Research article

Removal assessment of disinfection by-products (DBPs) from drinking water supplies by solar heterogeneous photocatalysis: A case study of trihalomethanes (THMs)

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A B S T R A C T

Solar heterogeneous photocatalysis was used to remove trihalomethanes (THMs) from drinking water. THMs, mainly trichloromethane (TCM), tribromomethane (TBM), bromodichloromethane (BDCM) and dibromochloromethane (DBCM) are one of the main class of disinfection by-products (DBPs). THMs were determined by HSGC-MS with detection limits (LODs) ranging from 0.5 μg L^{-1} to 0.9 μg L^{-1} for TCM and BDCM, respectively. Results show that a great proportion of THMs present in water are finally transferred to air as a result of their high volatility in the order TCM > BDCM > DBCM > TBM. The use of band-gap semiconductor materials (TiO_2 and mainly ZnO) used as photocatalysts in combination with $Na_2S_2O_8$ as electron acceptor and sulfate radical anion ($SO_4^{\bullet-}$) generator enhanced the photooxidation of all THMs as compared to photolytic test. The time required for 50% of THMs to disappear (DT_{50}) from water calculated for the most effective treatment (ZnO/$Na_2S_2O_8$) were 12, 42, 57 and 61 min for TCM, TBM, BDCM, and DBCM, respectively. Therefore, solar heterogeneous photocatalysis can be considered as an interesting strategy for THMs removal, especially in sunny areas like Mediterranean basin.

1. Introduction

As Leonardo Da Vinci said half a millennium ago, "*Water is the driving force of all nature*". Water is an essential natural resource for the sustainability of the life in our planet and disinfection treatment of drinking water (DW) is vital to supply pure water to citizens. The need to make water drinkable entails the inevitable disinfection to inactivate microorganisms (Kwarciak-Kozłowska, 2020). Chemical and physical methods used for water disinfection mainly include chlorination (Cl_2, NH_2Cl, $NHCl_2$, ClO_2 and/or $NaClO_3$) ozonation (O_3), UV light, potassium permanganate ($KMnO_4$), and/or nanofiltration (Dubey et al., 2020; Srivastav et al., 2020; Sinha et al., 2021). However, the appearance of many hazardous disinfection by-products (DBPs) is a noticeable concern worldwide (Prasad, 2020), especially in those methods involving chlorination, which is the typical method of disinfection to compare with other treatments. According to Chaukura et al. (2020), about 700 DBPs have been evidenced in DW. Chlorine (used as an oxidant over the last 100 years) is the main consistent disinfectant due to its cost-effectiveness, easy achievement, and lasting residual on the water supply network (Sadiq and Rodriguez, 2004). In addition to the chlorination parameters (time and chlorine dose), some factors such as pH, temperature, occurrence of other ions (Br^-, I^-) or chemical characteristics of natural organic matter (NOM) such as aromaticity and functionality are well-known to assess the impact on the level of DPBs generated (Kim and Yu, 2005; Ates et al., 2007; Al-Omari et al., 2014; Dubey et al., 2020; Sinha et al., 2021).

Among DBPs, trihalomethanes (THMs), haloacetic acids (HAAs) and haloacetonitriles (HANs), the three largest classes of DBPs by weight are the predominant classes reported in the chlorinated water. In many cases their occurrence is above the Maximum Admissible Concentration (MAC) in many countries worldwide causing adverse effects on human health (Dubey et al., 2020; Srivastav and Kaur, 2020; Sinha et al., 2021).

THMs are single-carbon substituted halogens (CHX_3) where X can be fluorine, chlorine, bromine or iodine or a grouping of them. However, only trichloromethane (TCM) or chloroform, and brominated THMs such as tribromomethane (TBM) or bromoform, bromodichloromethane (BDCM)

(BDCM) and dibromochloromethane (DBCM) are significant from the point of view of DW pollution. The amount of all these compounds is known as total THMs (TTHMs). TCM always has the highest concentration in DW, and frequently represented by more than 90% of the THMs. The pattern of THM amounts in chlorinated water is usually as follows: TCM > BDCM > DBCM > TBM (Brown, 2009; Durmishi et al., 2015; WHO, 2017). Valdivia-García et al. (2019) pointed out the strong seasonal correlation between THMs levels, water temperature and dissolved organic carbon (DOC) demonstrating how climate can influence THMs formation. Different analytical techniques are commonly used for the detection of THMs in water samples by direct aqueous injection, static/dynamic headspace, liquid-liquid extraction, headspace-solid phase microextraction or membrane-based sampling using gas chromatography (GC) coupled to mass spectrometers (MS) and electron capture (EC) as the most widely used detectors (Pérez-Pavón et al., 2008).

The widespread use of chlorine as a disinfectant applied as Cl_2 or hypochlorite salts generates HOCl, which then dissociates into OCl^- (Sadiq et al., 2002). HOCl has a higher reactivity than OCl^-, making it one of the most active oxidixing species (Frimmel and Jahnel, 2003). If Br^- and I^- initially exist in raw water, $HOCl/OCl^-$ oxidises Br^- and I^- to form $HOBr/OBr^-$ and HOI/OI^-, respectively, producing Br-DBPs and I-DBPs by different oxidation/substitution reactions with NOM ($HOCl/HOBr/HOI + NOM \rightarrow$ THMs + other halogenated DBPs).

