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UV/sulphite as alternative for UV/H_2O_2 for micropollutant degradation in drinking water

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ABSTRACT

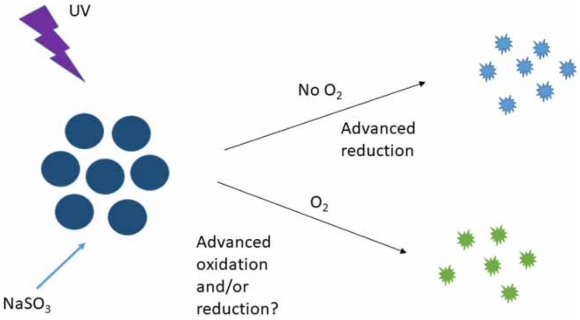
The UV/SO_3^{2-} process can be applied to convert organic micropollutants (OMP). The reaction is induced by UV photolysis of sulphite (preferably using a medium pressure (MP) UV lamp). Although in general it is assumed that the UV/SO_3^{2-} process is an advanced reduction process, our results show 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), HCO_3^- and NO_3^-, and thus was more effective in drinking water than in Milli-Q water. The reaction rate constants of the oxic UV/SO_3^{2-} process in general are lower than those of a UV/H_2O_2 process, but in cases where the use of H_2O_2 is not preferred, the UV/SO_3^{2-} process may be an interesting alternative.

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

HIGHLIGHTS

- UV/SO_3^{2-} process gives good degradation of organic micropollutants (OMP).
- Degradation takes place both under anoxic and oxic conditions.
- For some OMP oxic conditions are favorable for degradation.
- Higher degradation rate in drinking water than in ultrapure water.
- Possible alternative to UV/H_2O_2 process.

GRAPHICAL ABSTRACT



INTRODUCTION

Advanced oxidation processes (AOP) for the removal of organic micropollutants (OMP) from (drinking) water have obtained a lot of attention in the published 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 (Schoutteten *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 SO_3^{2-}, $S_2O_4^{2-}$, S^{2-} and 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-dichloroethane 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/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 $NaBH_4$ in combination with low pressure (LP) UV for the degradation of decabromodiphenyl ether. $NaBH_4$ for the removal of nitrophenol was described by Xiong *et al.* (2019). ARP seems to be an effective way to remove recalcitrant compounds, which often are difficult to remove by AOP. Yu *et al.* (2018a) and Wang & Liu (2019) showed that the efficiency of the UV/SO_3^{2-} system can be improved by adding iodide. Yang *et al.* (2020) conclude that ARP based on UV/sulphite is an effective process for the degradation of refractory contaminants. Important parameters affecting the efficiency are: pH, sulphite concentration, type of UV lamp (i.e. wavelength), UV dose, pollutant concentrations, DOM concentration, and the presence of ions. However, more research still is required, certainly for full-scale applications.

Sulphite shows a maximum UV absorbance at 220 nm, but experiments have been carried out with both LP (253.7 nm) and medium pressure (MP; 200–300 nm) UV-C lamps (Vellanki & Batchelor 2013; Vellanki *et al.* 2013; Duan & Batchelor 2014). The reactions taking place under anoxic conditions have been described in the published literature (Liu *et al.* 2013; Jung *et al.* 2014; Xiao *et al.* 2017c; Yazdanbakhsh *et al.* 2018; Yu *et al.* 2018a), 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 sulphur-containing organic molecules. Li *et al.* (2019) determined second order rate constants k_{eaq} by applying quantitative structure activity relationships (QSARs) for aliphatic and phenyl-based compounds. In the conversion of perchlorate by means of UV/SO_3^{2-} it was found that DOM competes with sulphite for 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 Cl_2 gas. This effect mainly can be observed at pH values of 9–11. The effectiveness of ARP appeared to increase with increasing sulphite and trichloroethylene concentrations (Qiwen *et al.* 2018).

According to Duan & Batchelor (2014) the quantum yield for the UV/SO_3^{2-} system is 0.018 ± 0.0018 mol/Einstein, whereas Xiao *et al.* (2017b) reported a value of 0.109 ± 0.001 mol/Einstein for hydrated electrons, and 0.034 ± 0.001 mol/Einstein for hydrogen radicals, when an LP UV lamp was used (for H_2O_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 ± 0.002 mol/Einstein, with a molar extinction coefficient for SO_3^{2-} of 18.14 mol^{-1} 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 Supplementary Information (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 $H^{\bullet}$.

