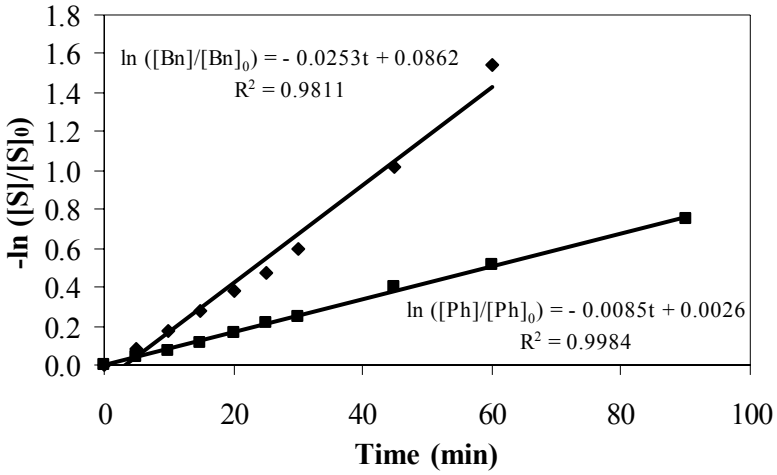


Figure 5.48: Evaluation of removal kinetics for experiment M-1
(♦ bentazone; ■ phenol)

It can be assumed that the effect of bentazone on mass transfer characteristics was more effective than phenol. The dissolved ozone concentrations for experiment M-1 were over than 2 mg/l during the whole oxidation period. An increase in the dissolved ozone concentration is expected to accelerate the reaction. However, the removal rates of both phenol and bentazone were decelerated in the experiment M-1. Therefore, other characteristics of the solution should be effective in modifying the rate constants.

As can be seen from the figure a good fit was observed for both phenol and bentazone for removal kinetics. However the overall removal rate constants found were different from the ones found for the single oxidation experiments. For multiple oxidation systems the rate constants decreased possibly due to the parallel oxidation of phenol and bentazone where solution characteristics were different. For the single oxidation of phenol at 75 mg/l initial concentration the rate constant was 0.0132 1/min for the same oxidation duration. For M-1 experiment the rate constant was found 0.0085 1/min.

The bentazone removal rate constant was determined as 0.0253 1/min for experiment M-1 while it was 0.0506 1/min for the single oxidation experiment of bentazone at the same initial concentration.

As discussed in Subsection 5.4.1 the accumulation of cis, cis-muconic acid affected the reduction rate of phenol. As noted before, bentazone reduction was decelerated from the beginning of the experiment M-1. This deceleration could be explained by the high concentration of cis, cis-muconic acid formed from the beginning of the oxidation

reaction. This high level of cis, cis-muconic acid concentration during the oxidation period had a retarding effect on bentazone removal rate in the experiment M-1.

As a conclusion, the main reason of decreasing the oxidation rate of phenol was figured out as the accumulation and the preferential oxidation of cis, cis-muconic acid. However, the decrease at the removal rate of bentazone can be attributed to the high level concentration of cis, cis-muconic acid from the beginning of the oxidation reaction.

The evaluation of removal kinetics for experiment M-2 is illustrated in Figure 5.49. The overall removal rate constants determined for phenol and bentazone for single oxidation experiments were 0.0132 and 0.0953 1/min while they were 0.0101 and 0.0396 1/min for experiment M-2 respectively. The general characteristics of the oxidation of phenol and bentazone are quite similar in the experiments M-1 and M-2.

