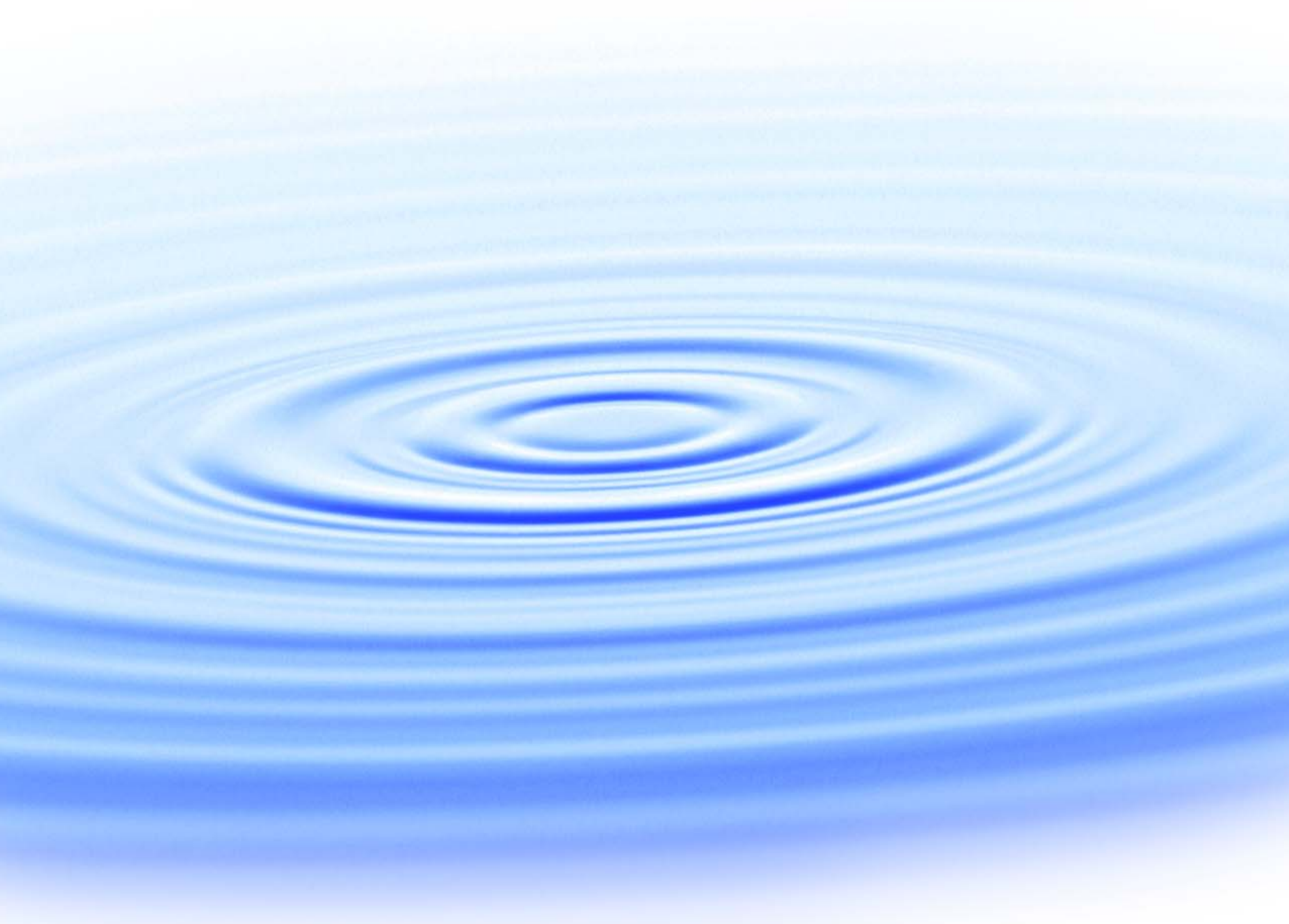
Oxidative Treatment of Organics in Membrane Concentrates



WateReuse Research Foundation

Oxidative Treatment of Organics in Membrane Concentrates

About the WateReuse Research Foundation

The mission of the WateReuse Research Foundation is to conduct and promote applied research on the reclamation, recycling, reuse, and desalination of water. The Foundation's research advances the science of water reuse and supports communities across the United States and abroad in their efforts to create new sources of high quality water through reclamation, recycling, reuse, and desalination while protecting public health and the environment.

The Foundation sponsors research on all aspects of water reuse, including emerging chemical contaminants, microbiological agents, treatment technologies, salinity management and desalination, public perception and acceptance, economics, and marketing. The Foundation's research informs the public of the safety of reclaimed water and provides water professionals with the tools and knowledge to meet their commitment of increasing reliability and quality.

The Foundation's funding partners include the Bureau of Reclamation, the California State Water Resources Control Board, the California Energy Commission, and the California Department of Water Resources. Funding is also provided by the Foundation's Subscribers, water and wastewater agencies, and other interested organizations.

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ABBREVIATIONS

AOP	Advanced oxidation process
APT	Applied Process Technologies, Inc.
BDOC	Biologically degradable organic carbon
$BDOC_5$	Five-day biologically degradable organic carbon
BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
DOC	Dissolved organic carbon
DOM	Dissolved organic material
ED	Electrodialysis
EDC	Endocrine-disrupting compound
EDAX	Energy-dispersive X-ray analysis
EDR	Electrodialysis reversal
EDTA	Ethylenediaminetetraacetic acid
EfOM	Effluent organic material
EE/O	Electrical energy per reaction order
Fe^{2+}	Ferric iron
Fe^{3+}	Ferrous iron
GC	Gas chromatography
H_2O_2	Hydrogen peroxide
$HO^{\cdot}$	Hydroxyl radical
$[HO^{\cdot}]_{SS}$	Steady-state hydroxyl radical concentration
kWh	Kilowatt-hour
K_{OW}	Octanol-water partition coefficient
LAS	Linear alkylbenzene sulfonate
LC	Liquid chromatography
m^3	Cubic meter
MF	Microfiltration
MGD	Million gallons per day
MS	Mass spectroscopy
MW	Molecular weight
MWCO	Molecular-weight cutoff
NF	Nanofiltration
NOM	Natural organic matter

O_3	Molecular ozone
*p*CBA	*para*-chlorobenzoic acid
PPCP	Pharmaceutical and personal care product
RO	Reverse osmosis
SAT	Soil aquifer treatment
SMP	Soluble microbial product
SOC	Synthetic organic chemical
SUVA	Specific UV absorbance at 254 nm
TDS	Total dissolved solids
TiO_2	Titanium dioxide
TOC	Total organic carbon
UF	Ultrafiltration
UV	Ultraviolet
UVA	UV absorbance
VRA	Volatile reactor assembly
WWTP	Wastewater treatment plant

FOREWORD

The WateReuse Research Foundation, a nonprofit corporation, sponsors research that advances the science of water reclamation, recycling, reuse, and desalination. The Foundation funds projects that meet the water reuse and desalination research needs of water and wastewater agencies and the public. The goal of the Foundation's research is to ensure that water reuse and desalination projects provide high-quality water, protect public health, and improve the environment.

A Research Plan guides the Foundation's research program. Under the plan, a research agenda of high-priority topics is maintained. The agenda is developed in cooperation with the water reuse and desalination communities including water professionals, academics, and Foundation Subscribers. The Foundation's research focuses on a broad range of water reuse research topics including:

- Defining and addressing emerging contaminants;
- Public perceptions of the benefits and risks of water reuse;
- Management practices related to indirect potable reuse;
- Groundwater recharge and aquifer storage and recovery;
- Evaluation and methods for managing salinity and desalination; and
- Economics and marketing of water reuse.

The Research Plan outlines the role of the Foundation's Research Advisory Committee (RAC), Project Advisory Committees (PACs), and Foundation staff. The RAC sets priorities, recommends projects for funding, and provides advice and recommendations on the Foundation's research agenda and other related efforts. PACs are convened for each project and provide technical review and oversight. The Foundation's RAC and PACs consist of experts in their fields and provide the Foundation with an independent review, which ensures the credibility of the Foundation's research results. The Foundation's Project Managers facilitate the efforts of the RAC and PACs and provide overall management of projects.

The Foundation's primary funding partners include the Bureau of Reclamation, California State Water Resources Control Board, the California Energy Commission, Foundation Subscribers, water and wastewater agencies, and other interested organizations. The Foundation leverages its financial and intellectual capital through these partnerships and funding relationships.

The use of membrane processes for wastewater treatment and reuse is rapidly expanding, especially the use of reverse osmosis (RO) membranes. RO membrane processes effectively remove organic, inorganic, and biological constituents, which accumulate in membrane concentrates. The goal of this project is to develop an oxidation process for removing organics in membrane concentrates. While previous projects have focused on issues associated with inorganic salts, utilities have few resources to treat organics or microbiological organisms present in membrane concentrates.

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They include the members of the research team and PAC members (as identified below), and the WateReuse Research Foundation's project managers, Josh Dickinson and Anna Durden. Kungyunk Park was a visiting postgraduate researcher from Korea during the time of this research and contributed to quantifying the hydroxyl radical conditions present during the oxidation of reverse osmosis concentrates. Applied Process Technology donated an integrated ozone-hydrogen peroxide system (HiPOx) for use on this project. Purifics, Inc. donated an integrated UV-TiO_2-ceramic membrane system (Photo-Cat^{TM}) for use on this project.

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EXECUTIVE SUMMARY

The use of membrane processes for wastewater treatment and reuse is rapidly expanding, especially the use of reverse osmosis (RO) membranes. RO membrane processes effectively remove organic, inorganic, and biological constituents, which accumulate in membrane concentrates. Therefore, membrane concentrates represent a significant concentrated point-source flow from the urban system into the environment. Considerable attention has focused on the impact of salts in membrane concentrates, but significantly less attention has been paid to the organic and biological constituents. The organic materials in membrane concentrates include organic matter in the carrier drinking water, refractory chemicals added by the public to wastewater (for example, pesticides, personal care products, pharmaceutical products, endocrine disruptors, etc.), and residuals from wastewater treatment processes (for example, soluble microbial products, partially biodegraded organics, and antiscaling chemicals). Removing these organics may become important in the future as the utilization of membranes for wastewater reuse grows.

PROJECT OBJECTIVES AND ORGANIZATION OF REPORT

The goal of this project is to develop an oxidation process for removing organics in membrane concentrates. While previous projects have focused on issues associated with inorganic salts, utilities have few resources to treat organics or microbiological organisms present in membrane concentrates. Three tasks were carried out to address the goal of the project:

1. Conduct a literature review and technical comparison of the technical and economic feasibility of existing and emerging oxidation processes for treating organics in membrane concentrates;
2. Conduct bench-scale screening of oxidation processes with the greatest potential for success; and
3. Optimize the most feasible oxidation process for treating RO membrane concentrate from a wastewater reclamation facility, and identify potentially limiting factors for implementing this technology.

This report is organized into five chapters that address these various objectives. Chapters 1 and 2 serve as an introduction to and literature review of the issues and potential processes that may oxidize organics. Chapter 3 describes the experimental and analytical methods employed during the project. Chapter 4 presents the results of screening several different oxidation processes for their ability to oxidize the organic matter present in an RO membrane concentrate. Chapter 5 investigates the optimization of one advanced oxidation process (AOP) (namely, titanium dioxide/UV irradiation) and its synergy with biological treatment. Chapter 6 summarizes the project, provides recommendations to utilities, and suggests follow-on research that will benefit the water reuse industry.

APPROACH

Several technologies capable of oxidizing organics were evaluated: 1) Fenton reactions with and without subsequent iron coagulation; 2) ozone with and without hydrogen peroxide; 3) UV irradiation alone, with hydrogen peroxide, or with titanium dioxide; and 4) wet chemical oxidation. Most of the research was conducted with concentrate from RO of partially denitrified wastewater at the City of Scottsdale Water Campus. The RO concentrate had a dissolved organic carbon (DOC) concentration of 40 to 50 mg/L and total-dissolved-solid (TDS) concentration of ~5500 mg/L. One membrane cleaning solution was also studied.

Oxidation experiments were conducted using bench-scale units. In addition to standard laboratory test systems, two proprietary AOP systems were evaluated. The first system (HiPOx from Applied Process Technology, Inc.) feeds hydrogen peroxide and ozone. The lab-scale unit supplies ozone as a gas to a rapidly recirculating sample (RO concentrate) spiked with high levels (100 to 1000 mg/L) of hydrogen peroxide. The second system (Photo-Cat^{TM} by Purifics, Inc.) is an integrated UV irradiation and ceramic membrane system that permits the internal recirculation of titanium dioxide.

Over the course of the study, RO concentrate was collected and subjected to treatment in the bench-scale reactors. The loss of DOC as a function of chemical dosage and energy input was monitored. Changes in other organic parameters (for example, UV absorbance at 254 nm, chemical oxygen demand, and concentrations of organic acids and biodegradable components) were also monitored. During selected experiments, the steady-state concentration of hydroxyl radicals was estimated using a probe compound (*para*-chlorobenzoic acid).

SUMMARY AND CONCLUSIONS

Processes that produced hydroxyl radicals were capable of oxidizing DOC to purgeable gases and biodegradable organics. UV/TiO_2 was selected as a sequential advanced oxidation biodegradation process because it lacks chemical reagents that could affect biological processes. UV radiation did not leave a residual, and titanium dioxide was easily separated using membranes. To achieve the 90% DOC removal goal for this project, biodegradation was incorporated, which reduced the energy dose requirements roughly by half. Thus, the project objective was achieved. Additional key summary points are given below.

Summary of Experiments Used to Screen the Effectiveness of DOC Removal from Wastewater RO Concentrate

- Iron coagulation removed less than 5% of the DOC in the RO concentrate.
- Applying the Fenton reaction at pH = 3 to 3.5 (10 mM Fe^{2+} and 10 mM H_2O_2) rapidly removed ~50% of the DOC in the RO concentrate. Raising the pH to 7.5 to 8.0 and allowing ferric iron to precipitate removed residual iron. Higher ferrous iron and hydrogen peroxide dosages might have yielded greater DOC removals.
- Ozonation (with hydrogen peroxide) of RO concentrate formed a white precipitate, probably calcite, because of a slight pH change and possibly also the cleavage of calcium-organic complexes or other microflocculation processes.
- Ozone addition, using a 0.7 mole H_2O_2/mole O_3 dose, oxidized and removed DOC. Ozone dosages of more than 1000 mg/L are necessary for approximately 75% removal of DOC in the RO concentrate. Up to this level of removal, DOC removal was nearly linear as a function of ozone dose. DOC removal was independent of when H_2O_2 was applied.
- UV/H_2O_2 achieved 40% DOC removal at a pH of 4, a UV dose of 12 kWh/m^3 with a 10 mM H_2O_2 dose. At pH levels of 7 and 10, UV/H_2O_2 removed less than 10% of the DOC.
- UV/TiO_2 achieved up to 95% DOC removal at a UV dose of 10.4 kWh/m^3 and was nearly independent of titanium dioxide doses between 1 and 5 g/L.
- Addition of H_2O_2 during UV/TiO_2 application did not significantly improve DOC removal.

- UVA percentage removal was greater than the DOC percentage removal, indicating preferential oxidation of carbon-carbon double bonds by the oxidation processes.

Because UV/TiO_2 was the easiest process to repeatedly conduct in the laboratory and achieved the highest DOC removal and best electrical energy per reaction order (EE/O), it was selected for optimization in the next phase of the research. The ozone process had problems with residual dissolved ozone and precipitates. Any hydrogen peroxide process would have needed to address residual hydrogen peroxide, which was considerable (10 to >100 mg/L), based on measurements.

Summary of Pulse Radiolysis Experiments Conducted to Estimate Reaction Rate Constants between the Hydroxyl Radical and Wastewater Organics

Pulse radiolysis research was conducted with other WateReuse-funded collaborators using the Department of Energy facilities at the University of Notre Dame Radiation Laboratory. The research was published in *Environmental Science and Technology* (Westerhoff et al., 2007) and is not reported here in detail because it was not part of the initial research plan. However, the research became extremely useful in the development of predictive models for the removal of organics in RO concentrate during AOP treatment.

Pulse radiolysis experiments were conducted on hydrophobic and hydrophilic acids and neutrals isolated from dissolved organic matter (DOM) samples from different sources (namely, stream, lake, and wastewater treatment plant). Absolute bimolecular reaction rate constants for the reaction of hydroxyl radicals ($^\bullet$OH) with DOM ($k_{^\bullet OH,\,DOM}$) were determined. The $k_{^\bullet OH,\,DOM}$ values are expressed as moles of carbon. Based on direct measurement of transient DOM radicals (DOM$^\bullet$) and competition kinetic techniques, both employing pulse radiolysis, the $k_{^\bullet OH,\,DOM}$ value for a standard fulvic acid from the Suwannee River purchased from the International Humic Substances Society was $(1.60 \pm 0.24) \times 10^8$ $M^{-1}s^{-1}$. Both pulse radiolysis methods yielded comparable $k_{^\bullet OH,\,DOM}$ values. The $k_{^\bullet OH,\,DOM}$ values for the seven DOM isolates from different sources ranged from 1.39×10^8 $M^{-1}s^{-1}$ to 4.53×10^8 $M^{-1}s^{-1}$ and averaged 2.23×10^8 $M^{-1}s^{-1}$ (equivalent to 1.9×10^4 [mg of C/L]$^{-1}s^{-1}$). More polar, lower-molecular-weight DOM isolates from wastewater have higher $k_{^\bullet OH,\,DOM}$ values.

Summary of Experimental Results for the Optimization of UV/TiO_2 Treatment plus Biodegradation for DOC Removal from Wastewater RO Concentrate

- UV/TiO_2 treatment removes nearly all of several pharmaceuticals from the RO concentrate to below the detection limits (1 ng/L).
- UV/TiO_2 treatment alone can achieve in excess of 90% DOC removal. Thus, the treatment meets our project goals. The rate of DOC removal is nearly zero-order (1.9 mg of DOC/L per kWh/m^3 or 0.53 kW-h-m^{-3}-[mg of DOC/L]$^{-1}$) up to 80% to 85% DOC removal. For higher DOC removals, the rate is also zero-order, but considerably more energy is required (0.67 kW-h-m^{-3}-[mg of DOC/L]$^{-1}$) to continue the oxidation of by-products that react slowly with hydroxyl radicals.
- No strong dependence on initial DOC concentration was observed for the zero-order rate loss of DOC. However, pH had a significant effect. A higher steady-state hydroxyl radical concentration ($[HO^\bullet]_{SS}$) was achieved at a pH of 5 than at a pH of 7 (the ambient pH of RO concentrate). The higher $[HO^\bullet]_{SS}$ occurred because of less scavenging by bicarbonate ion at the lower pH level. $[HO^\bullet]_{SS}$ was assessed using a hydroxyl radical probe (*para*-chlorobenzoic acid) spiked into RO concentrate. Values for $[HO^\bullet]_{SS}$ were on

the order of 0.2×10^{-13} M to 2×10^{-13} M in the lab UV reactors at pH = 7 and 5, respectively.

- In the lab UV system, UV/TiO_2 treatment produced biologically degradable organic carbon (BDOC). Without UV/TiO_2 treatment, less than 5% of the DOC in the RO concentrate was biodegradable. After UV/TiO_2 treatment, specific organic acids (oxalate, acetate, propionate, pyruvate, and formate) were present at concentrations from 100 to nearly 5000 mg of C/L. Other biodegradable materials also formed, because the measured BDOC content of samples after UV/TiO_2 treatment was always greater than the sum of the five measured organic acids. After UV/TiO_2 treatment using higher energy inputs, namely doses of 18 kWh-m^{-3} and 9 kWh-m^{-3}, the biodegradable fraction of the residual DOC increased to nearly 80% and 50%, respectively.
- The performances of the lab-scale UV system (1.8 L) and the larger-scale recirculating UV/TiO_2/ceramic membrane system (30-L Photo-Cat^{TM} system) were similar but clearly confirmed the order-of-magnitude energy inputs required to achieve DOC removal from RO concentrate. Both systems confirmed the production of significant amounts of BDOC material at dosages on the order of 5 to 15 kWh-m^{-3}.
- A preliminary economic analysis puts the energy cost for UV/TiO_2 treatment in the range of $1 to $8 per 1000 gal, depending upon the target final DOC concentration and whether biodegradation (medium filtration) is incorporated. Only the energy input for the UV system was considered because the energy used by the ceramic membrane system for TiO_2 recovery was assumed to be much lower than the UV system energy demand.

RECOMMENDATIONS FOR UTILITIES

RO and other high-solute-rejection membrane systems used for advanced treatment of wastewater produce concentrated waste streams containing salts, trace organics, and bulk, less characterized, organics. Discharge of these waste streams into the environment represents a point source of potential pollution. This research addresses the ability of oxidation and biological processes to significantly reduce the amount of organics present in RO concentrate before its discharge into the environment. Treatment of organics in RO concentrate is cost-effective because smaller volumes (namely, lower flowrates) of concentrated organics are treated. Although regulations do not yet exist for many organics in RO concentrates from wastewater treatment plants, they may in the future. From a broader ecosystem perspective, it may also be advantageous to treat refractory organics in RO concentrates before their release into surface waters, oceans, or even downstream regional wastewater treatment plants where trace organics (for example, estrogenic or other pharmaceutical compounds) may impact specific organisms or food chains.

The UV/TiO_2 system removed both bulk and trace organics in RO concentrate. The AOP decreased levels of pharmaceuticals and personal care products present in RO concentrate to less than 1 ng/L while decreasing bulk DOC from 40 mg/L to <10 mg/L. Experiments also demonstrated that the UV/TiO_2 system removed organics present in RO membrane cleaning solutions. However, these cleaning solutions have high organic carbon concentrations due to the surfactants they contain, so the UV dose required to achieve >90% DOC removal of these solutions is extremely high compared to that for the DOC in RO concentrate.

This study also demonstrated an integrated UV/TiO_2 system with a built-in ceramic membrane system (Photo-Cat by Purifics, Inc.) that can oxidize a significant fraction of DOC in RO concentrate to purgeable gases and biologically degradable organic material. Following this integrated system with a biological filter (sand, anthracite, or activated carbon) would reduce the electrical energy input for the UV system while achieving a high level (>90%) of DOC removal.

All AOPs will be more effective at lower pH levels because of hydroxyl radical scavenging by bicarbonate and carbonate species. The pH of the RO concentrate used in our study was approximately 7.0 (alkalinity = 1100 mg/L as $CaCO_3$). UV/TiO_2 treatment was significantly more effective at pH = 5 than at pH = 7 because of the reduced $HO^{\bullet}$ scavenging by bicarbonate at pH = 5, which leads to higher steady-state $HO^{\bullet}$ concentrations. It may be possible to better optimize the low-pH conditions required to prevent scale formation during RO treatment and those required to reduce $HO^{\bullet}$ scavenging during AOP treatment.

RECOMMENDATIONS FOR FUTURE RESEARCH

This research should initiate further efforts to reduce organics in RO concentrates before they are discharged to the environment or other wastewater treatment facilities. Potential future research efforts include:

- If salt rejection is not a primary objective for wastewater reuse, treatment by AOPs alone (without membranes) could become a viable approach for controlling organics. A comparison between integrated UV/TiO_2 systems (with ceramic membranes for TiO_2 separation) and tight membrane (RO and NF) systems is worthwhile to evaluate which system achieves overall reuse treatment goals at the lowest treatment costs. Ceramic membranes are effective at removing a wide variety of oocysts and bacteria, while UV disinfection effectively inactivates many viruses.
- Continuous-flow UV/TiO_2 treatment (pilot-scale) systems followed by simple biological filters (activated carbon) should be evaluated for posttreatment of RO concentrate prior to discharge to the environment.
- The cost-effectiveness of removing specific percentages (e.g., 10%, 50%) of the DOC from RO concentrate should be determined. Furthermore, DOC removal costs should also be balanced against the incremental benefits in reduction of potential toxicity or other ecological endpoints.
- The ability of UV/TiO_2 systems to reduce toxicity, rather than simply to remove DOC and specific compounds, should be investigated. A relationship between DOC removal and toxicity reduction would serve as useful guidance for utilities attempting to set target DOC levels for discharge of RO concentrates.
- The long-term usage of TiO_2 on membrane concentrates has not been evaluated but should be in the near future. Issues that should be addressed include 1) the long-term viability of TiO_2 structural (namely, friability) and oxidative properties, 2) accumulation of metals on TiO_2, and 3) disposal requirements for spent TiO_2.

CHAPTER 1

INTRODUCTION AND OBJECTIVES

1.1 STATEMENT OF PROBLEM

The use of membrane processes (microfiltration [MF], ultrafiltration [UF], nanofiltration [NF], reverse osmosis [RO], and electrodialysis [ED] reversal) for wastewater treatment and reuse is rapidly expanding. Membrane processes effectively remove organic, inorganic, and biological constituents, which then accumulate in membrane concentrates. As a result, membrane concentrates represent a significant concentrated point-source flow from the urban system into the environment. Utilities can treat these membrane concentrates and associated waste streams to minimize environmental impacts upon the disposal of this point-source flow. Considerable attention has focused on the impact of salts in membrane concentrates, but significantly less attention has been paid to the organics and biological constituents. The organic materials in membrane concentrates include organic matter in the carrier drinking water, refractory chemicals added by the public into wastewater (pesticides, personal care products, pharmaceutical products, endocrine disruptors, etc.), and residuals from wastewater treatment processes (for example, soluble microbial products [SMPs], partially biodegraded organics, and antiscaling chemicals). In addition, membrane concentrates contain biological materials (bacteria, viruses, oocysts, and cell fragments) that also represent a potential point source for control. Complete oxidation of all organics, including biological organisms, to carbon dioxide would represent the highest level of control. While complete oxidation may be cost-prohibitive, >90% organic oxidation may be feasible. Such a reduction would decrease the environmental impact of membrane concentrate disposal and potentially allow new uses of membrane concentrates that were previously limited by the presence of undesirable organics. In addition to oxidizing organics, the proposed oxidation technologies would achieve exceptionally high inactivation of bacteria and pathogens. This project lays a foundation for assessing potential treatment strategies for membrane concentrates, should this practice be deemed necessary to protect the environment in the future.

1.2 PROJECT OBJECTIVES

The goal of this project is to develop a posttreatment oxidation process to remove organics in membrane concentrates. While previous projects have focused on problems associated with inorganic salts, utilities have few resources to address organics or microbiological organisms present in membrane concentrates. Three tasks were carried out to address the goal of the project:

1. Conduct a literature review and technical comparison of the technical and economic feasibility of existing and emerging oxidation processes for treating organics in membrane concentrates;
2. Conduct bench-scale screening of oxidation processes with the greatest potential for success; and
3. Optimize the most feasible oxidation process for treating RO membrane concentrate from a wastewater reclamation facility, and identify potentially limiting factors for implementing this technology.

This report is organized into five chapters that address these various objectives. Chapters 1 and 2 serve as an introduction to and literature review of the issues and potential processes that may oxidize organics. Chapter 3 describes the experimental and analytical methods employed during the project. Chapter 4 presents the results from screening several different oxidation processes for their ability to oxidize organic matter present in RO membrane concentrate. Oxidation of organic matter involves both the formation of low-molecular-weight acids and purgeable gases, which are mainly carbon dioxide (namely, mineralization). Chapter 5 investigates the optimization of one advanced oxidation process (AOP) (namely, titanium dioxide/UV irradiation) and its synergy with biological treatment. Chapter 6 summarizes the project, provides recommendations to utilities, and suggests follow-on research that will benefit the water reuse industry.

CHAPTER 2

BACKGROUND

This chapter provides a literature review of the issues surrounding membrane concentrates, potential processes that may oxidize organics, and challenges to this type of research. A comparison of the technical and economic feasibilities of existing and emerging oxidation processes for treating organics in membrane concentrates is given.

2.1 WASTEWATER ORGANICS

Wastewater effluent organic matter (EfOM) contains a mixture of organic materials, including residual natural organic matter (NOM) present in the drinking water, biodegradable materials added by the public, SMPs produced by bacterial processes within the wastewater treatment plant (WWTP), and residual synthetic organic chemicals added by consumers and industry (surfactants, plasticizers, pharmaceuticals, personal care products, endocrine disruptors, etc.) that processes within the WWTP did not remove (Dignac et al., 2000; Drewes et al., 2002; Drewes et al., 1999; Fox, 2001). Drinking water serves as the "carrier" water for wastewater, and much of this drinking NOM passes through WWTPs. Depending upon the WWTP, the unit processes used (trickling filter, activated sludge, denitrification, etc.) will achieve variable removal efficiencies of the biodegradable organic matter added by the public (food, wastes, surfactants, etc.). SMPs are organic compounds generated by substrate metabolism and biomass decay during the biological treatment of water by bacteria (Barker et al., 1999; Barker and Stuckey, 1999). SMPs consist of macromolecules and cellular debris with protein and polysaccharide signatures. Adsorption or degradation within WWTPs partially or completely removes household and industrial chemicals, but their presence in effluents raises significant concern for aquatic and terrestrial organisms and potentially for humans as well (Daughton and Ternes, 1999; Snyder et al., 2003; Ternes, 1998; Ternes et al., 1999). Therefore, there is a need to minimize the amount of EfOM entering the environment to prevent adverse ecological or human impacts. This requirement includes the EfOM in membrane concentrates.