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. Schoutteten *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-}, $S_2O_4^{2-}$, S^{2-} and Fe^{2+}, also heterogeneous processes using n-types semiconductors like TiO_2, ZnO, Fe_3O_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 oxidant 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 distinguishes advanced oxidation and reduction processes, but also mentions 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 $SO_4^{\bullet-}$) and $SO_3^{\bullet-}$/$SO_5^{\bullet-}$ radicals play an important role. Reactions involved are shown in the Supplementary Information (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 under oxic 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_2O_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 LP (Philips TUV PL-L95/4P; 95 W HO) or 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 emits 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_2O_2 process was studied, using a concentration of 10 mg H_2O_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. In addition, 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 O_2 meter, type OXI 340i was used.

Under atmospheric conditions, the oxygen concentration was about 10 mg/L. A 10 g/L Na_2SO_3 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 HCO_3^-, NO_3^-, 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/cm^2.

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:

$$ln\left(\frac{C_0}{C}\right) = k * H' \tag{1}$$

In this equation C_0 is the initial concentration of a compound, C is its actual concentration in the aqueous phase and H' is the UV dose applied (mJ/cm^2). The factor time is incorporated in the UV dose. The reaction rate constant k (cm^2/mJ) depends on the type of reactions that occurs. In a UV/H_2O_2 process, in which besides photolysis also oxidation by hydroxyl radicals occurs, k can be described according to Equation (2):

$$k = k_{ox} + k_{phot} \tag{2}$$

In which k_{ox} is the reaction constant for the oxidation process, and k_{phot} is the reaction rate constant for the photolysis. For a UV/SO_3^{2-} process a similar formula can be applied ([3]):

$$k = k_{sulphite} + k_{phot} \tag{3}$$

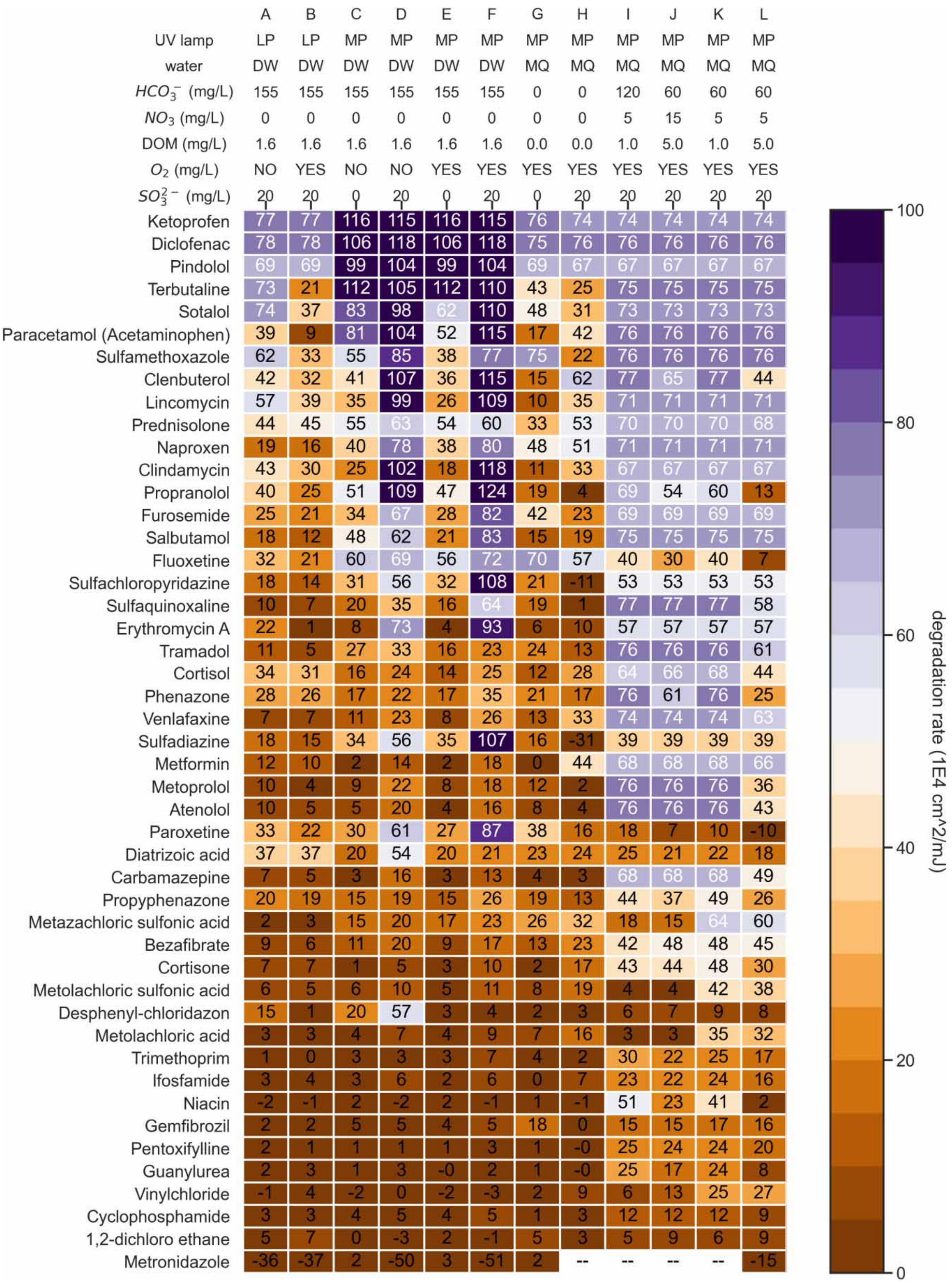
In which $k_{sulphite}$ is the reaction constant for the reactions caused by active compounds formed by the reaction of sulphite with UV radiation. Under oxic circumstances sulphite is completely converted into sulphate at UV doses ≥300 mJ/cm^2, as is shown in Figure SI1.