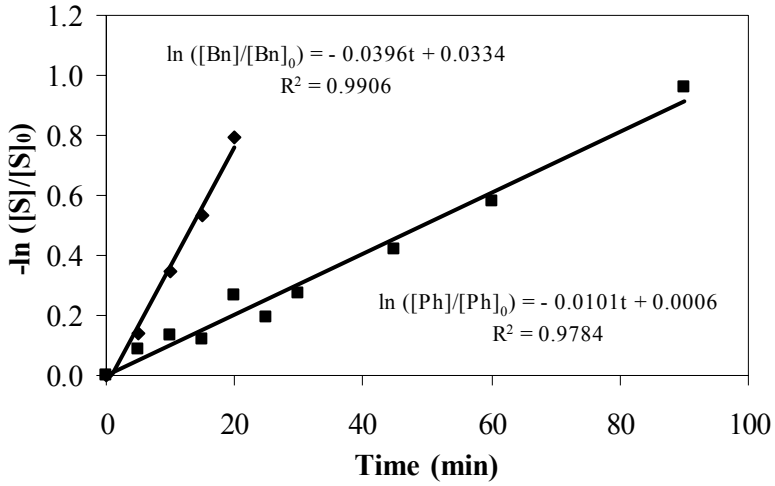


Figure 5.49: Evaluation of removal kinetics for experiment M-2
(♦ bentazone; ■ phenol)

As discussed in detail in Subsection 5.4.2, the dissolved ozone concentrations for experiment M-2 were higher than that measured for the same initial bentazone and phenol concentrations at single oxidation experiments. As can be seen from the Table 5.22, the maximum dissolved ozone concentration for experiment M-2 was reached at 30th minute and its level was 8.2 mg/l. For single oxidation experiment for phenol and bentazone the peak concentrations of dissolved ozone were, 3.3 mg/l and 7.2 mg/l respectively. From the results of measured dissolved ozone concentrations in the solution for experiment M-2 it can be said that the decreases in removal rates of phenol and bentazone cannot be attributed to the dissolved ozone concentrations in the solution

As can be seen from the figure the phenol removal rate decreased as compared to single oxidation of phenol. Though this decrease in phenol removal rate was not as high as that was observed for experiment M-1 (0.0085 1/min). The reason for that, in a similar manner to experiment M-1, may be the level of accumulation of cis, cis-muconic acid. In the single oxidation experiment P-3 the peak value of cis, cis-muconic acid was 3.92 mg/l, it increased to 9.21 mg/l for experiment M-1, while it was only 4.87 mg/l for experiment M-2, being slightly higher from 3.92 mg/l. Therefore, a relatively small decrease in phenol oxidation rate can be judged as demonstrated by the experiment M-2.

The decrease in bentazone removal rate was more pronounced for experiment M-2. This can also e explained by the level of cis, cis-muconic acid concentration in that it was only 0.3 mg/l in experiment B-1a which increased to 4.82 for experiment M-2.

The evaluation of removal kinetics for experiment M-3 is represented in Figure 5.50. For this set of the experiment the initial phenol and bentazone concentrations were 50 mg/l. The calculated overall removal rate constants for single oxidation experiments of phenol and bentazone were 0.0141 and 0.055 1/min respectively. As can be seen from the figure, the calculated the rate constants for experiment M-3 were lower than these values.

The dissolved ozone concentration profile of M-3 had a different pattern with compared to experiments M-1 and M-2. However the dissolved ozone concentrations were over 2 mg/l during the whole oxidation period. The peak concentration was 4.4 mg/l while they were 8.8 and 8.2 for experiments M-1 and M-2 respectively.

In this set of mixture experiment it should be also noted that the measured dissolved ozone concentrations were lower than that measured for single bentazone oxidation experiment of B-2. The measured dissolved ozone concentrations in experiment M-3 would slow down the removal rates of phenol and bentazone.

An evaluation of phenol removal rate constants of M-1, M-2 and M-3 can be made as follows; for M-3 experiment in a quite similar manner to those of M-1 and M-2 the phenol removal rate decreased in comparison with single oxidation experiment of P-2. However, the reduction in rate constant is less pronounced due to the fact that lower initial concentration of phenol with respect to experiment M-1 so having lower concentration of intermediates.

