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# The effect of suspended solids during UV/ hydrogen peroxide advanced oxidation of municipal wastewater

Laith Furatian

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**THE EFFECT OF SUSPENDED SOLIDS DURING UV/H<sub>2</sub>O<sub>2</sub> ADVANCED  
OXIDATION OF MUNICIPAL WASTEWATER**

BY

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THESIS

Submitted to the University of New Hampshire

in Partial Fulfillment of

the Requirements for the Degree of

Master of Science

in

Civil Engineering

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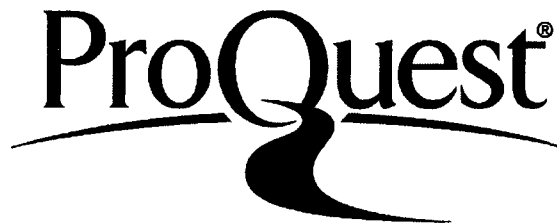
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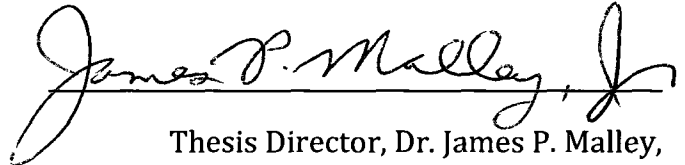
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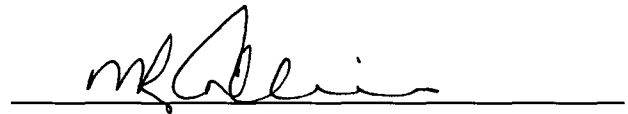


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Date

## Dedication

This work is dedicated to my mother.

الجنة تحت اقدم الامهات  
حديث نبوي

***"Heaven lies under the feet of mothers."***

*Hadith*

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## **ABSTRACT**

### **THE EFFECT OF SUSPENDED SOLIDS DURING UV/H<sub>2</sub>O<sub>2</sub> ADVANCED OXIDATION OF MUNICIPAL WASTEWATER**

By

Laith Furatian

University of New Hampshire, May, 2011

As wastewater and water reuse practices evolve to meet changing effluent requirements, the capabilities of various technologies to achieve treatment objectives merit investigation. This work examines the influence of suspended solids on the efficiency of the UV-H<sub>2</sub>O<sub>2</sub> advanced oxidation process to affect oxidation of organic contaminants in biologically wastewater effluents. Effluent samples from two conventional activated sludge plants were used to produce microfiltrates with 0.2 μm nylon filters. Para-chlorobenzoic acid (pCBA) was used as a probe compound to indirectly quantify the steady state OH concentration in samples spiked with H<sub>2</sub>O<sub>2</sub> and irradiated using a bench-scale UV collimated beam apparatus. An effluent sample from a membrane bioreactor was also evaluated. No significant difference in steady state OH concentration was observed between unfiltered and microfiltered samples, suggesting that suspended solids may not significantly contribute to hydroxyl radical scavenging in such effluents. Implications to the role of filtration are discussed.

## INTRODUCTION

The UV/H<sub>2</sub>O<sub>2</sub> advanced oxidation process (AOP) is more energy efficient for the removal of organic contaminants in water when the waters to be treated are highly transparent to light at 254 nm, and contain low amounts of dissolved organic matter and alkalinity. These conditions are common to reverse osmosis (RO) permeates and make the UV/H<sub>2</sub>O<sub>2</sub> AOP an attractive method of further treating such effluents for substances not fully removed by RO.

However, the RO process is energy intensive, with a specific energy of treatment ranging between 0.6 to 1.5 kWh/m<sup>3</sup> for the treatment of secondary effluents. Substantial chemical costs are involved in the maintenance of membrane systems, and the disposal of concentrates must be addressed (Pearce 2008). For many applications, RO permeates far exceed water quality requirements.

Since for many applications the required water quality is far below that of RO permeates, a lower quality water is often desirable for reuse purposes. A common wastewater reclamation scheme involves conventional biological treatment followed by filtration. Though removal of suspended solids via filtration generally results in a small reduction of UV absorbance, it is not known if such removal significantly alters the radical scavenging properties of the water, and thus the overall efficiency of a subsequent AOP. This work investigates whether filtration of

conventional secondary effluent improves the efficiency of the UV/ H<sub>2</sub>O<sub>2</sub> AOP for removal of organic pollutants in wastewater. Bench scale studies using unfiltered and microfiltered samples of secondary effluent were performed with a calibrated collimated beam apparatus to obtain results in terms of engineering parameters that may be interpreted in the context of full scale applications (Bolton et al. 2003). It is noted that this process targets primarily the soluble fraction of a contaminant. Results of these studies are not directly applicable to a contaminant found to be primarily associated with the particulate phase.

The goals of this work were thus (1) assessment of treatability of secondary effluent for removal of water soluble organic pollutants by direct use of the UV/H<sub>2</sub>O<sub>2</sub> AOP, (2) the effect of typical effluent suspended solids on treatment efficiency, and (3) comparison of the specific UV energy of treatment of this AOP applied to wastewater effluents.

Though the efficiency of the UV/H<sub>2</sub>O<sub>2</sub> AOP for removal of organic pollutants is lower when applied to biological effluents than when applied to RO permeates, if the primary contributions to OH scavenging in wastewater are identified, suitable pretreatments that target such components for removal may significantly improve AOP efficiency and avoid over treatment. Though beyond the scope of this work, comparison of alternative treatment schemes involves full economic analysis, of which operating energy is one crucial component.

## **CHAPTER I: LITERATURE REVIEW**

### **Background: Water, Energy and Reuse**

With population growth, traditional water resources are diminishing. Greater conservation and alternative sources are needed to satisfy demand. In more affluent societies, demand is increasingly met by desalination of sea water or the importation of water from distant watersheds, both of which require significant expenditures of energy (Allen et al, 1966; Argo, 1978; Hussein et al., 1999; Shon et al, 2009). As conventional energy resources continue to diminish as well, the production of both power and useful water require simultaneous consideration (Davis et al., 1967; Al-Mutaz, 2001; Forstmeier et al., 2007; Khamis, 2009). In some regions of the world, the situation is either quickly approaching or has already reached a crisis (Gleick, 1993; Darwish et al., 2005).

Many areas of the world are already dependent on desalination of sea water for much of their water needs. Generalized comparisons of water treatment options based on the price of produced water are complex (Blank et al. 2007). Since energy is a major cost component, meaningful comparisons of treatment options may be made on the basis of the specific energy of production, typically expressed in units of kilowatt-hours per cubic meter of treated water. The theoretical minimum energy required to obtain fresh water from seawater has been stated as  $0.7\text{kWh/m}^3$  (Shiffler, 2004), but for any practical system it is much higher. Most desalination in the world currently takes place in the Middle East where the primary method of

desalination is by thermal distillation (Suratt et al., 1996). In Kuwait, more than 93% of its fresh water needs are produced using the combination of steam turbines and multi-stage flash (MSF) distillation units in co-generation power desalting plants. The required energy per unit volume for desalination by MSF in Kuwait is 22 kWh/m<sup>3</sup> (Darwish et al., 2005), and MSF technology is set to dominate Kuwaiti desalination for several decades to come (Al-Bahou et al., 2007). The second most common method of desalination technology in the Middle East, also used in co-generation, is multiple-effect evaporation (MEF), reported to consume approximately 9 kWh/m<sup>3</sup> (Franquelin et al., 2001). Desalination by electro dialysis is reported to require 7 – 13 kWh/m<sup>3</sup> depending on salinity (Turek, 2002), with limited applications restricted to brackish waters (Suratt et al, 1996). However, virtually all new desalination plants utilize reverse osmosis (RO), with reported energy requirements ranging between 2-7 kWh/m<sup>3</sup> (Schiffler 2004; Darwish et al., 2005; Fritzmann et al., 2007; Pearce, 2008). These figures indicate only the energy cost involved, and do not include other operating costs such as chemicals for cleaning and disposal of concentrate. Recently, a method of desalination using microbial fuel cells has been reported in which electrical power and desalinated water are produced using bacteria and a source of biodegradable organic matter. Each fuel cell stage was demonstrated to remove up to 90% of the salt content while generating a maximum of 31 W/m<sup>3</sup>, with acetate as the bacterial substrate (Cao et al., 2009).

Considering the energy required in obtaining water by desalination, the incentive for reuse is clear. The reuse of wastewater conserves both water and energy. The

energy requirements of various forms of water and wastewater treatment have been extensively investigated by several firms and reviewed (Pearce, 2008). Below is a table summarizing the main findings for the energy costs involved in producing potable quality water from various sources, including surface water (i.e. rivers, lakes, reservoirs), municipal sewage, brackish water, and seawater. Municipal sewage treatments considered are conventional activated sludge (CAS), and membrane bioreactors (MBR). Pretreatment of RO feed water involves either conventional methods such as lime clarification and sand filtration, or the use of membrane-based microfiltration (MF) or ultrafiltration (UF). It has been argued (Pearce 2008) that the chemical costs of conventional pre-treatment for RO feed water are very high and thus less attractive than membrane based methods, consistent with what has been reported elsewhere (López-Ramirez et al. 2003).

**Table 1.1 – Specific energy usage for water and wastewater treatment (Pearce, 2008)**

	CAS (kWh/m <sup>3</sup> )	Pre-treatment (kWh/m <sup>3</sup> )	RO system (kWh/m <sup>3</sup> )	Total (kWh/m <sup>3</sup> )
Surface water				0.1-0.3
Wastewater	0.3-0.6	0.1-0.2	0.4-0.5	0.8-1.3
Wastewater MBR		0.8-1.0	0.4-0.5	1.2-1.5
Brackish <sup>a</sup>		0.1-0.3	0.6-0.9	0.8-1.0
Brackish <sup>b</sup>		0.3	1.3	1.7
Seawater		0.3-1.0	2.0-3.0	2.3-4.0

*a* TDS between 930 – 2200 ppm

*b* Tidal estuary

The energy of activated sludge treatment reported by Pearce is consistent with those reported elsewhere (Evans 1994; Burton 1996). MBR energy requirements

were lower than what was reported for a Kubota pilot system, involving 5 – 6 kWh/m<sup>3</sup> (Gil et al. 2010), but consistent with that reported elsewhere (Buer et al. 2010). Requirement of 0.1-0.2 kWh/m<sup>3</sup> for MF of CAS effluents is consistent with approximately 0.3 kWh/m<sup>3</sup> reported for UF treatment of secondary effluent (Bourgeois et al. 2001).

Based on the available information, the energy requirements for RO desalination of seawater are at least an order of magnitude greater than that typically needed to treat surface waters. It is also apparent that the recycling of wastewater, to comparable quality, requires at least half the energy needed for desalination of sea water. The application of RO based systems to wastewater treatment are thus a justifiable method of alleviating demand on more expensive water sources from an energy perspective, as suggested by some (Schaefer 2001).

In addition to energy expenditure, the implementation of water reuse relies on economic, social, and political considerations (Farooq 1981; Baumann 1983; Davenport 1994; Hartley 2006).

Two high profile examples of reuse applications include the Orange County Groundwater Replenishment System (GRS), in Orange County California, and the NEWater system of Singapore. Both systems were planned well in advance and based on extensive research and development (Allen et al. 1966; Allen 1979; Macpherson 2005; Tortahada 2006; PUB 2008).

Both systems are equipped to treat secondary municipal effluent by means of MF-RO systems, followed by ultraviolet (UV) radiation disinfection. In the case of



Orange County, the UV stage delivers sufficient energy to destroy trace chemical contaminants that have not been sufficiently removed by RO, in particular N-nitrosodimethylamine (NDMA) (Plumlee et al. 2008). These above mentioned systems are designed to produce water beyond the requirements of most drinking water standards, and are examples of planned indirect potable reuse.

Most wastewater reclaimed for reuse is used for non-potable applications, such as agricultural irrigation and the cooling of power plants. The required quality for such applications differ from those of potable reuse (Asano, 1986; Rebhun et al., 1988; Lazarova et al., 2005), and in general do not require the quality attained by RO permeates. Energy can be saved by avoiding over treatment of reclaimed water where possible. Yet, if the removal of any remaining contaminants in reclaimed wastewater is deemed necessary for a particular reuse application, additional treatment processes should be identified that avoid exceeding the cost of alternative water sources. For some organic pollutants, removal via advanced oxidation is among the few treatment methods available.

Intended use is not the only consideration in determining quality requirements.

Where agricultural irrigation exerts the largest demand of water resources, demand is not constant and depends on the agricultural growing cycles. A steady supply of treated water could be stored and drawn upon when needed, suggesting the use of aquifer storage (Asano 1993; Pyne 1995; Angelakis et al. 1999; Asano 2002; Al-Otaibi et al. 2007; Dillon et al. 2006). Treatment requirements before aquifer recharge with reclaimed wastewater merit careful consideration.

Among the complex mixture of dissolved, colloidal, and particulate organic matter present in treated wastewater, much of it is in a highly oxidized state and resistant to further biodegradation (Rickert et al. 1971; Chudoba 1987). The majority of effluent organic matter (EfOM) is composed of soluble microbial products (SMP) originating from the biological treatment process, in addition to smaller amounts of natural organic matter (NOM) originating from the drinking water source (Baker et al. 1999; Shon et al. 2006). This matrix also includes trace contaminants refractory to microbial degradation. Such contaminants are typically present at concentrations on the order of 1 µg/L and below and are thus often referred to as micropollutants.

Many effects of wastewater effluent upon aquatic ecology are well documented (Welch 1992), and the inability of conventional wastewater treatment to completely remove xenobiotic organic compounds has been investigated (Giger et al. 1981; Petrasek et al. 1983; Byrns 2001, Ternes et al. 2004). New knowledge regarding trace contaminants in wastewater and their fate in the environment continues to grow as analytical capabilities are advanced. The fate of micropollutants remaining in treated wastewater is conventionally left to the hydrological cycle for further breakdown and dilution in the environment. Many emerging contaminants, such as pharmaceuticals and personal care products are found to persist in the environment upon release, though their implications to environmental and human health are the subjects of ongoing research and debate (Daughton et al. 1999; Herberer 2002; et al. 2006; Radke et al. 2010). There is strong evidence that the estrogenicity of wastewater effluents have a profound impact on aquatic ecology (Jobling 1998; Sumpter 2005; Woodling 2006, Kidd et al. 2007, Jeffries et al. 2008). Some have

questioned the merit of advanced treatment of wastewater for removal of micropollutants, highlighting the inverse relationship between water quality and energy consumption (Jones et al. 2007). While information on emerging contaminants continues to grow, knowledge of legacy pollutants from a previous generation is also expanding (Fraser 2010). It is possible that emerging contaminants of today may be legacy contaminants of future generations, and a precautionary approach is suggested by some (Ternes et al. 2004). The spread of wastewater reclamation practices which curtail most, if not all, of the hydrological cycle may encourage a change in thinking on wastewater treatment standards, and an economic shift in what is feasible. In theory, rational changes to infrastructure and behavior may simultaneously improve the efficiency and quality of wastewater reclamation while reducing environmental impact of human activities. Some of the successful pollution prevention practices of industry (Overcash 2002) may prove useful in the treatment of municipal wastewater. Alternative methods to conventional wastewater practices that reduce water demand and minimize environmental impact include source separation and decentralized treatment and recycling (Larsen et al. 1996, 1997, 2001a, 2001b, 2004; Henze 1997; Otterpohl et al. 2002, 2003; Mauer et al. 2006; Oldenburg et al. 2007; Peter-Fröhlich et al. 2007; Chanan et al. 2009).

### **Chemical Oxidation of Organic Pollutants in Wastewater**

Returning to the question regarding further treatment of secondary effluents, the general question can be asked: if future regulations make it necessary, *how can*

*organic micropollutants of concern be removed from a matrix of effluent organic matter?*

For those compounds that are resistant to biological degradation, two general approaches may be considered for their removal from water. One approach uses physical removal of pollutants. These include membrane filtration, air stripping, activated carbon adsorption, and ion exchange. These methods do not destroy pollutants but transfer them to another phase, producing a waste stream whose disposal must be addressed. Such waste streams include RO concentrates, exhaust gases, spent carbon and ion exchange resin.

Rather than physical removal, another approach uses the chemical transformation of contaminants by oxidative means, to the extent that the toxicological properties of concern are sufficiently diminished. The ultimate end products of the oxidation of organic matter are carbon dioxide, water, and mineral acids, referred to as mineralization, though complete oxidation is often unnecessary. Conventional wastewater treatment uses biological oxidation to breakdown a large portion of organic matter. Effluent organic matter (EfOM) thus tends to be in a higher state of oxidation (Ricker et al. 1971) and generally less available to microorganisms as a carbon source. Consequently, compounds found in EfOM are less biodegradable and more refractory. Refractory compounds may be further oxidized by physical-chemical methods to disrupt chemical moieties making them more available for subsequent biodegradation. Since biological oxidation is more economical than physical-chemical methods, one method of removing refractory compounds while

minimizing overall treatment cost may involve a physical-chemical unit process located between two biological processes. The first biological process oxidizes easily biodegradable compounds that would compete with the refractory target pollutant during the physical-chemical process. The final biological process treats the biodegradable products formed by the physical-chemical process, should these still be of toxicological significance.

Common oxidants used in water treatment and their standard reduction potential ( $E^\circ$ ) are listed in Table 1.2.

**Table 1.2 – Oxidants used in water treatment and standard reduction potentials (Crittenden, 2005)**

Oxidant	$E^\circ$ (V)
$OH^\bullet$	2.59
$O_3$	2.08
$H_2O_2$	1.78
$MnO_4^-$	1.51
$HOCl$	1.48
$O_2$	1.27
$ClO_2$	0.80

It can be seen from Table 1.2 that the strongest oxidants available are the hydroxyl radical ( $OH^\bullet$ ) and ozone ( $O_3$ ). Though all these oxidants are able to fully mineralize most organic material, the reaction rates are in general too slow under conditions used in water treatment. The highest reaction rates observed are associated with the oxidants  $OH^\bullet$  and  $O_3$ . With most organic compounds,  $OH^\bullet$  reacts at near diffusion limited of  $10^9 \text{ M}^{-1}\text{s}^{-1}$  (Buxton, 1988). Reactions of  $O_3$  with organic matter are highly selective and reaction rates vary over a wide range ( $10^{-2} - 10^9 \text{ M}^{-1}\text{s}^{-1}$ ),

depending pH and the molecular structure of organic matter (Hoigné et al. 1976, 1983a, 1983b, 1985; Huber et al. 2003).

While extensively used for disinfection, HOCl reacts with natural organic matter at rates  $< 10^{-2} \text{ M}^{-1}\text{s}^{-1}$  (Gallard et al. 2002). In addition to low reaction rates, the oxidation of organic matter with HOCl produces undesirable by-products such as trihalomethanes (THMs) and haloacetic acids (HAAs), some of which are suspected human carcinogens. The reactivity of  $\text{ClO}_2$  with most organic compounds investigated was found to be very low ( $< 10^{-2} \text{ M}^{-1}\text{s}^{-1}$ ), with a few exceptions displaying reaction rates on the order of  $10^5 \text{ M}^{-1}\text{s}^{-1}$ , such as the estrogen  $17\alpha$ -ethinylestradiol (Hoigné et al. 1994; Huber et al. 2005). However, while the use of  $\text{ClO}_2$  avoids the formation of THMs and HAAs, the undesirable formation of chlorite ( $\text{ClO}_2^-$ ) and chlorate ( $\text{ClO}_3^-$ ) limit the dose of that can be used in water treatment (Crittenden et al, 2005). Little information in the literature can be found regarding the oxidation of organic matter in water treatment using  $\text{MnO}_4^-$  and  $\text{H}_2\text{O}_2$ . Studies involving oxidation of taste and odor compounds found reactivity of these oxidants to be comparable to HOCl (Lalezary et al. 1986; Glaze et al. 1990).

