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Application of the UV/H_2O_2 advanced oxidation process for municipal reuse water: bench- and pilot-scale studies

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Abstract

The occurrence of a variety of contaminants of emerging concerns (CECs) such as hormones and pharmaceuticals in municipal wastewater is an ongoing concern. In this study, UV/hydrogen peroxide (H_2O_2) was applied to treat the secondary effluent from Gold Bar Wastewater Water Treatment Plant in Edmonton, Alberta, Canada. Bench-scale tests were conducted to investigate the direct UV photolysis and UV/H_2O_2 oxidation of nine selected model micropollutants. The quantum yields at pH 7 were found to be between 0.0010 and 0.13. To investigate the effect of the water matrices, the degradation rate constants for 2,4-D and carbamazepine were determined in MilliQ water and wastewater. Overall, the estimated rates were higher in MilliQ water than those estimated in actual wastewater samples with differences of 34 and 37% for 2,4-D and carbamazepine, respectively. Differences in the pseudo first-order rate constants could be attributed to the matrix effects of the wastewater. The pilot-scale UV/H_2O_2 process did not appear to be able to remediate acute estrogenic activities in the reuse water to goldfish, whereas it had the potential to minimize the estrogenic effects of the reuse water in chronic exposures.

Keywords: micropollutants, endocrine disruption, estrogenic effects, reuse water, UV/H_2O_2 process, fluence-based degradation rate constant.

1 Introduction

Contaminants of emerging concerns (CECs) such as pharmaceuticals, hormones, pesticides, and personal care products have been found frequently around the world in wastewater effluents, surface waters, and groundwater [1, 2]. Although most of the CECs are typically present at low concentrations, their potential for additive and synergistic mixture effects can raise considerable toxicological concerns [3]. The release of these micropollutants into the environment may cause toxicity at any level of the biological systems [1]. As illustration, aquatic and terrestrial organisms are exposed to a broad range of natural and synthetic chemicals that interfere with the endocrine system and its physiology [4, 5]. The presence of CECs in treated municipal wastewater effluents has also been related to a number of adverse effects, including sexual development and behavioural changes which could affect the population fitness and survivability [6].

Several studies have reported that conventional water treatment processes are not able to remove micropollutants efficiently [7, 8]. For example, membrane filtration and activated carbon adsorption are highly effective processes for the removal of the majority of micropollutants. However, these processes are energy and material intensive, and the removal of polar organic compounds is limited when using activated carbon adsorption [9]. Moreover, the concentrate streams from membrane filtration need to be further treated and managed [10].

Because ultraviolet (UV)/hydrogen peroxide (H_2O_2) advanced oxidation processes (AOPs) have been found to be effective processes for the degradation of trace organic contaminants [11], the Gold Bar Wastewater Treatment Plant (WWTP) in Edmonton, Alberta, Canada, implemented a pilot-scale medium pressure (MP) UV/H_2O_2 AOP for further remediation of the wastewater effluent after conventional treatment processes coupled with ultrafiltration process. The objective of this study was, therefore, to assess the MP UV/H_2O_2 treatment of the Gold Bar municipal wastewater at both bench and pilot scale levels. The selected micropollutants were naproxen, carbamazepine, diclofenac, gemfibrozil, ibuprofen, caffeine, 2,4-Dichlorophenoxyacetic acid (2,4-D), 2,4-Dichlorophenol (2,4-DCP), and mecoprop (MCPP), which were chosen because of their frequent presence at relatively high detected concentrations (> 0.1 μg/L) in the final effluent of the Gold Bar WWTP [12]. The pseudo first-order rate constants and the second-order rate constants for the reaction between hydroxyl radicals (•OH) and the target compounds were determined in a quasi-collimated beam UV apparatus. To investigate the impact of the water matrix, the fluence-based pseudo first-order rate constants of 2,4-D and carbamazepine were estimated using a bench-scale UV/H_2O_2 process. The detoxification potential of a pilot-scale MP UV/H_2O_2 process was assessed through a real-time *in vivo* exposure of goldfish to reuse water. The endocrine disruption effects on goldfish sampled from the reuse water in each treatment were monitored in time intervals including spring, summer and fall of 2012. Estrogen-responsive genes that were monitored included estrogen receptors alpha 1 (ERα1), alpha 2 (ERα2), beta 1 (ERβ1), beta 2 (ERβ2) and nuclear progesterone receptor (NPR) at messenger ribonucleic acid (mRNA)