The occurrence of Br^- and dissolved organic matter (DOM) in DW justifies the formation of brominated THMs (Sadiq and Rodriguez, 2011). Their appearance in DW is a major problem because brominated are more hazardous than their chlorinated analogues (Richardson et al., 2007). Active bromine reacts with NOM more quickly than active chlorine, with highly brominated analogues appearing even at moderately low bromide level. Both species react with DOM to generate halogenated intermediates (Westerhoff et al., 2004).

The suitability of DW standards and their scrupulous implementation are extremely important issues to protect human health (WHO, 2017; Poleneni, 2020; Tsaridou and Karabelas, 2021). The main risk of THMs to citizens is the direct ingestion of DW, although other activities such as cooking, bathing, showering, etc. resulting from their volatilisation constitute an important source of exposure (Richardson et al., 2007; Rivera et al., 2012). The potential harmful effects of THMs to humans (De Castro Medeiros et al., 2019; Egwari et al., 2020; Sinha et al., 2021) led the US EPA to promulgate a MAC for THMs of 80 µg L^{-1} in DW (US EPA, 1998). Similarly, the EU has established a MAC of 100 µg L^{-1} (EC, 2020).

To reduce/remove THMs levels from DW, different methods aligned with biological or chemical technologies have been developed highlighting the notions of preventive action, through disinfectants other than chlorine or chlorine dose optimisation, and treatment action removing precursor materials by ion exchange resin or membrane filtration prior to chlorine addition. Once formed, coagulation/flocculation, adsorption, biological filtration, soil aquifer handling, ozonation/ultrafiltration, Advanced Oxidation Processes (AOPs) or hybrid treatment processes are some of the most commonly used methods to remove THMs from DW after disinfection (Zainudin et al., 2017; Sinha et al., 2021).

Currently, the development of solar photochemical processes is seen to be of dynamic significance, especially those where sunlight is used (Tsydenova et al., 2015; Chakrabarti, 2018). AOPs based on photocatalysis have proven to be an interesting tool to remove chemical and biological contaminants from water (Malato et al., 2009; Miklos et al., 2018; Aziz and Abu Amr, 2019). They have got substantial interest, especially heterogeneous photocatalysis (HP), defined as "chemical reactions induced by a solid material (photocatalyst) that absorbs suitable radiation and remains unaffected during the process" (Ahmad et al., 2016; Ahmed and Haider, 2018; Augugliaro et al., 2019). Among various semiconductor materials used as photocatalysts, TiO_2 (Aziz and Palaniandy, 2019; Gopinath et al., 2020) and ZnO (Lee et al., 2016; Ong

et al., 2018) are the most widely used for environmental solar applications. The major benefit of these technologies is that they attain the abatement/reduction of the pollutants by mineralization, unlike other conventional processes where the contaminant is only transferred to the environment (Ribeiro et al., 2015).

Organic pollutants are oxidised by extremely oxidant species, mainly hydroxyl radicals ($HO^\bullet$, $E_0 = 1.9$–2.8 V *vs.* NHE) and others including superoxide anion ($O_2^{\bullet -}$) and hydridodioxygen ($HO_2^\bullet$). In addition, sulfate anion radical, $SO_4^{\bullet -}$ ($E_0 = 2.5$–3.1 V *vs.* NHE) may also be engaged when peroxydisulfate ($S_2O_8^{2-}$) or peroxymonosulfate (HSO_5^-) are used as oxidants for environmental applications (Wacław et al., 2017; Wang and Wang, 2018). Both, $HO^\bullet$ and $SO_4^{\bullet -}$ with half-lives of 10^{-3} and 30–40 µs, respectively, are commonly involved in electron transfer reactions although the former may also react via hydrogen-atom abstraction (Olmez-Hanci and Arslan-Alaton, 2013).

Some studies have emphasised the removal of the precursors (mainly organic matter) responsible for generating THMs previously to disinfection process using AOPs (Sillanpää et al., 2018; Tak and Vellanki, 2019; Hariganesh et al., 2020; Sinha et al., 2021). However, scientific literature on the removal of THMs in DW through solar HP is very scarce. With this aim, we have assessed the effectivity of ZnO and TiO_2 as photocatalysts in combination with $Na_2S_2O_8$ as oxidant for the treatment of DW polluted with TCM, BDCM, DBCM and TBM under solar irradiation and at pilot plant scale in a sunny area such as southeast Spain.

2. Materials and methods

2.1. Chemicals, reagents and solvents

Analytical standards of THMs with >97% purity were purchased from Alfa Aesar (Karlsruhe, Germany). H_2O and CH_3OH (both HPLC-grade), $Na_2S_2O_8$, Na_2SO_4 and $Na_2S_2O_3$ all of them with a purity >98% were supplied by Scharlab (Barcelona, Spain). TiO_2 (70 anatase/30 rutile, 99.5%, BET 55 m^2 g^{-1}, size 32 nm, E_g 3.0 eV) P25 Aeroxide™ and ZnO (wurtzite, 99.99%, BET 7 m^2 g^{-1}, size 194 nm, E_g 3.1 eV) were provided by Nippon Aerosil Co Ltd. (Osaka, Japan) and Alfa Aesar (Karlsruhe, Germany), respectively. The photocatalysts were previously characterised by us (Fenoll et al., 2016) for Diffuse Reflectance Spectroscopy (DRS), X-Ray Diffractometry (XRD), Field Emission Scanning Electron Microscopy (FE-SEM), Energy Dispersive X-Ray (EDX) coupled to SEM and surface area following the Brunauer-Emmett-Teller (BET) method (Figure SM1).

