ARTICLE IN PRESS

Catalysis Today xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

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

Impact of TiO_2/UVA photocatalysis on THM formation potential

E.M. Rodríguez*, M.V. Gordillo, A. Rey, F.J. Beltrán

Departamento de Ingeniería Química y Química Física, Instituto Universitario de Investigación del Agua, Cambio Climático y Sostenibilidad (IACYS), Universidad de Extremadura, Av. Elvas s/n, 06006 Badajoz, Spain

ARTICLE INFO

Keywords:
TiO_2-Photocatalysis
THMFP
NOM
Phenolics
Quinones
Citric

ABSTRACT

In drinking water treatment plants, reduction of trihalomethane formation potential (THMFP) can be reached through precursor removal prior chlorine disinfection. In this work, the impact of TiO_2/UVA photocatalytic process on THMFP has been studied using different phenolics (phenol, resorcinol, catechol, hydroquinone and gallic acid) and citric acid as NOM surrogates. A solution of each surrogate was photocatalytically treated at pH 7 applying different UVA doses and then chlorinated. Resorcinol oxidation by TiO_2/UVA and THMFP reduction go hand in hand, indicating that the intermediates hardly form THMs when chlorinated. For the rest of surrogates, intermediates with medium-high specific THMFP (maximum values 40–120 μg $CHCl_3$ (mg DOC)$^{-1}$ for phenols; and ~1000 μg $CHCl_3$ (mg DOC)$^{-1}$ for citric acid) are initially formed and disappear at higher UVA doses. TiO_2/UVA treatment of water matrices with high and low specific UV absorption at 254 nm ($SUVA_{254}$) (Sigma-Aldrich humic acid, pH 7; and water from Villar del Rey reservoir; Badajoz-Spain), was also investigated. For surface water UVA doses higher than 5 kWh m^{-3} were needed to achieve a THMFP below 100 μg THM L^{-1}. During water treatment, an initial negative impact of AOPs in general and TiO_2/UVA in particular on THMFP is expected.

1. Introduction

Disinfection byproducts (DBPs) in drinking water arise from reactions of natural organic matter (NOM) and disinfectants, being trihalomethanes (THMs) and haloacetic acids (HAAs) considered the major DBPs formed on a mass basis during chlorination. Hydrophobic acid (HOA) and hydrophilic acid (HIA) fractions of NOM are the main THM precursors, HIA also being an important precursor of HAAs [1]. In water treatment plants removal of precursors by oxidation (O_3, ClO_2, AOPs), enhanced coagulation, adsorption onto activated carbon, membrane filtration, etc., prior chlorine disinfection, are classical routes to reduce THM formation potential (THMFP) [2–4]. In this sense, the effect of TiO_2 photocatalysis on DBP formation has been studied by different authors. Lee and Ohgaki [5] observed that TiO_2/UVC photocatalytic oxidation of different matrices (humic acid, with 4.9 mg L^{-1} of dissolved organic carbon (DOC_0); and surface waters with 1.1–3.5 mg L^{-1} DOC_0), caused an increase in THMFP at short treatment times. Liu et al. [6], indicated that application of TiO_2/UVA_{365nm} to humic acid (10 mg L^{-1} DOC_0) allowed 90% and 100% of DOC and A_{254nm} removal, respectively, after applying 17 kWh m^{-3}, whereas THMFP was reduced from ~600 μg L^{-1} to 280 μg L^{-1} at 6.8 kWh m^{-3}, and to 21 μg L^{-1} at 17 kWh m^{-3}. Also, Liu et al. [7] reported that THMFP and HAAFP in Myponga reservoir water (10 mg L^{-1} DOC_0 and about 560 μg L^{-1} THMFP and 400 μg L^{-1} HAAFP) when treated at the same conditions, were reduced to ~ 80 and 200 μg L^{-1}, respectively (with 6.8 kWh m^{-3}), and to less than 20 y 100 μg L^{-1}, respectively (with 17 kWh m^{-3}). Similarly, from their study about the treatment of two different surface waters (5.7 and 7.3 mg L^{-1} DOC) with TiO_2/UVC, Gerrity et al. [8] concluded that UV doses lower than 5 kWh m^{-3} led to important DOC and A_{254nm} removals but to an increase in THMFP. In this case, the authors reported that more than 40 kWh m^{-3} are necessary to reduce the THMFP below its initial value. Regardless of the application of a previous step (coagulation + flocculation + sedimentation; or microfiltration + GAC filtration), Mayer et al. [9] indicated that the photocatalytic treatment (TiO_2/UVC) of surface waters applying 5 kWh m^{-3} gives rise to an important increase in THMFP and HAAFP. The authors proposed doses higher than 80 kWh m^{-3} to effectively reduce the formation of these DBPs. In any case, the analyses of NOM before/after the photocatalytic treatment indicate a clear decrease in humic/fulvic content together with an increase of the hydrophilic fraction. The formation of short chain aldehydes and ketones in the latter has also been identified [[7],[9]].