levels, in spleen, liver and kidney as well as the mRNA levels in the liver of two genes (CYP19a and CYP19b) that encode aromatase.

2 Materials and methods

2.1 Chemicals

All the selected model compounds, including naproxen, carbamazepine, diclofenac, gemfibrozil, ibuprofen, caffeine, 2,4-D, 2,4-DCP, and MCPP, were obtained from Sigma Aldrich (at analytical grade). The reference compound *para*-chlorobenzoic acid (pCBA) was also obtained from Sigma Aldrich. 35% hydrogen peroxide (H_2O_2) was obtained from Fisher Scientific.

2.2 Bench-scale tests to estimate the rate constants and quantum yields

A quasi-collimated beam UV apparatus (Model PSI-I-120, Calgon Carbon Corporation, USA) equipped with a 1 kW medium pressure Hg-lamp (Calgon Carbon, Pittsburgh, PA, USA) was used to generate polychromatic UV light for the UV exposures. The irradiance was measured by a calibrated UV detector (International Light, Model SED240) connected to a radiometer (International Light, Model IL 1400A).

2.3 Bench-scale UV/H_2O_2 degradation for two model compounds in reuse water

The degradation experiments were conducted in 30 L of reuse water spiked with 150 μg/L 2,4-D or 120 μg/L carbamazepine, respectively. The photodegradation experiments were carried out in a cylindrical stainless steel Calgon Carbon (Moon Township, PA, USA) Rayox stirred-tank reactor equipped with a Rayox 1 kW medium pressure UV lamp in the center of a quartz sleeve. The average fluence rate (E_{avg}) in the reactor was calculated to be 11.5 mW/cm^2 using UVCalc® provided by Bolton Photosciences Inc. (Edmonton, AB, Canada).

2.4 Pilot-scale flow-through system for fish exposure experiments

The Gold Bar WWTP implemented a pilot-scale MP UV/H_2O_2 process, along with granular activated carbon (GAC) treatment process in parallel, for secondary effluent reuse studies. The production of reuse water from secondary effluent was achieved by a pilot-scale ultrafiltration (UF) system (Zenon ZeeWeed 500; pore size 0.04 μm; GE Water, Trevose, PA, USA). The UF effluent (reuse water) was passed through GAC and the UV/H_2O_2 systems (Trojan UVMAX K plus® with a fluence of 1,000 mJ/cm^2 and a H_2O_2 dose of 20 mg/L). Goldfish were exposed to effluents including: untreated UF reuse water; MP UV/H_2O_2; and GAC (control) processes in a flow-through system.

2.5 Goldfish exposure

The animal protocols for this study were approved by the University of Alberta Animal Care Research Ethics Committee in accordance with the Canadian Council for Animal Care Guidelines (CCAC) (Protocol # 557/10/12). Goldfish were purchased from Mt. Parnell Fisheries Inc. (Mercersburg, PA, USA) and maintained at the aquatic facility of the Department of Biological Sciences, University of Alberta for a minimum of three weeks prior to transfer to Gold Bar WWTP [13]. A total of 300 goldfish (50 fish per 150 L exposure tank, 2 tanks per experimental group) were exposed to reuse water, GAC (control) and UV/H_2O_2 treated effluents for a period of 60 days during spring, summer and fall in 2012. At day 7, 30 and 60 of each season, equal numbers of fish (3) from each exposure tank were removed, anesthetized with tricaine methane sulfonate and killed by cervical dislocation, dissected while their kidney, liver and spleen were aseptically removed and flash frozen in liquid nitrogen and stored at -80°C prior to gene expression analysis.

