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Influence of dissolved organic carbon source, photocatalyst identity and copper(II) ions on the formation of bromoform in irradiated titanium dioxide suspensions

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ABSTRACT

We report the irradiation of titanium dioxide suspensions (Hombikat UV100 and P25) under different conditions regarding the source of dissolved organic carbon (2,4-dihydroxybenzoic acid and brown water from a bog lake), and with and without added copper(II) ions. In contrast to P25 suspensions, we found no significant bromoform formation in Hombikat UV100 suspensions, likely because bromoform is degraded faster with Hombikat UV100 than with P25, preventing accumulation. In the case of P25 suspensions, the presence of 10 μM of added Cu^{2+} significantly inhibited bromoform formation. Bromoform was the only measurable trihalomethane (THM), even in the presence of 250 mg L^{-1} chloride ions. The concentrations of formed THM were below the limits for drinking water under all investigated experimental conditions.

1. Introduction

The formation of oxidation byproducts is an important problem in water treatment [1]. In particular, when the raw water contains elevated levels of bromide (Br^-), both inorganic and organic byproducts of toxicological relevance can be formed (e.g. bromate, bromoform) [2].

One oxidation technology which leads to relatively low formation of oxidation byproducts is heterogeneous photocatalysis with titanium dioxide as the photocatalyst [3–5]. This technique derives its effectivity as a water treatment technology largely from the formation of OH-radicals ($^\bullet$OH) on the photocatalytic surface from adsorbed OH^- and H_2O [6]. As a pretreatment, heterogenous photocatalysis has been shown to decrease the formation potential of trihalomethanes (THM) upon chlorination either through decreasing the dissolved organic carbon (DOC) content or through structural changes in the DOC [7–9].

We recently reported the formation of only small amounts of bromoform in the presence of elevated bromide ion concentrations [4] and the dependence of the amount and time scale of bromoform formation on the concentrations of photocatalyst, bromide ions and DOC [5]. The formation of bromoform in these systems is assumed to be the result of oxidation of bromide ions to HOBr [10] followed by subsequent bromination of the DOC and its brominated degradation intermediates (as evidenced by measurements of organically bound halogens adsorbable onto activated carbon), leading to bromoform formation as sketched in [4]. This proposition is consistent with the results in [5].

In the work presented here, we explore the influence of the identity of the photocatalyst and of the addition of copper(II) ions on the formation of bromoform in UV-irradiated TiO_2 suspensions. Furthermore, we compare the formation of bromoform from the model DOC-source used in [4,5] to bromoform formation using real aquatic natural organic matter (NOM).

2. Materials and methods

2.1. Chemicals

Hombikat UV100 was a gift from Sachtleben Chemie (Duisburg, Germany). P25 was provided by Degussa (Frankfurt am Main, Germany). Some basic data for these TiO_2 powders are given in Table 1. KBr (p.a. grade, Merck, Germany), 2,4-dihydroxybenzoic acid (purum, Fluka, Switzerland), copper sulfate (98%, Aldrich), and copper chloride ($CuCl_2{\cdot}H_2O$, p.a., Merck) were used as received. Ferric sulfate (p.a. grade, Fluka Chemika, Switzerland), potassium oxalate, sodium acetate, 1,10-phenanthroline (all p.a. grade, Merck, Germany), and sulfuric acid (95–97%) were used for actinometry.

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Table 1
Some characteristics of the commercially available P25 and Hombikat UV100 powders ([25] and manufacturer's specifications).

	P25	Hombikat UV100
Average particle diameter	20–30 nm	≈ 8 nm
BET surface area	50 ± 15 m^2 g^{-1}	> 250 m^2 g^{-1}
Crystal structure	Approximately 3/4 anatase and 1/4 rutile	anatase

2.2. Recirculation reactor

The experimental arrangement consisted of a 1 L glass vessel (reservoir) connected by polytetrafluoroethylene tubing to a pump, heat exchanger and reactor. The reactor consisted of a quarz glass tube into which a 14 W low presssure Hg lamp (Katadyn, Switzerland) was inserted. This was in turn coaxially fitted into a glass tube. The suspension was pumped into the space between the glass tubes and recycled into the reservoir. The reaction volume was ≈125 mL and the total aqueous volume of the system was ≈1.5 L. The temperature in all irradiation experiments was $21 \pm 1\,^{\circ}$C.

The lamp was turned on in a separate vessel for at least 20 min prior to the start of irradiation in order to insure a constant photon flux. The photon flux was 5×10^{-6} Einstein s^{-1} as estimated by chemical actinometry with potassium ferrioxalate performed according to [11].