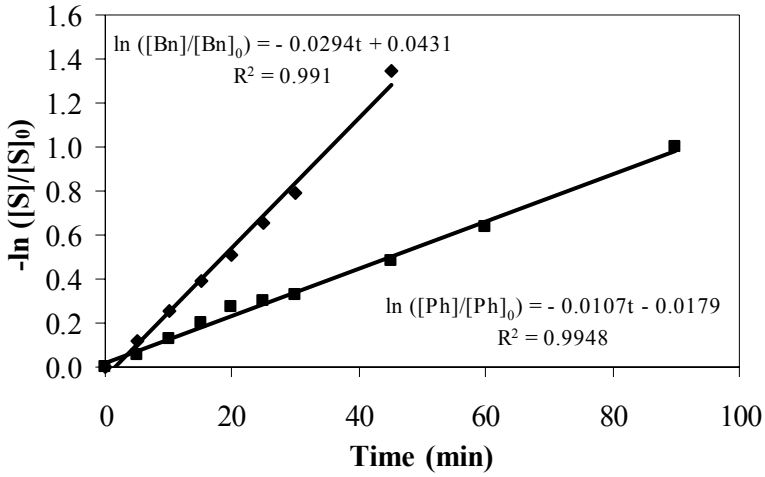


Figure 5.50: Evaluation of removal kinetics for experiment M-3
(♦ bentazone; ■ phenol)

The calculated bentazone removal rate constants for experiments M-1 and M-2 were 0.0253 and 0.0396 1/min respectively while it was 0.0294 1/min for experiment M-3. This is in accordance with the above explanations in that the level of cis, cis-muconic acid concentration in experiment M-3 oxidation was in between the levels observed for experiments M-1 and M-2.

Graphical representations of removal kinetics for experiment M-4 for both phenol and bentazone are illustrated in Figures 5.51.

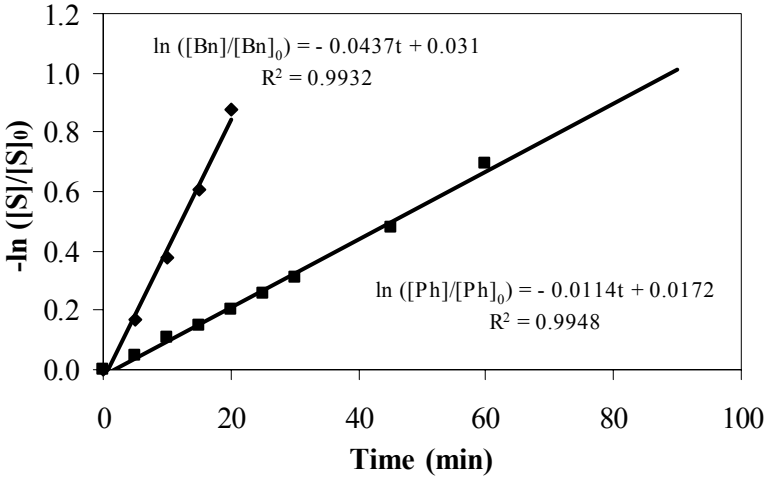


Figure 5.51: Evaluation of removal kinetics for experiment M-4
(♦ bentazone; ■ phenol)

The measured dissolved ozone concentrations in experiment M-4 were lower than that measured for experiment B1-a. However, 2 mg/l dissolved ozone concentration was observed at 10th minute and it remained over this concentration during the whole

oxidation period for experiment M-4. These lower dissolved ozone concentrations would also decrease the removal rates of phenol and bentazone in mixture experiment of M-4 compared to experiment B-1a.

For this set of the experiment the initial phenol and bentazone concentrations were 50 and 25 mg/l respectively. The calculated overall removal rate constant of single oxidation of phenol and bentazone (P-2 and B-1a) with the same initial concentrations were 0.0141 and 0.0953 1/min respectively. As can be seen from the figure the overall removal rate constant for phenol removal for experiment M-4 was 0.0114 1/min and lower than that found for experiment P-2 and the correlation coefficients were high enough for the experiments which can be attributed to the difference between levels of cis, cis-muconic acid concentrations of the two systems.