Carbonaceous biochemical oxygen demand (BOD) and chemical oxygen demand (COD) measurements are the most commonly reported surrogate for wastewater organics. However, many inorganics also exert COD, and BOD is only a measure of the oxygen consumption, not of the refractory organic content. Therefore, total or dissolved organic carbon (TOC or DOC) measurements more accurately quantify the EfOM concentration. Considerably fewer TOC and DOC data than BOD or COD concentrations are available for WWTP discharges. Recent research shows that the amount of DOC present in wastewater is a function of the level of treatment and that WWTPs that use denitrification can approach DOC levels observed in drinking water treatment plants (Figure 2.1) (Chen, 2007). Most wastewater reuse membrane systems use partially or completely denitrified wastewater effluent.

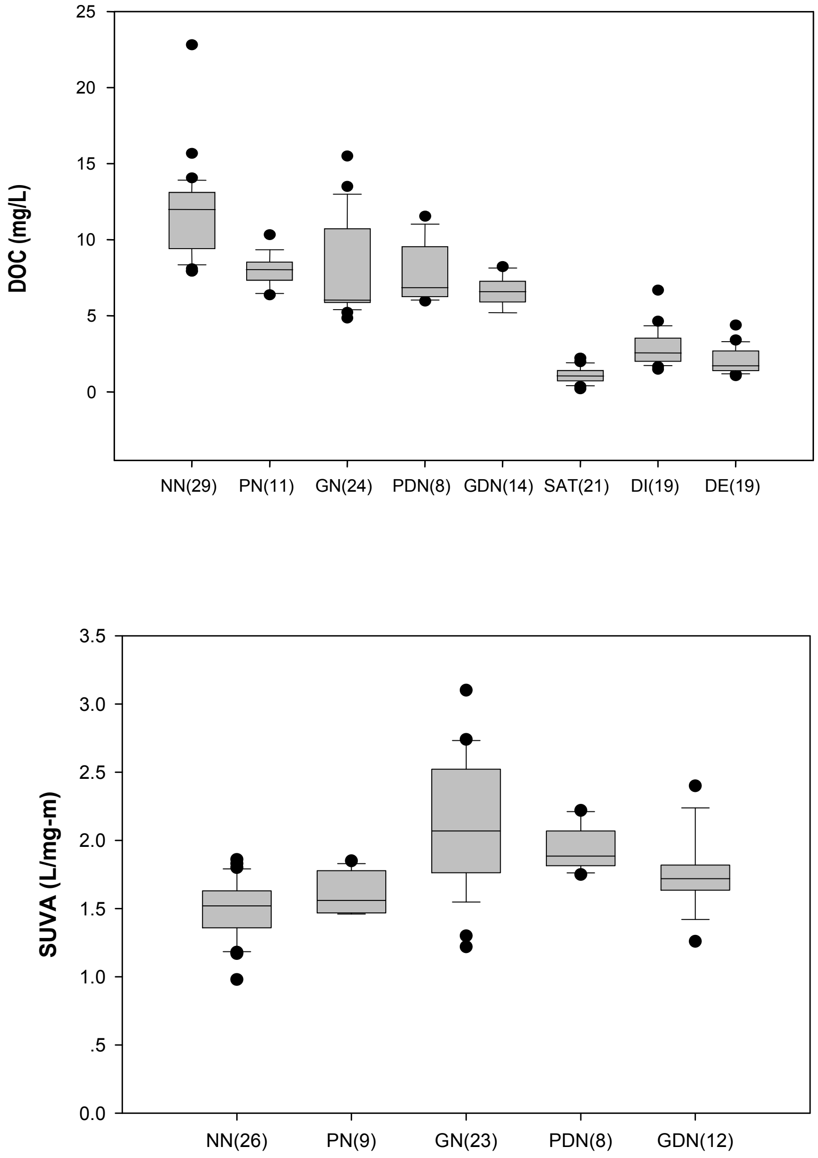


Figure 2.1. DOC and SUVA for several water sources. NN = nonnitrified wastewater; PN = partially nitrified wastewater; GN = good or well-denitrified wastewater; PDN = partially denitrified wastewater; GDN = well-denitrified wastewater; SAT = soil aquifer-treated wastewater; DI = drinking water treatment plant influent; and DE = drinking water treatment plant effluent (the values in the parentheses indicate the number of samples investigated).

EfOM can be characterized in several different ways, including bulk properties such as molecular weight or spectroscopic signature, group properties (proteins, carbohydrates, etc.), and compound-specific properties (for example, determined by mass spectroscopy) based on polarity, functionality, and mass. We have found that EfOM contains DOC with a wide range of molecular weights, that divalent cations affect sorption of organics onto biosolids, and that different polarity fractions of EfOM exhibit unique fluorescence and absorbance profiles (Esparza-Soto et al., 2006a; Esparza-Soto et al., 2006b; Esparza-Soto and Westerhoff, 2001; Esparza-Soto and Westerhoff, 2003; Pinney et al., 2000; Westerhoff and Anning, 2000). For example, based on ultrafiltration (UF) separation, effluent from several air-feed activated sludge systems exhibited a Gaussian molecular weight distribution, with most of the DOC (60%) in the intermediate size fraction of 500 to 3000 Da, while trickling filter effluents had >50% of the DOC in the >3000-Da size fraction. In some cases, simple measurements are the most useful. Specific ultraviolet absorbance (SUVA) at 254 nm measures the quantity of carbon-carbon double bonds (for example, aromatic carbon content) and is commonly used as a surrogate in assessing the likely efficiency of adsorptive processes (metal hydroxide precipitates, activated carbon media) at removing organics during water treatment. SUVA is the ratio of a water's UV absorbance at 254 nm to its DOC concentration. Generally, SUVA values of <2 L/mg of DOC-m are considered difficult for WWTPs to remove and do not even compel compliance with the Enhanced Coagulation requirement of the Surface Water Treatment Rule. The SUVA values of wastewater effluents are consistently lower and are similar to those of drinking water effluents that have already undergone adsorptive treatment (Figure 2.1).

2.2 ORGANIC COMPOSITION OF MEMBRANE CONCENTRATE

Membrane processes effectively remove organic, inorganic. and biological constituents from wastewater. Membrane systems generate two concentrated waste streams containing EfOM: 1) rejected materials (concentrate) and 2) backwashing and cleaning solutions.

2.2.1 Characteristics of Concentrate

The composition of a concentrate depends on the type of membrane used, recovery rate, and feed water characteristics. Concentrates from MF/UF contain suspended solids and colloidal particles, whereas NF and RO concentrates contain high concentrations of ions and small organic compounds, as shown in Table 2.1. Solute characteristics, such as molecular weight, molecular size (length and width), acid dissociation constant (pK_a), hydrophobicity/hydrophilicity ($\log K_{ow}$), and diffusion coefficient, affect their rejection in membrane systems. Ionic strength, pH, hardness, and the organic matter content of the feed water also affect solute rejection (Bellona et al., 2004; Drewes et al., 2005; Drewes et al., 2003; Yoon et al., 2006). Typical water recovery rates for RO systems are 35 to 50% for seawater desalination and 70 to 90% for brackish water desalination. The remaining fraction of the water is the concentrate, which contains the pollutants and compounds rejected by the membrane.

Table 2.1. Design Parameters and Performance of Membrane Processes[a]

Process	Pore Size (µm)	MWCO (Da)	NOM Removal (%)	Operating Pressure (kPa [psi])	Types of Contaminants Rejected
RO	NA	1–100	>99	1000–10,000 (150–1500)	Salts, synthetic organic chemicals, metal ions
NF	NA	200–1000	>95	350-1400 (50-200)	NOM, salts, protein
UF	0.001–0.1	1000–100,000	20	35–700 (5–100)	Bacteria, viruses, humic acid, colloidal particles
MF	0.1–10	>100,000	0	5-150 (1–20)	Large particles, bacteria, clay, humic acid, algae

[a]After Benjamin et al. (2002).

2.2.2 Antiscalants and Cleaning Agents

Antiscalants, which include polyphosphates, phosphonates, synthetic polymers, and proprietary formulated blends, usually are used to inhibit the precipitation of calcium carbonate or sulfate (Amjad, 1996; Darton, 2000). Antiscalants are generally organic compounds containing sulfonate, phosphonate, or carboxylic acid functional groups as well as chelating agents, as shown in Table 2.2. Dosages range between 2 and 10 ppm, depending on the scale-forming potential of the feed water, the recovery rate, and the antiscalant manufacturer's recommendations.

Table 2.2. Commonly Used Antiscalants[a]

Antiscalants	Acronym	Formula
Sodium tripolyphosphate	STPP	$Na_5P_3O_{10}$
Sodium hexametaphosphate	SHMP	$(NaPO_3)_6$
Amino tri(methylene phosphonic acid)	AMP	$N(CH_2PO_3H_2)_3$
1-Hydroxyethylidene-1,1-diphosphonic acid	HEDP	$CH_3(PO_3H_2)_2OH$
Ethylenediaminetetra (methylene phosphonic acid)	EDTMP	$(PO_3H_2CH_2)_2N(CH_2)_2N(CH_2PO_3H_2)_2$
Hexamethylenediaminetetra (methylene phosphonic acid)	HMPMP	$(CH_2PO_3H_2CH_2)_2N(CH_2)_6N(CH_2PO_3H_2)_2$
Diethylenetriaminepenta (methylene phosphonic acid)	DETMP	$N(CH_2)PO_3H_2[(CH_2)_2N(PO_3H_2)_2]_2$
2-Phosphonobutane 1,2,4-tricarboxylic acid	PBTC	$CH_2COOHC(PO_3H_2)COOH(CH_2)_2COOH$
Poly(acrylic acid)	PAA	$(CH_2CHCOOH)_n$
Poly(methacrylic acid)	PMAA	$(CH_2C[CH]_3COOH)_n$
Poly(maleic acid)	PMA	$(CHCOOHCHCOOH)_n$

[a]After Amjad (1996).

Chemical cleaning agents remove scaling and organic fouling from membranes. These cleaning agents include acids (such as phosphoric acid or citric acid), alkaline solutions (such as sodium hydroxide and potassium hydroxide), complexing agents (such as ethylenediaminetetraacetic acid [EDTA] and sodium hexametaphosphate), surfactants (such as linear alkylbenzene sulfonate [LAS] and sodium dodecyl sulfate), and enzymes. Table 2.3 lists the chemical cleaners commonly used in membrane systems. Commercial cleaning products are often mixtures of these compounds, but in most cases the actual composition is proprietary. Alkaline solutions increase the negative charge and thus the solubility of organic foulants. Metal chelating agents, such as EDTA, remove divalent cations from complex organic molecules and thus improve the cleaning of a fouled membrane. Surfactants are compounds that have both hydrophilic and hydrophobic groups and are semisoluble in both organic and aqueous solvents. LAS, the most common synthetic anionic surfactant, was first introduced as a biodegradable substitute for nonbiodegradable compounds such as alkylbenzene sulfonates. High concentrations of LAS may be difficult to biodegrade. AOPs such as UV/H_2O_2, Fenton reagent, UV/TiO_2, wet oxidation, and ultrasound have been used to degrade aqueous LAS (Abu-Hassan et al., 2005; Tabrizi and Mehrvar, 2006).

Table 2.3. Cleaning Agents for Membrane Systems[a]

Membrane Type	Foulant	Chemical Cleaning Agent
RO and MF	Scales (i.e., $CaCO_3$, $CaSO_4$, $BaSO_4$, $SrSO_4$, SiO_2)	Citric acid, HCl, phosphoric acid, or EDTA-based solution Clean silicate-based foulants with ammonium bifluoride-based solutions
	Colloidal clays/silts (i.e., SiO_2, $Fe[OH]_3$, $Al[OH]_3$, $FeSiO_3$)	EDTA- or BIZ-type detergents at high pH Clean silicate-based foulants with ammonium bifluoride-based solutions
	Biologicals (i.e., iron-reducing bacteria, sulfur-reducing bacteria, *Pseudomonas*)	EDTA- or BIZ-type detergents at high pH Shock disinfection with hydrogen peroxide, peracetic acid
	Organics (i.e., polyelectrolytes, oil, grease)	Detergents/surfactants, isopropanol
UF and MF	Fats and oils, proteins, polysaccharides, bacteria	0.5 N NaOH + 200 parts of chlorine per million
	DNA, mineral salts	0.1–0.5 M acid (acetic, citric, nitric)
	Fats, oils, proteins, biopolymers	0.1% sodium dodecyl sulfate, 0.1% Triton X-100
	Cell fragments, fats, oils, proteins	Enzyme detergents
	DNA	0.5% DNase
	Fats, oils, and grease	2–50% ethanol

[a] After Singh (2006).

2.3 USE OF MEMBRANES IN WATER REUSE

Reuse of wastewater will continue to expand over the next decades. While some reuse applications (irrigation, subsurface recharge, soil aquifer treatment) can accept settled or sand-filtered, partially denitrified wastewater effluent, membranes have become an integral part of many water reuse plants. Membrane systems can provide high removals of pathogens, salts, bulk organics, and trace organics from finished water. Rejection of these constituents is based on their size, polarity, and shape. Low-pressure MF (~ 0.2 μm) removes particulate matter based on size rejection. UF and NF operate at higher pressures than does MF and reject colloids and ions based on both size and steric (charge) interactions. While most membrane surfaces have a negative surface charge, significant adsorption of inorganics as well as of both bulk and trace organics can occur (Yoon et al., 2002a; Yoon et al., 2002b; Yoon et al., 2006). RO requires the highest operating pressures and rejects ions based on both charge and size. NF and RO generally require more extensive pretreatment (MF or medium filtration), pH control to inhibit precipitation of solids on membrane surfaces, and antiscalants. All membranes foul, in part because of bulk organics (for example, proteins and polysaccharides) in the feed water and biofilms that develop on membrane surfaces.

The benefits of membrane systems include the potentially high removals of salts, pathogens, and organics. However, membrane systems generate two concentrated waste streams containing EfOM: 1) membrane concentrates (materials rejected by the membranes) and 2) membrane cleaning solutions (backwashes, cleaning solutions). The volume of these waste streams is a function of water recovery rates (namely, efficiency) and backwashing or cleaning frequency. Higher applied membrane pressures are associated with "tighter" membrane pores and have lower water recovery rates. MF and UF membranes have 90% to >98% recovery rates, while RO, NF, and other applications (for example, ED) commonly have recovery rates of 70% to 85%. How to increase NF and RO recovery rates is currently the focus of considerable research. Higher recovery rates equate to higher concentration factors for the constituents of membrane concentrates. For example, an 85% recovery rate equates to a concentration factor of 6.7 for a compound completely rejected by the membrane. As utilities strive to maximize beneficial water use and minimize brine disposal, RO recoveries may increase to 95%, which would result in 20× concentration factors for organics and salts present in the RO feed water. Antiscalants (for example, polyacrylates, polyacrylic acids, or polyphosphates) are commonly added (~10 mg/L) to feed waters to inhibit precipitation (for example, calcium carbonate or sulfate) (Darton, 2000; Shih et al., 2004). While considerable research has and is focused on managing the high salt concentrations in the concentrates from tighter membranes (NF and RO), which result from these high concentration factors, the management and treatment of the organics (namely, EfOM and antiscalants) in these membrane concentrates also need to be considered.

Membranes must be cleaned to maintain reasonable flux rates. Depending on the type of membrane, various cleaning regimens are used at different frequencies. Hydraulic and air scour backwashing removes particulate, bacterial, and colloidal material from membrane surfaces, thus minimizing the cake development that leads to pore blockage. Acid (for example, phosphoric or citric acid) backwashing dissolves precipitates (for example, calcite) and some organic materials. Caustic backwashing desorbs other dissolved organics. Complexing agents (for example, EDTA, polyacrylates, and sodium hexametaphosphate) are used less frequently to remove inorganic and organic foulants. During wastewater reuse, each of these cleaning waste streams contains EfOM and other chemicals that should be managed prior to release into the environment. The hydraulic or air scour backwash could be returned to a WWTP process basin, but the other waste streams are usually disposed of in some other manner (see below).

The composition of membrane concentrates varies depending upon the type of membrane employed, recovery rate, and feed water composition. For example, the City of Scottsdale Water Campus pretreats partially nitrified-denitrified effluent using MF prior to RO, which operates at ~85% recovery efficiency. The total-dissolved-solid (TDS) concentration of the concentrate is 5560 mg/L with 2.6 mg of bromide/L, 46 mg of nitrate/L, and 64 mg of ammonia/L; the concentrate also has a pH of 7.7 and an alkalinity of 1110 mg/L as $CaCO_3$. It contains 50 mg of DOC/L and has a SUVA of 1.6 L/mg-m as well. These concentrations are consistent with a 6.6 concentration factor (namely, 85% recovery). The City of Scottsdale currently uses antiscalants and complexing agents in its membrane processes and sends all waste streams down a sewer to a regional WWTP. In the future, as more utilities practice water reuse using membranes, salt loadings may limit this discharge option (see discharge option section below), as they may encounter concern over point-source loadings of refractory EfOM.

2.4 DISPOSAL OF MEMBRANE CONCENTRATES

In 1993, a survey was conducted at 137 membrane-using drinking water plants in the continental United States of size greater than 95 m^3/day (Mickley et al., 1993). Of these plants, 73% were brackish water RO, 11% were NF, 11% ED, and the remaining 5% were seawater RO plants. The survey showed that the distribution of the disposal options was as follows:

- 48% disposal to surface water
- 23% disposal to the headworks of a WWTP
- 13% land application (including percolation)
- 10% disposal via deep well injection
- 6% evaporation ponds

While not discussed in this survey, ocean disposal is also widely viewed as a feasible option. Salt content is an important factor in each of the above disposal options, but very little attention has been paid to the presence of organics, especially of EfOM, which contains many trace compounds of potential human and ecosystem concern. Over the next decade, these organics may become a focus, which would necessitate further treatment before disposal.

Ocean disposal is the least expensive disposal method for areas that are near an ocean. California has proposed pipelines to transport membrane concentrates to an ocean outfall. For landlocked areas, however, the cost of such pipelines would be prohibitive. Furthermore, the potential risk of organics to the ocean ecosystem may be an issue in the future due to concerns regarding the fate of persistent organics.

Discharge of membrane concentrate to surface waters is a common disposal option. As long as surface water is available and the membrane concentrate can meet the discharge criteria, this option is cost-effective, and the large mixing volumes can handle relatively high-TDS membrane concentrates by dilution (Squire, 2000). However, membrane concentrate waste streams represent a concentrated point source of organic pollution, and the industry should consider treating them to prevent estrogenic, antibiotic, and other compounds from entering waterways. Although these compounds are currently unregulated, adverse aquatic ecosystem effects have been attributed to them.

Discharge of membrane concentrate to regional WWTPs can be viable if a WWTP is located nearby and can handle the salt loading. However, high-TDS water may have detrimental effects on wastewater treatment equipment, including the sewage treatment processes and the piping to the works. Because membrane concentrates are smaller-volume waste streams, posttreatment processes could be used to remove the organics of concern before the concentrate is discharged to a regional WWTP. Transformation of oxidized organics into biodegradable by-products (instead of complete mineralization) would also be beneficial if the concentrate is to be discharged to WWTPs. If some inorganics are oxidized (for example, bromide or ammonia), the species produced (for example, bromate or nitrate) would serve as electron acceptors and be reduced within the WWTP.

The feasibility of deep well injection (330 to 2600 m deep) is extremely site-specific since subsurface geological and groundwater conditions are the determining factors (Amjad, 1993). Deep well injection systems are required to have a backup disposal method, which could be another injection well or some other permissible form of membrane concentrate disposal (Witt and Ameno, 1989).

A typical example of land application is spray irrigation. The membrane concentrate is transported to an agricultural area and taken up by the crops. Even salty membrane concentrates may be viable for growing halophytes. The membrane concentrate may be pretreated or blended with other water sources, such as treated wastewater effluent, to generate a usable irrigation product. One limitation of this disposal method is that the membrane concentrate may contaminate groundwater or receiving surface waters. A backup disposal method is needed during periods of heavy rainfall.

Evaporation ponds are most appropriate for relatively warm and dry climates with high evaporation rates, level terrain, and low land costs (Mickley et al., 1993). At an evaporation pond in Arizona receiving cooling-tower blowdown using softened secondary effluent, the TOC was more than 200 mg/L, and it is unclear if the source of the organics was refractory EfOM, algal exudates, or antiscalants (Hou, 2004). Mechanical evaporation, such as that by a single-effect evaporator or vapor compression evaporator, could reach zero-liquid discharge, but the high cost due to the energy consumption, as well as the costs required for final salt or membrane concentrate disposal, makes this option less popular (Ahmed et al., 2000). However, some organics will coprecipitate with these solids (Hou, 2004), and removing the organics prior to such precipitation may increase the value of the recovered salts.

The Dewvaporation™ water treatment process, an energy-efficient patented technology, involves a carrier gas and purifies water through a humidification/dehumidification cycle. The anticipated salt concentration of effluents will rise from 5000 ppm to an estimated 300,000 ppm, reducing the size of the waste stream by more than a factor of 50, while producing distillation quality water as a side benefit. Reducing the size of the waste stream is an important consideration for customers needing to comply with zero-liquid-discharge regulations, as compliance proportionately reduces costs of disposal. One example of the Dewvaporation system is a 10,000-gal-per-day pilot plant that is funded in part by the Bureau of Reclamation and the City of Phoenix. The pilot plant will be installed and operated at the 23rd Avenue WWTP in Phoenix. RO effluent will be the feed water for the Dewvaporation unit. The 5000-ppm TDS RO effluent will be concentrated to more than 200,000 ppm of TDS, thereby reducing the membrane concentrate volume to 2% of the RO effluent (98% recovery). It may be appropriate to oxidize the organics prior to ultimate disposal of this concentrated slurry to prevent environmental contamination by EfOM in landfills or other locations. Oxidizing the organics may also allow the recovery of minerals, which have a higher value when they are not discolored by organics.

2.5 REMOVAL OF ORGANICS BY OXIDATION PROCESSES

Common disinfectants (free or combined chlorine, chlorine dioxide, and low-dose UV irradiation) are poor oxidants of organics, such as those comprising EfOM, but have other uses within treatment systems (Table 2.4). Stronger oxidants, including those involving molecular ozone (O_3), hydroxyl radicals ($HO^\bullet$), or various wet chemical oxidation reactants, are more likely to oxidize most of the EfOM to innocuous by-products. Much of the work on these stronger oxidation technologies to mineralize organics has occurred as part of research in the textile industry. For example, a wet oxidation process both with and without hydrogen peroxide (H_2O_2) achieved 90% TOC removal from a membrane concentrate of a dyeing waste stream (Lei et al., 1998), and sonication in the presence of copper sulfate could enhance the wet oxidation efficiency even more (Dhale and Mahajani, 1999). Fenton-like reactions with Nafion-Fe^{3+}/H_2O_2 achieved a 50% TOC reduction during treatment of an NF concentrate from a textile waste stream (Balanosky et al., 1999; Meric et al., 2005). The remainder of this section briefly describes these stronger oxidants and potential oxidation by-products.

Table 2.4. Oxidants and Their Applications in Water Treatment[a]

Purpose	Oxidants	Applications
Oxidation of reduced inorganic species	Chlorine, combined chlorine, hydrogen peroxide, permanganate, chlorine dioxide	Convert soluble metals such as Fe(III) and Mn(III) to insoluble forms Oxidize odorous sulfide Destroy metal organic complexes
Oxidation of organics	Ozone, AOPs, UV light, permanganate, chlorine dioxide	Destroy taste- and odor-causing compounds Destroy toxic organics [e.g., pesticides, benzene, trichloroethene, methyl tertiary-butyl ether] Eliminate color Reduce natural organic matter and disinfection by-product precursors
Coagulation aids	Ozone	Reduce amount of coagulant and improve coagulation process
Biocide agents	Ozone, chlorine, combined chlorine, iodine, UV light	Control nuisance growth, such as algae in pretreatment basins or reservoirs Serve as primary disinfectants to meet CT regulations

[a] After Crittenden et al. (2005).

Molecular ozone is a powerful oxidant, but it tends to selectively react with electron-rich carbon bonds (for example, C=C bonds). In previous work, we observed near-complete removal of aromatic carbon during ozonation of NOM, with production of aliphatic carbon enriched with oxygen functional groups, although only a 2% to 10% loss of TOC was observed at a dose of 2.5 mg of O_3/mg of TOC (Westerhoff et al., 1999). Ozone and $HO^{\bullet}$ oxidize organic carbon, generally resulting in lower-molecular-weight and more polar compounds (Anderson et al., 1986; Bose et al., 1994; Xiong et al., 1992). The principal oxidation by-products from NOM ozonation are aldehydes, ketones, and carboxylic acids, many of which are easily biodegradable. Excessive ozone-oxidation of NOM (7.5 mg of O_3/mg of C) transformed up to 40% of the TOC from NOM into 10 organic acids (acetic, formic, oxalic, gallic, malonic, fumaric, glycolic, hexanoic, phthalic, and valeric acids), while at lower ozone dosages ($\leq$ 2 mg of O_3/mg of C) these 10 organic acids accounted for less than 15% of the TOC (Edwards and Benjamin, 1992). Increased concentrations of C_1 through C_{14} aldehydes, several ketones, and C_1 through C_{24} carboxylic acids have also been identified after ozonation, solvent extraction, and gas chromatography with mass spectroscopy (GC/MS) analysis (Langlais et al., 1992; Miltner et al., 1992). Benoit and coworkers (1993) ozonated soil organic humic acids and methylated the residuals prior to GC/MS analysis (Benoit et al., 1993). They found that aliphatic compounds rich in oxygen were produced at high ozone dosages (6 mg of O_3/mg of C) while lower ozone doses yielded mainly benzene polycarboxylic acids and polyhydroxy benzene polycarboxylic acids.

In recent work involving ~60 endocrine disruptors (EDCs) and pharmaceuticals and personal care products (PPCPs), ozonation (1 to 2 mg of O_3/mg of TOC) oxidized most LC/MS/MS compounds by >80%. The exceptions were atrazine, meprobamate, and flame retardants, which do not contain aromatic moieties, and ibuprofen, which has an electron-withdrawing functional group on an aromatic ring. Several GC/MS/MS compounds exhibited minimal oxidation during ozonation (for example, chlordane, dieldrin, heptachlor epoxide, mirex, and musk ketone) (Westerhoff et al. 2005). Ozone oxidized steroids containing phenolic moieties (estradiol, ethynylestradiol, or estrone) more efficiently than it did those without phenolic moieties (androstenedione, progesterone, and testosterone). Hydroxyl functional groups donate electrons to aromatic rings, resulting in compounds that are more reactive with ozone than are nonaromatic ring structures or conjugated bonds with carboxyl or ketone functional groups. Addition of small amounts of H_2O_2 (0.025 mg of H_2O_2/mg of O_3) prior to ozonation generally improved the extent of EDC/PPCP oxidation by 5% to 15% as compared to ozone alone. Four compounds (androstenedione, atrazine, musk ketone, and testosterone) exhibited >20% higher oxidation in the presence of H_2O_2. H_2O_2 addition increases the rate of molecular ozone decay (namely, leads to lower molecular ozone concentrations) but increases $HO^\bullet$ concentrations. In experiments with 40 mJ/cm^2 from a medium-pressure UV lamp, a typical disinfectant dosage, significantly lower percentages of these EDC/PPCPs were oxidized than at a higher UV dosage of 1000 mJ/cm^2 (Snyder et al., 2005). UV/H_2O_2 was not explicitly studied. Thus, $HO^\bullet$ probably constitutes a major oxidation pathway for EDC/PPCPs during ozonation, which is consistent with reports that AOPs are promising systems for efficient removal of pharmaceuticals (Huber et al., 2003).

$HO^\bullet$ is produced by several processes (Table 2.5) that are usually referred to as AOPs (Table 2.6). $HO^\bullet$ produced during AOPs has high oxidative capacity and initiates a series of reaction mechanisms (namely, hydrogen abstraction/addition, oxygen addition, β scission, peroxy radical mechanisms, hydrolysis, etc.) that degrade organics. Both hydrogen abstraction and double-bond addition produce very reactive organic radicals that rapidly undergo subsequent oxidation. Most often they combine with dissolved oxygen to form peroxy organic radicals ($ROO^\bullet$) that undergo radical chain reactions that produce a variety of oxygenated by-products. AOPs can efficiently oxidize a wide range of organics (see Table 2.7).