### **Advanced Oxidation Processes Using Ozone or UV+**

Because of the ability of  $\text{OH}\cdot$  to oxidize most organic compounds unselectively and at near diffusion limited rates under ambient conditions, processes that utilize  $\text{OH}\cdot$  as the primary oxidant are referred to as Advanced Oxidation Processes (AOPs) (Glaze et al. 1987). Many AOPs that have been investigated (Carey 1992; Oppenländer 2003). The two most viable technologies for large scale water

treatment at this time involve the generation of OH• by means of O<sub>3</sub> or UV radiation in conjunction with H<sub>2</sub>O<sub>2</sub>, (Swain et al. 2008) referred to as O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> and UV/H<sub>2</sub>O<sub>2</sub> AOPs respectively.

### **Advanced Oxidation by O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>**

The addition of O<sub>3</sub> to water, in the presence of organic matter, results in the decomposition of O<sub>3</sub>, with an initial rapid phase of decomposition, followed by a slower phase (Staehelin et al. 1985). During the initial rapid phase of decomposition, O<sub>3</sub> decomposition generates OH• radicals (von Gunten 2003). During the slower second phase, O<sub>3</sub> is more stable and may persist for sufficient time to affect microbial disinfection. This second slow phase is typically seen in drinking water applications, where the organic carbon content and reactivity is relatively low. In wastewater, an O<sub>3</sub> residual is generally not observed at conventional doses, and while disinfection may still be achieved, significant doses are required to affect disinfection. The addition of H<sub>2</sub>O<sub>2</sub> accelerates the initial decomposition phase, and thus the generation of OH• for contaminant destruction (Staehelin et al. 1982). The presence of increased organic matter and bicarbonate/carbonate alkalinity, consume OH• and thus reduce the efficiency of micropollutant removal, a common issue in all AOPs (Oppenländer 2003).

Because of the relationship between organic content and initial O<sub>3</sub> demand, it is appropriate to normalize dose by dissolved organic carbon, expressed as g O<sub>3</sub>:g DOC (Huber et al. 2005). The addition of H<sub>2</sub>O<sub>2</sub> seems to provide little improvement on the use of O<sub>3</sub> during oxidation of wastewater (Snyder et al. 2006). In recent studies of

full scale implementations, several pharmaceutical micropollutants were significantly removed at doses of 0.5 – 0.6 g O<sub>3</sub>:g DOC (Hollender 2009). During treatment, the formation of the byproducts N-nitrosodiethylamine (NDMA) and bromate were observed. The specific energy consumption was reported as 0.035 kWh/m<sup>3</sup> or slightly more than 10% of the specific energy required for conventional wastewater treatment as stated in Table 1.1. The formation of bromate and brominated organics is consistently observed during ozonation of wastewater effluent (Kim et al. 2007, Wert et al. 2007). While methods to reduce bromate and other byproducts during ozonation exist (Rengao et al. 1997), such byproducts must be carefully considered. The formation of potentially harmful byproducts is a short coming of ozone based AOPs for many applications (Swain et al. 2008).

### **Advanced Oxidation by UV/H<sub>2</sub>O<sub>2</sub>**

Generation of OH• by UV/H<sub>2</sub>O<sub>2</sub> requires the absorption of photons by molecules of H<sub>2</sub>O<sub>2</sub>. While H<sub>2</sub>O<sub>2</sub> may be homogeneously distributed in a liquid under irradiation, the capacity of photons to propagate in the liquid is dependent on wavelength and wavelength specific absorption characteristics of the liquid medium. The greater the absorption of the liquid, the more the absorption of photons will be concentrated at the interface between the light source (lamp-sleeve system) and the liquid. Under ideal conditions, complete mixing ensures that all volume elements of the fluid in the reactor will receive the equivalent dose of photons or fluence.

Once photons have been absorbed by H<sub>2</sub>O<sub>2</sub>, excited-state molecules of H<sub>2</sub>O<sub>2</sub> must cleave and escape the solvent cage before recombination. The solvent cage reduces



the yield of OH• generation to half of that observed in the gas phase (Baxendale 1957), thus producing one radical per UV excited molecule of H<sub>2</sub>O<sub>2</sub>. Generated OH• react with most solutes at near diffusion limited rates. The average distance that OH• diffuses in the liquid before reacting has been estimated to be on the order of 1µm or less (Turchi et al. 1990). Thus, the generation by photolysis and use of OH• as an oxidant involves overcoming both photon and mass transfer limitations.

Organic carbon, carbonate, and bicarbonate compete with target pollutants to react with the generated OH•. The fundamental efficiency of the UV/H<sub>2</sub>O<sub>2</sub> AOP is thus governed by five main issues:

- absorbance of the liquid
- mixing
- molar absorptivity of H<sub>2</sub>O<sub>2</sub>
- quantum yield of H<sub>2</sub>O<sub>2</sub>
- reactivity of target pollutants with OH•
- competition for OH• between target pollutants and all other solutes.

**Absorbance of liquid:** The absorbtivity of ultrapure water to UV radiation in the range of 200 to 300 nm is very low relative to water containing organic and inorganic solutes (Quickenden et al. 1980). In the presence of solute molecules, photons entering the liquid may encounter a molecule and be absorbed, resulting in either the electronic excitation of the molecule or the breaking of bonds. Excited state molecules may emit a photon and return to the ground state or loose energy non-radiatively (Wayne 1988). Absorption of photons takes place on a time scale of

$10^{-15}$ - $10^{-18}$  s, and when photons of sufficient energy to break molecular bonds are absorbed, diatomic molecules do so within a time scale of  $10^{-13}$ - $10^{-14}$  s, the period of a single molecular vibration. Polyatomic molecules having absorbed such photons may accommodate the absorbed energy more easily and thus persist in an excited state for periods of  $10^{-8}$ s or more, during which time the absorbed energy may be dissipated without the breaking of bonds (Laidler 1987). Thus in water containing significant amounts of dissolved organic molecules, a significant portion of photons are absorbed and lost as heat. The attenuation of photon flux along the optical path into a non-scattering liquid is expressed by the Beer-Lambert law:

$$I = I_o e^{-\alpha' \ell} \quad (1)$$

Where

$I$  is the photon irradiance ( $\text{Es cm}^{-2} \text{s}^{-1}$ ) exiting the liquid after optical path length  $\ell$

$I_o$  is initial photon irradiance entering the liquid ( $\text{Es cm}^{-2} \text{s}^{-1}$ )

$\alpha'$  is the base  $e$  absorption coefficient for the liquid ( $\text{cm}^{-1}$ )

$\ell$  is distance into the liquid along the optical path ( cm )

The absorption coefficient is a function of the concentration of the dissolved solutes and their respective molar absorptivities (conventionally expressed in base 10):

$$\alpha = \varepsilon_1 C_1 + \varepsilon_2 C_2 + \dots = \sum \varepsilon_i C_i \quad (2)$$

Where

$\alpha$  is the base 10 absorptivity ( $\text{cm}^{-1}$ ) and  $\alpha' = 2.303 \alpha$ .

$\varepsilon_i$  is the decadic molar absorptivity of the  $i^{\text{th}}$  species ( $\text{M}^{-1}\text{cm}^{-1}$ )

$C_i$  is the concentration of the  $i^{\text{th}}$  species (M)

As natural waters and wastewater effluents are complex mixtures, only the total absorbance  $\alpha$  is generally measureable. The contribution to the total absorbance by added solutes can be made if the concentration and molar absorptivities are known, as in the case with  $\text{H}_2\text{O}_2$ . When the dissolved organic carbon (DOC) is known in mg/L, then the specific UV absorbance (SUVA) is equivalent to the value of  $\varepsilon$  for DOC, with appropriate modification of units.

**Photolysis of  $\text{H}_2\text{O}_2$ :** The average volumetric rate of photolysis of  $\text{H}_2\text{O}_2$  by a low pressure UV source can be expressed by the following (see appendix for derivation):

$$r_{\text{photolysis}} = -\frac{\phi \cdot \varepsilon \cdot C \cdot I_o \cdot (1 - 10^{-\alpha \ell})}{\alpha \cdot \ell} \quad (3)$$

Where

$\phi$  is the quantum yield of  $\text{H}_2\text{O}_2$  at 254 nm ( $\text{mol Es}^{-1}$ )

$\varepsilon$  is the decadic molar absorptivity of  $\text{H}_2\text{O}_2$  ( $\text{M}^{-1}\text{cm}^{-1}$ )

$C$  is the concentration of  $\text{H}_2\text{O}_2$  (M)

$I_o$  is the incident photonic irradiance ( $\text{Es cm}^{-2} \text{s}^{-1}$ )

$\alpha$  is total decadic absorptivity of the liquid ( $\text{cm}^{-1}$ )

$\ell$  is the depth into the liquid (cm)

When the absorbance is small ( $\alpha \ll 1$ ), the photolysis rate may be expressed as:

$$r_{\text{photolysis}} = -\frac{\phi \cdot f \cdot I_0}{\ell} \quad (4)$$

Where  $f$  is the fraction of absorbed photons which are absorbed by  $\text{H}_2\text{O}_2$ , and is expressed as  $f = \varepsilon \cdot C / \alpha$

A potentially useful feature of the use of UV radiation is that some contaminants are strong absorbers of UV and may be degraded by the action of UV light alone.

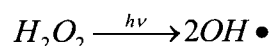
However, the rate of photolysis of any contaminant is a function of not only the molar absorptivity  $\varepsilon$ , but also the quantum yield  $\phi$ , which for most substances is relatively low (Stefan et al. 2004). The photolysis rate of any solute is proportional to the term  $\phi \cdot \varepsilon$ , as seen in equation 3. Table 1.3 shows photochemical data for several micropollutants, as well as  $\text{H}_2\text{O}_2$ , at 254 nm.

**Table 1.3 – Photolysis data for several micropollutants and  $\text{H}_2\text{O}_2$  at 254 nm**  
(Periera et al. 2007; Crittenden et al. 2005)

	$\varepsilon$ $\text{L mol}^{-1} \text{cm}^{-1}$	$\phi$ $\text{mol Es}^{-1}$	$\phi \varepsilon$ $\text{L Es}^{-1} \text{cm}^{-1}$
NDMA	1974	0.3	592
clofibric acid	400	0.0022	1
naproxen	4900	0.0297	146
carbamazepine	6070	0.0366	22
ciprofloxacin	12400	0.0701	869
ketoprofen	15450	0.0904	1397
iohexol	27620	0.1095	3024
$\text{H}_2\text{O}_2$	19	1	19

As can be seen from Table 1.3, the compound iohexol and ketoprofen are expected to be particularly labile to UV radiation and thus amenable to removal by UV photolysis. Photolysis has been found to be one of the few effective treatments for the contaminant NDMA (Swain et al. 2008). It is also clear that the low molar absorptivity  $\epsilon$  of  $\text{H}_2\text{O}_2$  at 254 nm is one of the shortcomings of the UV/ $\text{H}_2\text{O}_2$  AOP, compensated only by the high quantum yield. While the quantum yield of  $\text{H}_2\text{O}_2$  has been found to be relatively constant over the wavelength range 200 to 300 nm (Baxendale et al. 1957), its molar absorptivity increases in this range with decreasing wavelength (Morgan et al. 1988). It has been suggested that if a suitable source were available, using a wavelength of 220 nm would increase the molar absorptivity of  $\text{H}_2\text{O}_2$  by five-fold (Carey 1994). However, equation 4 above shows that the photolysis rate increases only if the fraction of photons absorbed by  $\text{H}_2\text{O}_2$  increases. Since the absorbance of organic matter increases rapidly with decreasing wavelength, the fraction absorbed by  $\text{H}_2\text{O}_2$  does not significantly increase with decreasing wavelength when significant organic matter is present. It may even decrease. It has also been suggested that the UV/ $\text{H}_2\text{O}_2$  AOP may be more efficient at higher pH, since hydrogen peroxide's conjugate base  $\text{HO}_2^-$  has a molar absorptivity of  $240 \text{ M}^{-1}\text{cm}^{-1}$  at 254nm (Andreozzi et al. 1999). However, the high pKa of 11.6 (Jones 1999) makes such pH adjustment costly, and the impact of alkalinity on reducing efficiency becomes more severe at higher pH, as will be discussed below.

The photolysis of  $\text{H}_2\text{O}_2$  generates  $\text{OH}\cdot$  with a quantum yield of 1.0 at 254 nm. This is half the theoretical yield of 2 due to the solvent cage effect present in the liquid state. The photolysis of  $\text{H}_2\text{O}_2$  can be described by:



Where  $h\nu$  is a photon at 254 nm. The generated  $OH\bullet$  react with solute  $S$  via hydrogen abstraction or the addition of double bonds to produce more oxidation products  $S'$ . The reaction rate is given by the second order hydroxyl radical rate constant for  $S$ ,  $k_{OH,S}$ .



The rate of  $OH\bullet$  consumption is proportional to the concentration of all solutes and their respective second order  $OH\bullet$  rate constants:

$$r_{consumption} = -(k_1 \cdot [S_1] + k_2 \cdot [S_2] + \dots) \cdot [OH\bullet] = -(\sum_i k_i \cdot [S_i]) \cdot [OH\bullet] \quad (5)$$

Where

$k_i$  is the second-order  $OH\bullet$  rate constants for the  $i^{\text{th}}$  solute species  $S$  ( $M^{-1}s^{-1}$ )

$[S]_i$  is the concentrations of the  $i^{\text{th}}$  solute (M)

The summed term  $\sum k[S]$  is referred to as the  $OH\bullet$  scavenging rate and is expressed in units of  $s^{-1}$ . The scavenging rate is inversely proportional to the average lifetime of the  $OH\bullet$  in water (Hoigné 1997).

When  $OH\bullet$  is continuously being generated by photolysis of  $H_2O_2$  and consumed near diffusion limited rates, then the steady-state condition may be assumed.

Under this assumption, the steady-state  $OH\bullet$  concentration may be determined and is given by the following expression (see appendix for derivation):

$$[OH\bullet]_{ss} = \frac{-\phi \cdot \varepsilon \cdot [H_2O_2] \cdot I_o}{\alpha \cdot \ell \cdot \sum_i k \cdot [S]_i} (1 - e^{-\alpha \ell}) \quad (6)$$

Where

$[OH\bullet]_{ss}$  is the steady-state concentration of  $OH\bullet$  (M)

$[H_2O_2]$  is the concentration of  $H_2O_2$  in solution (M)

And all other terms as defined previously.

The removal for a contaminant  $C$  from solution under UV irradiation in the presence of  $H_2O_2$  may then be expressed as:

$$\ln(C/C_o) = -k_{c,OH} \cdot [OH\bullet]_{ss} \cdot t \quad (7)$$

Where

$C$  is the concentration of the contaminant at time  $t$  (M)

$C_o$  is the initial concentration of contaminant (M)

$k_{c,OH}$  is the second order hydroxyl radical rate constant for the  
contaminant ( $M^{-1}s^{-1}$ )

$t$  is time of irradiation (s)

Equation (7) may also be written as  $\ln(C/C_o) = -k't$ , where  $k'$  is the pseudo-first order rate constant measured experimentally. Knowledge of the second order  $OH\bullet$  rate constant  $k_{c,OH}$ , allows the calculation of  $[OH\bullet]_{ss}$ .

A useful parameter in the evaluation of AOPs is the specific energy required to remove a contaminant by one order of magnitude (i.e. 90%), and is referred to as the *EE/O* or electrical energy per order (Bolton et al. 1996), defined as

$$EE/O = \frac{EED/V}{\log(C_i/C_f)} \quad (8)$$

Where

*EED/V* is the electrical energy consumed per volume of water treated (kWh/m<sup>3</sup>)

*C<sub>i</sub>* is the initial concentration of the pollutant (M)

*C<sub>f</sub>* is the final concentration of the pollutant (M)

The *EE/O* is typically expressed in units of kWh/m<sup>3</sup>-order. The lower value of *EE/O*, the more efficient the removal process.

While *EE/O* may be measured in practice for actual reactors, prediction of the *EE/O* for an actual reactor based on bench-scale collimated beam studies is difficult without information regarding the fluence distribution of the reactor. For collimated beam studies, treatability of various water matrices may be compared by comparison of the UV energy per order of magnitude reduction of a contaminant (*UVE/O*). The ratio of the *UVE/O* of two matrices will be a reasonable approximation to the ratio of the *EE/O* of the same matrices, under equivalent treatment conditions.



$$UVE/O = \frac{P_{UV} \cdot t/V}{\log(C_i/C_f)} \quad (9)$$

Where

$P_{UV}$  is the lamp radiant power at UV wavelengths (kW)

$t$  is the duration of irradiation or exposure (h)

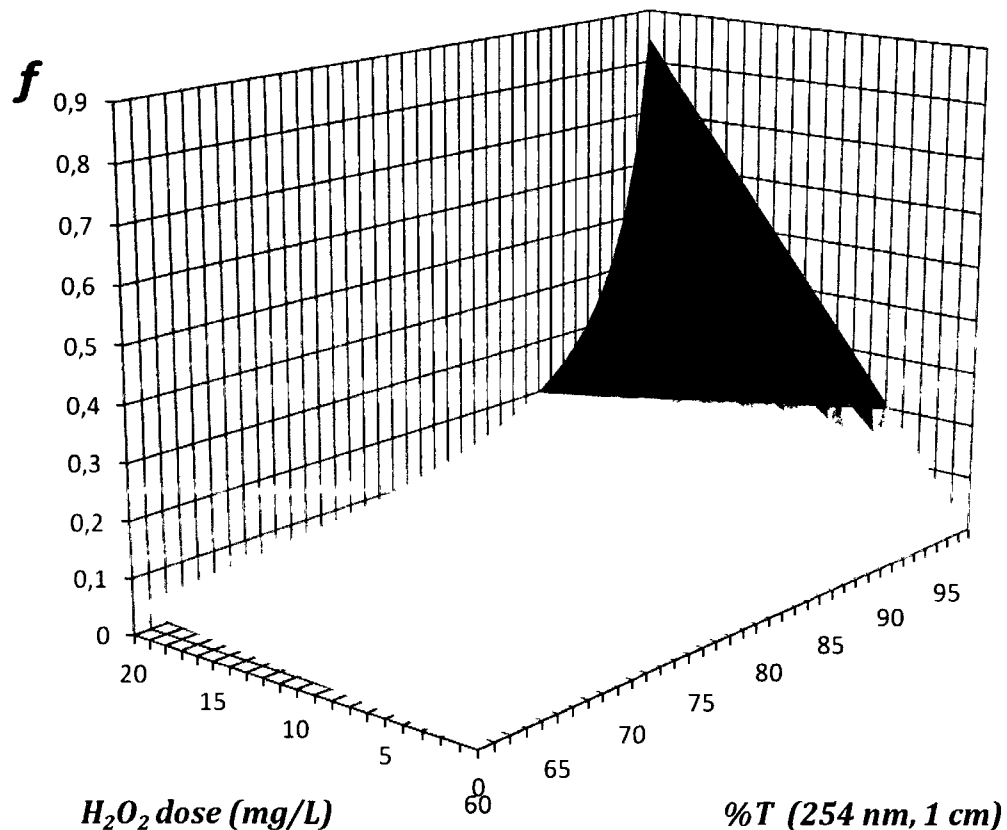
which gives equivalent units for  $UVE/O$  as for  $EE/O$ , namely kWh/m<sup>3</sup>-order. The relation between the two terms will be:

$$EE/O = (1/\eta) \cdot UVE/O \quad (10)$$

Where  $\eta$  is a function of the lamp and reactor efficiencies.

**Consideration of water absorbance:** One of the factors limiting the efficiency of the UV/H<sub>2</sub>O<sub>2</sub> AOP is the small fraction of photons absorbed by H<sub>2</sub>O<sub>2</sub>. This fraction is maximized in water matrices of low absorbance relative to H<sub>2</sub>O<sub>2</sub> at the wavelength considered. Thus, it is not surprising why this process is significantly more effective when applied to RO permeates, for which typical UV transmittance greater than 98% is observed (Chakraborti et al. 2007). Figure 1.1 indicates the fraction of photons absorbed by H<sub>2</sub>O<sub>2</sub> as a function of UV transmittance and H<sub>2</sub>O<sub>2</sub> dose.

