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Impact of Catalyst Load, Chemical Oxygen Demand and Nitrite on Disinfection and Removal of Contaminants During Catalytic Ozonation of Wastewater

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ABSTRACT

Calcium-silicate mineral Polonite® and aluminum-based catalyst (AL-1010S), previously identified as promising materials for catalytic ozonation, were used as catalysts to investigate the impact of some operating conditions (ratio ozone feed concentration to catalyst load) and wastewater characteristics (chemical oxygen demand - COD and nitrite - NO_2 concentration) on the disinfection and removal of contaminants of emerging concern (CECs) during catalytic ozonation of wastewater. Tests conducted in synthetic wastewater using two different ozone gas concentration (4 and 8 g (nm^3)) and 6 different catalyst loads provided ratios of 0.08, 0.11, 0.16, and 0.32. Results from the experiments indicated that the ratio of 0.11 was optimal and reached residual disinfection below 2 MPN mL^{-1} from the initial concentration of $5 \pm 2 \times 10^5$ MPN mL^{-1} and removal of atrazine (ATZ) above 80% from the initial concentration of 100±10 µg L^{-1} for an ozone dose of 41-45 mg L^{-1}. Catalytic ozonation with the selected materials enhanced disinfection and ATZ removal from synthetic wastewater (SWW) in comparison to non-catalytic ozonation by making the treatment performance less sensitive to increased chemical oxygen demand (COD) and nitrite (NO_2) in the matrix. Validation of the results in real wastewater effluents confirmed that catalytic ozonation enhanced disinfection. Catalytic ozonation using Polonite® and AL-1010S provided residual bacteria level of 0.6±0.42 MPN mL^{-1} and 0.29±0.41 MPN mL^{-1}, while non-catalytic ozonation lead to an average residual bacteria level of 1.26 ±0.09 MPN mL^{-1} for the same range of transferred ozone dose. However, under the conditions tested, a limited number of CECs were extracted at levels above the limits of quantification and further validation work is required to evaluate the performance of catalytic ozonation for the removal of CECs.

KEYWORDS

Catalytic ozonation, contaminants of emerging concern, wastewater treatment, disinfection, chemical oxygen demand, nitrite

1. Introduction

Protection of surface water from sources of contamination requires improvement of technologies used to treat wastewater. Contaminants of concern which may be discharged from wastewater treatment plants (WWTPs) along with treated wastewater include among others, pathogens and contaminants of emerging concern (CECs). CECs include compounds such as pharmaceutical and personal care products (PPCPs), endocrine disrupting compounds (EDCs), and pesticides, which have been reported to be present in effluent wastewater in North America, Europe, Asia, and Australia (Snyder 2008, Deblonde et al. 2011, Lee et al. 2013) in the range of ng L^{-1} and μg L^{-1} (Rodayan 2014, Yargeau et al. 2014, Westlund et al. 2017). Conventional biological and chemical wastewater treatment processes do not sufficiently eliminate many of these contaminants of concern and their transformation products, which are thus discharged in receiving streams (El-taliawy et al. 2017).

In the last decades, advanced oxidation processes (AOPs) gained attention as promising approaches to address the issue of CECs in wastewater. Catalytic ozonation is one of the AOPs utilizing interfacial reaction mechanisms and enhancing the formation of hydroxyl radicals ($^{\bullet}OH$), which then react with a larger variety of organic compounds than ozone (Snyder et al. 2006). Processes based on utilization of $^{\bullet}OH$ have a lower selectivity and thus enhance degradation of micropollutants, bacteria, pathogens, and viruses (Ikehata et al. 2006, Tondera et al. 2015, Gomes et al. 2017). Catalytic ozonation have the potential to lower the required ozone dose to reach and surpass treatment levels achieved using non-catalytic processes (Fontanier et al. 2005). Catalyst materials can attract the incoming ozone molecules to their surface and increase conversion of ozone into hydroxyl radicals through a series of step chain reactions. Catalytic ozonation can also affects the mass transfer of ozone into liquid (Nawrocki 2013).

In complex matrices such as wastewater, enhancement of the treatment efficiency with catalytic ozonation can be negatively affected by the presence of chemical oxygen demand (COD), total organic carbon (TOC), natural organic matter (NOM), nitrites (NO_2), scavenging compounds, or combination of these and other factors. Following the screening of several materials as potential catalysts for improved removal of CECs and *E.coli* (Kolosov et al. 2018), Polonite®, a calcium-silicate mineral, and aluminum-based metal oxide (AL-1010S), were selected for the further investigation in the present study. The objectives were: (1) To determine the optimal ratio of feed gas ozone concentration to catalyst loading for disinfection and removal of atrazine (ATZ); (2) To investigate the impact of important wastewater characteristics, including chemical oxygen demand (COD), nitrite (NO_2) concentration, and the hydraulic retention times (HRTs) on disinfection and removal of ATZ; (3) To validate the results obtained under controlled laboratory conditions, based on the use of synthetic wastewater (SWW), for the treatment of effluent wastewater collected at WWTPs.

2. Experimental

2.1. Materials and Reagents

Polonite®, developed by Ecofiltration Nordic AB, was provided by Prof. Gunno Renman from KTH – Royal Institute of Technology, Sweden. Polonite® is commercially sold for the removal of phosphorus from water and used for recycling nutrients in agriculture (Renman 2008). Aluminum based catalyst (AL-1010S) was developed by BASF and provided by Air Liquide, USA as part of a research project. Details about the composition of AL-1010S catalyst was not disclosed by our partners. All other chemicals used to prepare solutions and for analysis of samples were purchased from Sigma-Aldrich (Oakville, Ontario) and were of analytical grade (>97%) and used without any further purification. These catalysts were selected based on our previous work (Kolosov et al. 2018) and their composition and physical properties are reported in Kolosov et al. 2018.

2.2.Wastewater sources

2.2.1. Synthetic wastewater

Synthetic wastewater was prepared to mimic the effluent from wastewater treatment plants (WWTPs) and provide controlled conditions during the experiments. The baseline SWW, as used in our earlier work (Kolosov et al. 2018) was composed of the following chemicals added to Milli-Q water (MQW) (18.2 MΩ·cm): peptone (32 mg L^{-1}), meat extract (22 mg L^{-1}), and urea (6 mg L^{-1}). The solution was sterilized in an autoclave, then the following chemicals were added into the solution: $NaHCO_3$ (96 mg L^{-1}), $CaSO_4·2H_2O$ (60 mg L^{-1}), $MgSO_4$ (60 mg L^{-1}), KCl (4 mg L^{-1}), K_2HPO_4 (28 mg L^{-1}), $CaCl_2·2H_2O$ (4 mg L^{-1}), $MgSO_4·7H_2O$ (2 mg L^{-1}), and NaCl (7 mg L^{-1}). This mixture had a neutral pH (7.5±0.2) and a COD value of 65±5 mg L^{-1}. To provide variation in characteristics, the prepared SWW stock solution was diluted with MQW to the required composition. For the experiments based on SWW, bacteria (*E. coli [K-12 strain])* was cultured in a Lysogeny broth (LB) solution prepared by adding 2.0 g of Difco LB broth to 100 mL of MQW. The broth was autoclaved and inoculated with live bacteria in an aseptic environment and then incubated for 24 hours at 35°C and 110 RPM. After 24 hours, cell density was measured by spectrophotometry (Thermo-Scientific UV-Vis) at a wavelength of 600 nm. Inoculation of SWW was done to obtain an initial count of $5.0 \pm 3 \times 10^5$ cells mL^{-1}.

2.2.2. Municipal effluent wastewaters

Samples collected from the WWTPs were used in the validation experiments. The first WWTP (WWTP1) is situated in an off-island suburb of Montreal, QC, at the confluence of the Saint-Jacques River and the Saint Lawrence River. It treats an average flow of 65,000 m^3 day^{-1} of wastewater, which comes from a combined sewer system. The second WWTP (WWTP2) is situated in the southwestern Quebec region, east of Montreal and on the Yamaska river. WWTP2 treats wastewater from residential, commercial, and industrial sources, at an average flow of 56,000 m^3 day^{-1}. Effluent wastewater samples were collected in 1L plastic bottles and were then placed in a cooler for transportation to the laboratory. Upon arrival to the laboratory, a portion of each sample volume was placed in the -18°C freezer and the rest was stored in a refrigerator at 4°C for the experiments focused on disinfection that were performed within 24 hours of sample collection.

2.3. Experimental setup

Experiments were conducted in a continuous flow column reactor described in our earlier work (Kolosov et al. 2018). Briefly, it is composed of two CPVC columns (a 70 cm contact column followed by a 40 cm retention column used for sampling, both having a 4 cm ID). The system is equipped with a peristaltic pump (MasterFlex® L/S), digital gas flowmeter (ALICAT®) to measure gas flowrate coming into the system, two ozone analyzers (WEDECO®) to measure inlet and outlet ozone gas concentrations, an ozone destruct column to prevent any ozone discharge into the air, and a potassium iodide solution traps to capture any residual ozone. Ozone was produced by feeding dry air to a TrioGen® TOC C2B generator. Experiments were carried out at room temperature.

For catalytic ozonation experiments, the catalyst was placed in a stainless-steel mesh cylinder (2 mm mesh size, 3 cm ID) then submerged into the contact column above the gas-diffuser. Before introducing the ozone into the system, the contact column was filled with 700 mL of SWW or effluent wastewater and flowrate through the system was set according to the required hydraulic retention time (HRT).

2.4.Experimental design

2.4.1. Determination of optimal ozone to catalyst loading ratio and HRT

The optimal ratio of ozone feed gas concentration to catalyst loading was investigated using disinfection and removal of ATZ as criteria. ATZ was selected as a model compound because of its low removal efficiency during ozonation treatment, which would facilitate the detection of potentially enhanced removal due to the formation of the $^{\bullet}OH$ (Gomes et al. 2017). The catalysts loadings were selected to obtain the same ratios of feed gas ozone concentration to catalyst loading (0.08, 0.11, 0.16 and 0.32) for two different ozone gas concentration of 4 g $(nm^3)^{-1}$ (catalyst load of 12.5, 25, 37.5, and 50 g L^{-1}) and 8 g $(nm^3)^{-1}$ (catalyst load of 25, 50, 75, and 100 g L^{-1}). Two hydraulic flow rates (40 and 80 mL min^{-1}) were used to evaluate the potential impact of the HRT, 10 and 20 minutes, on treatment efficiency. In all experiments conducted the gas flowrate into the reactor was set at 1.0±0.05 L min^{-1}. Experiments were conducted in triplicate and each sample was analyzed in triplicate for disinfection and CECs concentration.

