# Novel Materials for Catalytic Ozonation of Wastewater for Disinfection and Removal of Micropollutants

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# Abstract

The purpose of this work was to identify novel materials that could be used for the catalytic ozonation of wastewater for improved removal of micropollutants and disinfection. The materials chosen for investigation were selected based on their commercial availability and composition characteristics that suggested that they could act as catalysts. Synthetic wastewater (SWW) was used to mimic municipal secondary effluent wastewater while obtaining constant and reproducible matrix characteristics. Polonite<sup>®</sup>, wollastonite, zeolite, TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (8%/92%), and AL-1010S (AlO<sub>2</sub>-based) were tested for their potential impact on efficiency of disinfection, based on the removal of E. coli bacteria and removal of contaminants of emerging concern (CECs), relative to conventional ozonation. Atrazine (ATZ), ibuprofen (IBP), naproxen (NPX), and gemfibrozil (GBZ) were used as indicator compounds. Zeolite and wollastonite did not promote disinfection and CECs removal; TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and AL-1010S provided improvement for both criteria, but to a lesser extent in SWW than in Milli-Q water; and Polonite<sup>®</sup> did not enhance the removal of CECs but led to the higher E. coli inactivation. These results suggest that Polonite<sup>®</sup>, AL-1010S, and TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> can act as catalysts and provide mechanisms to lower the ozone dose required to reach disinfection. The apparent kinetic constant of the reaction for the catalytic ozonation of ATZ, in the ultrapure water, was determined for Polonite<sup>®</sup>, TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and AL-1010S. The reusability of the catalysts was demonstrated over four consecutive cycles of 6 hours of treatment in a continuous flow ozonation system.

## **1** Introduction

The water demand is growing because of the expansion of the global population, while global warming and climate change negatively affect the availability of water and its quality (Dettinger et al., 2015; Hornberger et al., 2015). In addition, the list of contaminants of emerging concern (CECs) is expanding, creating new challenges to wastewater treatment facilities for identifying and developing approaches and technologies to mitigate the discharge of pollutants into the environment. New technologies are thus required to comply with, new or expected, more stringent regulations set by the governments and environmental agencies to protect our water resources. Switzerland is the first country that is working towards applying regulations and aims to achieve 80% removal of selected CECs during wastewater treatment (Mulder et al., 2015). Such regulations will pave the way for similar regulations in other countries, which would lead to improved quality of wastewater treatment and increased demand for effective treatment technologies.

Advanced Oxidation Processes (AOPs), which have garnered much attention in the wastewater treatment industry in the last decades, encompass processes based on free radicals, such as superoxide radical ( $^{\circ}O_2^{-}$ ), hydroperoxyl radical ( $^{\circ}HO_2$ ), hydroxyl radical ( $^{\circ}OH$ ), and alkoxyl radical ( $^{\circ}RO$ ) (Wang & Xu, 2012). Ozonation is a treatment that has been repeatedly proven as an effective method for disinfection

and removal of micropollutants and is considered as a tertiary wastewater treatment process for the removal of micropollutants (Kasprzyk-Hordern et al., 2003; Lee & von Gunten, 2010; von Gunten, 2003). The main drawbacks of ozonation for wastewater treatment are the potential of toxic transformation products formation, such as carboxylic acids and aldehydes (Martins et al., 2015), limited mineralization (Erol et al., 2009; Nawrocki & Kasprzyk-Hordern, 2010), selectivity of the reaction with ozone, and the low reaction rate constants (k) of some contaminants towards ozone (k<10 M<sup>-1</sup>s<sup>-1</sup>) (Broséus et al., 2009). Catalytic ozonation has the potential to overcome these limitations by opening different reaction pathways and potentially improve treatment efficiency.

Catalytic ozonation can be divided into homogeneous and heterogeneous processes that both promote the formation of hydroxyl radicals (R. Rosal et al., 2010). Heterogeneous catalytic ozonation commonly involves the use of metal oxides and supported metals (Gottschalk et al., 2000). Two mechanisms of heterogeneous catalytic ozonation generally contribute to the reactive systems: interfacial reaction and hydroxyl radical ('OH) mechanisms. These processes are based on the adsorption of the soluble ozone, properties of catalysts surfaces, and radical chain transfer reactions generating 'OH (Kasprzyk-Hordern et al., 2003; Roberto Rosal et al., 2011).

Over the recent years, catalytic ozonation studies searched for potential catalysts among metals (Al<sub>2</sub>O<sub>3</sub>-supported catalysts, TiO<sub>2</sub>, Ce/CeO<sub>2</sub>, Fe-based materials) (Guo et al., 2012) and materials containing metals in their structures, such as zeolites (Amir Ikhlag et al., 2012). Al<sub>2</sub>O<sub>3</sub>-supported catalysts enhanced the removal of some pharmaceuticals from aqueous solutions, such as effluent wastewater, synthetic wastewater (SWW), and ultrapure water (A. Ikhlaq et al., 2015; Roshani et al., 2014). TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> applied in catalytic ozonation enhanced the removal of para-chlorobenzoic acid (pCBA) and dimethyl phthalate from deionized water (Y. H. Chen et al., 2011). TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> promoted the formation of 'OH radicals, which is of interest for disinfection and removal of CECs from wastewater (K.-C. Chen & Wang, 2014; Y. H. Chen et al., 2011). Apparent kinetic modeling can be used to characterize the efficiency of the catalyst used during catalytic ozonation and the role played by 'OH radicals can be determined using radical scavengers, such as pCBA ( $k_{OH,pCBA} = 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) (Barry et al., 2014; Uslu et al., 2015). Polonite<sup>®</sup>, wollastonite, and zeolite have never been tested for catalytic ozonation, but we identified them as potential catalysts considering the presence of multiple metal oxides in their composition. Polonite® and wollastonite are calcium silicate minerals currently used for removing phosphates from wastewater. Zeolite is generally used in wastewater treatment as a filter medium for ammonia and heavy metal removal.