**Figure 1.1 – Fraction  $f$  of photons absorbed by  $H_2O_2$  for a range of %transmittance and  $H_2O_2$  concentrations at  $\lambda = 254\text{ nm}$**



**Components of Scavenging:** The OH radicals generated by photolysis of  $H_2O_2$  rapidly react with organic matter in the water matrix, described by equation (5) above. Target pollutants react with  $OH\cdot$  in competition with all other solutes, and thus the rate of pollutant oxidation is inversely proportional to the scavenging capacity of the matrix. Scavenging capacity may be divided into the organic matter contribution and the contribution due to alkalinity, primarily the bicarbonate ion

under neutral conditions. While the  $\text{OH}\cdot$  rate constant for bicarbonate and carbonate are well known, the contribution to scavenging by the organic matter is due to a complex mixture whose individual components are not readily determined. Consequently, scavenging may be divided into two components, one contribution from alkalinity, which is readily calculated from measured values, and the contribution of the organic matter, which must be determined as a bulk property in most cases. The organic contribution is found by measuring the total scavenging capacity and subtracting the contribution due to alkalinity.

Several comments should be made regarding  $\text{OH}\cdot$  scavenging by the bicarbonate/carbonate system. The  $\text{OH}\cdot$  rate constants for  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  are  $8.5 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$  and  $3.9 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$  respectively (Buxton 1988). While these are of lower magnitude compared with the rate constants of most organic compounds (typically  $10^8$ - $10^{10} \text{ M}^{-1}\text{s}^{-1}$ ), the concentration of  $\text{HCO}_3^-/\text{CO}_3^{2-}$  is usually several orders of magnitude higher than that of organic contaminants. Furthermore, it can be seen that  $\text{CO}_3^{2-}$  is almost 50 times as reactive as  $\text{HCO}_3^-$ , indicating that higher pH will result in a higher demand for OH radicals by the  $\text{HCO}_3^-/\text{CO}_3^{2-}$  system relative to neutral conditions, where virtually no  $\text{CO}_3^{2-}$  is present. Lastly, the reaction of  $\text{HCO}_3^-/\text{CO}_3^{2-}$  with  $\text{OH}\cdot$  results in the formation of  $\text{HCO}_3^{\cdot-}/\text{CO}_3^{2-\cdot}$  radicals. These radicals are oxidants that will react with organic matter at a wide range of rates ( $<10^3$ - $10^8 \text{ M}^{-1}\text{s}^{-1}$ ) highly dependent on molecular structure and tending to be well below the diffusion limited rates observed for  $\text{OH}\cdot$  (Chen et al. 1973). Exceptions exist, and organics such as those containing the indole moiety or aniline derivatives react with  $\text{HCO}_3^{\cdot-}$  at rates on the order of  $10^9 \text{ M}^{-1}\text{s}^{-1}$  (Chen et al. 1973, Larson et al. 2009). In

general, the presence of significant alkalinity results in the partial exchange of the near diffusion limited and unselective properties of the OH• radical for a generally much slower and highly selective oxidant.

Few reports of the scavenging capacity of various waters are available in the literature. A few will be cited here in order to illustrate typical magnitudes that may be encountered. Values of the scavenging of natural waters have been reported by one study (Huber et al. 2003), and are summarized in Table 1.4.

**Table 1.4-Scavenging capacity of natural waters (Huber et al. 2003)**

Source	DOC (mg/L)	Alkalinity <sup>a</sup> (mg/L)	$\Sigma k[S]_i \text{ (s}^{-1}) \times 10^{-4}$		
			DOC	Alkalinity	Total
well water	0.8	130	2.0	5.6	7.6
Seine River <sup>b</sup>	1.3	205	3.2	4.0	7.2
Lake Zurich	1.2	290	3.0	2.5	5.5
Finland lake	3.7	35	9.2	0.7	9.9

<sup>a</sup> shown here in units of mg/L as CaCO<sub>3</sub>, reported by Huber as mM HCO<sub>3</sub><sup>-</sup>  
<sup>b</sup> riverbank filtrate taken near Paris

Measured scavenging capacities were found in the range 5.5 – 9.9 ×10<sup>4</sup> s<sup>-1</sup>. It can be seen from Table 1.4 that, in all but one case, comparable contributions to scavenging capacity are made by both organic matter and alkalinity. Only in the high DOC-low alkalinity lake water from Finland does the organic matter dominate scavenging.

Other studies have reported on the scavenging from tertiary wastewater samples. Effluent samples taken from 8 wastewater treatment plants across five states of the

U.S.A. were found to have scavenging capacities in the range  $2.7 - 9.5 \times 10^5 \text{ s}^{-1}$  (Rosario-Ortiz et al. 2008), which are an order of magnitude larger than for the natural waters reported in Table 1.4. Those findings are summarized in Table 1.5, where the contribution of alkalinity and DOC reported have been used to calculate their respective contributions to the scavenging capacity. The alkalinity values are comparable to the natural waters considered above. The level of DOC found in the effluents, while higher, are still within an order of magnitude of those from the natural waters. Thus, the increase in reactivity of organic matter is suspected to be a possible cause of increased scavenging.

Another study of wastewater effluents found scavenging values to be even higher than those in Table 1.5 by one or two orders of magnitude, yet with comparable levels of organic matter and alkalinity (Wert et al. 2009). The cause of these large variations is not known. Based on these examples, for natural waters and wastewater effluents, total scavenging capacity is expected to span the range of  $10^4 - 10^6 \text{ s}^{-1}$ .

How does the  $\text{OH}\cdot$  scavenging of RO permeates compare to those of natural waters and wastewater effluents? This can be estimated based on the amount of alkalinity and DOC present in RO permeates and by the typical range of second-order hydroxyl radical rate constants for DOC. Since the organic matter of effluents (i.e. EfOM) are complex mixtures, the rate constant must be determined experimentally, yet it is possible to estimate the reasonable range for EfOM rate constants.

**Table 1.5-Scavenging capacity of wastewater effluents (Rosario-Ortiz 2008)**

<i>WWTP</i>	<i>DOC</i> ( <i>mg/L</i> )	<i>Alkalinity</i> ( <i>mg/L</i> )	$\Sigma k[S]_i \text{ (s}^{-1}\text{)} \times 10^{-5}$		
			<i>DOC</i>	<i>Alkalinity</i>	<i>Total</i>
1	8.5	224	8.2	0.4	8.6
2	6.3	178	5.8	0.3	6.1
3	6.6	133	2.5	0.2	2.7
4	6.4	131	2.5	0.2	2.7
5	11	98	9.3	0.2	9.5
6	20	222	4.5	0.4	4.9
7	8.7	161	7.7	0.3	8.0
8	7.1	206	3.6	0.4	4.0

While most rate constants are reported in units of  $M^{-1}s^{-1}$  (Buxton et al. 1988), experimental work has been done using NOM isolates, as well as humic and fulvic acids from the Suwannee river (Westeroff et al. 1998, Goldstone et al. 2002) for which rate constants are reported in units of  $L \text{ mgC}^{-1}s^{-1}$  as a result of the manner in which DOC is measured.

Rate constants of low molecular weight organics may serve to illustrate the rate constants to be expected, particularly in light of reports indicating that hydrophilic low molecular weight organics form a significant part of dissolved organic matter in biological effluents (Fujita et al. 1996, Ma et al. 2001). Table 1.6 lists several organic species with their rate constants converted to units of  $L \text{ mgC}^{-1}s^{-1}$ . The resulting rate constants are comparable to those of isolated humic substances and natural organic matter on a per carbon basis. Based on these data, a reasonable range for reactivity of organic matter with the  $OH\bullet$  radical can be taken as  $10^3 - 10^5 L \text{ mg}^{-1}s^{-1}$ .

**Table 1.6-Second order rate constants of low molecular weight organics**

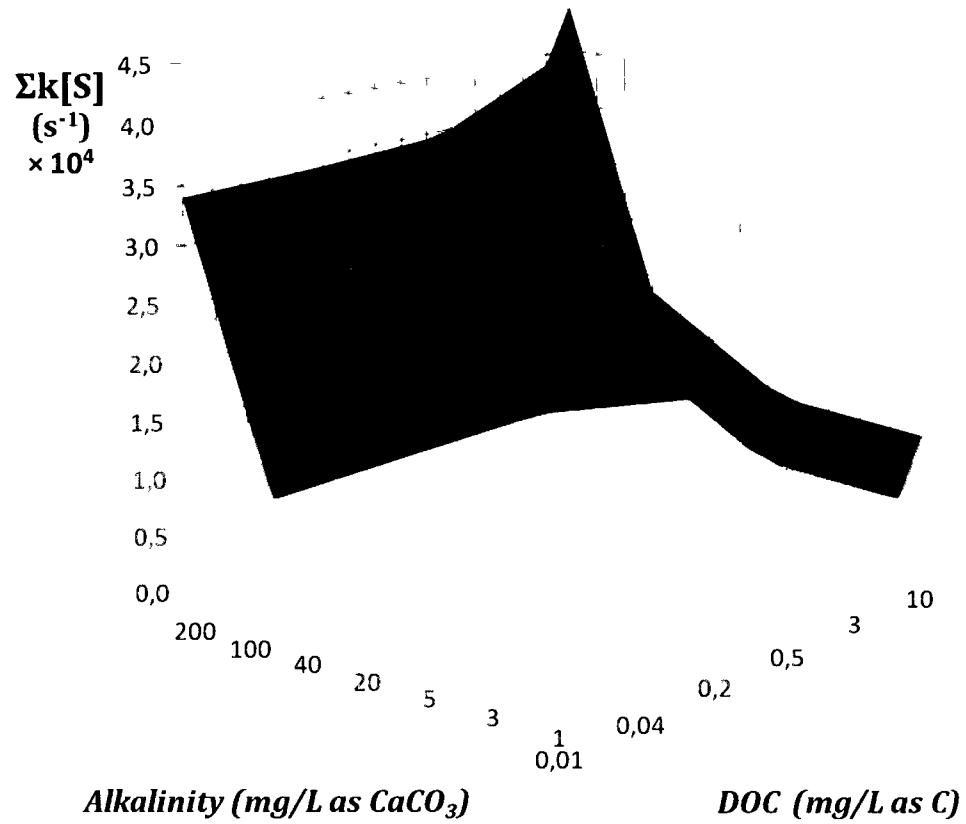
<b>Compound</b>	<b>MW g mol<sup>-1</sup></b>	<b>k<sub>OH,C</sub><sup>a</sup> M<sup>-1</sup>s<sup>-1</sup></b>	<b>k<sub>OH,C</sub> L mg C<sup>-1</sup> s<sup>-1</sup></b>
<i>acetate</i>	59	8.5 × 10 <sup>7</sup>	3.5 × 10 <sup>3</sup>
<i>formate</i>	45	3.2 × 10 <sup>8</sup>	2.7 × 10 <sup>4</sup>
<i>formaldehyde</i>	30	1.0 × 10 <sup>9</sup>	8.3 × 10 <sup>4</sup>
<i>oxalate</i>	89	7.7 × 10 <sup>6</sup>	3.2 × 10 <sup>2</sup>
<i>malonate</i>	102	3.0 × 10 <sup>8</sup>	8.3 × 10 <sup>3</sup>
<i>pyruvate</i>	87	3.1 × 10 <sup>7</sup>	8.6 × 10 <sup>2</sup>
<i>lactate</i>	89	3.0 × 10 <sup>8</sup>	8.3 × 10 <sup>3</sup>
<i>propionate</i>	73	8.2 × 10 <sup>8</sup>	2.3 × 10 <sup>4</sup>
<i>glucose</i>	180	1.5 × 10 <sup>9</sup>	2.1 × 10 <sup>4</sup>
<i>galactose</i>	180	2.0 × 10 <sup>9</sup>	2.8 × 10 <sup>4</sup>
<i>glucuronate</i>	193	3.0 × 10 <sup>9</sup>	4.2 × 10 <sup>4</sup>
<i>SR fulvic acid</i> <sup>b</sup>	-	-	2.7 × 10 <sup>4</sup>
<i>SR humic acid</i> <sup>b</sup>	-	-	1.9 × 10 <sup>4</sup>
<i>SR fulvic acid</i> <sup>c</sup>	-	-	3.1 × 10 <sup>4</sup>
<i>SR humic acid</i> <sup>c</sup>	-	-	6.8 × 10 <sup>4</sup>
<i>NOM</i> <sup>c</sup>	-	-	3.0 × 10 <sup>4</sup>

<sup>a</sup> Buxton et al. 1988, <sup>b</sup> Goldstone et al. 2002, <sup>c</sup> Westerhoff et al. 1999.

SR = Suwannee River

In order to visualize the effect of alkalinity, DOC, and the reactivity of the DOC on scavenging capacity, a series of plots are shown in Figures 1.2 -1.4. The regions on the plots associated with RO permeates include DOC amounts less than 0.5 mg/L, (Qin et al. 2005, Public Utilities Board of Singapore 2010) and alkalinity amounts less than 10 - 20 mg/L as CaCO<sub>3</sub> (Glucina et al. 2000, Padilla et al. 2010).

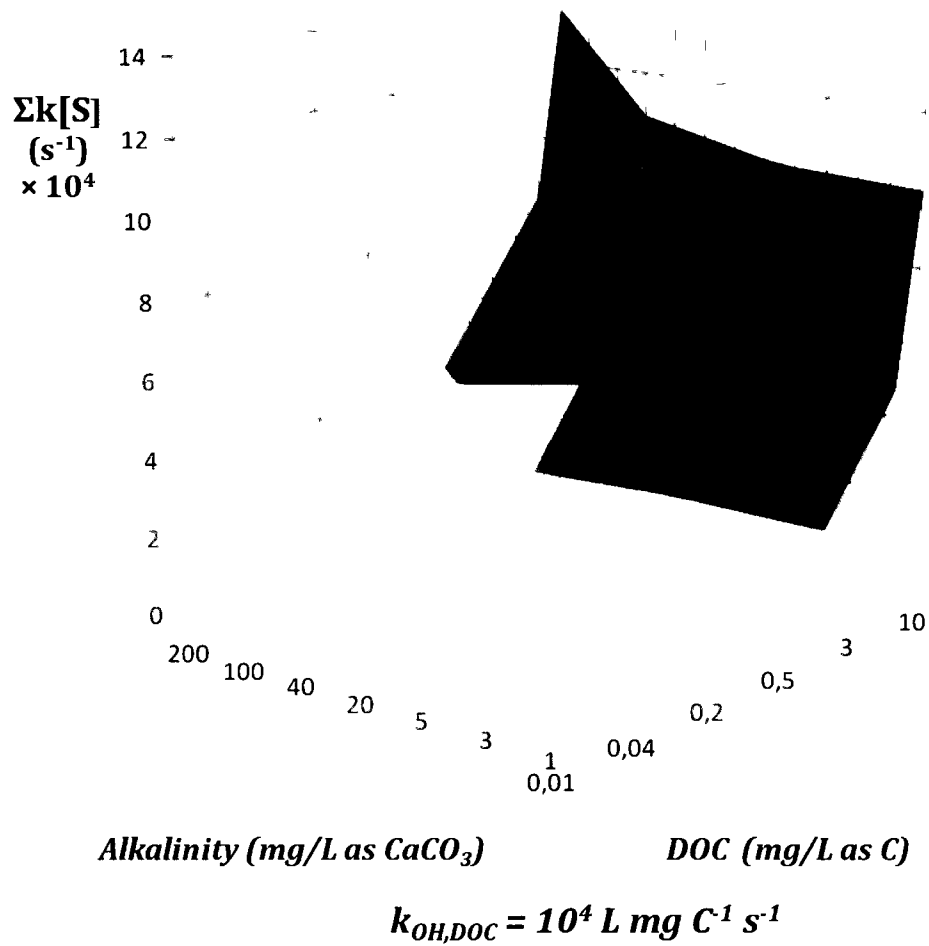
**Figure 1.2-Contribution to hydroxyl scavenging  $\Sigma k[S]_i$  from alkalinity and dissolved organic carbon at pH 7 and  $k_{OH,DOC} = 10^3 L mg C^{-1} s^{-1}$**



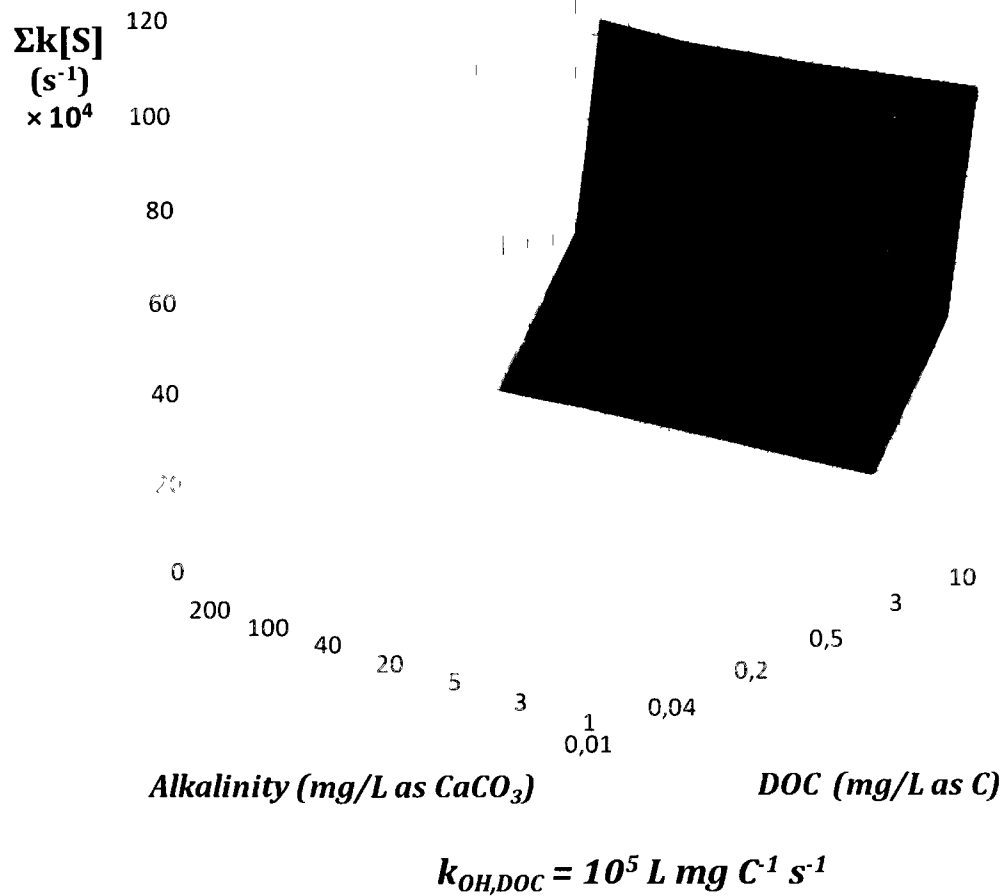
$$k_{OH,DOC} = 10^3 L mg C^{-1} s^{-1}$$



**Figure 1.3-Contribution to hydroxyl scavenging  $\Sigma k[S]_i$  from alkalinity and dissolved organic carbon at pH 7 and  $k_{OH,DOC} = 10^4 L mg C^{-1} s^{-1}$**



**Figure 1.4-Contribution to hydroxyl scavenging  $\Sigma k[S]_i$  from alkalinity and dissolved organic carbon at pH 7 and  $k_{OH,DOC} = 10^5 \text{ L mg C}^{-1} \text{ s}^{-1}$**

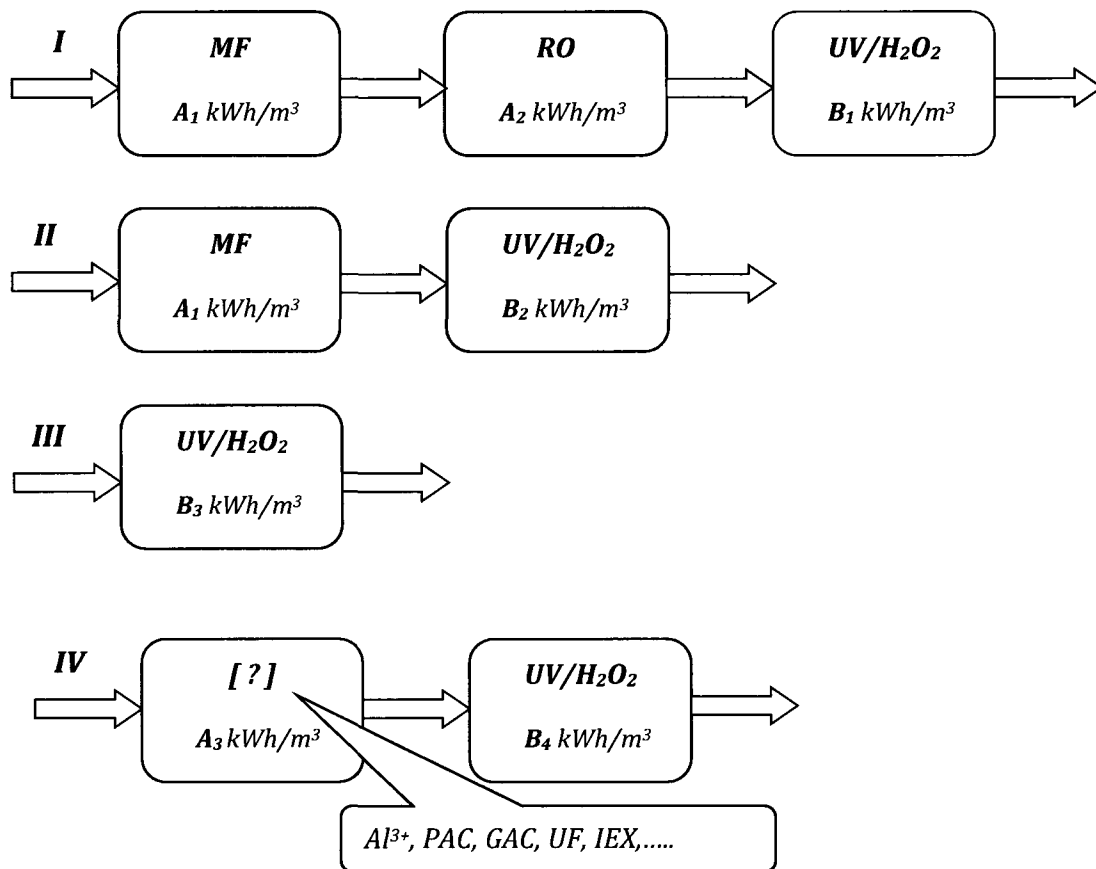


The importance of alkalinity on the scavenging capacity of a water matrix is highly dependent on the reactivity of the organic matter.