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/SO_3^2 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 pentoxifylline), resulting in less reliable data. For niacin and metronidazole analysis data did not always seem to be reliable, and for vinyl chloride 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 information (excel file). An overview of the reaction rate constants is given 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).



	A	B	C	D	E	F	G	H	I	J	K	L
UV lamp	LP	LP	MP	MP	MP	MP	MP	MP	MP	MP	MP	MP
water	DW	DW	DW	DW	DW	DW	MQ	MQ	MQ	MQ	MQ	MQ
HCO_3^- (mg/L)	155	155	155	155	155	155	0	0	120	60	60	60
NO_3 (mg/L)	0	0	0	0	0	0	0	0	5	15	5	5
DOM (mg/L)	1.6	1.6	1.6	1.6	1.6	1.6	0.0	0.0	1.0	5.0	1.0	5.0
O_2 (mg/L)	NO	YES	NO	NO	YES	YES	YES	YES	YES	YES	YES	YES
SO_3^{2-} (mg/L)	20	20	0	20	0	20	0	20	20	20	20	20
Ketoprofen	77	77	116	115	116	115	76	74	74	74	74	74
Diclofenac	78	78	106	118	106	118	75	76	76	76	76	76
Pindolol	69	69	99	104	99	104	69	67	67	67	67	67
Terbutaline	73	21	112	105	112	110	43	25	75	75	75	75
Sotalol	74	37	83	98	62	110	48	31	73	73	73	73
Paracetamol (Acetaminophen)	39	9	81	104	52	115	17	42	76	76	76	76
Sulfamethoxazole	62	33	55	85	38	77	75	22	76	76	76	76
Clenbuterol	42	32	41	107	36	115	15	62	77	65	77	44
Lincomycin	57	39	35	99	26	109	10	35	71	71	71	71
Prednisolone	44	45	55	63	54	60	33	53	70	70	70	68
Naproxen	19	16	40	78	38	80	48	51	71	71	71	71
Clindamycin	43	30	25	102	18	118	11	33	67	67	67	67
Propranolol	40	25	51	109	47	124	19	4	69	54	60	13
Furosemide	25	21	34	67	28	82	42	23	69	69	69	69
Salbutamol	18	12	48	62	21	83	15	19	75	75	75	75
Fluoxetine	32	21	60	69	56	72	70	57	40	30	40	7
Sulfachloropyridazine	18	14	31	56	32	108	21	-11	53	53	53	53
Sulfaquinoxaline	10	7	20	35	16	64	19	1	77	77	77	58
Erythromycin A	22	1	8	73	4	93	6	10	57	57	57	57
Tramadol	11	5	27	33	16	23	24	13	76	76	76	61
Cortisol	34	31	16	24	14	25	12	28	64	66	68	44
Phenazone	28	26	17	22	17	35	21	17	76	61	76	25
Venlafaxine	7	7	11	23	8	26	13	33	74	74	74	63
Sulfadiazine	18	15	34	56	35	107	16	-31	39	39	39	39
Metformin	12	10	2	14	2	18	0	44	68	68	68	66
Metoprolol	10	4	9	22	8	18	12	2	76	76	76	36
Atenolol	10	5	5	20	4	16	8	4	76	76	76	43
Paroxetine	33	22	30	61	27	87	38	16	18	7	10	-10
Diatrizoic acid	37	37	20	54	20	21	23	24	25	21	22	18
Carbamazepine	7	5	3	16	3	13	4	3	68	68	68	49
Propyphenazone	20	19	15	19	15	26	19	13	44	37	49	26
Metazachloric sulfonic acid	2	3	15	20	17	23	26	32	18	15	64	60
Bezafibrate	9	6	11	20	9	17	13	23	42	48	48	45
Cortisone	7	7	1	5	3	10	2	17	43	44	48	30
Metolachloric sulfonic acid	6	5	6	10	5	11	8	19	4	4	42	38
Desphenyl-chloridazon	15	1	20	57	3	4	2	3	6	7	9	8
Metolachloric acid	3	3	4	7	4	9	7	16	3	3	35	32
Trimethoprim	1	0	3	3	3	7	4	2	30	22	25	17
Ifosfamide	3	4	3	6	2	6	0	7	23	22	24	16
Niacin	-2	-1	2	-2	2	-1	1	-1	51	23	41	2
Gemfibrozil	2	2	5	5	4	5	18	0	15	15	17	16
Pentoxifylline	2	1	1	1	1	3	1	-0	25	24	24	20
Guanylurea	2	3	1	3	-0	2	1	-0	25	17	24	8
Vinylchloride	-1	4	-2	0	-2	-3	2	9	6	13	25	27
Cyclophosphamide	3	3	4	5	4	5	1	3	12	12	12	9
1,2-dichloro ethane	5	7	0	-3	2	-1	5	3	5	9	6	9
Metronidazole	-36	-37	2	-50	3	-51	2	--	--	--	--	-15

