UV/Sulphite as alternative for UV/H2O2 for micropollutant degradation in drinking water

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Abstract

The UV/SO32–/C032 process can be applied to convert organic micropollutants (OMP). The reaction is induced by UV-photolysis of sulphitesulphite (preferably using a MP UV lamp). Although in general it is assumed that the UV/SO32– process is an advanced reduction process, our results show degradation of OMP under both anoxic and oxic conditions. Several recalcitrant OMP even show higher degradation rates under oxic conditions than under anoxic conditions. This conversion is affected by the presence of dissolved organic carbon (DOC), HCO3–/C032 and NO3–/C032, and thus was more effective in drinking water than in Milli-Q water. The reaction rate constants of the oxic UV/SO32– process in general are lower than those of a UV/H2O2 process, but in cases were the use of H2O2 isn’t preferred, the UV/SO32– process may be an interesting alternative.

Key words: advanced oxidation/reduction, drinking water treatment, organic micropollutants, oxic/anoxic conditions, rate constants, UV/sulphitesulphite

Highlights

- UV/SO32– process gives good degradation of organic micropollutants (OMP).
- Degradation takes place both under anoxic and oxic conditions.
- For some OMP oxic conditions are favourable for degradation.
- Higher degradation rate in drinking water than in ultrapure water.
- Possible alternative to UV/H2O2 process.

Graphical Abstract

Introduction

Advanced oxidation processes (AOP) for the removal of organic micropolllutants (OMP) from (drinking) water have obtained a lot of attention in literature over recent years (Stefan 2017; Capodaglio 2020). However, not all compounds can effectively be oxidized, because in fact they already are in an oxidized state. This is the case for e.g. bromate (Jung et al. 2014; Xiao et al. 2017c) or halogenated organic compounds (Vellanki et al. 2013). By changing their properties by means of reduction, it may be possible to enhance their adsorption on...
activated carbon surfaces (Schouteten et al. 2016). In recent years some research has been done in this field, but it still is a largely unknown area.

Advanced reduction processes (ARP) can be characterized by the production of highly reactive reducing radicals. These can be generated by applying UV-C radiation (200–300 nm) to a solution of sulphite, dithionite, sulfide or ferrous ions (Hara et al. 1999; Duan & Batchelor 2014; Liu et al. 2014). Xiao et al. (2017c) give an overview of $\text{SO}_3^{2-}$, $\text{S}_2\text{O}_4^{2-}$, $\text{S}^2$ and $\text{Fe}^{2+}$ for the removal of bromate from water. Most types of water contain various compounds, like salts and natural organic matter (NOM). This NOM can be present as particulate organic matter (POM) and dissolved organic matter (DOM). The efficiency of treatment processes is affected by the presence of electron scavengers like nitrate and nitrite, and by UV absorbing compounds like DOM Liu et al. (2014) and Yoon et al. (2014) describe the conversion of 1,2-dichloro ethane by means of UV and the aforementioned ions. Yin et al. (2019) showed that a wavelength of 254 nm was more effective than 300 or 365 nm for the reduction of graphene oxide by means of UV/$\text{SO}_3^{2-}$. The removal of PFAS compounds by this process was studied by Bao et al. (2019) and Cui et al. (2020) wrote a review on the advanced reduction of PFAS by means of UV/sulphite and UV/iodide processes. Dong et al. (2018) used sodium sulphite or NaBH₄ in combination with LP UV for the degradation of decabromodiphenyl ether. NaBH₄ for the removal of nitrophenol was described by Xiong et al. (2018), and are shown in the supplementary information.