## **Treatment schemes for the removal of specific contaminants**

The use of RO in the reclamation of wastewater produces an effluent quality which greatly exceeds the requirements of many applications. Disposal of the concentrate is often costly and challenging. As an additional barrier to pollutants of concern, an AOP may follow the RO process. As the rejection of organic compounds, carbonate, and bicarbonate during reverse osmosis greatly increase the efficiency of the UV/H<sub>2</sub>O<sub>2</sub> AOP, this has been an attractive combination for some reuse applications (Deshmukh 2004).. While application of the UV/H<sub>2</sub>O<sub>2</sub> AOP directly to secondary or tertiary effluents requires more energy, the cost of additional energy may be offset by the high electrical and chemical costs of RO, as well as the cost of concentrate disposal. Thus the quantification of the required energy for comparable treatment of different water matrices is practical of interest. Furthermore, as the removal of suspended solids by MF is considered part of the pretreatment to RO, the influence of MF is of interest when considering AOP applications directly upon biological effluents. These energy considerations are summarized in Figure 1.5, in treatment schemes I to III. In scheme IV, alternative pretreatments are considered, particularly those that reduce the bulk absorbance and the amount of dissolved organic matter.

**Figure 1.5-Treatment schemes and energy required for equivalent treatment with respect to a particular contaminant, i.e.  $\log(C_i/C_f)$  .**



### Effect of Suspended Solids on the UV/ H<sub>2</sub>O<sub>2</sub> AOP

The application of MF to biological effluents removes particulate matter by sieve action, typically in the size range of 0.1 – 2  $\mu\text{m}$  and larger (Tchobanoglous et al 2003). This effectively reduces the measurable amount of suspended solids to below 1 mg L<sup>-1</sup>. In the effluents of activated sludge systems, such particles consist of biological floc, composed of bacterial cell aggregates, extracellular polymeric substance (EPS) and cell remnants in a porous network (Steiner et al. 1976, Smith et

al. 1984, Andreadakis 1993). Individual floc size ranges from 1 to 100  $\mu\text{m}$  or more and is typically measured on a dry weight basis as total suspended solids (TSS).

No information could be found in the literature regarding the effect of suspended solids on scavenging of  $\text{OH}\cdot$  radicals during advanced oxidation. Given the generally diffusion limited reaction rates of  $\text{OH}\cdot$  radicals with organic compounds, it can be reasoned that at the concentration of organics found in wastewater, that the  $\text{OH}\cdot$  radical diffuses a distance of the order of 0.01 to 1  $\mu\text{m}$  (Turchi et al. 1990). Thus, only those radicals generated within the immediate vicinity of the floc are affected by the presence of suspended solids. For the range of TSS found in conventional secondary effluent, the fractional volume occupied by floc is negligible compared to the volume of the bulk liquid. Thus the presence of suspended solids is predicted to have no effect on the scavenging capacity of the effluent and the steady-state concentration of  $\text{OH}\cdot$  radicals will depend only on the alkalinity, dissolved organic matter concentration and reactivity. In such a case, the MF process is predicted to have no effect on reducing scavenging capacity of the water. However, MF should slightly improve the UV absorbance, and thus increase the fraction of photons absorbed by  $\text{H}_2\text{O}_2$ . For cost comparison purposes, the AOP savings on lower energy and peroxide required to deliver an equally effective fluence to the microfiltrate should be compared to the additional capital and operating cost associated with the microfiltration process.

## CHAPTER II: MATERIALS AND METHODS

### Experimental Design

The research question of this work is:

Does the removal of suspended solids from biologically treated wastewater effluent improve the removal efficiency of organic pollutants by the UV/H<sub>2</sub>O<sub>2</sub> AOP?

To answer this question, bench scale studies were made of actual wastewater samples using a collimated beam apparatus and the use of the OH• radical probe compound, para-chlorobenzoic acid (pCBA). Treatment of unfiltered and microfiltered samples were made to measure the impact of suspended solids on treatment.

Wastewater samples were obtained from three wastewater treatment plants (WWTPs) in the city of London Ontario Canada during discreet sampling events on the same day. Two WWTPs (Pottersburg and Adelaide) use conventional activated sludge treatment and the third plant (Oxford) is a retrofitted membrane bioreactor (MBR). Grab samples were collected following clarification and prior to disinfection for all three plants.

Samples from the conventional plants were used to produce microfiltered samples in the lab. This resulted in five distinct water matrices available for study; two conventional secondary effluents, their corresponding microfiltrates, and the MBR effluent.

These five waters were immediately characterized for total suspended solids (TSS), chemical oxygen demand (COD), dissolved organic carbon (DOC), alkalinity, and UV absorbance at 254 nm ( $A_{254}$ ). Samples were then stored in brown glass bottles at 4°C till use. The probe compound pCBA was spiked into the aliquots of the samples prior to UV/H<sub>2</sub>O<sub>2</sub> treatment.

All five waters were tested in triplicate using the same collimated beam procedure to quantify the removal of pCBA with time. Dark reactions were simultaneously monitored for all subsamples. With TSS < 1 mg/L for microfiltered samples, a two level factorial experiment was performed with TSS as the factor. The treatment plants are treated as experimental blocks, with the MBR permeate available for comparison.

The measured removal of pCBA with time at a known H<sub>2</sub>O<sub>2</sub> concentration was used to calculate the steady-state OH• concentration  $[OH•]_{ss}$ . The  $[OH•]_{ss}$  and other known quantities are used to calculate the scavenging capacity  $\sum k_i[S]_i$ . The rate constant for the probe compound removal, as well as the calculate scavenging for each water matrix are the experimental responses to be compared.

Using a standardized collimated beam apparatus, it is possible to calculate the *UVE/O* for pCBA removal in each of the five waters serving as an additional response and a useful parameter to use in making comparisons in engineering terms.

### **Sampling and Sample Preparation**

Ten liter grab samples were gathered in autoclaved carboys, after rinsing in the water to be collected. Samples from all three plants were taken between 11am and 1pm on August 4<sup>th</sup> 2009, with no influence of storm events effecting plant operations.

Samples were transported to the lab and approximately 3 liters of microfiltrate was produced by vacuum filtration using prewashed 0.22  $\mu\text{m}$  nominal pore-size nylon filter pads (Millipore GNWP) in 50 ml portions. Each filter pad was prewashed with approximately 200 ml of deionized water prior to use. Including microfiltrates for Pottersburg and Adelaide effluents, approximately 2 liters of each of the five waters was stored at 4°C.

Samples of all five waters were measured for COD, DOC, and  $A_{254}$ . Microfiltrates were not tested for TSS or alkalinity, as microfiltration was found to produce TSS values below the detection abilities of the TSS test (<1mg/L). Tests also found that microfiltration did not affect any measureable change in alkalinity or pH.

A 100 ml aliquot of each sample was produced with a spike of pCBA stock solution to produce the appropriate initial probe compound concentration (400 to 500 ppb).



The sample was allowed to equilibrate to room temperature before addition of H<sub>2</sub>O<sub>2</sub> and the initiation of collimated beam experiments.

## **Wastewater Characterization**

### ***Chemical Oxygen Demand***

The chemical oxygen demand (COD) of each of the five experimental waters was measured in duplicate using the colorimetric method with the Hach COD heating block, Hach DR 2000 Spectrometer, and premade COD reagent vials for the ultralow COD range (0-100mg/L). Phthalic acid stock solution was used as a COD standard and ultrapure MilliQ water was used for COD blanks.

### ***Total Suspended Solids***

The total suspended solids (TSS) of the unfiltered and the MBR effluents were measured using Standard Method 2540 with 500ml of sample and 1µm nominal pore size filters (Fischer Scientific CG) prewashed with deionized water and dried in an oven at 100C°. The TSS measurements were performed in triplicate. It was found that the microfiltrates produced water with TSS values less than 1mg/L. The MBR effluent was also found to be free of measureable TSS.

### ***Dissolved Organic Carbon***

Dissolved organic carbon (DOC) was measured using the Shimadzu TOC analyzer after filtering all samples through 0.22µm nominal pore size filters. The analyzer uses the UV persulfate method of Standard Method 5310. Due to the potential incompatibility of particulate matter with the instrument, the TOC of the samples was not measured.

### ***Alkalinity***

Alkalinity was measured using Standard Method 2320 for raw effluents gathered from all three WWTPs. Confirmation was made that microfiltration in the lab did not alter the alkalinity or pH of the sample. Standard 0.2 N sulfuric acid was diluted in MilliQ water to 0.02 N and used to titrate 100 mL of sample to a pH of 4.5. The sample being titrated was kept mixed by a magnetic mixer and the pH was monitored using a pH meter (Oakton Vernon Hills II) suspended in the liquid. Titrations were performed in triplicate for each of the three effluents and the results reported in mg/L as CaCO<sub>3</sub>.

### ***Measurement of H<sub>2</sub>O<sub>2</sub>***

The measurement of H<sub>2</sub>O<sub>2</sub> was performed by the triiodide method (Klassen et al. 1994). Reagents were added to 1ml of sample and after a time of approximately 60 seconds, the resulting I<sub>3</sub><sup>-</sup> was measured spectrophotometrically at 351 nm (Hach DR 5000). Laboratory grade H<sub>2</sub>O<sub>2</sub> solution of 30% w/w (Sigma Aldrich) was kept at 4C° and used for all experiments after proper dilution in sample or ultrapure water. Ultrapure MilliQ water was used for all sample blanks.

### **Measurement of para-Chlorobenzoic Acid**

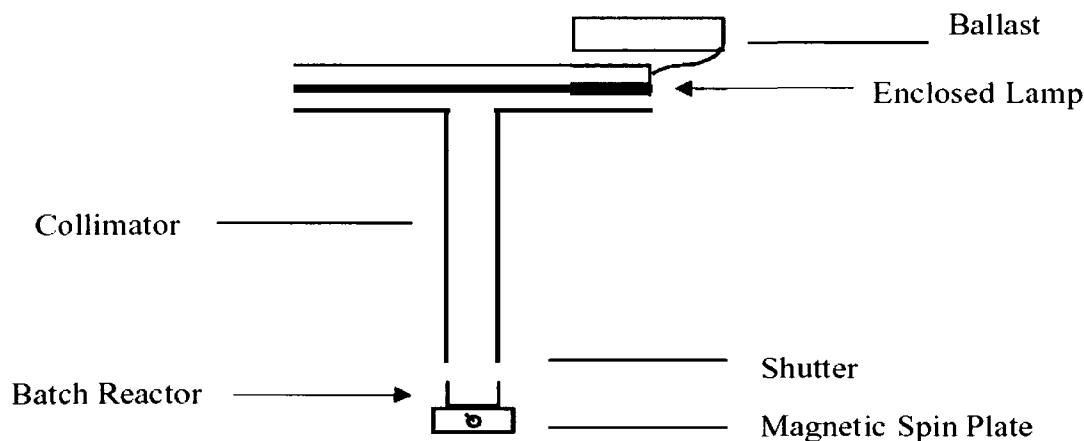
Measurement of the OH• radical probe compound para-chlorobenzoic acid (pCBA) was performed using reverse phase HPLC with UV photodetection (Waters Millford MA) and using a 25 cm long C18 column (Sigma Aldrich). Isocratic elution was performed using a mobile phase composition of 48 % acetonitrile and 52% water acidified to pH 2 with phosphoric acid. The HPLC grade acetonitrile was obtained from Caledon Chemicals (Mississauga ON). The mobile phase was made using MilliQ

water. Detection of pCBA was performed at 238 nm. Peak curve area was used to quantify pCBA concentration. Calibration curves were obtained using dilutions of stock lab grade pCBA solution. Wastewater samples to be analyzed for pCBA following collimated beam treatment were microfiltered with 0.22 micron filters (Millipore) directly into 1ml HPLC sample vials and placed in the refrigerator until the time of analysis, at most 3 hours from the time of sampling.

### Collimated Beam Apparatus and Experiments

A low pressure high output mercury amalgam lamp (Heraeus Hanau Germany) was used to produce a quasi-collimated beam apparatus according to procedures described in detail elsewhere (Bolton et al. 2003). The samples to be irradiated were placed in 5.5 cm inner diameter recrystalization dishes on a magnetic stir plate and adjustable jack stand, placed at the center of a collimating tube below the lamp housing (see Figure 2.1).

**Figure 2.1 - Collimated beam apparatus**



In order to accurately determine the fluence delivered to a liquid sample irradiated by the collimated beam, the central irradiance of the beam at the liquid surface must be measured and several calibration factors must be determined. These include factors to compensate for the non-uniformity of the irradiance across the irradiated liquid surface (Petri Factor), loss of energy due to reflection at the liquid surface (Reflection Factor), spatial spreading of the beam with depth of penetration (Divergence Factor), and the attenuation of light with depth of penetration due to absorbance (Water Factor), described in detail elsewhere (Bolton et al. 2003).

The irradiance of the collimated lamp light at 254nm was measured using a calibrated IL-1700 radiometer (International Light Peabody MA) with 230E detector, and with the calibration plane of the detector placed at the intended height of the liquid surface.

The scavenging capacity of a wastewater sample was measured as follows. An aliquot of 100 ml of sample was taken from refrigerated storage, placed in a volumetric flask and allowed approximately 20 minutes to equilibrate to room temperature. Known volumes of stock pCBA and  $H_2O_2$  solutions were delivered to the sample using calibrated micropipettes and mixed. Approximately 0.8mL of this sample was placed in an HPLC vial in order to measure the initial pCBA concentration actually obtained. The initial  $H_2O_2$  concentration and absorbance was measured. As  $H_2O_2$  contributes to the absorbance, the absorbance of the sample should be measured after  $H_2O_2$  addition for the purposes of accurate fluence calculation. The sample is divided between two recrystallization dishes. One dish will

be irradiated with the collimated beam and one dish will be stirred in absence of UV irradiation in order to monitor any dark reactions. The depth of the liquid in the irradiated dish is recorded. A timer is used to mark the start of the irradiation and approximately 0.8 ml samples are withdrawn from each dish by pipette at approximately 10 minute intervals until the end of the irradiation. Each sample is placed in a labeled HPLC vial. The peak area of the pCBA chromatograph at 238 nm is used to compute the concentration of pCBA for each time corresponding to dark and light reactions. At the end of the irradiation, the final absorbance and  $H_2O_2$  concentration is calculated for both light and dark reactions. The procedure is repeated in triplicate for each wastewater for which the scavenging term is to be determined.

### **Data Analysis**

Using the measured irradiance and calculated collimated beam calibration factors, the fluence delivered to each sample can be calculated. Using the HPLC calibration curve for pCBA, the concentration of the probe compound can be calculated at each sampling time for both light and dark reactions. Assuming pseudo-first order kinetics and steady-state conditions for the  $OH\cdot$  radical,  $[OH\cdot]_{ss}$  is calculated from the slope of each curve. The scavenging term corresponding to each pCBA curve is computed by a curve fitting optimization routine using the Excel solver and the theoretical expression relating  $[OH]_{ss}$  with scavenging and measured parameters.

## Preliminary- Experiments and Qualitative Observations

Before beginning collimated beam experiments, it was of interest to know whether significant removal of trace organic pollutants from unfiltered secondary effluents could be observed with this method using reasonable irradiation times and  $\text{H}_2\text{O}_2$  doses. The laboratory grade pharmaceutical acetaminophen (Sigma-Aldrich) was spiked into freshly collected secondary effluents from the Pottersburg WWTP, and dosed with 10 mg/L of  $\text{H}_2\text{O}_2$  before being irradiated for one hour under the collimated beam. The initial and final concentrations of acetaminophen were measured using liquid chromatography with UV detection at 230 nm and all other conditions equivalent to those described for measurement of the probe compound pCBA. Removal of acetaminophen was approximately 30% after an irradiation time of 40 minutes.

Due to concern that  $\text{H}_2\text{O}_2$  is unstable in the presence of large amounts of organic matter, it was of interest to know whether a significant demand in the  $\text{H}_2\text{O}_2$  would be observed upon dosing in unfiltered secondary effluent, as is observed for other oxidants such as chlorine. Unfiltered and microfiltered effluent were dosed with  $\text{H}_2\text{O}_2$  at amounts on the order anticipated during actual collimated beam experiments. No instantaneous demand was observed in either microfiltered or unfiltered effluents. Over the course of 2 hours of agitation on a stir plate, the amount of  $\text{H}_2\text{O}_2$  in the microfiltered samples showed no change. The  $\text{H}_2\text{O}_2$  level in the unfiltered effluent showed a gradual decrease on a scale of 1 mg/L over the

course of three hours, after an initial dose of approximately 10 mg/L . When these effluent samples were kept in sealed flasks in the dark at 4°C for 24 hours, no change in H<sub>2</sub>O<sub>2</sub> concentration was observed in the microfiltered effluent, whereas no remaining H<sub>2</sub>O<sub>2</sub> was detected in the unfiltered sample. Since the amount of dissolved organic matter was approximately 5 mg/L in these effluents and the suspended solids were approximately 10 mg/L, the above observations suggest that amount of organic matter in the samples does not explain the difference in H<sub>2</sub>O<sub>2</sub> stability. These observations may be explained by higher reactivity of organic matter in suspended solids towards H<sub>2</sub>O<sub>2</sub> relative to the reactivity of dissolved organic matter for H<sub>2</sub>O<sub>2</sub>, or by the presence of inorganic impurities in suspended solids that are catalytically active in the decomposition of H<sub>2</sub>O<sub>2</sub>.