2.3. Sample preparation

Two TiO_2 powders were used: P25 and Hombikat UV100. Water from Lake Hohloh (northern Black Forest, Germany) and 2,4-dihydroxybenzoic acid were used as sources of DOC. The characteristics of Lake Hohloh NOM have remained essentially constant over a sampling period of ≈ 20 years. This water consistently exhibits high DOC concentrations (≈ 25 mg L^{-1}) and low content of ions (electrical conductivity ≈ 40μ S cm^{-1}). For more details please refer to [12,13]. The titanium dioxide suspensions had the following composition:

- $\rho\,(TiO_2) = 1.5$ g L^{-1}
- $\rho_0\,(Br^-) = 3$ mg L^{-1}
- ρ_0 (DOC) = 1.1 mg L^{-1}

The samples were allowed to equilibrate for at least 15 min after contact with the TiO_2 before the start of irradiation (dark adsorption). It was confirmed by means of DOC measurements (Sievers TOC Analyzer 820, Sievers Instruments, Boulder, USA) that after this time, no significant changes occurred in the DOC concentration in the aqueous phase, signaling adsorption equilibrium. Because of the low DOC concentration and high concentration of TiO_2 and its buffer capacity, the pH of the suspensions remained in the range 6–7 throughout the course of the experiments.

For the experiments with added Cu^{2+}, a spike of 10 μM was used by adding an appropriate amount of $CuSO_4$ or $CuCl_2{\cdot}H_2O$ to Lake Hohloh water and let equilibrate for at least 3 d. This long time was allocated to allow for the complexation of the copper(II) ions with NOM [14,15]. This water was then used for the irradiation experiments.

2.4. Trihalomethanes (THM)

THMs were analyzed using headspace gas chromatography with electron capture detection on an HP 6890 system. The detection limits for $CHCl_3$, $CHCl_2Br$, $CHClBr_2$, and $CHBr_3$ were 0.4, 0.2, 0.5, and 0.8 μg L^{-1}, respectively. The samples were not pre-treated in any way prior to measurement, and were stored in air-tight vessels at 4 °C for no longer than 3 d before measurement.

2.5. Quantification of 2,4-dihydroxybenzoic acid (DHBA)

Measurements of DHBA were performed by reversed-phase high performance liquid chromatography (RP-HPLC) using an HP 1100 HPLC system as described in [4].

2.6. Quantification of DOC

Measurements of dissolved organic carbon were performed using a Sievers 820 TOC analyzer. The samples were previously filtered through 0.45 μm polycarbonate membrane filters (Millipore, Ireland). We note that this method can only quantify the organic carbon in solution. That is, the organic carbon that is adsorbed on the surface of TiO_2 cannot be directly accounted for.

2.7. Size exclusion chromatography

Filtered (0.45 μm) samples were analyzed using the apparatus described in detail in [16] using Toyopearl HW 50S resin (Tosoh Corp., Japan) as column packing and phosphate eluent (1.5 g L^{-1} $Na_2HPO_4{\cdot}2H_2O$ + 2.5 g L^{-1} KH_2PO_4) flowing at a rate of 1.5 mL min^{-1} as the mobile phase. Samples were diluted 1:10 prior to analysis. The dimensions of the column were: length = 250 mm, inner diameter = 20 mm.

3. Results and discussion

3.1. Natural versus model source of dissolved organic carbon

We previously showed that bromoform can be formed in irradiated titanium dioxide suspensions in the presence of both dissolved organic carbon (DOC) and bromide ions [5,4]. In those cases, DHBA was chosen as a model compound based on results by Boyce and Hornig [17], which revealed a high yield of bromoform upon bromination of DHBA. Furthermore, the structural features of DHBA make it a good model for humic acids, an important part of NOM [12]. Nevertheless, the formation of bromoform in irradiated TiO_2 suspensions containing real aquatic NOM as the source of DOC has not been shown to date.

In order to verify whether the results obtained with DHBA qualitatively and quantitatively follow the results obtained for a natural water, irradiation experiments were conducted with water from Lake Hohloh, a bog lake in the northern Black Forest (Germany) and compared to irradiation experiments with DHBA under otherwise identical conditions. We chose Lake Hohloh water because it has been extensively studied and used to characterize the properties of aquatic humic substances (e.g. [12]). Size exclusion chromatograms with DOC and UV detection are shown in Fig. 1. The experimental conditions were chosen on the basis of a parameter study [5], which showed that the combination of comparatively high concentrations of photocatalyst and bromide ions combined with a low DOC concentration give rise to increased formation of bromoform in irradiated TiO_2 suspensions. Thus, we expected a higher formation of bromoform compared to that reported in [4].