Total RNA was isolated from frozen tissue samples of kidney and spleen (~50 mg) using TRIzol RNA extraction reagent (Invitrogen; Thermo Fisher Scientific, Ottawa, ON, Canada). For RNA isolation of liver samples, a QIAGEN RNeasy® Mini Kit (QIAGEN, Toronto, ON, Canada) was used.

The mRNA abundance of five ER genes was measured in relation to the endogenous control, elongation factor 1 alpha (EF-1α), using quantitative PCR (qPCR, Applied Biosystems real-time PCR apparatus, Thermo Fisher Scientific). The qPCR Mastermix (2×) used in this study is a proprietary mix developed which is distributed by the Molecular Biology Service Unit (MBSU), in the Department of Biological Science at the University of Alberta, Edmonton, Canada. It contains Tris (pH 8.3), KCl, $MgCl_2$, Glycerol, Tween 20, DMSO, dNTPs, ROX as a normalizing dye, SYBR Green (Molecular Probes) as the detection dye, and an antibody inhibited Taq polymerase.

3 Results and discussion

3.1 Bench-scale UV/H_2O_2 degradation of model compounds

Medium pressure UV direct photolysis of solutions containing individual contaminants was performed to determine fluence-based first-order rate constants as well as quantum yields. With the addition of H_2O_2, the overall micropollutant degradation kinetics include a combination of UV direct photolysis and UV/H_2O_2 (•OH) oxidation that can be expressed by [14]:

$$\frac{-\mathrm{d}[\mathrm{P}]}{\mathrm{d}F} = (k_d^{'} + k_i^{'})[\mathrm{P}] = k_t^{'}[\mathrm{P}] \tag{1}$$

where k'_{d} is the fluence-based pseudo first-order rate constant for the direct photolysis of the micropollutant (P) and k_{i}' is the fluence-based pseudo first-order rate constant for UV/H_2O_2 oxidation that is a function of the second-order reaction rate constant for •OH attack (k_{OH}) and the steady-state concentration of •OH

($[\bullet OH]_{ss}$). The overall fluence-based pseudo first-order decay rate constants (k_t', cm^2/mJ) can be determined from the slope of a plot of $\ln([P_0]/[P])$ versus the fluence or UV dose, where $[P_0]$ and $[P]$ are the initial and final micropollutant concentrations in the wastewater. The fluence (F, mJ/cm^2) is calculated as the volume-averaged fluence rate (E_{avg} = 11.5 mW/cm^2) multiplied by the exposure time. The time-based pseudo first-order rate constant (k_d) for the direct photolysis of each compound can be obtained from the slope of a plot of $\ln([P_0]/[P])$ vs. reaction time for the direct photolysis.

The overall fluence-based pseudo first-order decay rate constants (k_t') and the quantum yield (Φ_C) for each compound are presented in fig. 1. The quantum yield is a fundamental parameter that quantifies the photon efficiency of a photochemical reaction. According to Stefan and Bolton [15] and assuming that the quantum yield is independent of wavelength, Φ_C can be determined from the fluence-based first-order rate constant.