**Scattering:** In order to determine the fluence (UV dose) provided to a particular water matrix, accurate knowledge of the matrix absorbance is required. It has been shown that for high levels of suspended solids, significant scattering of light at UV wavelengths take place, thus increasing the apparent absorbance when standard single pass spectrophotometers are used (Linden et al. 1998; Mamane et al. 2006). However, such scattered light is still germicidal and is still able to contribute to photolysis of H<sub>2</sub>O<sub>2</sub> and chemical contaminants, and thus should be included in the calculation of fluence. Measurement of absorbance with compensation for scattered light is performed with the use of an integrating sphere. The contribution of scattering to the apparent absorbance measurement was measured for secondary effluent used in this study. A Cary 100 spectrophotometer (Varian, Palo Alto CA) mounted with an integrating sphere (Lab Sphere, North Sutton NH) was used with a

1 cm quartz cuvette placed in the center of the sphere to exclude scattered light from the absorbance measurement, and in front of the sphere, along the optical path length to the detector, in order to include the scattered light for the absorbance reading. Unfiltered secondary effluent with a TSS of approximately 10 mg/L was used. Using five replicates each, the absorbance excluding scattering was  $0.114 \pm 0.005 \text{ cm}^{-1}$  ( $77.0 \pm 0.8 \text{ \%UVT}$ ) and including scattering was found to be  $0.115 \pm 0.002 \text{ cm}^{-1}$  ( $76.7 \pm 0.4 \text{ \%UVT}$ ). No significant scattering was observed for the level of TSS used in this work ( $< 10 \text{ mg/L}$ ).

Since the measurement of the probe compound involves the use of HPLC, all unfiltered effluent samples are microfiltered using a  $0.45 \text{ }\mu\text{m}$  filter before introduction into the sample vial for injection. To verify that no significant portion of the probe compound pCBA would be removed by sorption to the suspended solids during the exposures, an experiment was performed in which approximately  $300 \text{ }\mu\text{g/L}$  pCBA was spiked into ultrapure water ( $18 \text{ M}\Omega \text{ cm}$ ),  $0.22 \text{ }\mu\text{m}$  filtered secondary effluent, and unfiltered secondary effluent with an approximate suspended solids concentration of  $10 \text{ mg/L}$ . All three water qualities were agitated on mixing plates in parallel for three hours and samples taken at intervals to measure the concentration of pCBA present. No difference in pCBA concentration was observed after agitation for several hours, regardless of the water type. From this it can be concluded that no significant loss of the probe compound occurs due to adsorption during the time span of the experiments.



## CHAPTER III: RESULTS AND DISCUSSIONS

### Wastewater Characterization

Samples collected from three London Ontario WWTPs were brought in carboys to the lab for microfiltration and analysis. All tests were performed in either duplicate or triplicate. Table 3.1 presents a summary of wastewater characteristics.

*Table 3.1-Summary of water quality parameters*

<i>Water Matrix</i>	<i>COD mg/L</i>	<i>TSS mg/L</i>	<i>DOC mg/L</i>	<i>Alkalinity mg/L<sup>a</sup></i>	<i>A<sub>254</sub>/ %T cm<sup>-1</sup></i>	<i>pH</i>
<i>CAS<sub>1</sub></i>	63	7.5	4.6	103	0.209 / 62	7.1
<i>CAS<sub>1</sub> + MF</i>	55	<1	4.6	103	0.115 / 77	7.1
<i>CAS<sub>2</sub></i>	70	10	4.9	121	0.143 / 71	7.0
<i>CAS<sub>2</sub> + MF</i>	55	<1	4.9	121	0.104 / 79	7.0
<i>MBR</i>	48	<1	4.2	38	0.127 / 75	6.7

<sup>a</sup> expressed as CaCO<sub>3</sub>.

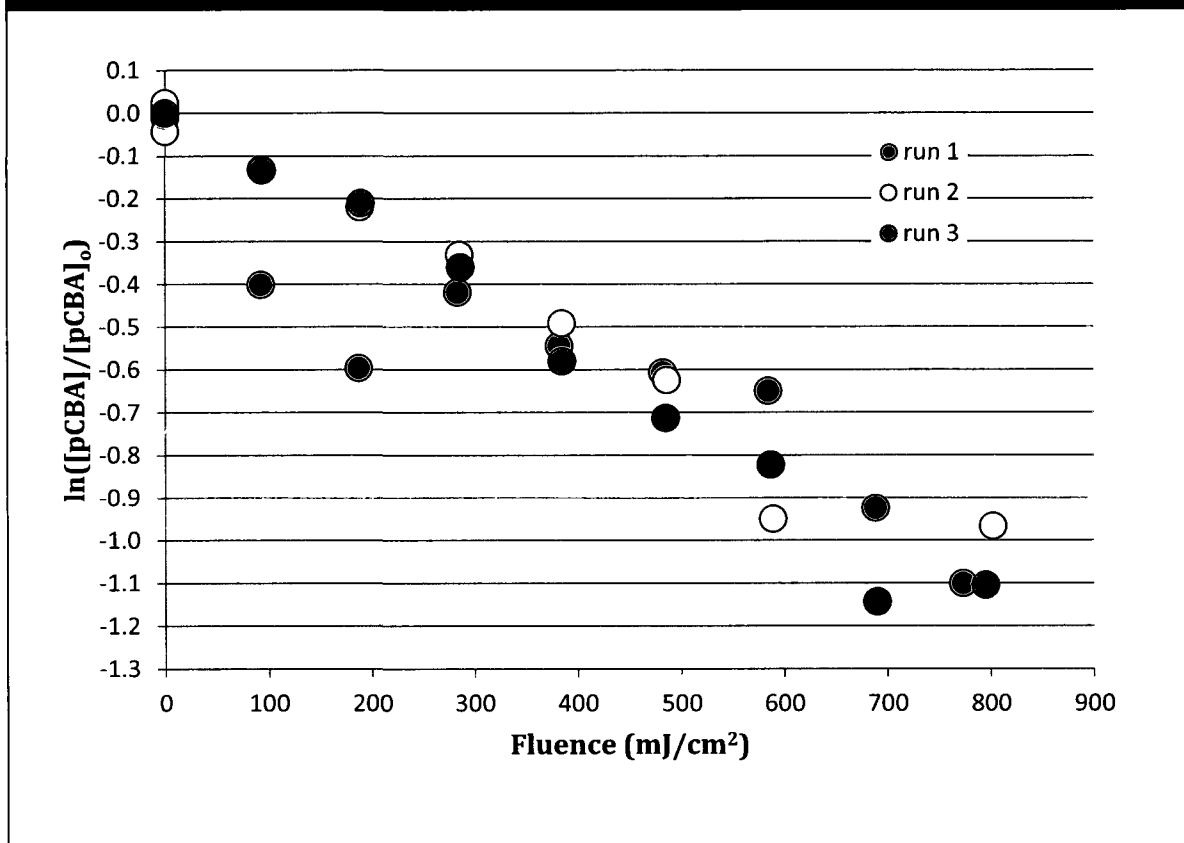
### Results of Collimated Beam Experiments

The concentration of the probe compound pCBA was monitored for all five water matrices during collimated beam experiments run in triplicate. Both light and dark reactions were monitored and raw data are tabulated in Appendix B.

**Pottersburg:** The Pottersburg Water Pollution Control Plant is a conventional activated sludge (CAS) WWTP unfiltered final effluent was subjected to the UV/H<sub>2</sub>O<sub>2</sub> by collimated beam after being dosed with approximately 13 mg/L of H<sub>2</sub>O<sub>2</sub> and being spiked with approximately 300 µg/L of pCBA. The removal of pCBA was

monitored in the sample being irradiated, and the experiments performed in triplicate. The results are presented in Figures 3.1 and Table 3.2.

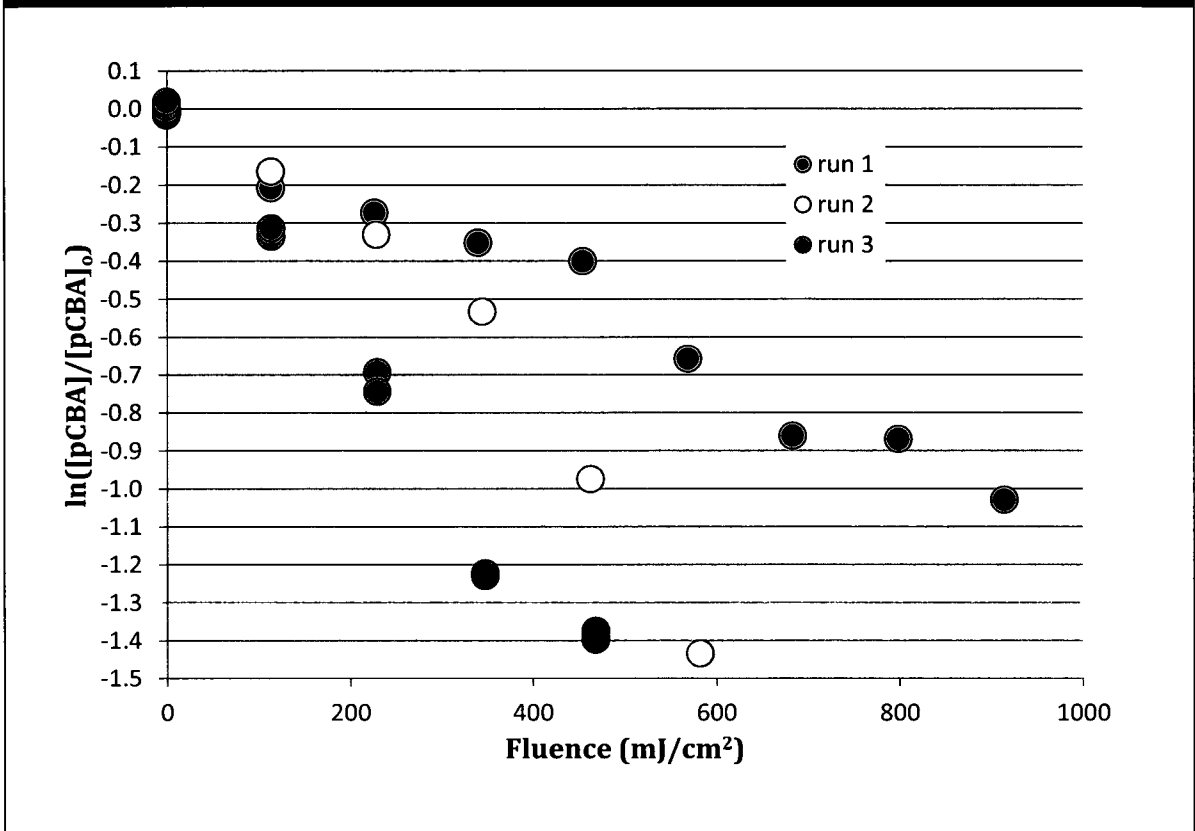
**Figure 3.1- The removal of the probe compound pCBA from unfiltered effluent from CAS<sub>1</sub> dosed with 13 mg/L H<sub>2</sub>O<sub>2</sub>.**



**Table 3.2 – First order rate constants for removal of pCBA from unfiltered secondary effluent (CAS<sub>1</sub>) for a H<sub>2</sub>O<sub>2</sub> dose of 13 mg/L**

$k_{pCBA} \times 10^{-4}$ (cm <sup>2</sup> /mJ)	run 1	run 2	run 3
Experiments	12 ± 2	15 ± 1	15 ± 1
(R <sup>2</sup> )	(0.87)	(0.96)	(0.98)
Average	14 ± 2		

**Figure 3.2- The removal of the probe compound pCBA from microfiltered effluent from CAS<sub>1</sub> dosed with 13 mg/L H<sub>2</sub>O<sub>2</sub>.**



**Table 3.3 - First order rate constants for removal of pCBA from microfiltered secondary effluent (CAS<sub>1</sub> + MF) for a H<sub>2</sub>O<sub>2</sub> dose of 13 mg/L**

$k_{pCBA} \times 10^{-4}$ (cm <sup>2</sup> /mJ)	run 1	run 2	run 3
Experiments (R <sup>2</sup> )	11 ± 1 (0.98)	23 ± 2 (0.95)	31 ± 1 (0.98)
Average	22 ± 2		

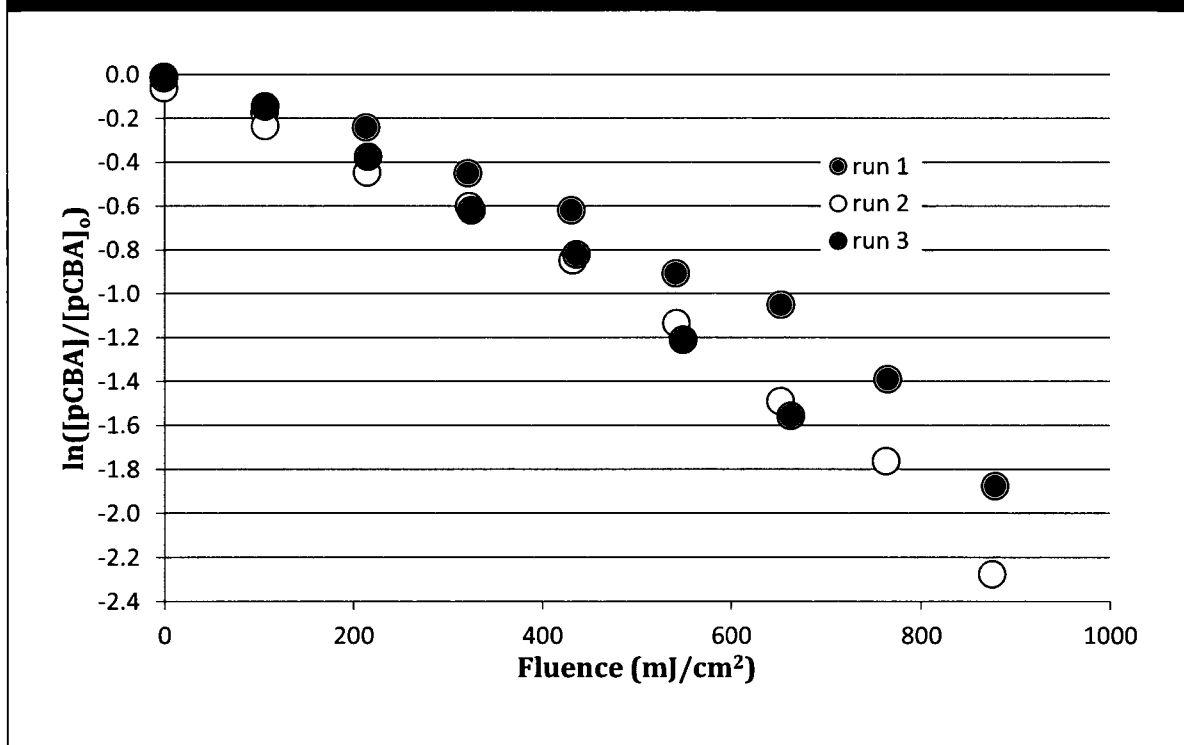
Rate constant values shown in the tables indicate the regression error for each run and their addition in quadrature for the average value.

The removal rate of pCBA can be expressed in terms of the fluence-based pseudo-first order rate constant ( $\text{cm}^2/\text{mJ}$ ).

The microfiltered effluent from Pottersburg was subjected to the same treatment as above, with the results presented in Figure 3.2 and Table 3.3.

**Adelaide:** The Adelaide WWTP final effluent was sampled on the same day and treated by the same method as the Pottersburg effluent. The unfiltered final effluent was monitored for pCBA removal as above. The results are presented in Figure 3.3 and Table 3.4 for filtered and Figure 3.4 and Table 3.5 for microfiltered samples.

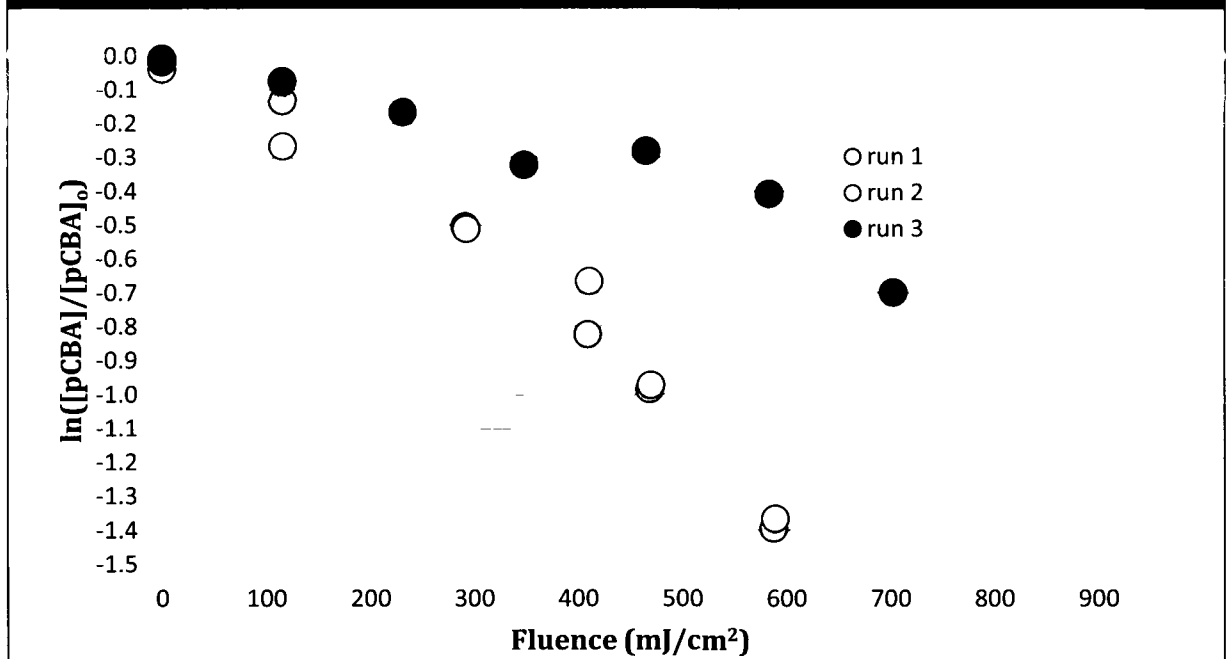
**Figure 3.3- The removal of the probe compound pCBA from unfiltered effluent from CAS<sub>2</sub> dosed with 13 mg/L H<sub>2</sub>O<sub>2</sub>.**



**Table 3.4 - First order rate constants for removal of pCBA from unfiltered secondary effluent (CAS<sub>2</sub>) for a H<sub>2</sub>O<sub>2</sub> dose of 13 mg/L**

$k_{pCBA} \times 10^{-4}$ (cm <sup>2</sup> /m)	run 1	run 2	run 3
Experiments (R <sup>2</sup> )	19 ± 1 (0.96)	29 ± 1 (0.98)	23 ± 1 (0.98)
Average	24 ± 2		