From the comparison of the calculated rate constants of bentazone removal (B-1a, M-2 and M-4) it can be said that increasing the initial phenol concentration increased the removal rate constant of 25 mg/l bentazone. This acceleration may be due to the parallel oxidation level of phenol with bentazone decreased with decreased initial phenol thus the intermediate concentration.

Graphical representations of removal kinetics for experiment M-5 for both phenol and bentazone are given in Figures 5.52.

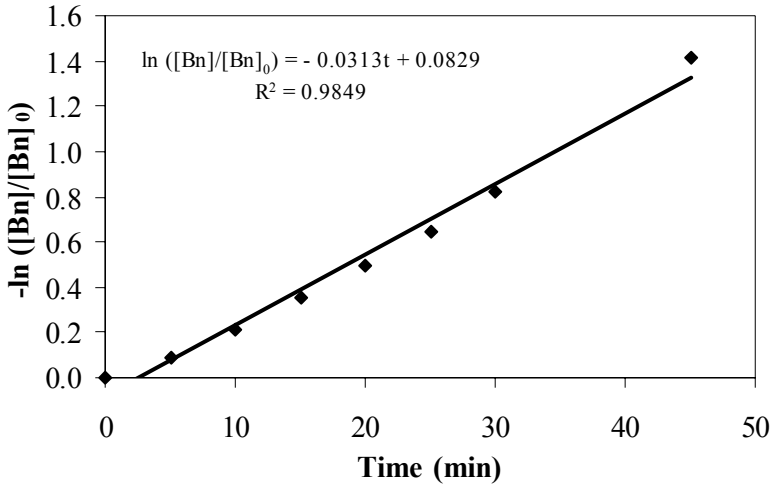


Figure 5.52: Evaluation of removal kinetics for experiment M-5 (♦ bentazone)

The dissolved ozone concentrations for experiment M-5 were higher than that measured for the same initial bentazone and phenol concentrations at single oxidation experiments. The maximum dissolved ozone concentration for experiment

M-5 was 14.6 mg/l. For single oxidation experiment for phenol (P-1a) and bentazone (B-3) these values were 7.3 mg/l and 9.1 mg/l respectively. From the dissolved ozone levels for single and mixture oxidation experiments, it can be concluded that the decreases in removal rates of phenol and bentazone cannot be attributed to the dissolved ozone concentrations in the solution

For experiment M-5 the phenol removal rate constant was not determined due to lower initial phenol concentration and the effect of formed phenol concentration as an intermediate from the oxidation of bentazone. In this set of the mixture experiment the initial bentazone concentration was 75 mg/l. The formed phenol concentration was 3.95 mg/l for single oxidation of bentazone at the same initial concentration.

As can be seen from the figure in this set of the mixture experiment the overall removal rate constant of bentazone oxidation was lower than that observed for single oxidation experiment of B-3. The bentazone oxidation occurred in parallel to phenol oxidation in multiple oxidation systems. The rate constants were 0.0506 1/min for experiment B-3 and 0.0313 for experiment M-5. As noted before the initial concentration of phenol was 75 mg/l for experiment M-1 and the overall removal rate constant was 0.0253 1/min. As can be seen from the results increasing the phenol initial concentration, decreased the removal rate constant of bentazone at experiment M-5. However this decrease was not proportional to the initial phenol concentration because the bentazone oxidation rates between M-1 and M-5 are relatively closer in spite of the fact the peak value of cis, cis-muconic acid was only 4.45 mg/l as compared to 9.21 mg/l for experiment M-1.

The removal kinetics evaluation for experiment M-6 is represented in Figure 5.53. For this set of the experiment the initial phenol and bentazone concentrations were 25 and 50 mg/l respectively.