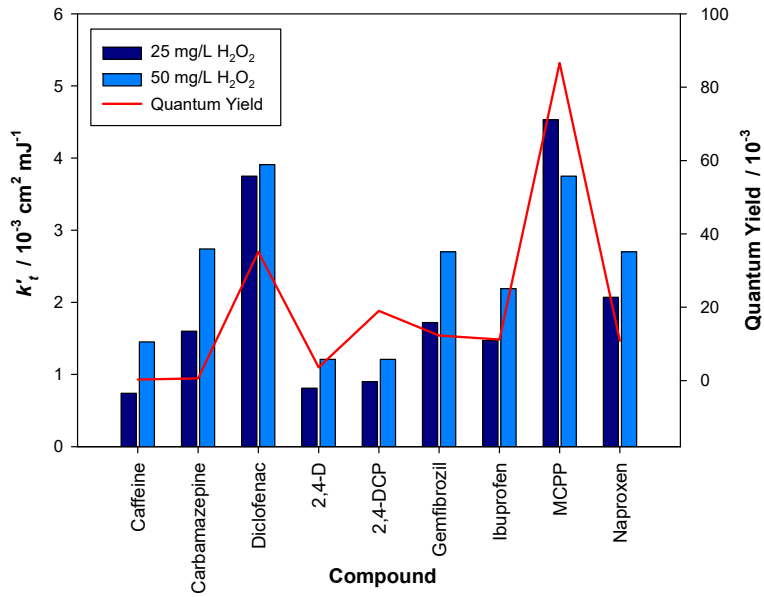

Figure 1: Overall fluence-based pseudo first-order decay rate constants (k_t') and quantum yield (Φ) for different CECs.

As shown in fig. 1, the increase of H_2O_2 enhanced the oxidation rate (i.e., increased k_t'). This enhancement can be attributed to the photolysis of H_2O_2, which generates •OH radicals. With the exception of MCPP, it can be seen clearly that the degradation rate constants at 50 mg/L H_2O_2 were all higher than those estimated at 25 mg/L H_2O_2. This can be explained from the fact that a higher H_2O_2 concentration results in higher absorption by H_2O_2, leading to a higher •OH radical generation rate, thereby promoting the •OH radical oxidation pathway. In these

cases, the pollutant degradation rates depend mainly on the rate of •OH radical formation and the second-order rate for the reaction between •OH radical and pollutants [16].

At H_2O_2 concentrations of 0, 25 and 50 mg/L, the degradation rate constant of each compound depended on the initial H_2O_2 concentration (fig. 2). In a certain concentration range, the first-order rate constant increased linearly with increasing H_2O_2 addition. However, the increase of the degradation rate constants would be attenuated (as is the case for MCPP) when the H_2O_2 concentration is in excess because H_2O_2 then becomes a scavenger by reacting directly with the •OH radicals, and the resulting product (HO_2•) from the reaction between H_2O_2 and the •OH radicals has lower oxidation capacity than •OH [17].

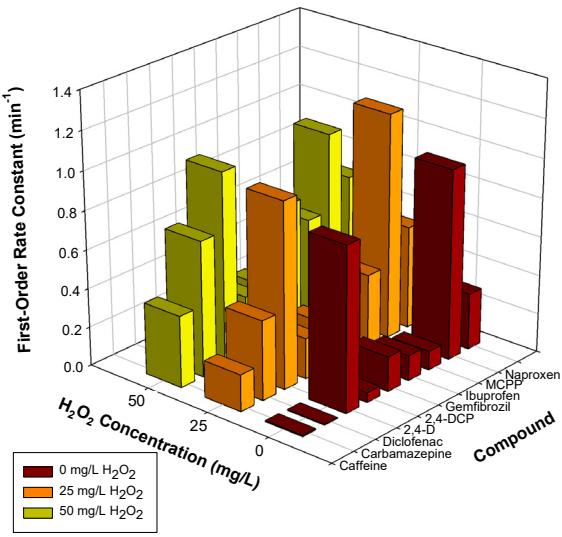

Figure 2: First-order rate constant of each compound at various initial H_2O_2 concentrations.