When both suspensions were irradiated (duplicate runs for each), we observed the steady formation of bromoform after a lag period. In the case of suspensions containing DHBA as DOC source, this lag phase lasted approximately 40 min, in good agreement with previous results [4,5]. The maximum concentrations were on the order of 15 μg L^{-1}. As expected, this was higher than reported in [4] (<10 μg L^{-1}). When using Lake Hohloh water as a DOC source, the lag time was approximately 20 min and the maximum bromoform concentrations were close to 20 μg L^{-1}. Both sets of results, shown

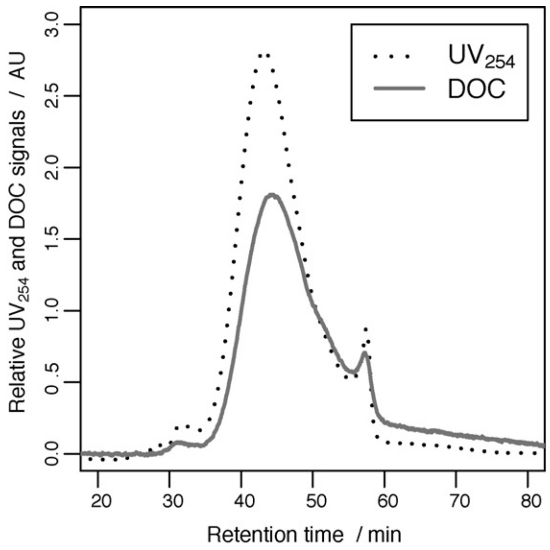

Fig. 1. Size exclusion chromatograms of Lake Hohloh water with DOC and UV (λ = 254 nm) detection.

in Fig. 2, are thus qualitatively very similar so that we expect the formation of bromoform to follow a similar curve when using other sources of refractory DOC.

Quantitatively, the difference in bromoform concentration was small (<5 μg L^{-1}). It should be noted that the plateau in both curves does not indicate the end of bromoform formation, because bromoform can also be degraded in irradiated TiO_2 suspensions [18]. Thus, the concentration level of the plateau is the result of the balance between formation and degradation of bromoform in UV-irradiated TiO_2 suspensions.

The decrease in DOC concentration was faster for suspensions containing DHBA than for those containing Lake Hohloh water: a decrease of ≈50% after 30 min and 70% after 60 min was observed for suspensions containing DHBA while only ≈ 10% were removed after 60 min for the suspensions containing Lake Hohloh. The lag phase, however, was shorter for suspensions containing the aquatic NOM than for those containing DHBA. Considering that the lag phase arises from the time required to break down the larger organic molecules into molecules containing only one carbon atom [4], the experimental results reveal that some molecules in the (on average larger but) highly heterogeneous NOM offer a shorter way to $CHBr_3$ than DHBA. These moieties are likely short, linear side chains in the NOM which do not have to undergo aromatic ring opening and subsequent degradation as is the case for DHBA [19].

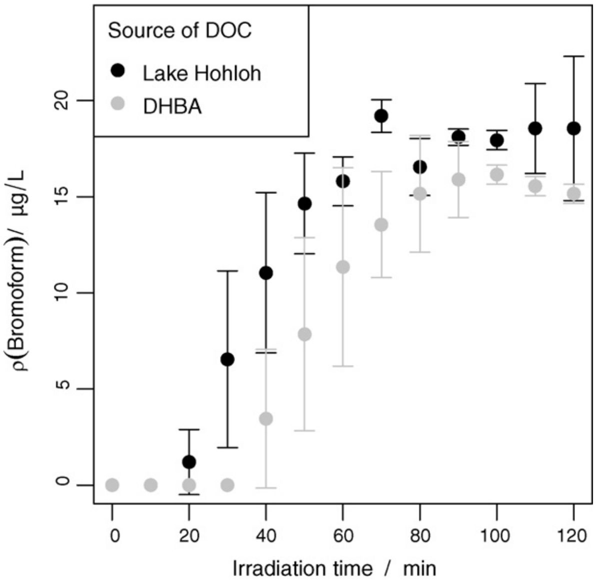

Fig. 2. Bromoform formation in irradiated titanium dioxide suspensions (P25) with DHBA and bog lake water as DOC source. ρ_0(DOC) = 1.1 mg L^{-1}, ρ_0(Br^-) = 3 mg L^{-1},ρ(TiO2)=1.5 g L^{-1}.

Table 2
Levels of bromoform observed in UV-irradiated suspensions of two different TiO_2-powders.