The dissolved ozone concentrations for experiment M-6 were lower than that measured for the same initial bentazone and phenol concentrations at single oxidation experiments. The maximum dissolved ozone concentration for experiment M-6 was 5.92 mg/l. This measured lower dissolved ozone concentrations would also decrease the removal rates of phenol and bentazone in mixture experiment of M-6.

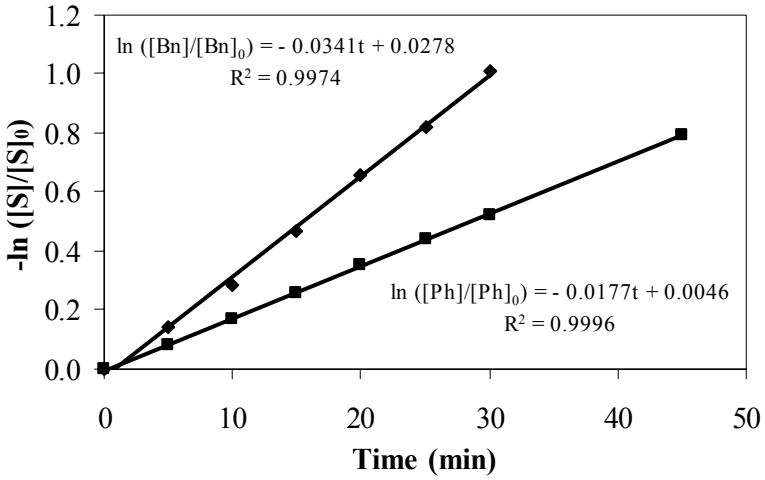


Figure 5.53: Evaluation of removal kinetics for experiment M-6
(♦ bentazone; ■ phenol)

In this set of the mixture experiment as noted before the initial bentazone concentration was 50 mg/l. The formed phenol concentration as an intermediate for experiment B-2 was 0.86 mg/l. The effect of formed phenol concentration as an intermediate from bentazone oxidation would not prevent from a kinetic evaluation of phenol removal. For experiment M-6 the phenol removal rate constant was 0.0177 1/min while it was 0.0288 1/min for experiment P-1a. In mixture experiment M-6, the difference between the formation rate and the oxidation rate of intermediates was different from the experiment P-1a. The peak values of cis, cis-muconic acid observed in experiments P-1a and M-6 were 1.58 mg/l and 4.9 mg/l respectively. As also noted before, the main reason of decreasing the oxidation rate of phenol compared with single oxidation experiments, was figured out as the accumulation and the preferential oxidation of cis, cis-muconic acid. Therefore the difference between cis, cis-muconic acid concentrations for experiments explained the change in the rate constants. A similar explanation was also valid as experiments M-6 and M-3 were compared.

In experiment M-6 the removal rate of bentazone slowed down with a smooth pattern during the oxidation period as compared to experiment B-2. The overall removal rate constant was reduced to 0.0341 (M-6) from 0.055 1/min (B-2). In the experiment M-3 the initial concentration of bentazone was 50 mg/l similar to experiment M-6 and its rate constant was 0.0294 1/min. It can be said that decreasing the phenol concentration from 50 mg/l down to 25 mg/l increased the removal rate constant of bentazone. The reduction in removal rate of bentazone can be due to the high level of

cis, cis-muconic acid concentration similar to other mixture experiments. The bentazone removal rate was decreased as a result of high level concentration of cis, cis-muconic acid from the beginning of the experiment.

Graphical representations of removal kinetics for experiment M-7a for both phenol and bentazone are given in Figures 5.54. For this set of the experiment the initial phenol and bentazone concentrations were 25 mg/l.