Table 2.5. Major Reactions That Produce $HO^\bullet$ in Various AOPs

Oxidation Process	Major Reaction
Fenton's reagent/H_2O_2	$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO\bullet$ $Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + \bullet OOH$
Ozone/H_2O_2	$2O_3 + H_2O_2 \rightarrow 2\ HO\bullet + 3O_2$
Ozone/UV	$O_3 + UV + H_2O \rightarrow 2HO\bullet + O_2$
H_2O_2/UV	$H_2O_2 + UV \rightarrow 2HO\bullet$ $HO\bullet + H_2O_2 \rightarrow HO_2 + H_2O$ $\bullet OOH + \bullet OOH \rightarrow H_2O_2 + O_2$
TiO_2/Photocatalysis	$TiO_2 + h\nu \rightarrow e^- + h$ $h^+ + OH^- \rightarrow HO\bullet$ $e^- + O_2 \rightarrow \bullet O_2$
Sonolysis	$H_2O +\ ))) \rightarrow \bullet H + HO\bullet$

Table 2.6. Advantages and Disadvantages of Various Oxidation Processes That Produce Hydroxyl Radicals in Decreasing Order of Preference[a]

Oxidation process	Advantages	Disadvantages
Hydrogen peroxide/ UV light	H_2O_2 is quite stable and can be stored on site for long periods prior to use.	H_2O_2 has very poor UV absorption characteristics. If the water matrix absorbs much UV light energy, then most of the light input to the reactor will be wasted. Requires specialized reactors. Residual H_2O_2 must be addressed.
Hydrogen peroxide/ ozone	Waters with poor UV-light transmission may be treated. Special reactors that are designed for UV illumination are not required.	Volatile organics will be stripped from the ozone contactor. Production of O_3 can be an expensive and inefficient process. Maintaining proper O_3/H_2O_2 dosages may be difficult. Low pH is detrimental to the process.
Titanium dioxide/ UV	Activated with near-UV light.	Fouling of the catalyst may occur. When used as a slurry, the TiO_2 must be recovered.
Ozone/UV	No need to maintain precise dosages of O_3/H_2O_2; residual oxidant will degrade rapidly (typical half life of O_3 is 7 min). Ozone absorbs more UV light than an equivalent dosage of hydrogen peroxide (~200 times more at 254 nm).	Must use O_3 and UV light to produce H_2O_2, which is the primary means of producing OH. Using O_3 to produce H_2O_2 is very inefficient as compared to just adding H_2O_2. Special reactors that are designed for UV illumination are required. Ozone in the off-gas must be removed. Volatile compounds will be stripped from the reactor.
Ozone/UV/H_2O_2	Processes that utilize the technology are commercially available; H_2O_2 promotes ozone mass transfer.	Specialized illumination reactors are required. Ozone in the off-gas must be removed. Volatile compounds will be stripped from the process.
Fenton reactions (Fe/ H_2O_2, photo-Fenton, or Fe/ ozone)	Commercially available processes; many innovative catalysts now available.	Process requires low pH. Commercially available processes utilize the technology
Sonolysis	The process may be used for waters that have low light penetration.	Technology is not available commercially and requires too much energy input.
Ozone/sonolysis	The process may have higher destruction rates than does sonolysis alone.	No commercial applications. Requires specialized reactor and significant amount of energy.
Supercritical water oxidation	Complete mineralization can be obtained for complex hazardous mixtures.	Requires very specialized reactor that operates at high pressure and consumes significant amount of energy. Corrosion can be significant with high chloride concentrations. Very expensive process that is normally designed for small flows.
Ozone/TiO_2	The process may have higher destruction rates than does TiO_2 alone.	No commercial applications.
Ozone/TiO_2/H_2O_2	The process may have higher destruction rates than does TiO_2 alone.	No commercial applications.
Pulsed corona discharges/nonthermal plasma	The process does not require elevated temperatures.	Works only in the gas phase.
Catalytic oxidation	For aqueous-phase applications, process does not require temperatures that are as high as supercritical water oxidation.	Only certain compounds in the aqueous phase may degrade. For gas phase applications, the production of dioxins and furans must be avoided.
Electron beam irradiation	The process does not require elevated temperatures.	No commercial applications. Requires specialized reactor and significant amount of energy.

[a] Adapted from Crittenden et al. (2005).

Table 2.7. Compound Classes, including Specific Examples, Oxidizable by PHCO[a]

Compound Class	Specific Examples
Aliphatic compounds	Linear alkanes such as methane, ethane, *n*-hexane, and dodecane Branched alkanes and cylcoalkanes such as isobutene and cyclohexane Olefins such as ethylene, butadiene, and cyclohexene
Halogenated aliphatic compounds	Partially chlorinated or brominated linear alkanes such as methylene chloride/bromide, chloroform, bromoform, 1,2-dichloroethane, 1,1,1-trichloroethane, and 1,1,2,2-tetrachloroethane; halogenated olefins such as vinyl chlorine/bromide and trichloroethylene Perchlorinated compounds such as carbon tetrachloride and perchloroethylene
Aromatic compounds	Plain or alkylated aromatic compounds such as benzene, naphthalene, toluene, xylenes, ethylbenzene, and biphenylene
Halogenated aromatic compounds	Polychlorinated aromatic compounds such as dichlorobenzene, benzyl chloride, chloronaphthalene, and polychlorinated biphenyls Pesticides and combustion products such as pentachlorophenol, lindane, dichlorodiphenyltrichloroethane, and dioxins
Oxygen-containing compounds	Aromatic and aliphatic alcohols such as phenol, catechol, ethanol, propanol, isopropanol, and decanol Aromatic and aliphatic aldehydes or ketones such as benzaldehyde, acetaldehyde, acetone, and methyl ethyl ketone Aromatic and aliphatic carboxylic acids such as benzoic acid, salicylic acid, acetic acid, butynic acid, and trichlochloracetic acid Aromatic and aliphatic ethers or esters such as ethyl ether, etyle acetate, and methyl methacrylate
Nitrogen-containing compounds	Aliphatic amines such as alkylamines, alkonylamines, and amino acids; aromatic amines such as aniline, atrazine, and pyridine Nitro compounds such as nitrobenzene and dinitrotoluene, nitrosamines such as nitrodimethylamine
Sulfur-containing compounds	Aliphatic and aromatic thioethers and mercaptans

[a]PHCO, photo-assisted heterogeneous catalytic oxidation processes. Table adapted from from Hand et al. (1995).

The following general pattern of oxidation is observed for AOPs: *Organic pollutant → Aldehydes → Carboxylic acids → Carbon dioxide and mineral acids*. Table 2.4 presents some of the significant by-products and the highest yields observed. The most significant by-products are the carboxylic acids because the second-order rate constants for these compounds are much lower than those for most organics. However, if adequate reaction time is provided, this time depending on the chemical type, chemical concentration, and AOP yield of hydroxyl radicals, then all by-products (>99% as measured by a TOC mass balance) are destroyed (Stefan and Bolton, 2002; Stefan et al., 1998; Stefan and Bolton, 2000a; Stefan et al., 2000b). Depending on the compound, these reaction times can be very long (namely, high oxidant dosages are needed). Some of these by-products are of concern, such as the halogenated acetic acids, which are formed from the oxidation of halogenated alkenes such as trichloroethene (Tables 2.8 and 2.9). With longer retention times and higher $HO^\bullet$ concentrations, however, these compounds can be destroyed. For example, it is possible to completely mineralize trichloroethylene in a few minutes of reaction time using an AOP that utilizes TiO_2, oxygen, and UV light (Zhang et al., 1994). UV/TiO_2 has been shown to achieve removals (~60%) of COD similar to those achieved by UF and slightly lower removals than RO (80%) does, when one is treating effluent from secondary and tertiary WWTPs (Al-Bastaki, 2004).

Table 2.8. Significant By-Products Observed after 2 Oxidation Processes[a]

Oxidation Process	By-Product	Molecular Formula
Ozone	Bromoform	$CHBr_3$
	Formaldehyde	HCHO
	Acetaldehyde	CH_3CHO
	Glyoxal	OHCCHO
	Methyl glyoxal	$CH_3COCOCHO$
	Glyoxylic acid	OHCCOOH
	Pyruvic acid	$CH_3COCOOH$
	Ketomalonic acid	HOOCCOCOOH
	Formate	$HCOO^-$
	Acetate	CH_3COO^-
	Oxalate	$OOCCOO^-$
	Bromate	BrO_3^-
UV/H_2O_2	Acetic acid	CH_3COOH
	Pyruvic acid	$CH_3COCOOH$
	Oxalic acid	OOCCOOH
	Pyruvaldehyde	$C_3H_4O_2$
	Formic acid	HCOOH
	Glyoxylic acid	OHCCOOH
	Hydroxyacetone	$CH_3C(O)CH_2OH$
	Formaldehyde	HCHO
	Acetaldehyde	CH_3CHO
	Methoxyacetic acid glyoxal	CH_3OCH_2COOH

[a]Adapted from Crittenden et al. (1999); Hammes et al. (2006).

Table 2.9. Some Observed AOP By-Products from Specific Compounds

Compound	Observed By-Products
Acetone	Major by-products (yield 10 to 30 mol%): acetic, pyruvic, and oxalic acids, pyruvaldehyde Minor by-products (yield 2 to 5 mol%): formic and glyoxylic acids, hydroxyacetone, formaldehyde
Methyl tertiary butyl ether	Major by-products: acetone, acetic acid, formaldehyde, tert-butyl formate (TBF), pyruvic acid, tert-butyl alcohol (TBA), 2-methoxy-2-methyl propionaldehyde (MMP), formic acid, methyl acetate Minor by-products: hydroxy- iso-butyraldehyde, pyruvaldehyde and hydroxyl- iso-butyric acid, oxalic acid
Dioxane	Major by-products: 1,2-ethanediol diformate, formic acid, oxalic acid, glycolic acid, acetic acid, formaldehyde, 1,2-ethanediol monoformate Minor by-products: methoxyacetic acid, glyoxal Very minor by-product: acetaldehyde
Trichloroethene	Major by-product: formic acid Minor by-product: oxalic acid Very minor by-products: 1,1-dichloroacetic acid, 1-monoacetic acid

Another potential problem with ozone or AOPs is the production of brominated by-products and bromate in waters containing bromide ion (Table 2.10 summarizes the relevant reactions). Ozone does not react directly with NOM to produce halogenated by-products, but it will react with bromide to form hypobromous acid (HOBr). HOBr can, in turn, react with NOM to form organic brominated by-products. The quantity of brominated by-products is determined by the bromide ion and TOC concentrations as well as the pH. $HO^{\bullet}$ can oxidize key intermediates (namely, OBr) in bromate formation and can thus be responsible for a significant portion of the bromate that forms. The complete pathway is described in the literature (von Gunten, 2003a; von Gunten, 2003b; von Gunten et al., 2001; Westerhoff et al., 1998a,b).

Table 2.10. Relevant Reactions for Bromate Formation

Process	Relevant Reactions
Ozonation	$O_3 + Br^- + H^+ \rightarrow HOBr + O_2$ $HOBr + TOC \rightarrow TOBr$ $O_3 + Br^- \rightarrow OBr^- + O_2$ $O_3 + OBr^- \rightarrow BrO_2^- + O_2$ $O_3 + OBr^- \rightarrow BrO_3^- + O_2$
AOP	$HOBr/OBr^- + HO^{\bullet} \rightarrow OBr^{\bullet} + H_2O/OH^-$ $OBr^{\bullet} + H_2O \rightarrow BrO_2^- + 2H^+$ $2OBr^{\bullet} + H_2O \rightarrow BrO^- + BrO_2^- + 2H^+$ $Br^- + HO^{\bullet} \rightarrow BrOH^-$ $BrOH^- + H^+ \rightarrow Br^{\bullet} + H_2O$ $Br^{\bullet} + OBr^- \rightarrow BrO^{\bullet} + Br^-$
Ozone or AOP with Ammonia	$NH_3 + HOBr \rightarrow NH_2Br + H_2O$

In several cases, photo- and electrochemical oxidation has been used to destroy organics in textile and landfill leachate membrane concentrates. Lei et al. (1998) achieved an 80% TOC reduction and 90% color removal from membrane concentrates from dyeing wastewater using a wet oxidation process with or without hydrogen peroxide. Fenton-like reactions with Nafion-Fe^{3+}/H_2O_2 achieved a 50% TOC reduction in the treatment of an NF concentrate from textile wastewater (Balanosky et al., 1999; Balanosky et al., 2000). Pollutants present in the RO concentrates (COD and color) also were successfully oxidized using boron-doped diamond (Van Hege et al., 2004); the average COD removal in those studies was 61%.

Ozone and the hydroxyl radical ($HO^{\bullet}$) can oxidize organic carbon to more biodegradable forms. Compared to ozone alone, O_3/H_2O_2 treatment generally improves oxidation of organics because H_2O_2 increases $HO^{\bullet}$ production. Ozonation and UV/H_2O_2 are promising processes for oxidation of pharmaceuticals in drinking water (Huber et al., 2003). Shon et al. (2006) reviewed applications of AOPs for EfOM in wastewater and found that the use of $O_3/H_2O_2/UV$ results in a shorter reaction time and requires less oxidant than do other AOPs. When photocatalysis and $FeCl_3$ are combined, DOC removal increases by up to 90%. A wide variety of organic contaminants are susceptible to destruction by UV/oxidation. In many cases, chlorinated hydrocarbons that are resistant to biodegradation can be treated effectively by UV/oxidation. Typically, easily oxidized organic compounds, such as those with double bonds (for example, trichloroethylene and vinyl chloride), as well as simple aromatic compounds (for example, toluene, benzene, xylene, and phenol), are rapidly destroyed in UV/oxidation processes.

Wet oxidation is an alternative technique for treating organic waste streams that are toxic or refractory to conventional biological treatments. The process is carried out in the liquid phase at relatively elevated temperatures (180 to 320 ^{o}C) and pressures (2 to 15 MPz) using a gaseous source of oxygen (Goi et al., 2006). To achieve less severe temperature and pressure conditions, the wet oxidation process can be enhanced by the use of a catalyst. The solid catalysts used are based on metallic salts (namely, copper sulfate and nitrate), noble metals (namely, Ru, Pd, Rh, and Pt) and metallic oxides (namely, CuO, MnO_2, CoO, ZnO, Al_2O_3, CeO_2, and TiO_2) (Santos et al., 2005). The high cost of this technique when applied to the complete oxidation of all organics in a waste stream is mainly due to the formation of low-molecular-mass carboxylic acids that are difficult to convert into CO_2 and H_2O. It has been suggested that a partial oxidation of organics may be followed by biological methods. The volatile reactor assembly is a three-phase cocurrent packed column that uses a stoichiometric excess of gas-phase oxygen as the oxidant and a noble metal catalyst. The ion-exchange- and adsorption-treated wastewater is heated (120 to 140 °C), pressurized (370 to 450 kPa), and fed into a packed column along with the oxygen feed stream. This wet oxidation process is used to oxidize polar, low-molecular-weight organic compounds such as acetic acid, acetone, ethanol, 1-propanol, 2-propanol, and propionic acid, which other treatment processes do not remove (Yang et al., 2003a; Yang et al., 2003b).

2.6 ECONOMIC EVALUATIONS OF AOPs

When different AOP technologies all achieve the removal of organic compounds to a certain degree, it is critical to compare their practical application. The electrical energy per reaction order (EE/O) measurement has been widely used for comparison of rough costs. The EE/O gives the electrical energy required to reduce the concentration of a pollutant by 1 order of magnitude for 1000 U.S. gal of water (Bolton et al., 2001). The corresponding values for batch operation and flow-through operation are calculated in equations 2.1 and 2.2, respectively.

$$EE/O = \frac{P \times t}{V \times \log(C_i / C_f)} \qquad \text{Batch operation} \qquad (2.1)$$

$$EE/O = \frac{P}{Q \times \log(C_i / C_f)} \qquad \text{Flow-through operation} \qquad (2.2)$$

where, *EE/O* denotes electrical efficiency per log order reduction, kWh/gal; *P* denotes energy dose, kW; *t* denotes reaction time, h; C_i denotes initial concentration, mg/L; C_f denotes final concentration, mg/L; *Q* denotes water flow rate, gal/h; and *V* denotes reactor volume, gal. This estimation makes the comparison of the treatment performances of different AOPs as simple as comparing the slopes on an energy-versus-log C_i/C_f graph. The steeper the slope, the more efficient is the selected advanced oxidation. However, when a certain target removal objective is set (>90% removal of DOC in this study), EE/O values derived from different removal ratios do not give an appropriate comparison. For example, given the same water flow, 5 kWh for 50% removal of DOC yields approximately half the EE/O that 40 kWh does for 95% DOC removal. Thus, the lower EE/O does not necessarily indicate the better treatment technology in this study. DOC removal as a function of energy dose (kWh/L, kWh/m^3) compares different AOPs more fairly.

An EE/O value of 10 kWh/L is considered to indicate an economically favorable process (Crittenden et al., 2005). Ozone doses can be converted into applied electrical power rates per unit volume of treated wastewater during ozonation by assuming an energy requirement of 10 kWh/lb of ozone generated. For example, when the EE/O of the H_2O_2/UV process is compared to that of the ozonation process, the EE/O of the H_2O_2/UV process turns out to be more cost-effective than ozonation for reactive dye bath effluent decolorization. The EE/O values of the H_2O_2/UV process and ozonation are 0.633 kWh/m^3 × order and 0.684kWh/m^3 × order, respectively (Alaton et al., 2002). The EE/O for the 1,2-dibromo-3-chloropropane oxidation process (H_2O_2/UV) was found to depend upon many factors (Crittenden et al., 1999). The study found that applying higher H_2O_2 dosages, reducing the inorganic carbonate concentration, and decreasing the pH can reduce the EE/O.

2.7 COMBINATION OF CHEMICAL OXIDATION WITH BIOLOGICAL TREATMENT

It is well-known that chemical oxidation processes (for example, ozonation) produce biologically degradable DOC (BDOC) or assimilable organic carbon (Langlais et al., 1992; Volk and Lechevallier, 2002). As a result, a subsequent treatment using biologically activated carbon can remove this BDOC and assimilable organic carbon. As discussed previously, AOPs produce lower-molecular-weight organic acids that may be readily degraded by biological activity. Lowering the molecular-weight distribution is important in enhancing the biodegradability of DOC because low-molecular-weight compounds are more easily transported across the cell membrane for metabolic enzymes to attack. Consequently, biological treatment after AOPs would degrade BDOC, resulting in further DOC removal.

2.8 SUMMARY OF RESEARCH NEEDS

The use of all types of membrane processes is rapidly expanding because their application may provide high removal efficiencies for organic, inorganic, and biological constituents. All membranes generate waste streams that contain higher-molecular-weight organic compounds (for example, NOM). Tighter membrane systems (for example, RO, NF, and ED) generate concentrates that also contain high salt contents, regulated synthetic organic compounds, and unregulated organic chemicals of potential concern (for example, estrogenic compounds). Numerous studies have focused on the inorganic salts in membrane concentrates, but less attention has been paid to their organic and biological constituents. Therefore, treatment of membrane concentrates to minimize the discharge into the environment of bulk organics, regulated synthetic organic chemicals, and unregulated organic contaminants of concern should be considered. Membrane concentrates represent a single, concentrated, relatively low-flowrate source of human-derived, water-soluble materials that could be treated to prevent their release into the environment. AOPs are promising treatment options to remove organics from membrane concentrates. In this study various AOPs are compared based on their removal of DOC as a function of time. Achievement of >90% organic oxidation may be more cost-effective than complete oxidation. In addition, following AOPs with biological treatment may achieve further DOC removal.

CHAPTER 3

EXPERIMENTAL AND ANALYTICAL METHODS

This chapter describes the source of the membrane concentrate tested and summarizes the experimental methods used to oxidize membrane concentrates. Details of analytical methods are also presented. All laboratory waters were prepared using nanopure water (NANOpure Infinity Ultra-pure Water System). All glassware was washed with Alconox detergent prior to acid washing and ashing at 550 °C. All chemicals were reagent grade and purchased from Fisher Scientific unless otherwise stated. Samples were held at 4 °C in glass bottles and analyzed within 7 days. Dissolved fractions were defined as passing a Whatman GF/F ashed filter.

3.1 SOURCE OF MEMBRANE CONCENTRATE AND CLEANING SOLUTION

Experiments were conducted with RO membrane concentrate used to treat wastewater in the City of Scottsdale (Water Campus). The 10-million-gal/day (10-MGD) facility treats denitrified wastewater by MF prior to RO treatment. Antiscalant is added prior to RO. The RO system operates at roughly 85% recovery. Currently the RO concentrate is discharged to a sanitary sewer that conveys this waste stream to a regional WWTP (91st Avenue WWTP, City of Phoenix). The RO membranes are periodically cleaned using surfactants, which are discharged to the sewer after use. Table 3.1 summarizes the typical RO concentrate water quality. RO concentrate from this site was collected multiple times for laboratory experiments throughout 2006 and 2007.

Table 3.1. Typical Water Quality of RO Concentrate

Parameter	Units	Value
DOC	mg/L	40
UVA at 254 nm	cm^{-1}	0.82
SUVA (UVA/DOC)	m^{-1} $(mg/L)^{-1}$	2.1
COD	mg/L	138
TDS	mg/L	5560
Conductance	μS/cm	10,000
Bromide	mg/L	2.6
Nitrate	mgN/L	46
Ammonia	mgN/L	64
Hardness	mg/L as $CaCO_3$	2357
Alkalinity	mg/L as $CaCO_3$	1110
pH		7.2

A 0.01% sodium alkylbenzene sulfonate cleaning solution was used in select UV irradiation tests. The City of Scottsdale Water Campus uses this cleaning solution for its RO system. Working stock solutions were prepared in nanopure water.

3.2 EXPERIMENTAL METHODS

3.2.1 Fenton and Fenton-like experiments

Fenton (Fe^{2+}/H_2O_2), Fenton-like (Fe^{3+}/H_2O_2), and ferric coagulation (Fe^{3+}) experiments were performed in a jar-test apparatus (PB-700; Phipps & Bird, Inc., Richmond, VA). Reagent chemicals were added to RO concentrate during rapid mixing (120 rpm), which continued during a reaction period. This process was followed by slow mixing (30 rpm) and settling as appropriate for each experiment.

3.2.2 Ozonation with H_2O_2 experiments

Ozone with hydrogen peroxide (O_3/H_2O_2) experiments were conducted using a lab-scale batch recirculation system (HiPOx system from Applied Process Technology, Pleasant Hill, CA) (Figure 3.1). Water was continuously recirculated with continuous gas (ozone/air) addition. The system is equipped with an ozone generator, a gaseous ozone concentration monitor, a gaseous ozone flow meter, a reactor, and an ozone destruction unit. Ozone gas was produced from pure oxygen. The system recirculates water with a constant feed of ozone gas. The ozone gas is diffused into the recirculating system prior to an in-line mixer. The volume of the recirculating reactor is 2 L. An access port in the recirculation loop permitted sample collection. During the experiments, ozone gas was applied continuously via an ozone gas injector. The H_2O_2 was added either to the mixed solution before ozone addition or into the sampling port during ozonation.

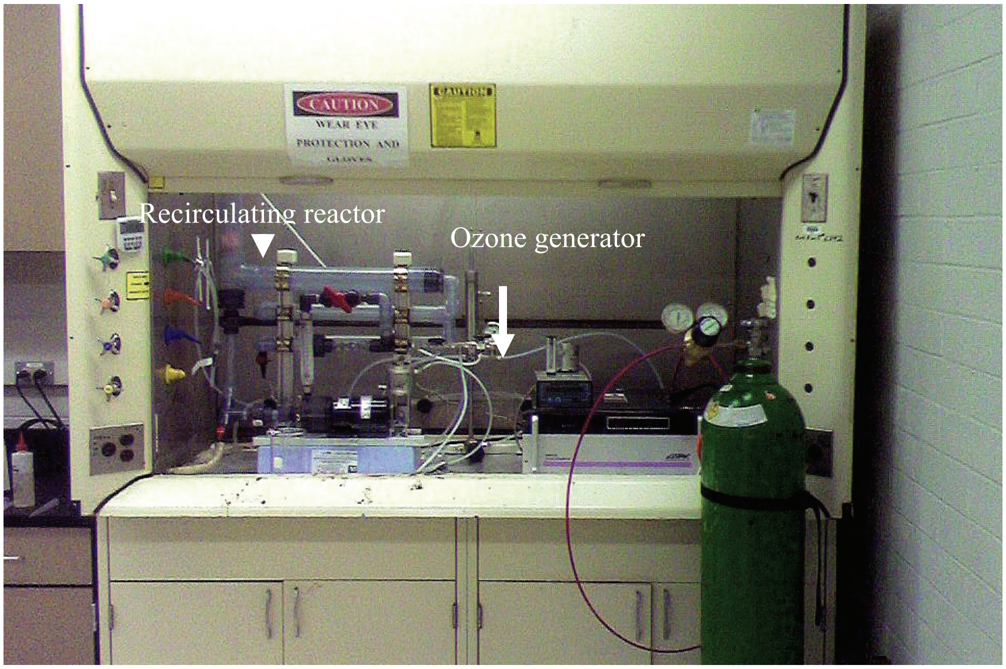


Figure 3.1. Lab-scale HiPOx system.

Using a spreadsheet provided with the equipment, ozone doses were determined based upon measured ozone gas-phase concentrations, gas feed rates, and volume of liquid in the system. H_2O_2 was present in most experiments, and no residual ozone was detected in the recirculation reactor.

3.2.3 Wet Oxidation

Figure 3.2 presents a schematic diagram of the apparatus used in wet oxidation. The main part of the system was a 300-mL stainless steel high-pressure vessel (Model 5500; Parr Instrument, Inc.) equipped with an electrical heating jacket, a temperature controller, a pressure transducer, and a magnetically driven four-blade turbine type impeller. The cooling water was controlled by a recirculating chiller system (FE500; Julabo).

Figure 3.2. Wet oxidation system.

The vessel was operated in batch mode. In a typical run, the reactor was loaded with an approximately 100- to 200-mL sample and a known amount of catalyst. Several commercial catalysts were tested, as well as one provided by Dr. Martin Reinhard at Stanford University. The reactor was then sealed, pressurized with oxygen, and heated to the desired temperature. Continuous mixing of the slurry at 300 to 500 rpm during the heating period allowed complete saturation of the slurry with oxygen before the beginning of the reaction. The starting time of the reaction is defined as when the desired temperature was reached. Samples were withdrawn periodically from the reactor, and special attention was given to the liquid sampling procedure to avoid contamination of the samples and/or losses of the liquid phase and catalyst. Liquid samples were filtered and then analyzed for the presence of DOC.

3.2.4 UV/H_2O_2 Experiments

A UV photolysis with H_2O_2 (UV/H_2O_2) reactor was constructed based upon the design of Hand et al. (1995). The system includes a light source, water bath with recirculating chiller, and four completely stirred reactor bottles (Figures 3.3 and 3.4). A 450-W mercury vapor lamp (Ace Glass, Inc.) is utilized as a UV source that produces monochromatic light at 254 nm. The light source is placed in an immersion well (Ace Glass, Inc.) and positioned in the center of the water bath. The water bath consists of an HDPE tank (Nalgene) covered with aluminum foil. The temperature of the system is controlled by a recirculating cooler system (FE500; Julabo). Four 1.8-L borosilicate bottles specially selected for optical clarity, interior surface smoothness, and the absence of glass imperfections (Wheaton) are placed in the water bath next to the light source. Magnetic stir bars located below the water bath provide control over mixing.