In the present study, five materials were evaluated as potential catalysts and the most promising ones were chosen for the further investigation. The potential of the materials was evaluated by testing their ability to enhance removal of the selected CECs in comparison to conventional ozonation and to facilitate disinfection, defined as 200 TC or *E. coli*/100 mL. The apparent kinetic constants for the removal of atrazine (ATZ) were determined for the most promising catalysts. A preliminary evaluation of the reusability of the selected materials was performed in a continuous flow reactor used to treat synthetic wastewater (SWW). The overall objective was to contribute to the development of improved technologies for the treatment of wastewater.

# 2 Experimental

# 2.1 Tested materials and target contaminants

Polonite<sup>®</sup>, a commercial product developed by Ecofiltration Nordic AB, was provided by Prof. Gunno Renman from KTH - Royal Institute of Technology, Sweden. Polonite® is obtained by high temperature heating of opoka, a natural calcium-silicate mineral, mined in southeastern Europe (Poland) and western Russia. The typical Polonite® composition includes: SiO<sub>2</sub> (40 % by weight), CaO (40%), Al<sub>2</sub>O<sub>3</sub> (6%), Fe<sub>2</sub>O<sub>3</sub> (2%), K<sub>2</sub>O (1%), MgO (1%), and other metal oxides such as TiO<sub>2</sub>, MnO<sub>2</sub>, P<sub>2</sub>O<sub>3</sub>. TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, a spherical particle composed of a TiO<sub>2</sub> core and Al<sub>2</sub>O<sub>3</sub> shell coating, was obtained from Yurui Chemical Co Ltd, Shanghai. The particles were composed of approximately 8% of TiO<sub>2</sub> and 92% of Al<sub>2</sub>O<sub>3</sub>. An AlO<sub>2</sub>-based product developed by BASF (product #AL-1010S) was provided by Air Liquide, USA. The exact composition of the material was not disclosed. This catalyst was provided later in the project, explaining the absence of data for that material in some of the early stage experiments. Wollastonite, a calcium silicate mineral, was provided by Canadian Wollastonite, Kingston, Ontario. It usually occurs as a common constituent of a thermally metamorphosed impure limestone. The typical composition of wollastonite consists of CaO (28%), SiO<sub>2</sub> (49%), Al<sub>2</sub>O<sub>3</sub> (10%), Fe<sub>2</sub>O<sub>3</sub> (4%), K<sub>2</sub>O (5%), MgO (2%), and a small fraction of MnO<sub>2</sub>, TiO<sub>2</sub> (% by weight) (Brogowski & Renman, 2004; Gustafsson et al., 2008). Zeolite, a silicate-based material containing alumina, was provided by ZeoCat Soluciones Ecológicas S.L.U, Spain. The exact chemical composition of zeolite is not available. Polonite<sup>®</sup>, wollastonite, and zeolite were sieved to retain only particle having a diameter of 2 to 4 mm. TiO<sub>2</sub>-AL<sub>2</sub>O<sub>3</sub> and AL-1010S were already provided with in pellets with a diameter of 3-4 mm. These materials contain Al<sub>2</sub>O<sub>3</sub> that has been previously shown to contribute to the removal of organic compounds during catalytic ozonation (Roshani, 2014, Pocostales, 2011, Ziylan-Yavas, 2017).

Atrazine (ATZ) ( $k_{03} = 6 [M^{-1} \cdot s^{-1}]$ ) (Martins et al., 2015), Gemfibrozil (GBZ) ( $k_{03} = 5 \times 10^4 [M^{-1} \cdot s^{-1}]$ ) (Gomes et al., 2017), Ibuprofen (IBP) ( $k_{03} = 9.1 [M^{-1} \cdot s^{-1}]$ ) (Gomes et al., 2017), and Naproxen (NPX) ( $k_{03} = 2 \times 10^5 [M^{-1} \cdot s^{-1}]$ ) (Gomes et al., 2017) were used as model compounds to monitor the removal of CECs during treatment considering that they have different reactivity towards ozone. Atrazine was selected for its lower reactivity towards ozone in order to facilitate the detection of the presence of other reaction mechanisms during catalytic ozonation. To facilitate the quantification of the target analytes, CECs were spiked in water at an initial concentration of 100-150 µg/L, which is in a range relevant to the range of concentrations found in effluent wastewaters (0.3-3.5 µg/L) (Westlund et al., 2017, Vieno et al. , 2014, Vidal-Dorsch et al., 2012). ATZ, IBP, GBZ, NPX, para-chlorobenzoic acid and chemicals used for the analysis of liquid ozone concentration were purchased from Sigma-Aldrich, Oakville, Ontario.

The *E. coli* K-12 bacteria strain was used in this research. The strain was kept at -80°C and cultured for each experiment when needed, using aseptic techniques and incubation for 24 hr prior to use in the experiments. For the experiments on the disinfection of SWW, *E. coli* was spiked in the range of 1 x  $10^5$  to 9 x  $10^5$  MPN/mL, which is 1 to 2Log higher than the count reported for effluent wastewaters.

# 2.2 Experimental setups

Two different ozonation systems were used to obtain the operating conditions required to meet the research objective: a semi-batch/batch and a continuous flow column. The semi-batch/batch system was used to determine the potential of the tested materials as catalysts (semi-batch regime) and apparent kinetics (batch regime). The continuous flow column system was used to investigate reusability of the materials. For both systems, ozone was produced using dry air fed to a TrioGen<sup>®</sup> TOC C2B (Ozonia) generator. Experiments were carried out at the room temperature and in triplicate, unless specified otherwise.