2.4.2. Impact of COD and NO_2 on treatment efficiency

Based on some of our unpublished studies on the effects of carbonates, nitrite, and total nitrogen on the ozonation of SWW for the disinfection of *E.coli*, nitrite, in the range of 1 to 5 mg L^{-1}, these characteristics were identified as factors impacting treatment efficiency. Experiments were thus conducted at initial levels of NO_2 of 0, 0.5, and 1.5 mg L^{-1} by spiking the SWW with appropriate amounts of concentrated sodium nitrite (0.1 M $NaNO_2$). The impact of COD on disinfection (initial *E. coli* concentration ranged $5\pm2 \times 10^5$ MPN mL^{-1}) and removal of ATZ (initial concentration of 100 µg L^{-1}) was also tested in the range of COD levels normally reported for secondary effluent (20±2, 40±3, and 70±5 mg L^{-1}). Based on optimal conditions identified in the previous section (2.4.1), the following conditions were used for these experiments: ratio of 0.11, ozone concentration 8 g $(nm^3)^{-1}$ and a catalyst loading of 75 g L^{-1}, HRTs of 10 and 20 minutes. Experiments were conducted in duplicate, due to the limited amount of catalyst, and each sample was analyzed in triplicate for disinfection and CECs concentration.

2.4.3. Validation in real wastewaters

Validation experiments using effluent wastewaters were also performed using optimal conditions identified in section 2.4.1 with SWW: ratio of 0.11, feed gas ozone concentration of 8 g $(nm^3)^{-1}$ and a catalyst loading of 75 g L^{-1}. But because of the more complex matrix, an HRT of 20 min was used to improve the contact time. Experiments were conducted using wastewater as collected (WWTP1) and wastewater spiked (WWTP2) with the compounds presented in Table 1, at initial concentration of 100 µg L^{-1} to facilitate the determination of the levels of removal. Experiments were conducted in triplicate and each sample was analyzed in triplicate for disinfection and CECs concentration.

2.5. CECs analysis

For experiments using SWW spiked with atrazine only, 1 mL of each sample was placed in a 1.5 mL safe-lock centrifuge tube and centrifuged at 14 200 rpm for 10 minutes. 0.5 mL of the supernatant was collected and stored at -18ºC until the further analysis. ATZ was analyzed by LC-HRMS (Accela 600 LC and LTQ XL Orbitrap mass spectrometer, Thermo Scientific, Waltham MA, USA) using the method described in our previous work (Kolosov et al. 2018). Briefly, 25µL was injected and separation was conducted at 40°C using a binary buffer system composed of 2mM ammonium formate and 0.1% formic acid in MQW (Solvent A) and methanol 0.1% formic acid (Solvent B). The gradient elution of A:B was 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). Electrospray ionization (Bisesi et al. 2014) in positive mode was used to detect ATZ.

For experiments using municipal wastewaters, after filtration (1.5 µm glass-fiber filters), 100 mL was transferred into a clean bottle for solid phase extraction (SPE) and spiked with a 100 µL of a mix of isotopes (500 µg L^{-1} in methanol) of each target analyte, as listed in Table 1. The surrogates were used to account to recovery during SPE and matrix effect during analysis. Oasis® MAX (Mixed-mode Anion eXchange) 6 cc cartridges were used to extract the target compounds. Target CECs were analyzed using the system described above but chromatographic separation was achieved using a Hypersil Gold column (50 Å~ 2.1 mm, 1.9 μm) with an in-line Direct-Connection UHPLC 0.2 μm filter. The elution was done at 0.3 mL min^{-1} using 5% methanol, 0.1% acetic acid in water (solvent A), and acetonitrile (solvent B) with a percentage of organic (B) changed as follows: 0 min (5%), 4 min (20%), 10 min (95%), 13 min (95%), 14 min (20%), 15 min (5%), and 18 min (5%). Detection was done in positive and negative ionization modes with a heated electrospray ionization (HESI) source. For Estrone, 17β-estradiol, and 17α-ethinylestradiol, ionization was performed in the negative mode using atmospheric-pressure chemical ionization (APCI), and a different gradient of water (solvent A) with acetonitrile (solvent B): percentage of organic (B) changed as follows: 0 min (40%), 8 min (60%), 11 min (40%).

Table 1. Targeted contaminants of emerging concern in the effluent wastewater collected at the WWTPs along with their respectively labelled surrogate.

COMPOUNDS	MW	SURROGATES
Atrazine (ATZ)	215.68	Atrazine-d5
Benzotriazole (BTZ)	119.13	Benzotriazole-d4
Mecoprop (MCP)	214.65	Mecoprop-d3
Carbamazepine (CBZ)	236.41	Carbamazapine-d10
Diclofenac (DFC)	296.15	Diclofenac-d3
Gemfibrozil (GBZ)	250.33	Gemfibrozil-d6
Ibuprofen (IBP)	206.28	Ibuprofen-d3
Naproxen (NPX)	230.26	Naproxen-d3
Sulfamethoxazole (SMX)	253.28	Sulfamethoxazole-d4
Triclosan (TCS)	289.54	Triclosan-d3
Trimethoprim (TMP)	290.32	Trimethroprim-d9
Venlafaxine (VLF)	277.41	Vanloflaxine-d6
17α-ethinylestradiol (EE2)	296.40	17α-ethinylestradiol-2,4,16-d4
17β-Estradiol (E2)	272.38	17β-Estradiol-2,4-d2
Estrone (E1)	270.37	Estrone-16,16-d2

2.6.Disinfection measurements

Analyses were performed using the Colilert method with a reagent from IDEXX laboratories (Westbrook, ME, USA) designed to measure total coliforms (TC) count (Jarvis et al., 2010). The detection limit for this method is 1 MPN mL^{-1} and the method is based on the following assumptions: (1) the target microorganisms do not repel each other; (2) the target microorganisms are randomly distributed in the water matrix; (3) the number of microorganisms in each quantum of inoculum are independent; (4) at least one viable target microorganism is present in every test tube (Jarvis et al., 2010). The disinfection criteria were 2 MPN mL^{-1} for experiments based on SWW inoculated with *E. coli* and 20 MPN mL^{-1} for experiments conducted using wastewater collected at WWTPs, which contained a large variety of bacteria.

2.7. Statistical analysis

Student's t-test was used to determine if the average removals of the tested conditions were significantly different ($p<0.05$). The data analysis was performed in Microsoft Excel using the SigmaXL add-in tool.

3. Results and Discussion

3.1. Effect of treatment conditions on the treatment efficiency

For each experiment, samples were collected at time 0, from the feed tank; at half the retention times (samples collected after 5 minutes ±3 seconds or 10 minutes ±3 seconds depending on the HRT) from the outlet of the system; and after completing a complete HRT cycle (samples collected after 10 minutes ±3 seconds and 20 minutes ±3 seconds of treatment depending on the HRT) from the outlet of the system. Treatment conditions were duplicated and results, presented in Tables S1 and S2 (Supplemental Material), are averages of the triplicates analysis of the duplicate experiments, along with average values obtained for each of the duplicate experiment. The transferred ozone dose (TOD) was calculated for each experiment to consider the mass transfer limitations related to the use of small ozonation systems and facilitate comparison of results. The desired efficiency criteria were set to >5.0 MPN Log units reduction for disinfection and >80% removal of ATZ.

Overall, results indicated that the presence of an increasing amount of catalyst in the system led to a higher TOD, further demonstrating the importance of measuring TOD for comparison of the results. Except at the lowest load of catalyst (ratio 0.32), catalytic ozonation with Polonite® and AL-1010S improved ($p<0.05$) both disinfection and ATZ removal compare to non-catalytic treatment under the same conditions. For the non-catalytic ozonation (ie. conventional ozonation), changes in HRT or concentration of ozone in the feed gas did not affect the disinfection efficiency.

However, the removal of ATZ was significantly enhanced ($p<0.05$) when using the higher concentration of ozone in the feed gas.

The impact of the treatment conditions is discussed in the following sections based on subsets of data summarizing results obtained at comparable TOD for the different ratios, ozone feed gas concentration and HRTs tested (Table 2). The efficiency of transfer in the system varied in function of the composition of the wastewater as well as the nature and amount of catalyst present. TOD values were considered equivalent when within ±4 mg L^{-1}.

Table 2. Comparison of disinfection and ATZ removal levels obtained at comparable TOD but using different HRT, ozone to catalyst ratios, ozone feed concentrations and catalysts (n=3).

Ozone to catalyst ratio	**TOD, mg L^{-1}**		**MPN Log_{10} Removal**		**ATZ removal, %**	
	Half cycle (20 min HRT)	**Full cycle (10 min HRT)**	**Half cycle (20 min HRT)**	**Full cycle (10 min HRT)**	**Half cycle (20 min HRT)**	**Full cycle (10 min HRT)**
Non-catalytic ozonation						
Ozonation 4 g $(nm^3)^{-1}$	22.1	22.4	2.3	2.9	17	22
Ozonation 8 g $(nm^3)^{-1}$	29.5	26.6	2.6	2.7	35	77
Catalytic ozonation with Polonite® 4 g $(nm^3)^{-1}$						
0.32	24.0	22.3	2.8	3.8	20[1]	45
0.16	28.4	29.2	2.3	3.6	31	84[1]
0.11	30.9	32.3	4.7	4.8	49	43
0.08	34.1	32.9	4.8	5.6	53	52
Catalytic ozonation with Polonite® 8 g $(nm^3)^{-1}$						
0.32	40.5	41.3	2.5	3.5	ND[2]	17[1]
0.16	38.4	38.7	3.5	5.5	99	99
0.11	45.2	41.5	5.5	5.5	87	97

0.08	46.4	46.9	5.6	5.3	84	97
Catalytic ozonation with AL-1010S 4 g $(nm^3)^{-1}$						
0.32	19.7	19.4	3.3	3.9	68	64
0.16	21.3	20.9	2.6	5.1	14	43
0.11	23.4	22.3	3.5	5.0	74	62
0.08	28.0	28.5	4.5	5.0	61	59
Catalytic ozonation with AL-1010S 8 g $(nm^3)^{-1}$						
0.32	24.7	28.7	2.2	3.2[1]	48[1]	48[1]
0.16	29.9	30.3	3.7	5.4	77	76
0.11	40.6	40.8	3.6	5.6	77	70
0.08	40.9	41.6	5.1	5.3	62	60

[1] No duplicate data available

[2] No data available

3.1.1. Effect of ozone feed gas concentration

During catalytic ozonation with AL-1010S disinfection, the use of a higher concentration of ozone in the feed gas (8 g nm^{-3}) did not impact the disinfection. Although the trend is not clear when looking at the data set, the statistical analysis indicated that the higher concentration of ozone in the feed gas led to a significant increase in ATZ removal ($p<0.05$).