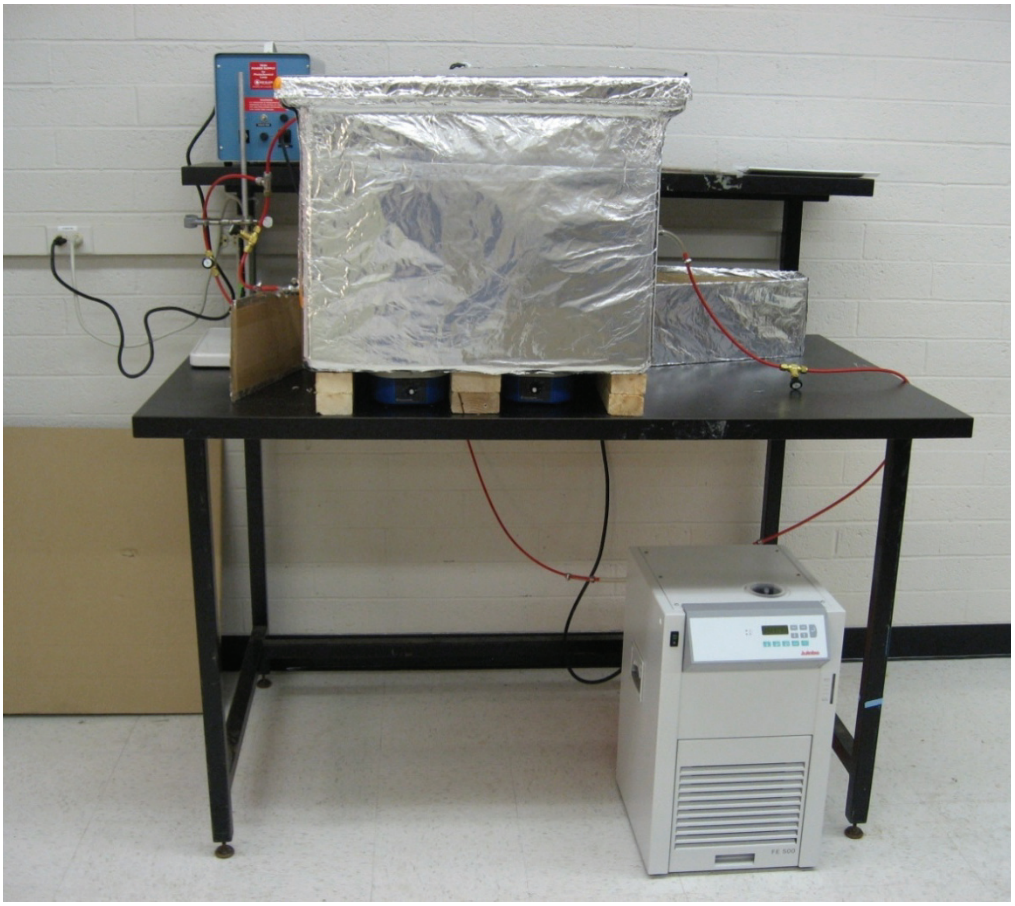


Figure 3.3. UV irradiation lab-scale system.

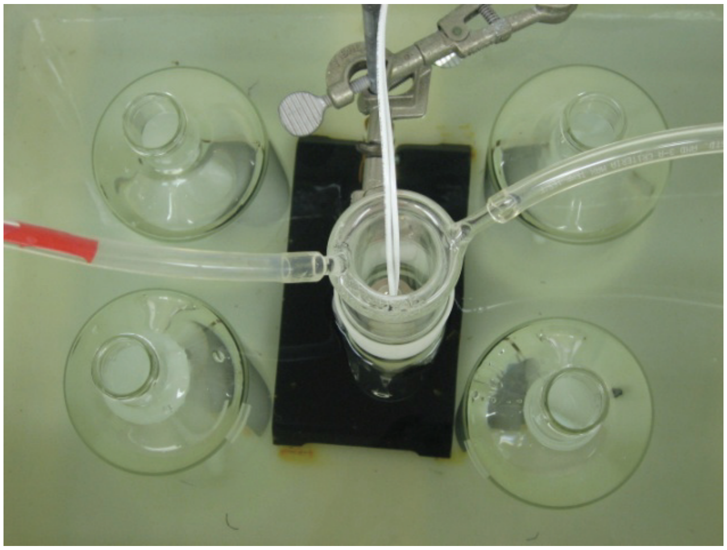


Figure 3.4. Downward view into water bath showing location of light source (center) and 4 reactor bottles.

3.2.4.1 UV Light Intensity Measurement

To estimate the light intensity received by the solution in the reactor, potassium ferrioxalate ($K_2[Fe\{C_2O_4\}_3]\cdot 3H_2O$) actinometry was used (Hatchard and Parker, 1956). A sulfuric acid solution containing 0.006 M potassium ferrioxalate was placed in the reactor and exposed to the light. Photolysis of ferrioxalate in sulfuric acid proceeds according to the following stoichiometry:

$$\left[Fe^{3+}\left(C_2O_4\right)_3\right]^{3-} \xrightarrow{hv} \left[Fe^{2+}\left(C_2O_4\right)_2\right]^{2-} + C_2O_4^{\ -} \qquad (3.1)$$

At 60-s intervals, samples were withdrawn from the reactor to measure the concentration of Fe^{2+}. The ferrous ion was measured by spectrophotometer (DR/2000; Hach) by using a phenanthroline method at 510 nm.

Figure 3.5 shows the Fe^{2+} concentration as a function of reaction time during the actinometry experiment. A clear linear relationship is observed between Fe^{2+} concentration and reaction time.

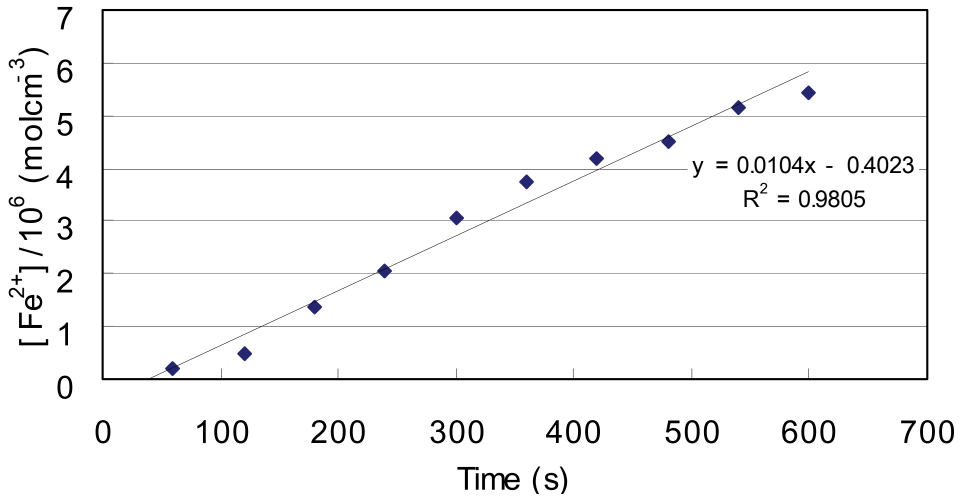


Figure 3.5. Formation of photogenerated Fe^{2+} with irradiation time.

The intensity of the UV source is estimated as 8.59 × 10^{-6} einstein/L·s (2.5 W/L) according to the following equation (and is consistent with previous publications using the same light source configuration, namely, Hand et al., 1995):

$$I = \frac{d[Fe^{2+}]/dt}{\Phi}$$

where,

I = light intensity (einsteins/L·s)

Φ = quantum yield of Fe^{2+} from the irradiation (1.21)

$d[Fe^{2+}]/dt$ = rate of formation of $[Fe^{2+}]$ in the photo process

From the results of an actinometry experiment, the UV dose of the system is estimated to be 22 mJ/s·cm^2. A user of this estimate assumes that one-half of the cylindrical reactor is exposed to the UV source. For example, $A = \pi rh = 327.26\ cm^2$, where A = surface area, r = radius (cm), h = height (cm) of the entire reactor volume (1.8 L). This value is an approximation, of course, but it is useful for comparing order-of-magnitude dosages from oxidation and disinfection.

3.2.4.2 UV Experiments with H_2O_2 and TiO_2

Test solutions were placed in the reactor bottles and mixed with hydrogen peroxide and titanium dioxide for 15 min before the UV lamp was turned on. Titanium dioxide (P25; Degusa) stock solution was sonicated for 15 min at 200 W/L to obtain a well-mixed suspension. Samples were withdrawn from the reactor using a 20-mL pipette and centrifuged for 5 min at 500 rpm (Thermo IEC; IEC Multi) to remove the TiO_2 catalyst from the solution.

3.2.4.3 Large-Scale Recirculating UV/TiO$_2$/Membrane System from Purifics (Photo-Cat)

UV/TiO$_2$ bench-scale experiments were conducted using the Photo-Cat system (Purifics ES, Inc.), which consists of a reactor, UV lamp (up to eight lamps), ceramic MF/UF, and automated control system (Figure 3.6). TiO$_2$ is continually circulated during the experiment and then separated using ceramic membranes. The manufacturer provided a spreadsheet for calculating the power. Operation in batch mode required 20-L samples of RO water to be added. A purge mode allows the system to be cleaned between runs.

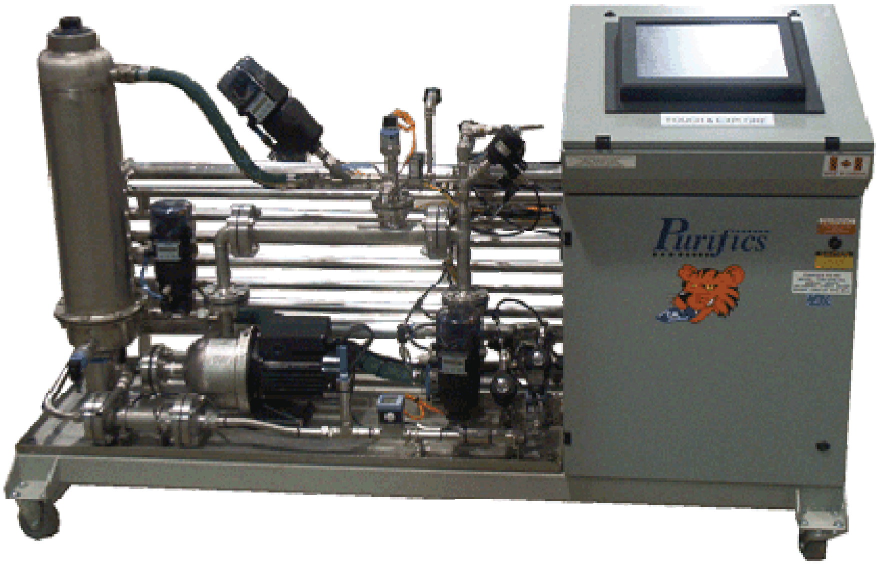


Figure 3.6. Photo-Cat system.

3.3 ANALYTICAL METHODS

General sample collection and handling were in accordance with the guidelines of Section 1060 of *Standard Methods* (Clesceri et al., 1998). All samples were filtered using a Whatman GF/F ashed glass fiber filter. For samples containing hydrogen peroxide, sodium thiosulfate was added to quench residual H_2O_2 because it was found to interfere with DOC measurements.

Table 3.2. Summary of Analytical Methods

Parameter	Instrument	Method
TOC	Shimadzu TOC 5050	High-temperature combustion (SM5310B)
UVA	Shimadzu Multispec 1501	Diode array
pH	Beckman Model 511201	Gel electrode (SM 4500-H+B)
Conductance	VWR Model 2052	SM2510B
Hardness	Hach Titration kit	Digital titrator with EDTA Method 8213
Alkalinity	Hach Titration kit	Digital titrator with phenolphthalein and total using sulfuric acid method 8203
Ozone residual	Hach AccuVac ampules	Indigo method 8311
Hydrogen peroxide	Hach hydrogen peroxide test kit model HYP-1	Titration/thiosulfate method
para-chlorobenzoic acid	Waters Alliance 2695 HPLC	UV detection
COD	DR5000 Hach spectrophotometer and Hach digestion block	Reactor digestion method 8000

3.5.1 BDOC$_5$

Biologically active sand was used to quantify the readily biodegradable fraction of organic carbon. Five-day BDOC (BDOC$_5$) was measured using the biologically active sand reactors described earlier (Allgeier and Summers, 1996). Briefly, 200 mL of clean sand was added to 1-L amber bottles (Figure 3.7). Glass wool permitted diffusion of air into the headspace and sample. A bacterial seed from the Scottsdale WWTP activated sludge system (return activated sludge) was added to each reactor for 1 day. The water (500 mL) was then replaced daily for 1 week and then every 3 days for 1 month to acclimate the reactors. The reactors were verified to be biologically active and stable when the DOC removal in each reactor achieved ±15% of the average removal.

3.5.2 Organic Acids

A Dionex DX-500 ion chromatograph was used to measure organic acids. The system includes a GP40 gradient pump, a CD20 conductivity detector (suppressed conductivity, Dionex ASRS Ultra II), an AS40 autosampler, and a Dionex AS11 HC column with an AG-11 guard column and Dionex ATC-3 trap column. Gradient elution occurred at a flow of 1.5 ml/min with the following concentrations: 0 to 10 min of 1 mM KOH; 10 to 16 min of linear 1 to 10 mM KOH; 16 to 20 min of linear 16 to 20 mM KOH; 20 to 30 min of linear 15 to 30 mM KOH; 30 to 40 min of linear 30 to 60 mM KOH; 40 to 42 min of 60 mM KOH; 42 to 44 min of linear 60 to 61 mM KOH; and 44 to 54 min of 1 mM KOH. The detected carboxylic acids were acetate, formate, propionate, pyruvate, and oxalate. Standards were prepared daily. The samples were analyzed within a few days of each experiment.

Figure 3.7. BDOC reactor with biologically active sand.

CHAPTER 4

COMPARISON OF OXIDATION STRATEGIES

This chapter compares the ability of several processes (oxidation and sorption to metal oxides) to remove DOC from RO concentrate. The goal is to demonstrate, under typical operating conditions, which process should be selected to investigate more thoroughly (namely, in Chapter 5). The processes compared here include:

- Sorption to metal oxides:
    - Iron precipitate
    - Titanium dioxide
- Advanced oxidation processes:
    - Fenton reaction
    - Wet chemical oxidation
    - Ozone/hydrogen peroxide
    - UV/hydrogen peroxide
    - UV/TiO_2

4.1 FENTON-RELATED PROCESSES

Experiments using the Fenton reaction (Fe^{2+} with H_2O_2) and Fenton-like (Fe^{3+} with or without H_2O_2) reactions were conducted to investigate the removal of DOC due to both the oxidation imparted by the Fenton reactions and sorption onto iron hydroxide precipitates. Initial experiments attempted to separate DOC removal by oxidation from DOC removal by precipitation. Subsequent tests investigated the kinetics of DOC removal during the Fenton reaction. While normally Fenton reactions are conducted only at low pH, it was deemed necessary to raise the pH to near-neutral should the RO concentrate ever be treated and discharged or put to additional beneficial use. Previous work by a graduate student also showed a benefit to raising the pH after a low-pH period in which oxidation occurs, based upon research on waste streams from colored dye-stuff manufacturing.

Table 4.1 summarizes the test conditions for the initial Fenton and Fenton-like experiments. Oxidation in the presence of hydrogen peroxide was conducted at pH = 3.5, but then the pH was increased (base addition) to 7.8 to facilitate iron hydroxide precipitation that could remove additional organics. The RO concentrate sample used for these experiments had a DOC of 40 mg/L (Table 4.2). DOC removal ranged from 8% to 12%. Strict coagulation alone exhibited the lowest DOC removal. Given the low SUVA of this water and potential for various inorganics to sorb (for example, phosphates), such low DOC removals are reasonable. Adding hydrogen peroxide and conducting the oxidation reaction at pH = 3.5 yielded a slight improvement in DOC removal. The best DOC, UVA, and COD removals occurred when one used ferrous iron and hydrogen peroxide at pH = 3.5, so further experiments focused only on Fenton-reaction-based conditions.

Table 4.1. Experimental Conditions for Fenton-Related Experiments

Parameter	Fenton Reaction	Fenton-like	Coagulation
Fe^{2+} dosage	5 mM	0	0
Fe^{3+} dosage	0	5 mM	5 mM
H_2O_2 dosage	5 mM	5 mM	0
Reaction time (min)	30	30	30
Reaction pH	3.5	3.5	7.8
Precipitation pH	7.8	7.8	7.8

Table 4.2. Results from Fenton-Related Experiments

		% Removed Relative to Initial Conditions		
Parameter	Initial Conditions	Fenton Reaction	Fenton-like	Coagulation
pH	6.8	*see Table 4.1*	*see Table 4.1*	*see Table 4.1*
UVA_{254} (1/cm)	0.816	34%	26%	14%
DOC (mg/L)	40.0	11%	13%	7%
COD (mg/L)	138	21%	12%	7%
SUVA (L/mg-m)	2.04	25%	15%	8%

To improve DOC removal, the ferrous iron and hydrogen peroxide dosages were increased (Table 4.3). In one experiment hydrogen peroxide was added only at the beginning of the reaction time. In the other test hydrogen peroxide was added both at the beginning of the experiment and after 21 min of reaction. The additional hydrogen peroxide was added based upon other experiments (not shown) that indicated complete consumption of hydrogen peroxide within 10 to 20 min of mixing of ferrous iron and hydrogen peroxide.

Table 4.3. Experimental Conditions for 2nd Set of Fenton Reaction Experiments

Parameter	Expt. F1	Expt. F2
Ferrous iron dosage (mM)	10	10
Hydrogen peroxide dosage (mM)		
Applied initially	10	7
Applied after 20 min	0	3
Initial pH	3.0 to 3.5	3.0 to 3.5
Reaction time at initial pH	30 min	30 min
Precipitation pH	7.8	7.8

Upon initiation of the experiments outlined in Table 4.3 (Figure 4.1), DOC removal occurred rapidly due to both oxidation and precipitation processes. Approximately 50% DOC removal was achieved. Providing longer low-pH-reaction times or staggering hydrogen peroxide addition did not appear to significantly improve DOC removal. Similar trends were observed for UVA removal (Figure 4.2), although the percentage of UVA removed was greater than that of DOC. Overall, UVA was reduced by nearly 75%.

Overall, Fenton reactions are capable of oxidizing organics in RO concentrate. High dosages of ferrous iron and hydrogen peroxide are necessary to achieve >50% DOC removal. Acidification of RO concentrate to pH = 3.5 was studied during the Fenton reactions; significant amounts of acid are required for well-buffered RO concentrate. After oxidation at low pH, base addition is necessary to neutralize the treated water and to remove iron as precipitated iron hydroxide.

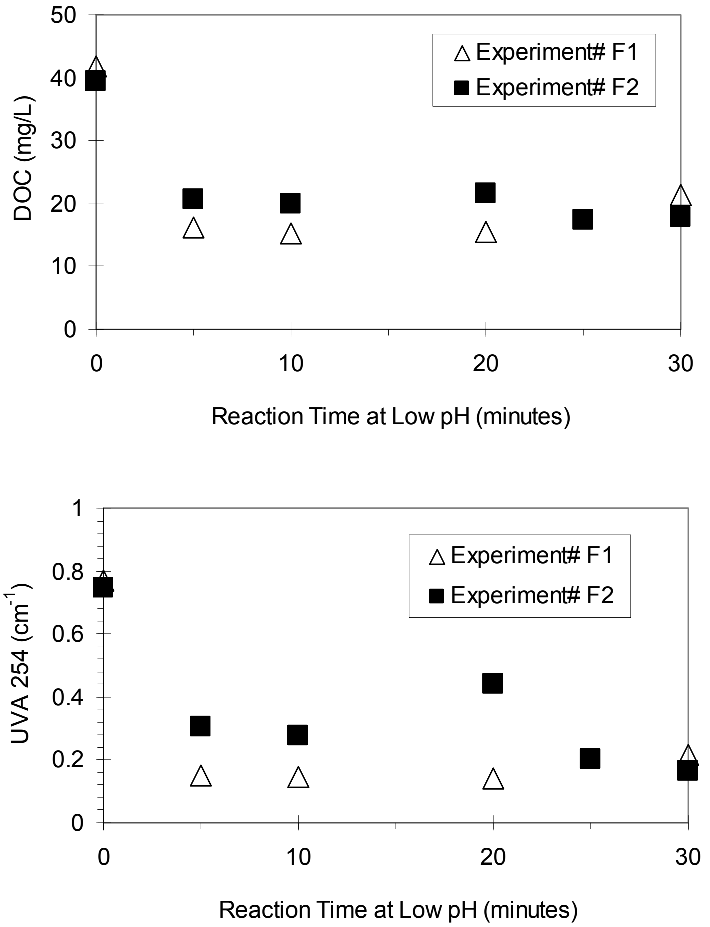


Figure 4.1. DOC and UVA removal during Fenton reaction treatment of RO concentrate.

4.2 WET CHEMICAL OXIDATION

Preliminary investigations with wet chemical oxidation were designed to validate this new experimental process in our laboratory. Wet chemical oxidation of phenol (5 g/L) was carried out (130 °C and 1.5 MPa in the presence or absence of a commercial catalyst) (Carriazo et al., 1988; Hamoudi et al., 1998). We used 2% wt Pd/Al_2O_3 obtained from Stanford University. Figure 4.2 illustrates the results. Based on DOC removal, phenol removal was < 5% without the catalyst but reached approximately 20% after 180 min in the presence of the catalyst. These results were consistent with the published work and validated the general operability of the laboratory wet chemical oxidation system.

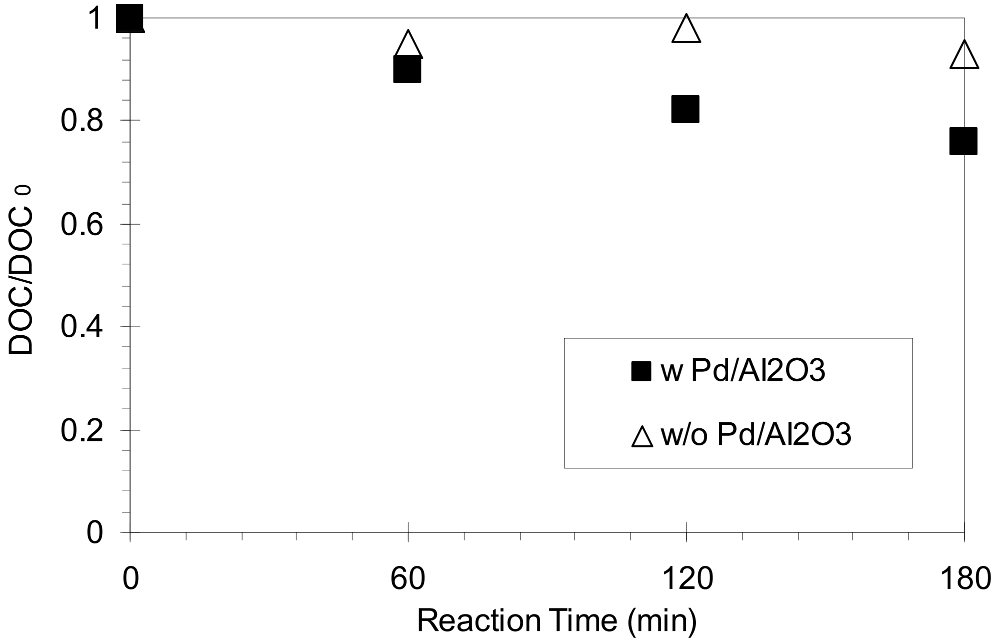


Figure 4.2. Effect of catalyst on phenol wet oxidation.

Wet chemical oxidation tests using RO concentrate were conducted in the presence or absence of catalyst at 100 °C and 0.3 MPa. DOC removal with the catalyst was only about 10%, whereas in the absence of the catalyst it was < 5%. The results were very similar to those in Figure 4.2.

Subsequent wet chemical oxidation tests with RO concentrate investigated the effects on DOC removal of varying the temperature (100 and 130 °C) and oxygen partial pressure (0.3 and 0.7 MPa) (Figure 4.3). The oxygen partial pressure requirement was estimated based on the COD of RO concentrate, which led to a pressure in excess of that required to oxidize carbon into carbon dioxide and water. Increasing the temperature and oxygen partial pressure resulted in greater DOC removals to a maximum of 50%. A zero-order loss of DOC was observed under the experimental conditions. If this rate continued, approximately 5 h of treatment would be required to achieve 90% removal. Of course, higher temperatures and/or oxygen partial pressures could be applied to try to improve the rate of DOC mineralization (namely, loss of organic carbon due to formation of carbon dioxide or purgeable carbonaceous compounds).

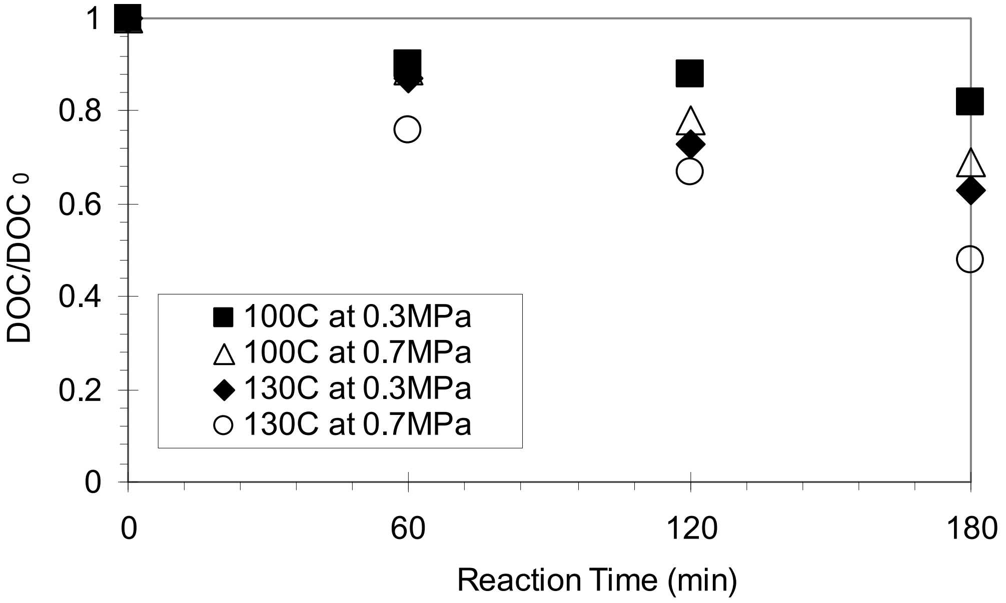


Figure 4.3. Effect of temperature and oxygen partial pressure on the removal of organics in RO concentrate by wet chemical oxidation.

4.3 ADVANCED OXIDATION USING OZONE AND HYDROGEN PEROXIDE

The HiPOx system is designed for use with both ozone and hydrogen peroxide, so no ozone-only experiments were conducted. In the lab HiPOx system, use of ozone alone would probably degrade the plastic tubing. Application of oxygen alone as a control (namely, the ozone generator was turned off) led to no detectable DOC removal. Subsequent experiments were conducted with fixed gas flowrates (50 to 200 mL/min) containing approximately 15% ozone by weight in the gas phase. With a constant gas application rate, longer gas addition durations result in higher applied ozone dosages. Samples for organic analysis were collected over time (namely, for increasing ozone dosages). Results from the HiPOx tests are presented in three parts:

- H_2O_2 applied at the beginning of the process
- H_2O_2 applied at the beginning and during the process
- Effect of pH

The target dosage for hydrogen peroxide and ozone was typically 0.7 mol of H_2O_2/mol of O_3. A 0.3% solution of hydrogen peroxide was used. The hydrogen peroxide was added at the beginning of the experiment, and then ozone was added for a fixed duration to achieve a specific ozone dose to yield the target ratio. Experiments were conducted at the ambient pH of the RO concentrate (pH = 7.5 to 8.0) unless otherwise noted. Select data will be presented to illustrate key conclusions from this work with the HiPOx system.

4.3.1 Hydrogen Peroxide Addition at Beginning of Experiment

Table 4.4 summarizes the test conditions. For reasons described later, experiments were conducted with both diluted and undiluted RO concentrate. Figure 4.4 presents data collected over time from the HiPOx system (namely, higher ozone dosages). Higher ozone dosages led to improved DOC and UVA removal during consumption of hydrogen peroxide. The rate of DOC loss was similar in experiments O1 through O5. At the highest ozone dose, DOC removal appeared to plateau at 70%, which corresponds to a final DOC concentration of 13.5 mg/L. None of the experiments achieved greater than 70% DOC removal. Ozone/hydrogen peroxide also destroyed UVA material (Figure 4.4). The maximum UVA removal was nearly 97%. A portion of the UVA at 254 nm can be attributed to part of the hydrogen peroxide absorption spectrum (Figure 4.5). Caution therefore needs to be taken when interpreting UVA data without DOC data. The loss of hydrogen peroxide as a function of ozone dose (Figure 4.4) appears to be nearly zero order (namely, changes linearly as a function of ozone dose). As hydrogen peroxide degrades, hydroxyl radicals (HO•) are produced. These HO• are primarily responsible for degradation of the organics.

Very high ozone dosages are applied here. Typical drinking water ozone dosages are on the order of 2 to 6 mg/L, which removes negligible DOC. To achieve high levels of DOC mineralization, higher ozone dosages are required (hundreds of milligrams per liter).