# 2.2.1 Semi-batch/batch system

The system presented in Figure 1 was designed to be operated as a semi-batch reactor to perform the screening of the materials for the catalytic ozonation of SWW. Experiments were conducted in a 1-L reactor connected to Wedeco<sup>®</sup> ozone analyzers for online monitoring of ozone concentration (g/Nm<sup>3</sup>) in the gas entering and leaving the vessel. The system was equipped with an Alicat<sup>®</sup> gas flowmeter (L/min) to monitor the feed gas to the reactor. Ozone was produced from dry air at the concentration of  $8.0 \pm 0.1$ g/Nm<sup>3</sup> and the Air/O<sub>3</sub> gas mixture was continuously bubbled (flowrate of  $1.0\pm0.1$  L/min) into the SWW (800 mL) through a sparger stone. The excess gas from the ozone generator was directed to a bubbling column and then to an ozone destruction column and potassium iodide (KI) solution traps used to prevent exposure to ozone. Reference conditions, i.e. conventional ozonation, were performed without any catalyst. For the catalytic ozonation experiments, the catalyst (25g or 50g) was placed into a stainless steel meshed holder attached to the lid of the reactor and submerged above the gas sparger. Continuous mixing was done using a magnetic stir bar at 500 RPM. Liquid samples (10 mL) were collected at time 0 and then at regular time intervals (every 4 min) until 20 min. Samples were analyzed for *E. coli* and for CECs.

For the kinetic studies, the same system was operated in batch mode. Milli-Q water (MQW) was used to prepare an ozone stock solution. Ozone was continuous sparged into the reactor with continuous mixing using a magnetic stir bar at 500 RPM. Temperature of the solution was maintained at 10±0.5 °C by placing the reactor in an ice bath in order to obtain increased solubility and stability of ozone in water during the experiment. The ozone stock solution was added to solutions to be treated with ozone in batch mode.



Figure 1. Schematic of the semi-batch/batch ozonation setup.

# 2.2.2 Continuous flow system

The continuous flow column reactor presented in Figure 2 consisted of two CPVC columns (4 cm ID) in series; a 70 cm high contact column followed by a 40 cm retention column used for sample collection. The system was equipped with a peristaltic pump (MasterFlex<sup>®</sup> L/S) to provide fixed SWW flowrate and residence time (RT) in the system. The ozonation system was equipped with the same flow meter and ozone analyzers as the semi-batch/batch system. The catalyst was placed in a holder made of stainless steel wire cloth with 2 mm openings and submerged into the contact column.

The SWW was fed into the contact column from the top port and provided counter-current liquidgas flow. The liquid leaving at the bottom of the contact column then entered the retention column from the top. Samples were collected through the sampling port at the bottom of the retention column. The offgas exiting at the top of the retention column was sent to the ozone analyzer and then the ozone destruction column.



Magnetic stir plate

Figure 2. Schematic of the continuous flow column ozonation setup

## 2.3 Synthetic wastewater

SWW was used to obtain a matrix representative of a secondary municipal effluent while obtaining a consistent matrix over the duration of the study. To prepare the SWW, the following chemicals were added into MQW: peptone (32 mg L<sup>-1</sup>), meat extract (22 mg L<sup>-1</sup>), and urea (6 mg L<sup>-1</sup>). The solution was sterilized in an autoclave, then the following chemicals were added into the solution: NaHCO<sub>3</sub> (96 mg L<sup>-1</sup>), CaSO<sub>4</sub>·2H<sub>2</sub>O (60 mg L<sup>-1</sup>), MgSO<sub>4</sub> (60 mg L<sup>-1</sup>), KCl (4 mg L<sup>-1</sup>), K<sub>2</sub>HPO<sub>4</sub> (28 mg L<sup>-1</sup>), CaCl<sub>2</sub>·2H<sub>2</sub>O (4 mg L<sup>-1</sup>), MgSO<sub>4</sub>·7H<sub>2</sub>O (2 mg L<sup>-1</sup>), and NaCl (7 mg L<sup>-1</sup>). The resulting solution had a pH of 7.6±0.2 and a COD value of 65±5 mg L<sup>-1</sup>. This recipe was adapted from Klamerth et al. 2010. All the chemicals were purchased from Sigma-Aldrich, Oakville, Ontario, were of analytical grade and were used without any further purification.

#### 2.4 Determination of apparent kinetics

The reaction between ozone and micropollutants can be described by direct or indirect reaction, i.e. through the reaction with  $O_3$  or 'OH. For example, degradation of atrazine can be described by the following reactions:

$$[O_3] + [C_{Atz}] \xrightarrow[kO_3]{} P \tag{1}$$

$$[^{\bullet}OH] + [C_{Atz}] \xrightarrow[kOH]{} P$$
(2)

The combined two reactions are commonly described by a general second-order equation (Acero et al., 2000):

$$-\frac{d[C_{Atz}]_t}{dt} = (k_{o3}[O_3]_t + k_{\cdot OH}[\cdot OH]_t) \times [C_{Atz}]_t$$
(3)

in which  $k_{O3}$  and  $k_{OH}$  are the reaction rate constants of ATZ with ozone and hydroxyl radicals, respectively. Since there is no direct approach for the quantitative measurement of 'OH concentration in the liquid phase, the quantification was done using the approach based on the use of a signal compound, parachlorobenzoic acid (pCBA) that was proposed by Elovitz & von Gunten, 1999. This approach is widely accepted and applied in studies of the ozone reaction kinetics (Acero et al., 2000; Lee & von Gunten, 2010; Roberto Rosal et al., 2011; Tong et al., 2010; Uslu et al., 2015). Contribution of the 'OH to the degradation of ATZ during the chemical reaction is described by Dodd et al. (Dodd et al., 2006) in the following manner:

$$f(\cdot OH) = \frac{k_{OH,Atz} \int_0^t [\cdot OH] dt}{k_{OH,Atz} \int_0^t [\cdot OH] dt + k_{O_3,Atz} \int_0^t [O_3] dt} = \frac{1}{1 + \frac{k_{O_3,Atz}}{k_{OH,Atz}} (\int_0^t [O_3] dt}}$$
(4)

The relationship between pCBA and 'OH can be used to indirectly quantify the 'OH concentration,

$$\int_0^t [\cdot OH] dt = \frac{-\ln\left(\frac{|pCBA|}{|pCBA|_0}\right)}{k \cdot OH, pCBA}$$
(5)