In order to determine the behavior of the different structures present in NOM Philippe et al. [10] investigated the impact of TiO_2 photocatalysis on THMFP using different surrogates: aminoacids (glutamic and aspartic acids, glycine, L-leucine and L-serine), carbohydrates (D-

---

* Corresponding author.
E-mail address: evarguez@unex.es (E.M. Rodríguez).

https://doi.org/10.1016/j.cattod.2017.12.018
Received 13 August 2017; Received in revised form 16 October 2017; Accepted 16 December 2017

Please cite this article as: Rodriguez, E.M., Catalysis Today (2017), https://doi.org/10.1016/j.cattod.2017.12.018

Nomenclature

ACE	Acetone
AOP	Advanced oxidation process
CAT	Catechol
CIT	Citric acid
CPC	Compound parabolic collector
DBP	Disinfection byproduct
DNPH	2,4-Dinitrophenylhydrazine
DOC	Dissolved organic carbon
DPD	*N,N′*-Diphenyl-*p*-phenylenediamine
EAS	Electrophilic aromatic substitution
ET	Electronic transfer
GAC	Granular activated carbon
GAL	Gallic acid
GC-ECD	Gas chromatography-Electron capture detector
HA	Humic acid
HAAs	Haloacetic acids
HAAFP	Haloacetic acids formation potential
HHQ	Hydroxyhydroquinone
HIA	Hydrophilic acid fraction of NOM
HOA	Hydrophobic acid fraction of NOM
HpBQ	Hydroxy-*p*-benzoquinone
HPLC-DAD	High performance liquid chromatography- diode array detector
HQ	Hydroquinone
HS	Headspace
NOM	Natural organic matter
3-OBA	3-Oxobutanoic acid
3-OPDA	3-Oxopentanedioic acid
pBQ	*p*-Benzoquinone
PHEN	Phenol
PHLO	Phloroglucinol
PI	Phenolic intermediates
PYR	Pyrogallol
$SUVA_{254}$	Specific UV absorbance at 254 nm (A_{254nm}/DOC)
SW	Surface water
THM	Trihalomethane
THMFP	Trihalomethane formation potential
s-THMFP	Specific trihalomethane formation potential (THMFP/DOC)
TOC	Total organic carbon
TPC	Total phenolic content

mannose and D-xilose) and phenolics (resorcinol and tannic acid). With the exception of L-leucine, the THMFP decreased throughout the treatment.

Taking into account all the above, the main objective of the present work is to evaluate the impact of TiO_2/UVA photocatalytic process, in terms of accumulated UVA energy per unit of volume (E_{UVA}, kWh m^{-3}), on THMFP using different phenolic compounds and citric acid as HOA and HIA NOM precursor surrogates. In addition, for a surface water treated by TiO_2/UVA followed by chlorination, the E_{UVA} needed to meet the legal requirements established by EU's drinking water standards (THMFP $< 100\,\mu g\,L^{-1}$) is determined.