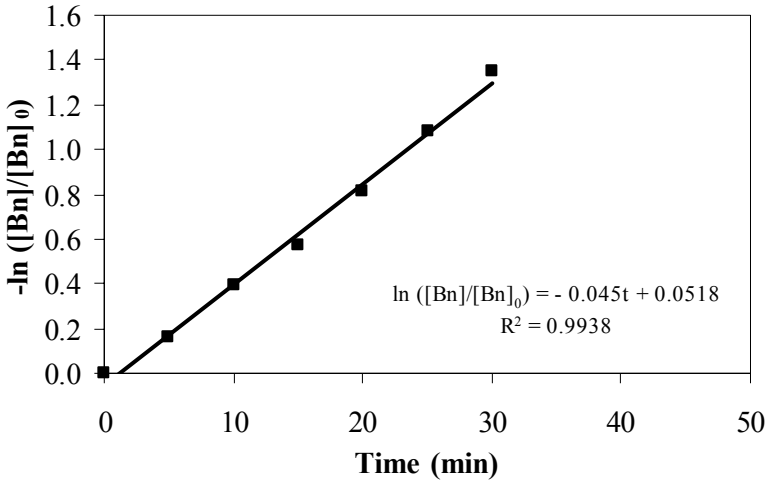


Figure 5.54: Evaluation of removal kinetics for experiment M-7a (♦ bentazone)

In this set of the experiment, bentazone removal fitted well the removal kinetics and the slope is smaller as compared to experiment B-1a which can be associated with the presence of higher concentration of cis, cis-muconic acid while ozone concentrations in the two experiments were comparable. On the other hand a comparison between experiments M-7a and M-6 also yielded a reasonable result in that the higher slope for bentazone oxidation can be explained by a relatively high ozone concentration as well as lower cis, cis-muconic acid concentration for M-7a. As for the phenol it was not possible to obtain a meaningful kinetics due to a sustained phenol concentration between 10-25 minutes. Another peculiarity in this case was a rapid removal of phenol between 25-30 minutes. But when in experiments P-1a and M-7a results compared, complete removal of phenol was seemed to be comparable.

In Table 5.23 summarized results of overall removal rate constants are given for both single and mixture oxidation experiments. The cis, cis- muconic acid concentrations are also given for the evaluation of the differences in rate constants.

Table 5.23: Summarized Results of Overall Removal Rate Constants

	Cis, cis-Muconic Acid Peak Concentration (mg/l)	**Rate Constant**	
	Phenol Experiments		
P-1a	1.58	0.0288	
P-1b	1.54	0.0848	
P-2	2.60	0.0141	
P-3	3.92	0.0132	
P-4	5.22	0.0133	
	Bentazone Experiments		
B-1a	0.28	0.0953	
B-1b	0.49	-	
B-2	0.66	0.0550	
B-3	0.99	0.0506	
B4	0.86	0.0440	
	Mixture Experiments		
		Phenol	Bentazone
M-1	9.21	0.0085	0.0253
M-2	4.87	0.0101	0.0396
M-3	6.45	0.0107	0.0294
M-4	4.78	0.0114	0.0437
M-5	4.45	-	0.0313
M-6	4.82	0.0177	0.0341
M-7a	2.90	-	0.0450
M-7b	3.70	-	

6. CONCLUSIONS

The main objective of this research is to understand the mechanism and process kinetics of ozonation reactions that lead evaluation of organic compounds oxidation when they are alone and in combination in the aqueous medium by molecular ozone under acidic conditions and in the bubble column reactors.

For the evaluation of the kinetic behavior and process of multiple substrate oxidation systems, organic compound removal, intermediate formation and removal, TOC removal pattern and dissolved ozone concentration in the solution are the parameters that need to be investigated. In the multiple substrate oxidation systems, the kinetics and reaction pattern of organic compounds can be different from the case they exist alone in the aqueous medium. This difference may originate from reaction patterns modified by the interaction between the oxidation of the substrate, formation and oxidation of intermediates as well as transport limitations which demonstrate itself in the profile of dissolved ozone concentration. Limited study exists in the literature for the evaluation of multiple substrate oxidation systems. One of the approaches is to find out relative rate constants of the two compounds reacting with ozone. This procedure is reliable when measuring the rates of fast reactions in aqueous solutions, and is based on the assumption that the reaction between the oxidant and the organic substrate follows an overall second-order kinetics, and more specially, of first order with respect to both reactants. However, this approach is not accurate because it does not account for the formation of intermediates and interaction between the oxidation of organic compounds.