DOC source	Photocatalyst	
	P25	Hombikat UV100
DHBA	≈ 15 μg L^{-1}	$\leq 3\mu$ g L^{-1}
Lake Hohloh	≈ 18 μg L^{-1}	Not detected

Further experiments with added chloride ions showed no formation of chlorinated THM for $\rho_0(Cl^-) = 250$ mg L^{-1}, when using DHBA as a DOC source. Thus, it appears that bromoform is the only important THM produced in UV-irradiated TiO_2 suspensions when both chloride and bromide are present in moderate concentrations. This preferential formation of bromoform follows from the results of Herrmann and Pichat [10], who reported that chloride ions are not oxidized in irradiated TiO_2 suspensions, in contrast to bromide ions, because the oxidation of X^- to X_2 is a required step in the formation of THM in this system [1,4].

The formation of iodinated THM was not considered here. However, this possibility remains open given that iodide ions are oxidized to a much larger extent than bromide ions (approximately a factor of 80) according to [10].

3.2. *Identity of the photocatalyst*

Having shown that the results obtained for suspensions containing DHBA and NOM are similar, we next sought to compare the formation of bromoform in irradiated TiO_2 suspensions when using different TiO_2 powders as photocatalysts, namely P25 and Hombikat UV100. These two photocatalyst powders exhibit different crystal structures and average primary particle sizes, as shown in Table 1.

Previous comparisons of these two TiO_2 powders regarding the degradation kinetics of organic pollutants, for example dichloroacetic acid [20] and X-ray contrast media [21], have revealed differences between the two. Although, Hombikat UV100 has the larger BET surface area, P25 often exhibits the higher activity, highlighting the effect of other factors such as crystal structure.

Thus, we hypothesized that the *formation* of bromoform as a byproduct of the degradation of organic material in the presence of bromide ions proceeds at different rates when using different TiO_2 materials. To test this, we irradiated TiO_2 suspensions of both powders in the presence of a model (DHBA) and a real (water from a bog lake—Lake Hohloh) source of dissolved organic carbon (DOC).

In contrast to the results shown above (Fig. 2) for the formation of bromoform in P25 suspensions with DHBA and Lake Hohloh water as sources of DOC, we found almost no formation of bromoform in Hombikat UV100 suspensions. Repeated irradiation experiments ($n \geq 2$ for each combination of DOC source and photocatalyst) led in most cases to bromoform concentrations well below 0.8 μg L^{-1}, and only in one sample for one experiment above this mark but less than 3 μg L^{-1}. The results are summarized in Table 2. In terms of DOC elimination, there was no difference between suspensions of P25 and of Hombikat UV100 containing DHBA in the first 30 min of irradiation: the DOC concentration decreased to

≈ 50% of the initial value in both cases. However, the DOC concentration remained essentially stable after this for Hombikat UV100 suspensions but decreased to ≈ 30% of the initial DOC concentration for P25 suspensions after 60 min of irradiation. There was no significant difference between the two photocatalysts when Lake Hohloh water was the source of DOC.

The observed levels of bromoform in the irradiated TiO_2 suspensions are the result of the competition for formation and degradation of bromoform. A simplified rate equation is thus

$$\frac{d[CHBr_3]}{dt} = -k_d[CHBr_3] + k_f[HOBr][P_{CHBr_3}] \qquad (1)$$

where k_d is the pseudo-first order rate constant for the degradation of bromoform in the irradiated TiO_2 suspensions, k_f the rate constant for the bromination reaction leading to $CHBr_3$, and P_{CHBr_3} is the sum of the concentrations of all direct $CHBr_3$ precursors; k_f is here assumed to be approx. the same for all precursors, and the main brominating agent is assumed to be HOBr.

As pointed out above, P25 and Hombikat UV100 have been found to degrade different compounds at different rates.

For this reason, we hypothesized that bromoform may also be degraded faster in Hombikat UV100 suspensions, preventing its accumulation in the irradiated Hombikat UV100 suspensions. To support this idea, we measured the degradation kinetics of bromoform in both P25 and Hombikat UV100 suspensions and found apparent first order kinetic constants of $k_{d,P25} = (8.6 \pm 1.3) \times 10^{-3}\,min^{-1}$ and $k_{d,Hombikat\,UV100} = (17.3 \pm 1.3) \times 10^{-3}$ min. Thus, the absence of bromoform in Hombikat UV100 suspensions may be due to a rapid depletion of the bromoform directly after formation. However, it is not possible to claim this conclusively because the rates of *formation* of bromoform with both photocatalysts are unknown.