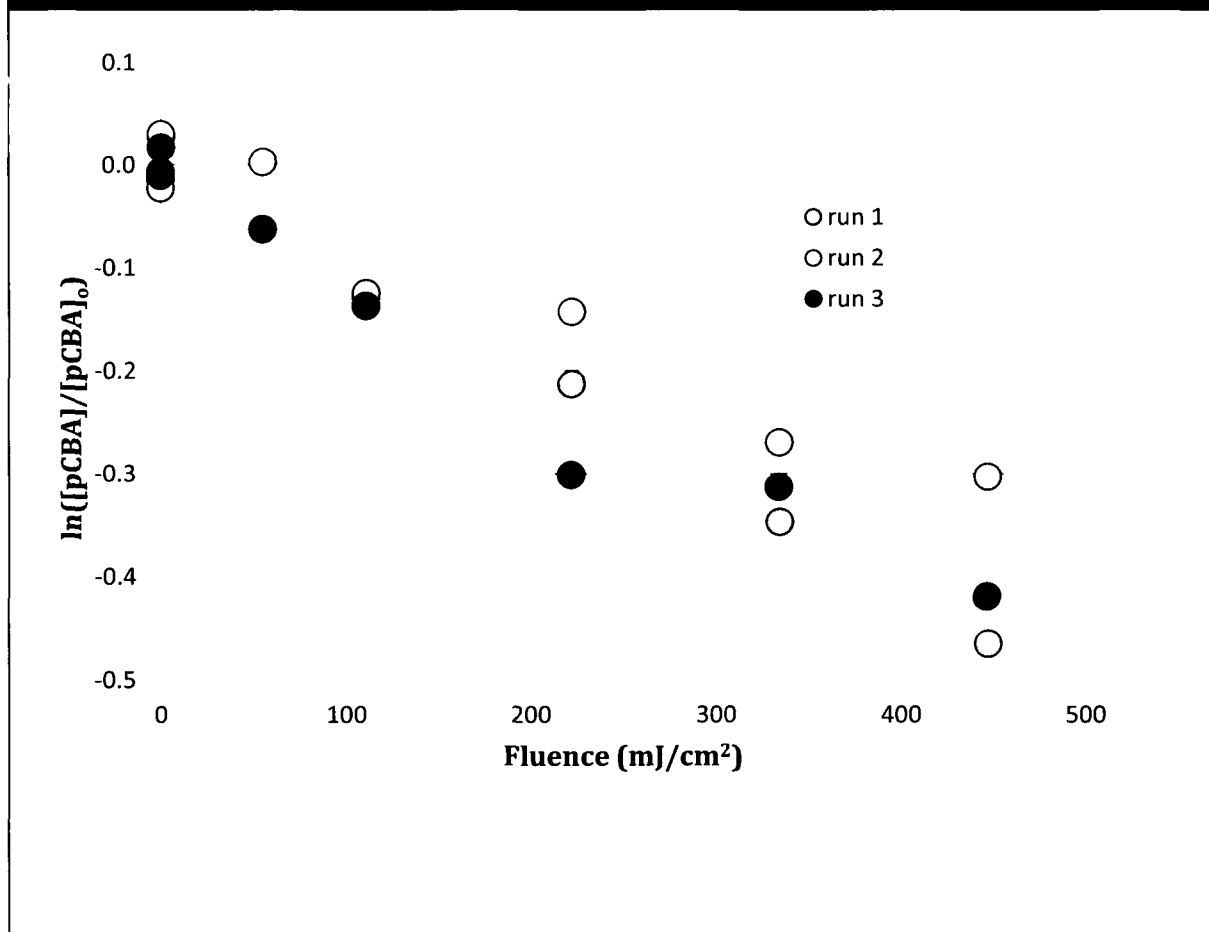
**Figure 3.4- The removal of the probe compound pCBA from microfiltered effluent from CAS<sub>2</sub> dosed with 13 mg/L H<sub>2</sub>O<sub>2</sub>.**



**Table 3.5 - First order rate constants for removal of pCBA from microfiltered secondary effluent (CAS<sub>2</sub>+MF) for a H<sub>2</sub>O<sub>2</sub> dose of 13 mg/L**

$k_{pCBA} \times 10^{-4}$ (cm <sup>2</sup> /m)	run 1	run 2	run 3
Experiments (R <sup>2</sup> )	23 ± 1 (0.99)	24 ± 2 (0.96)	9 ± 1 (0.91)
Average	18 ± 2		

**Figure 3.5- First order rate constants for removal of pCBA from membrane bioreactor permeate (MBR) for a H<sub>2</sub>O<sub>2</sub> dose of ~6.5 mg/L**



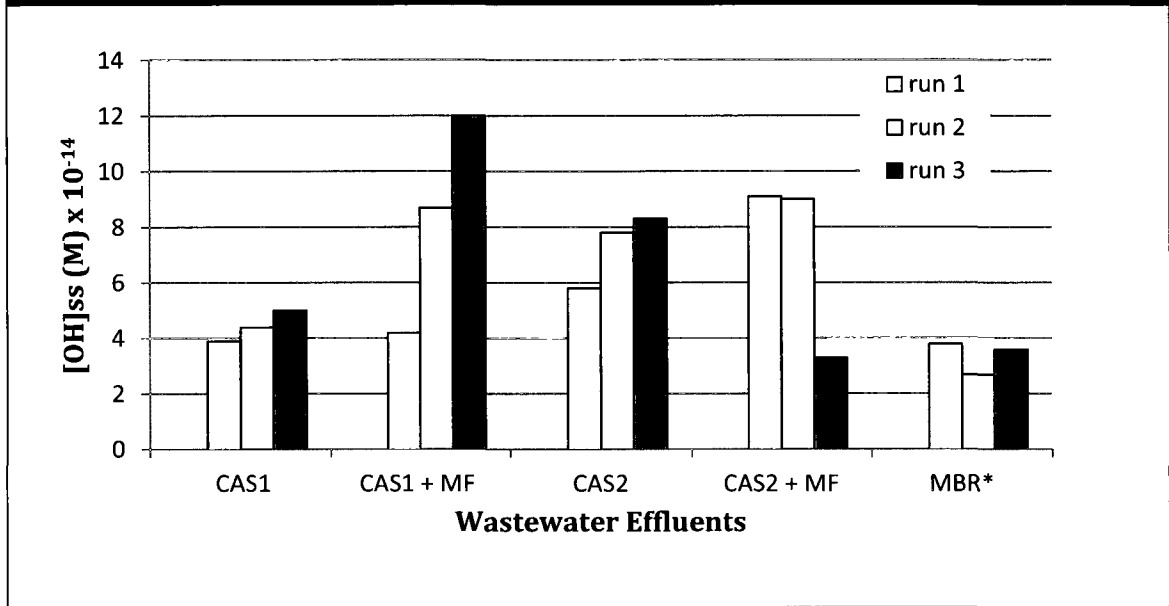
**Table 3.6 – First order rate constants for removal of pCBA from membrane bioreactor (MBR) effluent for a H<sub>2</sub>O<sub>2</sub> dose of ~6.5 mg/L**

$k_{pCBA} \times 10^{-4}$ (cm <sup>2</sup> /m)	run 1	run 2	run 3
Experiments (R <sup>2</sup> )	10 ± 1 (0.99)	7 ± 1 (0.94)	10 ± 1 (0.95)
Average	9 ± 1		

**Oxford** : The Oxford WWTP final effluent was also sampled for the same tests. The Oxford WWTP had been retrofitted one year prior to a membrane bioreactor (MBR) operation. For the collimated beam tests, the H<sub>2</sub>O<sub>2</sub> dose of 13 mg/L resulted in a rapid removal of pCBA such that only two samples could be captured on the same time scale before the concentration of pCBA decreased below the limit of quantitation (approximately 50 ppb). Thus in order to obtain sufficient data capture for the purpose OH• radical scavenging capacity, the concentration of H<sub>2</sub>O<sub>2</sub> was decreased by half to 6.5 mg/L. The results are presented in Figure 3.5 and Table 3.6.

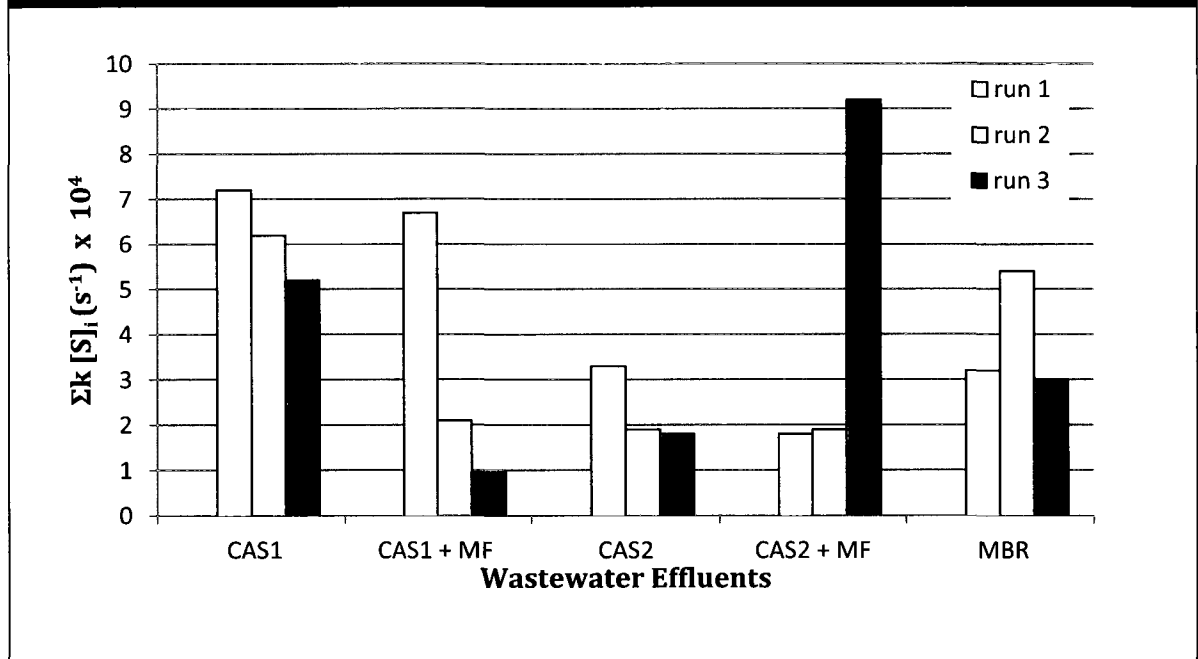
A general trend in the pCBA data observed for the two CAS effluents and their corresponding microfiltrates, are a high degree of repeatability for the experiments using CAS samples, and relatively higher amount of scatter for the microfiltrates. Because the microfiltrates were produced at one time, homogeneous subsamples are expected. No cause for this discrepancy was identified.

**Figure 3.6-Steady-state hydroxyl radical concentration measured via pCBA**



\* MBR runs used half the H<sub>2</sub>O<sub>2</sub> dose.

**Figure 3.7- Hydroxyl radical scavenging measured via pCBA**



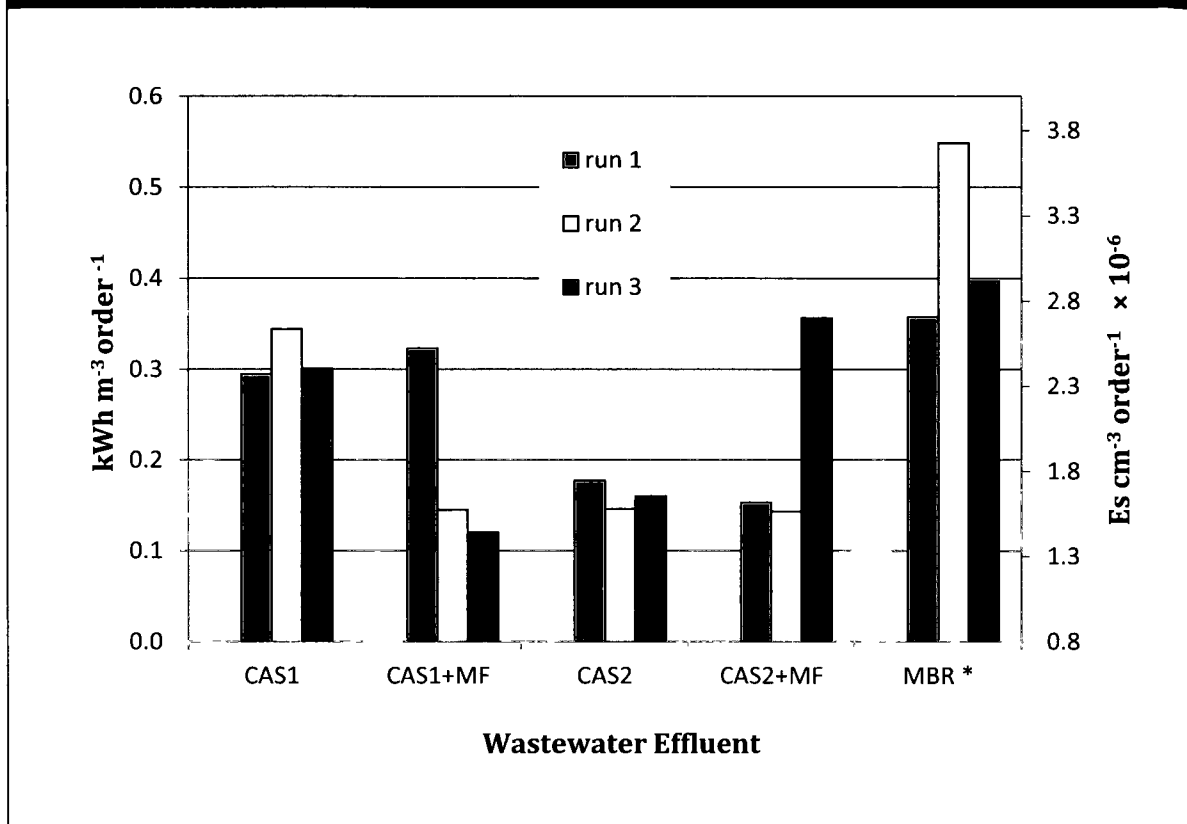


**Table 3.7 - Estimates of hydroxyl radical scavenging and contribution due to alkalinity**

<i>Water matrix</i>	<i>Alkalinity (mM HCO<sub>3</sub><sup>-</sup>)</i>	$\Sigma k_i[S]_i^a$ (s <sup>-1</sup> ) × 10 <sup>4</sup>	$k[\text{HCO}_3^-] / \Sigma k_i[S]_i$
<b>CAS<sub>1</sub></b>			
<i>Run1</i>	2.1	7.2	0.25
<i>Run2</i>	2.1	6.2	0.29
<i>Run3</i>	2.1	5.2	0.35
<b>Average</b>		<b>6.2</b>	<b>0.29±0.05</b>
<b>CAS<sub>1</sub> + MF</b>			
<i>Run1</i>	2.1	6.7	0.27
<i>Run2</i>	2.1	2.1	0.86
<i>Run3</i>	2.1	0.96	1.88
<b>Average</b>		<b>3.3</b>	<b>0.99±0.81</b>
<b>CAS<sub>2</sub></b>			
<i>Run1</i>	2.4	3.3	0.64
<i>Run2</i>	2.4	1.9	1.11
<i>Run3</i>	2.4	1.8	1.17
<b>Average</b>		<b>2.3</b>	<b>0.94±0.28</b>
<b>CAS<sub>2</sub> + MF</b>			
<i>Run1</i>	2.4	1.8	1.17
<i>Run2</i>	2.4	1.9	1.11
<i>Run3</i>	2.4	9.2	0.23
<b>Average</b>		<b>4.0</b>	<b>0.81±0.51</b>
<b>MBR</b>			
<i>Run1</i>	0.8	3.2	0.20
<i>Run2</i>	0.8	5.4	0.12
<i>Run3</i>	0.8	3.0	0.22
<b>Average</b>		<b>3.9</b>	<b>0.19±0.05</b>

<sup>a</sup> total scavenging including bicarbonate

**Figure 3.8- Estimates of specific UV Energy per order of probe compound pCBA (UVE/O) under irradiation at 254 nm.**



Based on the alkalinity values and the pH, the carbonate species concentrations may be determined and their contribution to the scavenging estimated. At the pH of the samples, the carbonate concentration can be assumed zero and the alkalinity composed entirely of bicarbonate. The second order hydroxyl radical rate constant for HCO<sub>3</sub><sup>-</sup> is 8.5x10<sup>6</sup> M<sup>-1</sup>s<sup>-1</sup>. The scavenging contributed by HCO<sub>3</sub><sup>-</sup> is shown in Table 3.7 in relation to the observed total scavenging in each run.

**Table 3.8-Summary of results (average  $\pm$  standard deviation, n=3)**

<b>Water Matrix</b>	<b><math>k_{pCBA}</math> (<math>\text{cm}^2/\text{mJ}</math>) <math>\times 10^{-4}</math></b>	<b><math>[\text{OH}]_{ss}</math> (<math>\text{M}</math>) <math>\times 10^{-13}</math></b>	<b><math>\Sigma k[S]_i</math> (<math>\text{s}^{-1}</math>) <math>\times 10^4</math></b>	<b>UVE/O <sup>a,b</sup> (<math>\text{kWh m}^{-3} \text{ order}^{-1}</math>)</b>
<b>CAS1</b>	<b><math>13 \pm 2</math></b>	<b><math>4.4 \pm 0.6</math></b>	<b><math>6 \pm 1</math></b>	<b><math>0.31 \pm 0.04</math></b>
<b>CAS1+MF</b>	<b><math>22 \pm 1</math></b>	<b><math>8 \pm 4</math></b>	<b><math>3 \pm 1</math></b>	<b><math>0.2 \pm 0.1</math></b>
<b>CAS2</b>	<b><math>22 \pm 2</math></b>	<b><math>7 \pm 1</math></b>	<b><math>2.3 \pm 0.8</math></b>	<b><math>0.21 \pm 0.05</math></b>
<b>CAS2+MF</b>	<b><math>19 \pm 9</math></b>	<b><math>7 \pm 3</math></b>	<b><math>4 \pm 4</math></b>	<b><math>0.2 \pm 0.1</math></b>
<b>MBR</b>	<b><math>9 \pm 2</math></b>	<b><math>3.4 \pm 0.6</math></b>	<b><math>4 \pm 1</math></b>	<b><math>0.4 \pm 0.1</math></b>

<sup>a</sup> relative to pCBA

<sup>b</sup>  $\text{H}_2\text{O}_2$  dose halved for MBR experiments

## Discussion

Reviewing the results presented in Tables 3.7 and 3.8, a few comments can be made. A means comparison of the UVE/O of filtered and unfiltered results via the t-test shows no statistical difference at the 95% confidence interval. With  $n=3$  for each matrix, means comparisons are expected to have low sensitivity to actual differences. But based on physical arguments presented earlier, the removal of suspended solids is not expected to produce a substantial difference in scavenging capacity and thus efficiency of the UV/ $\text{H}_2\text{O}_2$  AOP for biological effluents. The amount of suspended solids in the typical range observed in actual effluents does not appear to substantially increase the scavenging of  $\text{OH}\cdot$  radicals, though the slight increase in UV absorbance caused by floc does increase the amount of energy required to produce the same fluence. Thus the minor effect of UV absorbance on the AOP efficiency may be observed if more sensitive experiments are performed.

The total observed scavenging of the various waters tested show values consistent with Figures 1.3 and 1.4, namely that the reactivity of the effluent organic matter should be on the order of  $10^3$ - $10^4$  L mg<sup>-1</sup> s<sup>-1</sup>. This is also consistent with the rate constants expected for a number of typical low molecular weight organic compounds in wastewater listed in Table 1.6.

Alkalinity is a significant contribution to scavenging in all five water matrices. In particular, alkalinity dominates the scavenging in both effluents of the CAS<sub>2</sub> plant. Since the DOC of this plant is comparable to the others, the possibility that the reactivity of the DOC in this effluent is lower than the others cannot be excluded. In the case of the MBR effluent, for which alkalinity was low, the scavenging is comparable to the other effluents, suggesting the possibility that the soluble organic material from the MBR is of higher reactivity.

It has been reported elsewhere that the observed OH scavenging of wastewater is a function of molecular weight distribution of organic matter, with the most reactive fraction being that with molecular weight less than 1kDa (Dong et al. 2010). The EfOM of the MBR plant sampled may have a significantly different molecular weight distribution as compared to the other two conventional plants.

Additionally, nitrite has a high reactivity with OH radicals,  $1.0 \times 10^{10}$  L mol<sup>-1</sup> s<sup>-1</sup> (Buxton et al. 1988), but was not measured in this study. It is highly likely that significant differences in degree of nitrification existed between the plants at the time of sampling, with consequently varying amounts of nitrite in the effluent. For scavenging values on the order of  $10^4$  s<sup>-1</sup>, a nitrite concentration of 0.01 mg/L would

contribute approximately 10% of the observed scavenging. Thus, OH scavenging may be very sensitive to nitrite concentrations, particularly in the absence of denitrification. Future studies of AOP in wastewater should account for possible contribution of scavenging by nitrite. However, it is known that nitrite is readily oxidized to nitrate by chlorine during disinfection of wastewater, and that a chlorine residual forms only after the stoichiometric nitrite demand has been met (Snoeyink et al. 1980). The same may be true of the oxidation of nitrite by hydrogen peroxide. It has been reported that during the application of the Fenton reaction to landfill leachate, that the hydrogen peroxide alone was able to oxidize nitrite to nitrate (Kang et al. 2000).