In this study, phenol and bentazone were selected as model compounds for the experimental evaluations. In addition to the measurements of phenol and bentazone, the main intermediates formed, ozone concentration in the reactor and TOC measurements were also made in accordance with the aim of the study. Experiments were performed using synthetic solutions of the selected substrates in constant temperature room by a semi-batch glass reactor into which ozone is continuously bubbled to react with organic compounds at acidic pH (3.0).

The results obtained in the study have allowed formulating the following conclusions:

1) Cis, cis-muconic acid and hydroquinone were determined to be important intermediates formed during the ozone oxidation of phenol. Cis, cis-muconic acid and phenol were the intermediates monitored during the ozone oxidation of bentazone. The ratios of cis, cis-muconic acid to initial phenol concentrations were ranged between 7-5% while it was 6.4-10% for hydroquinone. The peak concentration of phenol was ranged between 1.21-5.70 mg/l for experiments conducted on 25-100 mg/l initial bentazone concentration. The peak values of cis, cis-muconic acid formed during the single bentazone oxidations were less than 1 mg/l for all experiments.

2) For single oxidation experiments of phenol and bentazone, the level of dissolved ozone in the bulk liquid and peak dissolved ozone concentrations increased with the increasing initial phenol and bentazone concentration. This variation seems to be reasonable considering the effect of organics on mass transfer characteristics. The observed dissolved ozone peak concentrations for single bentazone experiments were higher than those observed for phenol oxidation experiments. This indicated that the transport of ozone could be more readily provided for bentazone with regard to phenol. The peak dissolved ozone concentrations were ranged between 3.01 and 3.67 mg/l for phenol and 7.64-9.75 mg/l for bentazone for initial concentrations of 50-100 mg/l. During the course of the reaction, after peak values reached, dissolved ozone concentrations started to decrease upon further ozonation and reached an almost stationary concentration at around 2.0 mg/l through the end of measurements. The decrease in the dissolved ozone concentration can be attributed to the further ozonation of the intermediates and slowly reacting end products as well as diminishing ozone transport efficiency.

3) The TOC profiles during the oxidation exhibited a parallel change with the formation and oxidation of intermediates. In single phenol and bentazone oxidation experiments TOC removals were limited and were around 9-19% and 16-22% for phenol and bentazone, respectively at 3.0 mg/min ozone dosage. TOC removals became to be significant beyond the time where peak intermediate concentrations were obtained.

4) In the mixture experiments a steady removal pattern was observed for both phenol and bentazone for all concentrations studied except 25 mg/l initial concentration of both phenol and bentazone. The overall result of this study was that the rate of removal of both phenol and bentazone in mixture was less than their corresponding rates in the case of single oxidation experiments. For single phenol oxidation experiments, after 45 minutes a slowing down of the rate of phenol oxidation was observed for all mixture experiments with regard to single phenol oxidation experiments of the same initial concentrations. This deceleration affect decreased with decreasing initial bentazone concentration. The removal rate of bentazone slowed down with a smooth pattern during the oxidation period of mixture experiments. Increasing the phenol concentration extended the time needed for complete removal of bentazone. The modification of the removal rates in mixture experiments was explained considering the different profiles of intermediates and dissolved ozone concentration through the experiments.

5) The peak concentrations of cis, cis-muconic acid formed during the multiple substrate oxidation experiments increased with increasing initial phenol and bentazone concentration. The peak concentration of cis, cis-muconic acid was ranged between 2.9-9.21 mg/l for all mixture experiments (ca. 1-57-5.22 mg/l in single oxidation systems). The above increase in the accumulation of cis, cis-muconic acid with respect to single oxidation systems was attributed to affect the removal rate of phenol and bentazone in the mixture experiments. The effect of dissolved ozone concentration in the mixture experiments on the removal rate of phenol and bentazone was considered to be in a lesser extent than the effect of intermediates since in most of the cases dissolved ozone profiles of single and mixture experiments were not significantly different. The peak dissolved ozone concentrations were ranged between 4.39-14.65 mg/l for mixture experiments at 3.0 mg/min ozone dosage (ca. 3.01-14.01 mg/l for single phenol oxidation experiments and 7.64-17.31 mg/l for single bentazone oxidation experiments).