The effect of ozone feed gas concentration on treatment efficiency was more noticeable during the catalytic ozonation with Polonite®. The removals of ATZ at low ozone feed concentration were mainly in the range of 20-53% (except for one treatment condition with 84% removal) compare to a range of 84-99% (except for one treatment condition with 17% removal). The use of a feed gas concentration of 8 g nm^{-3}, allowed to reach the target elimination of ATZ > 80% in all conditions tested, except for the low ozone to catalyst loading ratio (0.32). The use of the higher ozone concentration in the feed gas also allowed to reach the disinfection criteria in 5 out of the 8 conditions tested, while disinfection was reached only for one set of conditions (0.08, HRT 10 min) when using the lower concentration of ozone in the feed gas (4 g nm^{-3}). These results are in alignment with an earlier study reporting that an increased ozone concentration enhanced the removal of some phthalates during catalytic ozonation with TiO_2 and Al_2O_3 catalysts (Mansouri et al., 2015). Beltran et al. 2002 reported an increase of the oxidation rate at higher ozone concentration, which also supports the higher efficiency obtained in the present study.

3.1.2. Effect of the ozone to catalyst loading ratio

During catalytic ozonation with Polonite® and AL-1010S, under low ozone feed gas concentrations, the ratios of 0.32 and 0.16 (lower amounts of catalyst) the criteria of performance were not met, except for AL-1010S at 0.16 ratio and HRT of 10 min but no replicate data is available for that condition. Ratios of 0.11 and 0.08 for AL-1010S catalyst provided complete disinfection in most conditions, while only a ratio of 0.08 allowed to reach disinfection during catalytic ozonation with Polonite®. For the whole range of ratios tested with a low ozone feed concentration, the target removal of ATZ was not attained. With the increased ozone feed gas concentration, the ratio of 0.16 also provided complete disinfection at an HRT of 10 min and ATZ was removed at > 76% but treatment performances were still improved at ratios of 0.11 and 0.08, especially for disinfection at an HRT of 20 min. These results indicated that the most efficient ratios of ozone concentration to catalyst loading are 0.11 and 0.08 for both materials. Reed et al. 2006 also reported that during the catalytic oxidation with silica and MnO_2 catalyst, the higher catalyst loading provided enhanced oxidation of acetone. They hypothesized that this was due to an increase surface area having the ability to produce oxidative species at the active sites on the metal surface. Considering the limited difference in efficiency between the two ratios, it was decided to continue the testing of the materials using the ratio based on the lower loading of catalyst required, ie. ratio of 0.11.

3.1.3. Effect of HRT

During catalytic ozonation with Polonite® and AL-1010S, at low ozone gas concentration, an HRT of 10 minutes provided a significant increase ($p<0.05$) in the disinfection, in comparison to an HRT of 20 min but had no effect on ATZ removal. With the increased ozone gas concentration the difference between half and full cycle was amplified, distinguishing the disinfection efficiency of both cycles. The complete disinfection was reached at ratio of 0.16 with the full cycle (HRT of 10 minutes) while the half-cycle efficiency was below set criteria. Though the ATZ removal was not affected by the change in HRT cycle. Similar trends were previously reported in the ozonation of effluent domestic wastewater, where the increase of the ozonation time with similar ozone dose lead to a minimal change of the treatment efficiency (Wang et al., 2008)

The higher efficiency observed at an HRT of 10 minutes might be explained by the increased hydraulic flowrate that enhanced the mixing of gas into liquid in the contact column and possibly facilitating the catalytic reaction (Le Sauze et al. 1993). Although a short HRT can decrease the ozone bubble size in liquid to improve the ozone gas–liquid mass transfer rate, at the same time, is shorten the contact time which might impact the efficiency (El-taliawy et al., 2017). The use of a longer HRT might be beneficial in the treatment of effluent wastewater, because of the complex matrix that is wastewater. Considering the limited differences observed between the two HRTs, it was decided to continue the testing of the performance with both HRT to provide a longer contact time in the column.

3.2. Effect of COD and NO_2 on treatment performance

Results of duplicate experiments for ozonation and catalytic ozonation performed using variable concentrations of COD and NO_2 are presented in Figures 1 and 2 for the HRT of 10 min, which was previously identified as providing improved efficiencies. Similar trends were observed with the HRT of 20 min and results are presented in the Supplemental Material (Figures S1 and S2). The variability between the duplicates experiments was in the range of 0-9% for the ATZ removal and disinfection. The results presented in Figures 1 indicate that for ATZ removal the wastewater characteristics impacted efficiency of catalytic ozonation, with declining levels of removal with respect to COD and NO_2 concentrations. Catalytic ozonation was also shown to be superior to conventional ozonation under certain treatment conditions, especially for one set of SWW characteristics: medium (40 mg L^{-1}) initial COD and high (1.5 mg L^{-1}) NO_2. Results presented in Figure 2, indicated that the disinfection was superior for catalytic ozonation except for treatment of the SWW having the lowest COD content and no or low concentration of NO_2 conditions. The lack of improvement for this specific set of conditions can be explained by the complete disinfection already reached with the non-catalytic ozonation treatment.

For the non-catalytic ozonation the increase in the COD and NO_2 content significantly impacted the efficiency of treatment with ATZ removal decreasing from 86% to 44% over the range of composition tested and the MPN removal decreasing from 5.2 MPN Log_{10} units to below 2 MPN Log_{10} units. Similarly, both factors affected the efficiency of the catalytic treatment with ATZ removal decreasing from 90% to 44% over the range of composition tested and the MPN removal decreasing from 5.8 MPN Log_{10} units to 3.2 MPN Log_{10} units. For both factors (COD and NO_2 concentration) the change in performance was not linearly correlated with the concentration.

The effect of COD was reported to be of concern for the conventional AOPs, including non-catalytic ozonation, because of the larger number of oxidants to be consumed with the increased COD concentration (Andreozzi et al., 1999). Lazarova et al. 2013 also reported the negative effect of wastewater quality, including increase of COD, on the disinfection during ozonation treatment (Lazarova at al., 2013). Nitrite ions are considered to be an efficient OH radical scavengers (Wang, 2012), which explain the decrease in efficiency observed with increasing NO_2 concentration. The presence of nitrite in the solution increases the ozone demand during ozonation treatment (Stapf et al, 2016) and since both the catalytic and non-catalytic ozonation are based on reaction with hydroxyl radicals, any other constituents scavenging oxidative species have the potential to limit the degradation of some CECs (Lee and von Gunten, 2010).

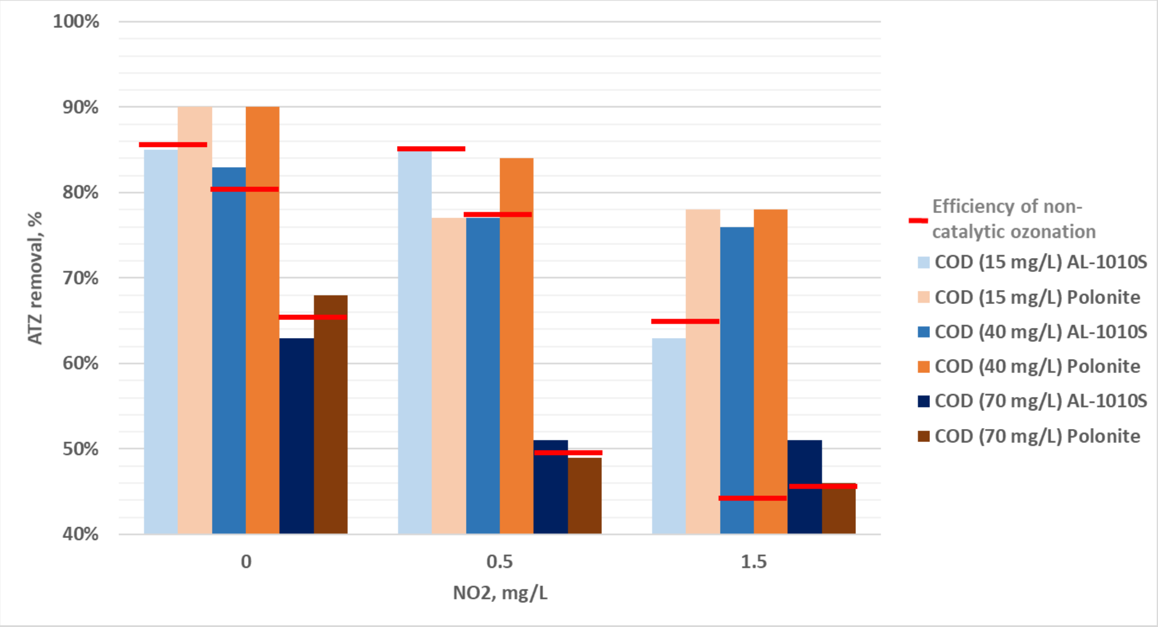


Figure 1. ATZ removal from SWW (10 min HRT) (n=2).