2. Experimental section

2.1. Chemicals

Resorcinol (RES), catechol (CAT), hydroquinone (HQ), phenol (PHEN), gallic acid (GAL), citric acid (CIT), p-benzoquinone (pBQ), phloroglucinol (PHLO), pyrogallol (PYR), hydroxyhydroquinone (HHQ), acetone (ACE) and THMs (trichloromethane, bromodichloromethane, dibromochloromethane and tribromomethane) were of analytical grade (Sigma-Aldrich). Humic acid (HA) sodium salt (Sigma-Aldrich), 3-oxopentanedioic acid (3-OPD, Sigma-Aldrich) and sodium hypochlorite (10% active chlorine, Panreac S.L) were of technical grade and used without further purification. Other reagents used were at least reagent grade. Water was purified by an ultrapure water system (Milli-Q, Millipore).

Surface water (SW) from Villar del Rey reservoir (Badajoz, Spain) was collected in May 2017. After being naturally decanted the SW was kept at 4 °C and used within 48 h. Main characteristics of SW are summarized in Table 1.

2.2. Experimental setup

Photocatalytic experiments under artificial UVA radiation were carried out in triplicate in a 250 mL Schott bottle provided with two 15 W black light lamps (λ_{max} 365 nm) located on both sides of the reactor. Intensity of UVA radiation entering the reactor was 1.51×10^{-6} einstein $(L\,s)^{-1}$ as determined by ferrioxalate actinometry [11]. In a typical experiment the reactor was loaded with 250 mL of aqueous solution of a given compound ($DOC_0 \sim 3.5\,mg\,L^{-1}$ for phenolics and CIT; between 3 and 6 mg L^{-1} for HA; pH_0 7 phosphate buffer 1 mM in all cases). After magnetic stirring an aliquot was taken for analysis. The catalyst (0.1 g L^{-1} TiO_2 P25 Evonik®) was then added and the suspension stirred in the dark for 30 min to reach the adsorption equilibrium. Meanwhile, the lamps were turned on to achieve the stationary emission regime. After the equilibrium period a sample was taken (t = 0) and the reactor exposed to UVA radiation for 2.5–3 h (total accumulated UV energy 1.2–1.5 kWh m^{-3}) for phenolics and citric acid; and

Table 1
Main characteristics of surface water (SW) from Villar del Rey reservoir (Badajoz, Spain).

Parameter	Value	Units
pH	7.2	–
Conductivity	112	$\mu S\,cm^{-1}$
Turbidity	1.9	NTU
TOC	6.0	mg L^{-1}
DOC	5.6	mg L^{-1}
IC	6.5	mg L^{-1}
Alkalinity[a]	54	mg L^{-1} $CaCO_3$
Cl_2 demand	3.9	mg L^{-1}
Specific Cl_2 demand	0.7	mg Cl_2 (mg DOC)$^{-1}$
TTHM	250 ± 20	μg THM L^{-1}
- $CHCl_3$	~230	μg L^{-1}
- $CHCl_2Br$	~20	
- $CHClBr_2$	< 10	
- $CHBr_3$	< 10	
s-THMFP	~43	μg THM (mg DOC)$^{-1}$
Total phenolic content, TPC[b]	0.2	mg L^{-1}
A_{220nm}	0.380	cm^{-1}
A_{254nm}	0.130	cm^{-1}
$SUVA_{254}$	2.3	L (mg DOC m)$^{-1}$
Cl^-	12.5	mg L^{-1}
Br^-	0.08	mg L^{-1}
NO_3^-	3.3	mg L^{-1}
$SO_4^=$	7.5	mg L^{-1}
NH_4^+	< 0.06	mg L^{-1}
Fe (total)	50	μg L^{-1}
Mn (total)	140	μg L^{-1}

[a] Calculated from IC content.

[b] As Phenol equivalents. Positive interferences cannot be disregarded ([14]).