2.2. Standard solutions

A stock standard solution (nominal concentration of 500 mg L^{-1} of each THM) was prepared in CH_3OH. An intermediate solution (10 mg L^{-1}) was prepared also in CH_3OH. Calibration standards (0.1–100 ng mL^{-1}) diluted in CH_3OH were prepared from the stock solutions directly in 20 mL vials. Solutions were kept in the dark at -18 °C for up to 30 days. Working standard solutions were prepared daily in ultra-pure water (18 mΩ). The water was sonicated for 15 min before use to remove any volatile components that might have interfered with subsequent analysis.

2.3. Experimental setup at pilot plant scale

The experiments were carried out during summer in a pilot facility located in a sunny area at the Agricultural Experimental Centre (University of Murcia) located between the coordinates 37° 59′ N and 1° 08′ W (Murcia, SE Spain). The small prototype used in this experiment (CPC technology) includes a mixing tank, a photoreactor module with five borosilicate tubes mounted on aluminium reflectors and an ultrafiltration membrane to recover the photocatalysts, as previously described by Vela et al. (2018). A scheme of the prototype is shown in Figure SM2.

Water (25 ± 2 °C) flows continuously from the tank in a closed circuit to achieve a uniform slurry. The values (W m^{-2}) of VIS-NIR, UVA, UVB, and UVC radiation were recorded by a pyranometer Delta Ohm HD 2102.2 (Caselle di Selvazzano, Italy) integrated in the facility.

Previously to the beginning of each assay, the DW (Table SM1) obtained from municipal network was strongly stirred by air stripping for 120 min (24–27 °C) with the tank uncovered before use to remove volatile organic compounds (VOCs). After this step, TTHMs was estimated to be 29 ± 12 µg L^{-1}. Coming up next, 150 L of water were spiked in the covered tank with the THMs (100 µg L^{-1} of each). Once homogenised by mechanical shaking (20 min) in the dark, 150 mg L^{-1} of TiO$_2$ or ZnO were added, and the mixture was homogenised (15 min) in dark conditions. Finally, Na$_2$S$_2$O$_8$ (250 mg L^{-1}) used to avoid e$^-$/h$^+$ recombination and generate sulfate radicals (SO$_4^{\bullet-}$) was added to the tank and the cover of the photoreactor module was removed. Water was circulated uninterruptedly to keep the photocatalyst appropriately stirred. An air compressor (250 L min^{-1}) provided air every 20 min (5 min running) because dissolved O$_2$ acts as an electron sink, generating O$_2^{\bullet-}$. During the lighting period (10–14 h) several samples were taken from 0 to 240 min. A photolytic test (in absence of photocatalysts and oxidant) was also performed. Three replications were carried out in each case.

2.4. Sample collection and preparation

Water samples were collected from the pilot plant in 500 mL amber glass bottles and stabilised by addition of sodium thiosulfate (125 mg per 100 mL of water) because it is a satisfactory dechlorinating agent that neutralises residual chlorine and prevents bactericidal effect during sample transit. Sample bottles were kept cold and immediately refrigerated (4 °C) until analysis of THMs, which was carried out usually within 24–48 h.

2.5. Headspace extraction

Screw-top headspace amber glass vials (20 mL) purchased from Sharlab (Barcelona, Spain) were used for headspace extractions. The total volume of each filtered (0.2 µm) sample was 10 mL leaving a headspace volume of 10 mL. In all cases, 1 g of sodium sulfate was added to increase volatilisation of the target compounds. After the vibratory shaking (10 s on, 60 s off/heating 80 °C for 30 min) period of the vials, the headspace was sampled, using a 2.5 mL syringe (1 mL injection volume), which was kept at 35 °C between aspiration and injection of the samples. Between samples, the syringe was flushed with N$_2$ for 10 s.

2.6. GC-MS conditions

A Thermo Trace Ultra gas chromatograph equipped with a Polaris Q-Ion Trap mass spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) using electron impact (EI) ionization at 70 eV and coupled to an autosampler TriPlus was used for analysis of THMs. The chromatographic column TR-V1 (30 m × 0.25 mm ID x 1.4 µm) coated with 6% cyanopropylphenyl polysiloxane was obtained from Thermo Fisher Scientific. The initial oven temperature was 50 °C (held for 2 min), raised up 220 °C at 10 °C min^{-1} (held for 2 min). The PTV injector (splitless, 30 s, 1/30) temperature was 250 °C, and the temperature of the ion source and transfer line was 225 °C. The carrier gas flow (Helium, 99.99%) was 1 mL min^{-1}. The multiplier voltage was 1300 V. A solvent delay of 2 min was used. Analyses were run in FS mode (45–250 *m/z*). To improve sensitivity, THMs were quantified in selected ion monitoring (SIM) mode. Retention times, evaluation of the mass spectral data of standards compared to a mass spectral database (NIST2005) and detailed diagnostics of ion fragments were used to identify THMs. Appropriate monitoring ions were selected based on their relative abundance. For each THM several monitoring ions (*m/z*) were selected for quantification and *confirmation,* as shown in Figure SM3: TCM (83, *85, 87*), TBM (173, *171, 175*), BDCM (83, *85, 129*) and DBCM (129, *127,*

131). The data acquisition was carried out running Thermo Scientific Xcalibur™ software.