Table 4.4. Experimental Conditions for HiPOx Tests

Experiment ID No.	Dilution of RO Water with Nanopure Water	Maximum Ozone Dosage (mg/L)	Initial H_2O_2 Dosage (mg/L)
O1	50%	340	296
O2	50%	310	176
O3	50%	485	258
O4	No dilution 100% RO concentrate	750	383
O5	No dilution 100% RO concentrate	1100	533

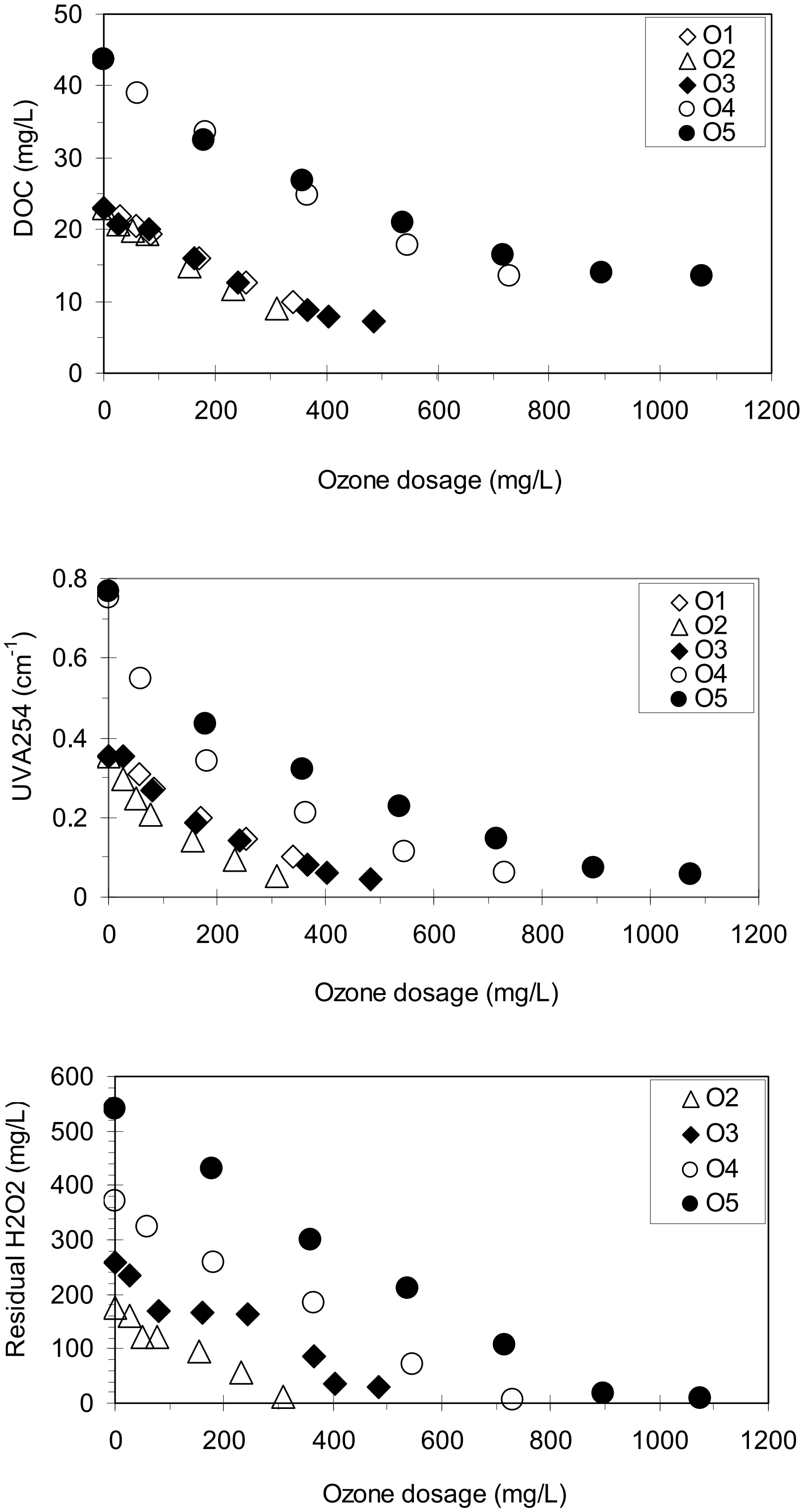


Figure 4.4. DOC, UVA$_{254}$, and H_2O_2 concentration profiles as functions of ozone dosages.

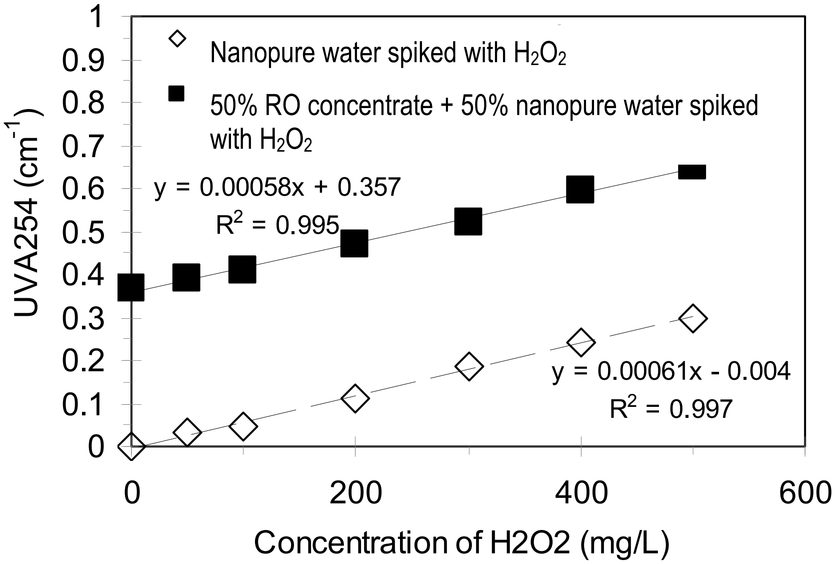


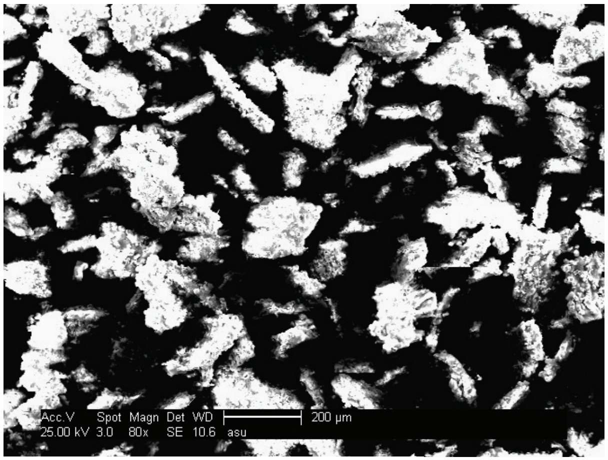
Figure 4.5. Influence of H_2O_2 on UVA measurements at 254 nm.

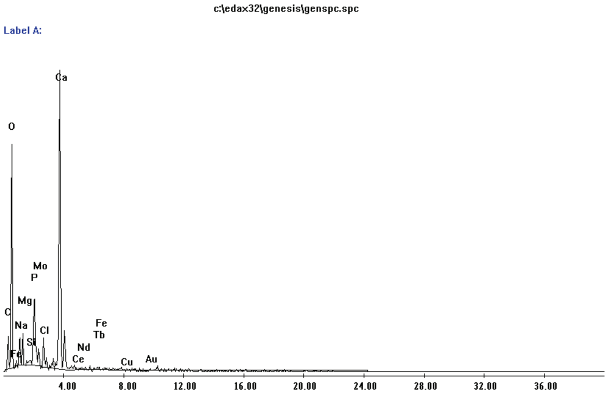
4.3.2 Analysis of White Precipitate Formed during HiPOx Tests

During ozonation with 100% RO concentrate, a dense white precipitate was observed to form over time in the HiPOx system. To determine the nature of this precipitate, the particulate matter suspended solids in ozonated and nonozonated RO concentrate were measured. Ozone (no hydrogen peroxide) was applied at a high dose in a small reactor (not the HiPOx system) at two different pH levels. Suspended solids in the samples were measured by filtration (Whatman GF/F), drying, and gravimetric determination. Increasing the pH of ozonated or nonozonated water led to the formation of more than 500 mg of suspended solids/L (Table 4.5). At pH = 7, ozonated RO concentrate had higher suspended solids than did nonozonated. This finding suggests that ozonation may be enhancing the formation of precipitates. Particulate material captured on the GF/F filter was analyzed by scanning electron microscopy and energy-dispersive X-ray analysis (Figure 4.6). The particulate matter appears crystalline and primarily contains calcium, carbon, oxygen, and phosphorus. The material is probably calcium carbonate, calcium phosphate, calcium silicate, and a precipitate of calcium and organic acids (for example, calcium oxalate). Greater particulate formation during ozonation may be due to a slight rise in pH due to off-gassing of dissolved carbon dioxide, cleavage of calcium bound to fulvic-like material, or formation of organic acids. The white precipitate did not form during UV irradiation experiments, suggesting that microflocculation of some type occurred during ozonation. The problem associated with formation of the white precipitate could be avoided completely by working with a 50% dilution of RO concentrate with nanopure water. This arrangement reduced the concentration of calcium and anions in solution, apparently to levels below the point at which they would precipitate. In a full-scale system, such dilution would not be feasible, but the precipitation may be controllable through acid addition. However, acid addition may have negative consequences on the formation of hydroxyl radicals from hydrogen peroxide because the dissociation of hydrogen peroxide is important for rapid formation of hydroxyl radicals.

Table 4.5. Suspended Solids in Raw and Ozonated RO Concentrate

Sample	pH	Suspended Solid Concn (mg/L)
RO concentrate	7	8.3 ± 0.7
	10	514 ± 13
Ozonated RO concentrate	7	23 ± 1
	10	564 ± 2





Element	Wt %
C	**16.4**
O	**49.29**
Na	2.91
Mg	2.49
Si	0.35
P	**3.76**
Mo	2.29
Cl	1.42
Ca	**17.8**
Ce	0.24
Nd	0.26
Tb	0.18
Fe	0.11
Au (from coating)	2.47

Figure 4.6. Scanning electron micrograph and EDAX analysis of the white precipitate formed during ozonation of RO concentrate.

4.3.3 Multiple Hydrogen Peroxide Applications

Because of the batch experimental setup of the HiPOx system, the ratio of H_2O_2 to ozone changes over time, eventually reaching the target of 0.7 mol/mol. Ozone continuously consumes hydrogen peroxide. To permit a better understanding of the dependence of DOC removal on ozone-to-hydrogen-peroxide ratios in the HiPOx system, hydrogen peroxide was added at the beginning of the experiment and then again later when the hydrogen peroxide ratio decreased.

Table 4.6 summarizes the conditions for experiments O6 through O9, which were conducted using RO retentate diluted by 50% with nanopure water to avoid the formation of precipitates.

Table 4.6. Experimental Conditions for HiPOx Tests using 50% Diluted RO Concentrate

Expt. No.	Maximum Ozone Dosage (mg/L)	Initial Hydrogen Peroxide Dosage at t = 0 (mg/L)	Additional Applied Hydrogen Peroxide Dosage at t = 25 min[a]
O6	565	340	296
O7	558	310	176
O8	585	485	258
O9	600	1100	533

[a] Corresponds to the time needed to reach half the maximum ozone dose.

Figure 4.7 illustrates the results. The slope of the hydrogen peroxide concentration versus ozone dose is approximately 0.5 mg of H_2O_2/mg of O_3 (0.7 mol of H_2O_2/mol of O_3). Overall, the change in hydrogen peroxide was nearly constant, no matter when it was applied. However, the interference of H_2O_2 on UVA at 254 nm was apparent when it was added for a second time because of the presence of a high H_2O_2 residual. DOC removal was constant in all four experiments, independent of when H_2O_2 was added. DOC removal plateaued at 60% to 65% removal.

4.3.4 Effect of pH

Dissociation of H_2O_2 into HO_2^- is important because HO_2^- reacts much more rapidly with ozone to form hydroxyl radicals. Thus, three pH levels were investigated (Table 4.7). Ozone and hydrogen peroxide dosages remained the same at each pH. Figure 4.8 illustrates the results. The pH has very little effect on DOC removal or changes in the hydrogen peroxide concentration as a function of ozone dose. Again, the maximum DOC removal approaches 65%.

Table 4.7. Experimental Conditions for HiPOx Tests using 50% Diluted RO

Experiment No.	pH	Maximum Ozone Dosage (mg/L)	Applied Hydrogen Peroxide Dosage at t = 0 (mg/L)	Applied Hydrogen Peroxide Dosage at t = 25 min (mg/L)[a]
O10	9	600	149	298
O11	10	600	149	298
O12	11	600	149	298

[a] Corresponds to the time needed to reach half the maximum ozone dose.

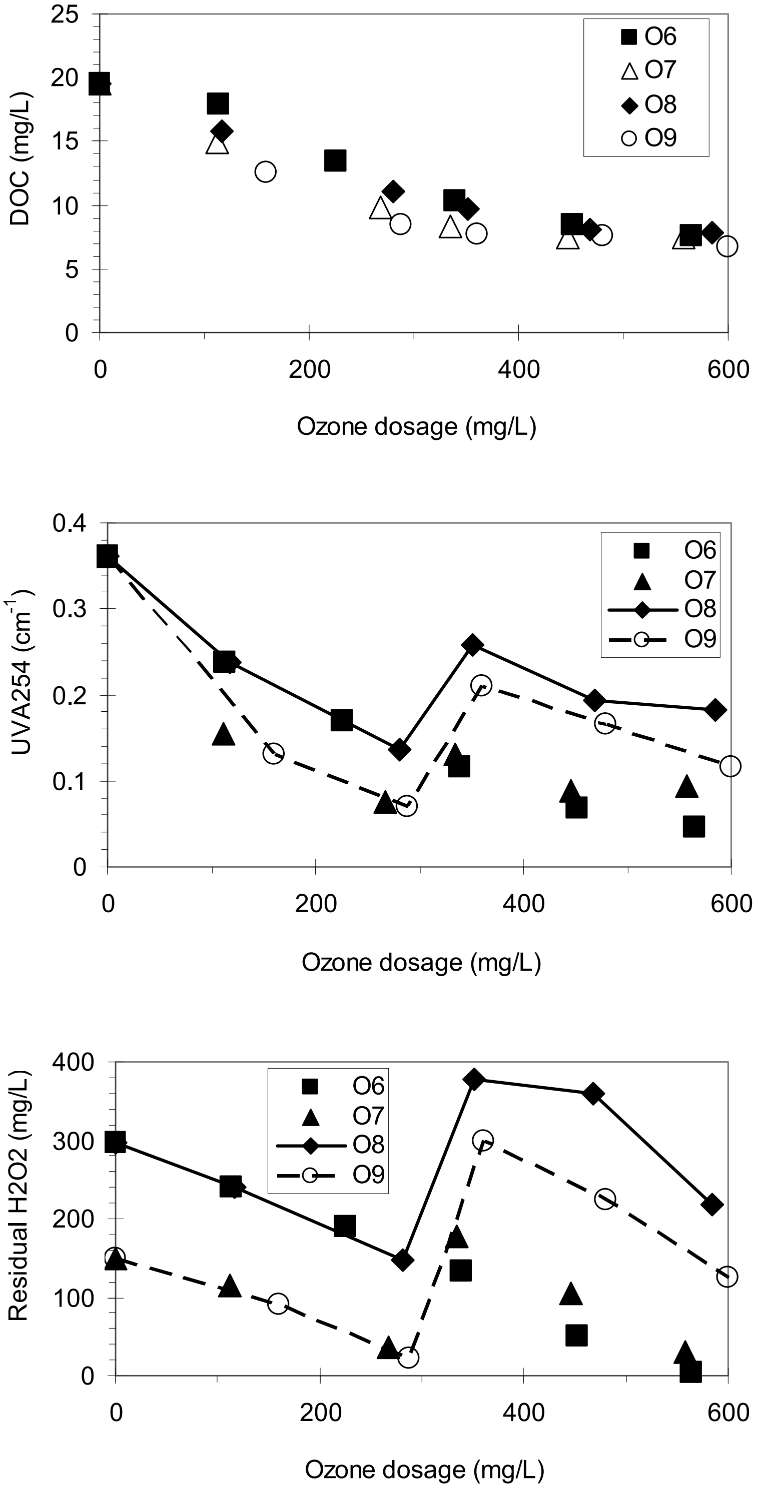


Figure 4.7. Changes in DOC, UVA, and H_2O_2 concentrations during oxidation with ozone.

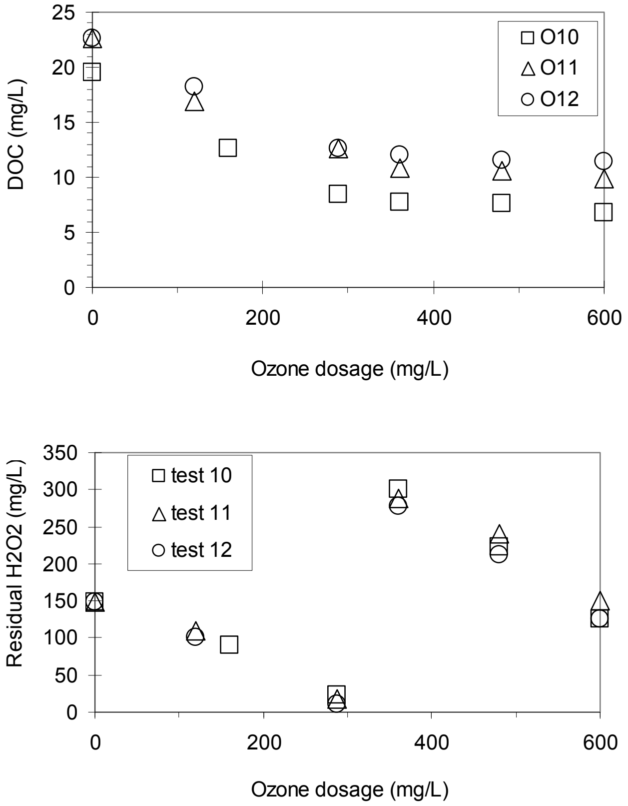


Figure 4.8. Effect of pH on DOC removal and loss of hydrogen peroxide during ozonation.

4.4 UV IRRADIATION EXPERIMENTS

Experiments were conducted in the lab-scale UV irradiation reactor with a low-pressure mercury lamp in the presence of hydrogen peroxide and titanium dioxide. Most experiments were conducted with diluted RO concentrate (50% RO concentrate plus 50% nanopure water). However, select experiments with 100% RO concentrate did not form white precipitates, as was observed during ozonation. Photolysis experiments were conducted over extended durations (up to 12 h) to reach high UV dosages in the laboratory system. However, such durations are not necessary in full-scale applications in which multiple higher-output lamps can be used.

4.4.1 UV/H_2O_2

To study the effect of pH and H_2O_2 concentration on the DOC removal efficiency, photolysis experiments were carried out for up to 11 h at various pHs and initial H_2O_2 doses. The concentration of H_2O_2 was calculated when the overall fraction of light (*F*) absorbed by water with a given background absorbance equaled 10%:

$$F = \frac{A_{H2O2}}{A_{H2O2} + A_{sample}} = 0.1 \tag{4.1}$$

A_{sample} = absorbance at wavelength λ of raw water ($0.4\ \text{cm}^{-1} \times l$)
A_{H2O2} = absorbance at wavelength λ of H_2O_2 ($\varepsilon_{H2O2} \times C_{H2O2} \times l$)

ε_{H2O2}= molar extinction coefficient of H_2O_2 at 254 nm (17.9 M^{-1} cm^{-1})
C_{H2O2}= concentration of H_2O_2 (M)
l = path length (= 1 cm)

Based upon this calculation, approximately 2.5 mM hydrogen peroxide should be added to the experimental solution. Inadvertently, higher levels of H_2O_2 were used (10, 20, and 100 mM), which possibly resulted in higher F values (0.34, 0.56, and 0.98, respectively). While much of the UV light was absorbed by H_2O_2, the hydrogen peroxide may have scavenged many of the hydroxyl radicals produced during this reaction. Figure 4.9 shows the results. At pH levels of 7 and 10, almost no DOC removal was observed, while up to 40% DOC removal was observed at pH = 4, independent of H_2O_2 dosage. At a low pH and longer irradiation times, higher DOC removal may be achievable.

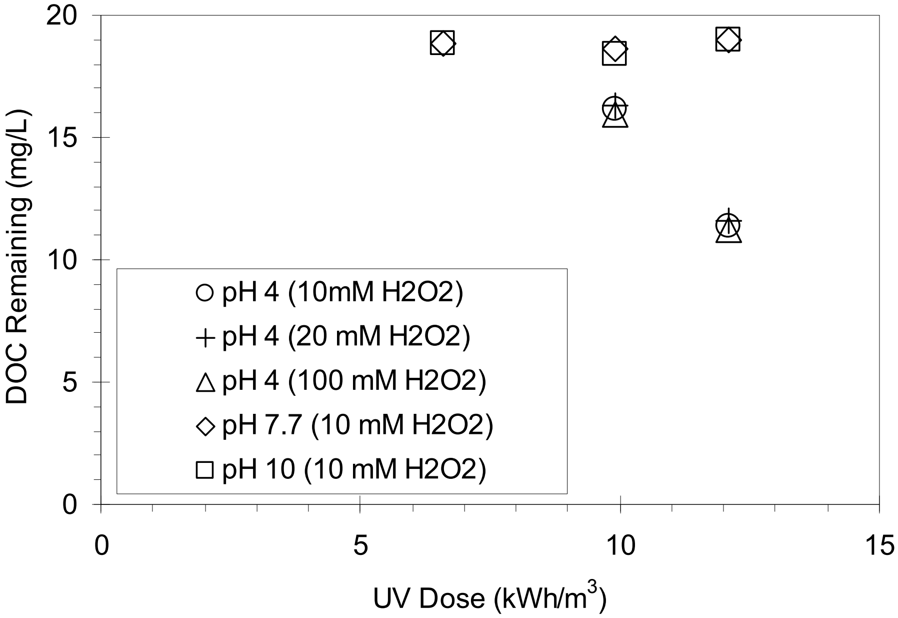


Figure 4.9. Effect of pH on DOC removal in UV/H_2O_2 treatment (initial DOC = 19 mg/L).

4.4.2 UV/TiO_2 Experiments

Several screening-level experiments were conducted with various UV dosages in the presence of 1 to 5 g of TiO_2/L (Figure 4.10). For TiO_2 dosages of 2 and 5 g/L, increasing the UV dosage improved DOC removal at ambient pH. When a fixed TiO_2 dosage of 2 g/L was used, the effect of pH was evaluated. Decreasing pH and increasing UV dosage improved DOC and UVA removal. UVA removal was higher than DOC removal, indicating preferential oxidation of organic matter with carbon-carbon double bonds.

Table 4.8. Effect of pH on DOC and UVA Percentage Removal as Function of UV Dosage[a]

pH	UV Dose (kWh/m^3)	DOC	UVA
4	2.2	12%	55%
4	4.5	37%	90%
7	2.2	8%	18%
7	4.5	16%	24%
10	2.2	5%	15%
10	4.5	8%	30%

[a] 2 g of TiO_2/L, 50% diluted RO concentrate, 19 mg of DOC/L, UVA of 0.030 cm^{-1}.

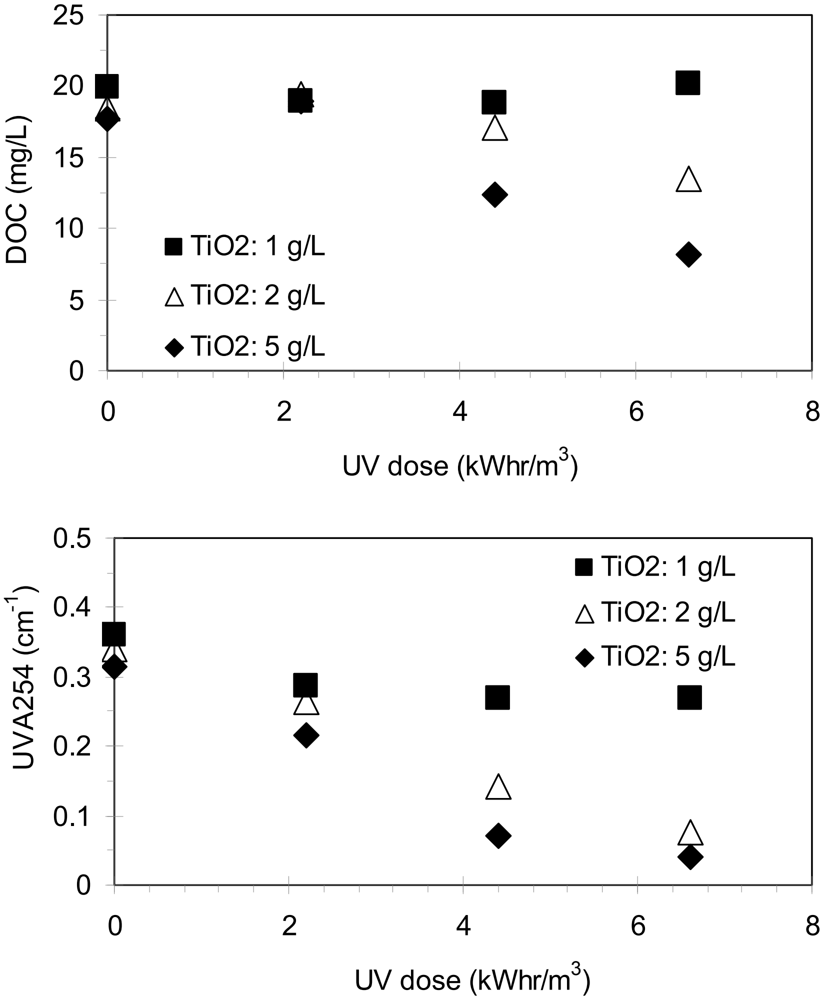


Figure 4.10. Effect of TiO_2 dose on DOC and UVA_{254} at ambient pH during UV irradiation.

4.4.3 Titanium Dioxide Adsorption

Adsorption of RO concentrate onto titanium dioxide was studied between pH = 5.0 and pH = 8.0. Titanium dioxide dosages comparable to those that would be applied during UV treatment (see below) were used (0.5 to 5 g/L). Batch tests with 10 h of contact time resulted in <5% DOC removal. Therefore, it was concluded that DOC adsorption onto TiO_2 was not a significant removal process.

4.4.4 UV/TiO_2/H_2O_2 Experiments

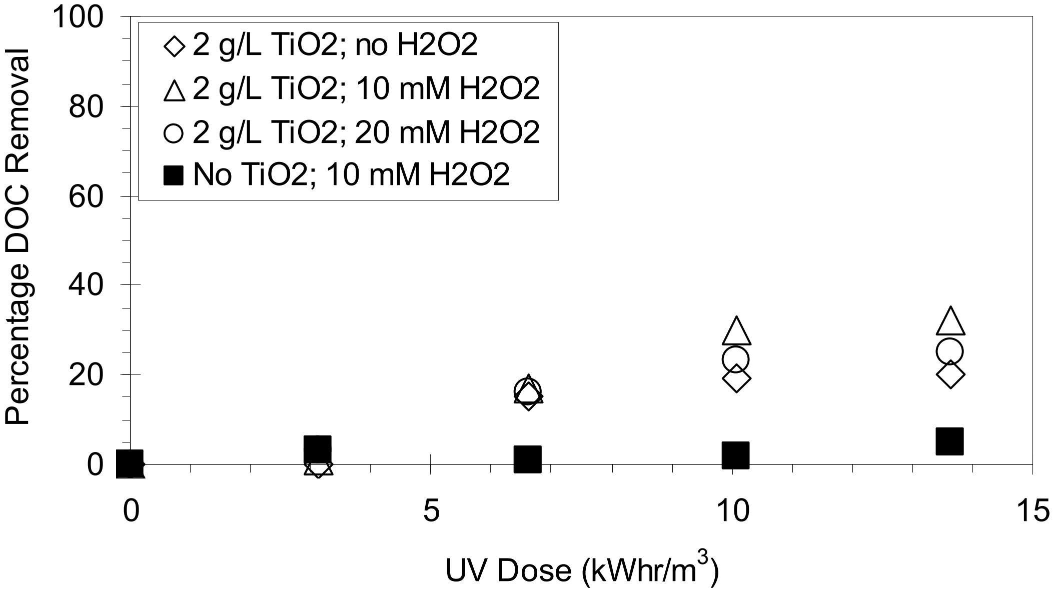
To compare the benefits, or synergy, of titanium dioxide and hydrogen peroxide, a series of tests was conducted at ambient pH (7.8) and reduced pH (5.0) (Table 4.9). Figure 4.11 illustrates the results. DOC removal was higher at pH = 5 than pH = 7.8. This result is probably because of hydroxyl radical scavenging by bicarbonate (discussed in Chapter 5). DOC removal without titanium dioxide addition was only 10% at pH = 7.8 and 30% at pH = 5.0. Therefore, titanium dioxide appears to be more effective than hydrogen peroxide. Marginal improvement in DOC removal was observed with the addition of hydrogen peroxide in conjunction with titanium dioxide. Similar trends were observed for UVA removal, although UVA removals that were higher than DOC removals did occur (not shown).