The  $R_c$  value describes the ratio of the concentration of 'OH to the concentration of O<sub>3</sub>. Therefore, a higher value indicates a higher proportion of 'OH in the reactive system:

$$R_c = \frac{[\cdot OH]}{[O_3]} = \frac{\int_0^t [\cdot OH] dt}{\int_0^t [O_3] dt}$$
(6)

Substituting (5) in (6)

$$R_{c} = \frac{\int_{0}^{t} [\cdot OH] dt}{\int_{0}^{t} [O_{3}] dt} = \frac{\frac{-\ln(\frac{|pCBA|}{|pCBA|_{0}})}{\frac{k_{OH,pCBA}}{\int_{0}^{t} [O_{3}]}}$$
(7)

[ 0D 4]

Finally, the overall reaction rate constant that is correlated to the ozonation treatment of ATZ can be described with the following equation:

$$k_{overall} = k_{O_3} + k_{OH} R_c \tag{8}$$

To determine the apparent reaction kinetics, 7.5 g of catalyst (AL-1010S, TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> or Polonite<sup>®</sup>) was placed inside the glass batch reactor (pre-cleaned with acetone and hexane solutions), and the reactor was filled with 250 mL of MQW. The MQW was enriched with O<sub>3</sub> for 30-45 minutes. The ozone concentration was monitored using the indigo method (4500-O3 OZONE [RESIDUAL] method from the Standard Methods for the Examination of Water and Wastewater) (American Public Health et al., 2005) and the gas bubbling was stopped when the target concentration (8 mg O<sub>3</sub>/l) was reached. The reactor was then placed on the magnetic stirring plate set at 500 rpm. ATZ solution (600  $\mu$ g/L), prepared in 50 mL of MQW, either with or without pCBA (Sigma-Aldrich, Oakville, Ontario), was added to the reactor containing the ozone solution and the catalyst. The injection port was immediately closed to limit the loss of ozone. Samples of 10 mL were taken after 2, 4, 6, 8, and 10 minutes using a syringe. The samples were analyzed for liquid ozone concentration, pH, ATZ, and pCBA concentration. For the ATZ analysis, each sample was spiked with 0.2 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> to quench any residual O<sub>3</sub> and stop the reaction between ozone and ATZ. For the control experiments (non-catalytic ozonation), catalyst was excluded from the protocol. The results were then analyzed using the approach described above to determine apparent kinetics and the contribution of hydroxyl radicals.

## 2.5 Reusability studies

A preliminary reusability study was performed over four cycles of use of each catalyst. Each cycle was conducted as a continuous 6 hours of treatment of SWW using the continuous flow column ozonation setup. 50 g of catalyst was placed into the stainless steel 2 mm mesh size socket and submerged into the contact column just above the sparger. Before introducing the ozone into the system, the contact column was filled, leaving the headspace for the gas to escape and to prevent overflow, with 700 mL of synthetic wastewater solution spiked with *E. coli* (1 x 10<sup>5</sup> to 9 x 10<sup>5</sup> MPN/mL) and ATZ (150 ±10 ppb). Samples were taken 3 times a day (after 1, 3 and 6 hours of operation) analyzed for *E. coli* and then stored at -18 °C until CEC analysis. At the end of each cycle, the system was washed with MQW, drained, and left to dry until the next day. For the control experiments, catalyst was excluded from the protocol and experiment proceeded as non-catalytic ozonation treatment.

# 2.6 Determination of the transferred ozone dose

For the continuous and semi-batch experiments, the transferred ozone dose (TOD) was calculated to take into account the mass transfer limitations associated with the use of a small ozonation systems. The ozone concentration measured in the feed-gas and off-gas were used to calculate the transferred ozone dose, using the following equation:

$$TOD = \sum \left( [O_3]_{in} - [O_3]_{out} \right) * Q_{gas} * t/V$$
(9)

where  $[O_3]_{in}$  is the ozone concentration in the feed gas to the reactor (mg/L),  $[O_3]_{out}$  is the ozone concentration in the off-gas that is leaving the reactor (mg/L),  $Q_{gas}$  is the gas flowrate (L/min), t is time (sec) and V the volume of solution (L). Results are presented as a function of the TOD.

#### 2.7 Quantification of CECs

Prior to chemical analysis, 1 mL of each sample was placed in a 1.5 mL plastic centrifuge tube that was centrifuged at 14 200 rpm for 10 minutes. A 0.5 mL aliquot of the supernatant was collected and

stored at -18 °C until the further analysis, and the rest was discarded. ATZ, IBP, GBZ, and NPX were analyzed using an LC-HRMS system, consisting of the Accela 600 LC System (Thermo Scientific, Waltham, MA, USA) in tandem with the LTQ XL Orbitrap mass spectrometer. Both, the LC and the MS, systems were controlled by the Thermo Xcalibur 2.0 software (Thermo Scientific, San Jose, CA, USA). A guard column (5mm x 2.1mm ID; 1.8µm) was used prior to the analytical column (50mm x 2.1mm ID; 1.8µm C18 Zorbax Eclipse Plus) (Agilent Technologies, Santa Clara CA, USA). Separation of the 25µL injected was conducted at 40°C with a binary buffer system composed of 2mM ammonium formate, 0.1% formic acid in MQW (Solvent A), and methanol 0.1% formic acid (Solvent B). A gradient elution at 0.3mL/min of A:B was conducted as follows: initial 95:5 (0-1 min), 75:25 (1-3.5 min), ramp to 80:20 (2.5-5 min), hold at 5:95 (5-8.5 min), and return to initial conditions 95:5 (8.5-10 min). Detection was performed using an electrospray ionization source (ESI) in a positive mode.

#### 2.8 Determination of the level of disinfection

Efficiency of disinfection was investigated by spiking SWW with *E. coli*. Bacteria were cultured in an LB broth solution, prepared by adding 2 g of Difco LB broth into 100 mL of MQW. The broth was autoclaved, inoculated with live bacteria in an aseptic environment, and then incubated for 24 hours at 35°C and 130 RPM. After 24 hours, cell density was measured by Thermo-Scientific UV-Vis spectrophotometer at the wavelength of 600 nm, and the bacteria was added into the SWW to obtain an initial count of 10<sup>5</sup> cells/mL. Analyses were performed using the Colilert method, designed to measure total coliforms count (Jarvis et al., 2010). The detection limit was found to be 1 MPN/mL.