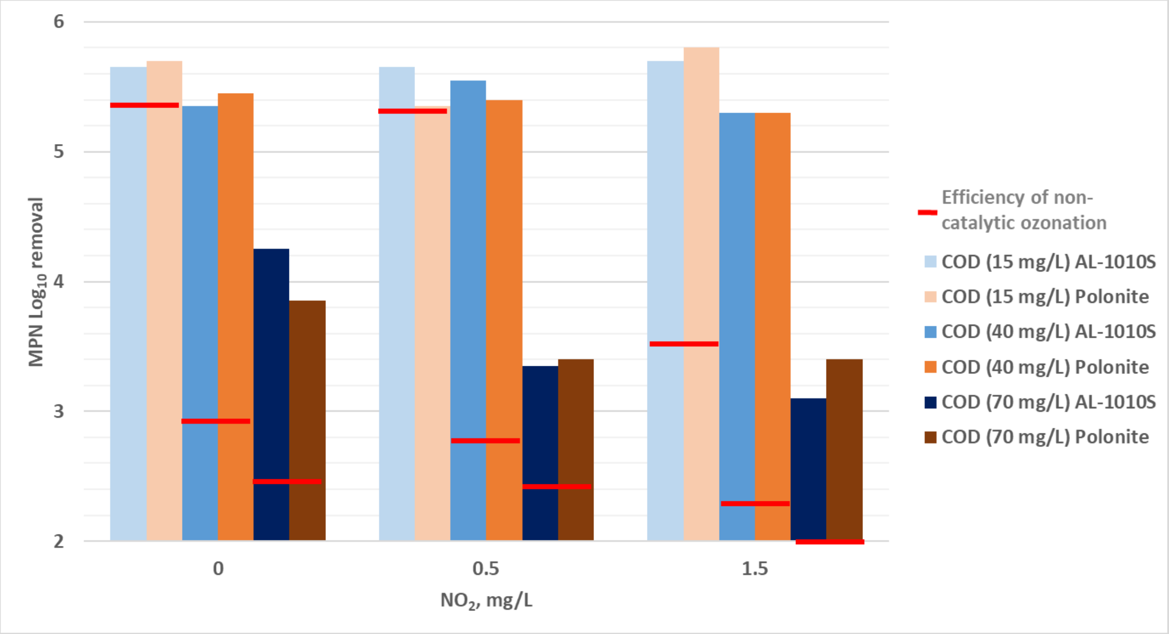


Figure 2. Disinfection of SWW (10 min HRT) (n=2).

To further investigate the effect of the combined COD and NO_2 factors on the treatment efficiency of catalytic ozonation, surface plots for the disinfection and ATZ removal were prepared (Figures 3 and 4). Results for the higher HRT (20 min), which reported similar trends, are presented in the Supplemental Material (Figures S3 and S4). The general conclusions drawn from the data is that the catalytic ozonation treatment with Polonite® and AL-1010S: 1. Over the range of conditions tested, COD had a greater effect on treatment performance than NO_2 for both disinfection (Figure 3) and ATZ removal (Figure 4) and ; 2. Catalytic ozonation was less affected by the variation in the COD or NO_2 content than conventional ozonation, which might be explained by the various reaction mechanisms having the ability to counteract to some extent the negative effect of increased COD and NO_2 concentrations. This effect was especially pronounced for disinfection for which the step decline in efficiency as a function of the COD content (Figure 3c) was damped for catalytic ozonation (Figure 3a and 3b). Catalytic ozonation thus has the potential to increase robustness of the process when treating wastewater of changing composition.

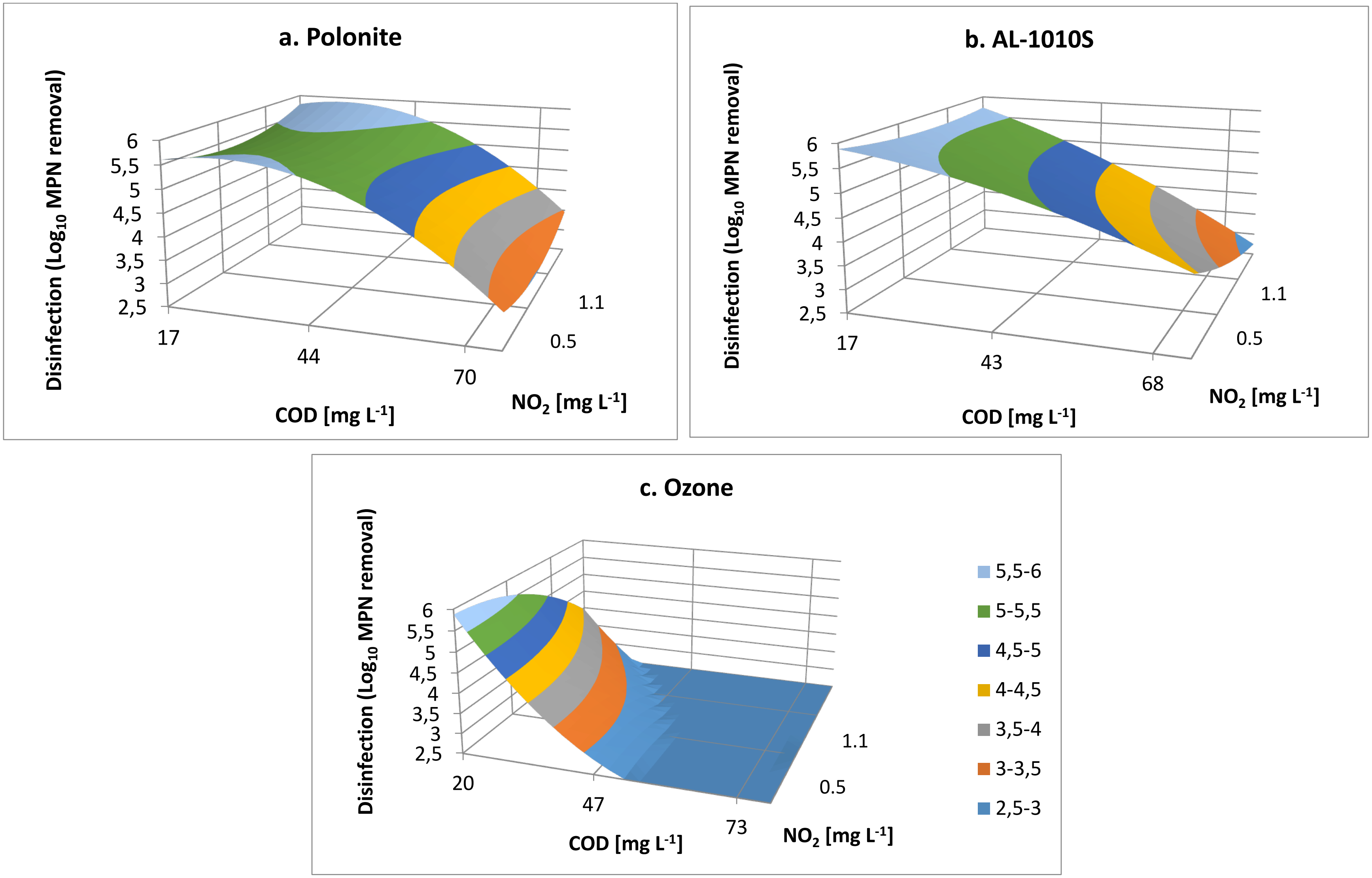
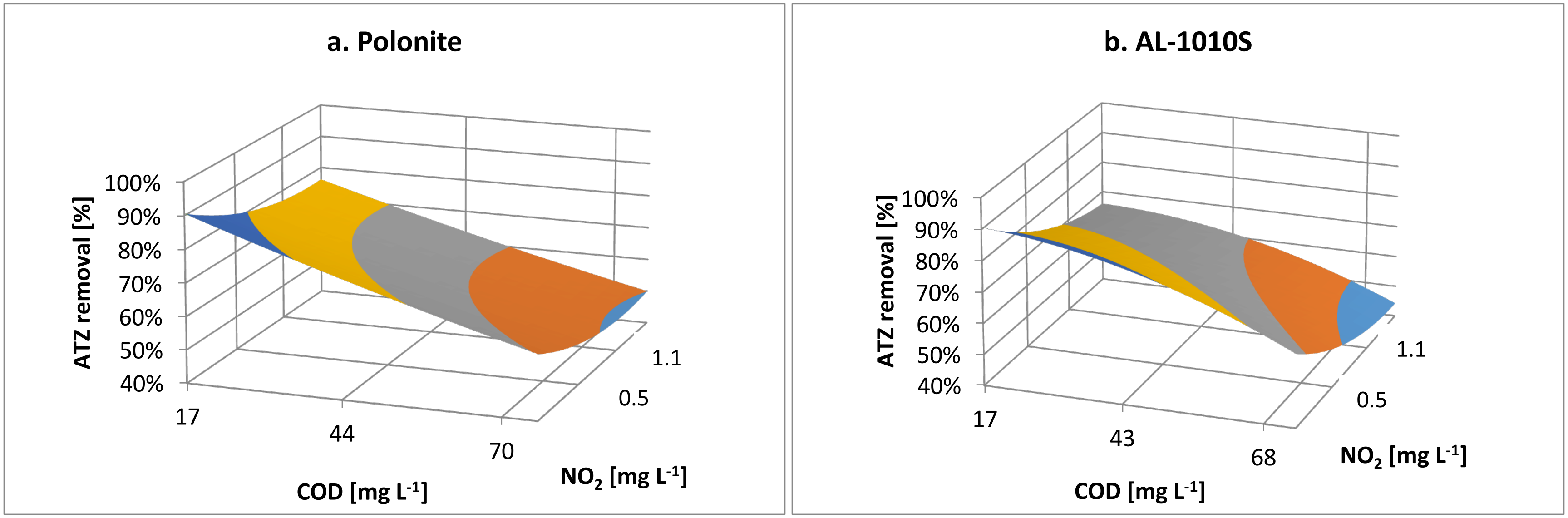

a. Polonite
Disinfection (Log_{10} MPN removal)
6
5,5
5
4,5
4
3,5
3
2,5
17
44
70
COD [mg L^{-1}]
1.1
0.5
NO_2 [mg L^{-1}]
b. AL-1010S
Disinfection (Log_{10} MPN removal)
6
5,5
5
4,5
4
3,5
3
2,5
17
43
68
COD [mg L^{-1}]
1.1
0.5
NO_2 [mg L^{-1}]
c. Ozone
Disinfection (Log_{10} MPN removal)
6
5,5
5
4,5
4
3,5
3
2,5
20
47
73
COD [mg L^{-1}]
1.1
0.5
NO_2 [mg L^{-1}]
5,5-6
5-5,5
4,5-5
4-4,5
3,5-4
3-3,5
2,5-3

Figure 3. Surface response plot of disinfection of SWW for different COD and NO_2 levels and an HRT of 10 minutes (n=2).