3.2 Rate constants for the reaction between the selected compounds and •OH radicals

A competition-kinetics method [18] was used to determine the second-order rate constant between the target compounds and •OH radicals (see table 1). *p*CBA was used as a reference compound because its second-order rate constant is widely accepted, with a value of 5.0×10^9 M^{-1} s^{-1} [19] and its direct photolysis is insignificant. The k_{OH} values for 2,4-D and carbamazepine agree well with the literature values. Very similar results were also obtained for ibuprofen, 2,4-DCP and caffeine compared to previous studies [20–22]. However, the values found for gemfibrozil, 2,4-DCP and MCPP appear to be different from the literature values. A possible reason could be that the published values were obtained by using other processes, such as γ radiolysis or ozonation. Because of various sources and

conditions, the •OH radical generation is often accompanied by other oxidants in the reacting system, which may include ozone, oxygen, the hydroperoxyl radical (HO_2•), and the peroxide radical anion. As a result, the exact role of the •OH radical is not clear. Other factors, such as reactor type, system geometry, reference compound used, pH value, and H_2O_2 concentration may also explain these differences.

Table 1: Second-order rate constants between the target compounds and •OH radicals.

Compound	$k_{OH}/10^9$ M^{-1} s^{-1}
Caffeine	4.10 ± 0.03
Carbamazepine	6.0 ± 0.1
Diclofenac	13.5 ± 0.1
2,4-D	4.4 ± 0.2
2,4-DCP	4.4 ± 0.1
Gemfibrozil	6.8 ± 0.1
Ibuprofen	5.25 ± 0.01
MCPP	6.46 ± 0.04
Naproxen	12.9 ± 0.6

3.3 Impact of the water matrix on the degradation rate constants

The pseudo-first order rate constants can be estimated as follows [19]:

$$-\frac{d[P]}{dt}=\frac{k_P[P]G_0\chi\Phi_{OH}/V}{k_P[P]+k_S[S]+k_{H_2O_2}[H_2O_2]}=k_t[P] \tag{2}$$

where Φ_{OH} is the quantum yield of the production of •OH radicals by H_2O_2 photolysis, V is the volume (L) of the aqueous solution, G_0 is the total photon flux (einstein/s) incident on the system in the wavelength range 200–400 nm, [S] is the concentration of scavengers, and χ is the fraction of the lamp emission absorbed by H_2O_2. k_{H2O2}, k_p and k_s are the time-based second-order rates for reaction of •OH with H_2O_2, the pollutant, and scavengers, respectively. This equation can be solved depending on the micropollutant being at trace (μg/L) versus elevated (mg/L) concentrations [23]. At trace concentrations, the eqn (2) becomes:

$$\frac{1}{k_t}=\frac{k_{H_2O_2}[H_2O_2]}{k_pG_0\chi\Phi_{OH}/V} \text{ or } k_t=\frac{k_pG_0\chi\Phi_{OH}/V}{k_{H_2O_2}[H_2O_2]} \tag{3}$$

As shown in eqn (3), the H_2O_2 concentration is the only factor that determines k_t and, therefore, it is nearly a constant under such circumstances. On the other hand, $1/k_t$ is proportional to the pollutant concentration [P] when the pollutant concentration is elevated:

$$\frac{1}{k_t} = \frac{k_{H_2O_2}[H_2O_2]}{k_P G_0 \chi \Phi_{OH} / V} + \frac{[P]}{G_0 \chi \Phi_{OH} / V} \quad (4)$$

In this case, k_t versus $[P]$ should yield approximately a straight line within a certain concentration range. As a result, this theoretical pseudo first-order rate constant k_t at trace concentration can be obtained from the intercept by plotting the rate constants versus concentration.

Because of their low quantum yields, the degradation of carbamazepine and 2,4-D by direct photolysis can be ignored [23]. Therefore, the degradation of carbamazepine and 2,4-D can be mainly attributed to the •OH mediated degradation pathway. A pseudo-first order degradation for carbamazepine and 2,4-D in the Goldbar reuse water was observed during the UV/H_2O_2 process using 20 mg/L H_2O_2, and the corresponding fluence-based degradation rate constants were found to be 0.87±0.04 and 0.60±0.04 × 10^{-3} cm^2/mJ, respectively (table 2).