2.7. Statistical analysis

The statistical software SigmaPlot (Systat, Software Inc., San Jose, CA) v.14 was used to fit the experimental data. To assess the influence of treatments on the disappearance of THMs from water, an analysis of variance (ANOVA) was performed by means of software IBM-SPSS Statistics (Armonk, NY) v.25 followed by Tukey's post-hoc test ($p < 0.05$).

3. Results and discussion

3.1. Analytical validation

The most commonly typical validation characteristics include specificity, accuracy (recovery, %), precision (RSD, %), linearity range, detection limit, quantitation limit, matrix effect and robustness (Magnusson and Ornemark, 2014). The specificity was assessed by examining blank water samples (n = 5) for the absence of interferences, which was confirmed, and no further interferences were observed in the retention time of the target analytes. The linear range of the method was assessed by plotting the relative peak area of each compound versus its concentration. Linear calibration curves were obtained for all THMs from 0.1 to 100 ng mL^{-1} as depicted in Figure SM2. The linearity range was assessed as a function of positive results of different tests (R > 0.99, normality, Durbin-Watson and constant variance). Thus, the curves obtained showed linearity throughout the calibration range. Recovery and precision were assessed by spiking blank samples at different spiking levels (2.5, 5 and 25 ng mL^{-1}). THMs recovery from spiked samples varied from 96.1 to 104.8%, with RSD <10% and intra- and inter-day RSD <8%. The lowest concentrations of each THM in a water sample that can be detected, but not inevitably quantified (LOD, S/N = 3) ranged from 0.5 ng mL^{-1} to 0.9 ng mL^{-1} for TCM and BDCM, respectively. On the other hand, the lowest THMs concentrations that can be determined with satisfactory precision and accuracy (LOQ, S/N = 10) varied from 1.6 ng mL^{-1} to 3.0 ng mL^{-1} for the same compounds. The matrix effect (ME, %) was calculated by comparing the slopes in the matrix (S_m) using blank extracts calibration solutions and pure solvent (S_s) (CH$_3$OH) calibration solutions (ME (%) = [S_m/S_s] – 1] x 100). In all cases, MEs were less than 20%, demostrating a low matrix influence. To ensure the accuracy, calibration standards were run multiple times during analytical determinations. Therefore, the method was performed accurately.

3.2. Volatilisation of THMs

The human exposure pathway to THMs includes ingestion, inhalation and dermal absorption, with volatilisation playing a key role in the three (Kim et al., 2004; Thurnau and Clar, 2017). According to Richardson (2005), dermal exposure and inhalation trough showering can lead to higher levels of THMs in the blood stream than ingestion. Therefore, it is assumed that THMs present in water are eventually transferred to the air a as result of their high volatility. For this reason, and previously to the photocatalytic experiments, we have carried out a simple assay under laboratory conditions to determine the volatilisation rate of THMs (100 g L^{-1}). For this purpose, distilled water samples (1 L, n = 3) were brought to 22 °C by using a thermostatic bath and a 2 L round bottom flask open to the atmosphere. As depicted in Fig. 1, the percentage of THMs removed after 4 h of stirring in darkness ranged from 86% to 54% for TCM and TBM, respectively, which is directly related to their Henry's LC and vapour pressures (TCM > BDCM > DBCM > TBM), as showed in Table 1. Similarly, Silva et al. (2013) showed a linear correlation (r = 0.995) of THM levels in water *vs* air with increasing Henry's LC. Therefore, it can be predicted that, as TCM is the most volatile, the TTHMs content in the aqueous phase would include a higher proportion of brominated species, which are more carcinogenic
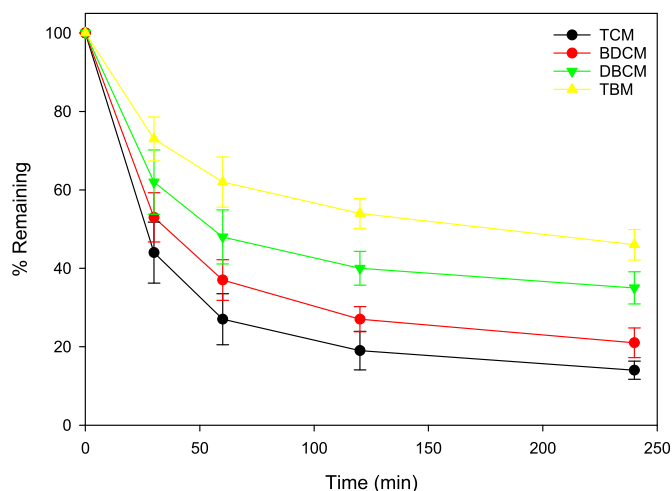
Fig. 1. Remaining percentages of THMs (100 µg L^{-1} of each one) from distilled water during stirring (240 min) in darkness at 22 ± 1 °C. Error bars denote standard deviation (n = 3).

and toxic (Richardson, 2003). Umphres et al. (1983) observed a 78%, 74%, 59% and 45% decrease in the input concentrations (100 µg L^{-1}) of TCM, BDCM, DBCM and TBM, respectively, at pilot-plant scale (air: water = 38:1, water loading = 21 mm s^{-1}, and bed packing depth = 2.4 m). As pointed out by Thurnau and Clar (2017), THMs amount has low effect on the volatilisation rates, while a linear relationship between temperature and volatilisation rate has been verified. Similar results were obtained by Pan et al. (2014).