#### **3** Results and Discussion

#### 3.1 Control experiments

Control experiments were performed to account for potential removal of CECs by adsorption of the catalyst or by the possible adsorption to surfaces of the reactor. Adsorption experiments for CECs removal (data presented in the Figure S1, Supplemental material) were conducted using MQW, spiked with four CECs at a concentration of 150  $\mu$ g/L for each compound and using 25 g of material per L of solution. Results indicated removals by adsorption of less than 13%. Removal obtained during the experiments must exceed these percentages in order to conclude that the reactive system contributed to the removal of the target compounds. The adsorption could be explained by the moderately log K<sub>ow</sub> values: 3.18 (NPX) (Hansch et al., 1995), 4.77 (GBZ), 3.97 (IBP), and 2.97 (ATZ) or by the possible complexation with metals presented in the materials (Rivera-Jiménez et al., 2010).

Control experiments were performed to evaluate the potential deactivation of bacteria in presence of the materials tested as potential catalysts. SWW was spiked with the CECs at 150 µg/L and *E. coli at*  $5\pm3 \times 10^5$  MPN/mL. The results (data presented in the Figure S2, Supplemental Material) indicated a slight reduction (max 0.5 MPN/mL) of the bacteria exposed to the material for 20 minutes, which was shown to be statistically insignificant based on a student's t-test ( $\alpha$ =0.05, n=2, p> 0.05).

# 3.2 Screening of materials

Catalytic ozonation experiments were conducted using MQW spiked with CECs at the concentration of 150  $\mu$ g/L and using the semi-batch reactor. Experiments were performed in MQW to evaluate the efficiency of the materials without any influence of more complex matrices that might bias

the screening of the materials. Ozone was sparged into the reactor for 10 minutes, and samples were collected at 0, 1, 2, 3, 4, 5, and 10 minutes. The average removal levels of CECs for duplicate experiments are presented in Figure 3.



**Figure 3.** Average removal of ATZ, GBZ, IBP and NPX (150 μg/L) in MQW vs TOD during ozonation (O<sub>3</sub>) or catalytic ozonation using 25 g/L of Polonite, TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, Wollastonite, Zeolite (n=2)

NPX, known to be reactive with ozone, was efficiently removed even at low doses of ozone and in absence of catalysts. However, the presence of catalysts allowed to reach higher removal levels of ATZ, GBZ, and IBP, for some ozone doses and materials, in comparison to ozone alone. Statistically significant (student *t*-test, p<0.05) increases in the removal levels were observed while using Polonite<sup>®</sup> (ATZ, GBZ, IBP), TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (ATZ, GBZ, IBP), wollastonite (GBZ, IBP), and Zeolite (GBZ). Zeolite also provided a significant increase in the removal of IBP but only at TOD > 12 mg O<sub>3</sub>/L. At doses above 10 mg O<sub>3</sub>/L, almost complete removal of the CECs was obtained using catalytic ozonation, while ozone alone removed less than 60% of the compounds, except for NPX that was removed at concentration lower than the limit of detection. The differences in trend between the different CECs can be explained by the reactivity of these compounds with ozone. ATZ and IBP have a low reaction rate with ozone k<sub>O3</sub><10 M<sup>-1</sup> s<sup>-1</sup> (Acero et al., 2000; Bing et al., 2015), while GBZ and NPX are highly reactive towards ozone with  $k_{O3} > 5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  (Gomes, 2017).

The pH behavior during treatment with each catalyst was investigated considering that pH can impact the ozone half-life in water, which in turn can influence the removal of contaminants (Kasprzyk-Hordern et al., 2003). During the ozonation in absence of any catalyst, pH of the solution decreased with the increasing TOD, as shown in Figure 4. The shift of pH to the acidic range can be explained by the formation of short chain acids and is favorable to the direct reaction between O<sub>3</sub> and the contaminants, as it was observed in other studies of ozonation of micropollutants in pure water (Martins, 2015). In presence of zeolite, the initial pH decreased to 4.5. In presence of wollastonite and TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, pH of the solution shifted to values between 6 and 7, while in presence of Polonite<sup>®</sup> pH increased above 10, due to the caustic nature of the mineral and reactive CaO phase (Gustafsson et al., 2008). The increase in pH creates favorable conditions for the formation of 'OH radicals and may contribute to better removal of compounds, considering that the reaction rate constants with 'OH radicals are higher than with ozone (ATZ k<sub>OH</sub> = 3 x  $10^9$  M<sup>-1</sup> s<sup>-1</sup> (Acero et al., 2000) and IBP k<sub>OH</sub> = 6 x  $10^8$  M<sup>-1</sup> s<sup>-1</sup> (Bing et al., 2015)).





#### 3.3 Disinfection of synthetic wastewater

Catalytic ozonation experiments for disinfection were carried out using the semi-batch reactor. SWW was spiked with *E. coli* to obtain an initial count in the range of  $2 \times 10^5$  to  $5 \times 10^5$  MPN/ml and two different loadings of catalyst 25 and 50 g/L were tested. Based on the quantification method used in this research, the Log unit reduction from the initial count should be equal or greater than 5.0 Log units to reach the target disinfection of less than 200 *E. coli*/100 mL. The results from the Colilert analyses are summarized in Figure 5.