Table 4.9. Experimental Matrix to Test Effects of TiO_2 and H_2O_2 Addition on DOC and UVA Removal during UV Treatment

Experiment No.	pH	TiO_2 Dose (g/L)	H_2O_2 Dose (mM)
UV1	7.8	2	0
UV2	7.8	2	10 (340 mg/L)
UV3	7.8	2	20 (680 mg/L)
UV4	7.8	0	10 (340 mg/L)
UV5	5.0	2	0
UV6	5.0	2	10 (340 mg/L)
UV7	5.0	2	20 (680 mg/L)
UV8	5.0	0	10 (340 mg/L)
UV9	5.0	2	100 (3400 mg/L)

4.5 COMPARISON OF ENERGY REQUIREMENTS TO ACHIEVE DOC REMOVAL

RO concentrate DOC removal per energy dose was compared for ozone and UV experiments. The analysis did not include Fenton reactions because the energy input is in manufacturing the chemicals and not in the on-site energy demand during treatment. The UV/TiO_2 process at pH = 4 to 5 achieves the highest removal and meets the project goal of >90% organic carbon removal. For comparable energy inputs, other AOPs achieved far less DOC removal.



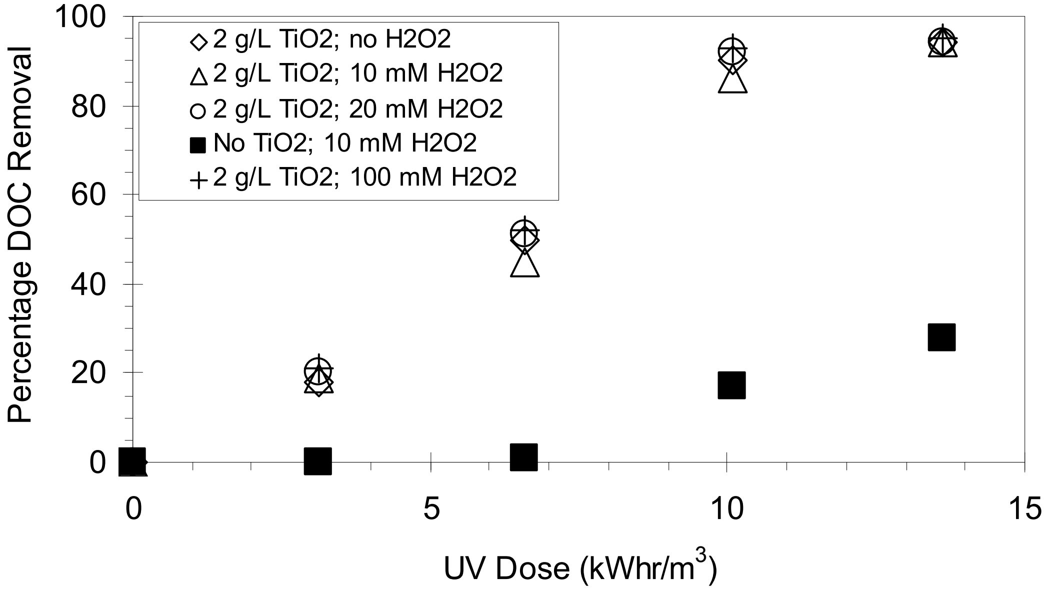


Figure 4.11. Effects of TiO_2 and H_2O_2 on percentage DOC removal during UV treatment (experiments UV1 through UV9).

4.6 UV/TiO_2 EXPERIMENTS WITH CLEANING SOLUTION

Figure 4.12 shows the UV/TiO_2 treatment (2 g/L, pH = 5) of 0.01% and 0.1% alkylbenzene sulfonate cleaning solution. The part of the DOC comprising alkylbenzene sulfonate appears to be readily oxidized at lower UV/TiO_2 dosages. Specifically, organics absorbing at 223 nm were preferentially removed. These results are consistent with literature that shows that hydroxyl radicals can partially oxidize this cleaning solution (Bagyo et al., 2004).

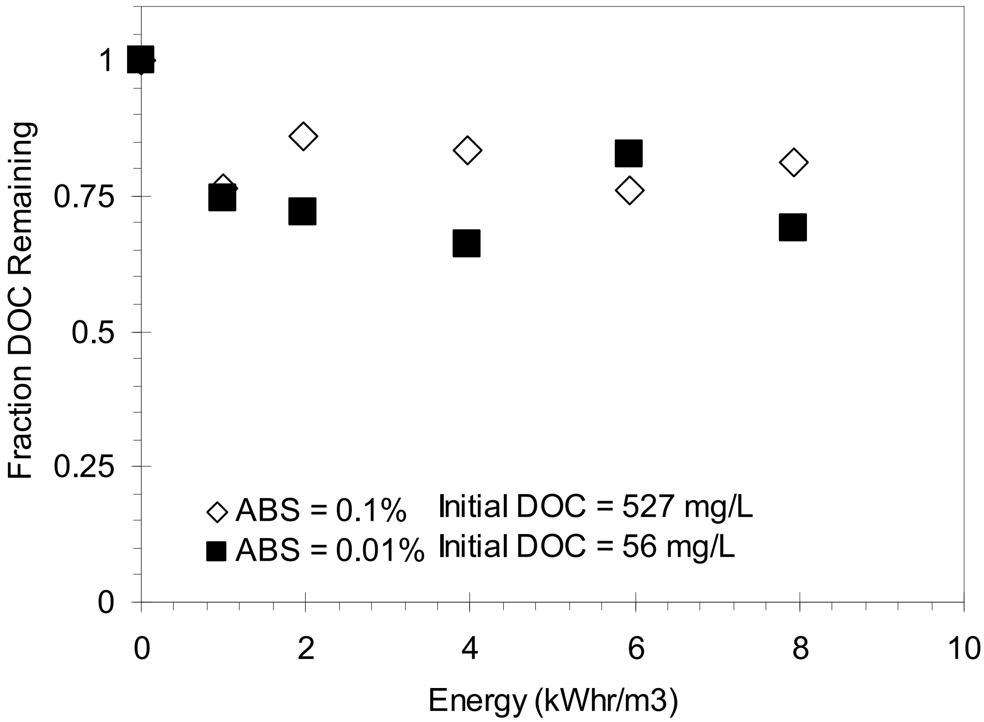


Figure 4.12. UV/TiO_2 DOC removal in alkylbenzene sulfonate cleaning solution.

4.7 SUMMARY

The goal of this chapter was to demonstrate which treatment processes could remove organic matter from RO concentrate and to select one technology to optimize in Chapter 5. The RO concentrate has a DOC of ~ 40 mg/L. The following results were presented:

- Iron coagulation removed less than 5% of the DOC in RO concentrate.
- Applying the Fenton reaction at pH = 3 to 3.5 (10 mM Fe^{2+} and 10 mM H_2O_2) rapidly removed ~50% of the DOC in RO concentrate. Raising the pH to 7.5 to 8.0 and allowing ferric iron to precipitate removed the residual iron. Higher ferrous iron and hydrogen peroxide dosages might have yielded greater DOC removals.
- Ozonation (with hydrogen peroxide) of RO concentrate formed a white precipitate, probably calcite, because of a slight pH change and possibly also because of cleavage of calcium-organic complexes or other microflocculation processes.

- When a dose of 0.7 mol of H_2O_2/mol of O_3 was used, ozone addition oxidized and removed DOC. Ozone dosages of more than 1000 mg/L are necessary to remove approximately 75% of the DOC in RO concentrate. Up to this level of removal, DOC removal was nearly linear as a function of ozone dose. DOC removal was independent of when H_2O_2 was applied.
- UV/H_2O_2 achieved 40% DOC removal at pH = 4, a UV dose of 11.8 kWh/m^3, and a H_2O_2 dose of 10 mM. At pH = 7 and 10, UV/H_2O_2 achieved less than 10% DOC removal.
- UV/TiO_2 achieved up to 95% DOC removal at a UV dose of 10.4 kWh/m^3; this finding was nearly independent of titanium dioxide dosage between 1 and 5 g/L.
- Addition of hydrogen peroxide during UV/TiO_2 application did not significantly improve DOC removal.
- In all cases the UVA percentage removal was greater than the DOC percentage removal, indicating preferential oxidation of carbon-carbon double bonds by all oxidation processes.

Hydroxyl radicals are the dominant oxidant responsible for destruction of organics in all AOPs studied. The UV/TiO_2 process achieved the highest DOC removal and best EE/O in our laboratory experiments. Furthermore, the addition of high hydrogen peroxide dosages led to handling problems associated with hydrogen peroxide residuals, which were present in kinetic samples for some analytical measurements. In addition, any hydrogen peroxide process would have to address residual hydrogen peroxide, which was considerable (10 to > 100 mg/L) based on measurements. Furthermore, the ozone process presented problems with residual dissolved ozone and precipitates. Thus, working with the UV/TiO_2 process in the laboratory was less complicated and reduced analytical concerns when compared to AOPs involving hydrogen peroxide. Therefore, the UV/TiO_2 process was selected for optimization in Chapter 5.

CHAPTER 5

OPTIMIZATION OF UV-TiO_2 AND BIODEGRADATION PROCESSES

In Chapter 4 the UV/TiO_2 process was selected for optimization of DOC and UVA removal from RO concentrate. Optimization includes developing a more thorough understanding of the effect of pH and HO• concentration on production of organic acids and of BDOC and on removal of trace organics in addition to removal of bulk DOC, as well as more understanding of the ability to scale up results.

5.1 VALIDATION OF UV/TiO_2 PROCESS

Figure 5.1 presents DOC and UVA removal during UV treatment with and without TiO_2 present. DOC removal is minimal (<5%) without TiO_2 and plateaus at 87% removal (residual DOC of 2.5 mg/L) with application of titanium dioxide. Clearly, titanium dioxide is required for effective oxidation. Hydroxyl radicals are produced during the UV/TiO_2 process. UVA is removed better than DOC is and reaches a plateau at roughly half the UV dose when the DOC residual plateaus. This finding suggests that UVA material is oxidized preferentially. Most AOPs will convert organics into the following sequence of by-products:

Bulk Organics → Aldehydes → Carboxylic acids → Carbon dioxide

The latter three by-products have low absorbance at 254 nm. Therefore, the UV/TiO_2 process in this reactor probably converted most of the bulk organics to by-products at a UV dose of around 4 to 6 kWh/m^3.

5.2 EFFECT OF INITIAL DOC CONCENTRATION

Experiments were conducted on diluted (50%) and undiluted RO concentrate (Figure 5.2). Diluting the RO concentrate by half only slightly changed the rate of DOC loss (2.7 versus 3.4 mg of DOC/kWh-m^{-3}). As discussed above, the UV/TiO_2 process reaches a DOC removal plateau. For the diluted RO concentrate, this result occurs at roughly 5 to 6 kWh/m^3, when the rate of DOC loss per UV dose decreases by nearly 85%. This finding probably reflects a shift from the dominant reactions being between bulk DOC and hydroxyl radicals to being between aldehydes or carboxylic acids and hydroxyl radicals, as the latter react much more slowly. The undiluted RO concentrate reaches a plateau at a higher UV dose (9 kWh/m^3), nearly twice the UV dose for twofold-higher DOC concentrations. Overall, the rate of DOC removal and the UV dose needed to convert the initial organic matter to oxidation products appear to have a linear relationship, and then a lower rate of destruction by UV radiation occurs for the oxidation products.

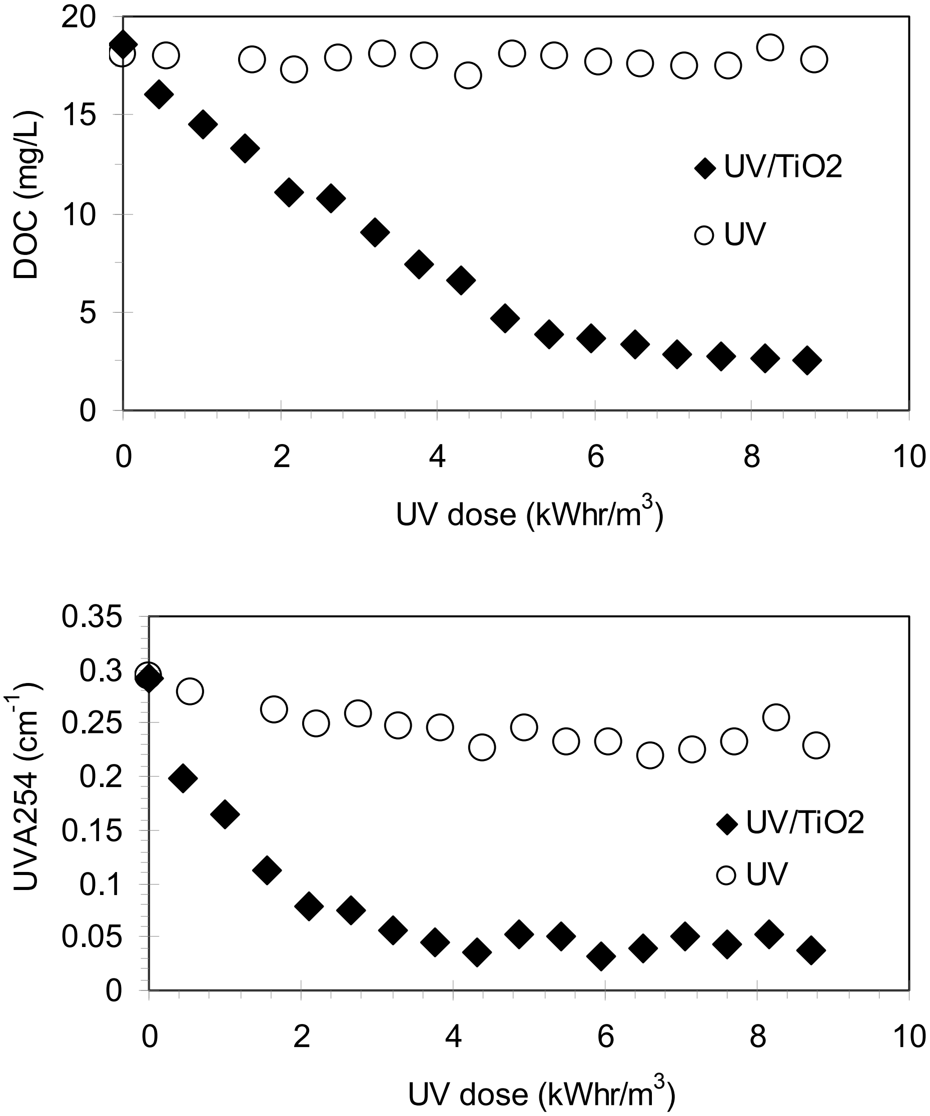


Figure 5.1. DOC and UVA254 as a function of energy input (i.e., reaction time with a fixed irradiation) with or without TiO_2 (pH = 5).

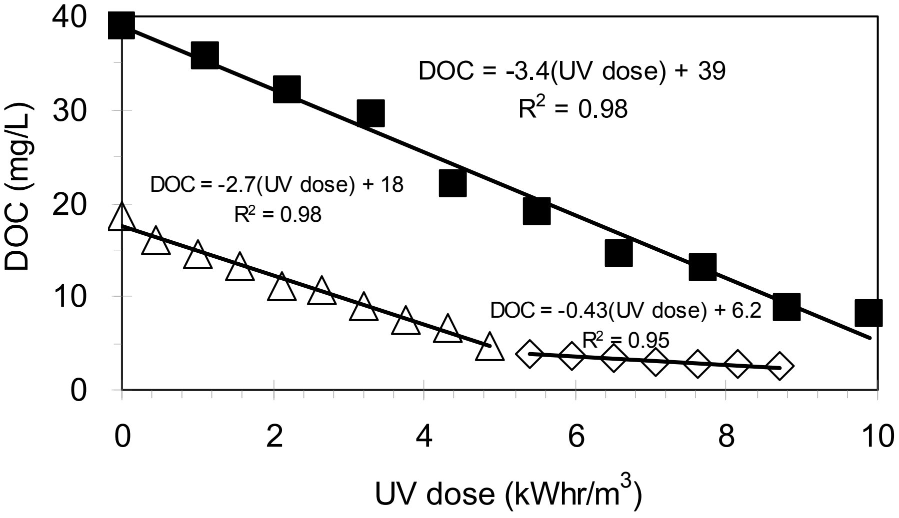


Figure 5.2. Effect of initial DOC concentration of RO concentrate on dependence between DOC loss and UV dose.

5.3 ESTIMATION OF HYDROXYL RADICAL STEADY-STATE CONCENTRATION

To quantify the steady-state $HO^{\bullet}$ concentration during UV/TiO_2 treatment in the reactors, *para*-chlorobenzoic acid (*p*CBA) was added to RO concentrate as an $HO^{\bullet}$ probe compound. This section presents how the use of an $HO^{\bullet}$ probe compound can yield steady-state $HO^{\bullet}$ concentrations along with experimental results. This information is critical in later understanding of the kinetics of organic matter oxidation.

The loss of *p*CBA over time can be described as follows:

$$\frac{d[pCBA]}{dt} = -k_{HO^{\bullet}/pCBA}[HO^{\bullet}][pCBA] \tag{5.1}$$

It is reasonable to assume that initially the UV/TiO_2 process operates with a near-steady-state production of $HO^{\bullet}$ radicals due to reactions between UV light and the titanium dioxide surface. *p*CBA is added at a low concentration (~5 μM) relative to DOC (1.5 mM as carbon) and therefore is not a significant $HO^{\bullet}$ radical scavenger. Thus, *p*CBA is a viable $HO^{\bullet}$ radical probe, and under steady-state $HO^{\bullet}$ concentrations ($[HO^{\bullet}]_{SS}$), Equation 5.1 becomes pseudo-first-order with respect to *p*CBA:

$$\frac{d[pCBA]}{dt} = -k'_{HO^{\bullet}/pCBA}[pCBA] \tag{5.2}$$

$$k'_{HO^{\bullet}/pCBA} = k_{HO^{\bullet}/pCBA}[HO^{\bullet}]_{SS} \tag{5.3}$$

The rate constant between *p*CBA and $HO^{\bullet}$ is $5.0 \times 10^{9}\ M^{-1}s^{-1}$ (Buxton et al., 1988). Therefore, $[HO^{\bullet}]_{SS}$ can be calculated as the ratio between the observed pseudo-first-order rate constant loss for *p*CBA ($k'_{HO^{\bullet}/pCBA}$) and $5.0 \times 10^{9}\ M^{-1}s^{-1}$:

$$k'_{HO^{\bullet}/pCBA} = k_{HO^{\bullet}/pCBA} \tag{5.4}$$

$$\left[HO^{\bullet}\right]_{SS} = \frac{k'_{HO^{\bullet}/pCBA}}{k_{HO^{\bullet}/pCBA}} = \frac{k'_{HO^{\bullet}/pCBA}\left(s^{-1}\right)}{5.0x10^{9}\left(M^{-1}s^{-1}\right)} \tag{5.5}$$

From Equation 5.2, the slope on a plot of ln (*p*CBA)/(*p*CPBA)$_0$ versus time yields the pseudo-first-order rate constant loss for *p*CBA ($k'_{HO^{\bullet}/pCBA}$).

Experiments were conducted using RO concentrate diluted by half with nanopure water and exposed to UV/TiO_2 at ambient pH and a reduced pH of 5. Figure 5.3 presents the rate of DOC loss and change in *p*CBA over time. The loss of DOC was consistent with previous observations: lower pH leads to more rapid DOC loss. Pseudo-first-order rate constants for the loss for *p*CBA ($k'_{HO^{\bullet}/pCBA}$) were $1.11 \times 10^{-4}\ s^{-1}$ at ambient pH and $8.8 \times 10^{-4}\ s^{-1}$ at pH = 5, almost eight times greater. The calculated values for $[HO^{\bullet}]_{SS}$ based on Equation 5.5 are then 2.2×10^{-14} M at ambient pH and 18×10^{-14} M at pH = 5 in the lab UV system with 2 g of TiO_2/L.

5.4 PRODUCTION OF BIODEGRADABLE ORGANIC MATTER DURING UV/TiO$_2$ TREATMENT

The formation of biodegradable organic matter was assessed via two methods. First, specific common organic acids produced during oxidation (namely, acetate, formate, oxalate, propionate, and pyruvate) were quantified. Second, BDOC tests using biologically acclimated sand reactors were conducted to quantify the total amount of biologically degradable material produced.

Both assessment means were conducted on multiple samples, and observed trends were consistent. Therefore, only a few of the experiments will be presented here. Figure 5.4 presents one set of experimental data. After applying nearly 9 kWh/m^3 of UV treatment, DOC had decreased from 39 to 8 mg/L. All five of the measured carboxylic acids were formed, with oxalate and propionate dominating. These results are consistent with observations during the ozonation of NOM (Langlais et al., 1991). Despite a gradual loss of DOC in the system, the individual organic acids reached their maximum concentrations with UV dosages of 2 to 4 kWh/m^3, while their sum reached its maximum at a dosage of 2.5 kWh/m^3. BDOC reactors should readily biodegrade all five of the carboxylic acids, and BDOC values did trend with their sum. BDOC tests contained roughly 3.5 mg more carbon per L than the sum of the five carboxylic acids. The additional material may have been other carboxylic acids, aldehydes, ketones, or other compounds. BDOC and carboxylic acid concentrations were in closer agreement over the UV dose range of 0 to 0.5 kWh/m^3 than during the rest of the UV experiment. These results suggest that although the DOC concentration declines gradually, significant transformation of the organic carbon is occurring.

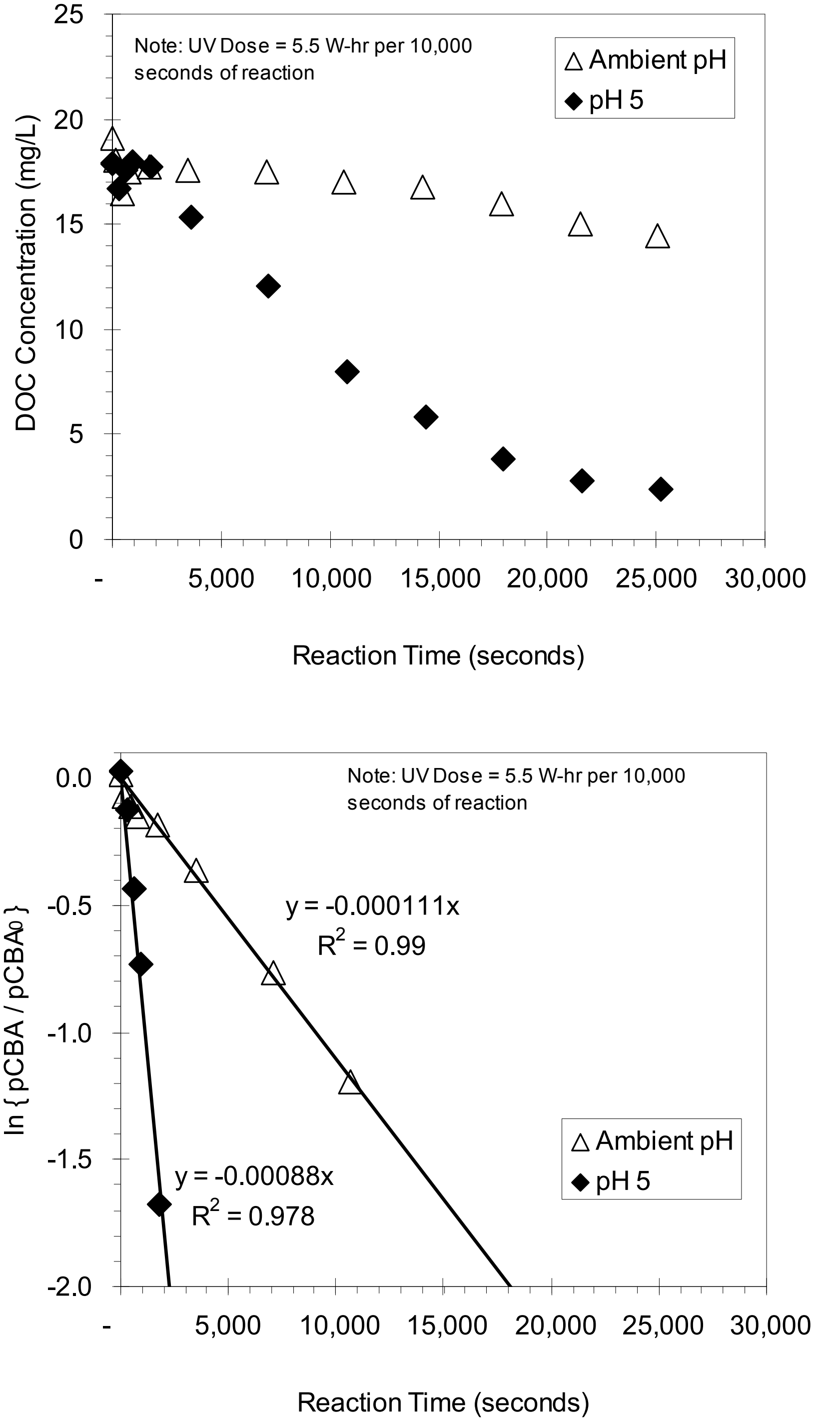


Figure 5.3. Change in DOC and *p*CBA over time during UV/TiO_2 treatment at two different pH levels (2 g of TiO_2/L).

Biodegradable oxidation products are formed after application of just a few watt-hours of UV irradiation. Therefore, a dual treatment was implemented. First, UV/TiO_2 treatment formed organic acids or other by-products. Then biodegradation removed these oxidation by-products.

Figure 5.5 illustrates the effect of this dual treatment. Samples were collected after different UV dosages and then subjected to biodegradation in BDOC reactors. The amount of BDOC material ranged from 2 to 12 mg/L. The greatest amount of BDOC was produced at a UV dose of 2 kWh/m^3. Increasing the UV dosage reduced the amount of BDOC material. Furthermore, at higher UV dosages, the percentage of DOC remaining that was biodegradable increased. At the highest UV dose applied (9.9 kWh/m^3) the DOC concentration was 8.1 mg/L but contained 6.1 mg of BDOC/L (namely, 75% of the DOC was biodegradable). After UV and BDOC treatment, the final DOC concentration was only 1.9 mg/L, representing a total DOC removal of 95%.

In designing a biological system to follow a UV/TiO_2 system, the kinetics of BDOC removal emerges as an important issue. Figure 5.6 illustrates the BDOC kinetics for 10 samples collected after different UV dosages. The largest amount of BDOC was produced at an intermediate UV dosage of 5.5 kWh/m^3, similar to the trend observed in Figure 5.5. However, the fastest removal (namely, rate of change in DOC/DOC_0 plot) occurred at higher UV dosages where a greater fraction of the DOC was present as carboxylic acids or other highly oxidized, easily degraded UV irradiation products. In most cases BDOC removal was nearly complete after 2 to 3 days. This contact time is specific to the BDOC reactor used in this study. In drinking water applications, $BDOC_5$ reactors mimic the DOC removal of full-scale biological filters with empty bed contact times of 4 to 8 min. Similar, small sand or activated carbon filters could be used on UV/TiO_2-treated RO concentrate as a means of removing BDOC.