3.3. Photolytic and photocatalytic kinetics

Unlike other DBPs, hydrolysis is not a common loss issue for THMs (Mabey and Mill, 1978) although it could contribute to their loss at elevated temperatures (>65 °C), especially for brominated species (Zhang et al., 2015a). However, some authors have demonstrated that THMs degrade photochemically, although bromine-substituted compounds are more sensitive than chlorinated analogues, ostensibly by photo-induced C–Br bond cleavage (Chen et al., 2010; Sinha et al., 2021). This is probably due to weaker bond-energy of C–Br (285 kJ mol^{-1}) than the C–Cl (327 kJ mol^{-1}) (Gilday et al., 2015). However, chlorinated THMs are more volatile than brominated species, as specified above.

Fig. 2 shows degradative curves obtained during the photolytic and photocatalytic trials. Mean values (W m^{-2}) of VIS-NIR, UVA, UVB and

UVC recorded at noon were 956.3 ± 31.2, 23.8 ± 2.2, 1.5 ± 0.3 and 0.2 ± 0.1, respectively, and a luminous flux per unit area of 101,547 ± 5084 lx. As can be observed, the use of photocatalysts in tandem with Na$_2$S$_2$O$_8$ enhanced the photooxidation of all THMs. The removal percentage (R %) at time t can be easily calculated as follows: R (%) = 100 − (C/C$_0$ x 100). As depicted, the percentages removed at the end of the photolytic test (240 min) ranged from 92% to 63% for TCM and TBM. The removal was in the order: TCM > BDCM > DBCM > TBM. Considering that the mixing tank has a headspace of about 250 L and that an air compressor was supplying air every 20 min, it is expected that a large proportion of THMs was removed by volatilisation during the irradiation time and consequently volatilisation will have a higher influence on their disappearance than photolysis. In addition, the percentage of de-chlorination and de-bromination measured as amount of Cl$^-$ and Br$^-$ ions (using a Dionex ICS-2100 ion chromatograph, Thermo Scientific, Waltham, MA, with an AS19 column and KOH as eluent) released into solution did not correlate with the amount of photodegraded THMs.

When photocatalysts were used, a significant ($p < 0.05$) higher effectiveness was observed for ZnO/Na$_2$S$_2$O$_8$ as compared to TiO$_2$/Na$_2$S$_2$O$_8$ for the degradation of chlorinated species (TCM, BDCM and DBCM), while no significant differences ($p < 0.05$) were detected for TBM (Fig. 2). In the case of TCM, only 3% of its initial concentration remained in water when ZnO/Na$_2$S$_2$O$_8$ was used after 60 min of treatment, while about 30% of TCM remained at the same time for TiO$_2$/Na$_2$S$_2$O$_8$ system. In the case of TBM, comparable amounts were recovered after 240 min of treatment, 2% and 4% for ZnO/Na$_2$S$_2$O$_8$ and TiO$_2$/Na$_2$S$_2$O$_8$, respectively. A similar photocatalytic oxidation pattern was observed for BDCM and DBCM for both photocatalysts, with percentages remaining at the end of the experiment (240 min) ranging from 5% (BDCM, ZnO/Na$_2$S$_2$O$_8$) to 14% (DBCM, TiO$_2$/Na$_2$S$_2$O$_8$). The primary experiments confirmed that the semiconductor amount affects the process because degradation increased with increasing load from 50 to 150 mg L^{-1} for both semiconductors (data not shown). A further increase in the loading (300 mg L^{-1}) weakly decreased the degradation rate, possibly due to the reversibility interaction between photocatalyst and pollutant and/or screening effect. On the other hand, to assess the effect of Na$_2$S$_2$O$_8$ on the degradation rate, two assays were carried out using different concentrations of the oxidant while conserving TiO$_2$ and ZnO loading at 150 mg L^{-1}. No significant differences ($p < 0.05$) were observed when the concentration of Na$_2$S$_2$O$_8$ was increased from 250 to 400 mg L^{-1} for both.

According to Liu et al. (2014), the pseudo-first order kinetic model is frequently suitable for describing the photocatalytic oxidation rate of many organic pollutants using semiconductor materials when substrate concentration is low. Thus, the apparent rate constant (k) can be calculated from the following equation (Eq. (1)):

Table 1
Main physical-chemical properties of the THMs studied (US EPA, 2017).