Conversion of organic micropollutants may be caused by either direct UV photolysis (applying UV-C radiation), by reduction by hydrated electrons, or reaction with the sulphite radicals formed in these reaction schemes. It has not yet become clear whether this results in the formation of sulfur containing organic molecules. Li et al. (2019) determined second order rate constants $k_{\text{rad}}$ by applying quantitative structure activity relationships (QSARs) for aliphatic and phenyl-based compounds. In the conversion of perchlorate by means of UV/$\text{SO}_3^{2-}$ it was found that DOM competes with sulphite for the UV radiation, and thus may hinder the conversion of perchlorate (Vellanki & Batchelor 2013; Duan & Batchelor 2014). At relatively high concentrations of humic acid (HA) (circa 5 mg/L) Jung et al. (2017) observed a lower reaction rate than in Milli-Q water, due to light absorption and scavenging. However, at HA concentrations of about 1 mg/L for the reduction of bromate reaction rates were found to be higher than in Milli-Q water. This may be caused by the formation of reactive HA compounds. Increasing pH values and temperature were found to increase the reaction rate, which was in accordance with findings of Liu et al. (2013) and Qiwen et al. (2018). However, the sulphite concentration was concluded to show an optimum, above which mixing problems hindered further increase of reaction rate (Vellanki & Batchelor 2013; Duan & Batchelor 2014; Dong et al. 2018). The hydrogen radical that can be formed can react quickly with chlorinated compounds, resulting in the formation of radicals and Cl₂ gas. This effect mainly can be observed at pH values of 9–11. The effectiveness of ARP appeared to increase with increasing sulphite and trichloro ethylene concentrations (Qiwen et al. 2018).

According to Duan & Batchelor (2014) the quantum yield for the UV/$\text{SO}_3^{2-}$ system is $0.018 \pm 0.0018$ mol/Einstein, whereas Xiao et al. (2017b) reported a value of $0.109 \pm 0.001$ mol/Einstein for hydrated electrons, and $0.034 \pm 0.001$ mol/Einstein for hydrogen radicals, when an LP UV lamp was used for $\text{H}_2\text{O}_2$ in combination with an LP UV lamp a quantum yield of 0.5 was reported by Wols et al. (2014b). According to Li et al. (2012) the quantum yield for the formation of hydrated electrons at 253.7 nm in anoxic Milli-Q water would be $0.116 \pm 0.002$ mol/Einstein, with a molar extinction coefficient for $\text{SO}_3^{2-}$ of $18.14 \text{ mol}^{-1} \text{ cm}^{-1}$.

As mentioned above, the pH plays an important role in UV advanced reduction processes. This is mainly due to the effect on the degree of dissociation of the sulphite, which results in a different UV absorption and radical formation (Jung et al. 2014; Xiao et al. 2017a, 2017b). At low pH values hydrated electrons may be scavenged according to Equation (5) in the sup. info (Yazdanbakhsh et al. 2018), which, however, results in the formation...
of a hydrogen radical. This seemed to have little effect on the degradation of trichlorophenol, as this was shown to be mainly caused by the sulphite radical. Yu et al. (2018b), however, showed that the advanced reduction of 2,4-
dichlorophenol UV/SO$_3^{2-}$ was most effective at pH 10. Yu et al. (2018a) studied the reaction of monochloroacetic acid with hydrated electrons, and found that a high pH favors the reduction process. Yu et al. (2019) showed that at pH 9.2 the reduction of diclofenac mainly was caused by e$_{aq}$ whereas at pH 6 the reaction was dominated by H$ullet$.

ARP may also be an interesting technology to deal with recalcitrant compounds like perfluoro acetic acid (PFOA). Zhang et al. (2015) studied the conversion of PFOA by means of UV/I$^-$, and observed an increasing reaction rate with increasing temperatures. Schouteten et al. (2016) compared the conversion of atrazine, carbamazepine, bromynil, diatrizoic acid and dinoseb by means of ARP and oxidation by ozone. As expected, they found ARP results in the formation of other types of products than oxidation. This indeed may result in better adsorption properties (e.g. for dinoseb and diatrizoic acid), but for atrazine and bromoxynil no effects, and for carbamazepine even less adsorption on activated carbon were observed. More research will be required to identify the (transformation) products of micropollutants in ARP.

Apart from homogeneous ARP, applying solutions of SO$_3^{2-}$, S$_2$O$_4^{2-}$, S$^2$– and Fe$^{2+}$, also heterogeneous processes using n-types semiconductors like TiO$_2$, ZnO, Fe$_2$O$_4$, CdS, SnO$_3$, WO$_3$ etc. can be used. During surface excitation both electrons and holes are formed, which can cause chemical reactions (Xiao et al. 2017c).