Figure 1 | Heatmap of rate constants k for photolysis and UV/SO$_3^2$ under oxic and anoxic conditions, using MP or LP UV lamps, in DW or MQ (with different concentrations of NO$_3^-$, HCO$_3$, and DOC. 'O$_2$' refers to oxic conditions.

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 clenbuterol the photolysis rate constant is clearly larger under anoxic conditions. In the published literature we only found one example in which photolysis was studied under both oxic and anoxic conditions (Al-Hassan & Al-Amro 1998). These authors used visible (VIS) and UV/VIS radiation, and found that under aerobic conditions VIS did not result in degradation of acridine orange hydrochloride hydrate, whereas under anaerobic conditions photolysis did occur. They also mentioned 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 nine 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 the published 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 (^{3}DOM*), 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 ^{3}DOM* 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 ^{3}DOM* with dissolved oxygen results in the formation of $^1O_2$ (McNeill & Canonica 2016), and intramolecular electron transfer between electron donors and receptors inside ^{3}DOM* was shown to produce reducing radical intermediates, which further react with dissolved oxygen to yield superoxide anions ($O_2^{\cdot -}$) (Li *et al.* 2017). Batista *et al.* (2016) also describe the role DOM can play in UV photolysis processes, and mention the formation of ^{3}DOM* with a formation rate of 6.83 to 14.70 $\times$ 10^8 mol/L/s, depending on the type of DOM applied (15 mg/L). Besides ^{3}DOM* also hydroxyl radicals ($k = 0.35–2.82 \times 10^{12}$ mol/L/s) and $^1O_2$ ($k = 6.65–20.3 \times 10^8$ mol/L/s) were formed. It is very likely that similar effects played a role here too.

UV/SO_3^{2-} processes

Although not for all compounds reliable values for reaction rate constant k in the UV/SO_3^{2-} 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 2. As expected, in DW for tramadol, metoprolol, diatrizoic acid, desphenylchloridozon, atenolol and metazachloric sulfonic acid the rate constant seems to be larger under anoxic conditions. However, surprisingly 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 SO_3^{2} to the mixture is illustrated in Figure 2. In DW the presence of SO_3^{2} does not seem to affect the conversion rate constant $k_{sulphite}$ for ketoprofen, gemfibrozil, pentoxifylline, guanylurea, vinyl chloride and cyclophosphamide (i.e. the difference between the k-value for photolysis and UV/SO_3^{2-} $\leq 2 \times 10^{-4}$ cm^2/mJ), independent of the presence of O_2. Under anoxic conditions the k-value is similar for trimethoprim, and under oxic conditions this is observed for terbutaline, diatrizoic acid and desphenylchloridzazone. The presence of SO_3^{2-} 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 SO_3^{2} 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 SO_3^{2}, and for 16 compounds a negative effect could be observed. Only for 19 OMP in this selection the presence of SO_3^{2-} 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 SO_3^{2-} 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 $^1O_2$, $O_2^{\cdot -}$ and $^{\cdot}OH$ (Semitsoglou-Tsiapou *et al.* 2016), and such reactions may have occurred here too, increasing the degradation rate. Second order reaction rate constants of $O_2^{\cdot -}$ have been reported in literature to be in the order of magnitude of 10^5–10^{10} $M^{-1}s^{-1}$ (Hayyan *et al.* 2016; Guo *et al.* 2021).

