Science of the Total Environment 651 (2019) 2139–2147

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Impact of catalyst load, chemical oxygen demand and nitrite on disinfection and removal of contaminants during catalytic ozonation of wastewater

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HIGHLIGHTS

- A shorter retention time provided better performance in disinfection and atrazine removal.
- The effect of ozone concentration in the feed gas differed depending on the catalyst.
- The catalysts dampened the negative effect of NO_2 and COD on efficiency of treatment.
- Treatment performance for disinfection was maintained when treating real wastewater.

GRAPHICAL ABSTRACT

	 **Polonite®** provided by Prof. Renman, KTH Royal Institute of Technology, Sweden	 **AL-1010S** provided by American Air Liquide, USA	 **Ozone** Generated in situ
Effect of O_3 concentration in feed gas	Strong	Strong ATZ removal only	Strong ATZ removal only
Effect of ratio O_3 to catalyst loading	Strong	Strong	Not applicable
Effect of HRT	Strong Disinfection only	Strong Disinfection only	No effect
Effect of COD	Moderate	Moderate	Strong
Effect of NO_2	Moderate	Moderate	Strong
Disinfection of effluent wastewater	Enhanced	Enhanced	Reference conditions
CEC removal from effluent wastewater	Insufficient results	Insufficient results	Reference conditions

ARTICLE INFO

Article history:
Received 24 July 2018
Received in revised form 21 September 2018
Accepted 27 September 2018
Available online 02 October 2018

Editor: Damia Barcelo

Keywords:
Catalytic ozonation
Contaminants of emerging concern
Wastewater treatment
Disinfection
Chemical oxygen demand
Nitrite

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.

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https://doi.org/10.1016/j.scitotenv.2018.09.394

However, under the conditions tested, a limited number of CECs were extracted at levels above the limits of quantification and further validation work required to evaluate the performance of catalytic ozonation for the removal of CECs.

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 and Yargeau, 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 (•OH), which then react with a larger variety of organic compounds than ozone (Snyder et al., 2006). Processes based on utilization of •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 affect 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}), $CaSO_4 \cdot 2H_2O$ (60 mg L^{-1}), $MgSO_4$ (60 mg L^{-1}), KCl (4 mg L^{-1}), K_2HPO_4 (28 mg L^{-1}), $CaCl_2 \cdot 2H_2O$ (4 mg L^{-1}), $MgSO_4 \cdot 7H_2O$ (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 h at 35 °C and 110 rpm. After 24 h, 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 1 L 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 h 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