The presence of a strong oxidator like oxygen may severely hinder ARP. Yazdanbakhsh et al. (2018) showed that the degradation of trichlorophenol, which was mainly attributed to the reaction with sulphite radicals, decreased from 95 to 75% due to the presence of oxygen. Also Yang et al. (2020) conclude that overall the presence of oxygen will have a negative influence on the reduction of micropollutants. Capodaglio (2020), however, not only distinguish advanced oxidation and reduction processes, but also mention AORP: combined advanced oxidation and reduction processes. In oxygen containing water solvated electrons can react with oxygen to form hydroxyl radicals. Thus, AORP combine both types of radical reactions to directly degrade contaminants. These processes may be less energy efficient, but show a wide applicability range. Cao et al. (2021) demonstrated that the UV/SO$_3^{2-}$ process in the presence of oxygen can act as an advanced oxidation process for the degradation of iopamidol, in which oxysulfur radicals (including SO$_4^{2-}$) and SO$_3^{2-}$/SO$_5^{2-}$ radicals play an important role. Reactions involved are shown in the sup. Info (Equations (10)–(13)).

As also Dutch sources for drinking water contain more and more recalcitrant OMP, the question was raised whether UV/SO$_3^{2-}$ may be a solution to this problem. Most research on UV/SO$_3^{2-}$ processes described so far was carried out under anoxic conditions. For full scale application in e.g. drinking water treatment, this may be a disadvantage. However, based on the findings presented above, the question was asked whether the UV/SO$_3^{2-}$ would be effective for the removal of OMP from drinking water underoxic conditions. In the present research we investigated the possibilities of the UV/SO$_3^{2-}$ process for the removal of recalcitrant organic micropollutants from drinking water. We studied the effects of the presence of oxygen, UV-C wavelength, and matrix conditions on the removal rate. Furthermore for a selection of micropollutants, which are often encountered in Dutch sources of drinking water, we compared the effect of the UV/SO$_3^{2-}$ process with that of the well-known UV/H$_2$O$_2$ advanced oxidation process.

**METHODS**

**Experimental set-up**

Experiments were carried out in a collimated beam apparatus (CB) (Hofman-Caris et al. 2012), equipped with either a low pressure (LP; Philips TUV PL-L95/4P; 95 W HO) or medium pressure (MP; Philips HOK 20/100; 2 kW) UV lamp. The LP lamp emits radiation with a wavelength of 253.7 nm, whereas the MP lamps emit a range of wavelengths between 200 and 300 nm. Two series of experiments were carried out: (1) with a set of previously studied micropollutants (Wols et al. 2013), and (2) with a set of often encountered recalcitrant micropollutants in sources for drinking water. The organic micropollutants studied, their molecular structures, starting concentrations and producers are shown in table SI2. Analyses were carried out at the KWR laboratory as previously reported (Wols et al. 2015). In the second series, apart from UV/SO$_3^{2-}$ also a UV/H$_2$O$_2$ process was studied, using a concentration of 10 mg H$_2$O$_2$/L.

For experiments under low oxygen concentrations, a perforated plastic ring was placed above the petri dish in de CB set-up. This ring was used to create a nitrogen atmosphere on top of the petri dish during experiments.
Besides, before the start of the experiment the solutions were bubbled with helium for 10 minutes. In this way, an oxygen concentration of 1.1 mg/L was obtained, which increased to 1.4 mg/L during the experiments. For this purpose a WTW O2 meter, type OXI 340i was used. Under atmospheric conditions, the oxygen concentration was about 10 mg/L. A 10 g/L Na2SO3 solution was added to the test solution.

Water and chemicals
Experiments were carried out in tap water of the city of Nieuwegein (DW), Milli-Q, and Milli-Q with additions of HCO3−, NO3−, and/or DOC (Alfa Aesar, sodium humic acid containing 50–60% humic acids; stock solution 400 g mixed with 100 ml Milli-Q and filtrated over 0.45 μm filters). The second series of experiments was carried out in DW. Details on the water composition are shown in table SI1 of the supplementary information.