# Figure 5. Average *E. coli* $Log_{10}$ MPN removal during ozonation and catalytic ozonation using two different doses of catalysts 25 and 50 mg/L. (error bars = standard deviation, n = 3)

When Polonite<sup>®</sup>, TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, AL-1010S, and Zeolite were used in quantity of 25 g catalyst/L, the disinfection criteria was reached at a TOD of 34 - 39 mg/L, which is smaller than the values obtained for the conventional ozonation (38 - 49 mg/L of TOD). Polonite<sup>®</sup>, TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, AL-1010S, and to a lesser extent zeolite, provided an improved disinfection for a given ozone dose in comparison to non-catalytic ozonation. However, the use of wollastonite did not improve the disinfection in comparison to non-catalytic ozonation. SWW matrix facilitated the transfer of ozone into the solution with transferred doses of ozone of 46-50 mg/L in SWW compared to 27-30 mg/L in MQW using the same operating conditions (O<sub>3</sub> gas concentration =  $8.0\pm0.1 \text{ g/m}^3$  and gas flowrate of  $1.0\pm0.1 \text{ L/min}$  for 20 minutes of ozone sparging into the reactor). During treatment, the pH was also affected differently depending on the material tested: for zeolite, wollastonite, AL-1010S, and TiO<sub>2</sub>-AL<sub>2</sub>O<sub>3</sub> the pH decreased from 7.6±0.2 to 7.2±0.1, for Polonite<sup>®</sup> the pH increased up to 9.8±0.1, while for non-catalytic ozonation the pH decreased to 7.1±0.1.

The use of 50 g catalyst/L allowed to reduce the TOD required to reach disinfection under certain conditions. Polonite<sup>®</sup> and AL-1010S catalysts reduced the required TOD to 25 - 28 mg/L, corresponding to a 30-50% reduction in TOD. TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> used with a TOD > 20 mg/L also showed a statistically significant (p<0.05) effect on the removal of *E. coli*. At the higher catalyst loading (50 g/L) and for a TOD of 10 mg/L, wollastonite and zeolite provided an improved disinfection compared to non-catalytic ozonation treatment, but that effect was diminished with further increases in TOD. At this higher catalyst load, the pH was also affected differently depending on the material tested: zeolite and wollastonite led to a decrease of pH to  $7.3\pm0.1$ , AL-1010S, and TiO<sub>2</sub>-AL<sub>2</sub>O<sub>3</sub> stabilized the pH, while Polonite® increased the pH up to  $10.0\pm0.1$ .

The increased efficiency, observed under certain conditions, can be explained by the increased availability of oxidizers formed in presence of the catalysts that can oxidize the cell membranes of the microorganisms, causing the rupture of the membranes, affecting the cell viability, and contributing to the disinfection (Jyoti & Pandit, 2004).

## 3.4 CECs removal from synthetic wastewater

The CECs removal from the SWW was determined from the same experiments as the ones described for disinfection and results are reported in Figure S3 (Supplemental material) for a catalyst load of 25 g/L and Figure 6 for a load of 50 g/L. The more complex SWW matrix reduced the level of CECs removal obtained at a given TOD compare to MQW (Figure S3 compared to Figure 3); for example, ATZ in SWW was removed at 10-20% for a TOD of 10 mg/L in both the presence or absence of catalysts; while in MQW (Figure 3) ATZ was removed below detection limits in the presence of Polonite<sup>®</sup> and TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>. This can be explained by competing reactions with other constituents in the matrix or scavenging effects (Elovitz & von Gunten, 1999). It is also possible that the presence of the various compounds in the matrix affected the activity of the material surface sites. In addition, with the pH shifting to the alkaline range, HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>-2</sup> become dominant and can act as radical scavengers (rate constant of k<sub>OH</sub> = 1.5 x 10<sup>7</sup> M<sup>-1</sup>s<sup>-1</sup> for HCO<sub>3</sub><sup>-</sup> and k<sub>OH</sub> = 4.2 x 10<sup>8</sup> M<sup>-1</sup>s<sup>-1</sup> for CO<sub>3</sub><sup>2-</sup> (Kasprzyk-Hordern et al., 2003)), limiting the reaction between CECs and 'OH radicals formed. The salts used in the preparation of SWW, CaSO<sub>4</sub>·2H<sub>2</sub>O, MgSO<sub>4</sub>, K<sub>2</sub>HPO<sub>4</sub>, and MgSO<sub>4</sub>·7H<sub>2</sub>O, can also affect the availability of 'OH radicals (Amir Ikhlaq et al., 2012).

The use of 25 g/L of catalyst (Figure S3) indicated that NPX and GBZ were efficiently removed by all treatments and that catalytic ozonation did not improve the removal of these two compounds. However, Polonite<sup>®</sup> and TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> significantly (p<0.05) increased the removal of IBP; and TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> significantly improved the removal of ATZ. Wollastonite and zeolite did not improve the removal of any CECs in comparison to ozonation. When a higher amount of catalyst was used, 50 g/L (Figure 6), a statistically significant (p<0.05) increase in the removal was obtained only in presence of TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> for ATZ, which is the less sensitive to direct reaction with ozone. These results do not provide clear evidence that catalytic ozonation improved the removal of the selected compounds in comparison to non-catalytic ozonation. A negative effect (p<0.05) was even observed for the removal of CECs at the highest load of wollastonite, which could not be explained. Although higher removals were seldomly observed, further investigation would be required to determine if the amount and nature of the transformation products formed were affected by the use of the catalysts. This aspect is important considering that transformation products might contribute to the residual toxicity of the treated wastewater.



**Figure 6**. Average removal of ATZ, GBZ, IBP and NPX (150  $\mu$ g/L) in SWW as a function of TOD during ozonation (O<sub>3</sub>) and catalytic ozonation using 50 g/L of Polonite, TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, Wollastonite, Zeolite, AL-1010S. (n = 3, Error bars = Standard deviation)

Experiments with adjusted initial pHs were conducted to evaluate if the change in pH, caused by the catalysts added into SWW might be the main factor leading to improved efficiency of the treatment. SWW was spiked with ATZ, GBZ, IBP, and NPX at the concentration of  $110\pm10 \mu g/L$  and initial *E. coli* of  $6\pm2 \times 10^5$  MPN/ml. Using 0.1M NaOH or 0.1M H<sub>2</sub>SO<sub>4</sub> solutions, pH was adjusted to conduct experiments at two different pHs:  $10.0\pm0.1$  (to obtain a similar pH to the highest one obtained in presence of a catalyst) and  $7.5\pm0.1$ . Non-catalytic ozonation experiments were carried in the same conditions as the ones described in Sections 3.3 and 3.4, and results are summarized in Table 1.