a. Polonite

b. AL-1010S

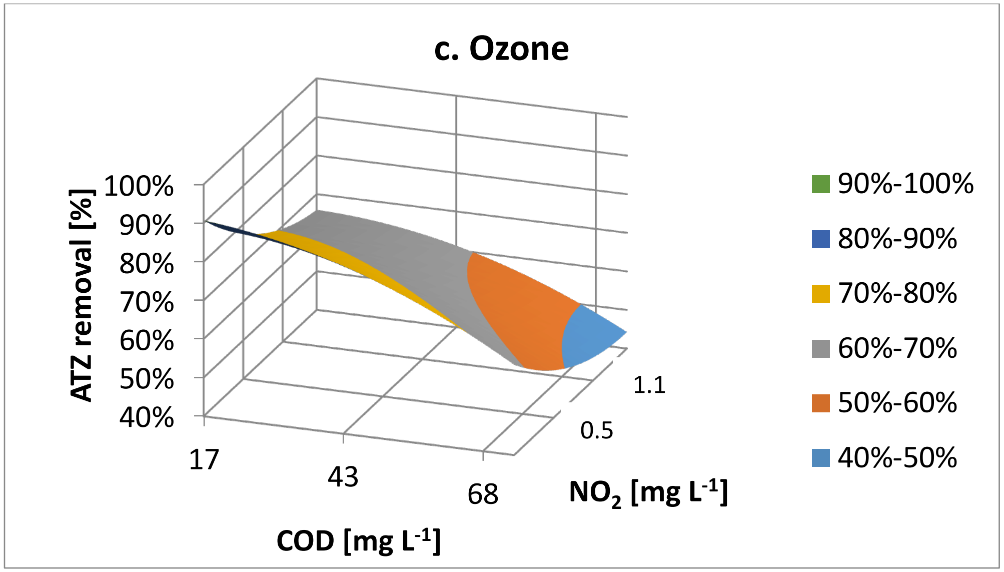


Figure 4. Surface response plot of ATZ removal from SWW for different COD and NO_2 levels and an HRT of 10 minutes (n=2)

3.3.Validation of performance when treating municipal effluent wastewater

Considering that real wastewater has a more complex matrix than SWW, the efficiency of treatment at optimal conditions was validated by treating wastewater effluents from two different plants. Triplicate analysis indicated the following characteristics of the wastewaters collected: WWTP1: 39.6±1.5 mg L^{-1} COD, NO_2 concentration of 1.46± 0.01 mg L^{-1} and pH of 7.43±0.1 and for WWTP2: 62±2 mg L^{-1} COD, NO_2 concentration of 1.07± 0.01 mg L^{-1} and pH of 7.68±0.01. These characteristics were in the range of the conditions tested with SWW, which were 40±3, and 70±5 mg L^{-1} and NO_2 of 0.5 and 1.5 mg L^{-1}.

The treatment of real wastewater rather than SWW led to different changes in pH: for AL-1010S, the pH dropped from 7.3 to 7.2 in SWW while it increased from 7.4 to 7.81 in wastewater; for Polonite®, the pH increased from 7.3 to 9.9 in SWW while it increased from 7.4 to 9.5 in wastewater. Similarly, during non-catalytic ozonation, the pH decreased from 7.3 to 7.0 in SWW, while it increased from 7.4 to 7.8 in wastewater. The difference in the pH shift during treatment might affect the formation of $^{\bullet}OH$ radicals during the ozonation and catalytic ozonation processes and suggest the formation of different transformation products. The effluent wastewater matrix impacted the transfer of ozone into the system and consequently, under the same operating conditions as in the SWW experiments, lower TODs were obtained. During the SWW treatment, average TOD were 70, 68, and 70.5 mg L^{-1} for catalytic ozonation with AL-1010S, Polonite®, and non-catalytic ozonation, while during treatment of the WWTP effluents the TODs were 43.3 (WWTP1) and 41.7 (WWTP2) mg L^{-1}, 50 (WWTP1) and 46.7 (WWTP2) mg L^{-1} and 46.3 (WWTP1) and 43.4 (WWTP2) mg L^{-1}, for the respective treatments. It is hypothesised that constituents present in the wastewater might be blocking available surface sites of the catalysts, limiting the transfer of ozone in solution, or that constituents in the wastewater is limiting the transfer of ozone, that was also reported in other studies of catalytic ozonation using different metals (Nawrocki, 2010; Sui et al., 2010).

Figure 5 presents the results of the validation experiments conducted with effluent collected at WWTP1, using the optimal condition identified in previous sections: ozone gas concentration of 8±0.1 g $(nm^3)^{-1}$ and ratio of catalyst to ozone concentration of 0.11 as well as an HRT of 20 min to provide sufficient contact time to treat the more complex matrix. The blue line represents the initial MPN Log_{10} value measured in the effluent wastewater before any treatment. No significant adsorption on the catalytic materials was observed after 20 minutes ($p>0.05$), suggesting that the significantly lower bacterial contents ($p<0.05$) observed during ozonation and catalytic ozonation occurred through the ozone/hydroxyl radical reactions rather than by binding to the catalyst surface or the surface of the reactor. Better disinfection was obtained with the catalytic ozonation treatments ($p<0.05$) with AL-1010S leading to a residual bacteria level of 0.6±0.42 MPN mL^{-1} with one case of complete disinfection and Polonite® leading to a residual value of 0.29±0.41 MPN mL^{-1} with two out of three experiments providing complete disinfection, while non-catalytic ozonation lead to an average residual bacteria level of 1.26 ±0.09 MPN mL^{-1}.

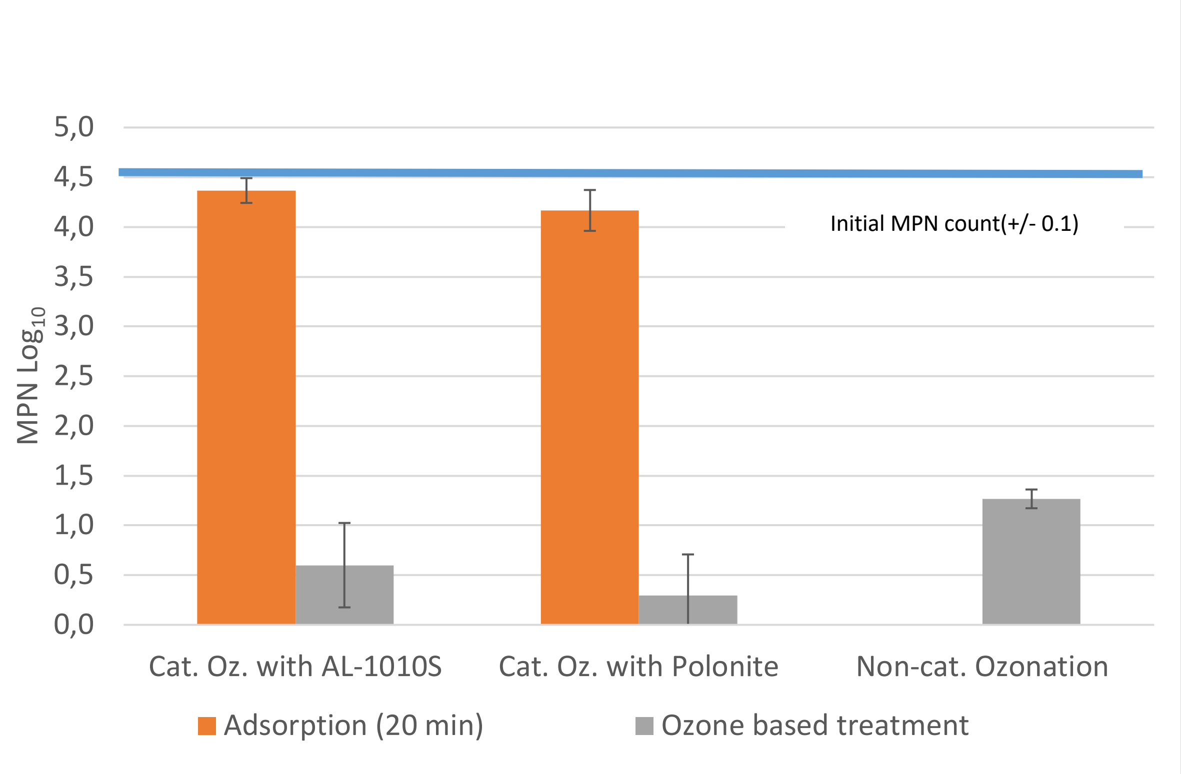


Figure 5. MPN mL^{-1} count after 20 minutes of exposure to the catalysts (adsorption), ozonation and catalytic ozonation performed at ratio 0.11 and 8 g $(nm^3)^{-1}$ozone feed gas concentration (n=3, error bars=standard deviation).

The removal of CECs in the effluent wastewater was investigated by monitoring the concentrations of native compounds in the effluent of WWTP1 and monitoring the concentrations of compounds spiked at 100 μg L^{-1} in the effluent of WWTP2 (list provided in Table 1) to increase the probability of being able to calculate removals. For both experiments (native and spiked), the recoveries during solid phase extraction were low and only the compounds with recoveries > 10% were considered (E2 35%, EE2 18%, VLF 68%, CBZ 18%, NPX 14%, TCS 15%, TMP 64% and MCP 33%). The chemical analysis included the whole list of target compounds but only compounds detected at concentrations above their limits of detection are reported in Table 3.

Table 3. Removal of the selected CECs from the effluent wastewater collected at WWTP1 (average of n=3) and WWTP2 (spiked at 100 ug L^{-1}, average of n=2) during ozonation and catalytic ozonation performed at ratio of 0.11, ozone concentration of 8 g $(nm^3)^{-1}$, and 20 min HRT.