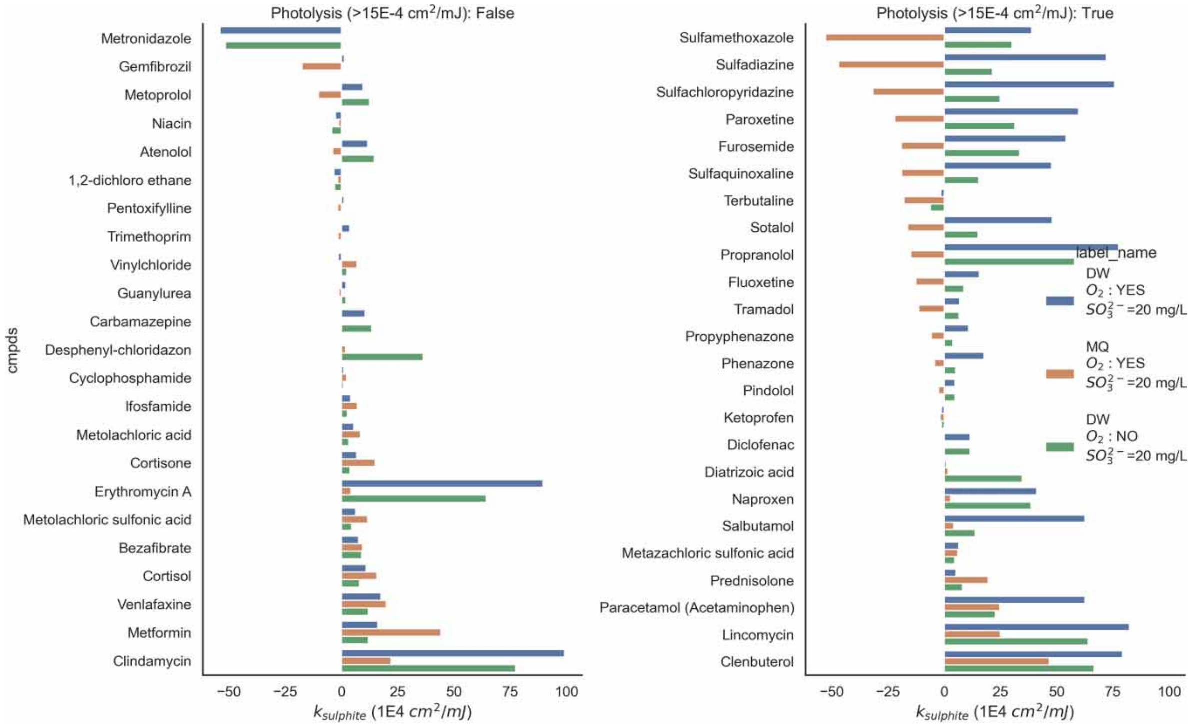


Figure 2 | $k_{sulphite}$, applying MP UV-lamps (200–300 nm) in DW under oxic and anoxic conditions and in MQ under oxic conditions.

The results suggests 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^{2-} 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^{2-} 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 1.

For 50% of the OMP tested in this study the presence of oxygen did not affect the k-value for the UV/SO_3^{2-} 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 vinyl chloride 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 desphenylchloridazon and paracetamol anoxic circumstances seem to result in a higher conversion, whereas for several other compounds (gemfibrozil, furosemide, cyclophosphamide, cortisone, venlafaxine, trimethoprim, sulfaquinoxaline, sulfadiazine, sulfachlorpyridazine, 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^{2-} 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^{2-} process. Increasing the NO_3^- content in our experiments from 5 to 15 mg/L (column L versus J) also does not affect the k-value of the UV/SO_3^{2-} 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^{2-} 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 $SO4^{\cdot -}$ ($k = 6.8 \times 10^3$ 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) does not 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^{2-} 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_2O_2. An advantage is that no excess H_2O_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 does not have to be removed after the reaction. Besides, storage and handling of H_2O_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).