The annual performance reports for the year 2009 for the wastewater treatment plants used in this study have been made available by the City of London Ontario on the World Wide Web (City of London Sewage Treatment 2010). Weekly measurements were made for ammonia, nitrate, and alkalinity in the effluents of the three plants. The trends seen in the period from July to October 2009 confirm the possibility of varying degrees of nitrification. The effluent ammonia levels were all within 0.001 to 0.008 mg-N/L. The nitrate levels at CAS1 (Pottersburg) and CAS2 (Adelaid) averaged around 10 and 15 mg-N/L respectively. The MBR plant (Oxford) had the highest average nitrate value at about 25 mg-N/L between July and October, and also the lowest ammonia effluent value of 0.001 mg-N/L. These differences in nitrification were further confirmed by the average alkalinity values for Pottersburg, Adelaid, and Oxford, being 100, 120, and 40 mg/L as CaCO<sub>3</sub> respectively. Thus, while nitrite levels were not reported, it is likely that the nitrite concentration in the fresh

effluent may have been in the range of 0.01 to 1 mg-N/L. Were effluent nitrite not oxidized to nitrate by hydrogen peroxide, it would likely have had a significant effect on the OH radical concentration during the application of the AOP.

If the removal of a target contaminants by the UV/H<sub>2</sub>O<sub>2</sub> AOP is not influenced by suspended solids, then the filtration unit process may be freely relocated elsewhere in the treatment scheme. For example, filtration may take place following the AOP, possibly utilizing biologically active filtration in order to further oxidize more biodegradable products from the AOP.

## CHAPTER IV: CONCLUSIONS AND RECOMMENDATIONS

Some remarks can be made.

1. Removal of trace organic pollutants was observed after direct application of UV/H<sub>2</sub>O<sub>2</sub> to biological effluents under bench-scale collimated beam conditions.
2. No significant effect could be observed for the influence of suspended solids (< 10 mg/L ) on AOP efficiency during the applied treatments under bench scale conditions.
3. Observed scavenging in effluent wastewater samples from three plants appear to involve both dissolved organic matter and alkalinity. The degree of influence of these two factors differs in the three waters, with some waters appearing to be dominated by alkalinity or possibly an unknown parameter.

Recommendations:

1. Assess treatment of water sampled from reuse facilities using MF, UF, RO processes and comparing the energy cost of target compound removal in terms of EE/O.
2. Gather energy consumption or electrical cost data from such facilities as the Orange County Ground Water Replenishment System for various unit

processes (MF and RO) to better quantify the improvement in water quality and scavenging from the perspective of the AOP.

3. Test the influence of reduction of UV absorbance and removal of low molecular weight organic acids by physical chemical methods prior to UV/H<sub>2</sub>O<sub>2</sub>
4. Perform life cycle analysis of both UV/H<sub>2</sub>O<sub>2</sub> AOP and ozonation of wastewater effluents, including cost of bromate mitigation.
5. Compare production of nitrogenous disinfection byproducts by both UV/H<sub>2</sub>O<sub>2</sub> and ozonation of wastewater effluents.
6. Test treatability of compounds found to have higher reactivity with the bicarbonate radical and confirmation that the alkalinity does not impede this process.



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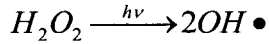
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## APPENDIX A: DERIVATION OF IMPORTANT EQUATIONS

### Photolysis of H<sub>2</sub>O<sub>2</sub> reaction



Peroxide molecules are split by photons of 254 nm, with a quantum yield of  $\Phi = 1$ , half the theoretical amount due to the cage effect.

### Photonic irradiance or Beer-Lambert law (Es/cm<sup>2</sup> s)

$$I = I_o e^{-\alpha'x}$$

This expression relates the remaining photonic irradiance  $I$  after traversing a distance  $x$  through a medium of absorptivity of  $\alpha'$ , with an initial photonic irradiance  $I_o$  at the lamp to liquid interface. The rate of decrease of the photonic irradiance  $I$  with distance  $x$  traversed into the liquid equals the rate of photonic absorption per volume  $I_a$  from the lamp-air-liquid interface to the point  $x$ .

### Rate of photon absorption per volume of liquid at distance $x$ from the lamp-liquid interface (Es / cm<sup>3</sup> s)

$$I_a = -\frac{dI}{dx} = \alpha' I_o e^{-\alpha'x}$$

### Volume rate of photolysis of H<sub>2</sub>O<sub>2</sub> from liquid interface to position $x$ in the liquid.

$$r_x = -\phi \cdot f \cdot I_a$$

$$r_{avg,\ell} = \frac{\int_0^\ell r_x dx}{\int_0^\ell dx} = \frac{1}{\ell} \int_0^\ell r_x dx = -\frac{1}{\ell} \int_0^\ell \phi \cdot f \cdot I_a \cdot dx = -\frac{1}{\ell} \int_0^\ell \phi \cdot f \cdot \alpha' \cdot I_o \cdot e^{-\alpha'x} \cdot dx$$

$$r_{avg,\ell} = \frac{\phi \cdot f \cdot I_o}{\ell} (1 - e^{-\alpha' \ell})$$

where  $f$  is the fraction of photons absorbed by  $H_2O_2$  compared to the total photon absorption of the liquid

$$f = \frac{\varepsilon' [H_2O_2]}{\alpha'}$$

$$r_{avg,\ell} = \frac{\phi \cdot \varepsilon' [H_2O_2] \cdot I_o}{\alpha' \cdot \ell} (1 - e^{-\alpha' \ell})$$

$$r_{avg,\ell} = \phi \cdot \varepsilon' [H_2O_2] \cdot \frac{E_o}{U} \cdot \frac{(1 - e^{-\alpha' \ell})}{\alpha' \ell}$$

or

$$r_{avg,\ell} = \phi \cdot \varepsilon \cdot [H_2O_2] \cdot \frac{E_o}{U} \cdot \frac{(1 - 10^{-\alpha \ell})}{\alpha \cdot \ell}$$

where

$$\alpha' = 2.303 \cdot \alpha$$

$$\varepsilon' = 2.303 \cdot \varepsilon$$

$$e^{-\alpha' \ell} = 10^{-\alpha \ell}$$

### Steady-state OH concentration $[OH]_{ss}$

To express the OH radical concentration, under the steady-state assumption, the rate of generation of OH radicals (photolysis of  $H_2O_2$ ) is equal the rate of consumption of OH radicals (scavenging by solutes reactive with OH radicals).

$$r_{generation} = \frac{d[OH \bullet]}{dt} = -\frac{d[H_2O_2]}{dt} = \phi \cdot \varepsilon \cdot [H_2O_2] \cdot \frac{E_o}{U} \cdot \frac{(1 - 10^{-\alpha \ell})}{\alpha \cdot \ell}$$

$$r_{consumption} = -\frac{d[OH \bullet]}{dt} = (k_1 \cdot [S_1] + k_2 \cdot [S_2] + \dots + k_i \cdot [S_i]) \cdot [OH \bullet] = \sum_i k_i \cdot [S_i] \cdot [OH \bullet]$$

$$r_{\text{generation}} = r_{\text{consumption}}$$

$$[OH \bullet]_{SS} = \frac{\phi \cdot \varepsilon \cdot [H_2O_2] \cdot \frac{E_o}{U} \cdot \frac{(1 - 10^{-\alpha \ell})}{\alpha \cdot \ell}}{\sum_i k_i \cdot [S_i] + k_{H_2O_2} \cdot [H_2O_2]}$$

## APPENDIX B: EXPERIMENTAL DATA

### B.1 Water quality

#### Total Suspended Solids (TSS)

Measured using 500ml samples of effluent taken on April 4<sup>th</sup> 2009 London Ontario.

WWTP	Final weight (g)	Initial weight (g)	Net weight (g)	TSS (mg/L)
<i>Pottersburg</i>	0.3792	0.3755	0.0034	7.4
<i>(CAS<sub>1</sub>)</i>	0.3813	0.3775	0.0038	7.6
<b>Average ± standard deviation</b>				<b>7.5 ± 0.1</b>
<i>Adelaide</i>	0.3831	0.3778	0.0053	10.6
<i>(CAS<sub>2</sub>)</i>	0.3755	0.3706	0.0049	9.8
<b>Average ± standard deviation</b>				<b>10.2 ± 0.6</b>
<i>Oxford</i>	0.3696	0.3698	-	<1
<b>(MBR)</b>				
<i>Microfiltrates (0.22 μm pore size) produced TSS &lt; 1 mg/L as expected (test used 1 μm pore size filter pad).</i>				



## Alkalinity

Measured using 100ml samples of effluent taken on April 4<sup>th</sup> 2009, London Ontario, by titration to pH 4.5 with 0.02N sulfuric acid.

WWTP	<i>pH initial</i>	<i>Initial volume</i> (mL)	<i>Final volume</i> (mL)	<i>Volume</i> (mL)	<i>Alkalinity</i> mg/L as Ca CO <sub>3</sub>
<b>Pottersburg</b>	7.3	12.2	1.5	10.7	107
<b>(CAS<sub>1</sub>)</b>	7.0	12.4	2.3	10.1	101
	7.0	10.4	0.3	10.1	101
<b>Average ± standard deviation</b>					<b>103 ± 3</b>
<b>Adelaide</b>	7.0	12.9	0.3	12.6	126
<b>(CAS<sub>2</sub>)</b>	7.1	12.1	0.1	12.0	120
	7.1	12.6	0.8	11.8	118
<b>Average ± standard deviation</b>					<b>121 ± 4</b>
<b>Oxford</b>	6.8	3.9	0.1	3.8	38
<b>(MBR)</b>	6.7	7.7	3.9	3.8	38
					<b>38 ± 1</b>

*No effect on alkalinity or pH was found for microfiltered samples.*

## Chemical Oxygen Demand

Measured by Hach COD test kit, using closed reflux method in prepared sample vials

WWTP	COD mg/L as O <sub>2</sub>
<i>Pottersburg</i>	63
<i>(CAS<sub>1</sub>)</i>	
<i>Pottersburg Microfiltrate</i>	55
<i>(CAS<sub>1</sub>+MF)</i>	
<i>Adelaide</i>	70
<i>(CAS<sub>2</sub>)</i>	
<i>Adelaide Microfiltrate</i>	55
<i>(CAS<sub>2</sub>+MF)</i>	
<i>Oxford</i>	48
<i>(MBR)</i>	

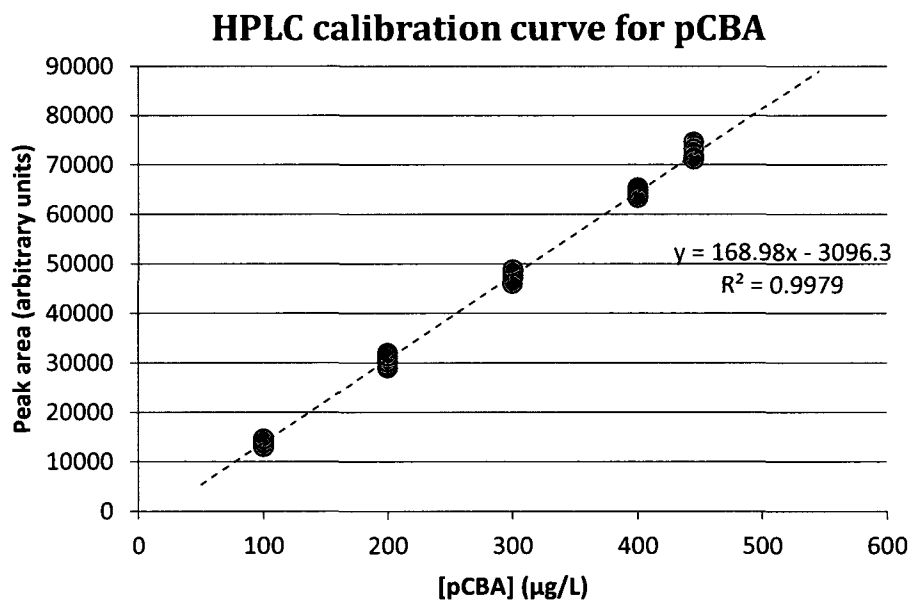
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*Deionized water blanks used to zero instrument before readings of COD*

## B.2 HPLC calibration curve for pCBA

[pCBA] μg/L	peak area*	[pCBA] μg/L	peak area*	[pCBA] μg/L	peak area*
445	74551	300	47607	100	13497
445	71785	300	47043	100	14542
445	73168	300	48321	100	13954
445	71362	300	48798	100	12969
445	71033	300	45949	100	14478
400	65311	200	28952		
400	64745	200	30890		
400	64197	200	31964		
400	63579	200	30158		
400	63270	200	31333		

\* arbitrary units for peak area



### B.3 Collimated Beam Petri Factor

<b><i>y</i>-position (cm)</b>	<b><i>meter reading</i> (mW/cm<sup>2</sup>)</b>	<b><i>x</i>-position (cm)</b>	<b><i>meter reading</i> (mW/cm<sup>2</sup>)</b>
-3.0	0.273	-3.0	0.249
-2.5	0.281	-2.5	0.266
-2.0	0.274	-2.0	0.270
-1.5	0.269	-1.5	0.272
-1.0	0.265	-1.0	0.274
-0.5	0.266	-0.5	0.278
0.0	0.272	0.0	0.278
0.5	0.279	0.5	0.264
1.0	0.287	1.0	0.261
1.5	0.293	1.5	0.258
2.0	0.298	2.0	0.254
2.5	0.272	2.5	0.231
3.0	0.086	3.0	0.082

*Center irradiance* = 0.275 mW/cm<sup>2</sup>

*Petri Factor* = 0.976

*Reflection Factor* = 0.975

*Divergence Factor* = 0.934

## B.4 Collimated Beam Experiments with pCBA

**Pottersburg WWTP unfiltered secondary effluent**

**Run 1 of 3**

time (min)	light reaction					dark reaction				
	peak area	[pCBA] ( $\mu\text{g/L}$ )	$\ln(C/C_0)$ <sup>a</sup>	$\alpha$ ( $\text{cm}^{-1}$ ) <sub>b</sub>	[H <sub>2</sub> O <sub>2</sub> ] ( $\text{mg/L}$ ) <sub>b</sub>	peak area	[pCBA] ( $\mu\text{g/L}$ )	$\ln(C/C_0)$ <sup>a</sup>	$\alpha$ ( $\text{cm}^{-1}$ )	[H <sub>2</sub> O <sub>2</sub> ] ( $\text{mg/L}$ )
0	46160	291	0.0164	0.212	13.7	46160	291	0.0164	0.212	13.7
0	45174	286	-0.0052	0.212	13.7	45174	286	-0.0052	-	-
0	44899	284	-0.0113	0.212	13.7	44899	284	-0.0113	-	-
10	30382	198	-0.4019	0.203	13.4	40001	255	-0.1269	-	-
20	25001	166	-0.5968	0.194	-	42119	268	-0.0753	-	-
30	29847	195	-0.4197	0.185	12.7	48745	307	0.0708	-	-
40	26330	174	-0.5451	0.176	12.4	42692	271	-0.0617	-	-
50	24737	165	-0.6075	0.166	12.0	46874	296	0.0317	-	-
60	23700	159	-0.6503	0.157	11.7	43906	278	-0.0337	-	-
70	18009	125	-0.9249	0.148	11.4	45702	289	0.0064	-	-
78	15097	108	-1.1013	0.141	11.2	47720	301	0.0496	0.199	12.0

<sup>a</sup>  $C=[\text{pCBA}]$  and  $C_0$  based on average of separate injections of sample at  $t = 0$  min.

<sup>b</sup> initial and final values measured and intermediate values interpolated

**Pottersburg WWTP unfiltered secondary effluent**  
**Run 2 of 3**

time (min)	light reaction					dark reaction				
	peak area	[pCBA] ( $\mu\text{g/L}$ )	$\ln(C/C_0)$ <sup>a</sup>	$\alpha$ ( $\text{cm}^{-1}$ ) <sub>b</sub>	[H <sub>2</sub> O <sub>2</sub> ] ( $\text{mg/L}$ ) <sub>b</sub>	peak area	[pCBA] ( $\mu\text{g/L}$ )	$\ln(C/C_0)$ <sup>a</sup>	$\alpha$ ( $\text{cm}^{-1}$ )	[H <sub>2</sub> O <sub>2</sub> ] ( $\text{mg/L}$ )
0	46313	292	0.0180	0.210	13.2	46313	292	0.0180	0.210	13.2
0	46582	294	0.0237	0.210	13.2	46582	294	0.0237	-	-
0	43573	276	0.0430	0.210	13.2	43573	276	-0.0430	-	-
10	39887	254	0.1314	0.200	12.9	42538	270	-0.0671	-	-
20	36468	234	0.2210	0.191	12.7	45838	290	0.0076	-	-
30	32651	212	-0.3320	0.181	12.5	47010	297	0.0329	-	-
40	27811	183	0.4921	0.171	12.2	47997	302	0.0537	-	-
50	24346	162	0.6251	0.161	12.0	44085	279	-0.0314	-	-
60	17590	122	0.9502	0.152	11.7	43491	276	-0.0449	-	-
70	-	-	-	0.142	11.3	48226	304	0.0584	-	-
80	17296	121	-0.967	0.132	13.2	44121	279	-0.0305	0.198	11.9

<sup>a</sup> C=[pCBA] and C<sub>0</sub> based on average of separate injections of sample at t = 0 min.

<sup>b</sup> initial and final values measured and intermediate values interpolated

**Pottersburg WWTP unfiltered secondary effluent  
Run 3 of 3**

time (min)	light reaction					dark reaction				
	peak area	[pCBA] ( $\mu\text{g/L}$ )	$\ln(C/C_0)$ <sup>a</sup>	$\alpha$ ( $\text{cm}^{-1}$ ) <sub>b</sub>	[H <sub>2</sub> O <sub>2</sub> ] ( $\text{mg/L}$ ) <sub>b</sub>	peak area	[pCBA] ( $\mu\text{g/L}$ )	$\ln(C/C_0)$ <sup>a</sup>	$\alpha$ ( $\text{cm}^{-1}$ )	[H <sub>2</sub> O <sub>2</sub> ] ( $\text{mg/L}$ )
0	48997	308	0	0.205	13.2	48997	308	0	0.205	13.2
10	42859	272	-0.1338	0.198	13.0	47029	297	-0.0410	-	-
20	39659	253	-0.2114	0.190	12.8	46438	293	-0.0536	-	-
30	34153	220	-0.3609	0.183	12.7	46691	295	-0.0482	-	-
40	27423	181	-0.5804	0.175	12.5	48696	307	-0.0062	-	-
50	24002	160	-0.7136	0.168	12.3	47064	297	-0.0403	-	-
60	21514	146	-0.8231	0.160	12.1	49367	310	0.0075	-	-
70	15618	111	-1.1433	0.153	12.0	50590	318	0.0320	-	-
80	16227	114	-1.1051	0.145	11.8	43789	277	-0.1124	0.192	12.2

<sup>a</sup> C=[pCBA] and C<sub>0</sub> based on average of separate injections of sample at t = 0 min.

<sup>b</sup> initial and final values measured and intermediate values interpolated

**Pottersburg WWTP microfiltered effluent**

**Run 1 of 3**

time (min)	light reaction					dark reaction				
	peak area	[pCBA] ( $\mu\text{g/L}$ )	$\ln(C/C_0)$ <sup>a</sup>	$\alpha$ ( $\text{cm}^{-1}$ ) <sub>b</sub>	$[\text{H}_2\text{O}_2]$ ( $\text{mg/L}$ ) <sub>b</sub>	peak area	[pCBA] ( $\mu\text{g/L}$ )	$\ln(C/C_0)$ <sup>a</sup>	$\alpha$ ( $\text{cm}^{-1}$ )	$[\text{H}_2\text{O}_2]$ ( $\text{mg/L}$ )
0	54242	339	0.0090	0.116	13.2	54242	339	0.0090	0.116	13.2
0	53271	334	-0.0091	0.116	13.2	53271	334	-0.0091	-	-
10	43640	277	-0.2085	0.115	13.1	54964	344	0.0222	-	-
20	40934	261	-0.2725	0.113	13.0	54131	339	0.0069	-	-
30	37811	242	-0.3519	0.112	12.9	53138	333	-0.0116	-	-
40	36029	232	-0.4001	0.110	12.8	54297	340	0.0100	-	-
50	27841	183	-0.6580	0.109	12.8	57791	360	0.0724	-	-
60	22737	153	-0.8605	0.107	12.7	54425	340	0.0124	-	-
70	22546	152	-0.8689	0.106	12.6	54643	342	0.0164	-	-
80	19200	132	-1.0296	0.104	12.5	54862	343	0.0204	0.118	13.3

<sup>a</sup>  $C=[\text{pCBA}]$  and  $C_0$  based on average of separate injections of sample at  $t = 0$  min.