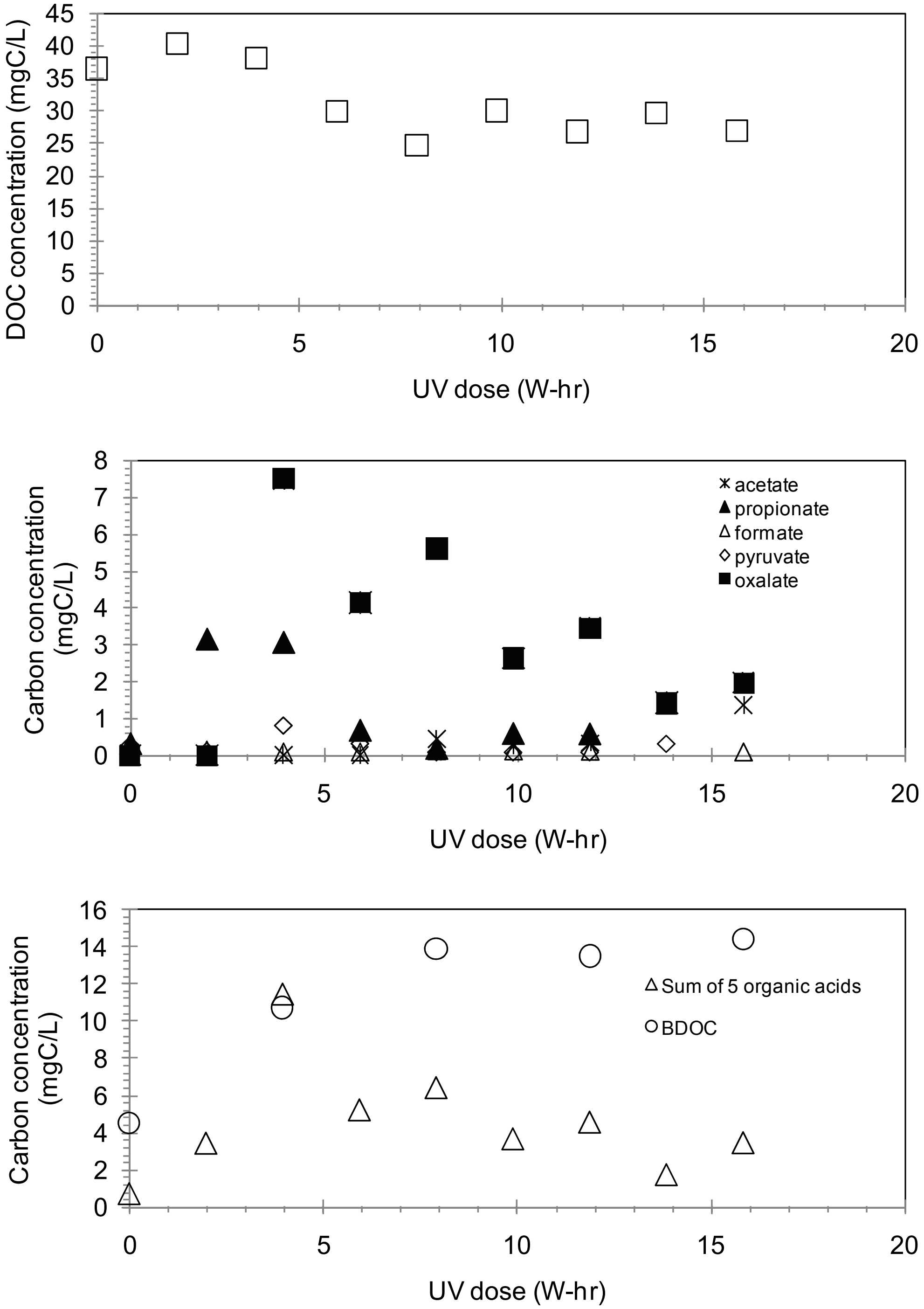
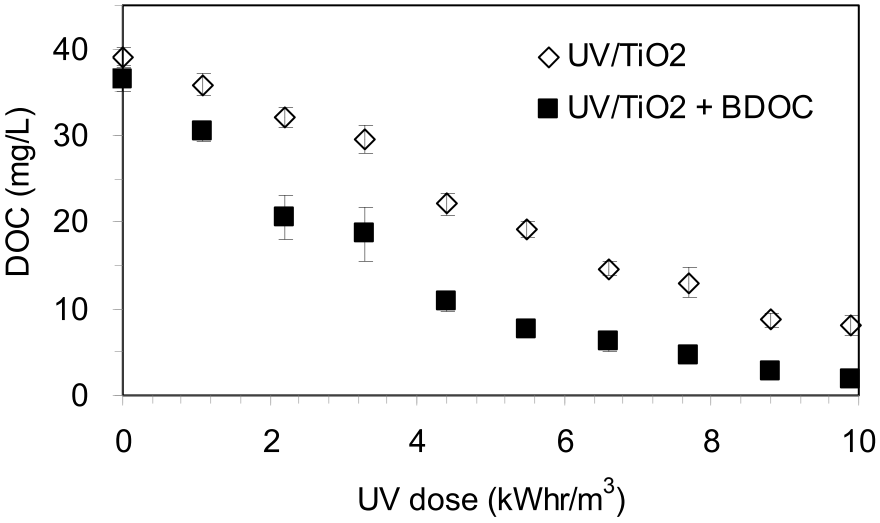


Figure 5.4. Loss of DOC and formation of organic acids and BDOC material from undiluted RO concentrate during UV/TiO_2 process with 4 g of TiO_2/L at pH = 5.



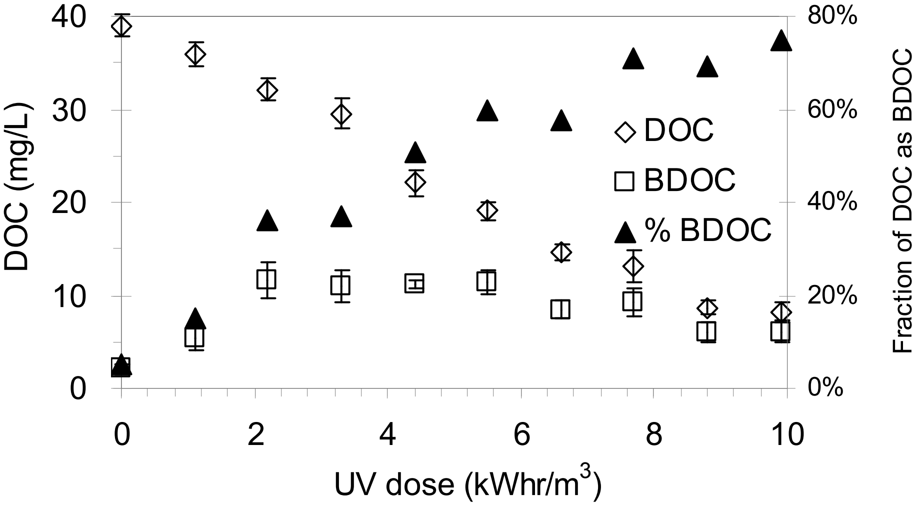


Figure 5.5. Effect of dual treatment (UV/TiO$_2$ followed by biodegradation in BDOC reactors) at pH = 5 with 2 g of TiO$_2$/L.

5.5 LARGER-SCALE UV/TiO_2 REACTOR WITH CERAMIC TiO_2 RECOVERY SYSTEM (PURIFICS Photo-Cat)

Initial experiments with the Photo-Cat system were conducted using a model organic compound (potassium hydrogen phthalate) at a DOC concentration of 25 mg/L because large volumes (20 to 35 L) were required, which would involve considerable water hauling from the Scottsdale RO facility. When potassium hydrogen phthalate was used, a zero-order DOC loss as a function of applied UV dosage (0.86 mg/W-h) was observed for TiO_2 dosages of 0.5 and 1 g/L at pH = 7. This rate was independent of TiO_2 dosage. The rate increased by nearly 5% when the pH was reduced to 5 from pH = 7. Therefore, further experiments were conducted with diluted RO concentrate at pH = 5 with 0.5 g of TiO_2/L.

Experiments with one-third RO concentrate (two-thirds nanopure water) at pH = 5 were conducted to evaluate the ability of the ceramic membrane filter to retain TiO_2 and DOC. DOC levels were measured in the water before and after the ceramic filter, and no significant difference was observed. Multiple samples collected at up to 70 kWh/m^3 exhibited a pseudo-zero-order DOC loss rate of 0.11 mg of DOC/L per kWh/m^3 of applied energy.

Organic carbon was oxidized in the Photo-Cat system (Figure 5.7). Higher UV doses resulted in greater DOC loss. Samples collected over time (variable UV doses) were also analyzed for BDOC content. A maximum BDOC content of 8 mg/L was observed at an applied UV dosage of 30 kWh/m^3. This BDOC represented ~70% of the DOC remaining after UV treatment. At the highest applied UV dose (75 kWh/m^3), the DOC concentration after UV treatment was 8 mg/L and contained 6 mg of BDOC/L. Therefore, after combined UV treatment and biodegradation, the final DOC concentration was 2 mg/L, representing a 91% removal of DOC.

A direct comparison of the Photo-Cat system and lab UV system is complicated because of how the UV dosages were computed. Actinometry was conducted on the lab UV system, whereas in the Photo-Cat system the sum of the outputs from each 75-W lamp, assuming 30% lamp efficiency, was used as the applied UV dosage. Figure 5.8 compares the DOC removed during UV treatment alone and in conjunction with BDOC reactors for the two systems. Both systems remove DOC, although the results are not perfectly scalable unless further equalization of the UV dosages is undertaken. Actinometry of the Photo-Cat system was not undertaken because of resource constraints but would be necessary for future research. However, at any given DOC concentration, after UV treatment the fraction of the DOC remaining that is biologically degradable is nearly equivalent for the lab UV and Photo-Cat systems.

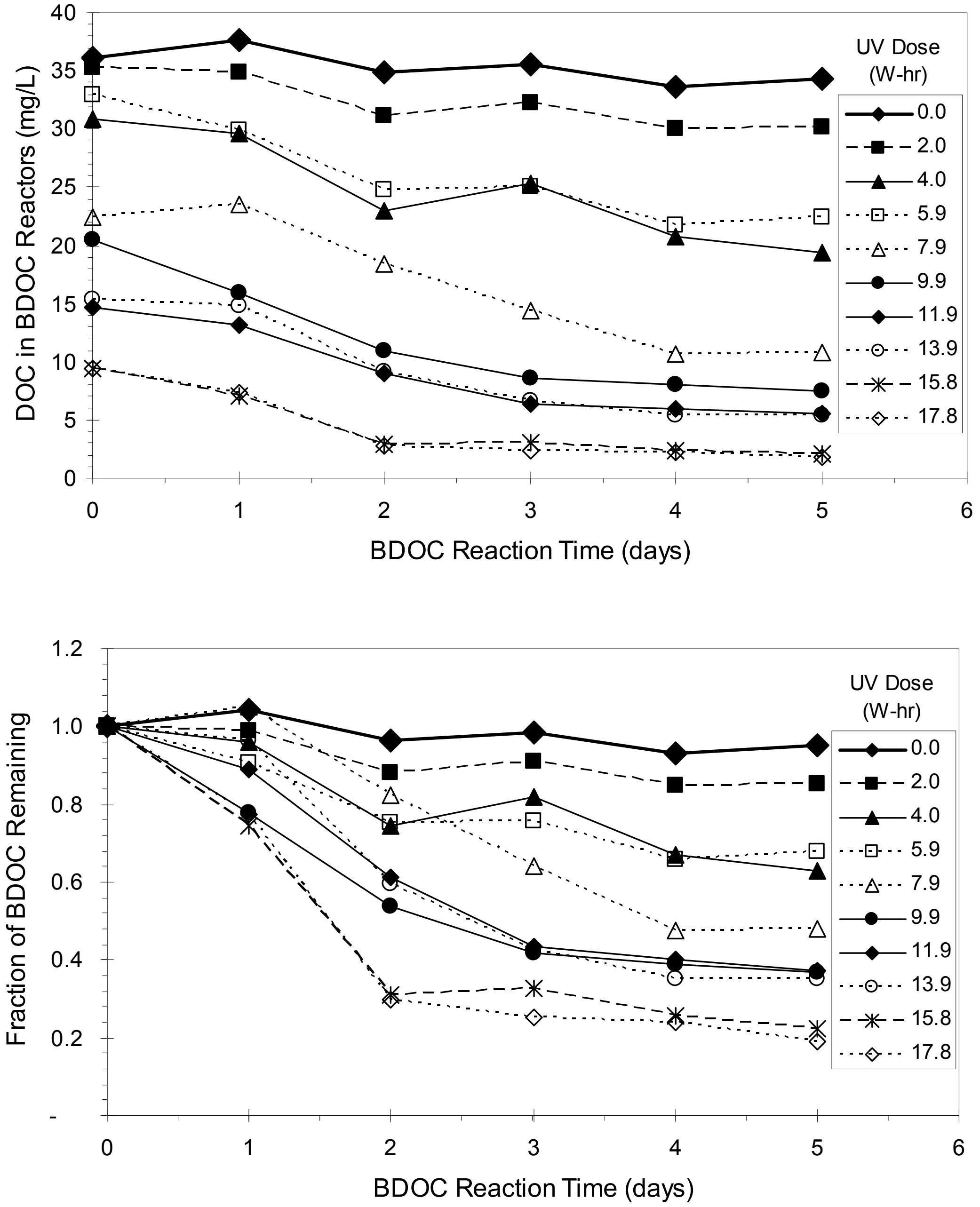


Figure 5.6. BDOC kinetics for 10 samples irradiated with increasingly longer UV dosages at pH = 5 and with 2 g of TiO_2/L. The top plot shows the kinetics of DOC removal for BDOC reactors starting with different initial DOC values induced by different amounts of energy input into the UV/TiO_2 system. The bottom plot normalizes the kinetics of DOC removal to the initial DOC concentration.

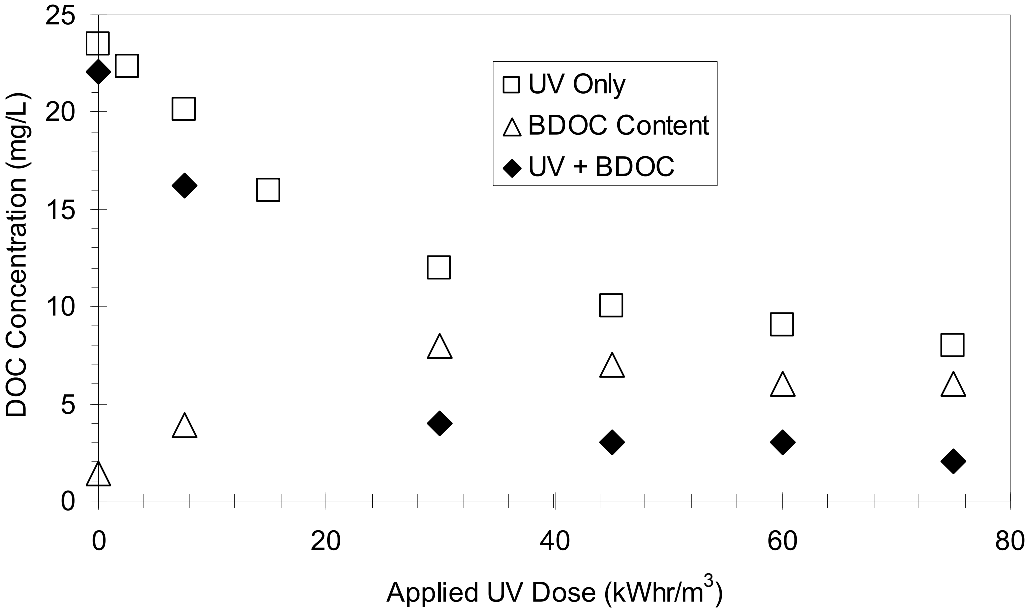


Figure 5.7. Loss of DOC in Photo-Cat system alone and with subsequent biodegradation in BDOC reactors (pH = 5, 0.5 g of TiO_2/L).

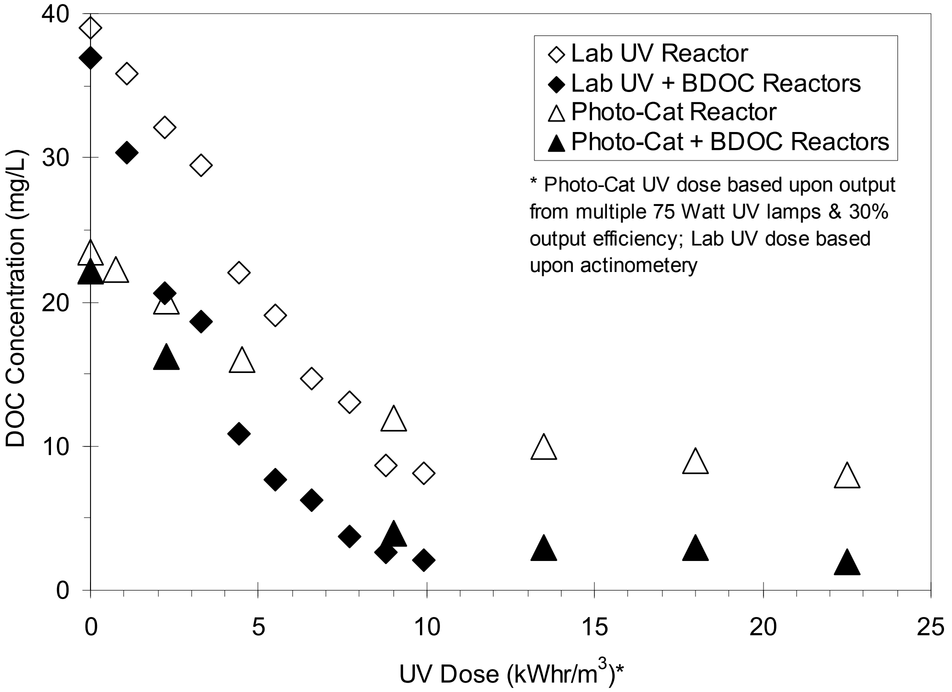


Figure 5.8. Comparison of DOC removal by UV alone (lab UV and Photo-Cat) and of that by a combination of UV treatment and BDOC reactors.

3

5.6 REMOVAL OF PHARMACEUTICAL COMPOUNDS IN RO RETENTATE BY UV/TiO_2

Before and after treatment by the Photo-Cat system, samples were collected for LC/MS/MS analysis (API 4000 instrument, solid-phase extraction) for several pharmaceuticals (Table 5.1). Because of a change in personnel, the precise time (namely, UV dose) when the samples were collected is not available. The times are believed to be after 5 and 50 kWh/m^3. UV/TiO_2 treatment removes nearly all of the tested pharmaceuticals to below detection limits (1 ng/L).

Table 5.1. Summary of Pharmaceuticals Present in 50% Diluted RO Concentrate before (Duplicate Influent Samples) and after (Duplicate Treated Samples) UV/TiO_2 Treatment using the Photo-Cat System

	Concn (ng/L)			
Compound	**Influent No. 1**	**Influent No. 2**	**Treated No. 1**	**Treated No. 2**
Ibuprofen	2	0	0	0
Naproxen	5	5	0	0
Dilantin	89	93	0	0
Triclosan	7	7	0	0
Diclofenac	1	1	0	0
Caffeine	6	5	0	0
Carbamazepine	383	470	0	0
Cotinine	4	60	0	0
Diazepam	6	7	0	0
Fluoxetine	11	18	0	5
Hydrocodone	3	4	0	0
Meprobamate	700	620	1	1
Oxybenzone	5	5	2	0
Sulfamethoxazole	23	16	0	0
DEET	272	310	0	0
Trimethoprim	36	23	0	0
Diuron	3	3	0	0
Atrazine	2	2	0	0

5.7 MODELING DOC LOSS DURING UV/TiO_2 OXIDATION IN LAB REACTORS

5.7.1 Comparison of DOC Loss Rates

Several experiments are plotted together in Figure 5.9 and fit by pseudo-zero-order relationships. The slopes of these are the zero-order rate constants (*k*, [mg/L]/s). The average *k* value at pH = 5 (0.00093 [mg/L]/s) is nearly four times greater than the average at ambient pH = 7 (0.00024 [mg/L]/s). Values for *k* tend to increase with TiO_2 dosages of 5 g/L relative to 2 g/L, but dependence upon initial DOC concentration is minimal. These rates will be used in the subsequent modeling section. Zero-order reactions have previously been observed for the loss of DOC during UV/TiO_2 treatment (Hand et al., 1995).

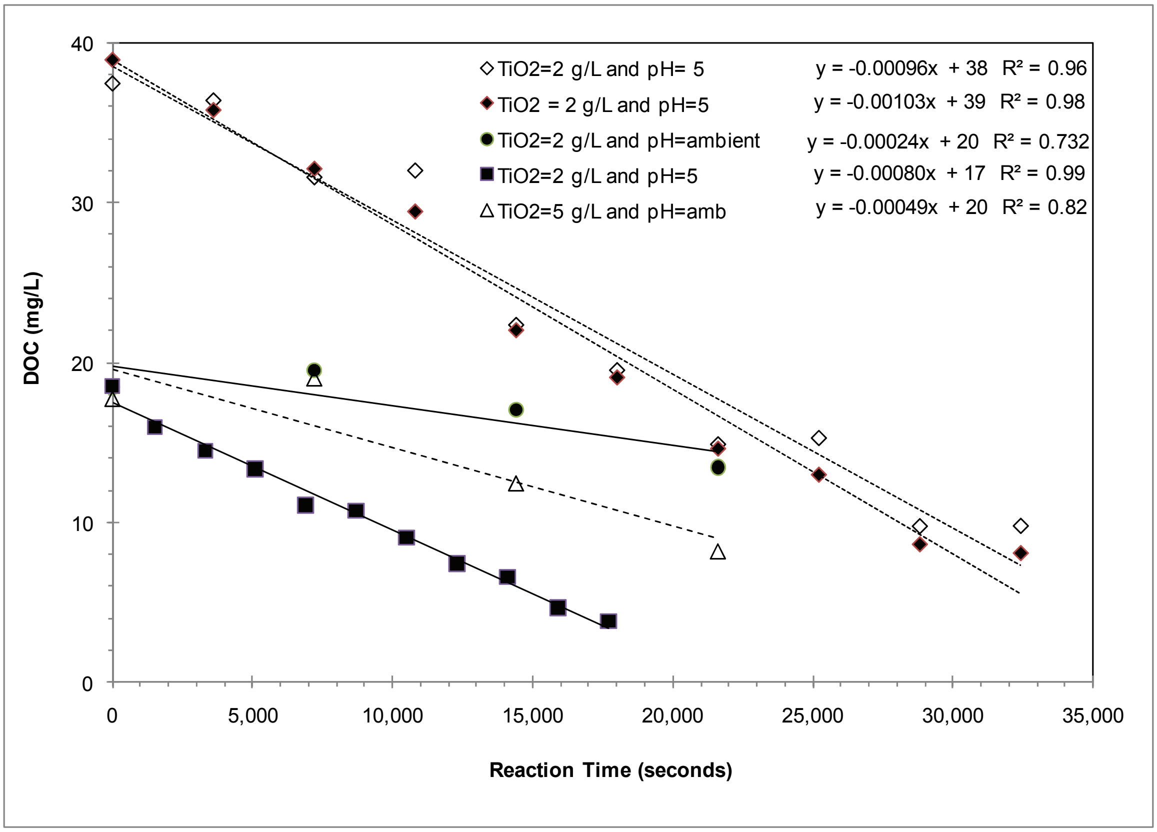


Figure 5.9. Summary of UV/TiO_2 experiments with RO concentrate from the lab UV reactor fitted with pseudo-zero-order rate laws.

5.7.2 Kinetic Modeling

A series of equations were developed to represent the observed trends in DOC loss and the transient formation of organic acids under steady-state $HO^{\bullet}$ concentrations, as observed in *p*CBA experiments. All species in the models were accounted for on a mole-of-carbon basis. Reactions are balanced for carbon only; no attempt to account for noncarbon species was undertaken. Steady-state $HO^{\bullet}$ concentrations were used, and the stoichiometry for the number of $HO^{\bullet}$ molecules required to oxidize the organics was not specifically considered. The following reactions were considered:

$$DOM + HO^{\bullet} \xrightarrow{4x10^{8}\,M^{-1}s^{-1}} 0.9[DOM\_oxid] + 0.1[Oxalate]$$

$$[DOM\_oxid] + HO^{\bullet} \xrightarrow{4x10^{8}\,M^{-1}s^{-1}} 0.1[Acetate] + 0.2[\mathrm{Pr}\,opionate] + 0.7[CO_2]$$

$$[Oxalate] + HO^{\bullet} \xrightarrow{3.85x10^{6}\,M^{-1}s^{-1}} [CO_2]$$

$$[Acetate] + HO^{\bullet} \xrightarrow{3.67x10^{7}\,M^{-1}s^{-1}} [CO_2]$$

$$[\mathrm{Pr}\,opionate] + HO^{\bullet} \xrightarrow{4x10^{8}\,M^{-1}s^{-1}} [CO_2]$$

In the above equations, dissolved organic matter (DOM) present in RO concentrate reacts with $HO^{\bullet}$ such that 90% of its carbon is incorporated into an unknown oxidized form of DOM (DOM_oxid) and 10% into oxalate. This distribution was selected to approximate the observed formation of oxalate in laboratory experiments. The unknown oxidized form of DOM (DOM_oxid) reacts further with $HO^{\bullet}$ to produce a distribution of products. The values of 10% acetate and 20% propionate are again based upon experimental observations, and the remaining 70% eventually produces carbon dioxide by non-rate-limiting reactions. Direct reactions between the three organic acids and $HO^{\bullet}$ were assumed to be the rate-limiting step in the production of carbon dioxide or other volatile species. The rate constants annotated with each reaction are from the literature for oxalate, acetate, and propionate (expressed on a mole-of-carbon basis). The second-order rate constant between DOM and $HO^{\bullet}$ is based on research conducted with organic matter isolates from wastewaters as part of this project. Details of the pulse radiolysis research are presented elsewhere (Westerhoff et al., 2007). Table 5.2 summarizes the relevant rate constants obtained from that work.

Table 5.2. 2nd-Order Rate Constants for $^{\bullet}OH$ Reaction with DOM Isolates

DOM Isolate Description	$k_{^{\bullet}OH,\,DOM}$ **($10^{8}\,M^{-1}s^{-1}$)**
Suwannee River Fulvic Acid	1.39 ± 0.16
Suwannee River Fulvic Acid	1.87 ± 0.07
Suwannee River Fulvic Acid	1.55 ± 0.04
Saguaro Lake Hydrophobic Acid	1.73 ± 0.04
Saguaro Lake Transphilic Acid	1.45 ± 0.02
Saguaro Lake Hydrophobic Neutral	2.18 ± 0.13
Nogales WWTP Hydrophobic Neutral	1.72 ± 0.13
Nogales WWTP Transphilic Neutral	4.53 ± 0.54
Nogales WWTP Transphilic Acid	3.63 ± 0.31

Figures 5.10 and 5.11 illustrate the modeling results, which were obtained using a computer package from EAWAG (AquaSim). DOC represents the sum of the residual RO concentrate DOM, unknown oxidized forms of DOM (DOM_oxid), and the organic acids. A pseudo-zero-order rate of DOC loss in Figure 5.10 of 7.92 × 10^{-8} mol of C/L-s (0.00095 [(mg of C/L)/s]) was obtained, which closely matches similar rates summarized in Figure 5.9 that use an $[HO^{\bullet}]_{SS}$ of 3.8 × 10^{-13} M. This $[HO^{\bullet}]_{SS}$ is only slightly higher than the value of 1.8 × 10^{-13} M obtained from the *p*CBA experiments (Figure 5.3). The model simulates the transient intermediate oxidized organic carbon forms and the production of carbon dioxide. The results correspond well with the BDOC findings, which suggest that a significant fraction of the DOC in solution is biodegradable at higher UV doses (namely, exposure times) (Figure 5.5). Therefore, the model appears to be a useful tool for beginning to understand the disposition of carbon in RO concentrate. Much more model development would need to occur to validate the model. Once validated, however, the modeling equations could be integrated with other reactions (for example, bromate formation reactions).

5.8 ECONOMIC BENEFITS OF UV/TiO_2 AND BIODEGRADATION

In an attempt to better define the potential treatment costs, Figure 5.12 predicts the costs of the energy inputs needed to meet specific final DOC treatment goals for the example of RO concentrate (40 mg/L) treated at pH = 5 by UV/TiO_2. The costs for the ceramic membrane or acid addition, which are minor, are not included. Only the electrical energy cost for the UV system was considered because this factor was the primary energy requirement. The added benefit of biodegradation is evident in the bottom plot. For example, if the target final DOC concentration is 10 mg/L, the energy required to operate a UV/TiO_2 system would be on the order of $6/1000 gal. However, if a lower UV dose is applied to the RO concentrate and then it is biologically treated (namely, using a medium filter), the cost to achieve a 10-mg/L final DOC concentration would decrease by 30% to roughly $4/1000 gal. This economic analysis has numerous inherent assumptions, but its creators attempt to illustrate the relative cost of this treatment and the benefit of incorporating biodegradation after UV/TiO_2 treatment.

5.9 SUMMARY

This chapter presents data showing that greater than 95% removal of the DOC in RO concentrate is possible through treatment by UV/TiO_2 followed by biodegradation. Key findings include:

- UV/TiO_2 treatment removes nearly all of several pharmaceuticals from the RO concentrate to below detection limits (1 ng/L).
- UV/TiO_2 treatment alone can achieve in excess of 90% DOC removal. Thus, the treatment meets our project goals. The rate of DOC removal is nearly zero-order (1.9 mg of DOC/L per kWh/m^3 or 0.53 kWh-m^{-3}-[mg of DOC/L]$^{-1}$) up to 80% to 85% DOC removal. If one seeks to achieve higher DOC removals, the rate is also zero order, but considerably more energy is required (0.67 kWh-m^{-3}-[mg of DOC/L]$^{-1}$) to continue oxidation of by-products that react slowly with hydroxyl radicals.
- No strong dependence on initial DOC concentration was observed for the zero-order rate loss of DOC. However, pH had a significant effect. A higher steady-state hydroxyl radical concentration ($[HO^{\bullet}]_{SS}$) was achieved at pH = 5 than at pH = 7 (the ambient pH of the RO concentrate) because of less scavenging by bicarbonate ion at the reduced pH level. $[HO^{\bullet}]_{SS}$ was assessed using a hydroxyl radical probe (*p*CBA) spiked into the RO concentrate. Values for $[HO^{\bullet}]_{SS}$ were on the order of 0.2 × 10^{-13} to 2 × 10^{-13} M in the lab UV reactors at pH = 7 and 5, respectively.