Nevertheless, the rate of formation of bromoform may be estimated for P25 suspensions by using Eq. (1). At the plateau observed in Fig. 2, the overall rate of bromoform formation $d[CHBr_3]/dt \approx 0$ and $k_d[CHBr_3] \approx k_f[HOBr][P_{CHBr_3}]$. Thus, bromoform is being formed and degraded at a rate of ≈ 0.7 nmol L^{-1} min^{-1}. This corresponds to approximately one bromoform formation/degradation reaction per liter of TiO_2 suspension for every 4×10^5 photons entering the system (the input into each sample is ≈ 3×10^{18} photons per second). An estimation of the rate of formation in Hombikat UV100 suspensions is not possible because $[CHBr_3] \approx 0$ in all experiments.

This strong difference in byproduct formation with the two different TiO_2 powders may be of practical significance for the use of heterogeneous photocatalysis for the treatment of bromide-containing water.

3.3. *Influence of added copper(II) ions*

The main geogenic precursor of bromoform in oxidative water treatment is natural organic matter (NOM). Because bromoform only contains one carbon atom, it appears as a relatively late product of the oxidation of NOM in the presence of bromide ions (cf. lag time in Fig. 2). We hypothesized that any factor having an effect on the degradation kinetics of NOM would have an effect on the rate of production of bromoform.

One such factor is the concentration of copper(II) ions. Addition of Cu^{2+} has been shown to slow down the mineralization of humic acids by $^{\bullet}OH$ (H_2O_2 process, see [22]) and current results in our laboratory [23] show that the photocatalytic degradation of NOM is slowed down in the presence of added Cu^{2+}[23]. Thus, we compared the formation of bromoform with and without added Cu^{2+} (10 μM). For these experiments, bog lake water served as the DOC source.

While the samples without added Cu^{2+} showed up to approximately 20 μg L^{-1} bromoform (cf. Fig. 2), the irradiated samples with $c_{added}(Cu^{2+})$ = 10 μM showed very little formation of bromoform (<5 μg L^{-1}, $n = 2$), as seen in Fig. 3.

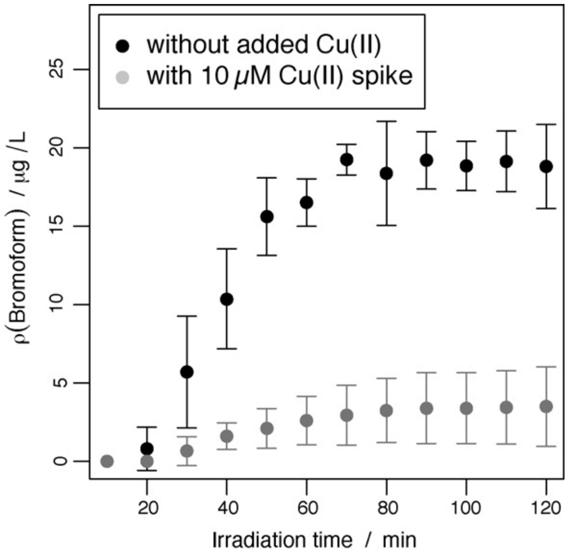

Fig. 3. Bromoform formation in irradiated P25 suspensions (with Lake Hohloh water as DOC source) with and without a spike of 10 μ mol L^{-1} Cu(II).

Because copper(II) ions are known to build very stable coordination compounds with NOM [24], it is attractive to assume that the decreased bromoform formation is due to the changes in transformation of the NOM brought about by the presence of Cu^{2+}[23], which in turn could lead to a decreased concentration of appropriate THM precursors.

4. Conclusions

The amount of bromoform produced in titanium dioxide suspensions containing elevated fresh water bromide ion concentrations and dissolved organic carbon is strongly affected by:

- the identity of the photocatalyst powder used, and by
- the presence of copper(II) ions.

In particular, both the use of Hombikat UV100 as a photocatalyst and the addition of Cu^{2+} led to a large decrease in the observed bromoform concentrations (in all cases < 5 μg L^{-1} compared to up to ≈ 20 μg L^{-1} when using Lake Hohloh water as DOC source).

Despite the large differences observed in bromoform formation under different experimental conditions, the absolute amounts were invariably far below the prescribed limit for trihalomethanes (THM) in drinking water, even in the presence of 250 mg L^{-1} of chloride ions. This observation underlines the potential of heterogeneous photocatalysis as an alternative oxidative step in the treatment of water for human consumption, because it can effectively oxidize a large variety of organic pollutants and shows a low potential for THM formation. Further studies should investigate the formation of other potentially harmful reaction byproducts.

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