<sup>b</sup> initial and final values measured and intermediate values interpolated



**Pottersburg WWTP microfiltered effluent  
Run 2 of 3**

time (min)	light reaction					dark reaction				
	peak area	[pCBA] ( $\mu\text{g/L}$ )	$\ln(C/C_0)$ <sup>a</sup>	$\alpha$ ( $\text{cm}^{-1}$ ) <sub>b</sub>	[H <sub>2</sub> O <sub>2</sub> ] ( $\text{mg/L}$ ) <sub>b</sub>	peak area	[pCBA] ( $\mu\text{g/L}$ )	$\ln(C/C_0)$ <sup>a</sup>	$\alpha$ ( $\text{cm}^{-1}$ )	[H <sub>2</sub> O <sub>2</sub> ] ( $\text{mg/L}$ )
0	49250	310	-0.0013	0.115	13.2	49250	310	-0.0013	0.115	13.2
0	49365	310	0.0011	0.115	13.2	49365	310	0.0011	-	-
0	49325	310	0.0002	0.115	13.2	49325	310	0.0002	-	-
10	41811	266	-0.1650	0.109	12.9	48493	305	-0.0168	-	-
20	35416	228	-0.3310	0.104	12.7	51657	324	0.0464	-	-
30	28945	190	-0.5328	0.098	12.4	53010	332	0.0723	-	-
40	18605	128	-0.9748	0.093	12.1	51238	322	0.0383	-	-
50	11745	88	-1.4348	0.087	11.9	52898	331	0.0708	-	-
60	<LOQ	-	-	-	-	49728	313	0.0084	-	-
70	<LOQ	-	-	-	-	47997	302	-0.0271	-	-
80	<LOQ	-	-	-	-	52669	330	0.0658	0.117	13.2

<sup>a</sup> C=[pCBA] and C<sub>0</sub> based on average of separate injections of sample at t = 0 min.

<sup>b</sup> initial and final values measured and intermediate values interpolated

**Pottersburg WWTP microfiltered effluent**  
**Run 3 of 3**

time (min)	light reaction					dark reaction				
	peak area	[pCBA] ( $\mu\text{g/L}$ )	$\ln(C/C_0)$ <sup>a</sup>	$\alpha$ ( $\text{cm}^{-1}$ ) <sub>b</sub>	$[\text{H}_2\text{O}_2]$ ( $\text{mg/L}$ ) <sup>b</sup>	peak area	[pCBA] ( $\mu\text{g/L}$ )	$\ln(C/C_0)$ <sup>a</sup>	$\alpha$ ( $\text{cm}^{-1}$ )	$[\text{H}_2\text{O}_2]$ ( $\text{mg/L}$ )
0	50156	315	-0.0098	0.115	13.1	50156	315	-0.0098	0.115	13.1
0	49845	313	-0.0160	0.115	13.1	49845	313	-0.0160	-	-
0	50990	320	0.0067	0.115	13.1	50990	320	0.0067	-	-
0	51604	324	0.0187	0.115	13.1	51604	324	0.0187	-	-
10	36195	233	-0.3360	0.107	12.9	51752	325	0.0216	-	-
10	37008	237	0.3138	0.107	12.9	52861	331	0.0428	-	-
20	25323	168	0.6932	0.099	12.6	52403	328	0.0341	-	-
20	24065	161	-0.7442	0.099	12.6	52638	330	0.0385	-	-
30	14803	106	-1.2301	0.090	12.4	53479	335	0.0544	-	-
30	14908	107	-1.2230	0.090	12.4	52034	326	0.0270	-	-
40	12810	94	-1.3747	0.082	12.2	50177	315	-0.0094	-	-
40	12517	92	-1.3978	0.082	12.2	50769	319	0.0024	0.117	12.9

<sup>a</sup>  $C=[\text{pCBA}]$  and  $C_0$  based on average of separate injections of sample at  $t = 0$  min

<sup>b</sup> initial and final values measured and intermediate values interpolated

**Adelaide WWTP unfiltered secondary effluent  
Run 1 of 3**

time (min)	light reaction					dark reaction				
	peak area	[pCBA] ( $\mu\text{g/L}$ )	$\ln(C/C_0)$ <sup>a</sup>	$\alpha$ ( $\text{cm}^{-1}$ ) <sub>b</sub>	[H <sub>2</sub> O <sub>2</sub> ] ( $\text{mg/L}$ ) <sup>b</sup>	peak area	[pCBA] ( $\mu\text{g/L}$ )	$\ln(C/C_0)$ <sup>a</sup>	$\alpha$ ( $\text{cm}^{-1}$ )	[H <sub>2</sub> O <sub>2</sub> ] ( $\text{mg/L}$ )
0	53919	337	0.0263	0.145	13.0	53919	337	0.0263	0.145	13.0
0	51897	325	-0.0119	0.145	13.0	51897	325	-0.0119	-	-
0	51742	325	-0.0149	0.145	13.0	51742	325	-0.0149	-	-
10	44185	280	-0.1728	0.141	12.3	50692	318	-0.0354	-	-
20	41304	263	-0.2402	0.137	11.7	50466	317	-0.0399	-	-
30	33450	216	-0.4511	0.132	11.1	53601	336	0.0204	-	-
40	28266	186	-0.6195	0.128	10.5	53034	332	0.0098	-	-
50	21204	144	-0.9070	0.124	10.0	53533	335	0.0191	-	-
60	18355	127	-1.0513	0.120	9.5	52135	327	-0.0073	-	-
70	13078	96	-1.3903	0.115	9.0	53399	334	0.0166	-	-
80	8046	66	-1.8760	0.111	8.5	51799	325	-0.0138	0.126	8.8

<sup>a</sup>  $C=[\text{pCBA}]$  and  $C_0$  based on average of separate injections of sample at  $t = 0$  min.

<sup>b</sup> initial and final values measured and intermediate values interpolated

**Adelaide WWTP unfiltered secondary effluent  
Run 2 of 3**

time (min)	light reaction					dark reaction				
	peak area	[pCBA] ( $\mu\text{g/L}$ )	$\ln(C/C_0)$ <sup>a</sup>	$\alpha$ ( $\text{cm}^{-1}$ ) <sub>b</sub>	[H <sub>2</sub> O <sub>2</sub> ] ( $\text{mg/L}$ ) <sub>b</sub>	peak area	[pCBA] ( $\mu\text{g/L}$ )	$\ln(C/C_0)$ <sup>a</sup>	$\alpha$ ( $\text{cm}^{-1}$ )	[H <sub>2</sub> O <sub>2</sub> ] ( $\text{mg/L}$ )
0	56944	355	0.0411	0.141	13.7	56944	355	0.0411	0.141	13.7
0	51394	322	-0.0615	0.141	13.7	51394	322	-0.0615	-	-
0	55617	347	0.0175	0.141	13.7	55617	347	0.0175	-	-
10	43190	274	-0.2354	0.138	12.9	54205	339	-0.0082	-	-
20	34918	225	-0.4480	0.135	12.1	53443	335	-0.0224	-	-
30	29971	196	-0.6008	0.132	11.4	51733	324	-0.0549	-	-
40	23417	157	-0.8475	0.130	10.7	51605	324	-0.0574	-	-
50	17565	122	-1.1351	0.127	10.1	55722	348	0.0194	-	-
60	12306	91	-1.4909	0.124	9.5	56730	354	0.0373	-	-
70	9369	74	-1.7636	0.121	8.9	54315	340	-0.0062	-	-
80	5610	52	-2.2764	0.118	8.4	53734	336	-0.0169	0.139	8.8

<sup>a</sup>  $C=[\text{pCBA}]$  and  $C_0$  based on average of separate injections of sample at  $t = 0$  min.

<sup>b</sup> initial and final values measured and intermediate values interpolated

**Adelaide WWTP unfiltered secondary effluent  
Run 3 of 3**

time (min)	light reaction					dark reaction				
	peak area	[pCBA ) ( $\mu\text{g/L}$ )	$\ln(C/C_0)$ <sup>a</sup>	$\alpha$ ( $\text{cm}^{-1}$ ) <sub>b</sub>	[H <sub>2</sub> O <sub>2</sub> ] ( $\text{mg/L}$ ) <sup>b</sup>	peak area	[pCBA] ( $\mu\text{g/L}$ )	$\ln(C/C_0)$ <sup>a</sup>	$\alpha$ ( $\text{cm}^{-1}$ )	[H <sub>2</sub> O <sub>2</sub> ] ( $\text{mg/L}$ )
0	51444	323	-0.0093	0.142	13.0	51444	323	-0.0093	0.142	13.0
0	53210	333	0.0244	0.142	13.0	53210	333	0.0244	-	-
0	51125	321	-0.0155	0.142	13.0	51125	321	-0.0156	-	-
10	44932	284	-0.1447	0.136	12.2	50232	316	-0.0332	-	-
20	35721	230	-0.3741	0.131	11.4	55080	344	0.0590	-	-
30	27966	184	-0.6188	0.125	10.7	52282	328	0.0068	-	-
40	22884	154	-0.8194	0.119	10.0	52315	328	0.0075	-	-
50	15468	110	-1.2111	0.114	9.4	52947	332	0.0195	-	-
60	10931	83	-1.5582	0.108	8.8	51592	324	-0.0065	-	-
70	<LOQ	-	-	-	-	51293	322	-0.0123	-	-
80	<LOQ	-	-	-	-	54424	340	0.0470	0.134	9.1

<sup>a</sup>  $C=[\text{pCBA}]$  and  $C_0$  based on average of separate injections of sample at  $t = 0$  min.

<sup>b</sup> initial and final values measured and intermediate values interpolated

**Adelaide WWTP microfiltered effluent**  
**Run 1 of 3**

time (min)	light reaction					dark reaction				
	peak area	[pCBA] ( $\mu\text{g/L}$ )	$\ln(C/C_0)$ <sup>a</sup>	$\alpha$ ( $\text{cm}^{-1}$ ) <sub>b</sub>	$[\text{H}_2\text{O}_2]$ ( $\text{mg/L}$ ) <sup>b</sup>	peak area	[pCBA] ( $\mu\text{g/L}$ )	$\ln(C/C_0)$ <sup>a</sup>	$\alpha$ ( $\text{cm}^{-1}$ )	$[\text{H}_2\text{O}_2]$ ( $\text{mg/L}$ )
0	54265	339	-0.011	0.104	13.2	54265	339	-0.011	0.104	13.2
0	53573	335	-0.023	0.104	13.2	53573	335	-0.023	-	-
0	56678	354	0.033	0.104	13.2	56678	354	0.033	-	-
10	47928	302	-0.1347	0.101	13.0	53423	334	-0.0262	-	-
25	33104	214	-0.5047	0.097	12.6	57687	360	0.0506	-	-
35	24066	161	-0.8240	0.094	12.4	53656	336	-0.0218	-	-
40	20463	139	-0.9858	0.092	12.3	52253	328	-0.0483	-	-
50	13592	99	-1.3949	0.089	12.0	54393	340	-0.0082	-	-
60	10488	80	-1.6542	0.086	11.8	54967	344	0.0023	-	-
70	8187	67	-1.9019	0.083	11.6	56615	353	0.0319	-	-
80	<LOQ	-	-	-	-	57125	356	0.0409	0.106	11.6

<sup>a</sup>  $C=[\text{pCBA}]$  and  $C_0$  based on average of separate injections of sample at  $t = 0$  min.

<sup>b</sup> initial and final values measured and intermediate values interpolated

**Adelaide WWTP microfiltered effluent  
Run 2 of 3**

time (min)	light reaction					dark reaction				
	peak area	[pCBA] ( $\mu\text{g/L}$ )	$\ln(C/C_0)^a$	$\alpha$ ( $\text{cm}^{-1}$ ) <sub>b</sub>	$[\text{H}_2\text{O}_2]$ ( $\text{mg/L}$ ) <sup>b</sup>	peak area	[pCBA] ( $\mu\text{g/L}$ )	$\ln(C/C_0)^a$	$\alpha$ ( $\text{cm}^{-1}$ )	$[\text{H}_2\text{O}_2]$ ( $\text{mg/L}$ )
0	53382	334	0.0462	0.102	13.1	53382	334	0.0462	0.102	13.1
0	48967	308	-0.0400	0.102	13.1	48967	308	-0.0400	-	-
0	50569	318	-0.0078	0.102	13.1	50569	318	-0.0080	-	-
10	39001	249	-0.2677	0.099	12.8	48578	306	-0.0481	-	-
25	30529	199	-0.5126	0.095	12.4	48506	305	-0.0496	-	-
35	26160	173	-0.6671	0.093	12.1	49043	309	-0.0386	-	-
40	19253	132	-0.9736	0.091	12.0	50463	317	-0.0101	-	-
50	12999	95	-1.3664	0.089	11.8	54730	342	0.0711	-	-
60	8936	71	-1.7412	0.086	11.5	51778	325	0.0157	-	-
70	<LOQ	-	-	-	-	52458	329	0.0287	-	-
80	<LOQ	-	-	-	-	49902	314	-0.0212	0.110	13.2

<sup>a</sup>  $C=[\text{pCBA}]$  and  $C_0$  based on average of separate injections of sample at  $t = 0$  min.

<sup>b</sup> initial and final values measured and intermediate values interpolated

**Adelaide WWTP microfiltered effluent  
Run 3 of 3**

time (min)	light reaction					dark reaction				
	peak area	[pCBA] ( $\mu\text{g/L}$ )	$\ln(C/C_0)^a$	$\alpha$ ( $\text{cm}^{-1}$ ) <sub>b</sub>	$[\text{H}_2\text{O}_2]$ ( $\text{mg/L}$ ) <sup>b</sup>	peak area	[pCBA] ( $\mu\text{g/L}$ )	$\ln(C/C_0)^a$	$\alpha$ ( $\text{cm}^{-1}$ )	$[\text{H}_2\text{O}_2]$ ( $\text{mg/L}$ )
0	55034	344	0.0293	0.106	13.2	55034	344	0.0293	0.106	13.2
0	52452	329	-0.0188	0.106	13.2	52452	329	-0.0188	-	-
0	52850	331	-0.0112	0.106	13.2	52850	331	-0.0112	-	-
10	49563	312	-0.0754	0.104	13.1	52891	331	-0.0104	-	-
20	45228	286	-0.1669	0.101	13.0	53940	338	0.0092	-	-
30	38663	247	-0.3238	0.099	12.9	57051	356	0.0653	-	-
40	40328	257	-0.2816	0.096	12.8	51204	321	-0.0428	-	-
50	35534	229	-0.4082	0.094	12.7	54860	343	0.0261	-	-
60	26539	175	-0.7000	0.091	12.6	55793	349	0.0430	0.115	13.2

<sup>a</sup>  $C=[\text{pCBA}]$  and  $C_0$  based on average of separate injections of sample at  $t = 0$  min.

<sup>b</sup> initial and final values measured and intermediate values interpolated



**Oxford WWTP membrane bioreactor (MBR) permeate  
Run 1 of 3**

time (min)	light reaction					dark reaction				
	peak area	[pCBA] ( $\mu\text{g/L}$ )	$\ln(C/C_0)^a$	$\alpha$ ( $\text{cm}^{-1}$ ) <sub>b</sub>	[H <sub>2</sub> O <sub>2</sub> ] ( $\text{mg/L}$ ) <sup>b</sup>	peak area	[pCBA] ( $\mu\text{g/L}$ )	$\ln(C/C_0)$ <sup>a</sup>	$\alpha$ ( $\text{cm}^{-1}$ )	[H <sub>2</sub> O <sub>2</sub> ] ( $\text{mg/L}$ )
0	50636	318	-0.0140	0.125	6.5	50636	318	-0.0140	0.125	6.5
0	50627	318	-0.0142	0.125	6.5	50627	318	-0.0142	-	-
0	52786	331	0.0276	0.125	6.5	52786	331	0.0276	-	-
10	45169	286	-0.1283	0.122	6.4	54316	340	0.0562	-	-
20	41486	264	-0.2133	0.119	6.3	52338	328	0.0191	-	-
30	36297	233	-0.3469	0.116	6.2	53325	334	0.0378	-	-
40	32253	209	-0.4651	0.113	6.1	54139	339	0.0529	0.125	6.3

<sup>a</sup>  $C=[\text{pCBA}]$  and  $C_0$  based on average of separate injections of sample at  $t = 0$  min.

<sup>b</sup> initial and final values measured and intermediate values interpolated

**Oxford WWTP membrane bioreactor (MBR) permeate  
Run 2 of 3**

time (min)	light reaction					dark reaction				
	peak area	[pCBA] ( $\mu\text{g/L}$ )	$\ln(C/C_0)^a$	$\alpha$ ( $\text{cm}^{-1}$ ) <sub>b</sub>	$[\text{H}_2\text{O}_2]$ ( $\text{mg/L}$ ) <sup>b</sup>	peak area	[pCBA] ( $\mu\text{g/L}$ )	$\ln(C/C_0)^a$	$\alpha$ ( $\text{cm}^{-1}$ )	$[\text{H}_2\text{O}_2]$ ( $\text{mg/L}$ )
0	52731	330	-0.0078	0.124	6.5	52731	330	-0.0078	0.124	6.5
0	51946	326	-0.0228	0.124	6.5	51946	326	-0.0228	-	-
0	54753	342	0.0298	0.124	6.5	54753	342	0.0298	-	-
5	53267	334	0.0023	0.123	6.5	53612	336	0.0088	-	-
10	46904	296	-0.1249	0.122	6.4	54616	342	0.0273	-	-
20	46059	291	-0.1431	0.120	6.4	53336	334	0.0036	-	-
30	40579	258	-0.2697	0.117	6.3	54253	339	0.0207	-	-
40	39245	251	-0.3032	0.115	6.3	54246	339	0.0205	0.125	6.5

<sup>a</sup>  $C=[\text{pCBA}]$

<sup>b</sup> initial and final values measured and intermediate values interpolated

**Oxford WWTP membrane bioreactor (MBR) permeate  
Run 3 of 3**

time (min)	light reaction					dark reaction				
	peak area	[pCBA] ( $\mu\text{g/L}$ )	$\ln(C/C_0)^a$	$\alpha$ ( $\text{cm}^{-1}$ ) <sub>b</sub>	$[\text{H}_2\text{O}_2]$ ( $\text{mg/L}$ ) <sup>b</sup>	peak area	[pCBA] ( $\mu\text{g/L}$ )	$\ln(C/C_0)$ <sup>a</sup>	$\alpha$ ( $\text{cm}^{-1}$ )	$[\text{H}_2\text{O}_2]$ ( $\text{mg/L}$ )
0	61595	383	-0.0104	0.125	5.9	61595	383	-0.0104	0.125	5.9
0	61819	384	-0.0068	0.125	5.9	61819	384	-0.0068	-	-
0	63311	393	0.0170	0.125	5.9	63311	393	0.0170	-	-
5	58448	364	-0.0629	0.124	5.9	59868	373	-0.0389	-	-
10	54269	339	-0.1371	0.123	5.8	61332	381	-0.0147	-	-
20	46044	291	-0.3014	0.120	5.7	61766	384	-0.0077	-	-
30	45519	288	-0.3129	0.118	5.7	62548	388	0.0049	-	-
40	40928	261	-0.4192	0.115	5.6	62197	386	-0.0007	0.125	5.8

<sup>a</sup>  $C=[\text{pCBA}]$

<sup>b</sup> initial and final values measured and intermediate values interpolated