UV doses applied in both series of experiments ranged from 0 to 600 mJ/cm².

RESULTS AND DISCUSSION
Reaction kinetics
In general, the conversion of a compound by UV radiation can be described with Equation (1). This also is the case for the conversion of sulphite into sulphate, with a redox potential of −0.20 and −0.86 V respectively.

\[
\ln \left( \frac{C_0}{C} \right) = k \times H'
\]  

(1)

In this equation C0 is the initial concentration of a compound, C is its actual concentration in the aqueous phase and H’ is the UV dose applied (mJ/cm²). The factor time is incorporated in the UV dose. The reaction rate constant k (cm²/mJ) depends on the type of reactions that occur. In a UV/H2O2 process, in which besides photolysis also oxidation by hydroxyl radicals occurs, k can be described according to Equation (2)

\[
k = k_{ox} + k_{phot}
\]  

(2)

In which kox is the reaction constant for the oxidation process, and kphot is the reaction rate constant for the photolysis. For a UV/SO32− process a similar formula can be applied ([3]):

\[
k = k_{sulphite} + k_{phot}
\]  

(3)

In which ksulphite is the reaction constant for the reactions caused by active compounds formed by the reaction of sulphite with UV radiation. Under oxic circumstances sulphite is completely converted into sulfate at UV doses ≥300 mJ/cm², as is shown in figure SI1.

Direct reaction of OMP with sulphite
Experiments were carried out using a set of 47 pharmaceuticals and other often encountered organic micropollutants in sources for drinking water (see table SI2 in the supplementary information). As sulphite is an oxidant, it is possible that it may directly react with e.g. OMP, or that the presence of sulphite may interfere with the analyses of the OMP (Wols et al. 2013). The effect of sulphite addition in general is shown to be small or negligible, and in general within the experimental uncertainty (figure SI2). The k values for photolysis and the UV/SO32− process were calculated, both under oxic and under anoxic conditions. For some compounds (like diclofenac, ketoprofen and pindolol) concentrations were decreased below the reporting limit under irradiation, and for other compounds hardly any degradation could be observed (e.g. for guanylurea and pentoxyfylline), resulting in less reliable data. For niacin and metronidazole analysis data didn’t always seem to be reliable, and for vinylchloride no reliable data could be obtained because of its volatility in the collimated beam set-up. This explains the negative values calculated. All concentrations measured in this series are shown in supplementary info (excel file). An overview of the reaction rate constants is given in in a heat map (Figure 1).

Effect of oxygen on photolysis
The photolysis rate constants for the compounds studied are shown in Figure 1 (columns C, E and G).
It can be observed that for 33 out of 47 compounds in DW the photolysis rate constant seems to be independent of the presence of oxygen (columns A and B in Figure 1), as would have been expected. However, for tramadol, sotalol, salbutamol, paracetamol, lincomycin, furosemide, desphenylchloridazon, clindamycin and Paracetamol (Acetaminophen) the photolysis rate constant is significantly different between oxic and anoxic conditions.

**Figure 1** | Heatmap of rate constants $k$ for photolysis and UV/\(\text{SO}_3\) under oxic and anoxic conditions, using MP or LP UV lamps, in DW or MQ (with different concentrations of \(\text{NO}_3\), \(\text{HCO}_3\), and \(\text{DOC}\).

O\(_2\) refers to oxic conditions.

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clenbuterol the photolysis rate constant is clearly larger under anoxic conditions. In literature we only found one example where photolysis was studied under both oxic and anoxic conditions (Al-Hassan & Al-Amro 1998). These authors used VIS and UV/VIS radiation, and found that under aerobic conditions VIS didn’t result in degradation of acridine orange hydrochloride hydrate, whereas under anaerobic conditions photolysis did occur. They also mention that UV photolysis occurred under aerobic conditions. Obviously, different reaction mechanisms are involved, involving e.g. active oxygen radicals under oxic conditions, as has been reported before (Semitsoglou-Tsiapou et al. 2016). These might also act as radical scavengers, decreasing the reaction rate in some cases.