6) TOC removals for all experiments indicated limited amount of mineralization, thus existence of slowly oxidizable end products. In mixture oxidation experiments TOC removals at the time that cis, cis-muconic acid peak was observed were always slightly higher than sum of respective single oxidation

TOC removals of phenol and bentazone except for the systems with 25 mg/l initial phenol. In mixture oxidation experiments TOC removals were limited and were around 11-20% at 3.0 mg/min ozone dosage.

7) Mathematical modeling of the system was attempted though the use of simultaneous differential equations representing all the variables involving in the system however, none of the models yielded a satisfactory approximation due to highly variable character of the system as well as insufficient data particularly concerning the intermediate formation and also variations at volumetric mass transfer coefficient. Therefore an overall substrate removal modeling was carried out employing the following formula for both single and mixture systems.

$$\frac{d[S]}{dt} = -k \quad [S] \qquad \textbf{(6.1)}$$

8) The overall substrate removal rate constants of single ozonation of phenol have been found ranging between 0.0133-0.0288 1/min at 3.0 mg/min ozone dosage whereas bentazone removal rates ranged between 0.044-0.0953 1/min at the same ozone dosage.

9) For the oxidation of mixtures the same kinetic approach was applied. The overall substrate removal rate constants of both phenol and bentazone were found to be always lower than those obtained for single substrate oxidation kinetics. These changes in the removal rate constants were related to accumulation of intermediates, particularly cis, cis-muconic acid for the phenol oxidation. The decrease in the overall substrate removal rate constants, for the mixture experiments studied was in the order of 60-70% for phenol and about 50% for bentazone which indicated a significant difference.

As summarized above the thesis study indicated several points that should be taken into consideration in the evaluation of ozone oxidation systems. An overall assessment of the outcomes of the study yields the following as the basic points related to the mechanisms of the ozone oxidation of multiple substrate oxidation systems:

In the multiple substrate oxidation systems, the process kinetics and reaction pattern of organic compounds found to be different from the case they exist alone in the aqueous medium. This difference was attributed to reaction patterns modified by the

interaction between the oxidation of the substrates, formation and oxidation of intermediates as well as the variations at overall mass transfer coefficient ($k_L a$). The variation in volumetric mass transfer coefficient due to the surface active character of the substrates, also the removal of the initial compound and formation of intermediates during the course of the oxidation reactions, the mass transfer characteristics of the reactor becomes different at each oxidation period. In these circumstances the derived equations for the modeling of ozonation process need to be modified for each oxidation period. However, the expression of $k_L a$ value by differential equations is very difficult. The modeling approaches used in the literature do not consider this variation in $k_L a$ value therefore these models would not be appropriate for the modeling of ozone oxidation processes. For a better understanding of the system, the $C*t$ parameter can also be evaluated where C is the applied ozone dosage (mg/min) and t is the reaction time in which organic compound is removed completely (min).

Recommended further studies in this area for a thorough understanding and quantitative evaluation of ozone oxidation of multiple substrate systems:

- To carry out further investigation for the evaluation of the relationship between the applied ozone dosage and the reaction time
- To identify and quantify the unknown intermediates to evaluate a more realistic picture of the ozone oxidation systems and process kinetics
- To follow the concentration of ozone gas outlet of the reactor to evaluate ozone utilization for the ozone oxidation systems
- To model the mass transfer of ozone with changing $k_L a$ values depending on surface active character of the substrate and end product composition

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BIBLIOGRAPHY

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