	CBZ	**E2**	**EE2**	**MCP**	**NPX**		**TMP**	**TCS**	**VLF**	
	WWTP 1 $C_0 = 0.22±0.02$ µg L^{-1}	WWTP 1 $C_0 = 0.12±0.03$ µg L^{-1}	WWTP 1 $C_0 = 0.3±0.27$ µg L^{-1}	WWTP 2 $C_0 = 57±2.7$ µg L^{-1}	WWTP 1 $C_0 = 0.75±0.23$ µg L^{-1}	WWTP 2 $C_0 =125.3±19.1$ µg L^{-1}	WWTP 2 $C_0 =118±13$ µg L^{-1}	WWTP 2 $C_0 = 134.9±2.4$ µg L^{-1}	WWTP1 $C_0 = 0.42±0.04$ µg L^{-1}	WWTP 2 $C_0 = 86.8±5.9$ µg L^{-1}
AL-1010S	100%	77%	96%	84%	100%	75%	100%	11%	99%	100%
Polonite®	100%	71%	98%	79%	100%	73%	100%	NF	99%	97%
Ozonation	100%	88%	100%	67%	100%	63%	100%	15%	100%	96%

The results suggest limited enhancement of removal of CECs during catalytic ozonation with E2 being better removed during the non-catalytic treatment of wastewater from WWTP1 and only MCP being removed at higher levels during catalytic ozonation of the wastewater collected at the WWTP2 with AL-1010S (84%) and Polonite® (79%), which are higher than the removal of 67% obtained during non-catalytic ozonation ($p<0.05$). The absence of significant differences between the two treatments might be hidden by the fact that the ozone doses tested provided high removals of most target contaminants even for conventional ozonation. The reaction rates of the target CECs with ozone are ranging between 3.3×10^4 to 4×10^7 M^{-1} s^{-1} (Deborde et al. 2005, Vieno et al. 2014), with the exception to MCP with a lower reactivity towards ozone, 1×10^2 M^{-1} s^{-1} (Giraudo et al. 2017). The observed increased removal of MCP with catalytic ozonation might be explained by the enhanced formation of hydroxyl radicals contributing its removal. Considering the limited number of compounds that were successfully quantified, it is difficult to conclude on the overall efficiency of catalytic ozonation for the removal of CECs and further investigation is required.

4. Conclusion

The present research investigated the disinfection and removal of contaminants by catalytic ozonation using Polonite® and AL-1010S as catalysts to determine the effect of wastewater characteristics (COD and NO_2 content) and operating conditions (concentration of ozone in feed gas and ratio of ozone concentration to catalyst loading) on disinfection and removal of CECs. The main conclusions are:

- The use of the shorter HRT provided better performance. It would be interesting to investigate at larger scale the reasons for such improved performance, which was not possible using the current laboratory setup.
- The effect of the concentration of ozone in the feed gas was different depending on the catalyst (limited effect with AL-1010S but increased performance at high concentration for Polonite®). This suggest that optimization of this process parameter might be catalyst-dependent.
- The effect of the catalyst on the treatment performance compared to conventional ozonation was observed only at ratios of ozone feed gas concentration to catalyst loading of 0.11 and 0.08. No significant difference was observed at these ratios and a ratio of 0.11 was considered as optimal, which correspond a catalyst loading of 75 g when using 8 g $(nm^3)^{-1}$ ozone feed gas concentration and catalyst loading of 37.5 g with 4 g $(nm^3)^{-1}$ ozone feed gas concentration.
- Both NO_2 and COD concentrations greatly impacted efficiency of treatment but the use of AL-1010S or Polonite® rendered the process less sensitive to these wastewater characteristics.
- Treatment performance for disinfection were maintained when treating real wastewater. However, except for the higher removal of MCP during catalytic ozonation of wastewater, the limited number of CECs that were quantifiable in the matrix impose further testing before concluding on treatment performance for CEC removal.

5. Acknowledgment

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6. References

Andreozzi, R., Caprio, V., Insola, A., and Marotta, R. (1999). Advanced oxidation processes for water purification and recovery. *Catalysis Today, 53*(1), 51-59.

Beltrán, F. J., Rivas, J., Alvarez, P., and Montero-de-Espinosa, R. (2002). Kinetics of heterogeneous catalytic ozone decomposition in water on an activated carbon. *Ozone: Science and Engineering*, 24(4), 227-237.

Bisesi, J. H., W. Bridges and S. J. Klaine (2014). "Effects of the antidepressant venlafaxine on fish brain serotonin and predation behavior." *Aquatic Toxicology* **148**: 130-138.

Deblonde, T., C. Cossu-Leguille, P. Hartemann and F. Cannes (2011). "Emerging pollutants in wastewater: A review of the literature." *International Journal of Hygiene and Environmental Health* **214**(6): 442-448.

Deborde, M., S. Rabouan, J. P. Duguet and B. Legube (2005). "Kinetics of aqueous ozone-induced oxidation of some endocrine disruptors." *Environmental Science and Technology* **39**(16): 6086-6092.

El-taliawy, H., M. Ekblad, F. Nilsson, M. Hagman, N. Paxeus, K. Jönsson, M. Cimbritz, J. la Cour Jansen and K. Bester (2017). "Ozonation efficiency in removing organic micro pollutants from wastewater with respect to hydraulic loading rates and different wastewaters." *Chemical Engineering Journal* **325**: 310-321.

Fontanier, V., S. Baig, J. Albet and J. Molinier (2005). "Comparison of Conventional and Catalytic Ozonation for the Treatment of Pulp Mill Wastewater." *Environmental Engineering Science* **22**(2): 127-137.

Giraudo, M., G. Cottin, M. Esperanza, P. Gagnon, A. O. D. Silva and M. Houde (2017). "Transcriptional and cellular effects of benzotriazole UV stabilizers UV-234 and UV-328 in the freshwater invertebrates Chlamydomonas reinhardtii and Daphnia magna." *Environmental Toxicology and Chemistry* **36**(12): 3333-3342.

Gomes, J., Costa, R., Quinta-Ferreira, R. M., and Martins, R. C. (2017). Application of ozonation for pharmaceuticals and personal care products removal from water. *Science of the Total Environment*, 586, 265-283.

Ikehata, K., N. Jodeiri Naghashkar and M. Gamal El-Din (2006). "Degradation of Aqueous Pharmaceuticals by Ozonation and Advanced Oxidation Processes: A Review." *Ozone: Science and Engineering* **28**(6): 353-414.

Kolosov, P., M.-L. Peyot, and V. Yargeau (2018). "Novel Materials for Catalytic Ozonation of Wastewater for Disinfection and Removal of Micropollutants." *Science of The Total Environment,644, 1207-1218.*

Lazarova, V., Liechti, P.-A., Savoye, P., and Hausler, R. (2013). Ozone disinfection: main parameters for process design in wastewater treatment and reuse. *Journal of Water Reuse and Desalination*, **3**(4), 337-345.

Le Sauze, N., A. Laplanche, N. Martin and G. Martin (1993). "Modelling of ozone transfer in a bubble column." *Water Research* **27**(6): 1071-1083.

Lee, Y., and von Gunten, U. (2010). "Oxidative transformation of micropollutants during municipal wastewater treatment: Comparison of kinetic aspects of selective (chlorine, chlorine dioxide, ferrateVI, and ozone) and non-selective oxidants (hydroxyl radical)." *Water Research, 44*(2), 555-566.

Lee, Y., D. Gerrity, M. Lee, A. E. Bogeat, E. Salhi, S. Gamage, R. A. Trenholm, E. C. Wert, S. A. Snyder and U. Von Gunten (2013). "Prediction of micropollutant elimination during ozonation of municipal wastewater effluents: use of kinetic and water specific information." *Environmental Science and Technology* **47**(11): 5872-5881.

Mansouri, L., Sabelfeld, M., Geissen, S.-U., and Bousselmi, L. (2015). Catalytic ozonation of model organic compounds in aqueous solution promoted by metallic oxides. *Desalination and Water Treatment*, **53**(4), 1089-1100.

Nawrocki, J. (2013). "Catalytic ozonation in water: Controversies and questions. Discussion paper." *Applied Catalysis B: Environmental* **142**: 465-471.

Nawrocki, J., and Kasprzyk-Hordern, B. (2010). "The efficiency and mechanisms of catalytic ozonation." *Applied Catalysis B: Environmental* , **99**(1-2), 27-42.

Reed, C., Lee, Y. K., and Oyama, S. T. (2006). "Structure and oxidation state of silica-supported manganese oxide catalysts and reactivity for acetone oxidation with ozone." *The Journal of Physical Chemistry B*, **110**(9), 4207-4216.

Renman, A. (2008). "On-site wastewater treatment: Polonite and other filter materials for removal of metals, nitrogen and phosphorus (Doctoral dissertation, KTH), Stokholm, Sweden."

Rodayan, A. (2014). "Presence and Fate of Drugs of Abuse in Environmental Waters and Engineered Systems" (Doctoral dissertation, McGill University Libraries), Montreal, Canada.

Snyder, S. A. (2008). "Occurrence, Treatment, and Toxicological Relevance of EDCs and Pharmaceuticals in Water." *Ozone: Science and Engineering* **30**(1): 65-69.

Snyder, S. A., E. C. Wert, D. J. Rexing, R. E. Zegers and D. D. Drury (2006). "Ozone oxidation of endocrine disruptors and pharmaceuticals in surface water and wastewater." *Ozone: Science and Engineering* **28**(6): 445-460.

Stapf, M., Miehe, U., and Jekel, M. (2016). Application of online UV absorption measurements for ozone process control in secondary effluent with variable nitrite concentration. *Water Research*, *104*, 111-118.

Sui, M., Sheng, L., Lu, K., and Tian, F. (2010). "FeOOH catalytic ozonation of oxalic acid and the effect of phosphate binding on its catalytic activity." *Applied Catalysis B: Environmental*, **96**(1-2), 94-100.

Tondera, K., K. Klaer, J. Gebhardt, J. Wingender, C. Koch, M. Horstkott, M. Strathmann, L. Jurzik, I. A. Hamza and J. Pinnekamp (2015). "Reducing pathogens in combined sewer overflows using ozonation or UV irradiation." *International Journal of Hygiene and Environmental Health* **218**(8): 731-741.

Tong, S., R. Shi, H. Zhang and C. Ma (2010). "Catalytic performance of Fe3O4-CoO/Al2O3 catalyst in ozonation of 2-(2, 4-dichlorophenoxy) propionic acid, nitrobenzene and oxalic acid in water." *Journal of Environmental Sciences* **22**(10): 1623-1628.

Vieno, N., and Sillanpää, M. (2014). "Fate of diclofenac in municipal wastewater treatment plant—a review." *Environment International*, 69, 28-39.

Wang, J. L., and Xu, L. J. (2012). "Advanced Oxidation Processes for Wastewater Treatment: Formation of Hydroxyl Radical and Application." *Critical Reviews in Environmental Science and Technology, 42*(3), 251-325.

Wang, S., Ma, J., Liu, B., Jiang, Y., and Zhang, H. (2008). "Degradation characteristics of secondary effluent of domestic wastewater by combined process of ozonation and biofiltration." *Journal of Hazardous Materials*, ***150***(1), 109-114.