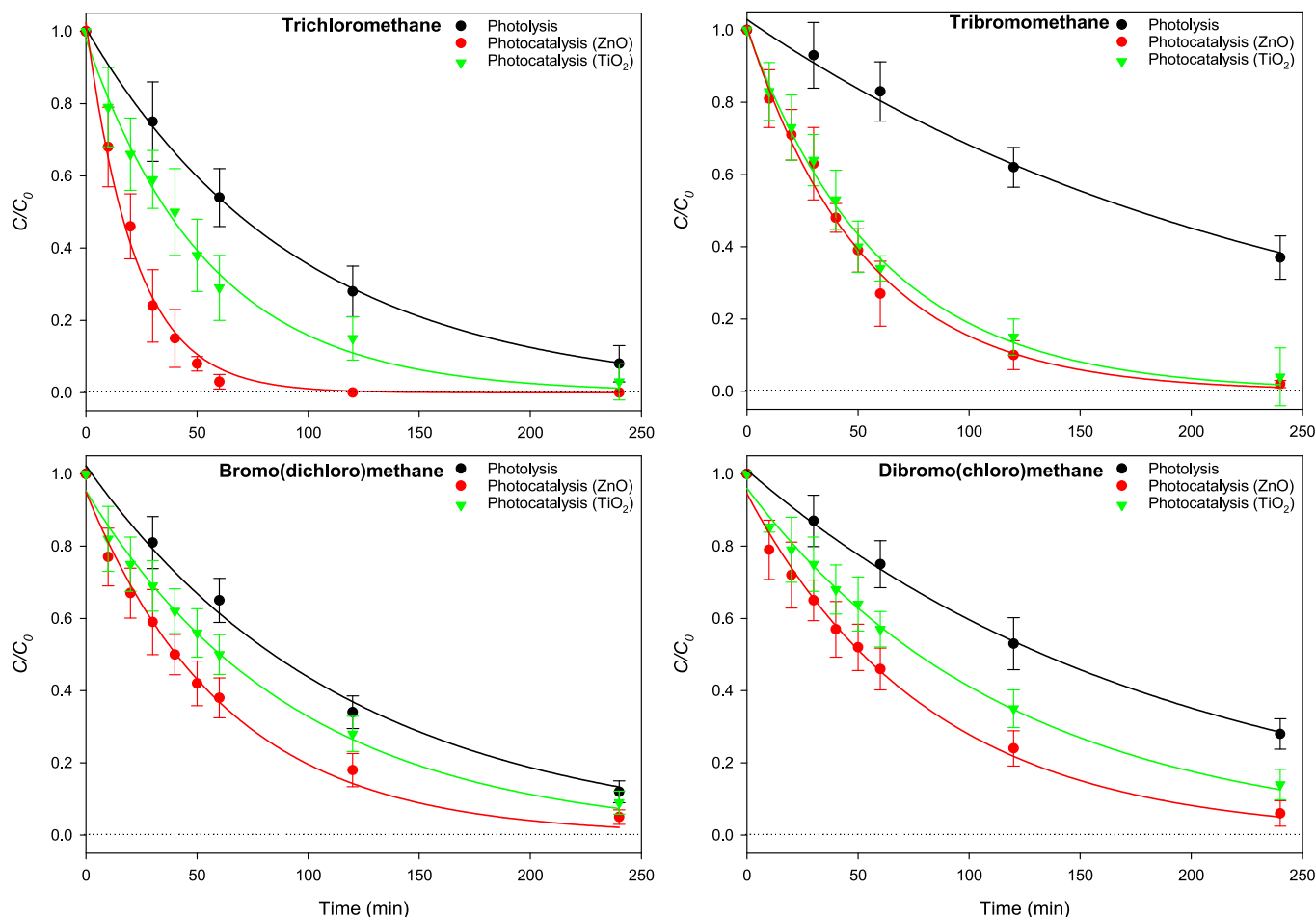| Compound (CAS)	Structure	Formula	Molecular weight	Water solubility (mg L^{-1}, 25 °C)	Log K$_{OW}$	Henry's Law Constant (Pa m^3 mol^{-1})	Vapour pressure (Pa, 25 °C)	Boiling point (°C)
TCM (67-66-3)		CHCl$_3$	119.4	7950	2.0	3.72×10^2	2.63×10^4	61
TBM (75-25-2)		CHBr$_3$	252.7	3100	2.4	5.42×10^1	7.20×10^2	149
BDCM (75-27-4)		CHBrCl$_2$	163.8	3030	2.0	2.15×10^2	7.65×10^3	90
DBCM (124-48-1)		CHBr$_2$Cl	208.3	2700	2.2	7.93×10^1	2.09×10^3	120

Fig. 2. Exponential decay of THMs during photolytic and photocatalytic experiments using ZnO (150 mg L^{-1}) and TiO$_2$ (150 mg L^{-1}) in tandem with Na$_2$S$_2$O$_8$ (1 mM) under natural sunlight at pilot plant scale. Error bars denote standard deviation (n = 3).

$$-\frac{dC}{dt} = kC \rightarrow C_t = C_0 e^{-kt} \rightarrow ln\ C_t = ln\ C_0 - kt \rightarrow\ \ ln\frac{C_0}{C_t} =\ kt \qquad \text{(Eq. 1)}$$

where t is the reaction time (min), C_0 the initial concentration (μg L^{-1}) of THMs and C_t the residual concentration (μg L^{-1}) of them at time t.