A comparison of the photolysis rate constants under aerobic conditions in DW and MQ (columns E and G in Figure 1) shows that in 14 cases in DW rate constants are higher than in MQ, in 9 cases the rate constants are a little higher in MQ than in DW, and in 24 cases the values are identical. It is likely that photolysis products of DOM may have played a role in the degradation of the pharmaceuticals present, causing the differences, but no general effects can be observed, as the DOM photolysis products are more selective (probably due to their complex molecular structures). In literature several types of effects of DOM on the degradation of organic compounds can be found. Liu et al. (2016) showed that DOM can have a slightly inhibiting effect on the UV photolysis of oxytetracycline, which was attributed to light scattering. Song et al. (2021) noticed that DOM can play several roles in the photolysis of tetracycline. It can promote the formation of hydroxyl radicals and generate triplet-excited state DOM (3DOM*), enhancing the indirect photolysis. However, it may also inhibit the reaction of OMP by an inner filter effect and interaction with the OMP in question. It was found that 3DOM* plays an important role in the photodegradation of e.g. acetaminophen (Li et al. 2017), betablockers (Wang et al. 2012) and BDE-153 (Wang et al. 2016). Reaction of 3DOM* with dissolved oxygen results in the formation of O2· (McNeill & Canonica 2016), and intramolecular electron transfer between electron donors and receptors inside 3DOM* was shown to produce reducing radical intermediates, which further react with dissolved oxygen to yield superoxide anions (O2−·) (Li et al. 2017). Batista et al. (2016) also describe the role DOM can play in UV photolysis processes, and mention the formation of 3DOM* with a formation rate of 6.83 to 14.70 × 108 mol/L/s, depending on the type of DOM applied (15 mg/L). Besides 3DOM* also hydroxyl radicals (k = 0.35–2.82 × 1012 mol/L/s) and O2· (k = 6.65–20.3 × 108 mol/L/s) were formed. It is very likely that similar effects played a role here too.

UV/SO32− processes

Although not for all compounds reliable values for reaction rate constant k in the UV/SO32− process in DW could be obtained, for most compounds both under oxic and anoxic conditions a k value could be calculated, as shown in Figure 3. As expected, in DW for tramadol, metoprolol, diatrizoic acid, desphenylchloridozon, atenolol and especially metronidazole, independent of the presence of oxygen. For all other compounds in this study, however, it seems that for much more OMP the rate constant is higher under oxic conditions then under anoxic conditions.

The effect of the addition of SO32− to the mixture is illustrated in Figure 2. In DW the presence of SO32− doesn’t seem to affect the conversion rate constant ksulphitesulphite for ketoprofen, gemfibrozil, pentoxyfylline, guanylurea, vinylchloride and cyclophosphamide (i.e. the difference between the k value for photolysis and UV/SO32− ≤2×10−4 cm²/mj), independent of the presence of O2. Under anoxic conditions the k value is similar for trimethoprim, and under oxic conditions this is observed for terbutaline, diatrizoic acid and desphenylochloridazone. The presence of SO32− appears to have a negative effect on the k value in DW for niacin, 1,2-dichloro ethane and especially metronidazole, independent of the presence of oxygen. For all other compounds in this study, however, the rate constant in DW increases by the interaction with SO32− and UV. For MQ, under oxic conditions, however, different effects can be observed. Here for 11 of the 47 OMP hardly any effects could be observed for the interaction with SO32−, and for 16 compounds a negative effect could be observed. Only for 19 OMP in this selection the presence of SO32− enhanced the conversion of OMP in MQ, whereas this was the case for 36 compounds (anoxic conditions) or 34 compounds (oxic conditions) in DW. This clearly shows that the positive effect of SO32− is related to the presence of other compounds in the aqueous matrix. From literature it is known that photolysis of DOM may also result in the formation of radical species O2·, O2· and OH (Semitsoglou-Tsiapou et al. 2016), and such reactions may have occurred here too, increasing the degradation rate. Second order reaction rate constants of O2· have been reported in literature to be in the order of magnitude of 105–1010 M−1s−1 (Hayyan et al. 2016; Guo et al. 2021).
**Figure 2** | $k_{\text{so}_{2}}$, applying MP UV-lamps (200–300 nm) in DW under oxic and anoxic conditions and in MQ under oxic conditions.