**Table 1.** Average removal of CECs and *E. coli* in SWW adjusted to different initial pHs prior to ozonation performed at a TOD of 50 mg/L.

	Average removal $(n=3) \pm STD$ during non-catalytic ozonation				
pH of treated SWW	Log <sub>10</sub> MPN Removal	ATZ	GBZ	IBP	NPX
рН 10	$2.90\pm0.35$	$54\%\pm8\%$	no longer detected	$59\%\pm14\%$	no longer detected
рН 7.5	$4.67\pm0.15$	55% ±4%	no longer detected	$57\% \pm 2\%$	no longer detected

Disinfection was affected by the increase in pH and resulted in a decrease of 2 Log units in the alkaline conditions but the analysis of the CECs indicating that the same levels of removal were obtained at both pHs. These results indicate that the increase in pH observed during catalytic ozonation using Polonite<sup>®</sup> cannot alone explain the higher removals obtained and suggest that mechanisms based on catalysis and other reactive species are playing a significant role.

# 3.5 Reusability of the most promising catalysts

The reusability of Polonite<sup>®</sup>, TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, and AL-1010S was investigated over consecutive cycles in the continuous flow system. SWW was spiked with ATZ at the concentration of 100  $\mu$ g L<sup>-1</sup> and *E. coli* to obtain an initial count in the range of 2 x 10<sup>5</sup> to 5 x 10<sup>5</sup> MPN/ml. The system was operated over four cycles of 6 hours. Disinfection and ATZ removal results are reported as values normalized to the transferred ozone dose (TOD) for each time point using the following equation (10):

$$Log MPN_{removal, normalized} = \frac{Log MPN_{removal, calculated \times TOD}}{TOD_{target}}$$
(10)

where the TOD was calculated for each cycle, and the  $TOD_{target}$  was determined as the expected value for the selected conditions. For all three materials and over the four consecutive cycles, catalytic ozonation provided greater disinfection than conventional ozonation (Figure 7, ozonation being represented by the grey area). However, the target disinfection (5 MPN log unit) was reached only four times. The average TOD values recorded per cycle were: 28.6±1.4 mg/L (TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>), 30.7±3.8 (AL-1010S), 28.3±2.5 mg/L (Polonite), and 32±1.1 mg/L (non-catalytic ozonation). Commercially available TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> provided a stable level of disinfection over the four treatment cycles, with an average removal of 4.11 MPN Log units, compared to the average removal of 2.24 MPN Log units for non-catalytic ozonation. Polonite<sup>®</sup> provided the least stable efficiency with averages of normalized log MPN removal over each cycle of 5.11, 4.61, 4.56, 4.34 Log units. The decrease in the efficiency might be attributed to the decrease of the pH in the collected samples with every consequent cycle, e.g. (9.32, 9.2, 8.7, 8.1), which can be attributed to the dissolution of reactive CaO phase (Gustafsson et al., 2008). The decrease during the fourth cycle observed with Polonite<sup>®</sup> and TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> might be associated with the exhaustion of the material and/or saturation of the active sites on the surface of catalysts. During catalytic ozonation with AL-1010S catalyst, the efficiency increased in each consecutive cycle, reaching the highest efficiency and meeting the target disinfection criteria in the fourth cycle. This might be explained by an activation of the catalyst surface by exposure to ozone.



Figure 7. Average normalized log MPN removal over 4 consecutive cycles of catalytic ozonation using the same catalytic material in SWW. (n=2, Grey area represents average log MPN removal for ozonation  $\pm$  STD).

For all three materials and over the four consecutive cycles, catalytic ozonation provided greater removal of ATZ than conventional ozonation (Figure 8, ozonation being represented by the grey area). The ATZ removal with catalytic ozonation ranged from 72% to 100% and the removal exceed the removal by ozonation in 30 out of the 39 runs. Polonite<sup>®</sup> and TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> had slightly better results than AL-1010S that did not equal the removal obtained with ozonation alone in several runs. In every cycle and for all three materials, a decline in the removal of ATZ was observed, which is opposite to the increasing efficiency during each cycle of disinfection. The difference in trend over the successive cycles for the removal of ATZ removal and disinfection suggests that different reaction mechanisms are dominant for

each criterion. A possible explanation for this decline is a partial exhaustion of the catalyst and/or a saturation of the available surface sites during each 6hr cycle. We can hypothesize that the washing of the catalysts with MQW between cycles might have contributed to the recovery of the efficiency at the beginning of each cycle. Normalized to the TOD, ATZ removal values for TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, AL-1010S, Polonite<sup>®</sup>, and non-catalytic ozonation were 94%, 89%, 96% and 84%, respectively.



Figure 8. Average normalized ATZ removal over 4 consecutive cycles of catalytic ozonation using the same catalytic material in SWW. (n=2, Grey area represents average log MPN removal for ozonation  $\pm$  STD).

# 3.6 Apparent kinetics of catalytic ozonation of ATZ

Apparent kinetics was investigated using the batch reactor. Ozone concentration in the MQWbased ozone stock solution was measured at 8.79 mg/L (0.18 mmol/L) with standard deviation of 0.33 mg/L (0.0068 mmol/L). ATZ was spiked into the reactor to obtain the initial concentration of 108  $\mu$ g/L (0.0005 mmol/l) with standard deviation of 4.7  $\mu$ g/L (0.00002 mmol/L) between experiments. For experiments investigating the role of hydroxyl radicals in the removal of ATZ in these catalytic systems, pCBA was added at initial concentration of 11.5 mg/L (0.073 mmol/L), to quench any available •OH radical formed during the ozonation of the solution, with standard deviation of 0.59 mg/L (0.0038 mmol/L). The temperature changed from 10.5±0.7 °C to 9.6 ±0.6 °C during the 10 minutes of the experiments. The pH was also monitored and recorded for each experiment and will be discussed later.