Westlund, P., and Yargeau, V. (2017). "Investigation of the presence and endocrine activities of pesticides found in wastewater effluent using yeast-based bioassays." *Science of The Total Environment*, 607, 744-751.

Yargeau, V., Taylor, B., Li, H., Rodayan, A., and Metcalfe, C. D. (2014). "Analysis of drugs of abuse in wastewater from two Canadian cities." *Science of The Total Environment*, 487, 722-730.

Supplemental Material

Table S1. Disinfection and ATZ removal levels for ozone to catalyst loading ratios at ozone feed gas concentration of 4 g $(nm^3)^{-1}$

OZONE TO CATALYST RATIO	High HRT								Low HRT							
	TOD, mg/l	Sampling Time, min	Average MPN Removal	Replicate 1	Replicate 2	Average Atrazine removal, %	Replicate 1	Replicate 2	TOD, mg/l	Sampling Time, min	Average MPN Removal	Replicate 1	Replicate 2	Average Atrazine removal, %	Replicate 1	Replicate 2
Non-catalytic ozonation																
0	**22.1**	*10*	2.3	2.1	2.4	17	16	17	**11.2**	*5*	2.4	2.3	2.4	7	1	13
	44.0	*20*	2.6	2.0	3.2	26	19	33	**22.4**	*10*	2.9	2.7	3.1	22	11	33
Polonite® catalyst, Ozone concentration in feed gas 4 g $nm^{3\ -1}$																
0.32	**24.0**	*10*	2.8	2.3	3.3	20*	36	4	**11.3**	*5*	3.8	3.3	4.2	40	40	40
	47.7	*20*	3.3	3.0	3.6	52	49	54	**22.3**	*10*	3.8	3.4	4.2	45	43	46
0.16	**28.4**	*10*	2.3	2.3	2.3	31	4	57	**14.8**	*5*	3.0	2.8	3.2	60**	60	
	56.6	*20*	2.9	2.8	3.0	39	10	68	**29.2**	*10*	3.6	3.2	3.9	84**	84	
0.11	**30.9**	*10*	4.7	3.6	5.7	49	49	49	**15.8**	*5*	3.8	3.7	3.9	42	41	42
	61.6	*20*	5.7	5.6	5.7	54	53	55	**32.3**	*10*	4.8	4.4	5.2	43	43	43
0.08	**34.1**	*10*	4.8	3.7	5.9	53	52	53	**16.3**	*5*	5.0	4.6	5.3	51	47	54
	66.9	*20*	5.7	5.4	5.9	60	56	64	**32.9**	*10*	5.6	5.3	5.9	52	44	60
AL-1010S catalyst, Ozone concentration in feed gas 4 g $nm^{3\ -1}$																
0.32	**19.7**	*10*	3.3	3.2	3.3	68	61	75	**9.8**	*5*	3.2	3.3	3.1	63	62	63
	39.1	*20*	4.0	3.9	4.0	79	78	79	**19.4**	*10*	3.9	3.7	4.0	64	63	65
0.16	**21.3**	*10*	2.6	2.4	2.8	14	3	24	**10.7**	*5*	4.3	3.5	5.0	26	14	37
	39.5	*20*	3.2	3.0	3.3	41	21	61	**20.9**	*10*	5.1	5.0	5.2	43	29	57
0.11	**23.4**	*10*	3.5	3.2	3.8	74	70	78	**11.4**	*5*	5.0	5.0	5.0	58	55	60
	47.3	*20*	4.5	3.9	5.1	77	75	78	**22.3**	*10*	5.0	5.0	5.0	62	60	63
0.08	**28.0**	*10*	4.5	3.7	5.2	61	52	70	**14.1**	*5*	5.0	5.0	5.0	55	51	58
	56.1	*20*	5.4	5.2	5.6	71	63	78	**28.5**	*10*	5.0	5.0	5.0	59	56	62

[*] Unexpected low recoveries of one replicate

[**] No duplicate data available

Table S2. Catalytic and non-catalytic ozonation experiments for at ozone feed gas concentration of 8 g $(nm^3)^{-1}$

OZONE TO CATALYST RATIO	High HRT								Low HRT							
	TOD, mg/l	Sampling Time, min	Average MPN Removal	Replicate 1	Replicate 2	Average Atrazine removal, %	Replicate 1	Replicate 2	TOD, mg/l	Sampling Time, min	Average MPN Removal	Replicate 1	Replicate 2	Average Atrazine removal, %	Replicate 1	Replicate 2
Non-catalytic ozonation																
0	**29.5**	***10***	2.6	2.4	2.8	35	1	68	**13.5**	***5***	2.7	2.4	2.9	59	55	63
	53.8	***20***	3.4	3.3	3.4	87	80	93	**26.6**	***10***	3.1	2.7	3.4	77	75	79
Polonite® catalyst, Ozone concentration in feed gas 8 g nm$^{3\ -1}$																
0.32	**40.5**	***10***	2.5	2.5	2.5	***			**25.7**	***5***	3.2	3.2	3.2	3*	3	
	75.4	***20***	2.8	2.8	2.8	72*	72		**41.3**	***10***	3.5	3.5	3.5	17*	17	
0.16	**38.4**	***10***	3.5	2.9	4.1	99	98	100	**19.8**	***5***	4.7	4.0	5.3	95	89	100
	76.7	***20***	5.4	5.1	5.7	100	100	100	**38.7**	***10***	5.5	5.3	5.7	99	98	100
0.11	**45.2**	***10***	5.5	5.3	5.7	87	86	87	**21.6**	***5***	5.5	5.4	5.6	94	94	94
	83.7	***20***	5.5	5.3	5.7	88	86	89	**41.5**	***10***	5.5	5.4	5.6	97	96	98
0.08	**46.4**	***10***	5.6	5.5	5.6	84	83	85	**24.2**	***5***	5.3	5.0	5.5	93	92	93
	85.7	***20***	5.6	5.5	5.6	86	85	87	**46.9**	***10***	5.3	5.0	5.5	97	95	98
AL-1010S catalyst, Ozone concentration in feed gas 8 g nm$^{3\ -1}$																
0.32	**24.7**	***10***	2.2**	2.2		48**	48		**14.2**	***5***	3.2**	3.2		39**	39	
	51.4	***20***	4.7**	4.7		66**	66		**28.7**	***10***	3.2**	3.2		48**	48	
0.16	**29.9**	***10***	3.7	3.6	3.8	77	68	86	**15.8**	***5***	3.6	3.4	3.7	76	74	77
	55.1	***20***	5.5	5.5	5.5	88	85	90	**30.3**	***10***	5.4	5.1	5.7	76	75	77
0.11	**40.6**	***10***	3.6	3.1	4.0	77	72	82	**21.1**	***5***	5.6	5.4	5.8	71	63	78
	78.4	***20***	5.4	5.0	5.7	86	79	92	**40.8**	***10***	5.6	5.4	5.8	70	61	79
0.08	**40.9**	***10***	5.1	5.0	5.2	62	53	70	**21.6**	***5***	5.3	5.2	5.3	57	53	60
	80.2	***20***	5.1	5.0	5.2	74	70	77	**41.6**	***10***	5.3	5.2	5.3	60	56	63

*No duplicate data available

**No duplicate data available

***Failed to detect ATZ in the sample

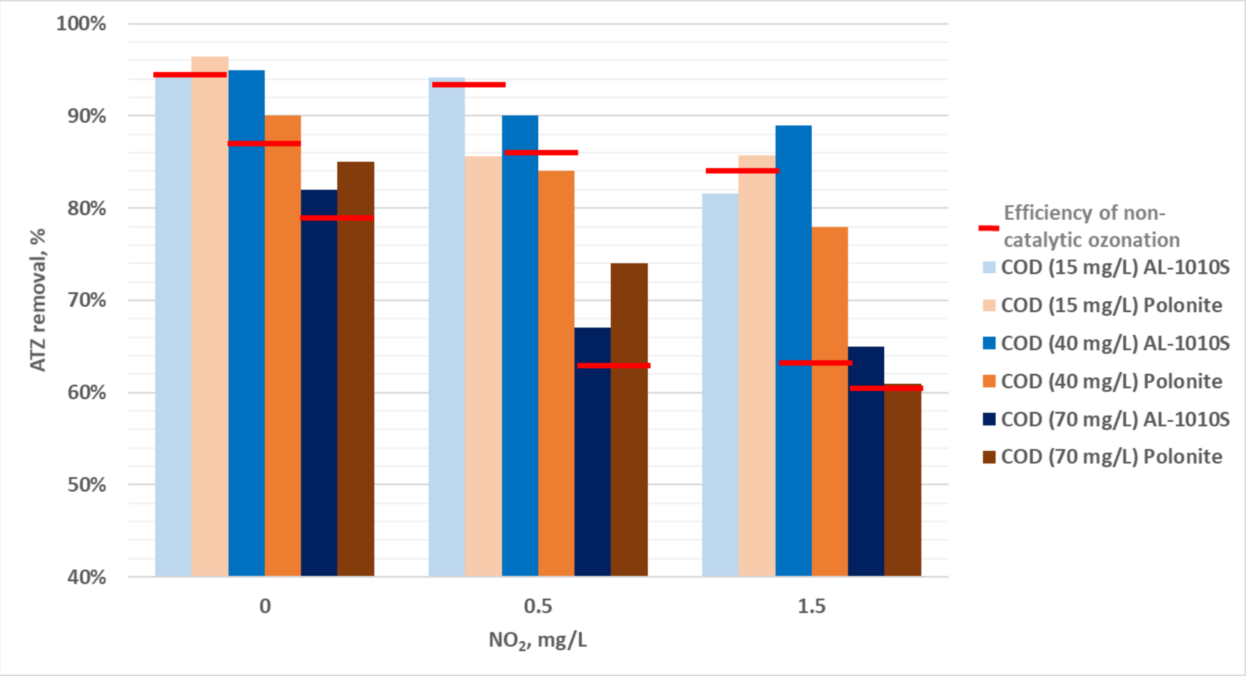

Figure S1. ATZ removal from SWW (20 min HRT) (n=2).