| Compound                  | Water Type | A | B | C | D | E |
|---------------------------|------------|---|---|---|---|---|
| Metronidazole             | DW         | 64| 70| 77| 75| 76|
| Gemfibrozil               | DW         | 61| 68| 74| 76| 77|
| Metoprolol                | DW         | 32| 34| 36| 35| 48|
| Niacin                    | DW         | 17| 23| 25| 30| 42|
| Atenolol                  | DW         | 17| 18| 22| 24| 36|
| 1,2-dichloroethane        | DW         | 20| 21| 19| 22| 22|
| Pentoxifylline            | DW         | 7 | 12| 15| 17| 31|
| Trimethaphrin             | DW         | 8 | 11| 13| 13| 31|
| Vinychloride              | DW         | 6 | 9 | 12| 16| 27|
| Guanurea                  | DW         | 4 | 5 | 6 | 7 | 23|
| Carbamazepine             | DW         | 2 | 3 | 6 | 6 | 23|
| Desfenerchloridazon       | DW         | 2 | 5 | 6 | 8 | 18|
| Diglyme                   | DW         | 7 | 0 | 4 | 2 | 24|
| 2,6 Dichloorbenzamide (BAM)| DW | 5 | 3 | 6 | 4 | 16|
| Triglyne                  | DW         | 5 | 1 | 2 | 4 | 23|
| N,N-dimethyl/sulfamide (DMS)| DW | 0 | 1 | 2 | 4 | 4|

**Figure 3** | $k$-values for the UV/SO$_3$$^-$ process in DW, series 2.
The results suggest that it is not (only) a reduction process that is taking place, as in that case it would have been favored by the absence of oxygen. This is in accordance with the findings of Cao et al. (2021).

Effect of wavelength in UV/SO$_3^-$ processes

The molar absorbance of sulphite as a function of wavelength is shown in Figure SI3. As sulphite has a maximum UV absorbance below 220 nm (see Figure SI3), it was expected that MP UV lamps would give better results than LP UV lamps in the UV/SO$_3^-$ process. This was checked for the micropollutants present, using tap water from the city of Nieuwegein, a sulphite dose of 20 mg/L and a UV dose of 600 mJ/cm$^2$. The results are shown in columns B and F (aerobic conditions) and A and D (anaerobic conditions) in Figure 3.

For 50% of the OMP tested in this study the presence of oxygen didn’t affect the k-value for the UV/SO$_3^-$ process with LP UV-lamps, and for 50% the absence of oxygen was shown to result in a higher k-value, which is opposite to the results obtained with MP UV lamps. Only for vinylchloride k seemed to be higher under oxic than under anoxic conditions, but this result may have been affected by the high volatility of vinylchloride.

In general, it can be seen that MP radiation results in a higher conversion than LP radiation, as expected. Furthermore, for desphenychloridazon and paracetamol anoxic circumstances seem to result in a higher conversion, whereas for several other compounds (gemfibrozil, furosemide, cyclofosfamide, cortisone, venlafaxine, trimethoprim, sulamguinoxaline, sulfadiazine, sulfachloropyridazine, salbutamol, propyphenazone and phenazone) the opposite is observed, regardless of the type of UV lamp. Finally, there are some compounds which show a different behavior depending on the type of UV lamp. For diatrizoic acid, and metazachloric sulfonic acid oxic conditions seemed to be favorable for LP lamps and anoxic conditions for MP lamps, whereas for cortisol, tramadol, propranolol and paroxetine the opposite was observed. These results also indicate that it is not simply a matter of photolysis and reduction, but that other reactions, involving oxygen, also play a role in the degradation process.

Effect of water composition

As shown above the matrix composition clearly affects the UV/SO$_3^-$ process. The effects of nitrate, hydrogen carbonate and DOC concentration in MQ was tested under oxic conditions. Increasing the HCO$_3^-$ concentration from 60 to 120 mg/L (column K versus I) has a strong negative effect on the k-value for metazachloric sulfonic acid, metolachlor sulfonic acid, metolachloric acid and vinyl chloride. This may indicate that radical scavenging by carbonate plays a role in the conversion of these compounds. For all other compounds tested here no or only small effects can be observed.