With low adsorption of ATZ on the surface of selected catalysts (<10%), and low kinetic reaction with ozone, the catalytic ozonation might have contributed to the removal of ATZ (in addition to direct reaction between ozone and ATZ) through the indirect ozonation mechanism, i.e. formation and utilization

of 'OH radicals. Non-catalytic and catalytic ozonation experiments, with and without the presence of the scavenging compound pCBA, were thus performed to determine the contribution of 'OH to the removal of ATZ. Results were analyzed to determine if the removal of ATZ followed a 2<sup>nd</sup> or a 1<sup>st</sup> order reaction.

Results compiled in Figure 9 indicate different removal profiles as a function of time using ozonation or catalytic ozonation performed with the different materials tested as catalysts (AL-1010S, TiO<sub>2</sub>Al<sub>2</sub>O<sub>3</sub>, Ozone and Polonite). The removal profiles were significantly affected by the addition of the 'OH scavenger (pCBA). These results demonstrate that 'OH played a significant role in all cases of catalytic and non-catalytic ozonation treatment. For the catalytic systems, 'OH had a greater contribution in presence of TiO<sub>2</sub>-AL<sub>2</sub>O<sub>3</sub>, AL-1010S, and Polonite<sup>®</sup> with decreases of 45%, 55%, and 72% of the removal after 8 min in presence of pCBA, compared to decreases of 35% for ozone. These results suggest that in presence of the catalysts, the 'OH did play a more significant role than during ozonation.



**Figure 9**. Average ATZ concentration as a function of time during ozonation or catalytic ozonation in presence and absence of a scavenger pCBA in MQW (n=3, error bars = Standard deviation)

Using the approach developed by Elovitz & von Gunten, 1999, the apparent kinetic rate constant for the reaction between O<sub>3</sub> and •OH with ATZ in the presence of catalysts was determined for each catalyst and

summarized in Table 2. These values further demonstrate the reduced ability of the system to remove ATZ when •OH are scavenged.

	$\frac{k_{apparent}, pCBA}{(R^2)} M^{-1} s^{-1}$	$k_{apparent}$ , $M^{-1} s^{-1}$ $(R^2)$
Polonite	n/a	5 x 10 <sup>9</sup> (0.97)
TiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	8.77 (0.86)	6 x 10 <sup>9</sup> (0.89)
AL-10108	6.53 (0.9)	5 x 10 <sup>9</sup> (0.7)
Ozone alone	5.31 (0.92)	4 x 10 <sup>9</sup> (0.83)

**Table 2.** Apparent reaction rate constants for catalytic and non-catalytic ozonation of ATZ in absence and presence of the hydroxyl radical scavenger.

During the non-catalytic ozonation, pH of the MQW dropped from pH  $5.0\pm0.2$  to pH  $4.0\pm0.1$ , while catalytic ozonation with TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and AL-1010S catalysts increased the pH from  $5.0\pm0.2$  to  $6.9\pm0.2$  and  $7.6\pm0.3$ , respectively. With the presence of Polonite<sup>®</sup>, the pH of the solution increased to pH  $9.9\pm0.2$ . Therefore, it created an alkaline environment that was less favorable for the ozone stability in the solution. Theoretically, the generated ozone was converted to •OH, which explains the inability to calculate the  $f_{OH}$  for the catalytic ozonation with Polonite<sup>®</sup> that was scavenged in the reaction with the pCBA. For all other cases, the contribution of •OH radicals to the degradation of ATZ, was more than 65%, and the remaining being removed either by direct reaction with ozone or other possible catalytic reactions.

# 4 Conclusions

This work allowed the identification of three materials demonstrating a potential for use in catalytic ozonation: Polonite<sup>®</sup>, TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, and AL-1010S. Polonite<sup>®</sup> had the most important effect on lowering of the TOD required for disinfection but did not impact the removal of CECs. AL-1010S and TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> also improved the removal of *E. coli* but had limited impact on CECs removal. Zeolite and wollastonite provided limited effects in the range of conditions tested.

The second-order constants were investigated for the reaction between ozone and ATZ with the presence of Polonite<sup>®</sup>, TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, and AL-1010S catalysts. The treatment of ATZ during the catalytic ozonation with TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> had the faster rate of the removal in MQW. Results from scavenging experiments supported the hypothesis that the OH radicals play an important role in the removal of compounds with low reactivity towards ozone. Further investigation is required for extrapolation to other types of reactor and scale of treatment.

The reusability of the catalysts for disinfection purposes showed that AL-1010S and TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> can be reused without losing their efficiency in several cycles, even with a moderately high initial *E. coli* counts (3.9 to 4.1 MPN Log removal). Polonite<sup>®</sup> was the most efficient material in the first cycle but

exhibited a declining efficiency over four consecutive cycles while maintain a relatively stable removal of ATZ (> 90%). Catalytic ozonation with AL-1010S and TiO<sub>2</sub>-AL<sub>2</sub>O<sub>3</sub> was less stable in the continuous flow system.

This study demonstrated the potential of selected catalysts to improve treatment of wastewater by catalytic ozonation, especially for disinfection and to some extent CEC removal, which may help to meet more stringent regulations for disinfection and removal of micropollutants. Further investigation is however required to investigate the nature and/or toxicity of transformation products that could be formed during the catalytic ozonation, validate the performance in real wastewater and evaluate the economic viability of catalytic ozonation for wastewater treatment.

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# **Supplemental Material**



**Figure S1.** Removal of ATZ, GBZ, IBP, and NPX by adsorption on catalyst surface or other surfaces of the reactor.



**Figure S2.** Average *E.coli* log reduction as a function of time of exposure to the materials tested as potential catalysts without ozone (n=2)



**Figure S3.** Average removal of ATZ, GBZ, IBP and NPX (150  $\mu$ g/L) in SWW as a function of TOD during ozonation (O<sub>3</sub>) and catalytic ozonation using 25 g/L of Polonite, TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, Wollastonite, Zeolite, AL-1010S. (n = 3, Error bars = Standard deviation)



**Figure S4.** Change in TOD over the course of 1 cycle (6 hours of continuous operation) (n=4 or 5 for catalytic ozonation and n=2 for ozonation alone).