- In the lab UV system, UV/TiO_2 treatment produced BDOC. Without UV/TiO_2 treatment, less than 5% of the DOC in the RO concentrate was biodegradable. After UV/TiO_2 treatment, specific organic acids (oxalate, acetate, propionate, pyruvate, and formate) were present at concentrations from 100 to nearly 5000 mg of C/L. Other biodegradable materials also must have formed because the BDOC content of samples after UV/TiO_2 treatment was always greater than the sum of the five measured organic acids. After addition of higher energy inputs during the UV/TiO_2 treatment, the biodegradable fraction of the residual DOC increased to nearly 80% (after a dose of 18 kWh-m^{-3}) and to 50% (after a dose of 9 kWh-m^{-3}).
- The performance of the lab UV system (1.8 L) and that of a larger-scale recirculating UV/TiO_2/ceramic membrane system (30-L Photo-Cat system) were similar but clearly confirmed the order-of-magnitude energy inputs required to achieve DOC removal from RO concentrate. Both systems confirmed the production of significant amounts of BDOC material at dosages on the order of 5 to 15 kWh-m^{-3}.
- A preliminary economic analysis puts the energy cost for UV/TiO_2 treatment in the range of \$1 to \$8 per 1000 gal, depending on the target final DOC concentration and if biodegradation (medium filtration) is incorporated. For example, if the target final DOC concentration is 10 mg/L, the energy required to operate a UV/TiO_2 system would be on the order of \$6/1000 gal. However, if a lower UV dose is applied and if then the RO concentrate is biologically treated (namely, using a medium filter), the cost to achieve a 10-mg/L final DOC concentration would decrease by 30% to roughly \$4/1000 gal.
- Figure 5.13 presents a schematic of the sequence of processes that could be combined to treat organics in RO concentrates.

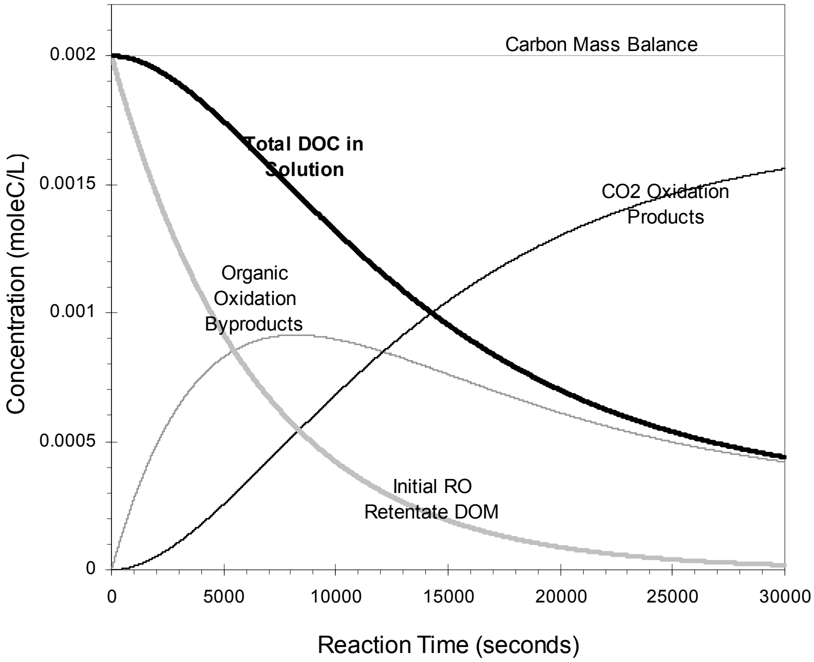


Figure 5.10. Simulation of changes in concentrations of carbon products during UV/TiO$_2$ treatment under steady-state HO$^\bullet$ conditions.

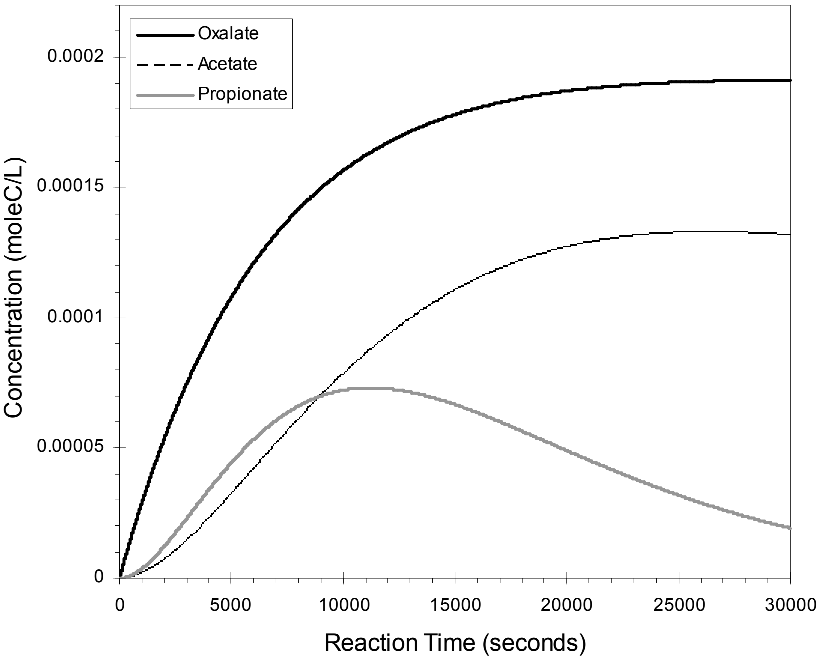


Figure 5.11. Simulation of changes in organic acid concentrations during UV/TiO$_2$ treatment under steady-state HO$^\bullet$ conditions.

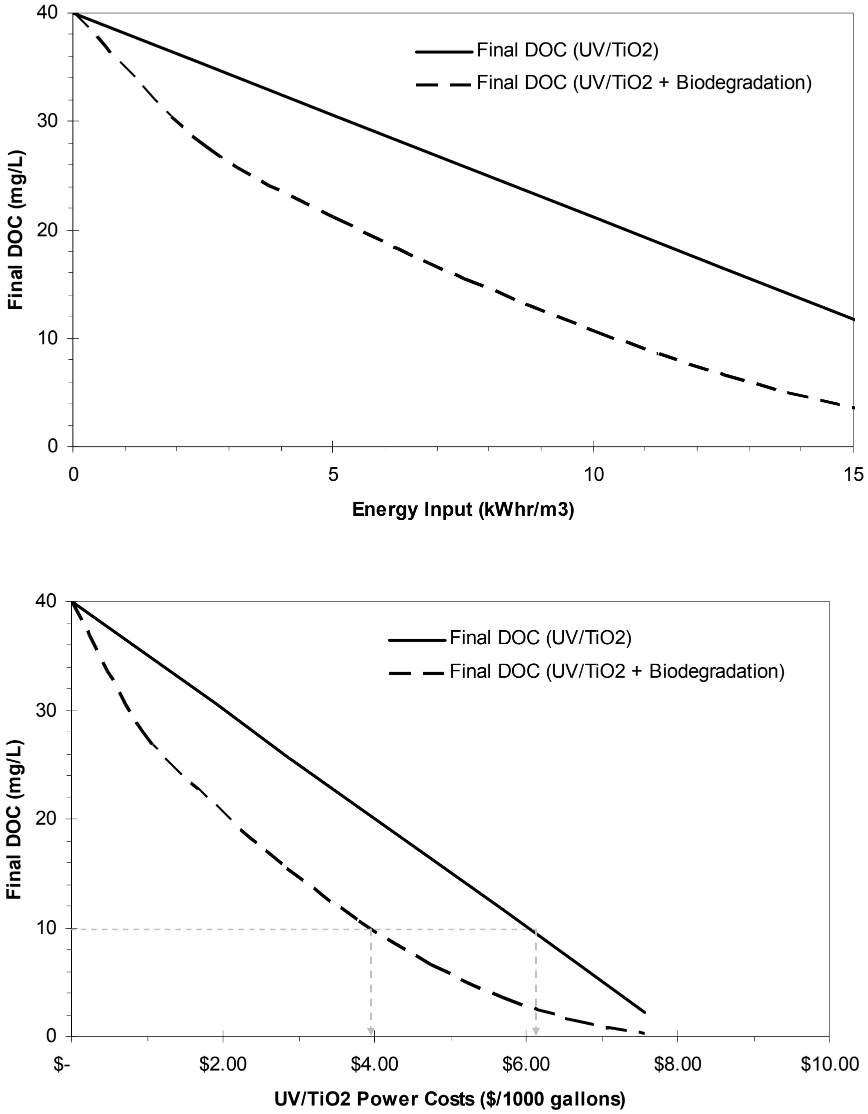


Figure 5.12. Economic evaluation of a UV/TiO_2 system (pH = 5), with and without biodegradation, that achieves specific final DOC concentrations (calculated using $0.10/kWh). Only the energy needed for the UV system was considered.

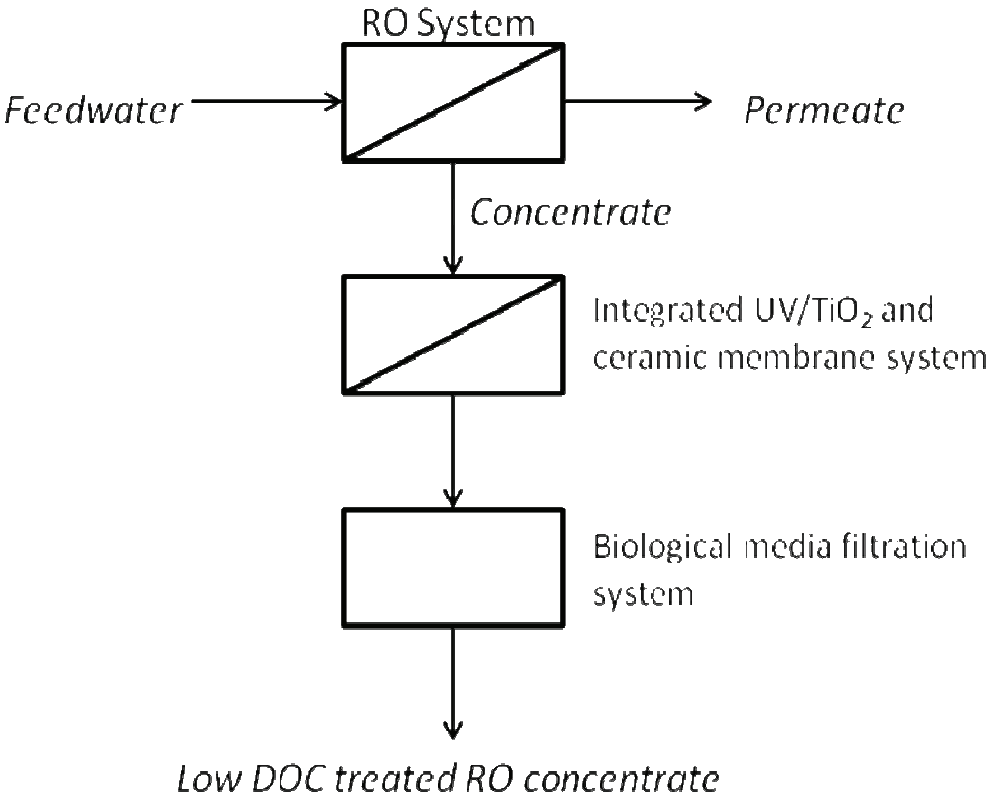


Figure 5.13. Schematic of potential treatment system for managing removal of organics from RO concentrate.

CHAPTER 6

SUMMARY AND RECOMMENDATIONS FOR UTILITIES AND FUTURE RESEARCHERS

6.1 SUMMARY AND CONCLUSIONS

Several technologies capable of oxidizing organics were evaluated: 1) Fenton and Fenton-like reactions with and without subsequent iron coagulation; 2) ozone with and without hydrogen peroxide; 3) UV irradiation alone, with hydrogen peroxide, or with titanium dioxide; and 4) wet chemical oxidation. Most of the research was conducted with RO concentrate from partially denitrified wastewater at the City of Scottsdale Water Campus. Oxidation experiments were conducted using bench-scale units. Processes that produced hydroxyl radicals were capable of oxidizing DOC, facilitating its removal as purgeable gases, and producing biodegradable organics. UV/TiO_2 was selected as a sequential AOP-biodegradation process because of its lack of chemical reagents that could affect biological processes. UV treatment did not leave a residual, and titanium dioxide was easily separated using membranes. To achieve the 90% DOC removal goal for this project, incorporation of biodegradation roughly halved the energy dose requirements. Thus the project objective was achieved. Additional key summary points are given below.

6.1.1 Summary of Experiments Used to Screen Effectiveness for DOC Removal from Wastewater RO Concentrate

- Iron coagulation removed less than 5% of the DOC in RO concentrate.
- Applying the Fenton reaction at pH = 3 to 3.5 (10 mM Fe^{2+} and 10 mM H_2O_2) rapidly removed ~50% of the DOC in the RO concentrate. Raising the pH to 7.5 to 8.0 and allowing ferric iron to precipitate removed residual iron. Higher ferrous iron and hydrogen peroxide dosages might have yielded greater DOC removals.
- Ozonation (with hydrogen peroxide) of RO concentrate formed a white precipitate, probably calcite, because of a slight pH change and possibly the cleavage of calcium-organic complexes or other microflocculation processes.
- Ozone addition using a 0.7-mol-of-H_2O_2/mol-of-O_3 dose oxidized and removed DOC. Ozone dosages of more than 1000 mg/L are necessary to remove approximately 75% of the DOC in RO concentrate. Up to this level of removal, DOC removal was nearly linear as a function of ozone dose. DOC removal was independent of the time when H_2O_2 was applied.
- UV/H_2O_2 achieved 40% DOC removal at pH = 4, a UV dose of 11.8 kWh/m^3, and an H_2O_2 dose of 10 mM. At pH = 7 and 10, UV/H_2O_2 achieved less than 10% DOC removal.
- UV/TiO_2 achieved up to 95% DOC removal at a UV radiation dose of 10.4 kWh/m^3 and was nearly independent of titanium dioxide doses between 1 and 5 g/L.
- Addition of hydrogen peroxide during UV/TiO_2 application did not significantly improve DOC removal.
- In all cases the UVA percentage removal was greater than the DOC percentage removal, indicating preferential oxidation of carbon-carbon double bonds by all oxidation processes.

The ozone process had problems with residual dissolved ozone and precipitates. Anyone using a hydrogen peroxide process would have needed to address residual hydrogen peroxide, which was considerable (10 to > 100 mg/L) in these experiments. Because UV/TiO_2 was the easiest process to repeatedly conduct in the laboratory and achieved the highest DOC removal and best EE/O, it was selected for optimization in the next phase of the research.

6.1.2 Summary of Pulse Radiolysis Experiments Conducted to Estimate Reaction Rate Constants between the Hydroxyl Radical and Wastewater Organics

Research was conducted with other WateReuse-funded collaborators by using the Department of Energy facilities at the University of Notre Dame Radiation Laboratory. The research was published in *Environmental Science and Technology* and is not reported here in detail because it was not part of the initial research plan (Westerhoff et al., 2007). However, the research became extremely useful in the development of predictive models for the removal of organics in RO concentrate during AOP treatment.

Pulse radiolysis experiments were conducted on hydrophobic and hydrophilic acids and neutrals isolated from DOM samples from different sources (namely, stream, lake, and WWTP). Absolute bimolecular reaction rate constants for the reaction of hydroxyl radicals ($^\bullet OH$) with DOM ($k_{^\bullet OH, DOM}$) were determined. $k_{^\bullet OH, DOM}$ values are expressed as moles of carbon. Based on the direct measurement of transient DOM radicals ($DOM^\bullet$) and competition kinetic techniques, both of which used pulse radiolysis, the $k_{^\bullet OH, DOM}$ value for a standard fulvic acid from the Suwannee River purchased from the International Humic Substances Society was $(1.60 \pm 0.24) \times 10^8\ M^{-1}s^{-1}$. Both pulse radiolysis methods yielded comparable $k_{^\bullet OH, DOM}$ values. The $k_{^\bullet OH, DOM}$ values for the seven DOM isolates from different sources ranged from $1.39 \times 10^8\ M^{-1}s^{-1}$ to $4.53 \times 10^8\ M^{-1}s^{-1}$ and averaged $2.23 \times 10^8\ M^{-1}s^{-1}$ (equivalent to 1.9×10^4 $[\text{mg of C/L}]^{-1}s^{-1}$). More polar, lower-molecular-weight DOM isolates from wastewater have higher $k_{^\bullet OH, DOM}$ values.

6.1.3 Summary of Experimental Results to Optimize UV/TiO_2 Treatment plus Biodegradation for DOC Removal from Wastewater RO Concentrate

- UV/TiO_2 treatment removes from RO concentrate nearly all of several pharmaceuticals to below detection limits (1 ng/L).
- UV/TiO_2 treatment alone can achieve in excess of 90% DOC removal. Thus, the treatment meets our project goals. The rate of DOC removal is nearly zero order (1.9 mg of DOC/L per kWh/m^3 or 0.53 kWh-m^{-3}-$[\text{mg of DOC/L}]^{-1}$) up to 80% to 85% DOC removal. To achieve higher DOC removals, the rate is also zero order, but considerably more energy is required (0.67 kWh-m^{-3}-$[\text{mg of DOC/L}]^{-1}$) to continue the oxidation of by-products that react slowly with hydroxyl radicals.
- No strong dependence on initial DOC concentration was observed for the zero-order rate loss of DOC. However, pH had a significant effect. A higher steady-state hydroxyl radical concentration ($[HO^\bullet]_{SS}$) was achieved at pH = 5 than at pH = 7 (the ambient pH of the RO concentrate) because of less scavenging by bicarbonate ion at the reduced pH level. $[HO^\bullet]_{SS}$ were assessed using a hydroxyl radical probe (*p*CBA) spiked into RO concentrate. Values for $[HO^\bullet]_{SS}$ were on the order of 0.2×10^{-13} M to 2×10^{-13} M in the lab UV reactors at pH = 7 and 5, respectively.
- In the lab UV system, UV/TiO_2 treatment produced BDOC. Without UV/TiO_2 treatment, less than 5% of the DOC in the RO concentrate was biodegradable. After UV/TiO_2 treatment, specific organic acids (oxalate, acetate, propionate, pyruvate, and formate) were present at concentrations from 100 to nearly 5000 mg of C/L. Other biodegradable

materials also formed because the BDOC content of the samples after UV/TiO_2 treatment was always greater than the sum of the five measured organic acids. When one used higher energy inputs in the UV/TiO_2 treatment, the biodegradable fraction of the residual DOC increased to nearly 80% after a dose of 18 kWh-m^{-3} and to 50% after a dose of 9 kWh-m^{-3}.

- The performance of the lab UV system (1.8 L) and that of the larger-scale recirculating UV/TiO_2/ceramic membrane system (30-L Photo-Cat system) were similar but clearly confirmed the order-of-magnitude energy inputs required to remove DOC from RO concentrate. Both systems confirmed the production of significant amounts of BDOC material at UV dosages on the order of 5 to 15 kWh-m^{-3}.
- A preliminary economic analysis puts the energy cost for UV/TiO_2 treatment in the range of $1 to $8 per 1000 gal at pH = 5, depending upon the target final DOC concentration and if biodegradation (medium filtration) is incorporated. Only the energy input for the UV system was considered because the energy used by the ceramic membrane system for TiO_2 recovery was assumed to be much lower than the UV system energy demand. Costs would increase if the system was operated at higher pH because of hydroxyl radical scavenging by carbonate and bicarbonate species.

6.2 RECOMMENDATIONS FOR UTILITIES

RO and other high-solute-rejection membrane systems used for advanced treatment of wastewater produce concentrated waste streams containing salts, trace organics, and bulk, less characterizable organics. Discharge of these waste streams into the environment represents a point source of potential pollution. This research addresses the ability of oxidation and biological processes to significantly reduce the amount of organics present in RO concentrate before its discharge into the environment. Treatment of organics in RO concentrate is probably a wise decision because it is cost-effective to treat smaller volumes (namely, lower flowrates) of concentrated organics. Although regulations do not yet exist for many organics in RO concentrates from WWTPs, they may in the future. It may also be advantageous from a broader ecosystem perspective to treat refractory organics in RO concentrate before their release into surface waters, oceans, or even downstream regional WWTPs.

The UV/TiO_2 system removed both bulk and trace organics in RO concentrate. The AOP decreased levels of PPCPs present in RO concentrate to less than 1 ng/L, while bulk DOC decreased from 40 mg/L to <10 mg/L. Experiments also demonstrated that the UV/TiO_2 system removed organics present in RO membrane cleaning solutions. However, these cleaning solutions have high organic carbon concentrations due to the surfactants they contain, so the UV dose required to achieve >90% DOC removal for these solutions is extremely high compared to that of the DOC in RO concentrate.

This study demonstrated an integrated UV/TiO_2 system with a built-in ceramic membrane system (Photo-Cat; Purifics, Inc.) that can oxidize a significant fraction of the DOC in RO concentrate to purgeable gases and biologically degradable organic material. Following this integrated system with a biological filter (sand, anthracite, and activated carbon) would reduce the electrical energy input for the UV system while achieving a high level (>90%) of DOC removal.

All AOPs will be more effective at lower pH levels because of hydroxyl radical scavenging by bicarbonate and carbonate species. The pH of the RO concentrate used in our study was approximately 7.0 (alkalinity = 1100 mg/L as $CaCO_3$). UV/TiO_2 treatment was significantly more effective at pH = 5 than at pH = 7 because of the reduced hydroxyl radical scavenging by bicarbonate. It may be possible to better optimize the low-pH conditions required to prevent scale formation during RO treatment and those required to reduce $HO^\bullet$ scavenging during AOP treatment.

6.3 RECOMMENDATIONS FOR FUTURE RESEARCH

This research should initiate further efforts to reduce organics in RO concentrates before they are discharged to the environment or other wastewater treatment facilities. Potential future research efforts include:

- If salt rejection is not a primary objective for wastewater reuse, treatment by AOPs alone (without membranes) could become a viable approach for controlling organics. A comparison between integrated UV/TiO_2 systems (with ceramic membranes for TiO_2 separation) and tight membrane systems (RO and NF) is worthwhile to evaluate which system achieves overall reuse treatment goals at the lowest treatment costs. Ceramic membranes are effective at removing a wide variety of oocysts and bacteria, while UV disinfection effectively inactivates many viruses.
- Continuous-flow UV/TiO_2 treatment (pilot-scale) systems followed by simple biological filters (activated carbon) should be evaluated for treatment of RO concentrate prior to discharge to the environment.
- The cost effectiveness of removing 10%, 25%, 50%, 75%, 90%, etc. of the DOC in RO concentrate should be determined. However, it is also important to pair the cost for this DOC removal with the incremental benefits in the reduction of toxicity or other ecological endpoints.
- The ability of UV/TiO_2 systems to reduce toxicity, rather than just the amounts of DOC and specific compounds, should be investigated. A relationship between DOC removal and toxicity reduction would serve as useful guidance for utilities attempting to set target DOC levels for discharge of RO concentrates.
- The long-term usage of TiO_2 on membrane concentrates has not been evaluated but should be in the near future. Issues that should be addressed include 1) long-term viability of TiO_2 structural (namely, friability) and oxidative properties, 2) accumulation of metals on TiO_2, and 3) disposal requirements for spent TiO_2.

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APPENDIX

ESTIMATION OF UV IRRADIANCE DOSAGES

Below is an energy output relationship for the lamp used in the bench-scale UV irradiation experiments (from the manufacturer) and calculations converting the total energy output to units of W/L. Actinometry experiments were used to determine the total incident light irradiance. Calculation of total energy (kWh/m^3) input into the reactors involved multiplying 1.1 W/L by the reactor volume (1.8 L) and irradiation time (hours), with appropriate unit conversions of 1000 W per kW and 1000 L per m^3.

UV irradiation intenstiy h 6.62E-34 N 6.02E+23
c 3.00E+08

Wavelength	angstroms = 0.1nm	nm=10^{-9}m	Radiated energy		photon energy, E			einstein/s
angstroms	nm	m	w	%	(J)	photons/sec	%	mole photon/sec
13673	1367.3	1.37E-06	2.6	1.5	1.45E-19	1.79E+19	4.4	2.97E-05
11287	1128.7	1.13E-06	3.3	1.9	1.76E-19	1.88E+19	4.6	3.12E-05
10140	1014.0	1.01E-06	10.5	6.0	1.96E-19	5.36E+19	13.0	8.91E-05
5780	578.0	5.78E-07	20.0	11.4	3.44E-19	5.82E+19	14.2	9.67E-05
5461	546.1	5.46E-07	24.5	13.9	3.64E-19	6.74E+19	16.4	1.12E-04
4358	435.8	4.36E-07	20.2	11.5	4.56E-19	4.43E+19	10.8	7.36E-05
4045	404.5	4.05E-07	11.0	6.3	4.91E-19	2.24E+19	5.4	3.72E-05
3660	**366.0**	3.66E-07	25.6	14.6	5.43E-19	4.72E+19	11.5	7.84E-05
3341	**334.1**	3.34E-07	2.4	1.4	5.94E-19	4.04E+18	1.0	6.71E-06
3130	**313.0**	3.13E-07	13.2	7.5	6.35E-19	2.08E+19	5.1	3.46E-05
3025	**302.5**	3.03E-07	7.2	4.1	6.57E-19	1.10E+19	2.7	1.82E-05
2967	**296.7**	2.97E-07	4.3	2.4	6.69E-19	6.42E+18	1.6	1.07E-05
2894	**289.4**	2.89E-07	1.6	0.9	6.86E-19	2.33E+18	0.6	3.87E-06
2804	**280.4**	2.80E-07	2.4	1.4	7.08E-19	3.39E+18	0.8	5.63E-06
2753	**275.3**	2.75E-07	0.7	0.4	7.21E-19	9.70E+17	0.2	1.61E-06
2700	**270.0**	2.70E-07	1.0	0.6	7.36E-19	1.36E+18	0.3	2.26E-06
2652	**265.2**	2.65E-07	4.0	2.3	7.49E-19	5.34E+18	1.3	8.87E-06
2571	**257.1**	2.57E-07	1.5	0.9	7.72E-19	1.94E+18	0.5	3.23E-06
2537	**253.7**	2.54E-07	5.8	3.3	7.83E-19	7.41E+18	1.8	1.23E-05
2482	**248.2**	2.48E-07	2.3	1.3	8.00E-19	2.87E+18	0.7	4.77E-06
2400	**240.0**	2.40E-07	1.9	1.1	8.28E-19	2.30E+18	0.6	3.81E-06
2380	**238.0**	2.38E-07	2.3	1.3	8.34E-19	2.76E+18	0.7	4.58E-06
2360	**236.0**	2.36E-07	2.3	1.3	8.42E-19	2.73E+18	0.7	4.54E-06
2320	**232.0**	2.32E-07	1.5	0.9	8.56E-19	1.75E+18	0.4	2.91E-06
2224	**222.4**	2.22E-07	3.7	2.1	8.93E-19	4.14E+18	1.0	6.88E-06
total			175.8	100.0	1.5E-17	4.1E+20	100.0	6.83E-04
UV			83.7	47.6	**1.3E-17**	**1.3E+20**	**31.3**	**2.14E-04**

photon mole = einstein = 6.23*10^{23} photons/mole

E = hv

E: energy for photolysis reaction, J
h: Plank's constant, 6.62*10^{-34}J·s
v: frequency of light, s^{-1}

λ=c/v

λ: wavelength of light, m
c: speed of light, 3.00*10^{8}m/s

E = hc/λ

numbers of photon arriving per second

Power/photon energy =
Watts/Joules = photons/sec

from actinometry experiment,

total incident light intensity	8.6*10^{-6} einstein/Ls
UV incident light intensity	**2.7*10^{-6}einstein/Ls (31.3%)**

$$\frac{2.7*10^{-6}\ \text{einstein}}{\text{Ls}}\ \Bigg|\ \frac{4.0*10^{5}\text{J}}{\text{einstein}} = 1.1\ \text{J/s·L} \quad = 1.1\ \text{W/L}$$

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