Liu et al. (2016) already showed that nitrate may enhance the photolysis of OMP by the formation of hydroxyl radicals. However, according to Liu et al. (2014) increasing the NO$_3^-$ concentration from 0 to 25 mg/L hardly affected the reaction rate constant for vinylchloride in the UV/SO$_3^-$ process. Increasing the NO$_3^-$ content in our experiments from 5 to 15 mg/L (column L versus J) also doesn’t affect the k-value of the UV/SO$_3^-$ process for 25 compounds, and results in a higher k-value for 18 compounds. However, for metazachloric sulfonic acid, metolachlor sulfonic acid, metolachloric acid and vinyl chloride the opposite effect was observed. This again shows that radical scavenging is an important factor in the conversion of these four compounds, as it was in the case of HCO$_3^-$ . However, for the other OMP the presence of NO$_3^-$ may even have a positive effect on the OMP removal.

Duan & Batchelor (2014) have found that at a wavelength of 222 nm k values for the removal of perchlorate by the UV/SO$_3^-$ process decreased from 0.087 to 0.030 h$^{-1}$ with DOM content increasing from 0 to 30 mg/L. At a wavelength of 253.7 nm k decreased from 0.1 (no DOM) to 0.0033 h$^{-1}$ (50 mg DOM/L). Cao et al. (2021) concluded that the presence of DOM inhibited the degradation of iopamidol and the degradation efficiency decreased from 79.9% to 64.2% as the concentration of DOM increased from 0 to 1.5 mg/L, caused by DOM capturing SO$_4^{2-}$ (k = 6.8 x 10$^3$ L·mg·C$^{-1}$·s$^{-1}$). According to Zhou et al. (2017) the presence of DOM inhibits the degradation of compounds by sulphate radicals. Increasing the DOC content of the solution from 1 to 5 mg/L in our experiments (column K versus L) doesn’t seem to affect the k-values for 28 compounds, and significantly decreases the values for 19 compounds. Summarizing it can be concluded that the combined effects of low concentrations of HCO$_3^-$, NO$_3^-$ and DOC significantly enhance degradation of most compounds. It seems that the presence of DOC, NO$_3^-$ and HCO$_3^-$ results in the formation of other radicals, with may react effectively with certain compounds. Furthermore, a different DOC-composition in the MQ-experiments (with artificially added DOC) than in de DW experiments may also have played a role, but this should be further investigated.
**Application in drinking water treatment**

These results shown above indicate that the UV/SO$_3^2$ process probably is not a simple reduction process. Although at this moment it still is not clear which processes actually are occurring, the higher conversions observed under oxic conditions indicate that oxidative reactions likely are taking place where (activated) oxygen radicals play a role. One of the questions to be answered is whether sulfonated compounds may be formed under these circumstances.

For water treatment it might be very interesting if UV/SO$_3^2$ could be used to remove organic micropollutants instead of UV/H$_2$O$_2$. An advantage is that no excess H$_2$O$_2$ will have to be removed in an additional filtration step. The maximum sulphate concentration in DW is 150 mg/L in the Netherlands, so unless the water already contained a relatively high concentration sulphate, this doesn’t have to be removed after the reaction. Besides, storage and handling of H$_2$O$_2$ would require specific safety measures, which are not required when NaSO$_3$ is used. In order to check the applicability of the UV/SO$_3^2$ process in water treatment, additional experiments (series 2) were carried out in tap water (DW) under oxic conditions, applying a MP-UV dose of 600 mJ/cm$^2$ and a SO$_3^2$ concentration of 0 to 60 mg/L. The removal of very recalcitrant organic micropollutants, often encountered in sources for drinking water in the Netherlands, was studied. The results are shown in a heatmap (Figure 3).

For the UV/H$_2$O$_2$ process the optimum H$_2$O$_2$ concentration of 10 mg/L for this water matrix has been applied (Wols et al. 2014a, 2015). All experiments were carried out in drinking water.