Following the above equation, the time required for X% of THMS to disappear (Disappearance Time, DTx) from the water can be calculated following Eq. (2):

$$DT_x = ln\left(\frac{100}{100-x}\right)\Big/ k \qquad \text{(Eq. 2)}$$

The photocatalytic degradation of THMs in DW obeys to a first order kinetics. In agreement to this model, the statistical parameters obtained after fitting are shown in Table 2. As can be observed the R^2 values were ≥0.98 in all cases with $S_{Y/X} \leq 0.2$ in the most adverse case. The relationship k_{ZnO}/k_{TiO2} ranged from 4 (TCM) to 1.2 (TBM and BDCM). For

both photocatalysts, the degradation rate was in the order TCM > TBM > BDCM > DBCM. Following first-order degradation model, calculated DT$_{50}$ values for the most efficient treatment (ZnO/Na$_2$S$_2$O$_8$) were 12, 42, 57 and 61 min for TCM, TBM, BDCM, and DBCM, respectively. ZnO is an attractive photocatalyst because it is more cost-effective (its production cost is up to 75% lower than TiO$_2$) and can be excited by a broad UV spectrum (245 nm–380 nm) compared to TiO$_2$ (Akhmal Saadon et al., 2016). One drawback to consider is that TiO$_2$ absorbs a slight fraction of the solar spectrum in the UV region (3.6%–5.2%) depending on the weather conditions (Zhang et al., 2015b). ZnO is widely used because it has a band gap energy (E_g) very similar to TiO$_2$, higher quantum efficiency, deep violet/borderline UV absorption and large excitation binding energy (60 meV) (Lee et al., 2016; Ong et al., 2018).

On the other hand, among different AOPs, sulfate radical-based processes (SO$_4^{\bullet-}$-AOPs) have been achieving attention as an operative

Table 2
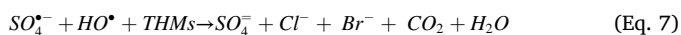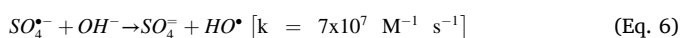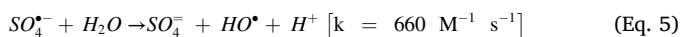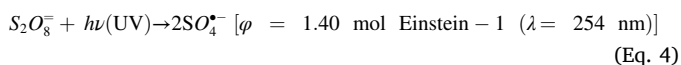Kinetic parameters (k in min^{-1}; DT in min) calculated for the photolytic and photocatalytic degradation of THMs under natural sunlight irradiation according to the pseudo-first order model (n = 3).

THM	Photolysis					Photocatalysis (ZnO/Na$_2$S$_2$O$_8$)					Photocatalysis (TiO$_2$/Na$_2$S$_2$O$_8$)				
	R	ln C/C_0	k	$S_{Y/X}$	DT$_{50/90}$	R	ln C/C_0	k	$S_{Y/X}$	DT$_{50/90}$	R	ln C/C_0	k	$S_{Y/X}$	DT$_{50/90}$
TCM	0.9998	−0.0127	0.0106	0.02	65/217	0.9779	−0.2330	0.0569	0.20	12/40	0.9894	0.1450	0.0143	0.12	48/161
TBM	0.9957	−0.0375	0.0043	0.03	161/535	0.9874	0.0849	0.0166	0.15	42/139	0.9865	0.1114	0.0135	0.13	51/171
BDCM	0.9972	−0.0437	0.0090	0.05	77/256	0.9911	0.1672	0.0121	0.09	57/190	0.9980	0.0782	0.0098	0.03	71/235
DBCM	0.9994	−0.0156	0.0054	0.01	128/426	0.9983	0.0829	0.0114	0.04	61/102	0.9978	0.0576	0.0080	0.03	87/288

$S_{Y/X}$: Standard deviation of the y-intercept (ln C/C_0) of the regression line (standard error of estimate).

tool to eliminate different emerging pollutants in water (Wang and Wang, 2018). In the absence of suitable electron acceptors, the recombination step is the predominant step that limits the quantum yield (Ahmed et al., 2011). $Na_2S_2O_8$ acts as an electron acceptor, avoiding the recombination e_{CB}^-/h_{VB}^+ (Eq. (3)). In addition, $Na_2S_2O_8$ produces $SO_4^{\bullet-}$ by breaking the O–O bond resulting from absorption of heat energy or UV light (Eq. (4)), and $HO^\bullet$ in accordance with the following equations (Eqs. (5) and (6)) (Matzek and Carter, 2016). Finally, $SO_4^{\bullet-}$ and $HO^\bullet$ promote the mineralization of the THMs (Eq. (7)).

$$S_2O_8^= + 2H^+ + 2e^- \rightarrow 2HSO_4^- \qquad \text{(Eq. 3)}$$

$$S_2O_8^= + h\nu(\text{UV}) \rightarrow 2SO_4^{\bullet-} \ [\varphi = 1.40 \ \text{mol Einstein} - 1 \ (\lambda = 254 \ \text{nm})] \qquad \text{(Eq. 4)}$$

$$SO_4^{\bullet-} + H_2O \rightarrow SO_4^= + HO^\bullet + H^+ \ [\text{k} = 660 \ \text{M}^{-1} \ \text{s}^{-1}] \qquad \text{(Eq. 5)}$$

$$SO_4^{\bullet-} + OH^- \rightarrow SO_4^= + HO^\bullet \ [\text{k} = 7\text{x}10^7 \ \text{M}^{-1} \ \text{s}^{-1}] \qquad \text{(Eq. 6)}$$

$$SO_4^{\bullet-} + HO^\bullet + THMs \rightarrow SO_4^= + Cl^- + Br^- + CO_2 + H_2O \qquad \text{(Eq. 7)}$$

The main concern when using $Na_2S_2O_8$ as an oxidant is the increase in $SO_4^=$ due to the transformation of $S_2O_8^\equiv \rightarrow 2 \ SO_4^=$ during the photoprocess. In our case, we have observed an increase in the concentration of $SO_4^=$ from 129 to 230 mg L^{-1} (TiO_2) and 210 mg L^{-1} (ZnO) at the end of the treatments. If drinking water contains high $SO_4^=$ levels (>500 mg L^{-1}) some negative effects such as gastrointestinal disturbances and a perceptible taste have been reported. In addition, such levels may contribute to corrosion of the supply network. However, no health-based guideline value for $SO_4^=$ in drinking water has been proposed (WHO, 2017).