The pseudo first-order rate constants k_t for trace concentrations obtained from the model described by Shu *et al*. [24] for 2,4-D and carbamazepine are 0.35 min^{-1} and 0.56 min^{-1}, respectively. Using the above approximation approach, the calculated fluence-based constants were estimated to be 1.39×10^{-3} and 0.91×10^{-3} cm^2/mJ for carbamazepine and 2,4-D in MilliQ water, respectively (table 2). Through this approach, it is possible to compare the estimated and observed degradation rate constants for 2,4-D and carbamazepine in MilliQ water versus wastewater. Overall, the estimated rates were higher than those obtained in actual wastewater samples for both micropollutants with differences of 34 and 37% for 2,4-D and carbamazepine, respectively. Differences in the pseudo first-order rate constants can be attributed to the matrix effects of the wastewater such as the presence of total organic carbon and bicarbonate, recovery errors in the solid-phase extraction step, and different H_2O_2 concentrations applied in the MilliQ water (25 mg/L) and in the wastewater (20 mg/L). The approach described above could also be applied to predict the degradation efficiency of the UV/H_2O_2 process for other micropollutants of concern in wastewater, where advanced analytical chemistry technology is not readily available [24]. In addition, by using the fluence-based rate constants presented in this study, the results can be compared between UV reactors at various scales since the fluence is the only parameter needed for comparative purposes.

Table 2: Fluence-based rate constant for carbamazepine and 2,4-D.

Compound	Fluence-based rate constant	
	MilliQ water (cm^2/mJ)	Reuse water (cm^2/mJ)
Carbamazepine	1.39×10^{-3}	0.87×10^{-3}
2,4-D	0.91×10^{-3}	0.60×10^{-3}

3.4 Estrogen-responsive receptor gene expressions in fish tissues

The physiological impact of mixtures of contaminants in effluents on exposed goldfish were measured via the expression levels of ERα1, ERα2, ERβ1, ERβ2

and NPR for tissues including liver, kidney and spleen over different seasons (spring, summer and fall) and exposure durations (7, 30 and 60 days).

The results indicated that during spring operations, the 7-day exposure of fish to reuse water caused a significant down-regulation in mRNA levels of ERα2, ERβ2 and NPR in the kidney and ERα1 and NPR in the liver (data not showed). By comparison, the expression levels of ER genes in the spleen exposed to reuse water, were similar to those in fish and GAC process treated reuse water after 7 days' exposure. On the other hand, the mRNA levels of ERs in the kidney of fish exposed to effluent with UV/H_2O_2 treatment (7 days) showed an up-regulation trend for ERα2, ERβ1, ERβ2 and NPR compared to those in reuse water, indicating that the UV/H_2O_2 treatment of reuse water was effective in remediating endocrine disruption after acute exposure. Prolonged exposure (60 days) of goldfish in reuse water further suppressed some genes particularly in kidney and spleen, revealing sub-chronic inhibition effects of the reuse water to the goldfish. The results of this study illustrated that reuse water with the UV/H_2O_2 treatment showed no obvious reduction of estrogenic impact on fish after a prolonged exposure in spring [24].

The UV/H_2O_2 process also showed an estrogenic impact remediation potential, particularly in kidney and spleen of goldfish during summer operations by restoring the ER gene expressions to the control level. The varied performance of the UV/H_2O_2 process may arise from the fact that the composition of estrogenic substances in reuse water may differ seasonally. The spring melt runoff and heavy rain events occurring during spring period in Edmonton could result in a sharp increase of estrogenic substances and metals, simply because these substances are adsorbed in the soil and the sediments washed into the sewage system, and eventually they end up in the Gold Bar WWTP [12].