Some small differences in k-values for compounds in series 1 and 2 (Figures 3 and 5) can be explained by a slightly different water quality (see Table SI1) or a different DOM composition, as samples were taken in another season. However, in general the results are in fairly good accordance.

As expected, for most compounds photolysis rate constants are $<10^{-4}$ cm$^2$/mJ. Only for MCPA and MCPP photolysis showed a $k_{photolysis} > 60^{-4}$ cm$^2$/mJ.

The values for $k_{sulphitesulphite}$ in series 2 are shown in Figure 4.

Increasing the SO$_3^2$ concentration seems to have no or even a negative effect on the k-values for triglyme, BAM, diglyme, desfenylchloridazon and acesulfame K. For all other compounds studied in this series the k-values increased, especially for dimethenamid.

![Figure 4](http://iwaponline.com/ws/article-pdf/doi/10.2166/ws.2021.164/894999/ws2021164.pdf)
In general, the UV/H₂O₂ process appears to be more effective than the UV/SO₃²⁻ process, although for some compounds, like diatrizoic acid, dimethenamid, MCPA, and MCPP the differences are negligible. Increasing the sulphite concentration from 20 to 60 mg/L (0.16–0.48 mmol/L) results in increasing reaction rate constants. This is in accordance with the results reported earlier by (Qiwen et al. 2018), and would be expected if photolysis of sulphite was to initiate the micropollutant degradation. The sulphite concentration is in the same order of magnitude as the H₂O₂ concentrations: 10 mg H₂O₂/L equals 0.29 mmol/L, and every H₂O₂ can form two hydroxyl radicals.

From the present data it is not possible to draw conclusions on the formation of transformation products. It seems that all sulphite is converted into sulfate, but as the sulphite and sulfate concentrations are three orders of magnitude higher than the micropollutants concentrations, this doesn’t exclude the possibility that low concentrations of sulphur containing compounds may have been formed.

According to Capodaglio (2020) AORP may seem less efficient than the conventional AOP, but shows a wide applicability range. The present results seem to indicate that the UV/SO₃²⁻ process under oxic conditions also may be regarded as an AORP, with an applicability range suitable for drinking water treatment. Although the process seems to be less generally applicable than e.g. the UV/H₂O₂ process, it may be considered to apply the UV/ SO₃²⁻ process in addition to other processes, for the removal of some recalcitrant compounds, or for the specific treatment of water with certain contaminants.

CONCLUSIONS

As expected, the UV/SO₃²⁻ process can be applied to convert OMP. The reaction is started by photolysis of sulphite, which is in accordance with the observation that MP UV lamps give a higher micropollutant degradation than LP UV lamps.

OMP degradation by UV/SO₃²⁻ was observed under both anoxic and oxic conditions. Surprisingly, many OMP showed higher degradation under oxic conditions. This leads to a new hypothesis, that UV/SO₃²⁻ is an AORP under oxic conditions. Oxygen radicals and ³DOM⁺ probably play an important role. This will further have to be investigated.

A broad range of recalcitrant organic micropollutants can be degraded by oxic UV/SO₃²⁻. In DW better results were obtained than in MQ. The conversion is affected by the presence of DOC, HCO₃⁻ and NO₃⁻. Low concentrations of these compounds in MQ significantly enhance the degradation of OMP, possibly due to radicals like ³DOM⁺. Increasing the nitrate concentration has a small (positive) effect on the micropollutant degradation, but increasing the TOC or HCO₃⁻ concentration has no or only a small negative effect, due to scavenging.

The UV/H₂O₂ process in general results in higher reaction rate constants than the UV/SO₃²⁻ process, although for some compounds, like diatrizoic acid, dimethenamid, MCPA and MCPP rate constants are similar. However, the UV/ SO₃²⁻ process may be an interesting alternative. The sulfate concentration formed in general will be below drinking water standards.

More research will be required to elucidate the exact reactions taking place, and which transformation products may be formed. Also the role of DOC concentration and composition will have to be studied in more detail. This will show whether the UV/ SO₃²⁻ process indeed may be an effective alternative treatment method for drinking water production.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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