As mentioned above, the scientific literature on the effectiveness of AOPs in reducing THMs is scarce. Hwangbo et al. (2019) found 22% dechlorination and 100% debromination as theoretical amount of Cl^- and Br^- ions that can be released from photocatalysed THMs using 1 g L^{-1} of ZnO (pH 7.0 and 365 nm) for 24 h and 90% dechlorination of TCM when no brominated analogues are present. Other authors have pointed out 92–100% removal of THMs (at 200 μg L^{-1} initial concentrations) with 0.1% of 40% w/w H_2O_2 and 90 min of UV exposure (Rudra et al., 2005). The results achieved by Zhang et al. (2021) indicate that heterogeneous Fenton-like process followed by granular activated carbon filtration constitutes a suitable technology to remove THMs. Xiao et al. (2016) reported that UV/$Na_2S_2O_8$ is the most cost-effective procedure for abatement of other DBPs (I-HAAs) related to other UV-based AOPs. Further results indicated the photocatalytic activity of carbon-doped g-C_3N_4 for the removal the TTHMs with the reaction rate constant of 0.0104 min^{-1} (Chang et al., 2019).

3.4. Cost estimate for water treatment

A comparison of the treatment cost for both systems (ZnO/$Na_2S_2O_8$ and TiO_2/$Na_2S_2O_8$) under the same experimental conditions is showed in Table SM2. Bearing in mind that the SE Spain receives about 3000 h of sunlight per year, the average of useful minutes of the pilot plant (*UM*) is 480 min day^{-1}, and the number of days of use per year is 240 (according to weather conditions), the treatment capacity (*TC*) of our system was calculated according to the following equation (Eq. (8)):

$$TC \ \left(L \ year^{-1}\right) = \frac{(UM \ x \ V \ x \ 240)}{DT_{90}} \qquad \text{(Eq. 8)}$$

where *V* is the volume of water treated (150 L) and DT_{90} is the amount of time required for 90% of the initial THM concentration to dissipate. In our case, the selected DT_{90} was the corresponding to the compound with higher value according to Table 2 (190 min for BDCM and 288 min for DBCM in ZnO and TiO_2 systems, respectively).

Consequently, the treatment cost was estimated to be 54 € m^{-3} for

the ZnO/$Na_2S_2O_8$ system and 78 € m^{-3} for the TiO_2/$Na_2S_2O_8$ system. The significant differences found in cost between both treatments are attributed to the high reaction rate observed for the studied compounds by treatment with ZnO.

4. Conclusions

THMs such as TCM and other brominated compounds (BDCM, DBCM and TBM) are mainly generated as DBPs during chlorination of raw water. Although DW chlorination offers many benefits, THMs have received the most scientific and regulatory attention owing to their widespread occurrence and reported human health concerns. They constitute an undesirable group of VOCs formed by the reaction of disinfectants with inorganic and organic matter. According to experimental models, they are suspected to be genotoxic and carcinogenic substances with negative acute reproductive effects that constitute health hazard. Therefore, low-cost and environmentally friendly methods are required to detoxify DW to avoid damage to the human health and environment, prior to its distribution through the water supply network.

Although THMs are very volatile (the percentage of THMs removed after 4 h of stirring in darkness ranged from 86% to 54% for TCM and TBM, respectively) and photodegradable compounds, the use of solar heterogeneous photocatalysis by means of commercially available photocatalysts, such as band-gap semiconductor materials like ZnO and TiO_2, in combination with a strong oxidant like $Na_2S_2O_8$ considerably enhances their disappearance in DW. The main benefit/advantage of AOPs is that they accomplish the abatement or at least the decrease of the pollutant content by mineralization, while other conventional processes only transfer them from one place to another. The percentages removed at the end of the photolytic test (240 min) ranged from 92% to 63% for TCM and TBM (TCM > BDCM > DBCM > TBM). When photocatalysts were used, a higher effectiveness of ZnO/$Na_2S_2O_8$ compared to TiO_2/$Na_2S_2O_8$ was observed for the degradation of chlorinated species (TCM, BDCM and DBCM), while no significant differences were detected for TBM. This is of special interest in countries/areas with water scarcity but receiving a great amount of sunshine (a renewable, inexhaustible and pollution-free energy source) such as some areas of the Mediterranean basin, like SE Spain, although the treatment cost ranged from 54 to 78 € m^{-3} for the ZnO/$Na_2S_2O_8$ and TiO_2/$Na_2S_2O_8$ systems, respectively.

Author statement

Gabriel Pérez-Lucas: Conceptualization, Investigation, Formal analysis, Writing – original draft. **Marina Martínez-Menchón:** Investigation, Formal analysis, Data curation. **Nuria Vela:** Investigation, Formal analysis, Data curation. **Simón Navarro:** Conceptualization, Investigation, Formal analysis, Validation, Writing – original draft, Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi. org/10.1016/j.jenvman.2022.115936.

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