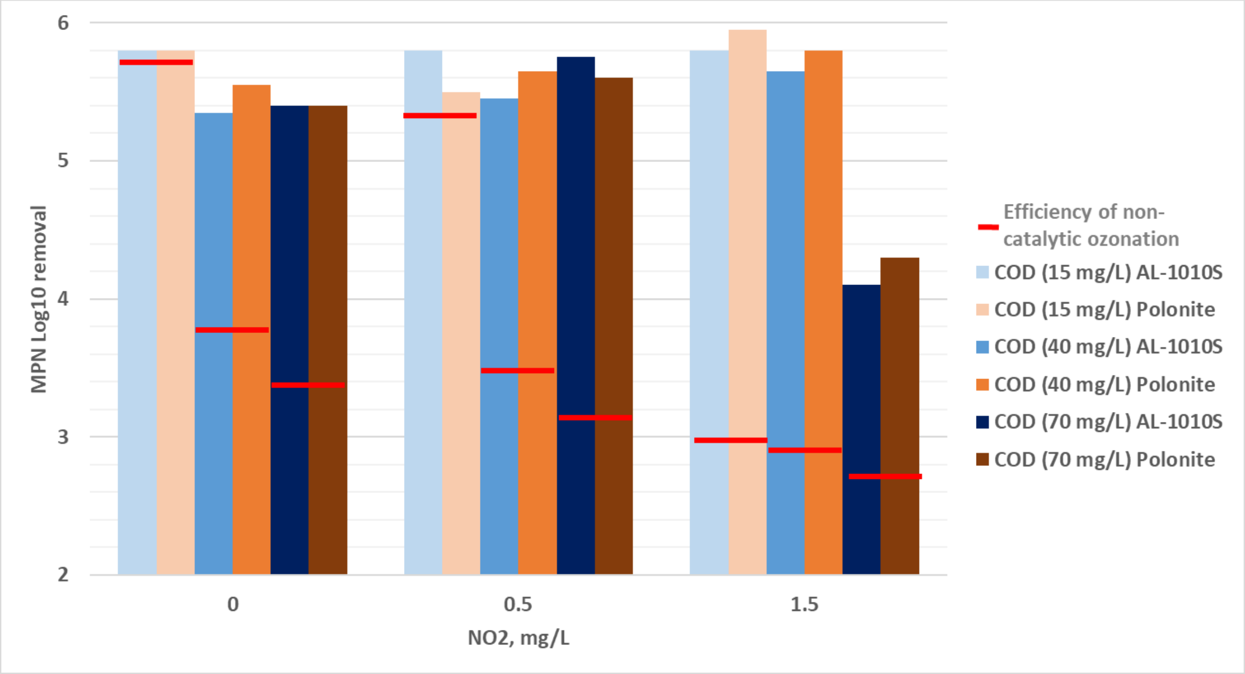

Figure S2. Disinfection of SWW (20 min HRT) (n=2).

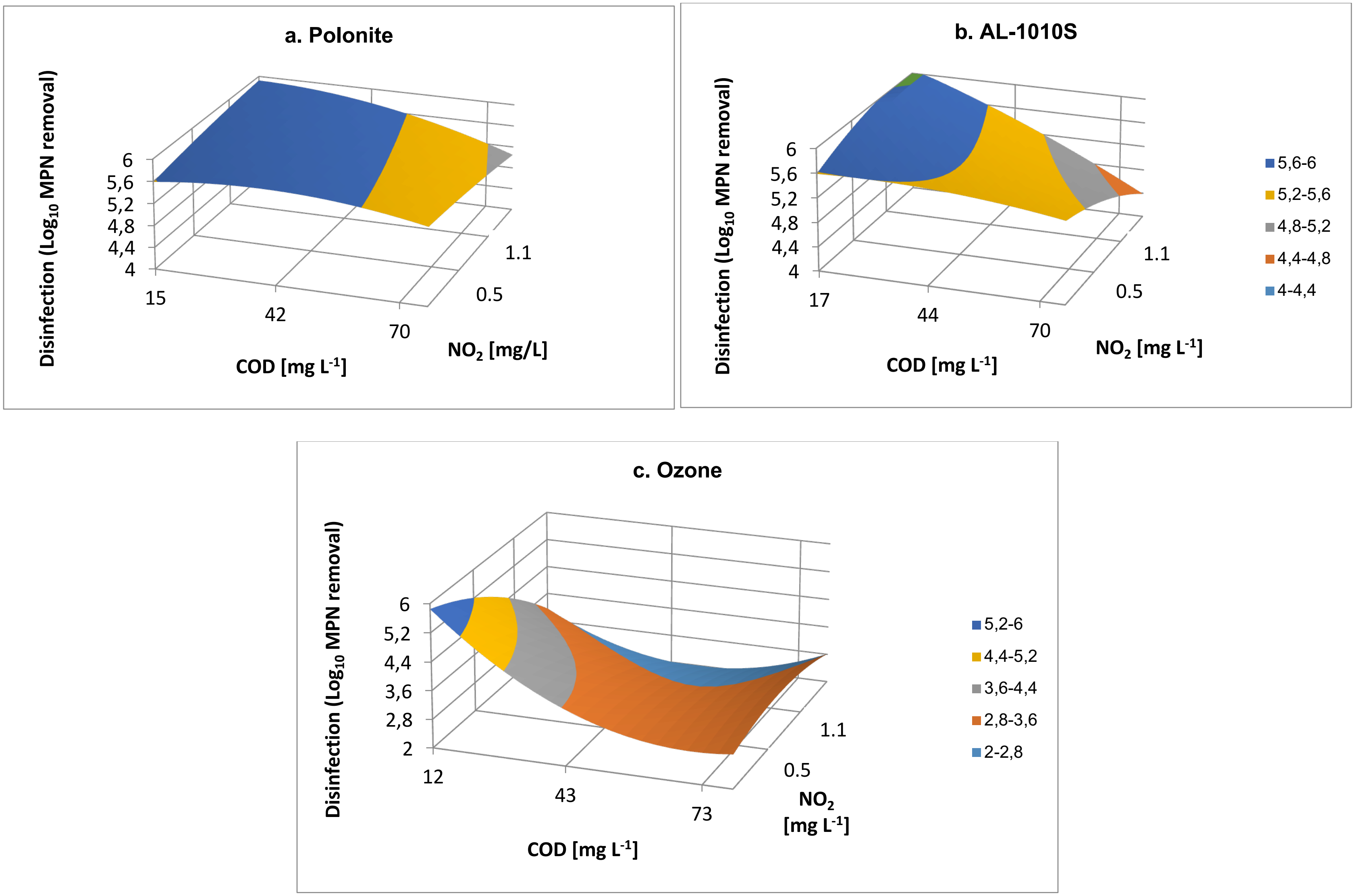

Figure S3. Surface response plot of disinfection of SWW profile (20 min HRT) (n=2).

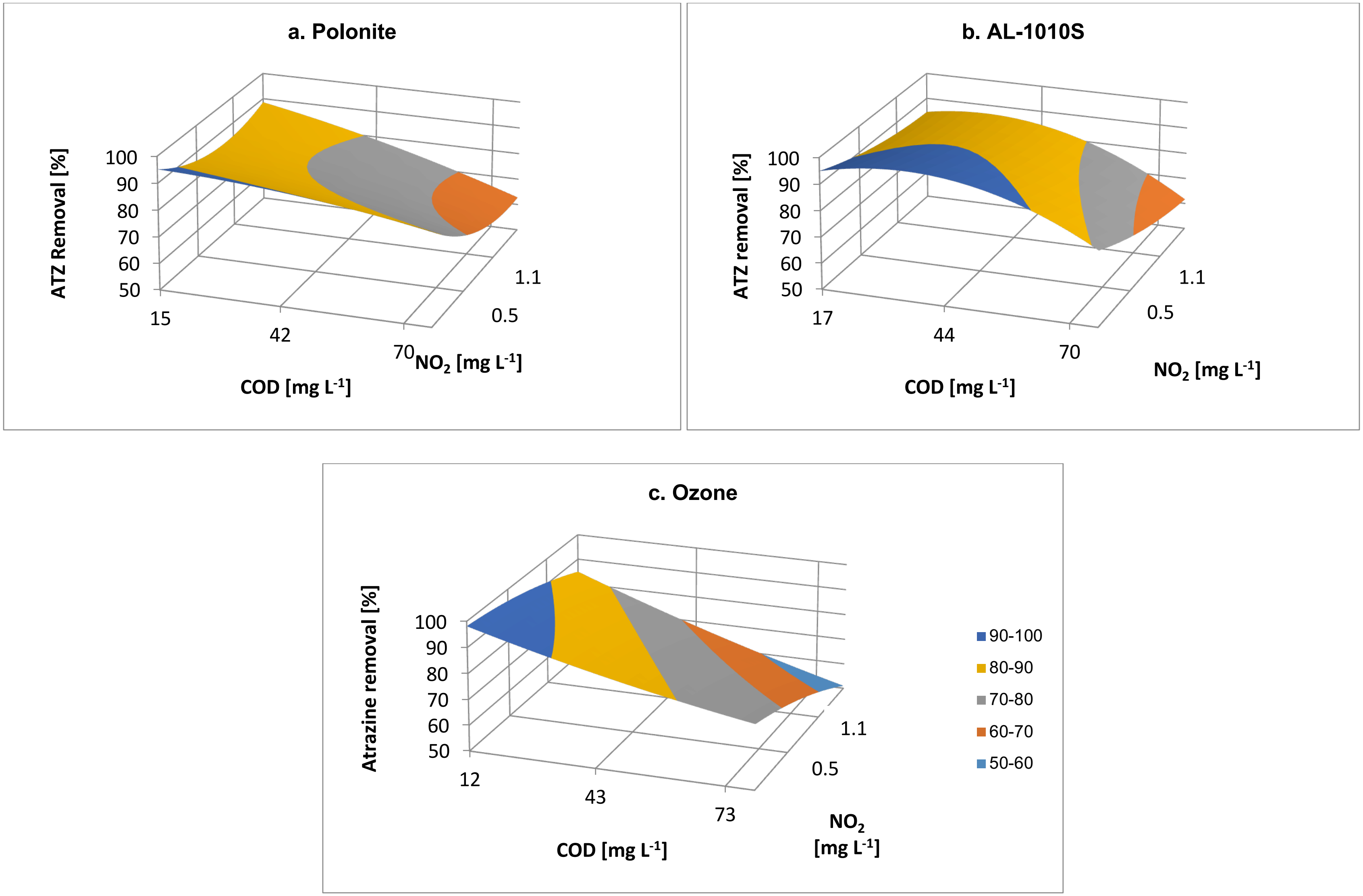

Figure S4. Surface response plot of ATZ removal from SWW profile (20 min HRT) (n=2).