There was also no clear evidence indicating that the UV/H_2O_2 treatment of reuse water would further induce sub-chronic estrogenic effects to goldfish [24]. The ERα and ERβ protein had a very high binding specificity for estrogenic chemicals, leading to a diverse level of ER subtypes expression in different tissues. However, this binding affinity and tissue distribution of ERα, ERβ and NPR in goldfish over the exposure period was not clearly observed.

3.5 The expression of CYP 19 gene

The mRNA levels of the CYP19 gene in the liver of goldfish were measured after exposure for 7, 30 and 60 days to reuse, GAC treated (control) and UV/H_2O_2 treated reuse water during spring, summer and fall of 2012**.** In spring (fig. 3), the expression of aromatase genes CYP19a and CYP19b was found significantly elevated for fish exposed 7 days in reuse water, while CYP19a and 19b gene abundance of fish exposed in UV/H_2O_2 treated reuse water remained at the control level for this short term exposure. Prolonged exposure (7 and 30 day) of fish in reuse water lowered the mRNA level of CYP19a and 19b. The UV/H_2O_2 treatment of reuse water did not seem to ameliorate both of the aromatase encoding genes for the long term exposure [24]. An exception was observed for fish in UV/H_2O_2 treated reuse water after 60 days a significant down-regulation in the mRNA level of CYP19b was observed compared to those in the control goldfish samples. Similar results were observed for summer and fall (data not shown).

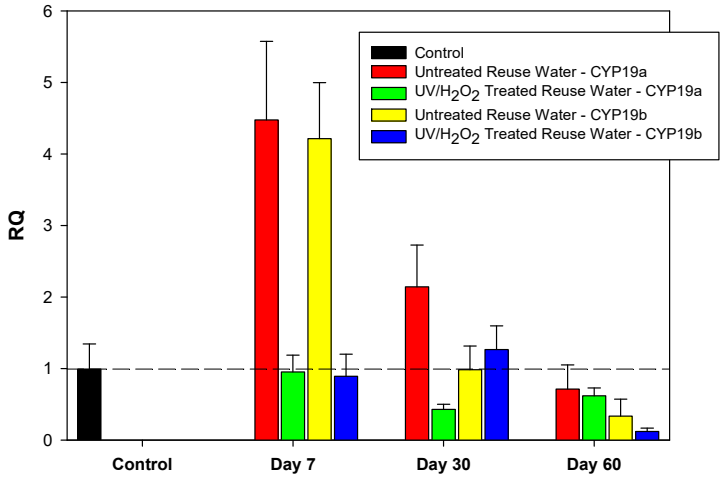

Figure 3: Quantitative PCR gene expression of aromatase gene CYP19a and CYP19b in the liver of goldfish exposed to GAC treated reuse water (control); untreated reuse water; and UV/H_2O_2 treated reuse water during spring 2012. Whiskers reflect standard error.

4 Conclusions

Low concentrations of CECs in municipal wastewater treatment plant effluents affect the possibility to reuse these waters. A potential candidate for tertiary municipal wastewater treatment of these CECs is UV/H_2O_2. In this study, a new approach was presented to predict the fluence-based degradation rate constants of environmentally occurring micropollutants, including carbamazepine and 2,4-D in a medium pressure (MP) UV/H_2O_2 system based on a previous bench-scale investigation. This approach could be used to estimate the performance of the MP UV/H_2O_2 process for degrading trace CECs found in municipal wastewater.

By using *in vivo* biomonitoring assays, both acute and sub-chronic endocrine disruptions were observed in liver, spleen and kidney of goldfish exposed in the reuse water. The pilot-scale UV/H_2O_2 process did not appear to be capable of remediating acute estrogenic activities in the reuse water as shown by impact on goldfish, whereas it has the potential to minimize the estrogenic effects of the reuse water in the chronic exposures (e.g., 60 days). Because the performance of UV/H_2O_2 process was UV fluence and H_2O_2 dependent, further optimization of this process may be required to remediate the estrogenic activity in wastewater.

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