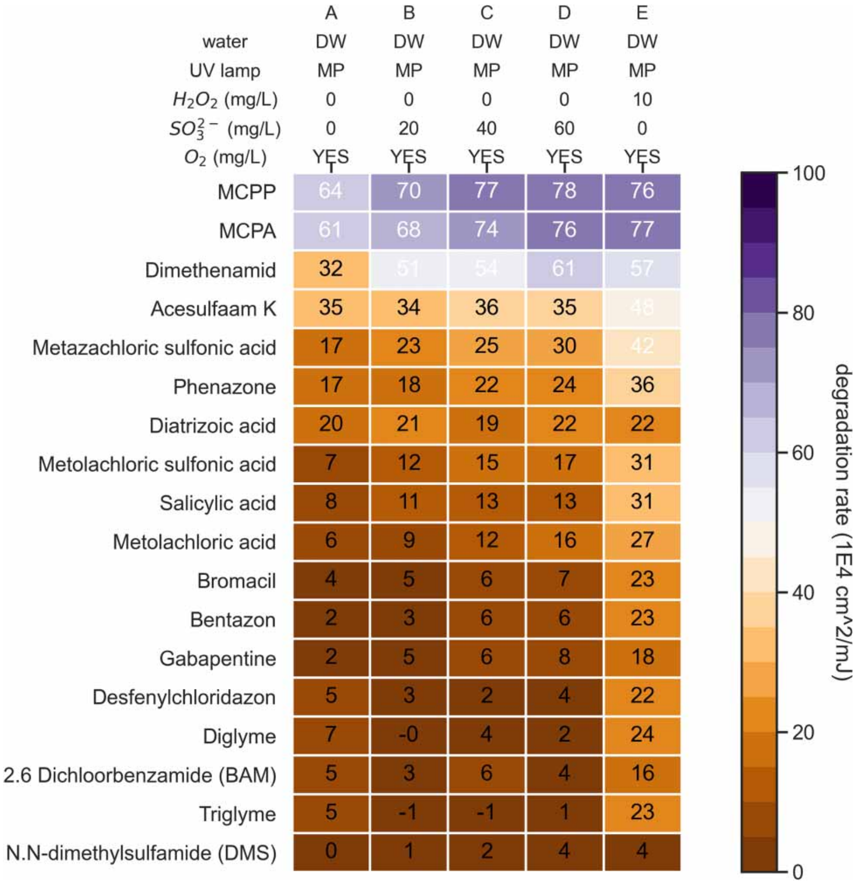
For the UV/H_2O_2 process the optimum H_2O_2 concentration of 10 mg/L for this water matrix has been applied (Wols *et al.* 2014a, 2015). All experiments were carried out in drinking water.

Some small differences in k-values for compounds in series 1 and 2 (Figures 3 and 4) 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 $<10 \times 10^{-4}$ cm^2/mJ. Only for MCPA and MCPP photolysis showed a $k_{photolysis} > 60 \times 10^{-4}$ cm^2/mJ.

The values for $k_{sulphite}$ 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.



	A	B	C	D	E
water	DW	DW	DW	DW	DW
UV lamp	MP	MP	MP	MP	MP
H_2O_2 (mg/L)	0	0	0	0	10
SO_3^{2-} (mg/L)	0	20	40	60	0
O_2 (mg/L)	YES	YES	YES	YES	YES
MCPP	64	70	77	78	76
MCPA	61	68	74	76	77
Dimethenamid	32	51	54	61	57
Acesulfaam K	35	34	36	35	48
Metazachloric sulfonic acid	17	23	25	30	42
Phenazone	17	18	22	24	36
Diatrizoic acid	20	21	19	22	22
Metolachloric sulfonic acid	7	12	15	17	31
Salicylic acid	8	11	13	13	31
Metolachloric acid	6	9	12	16	27
Bromacil	4	5	6	7	23
Bentazon	2	3	6	6	23
Gabapentine	2	5	6	8	18
Desfenylchloridazon	5	3	2	4	22
Diglyme	7	-0	4	2	24
2.6 Dichloorbenzamide (BAM)	5	3	6	4	16
Triglyme	5	-1	-1	1	23
N.N-dimethylsulfamide (DMS)	0	1	2	4	4

Figure 3 | k-values for the UV/SO_3^{2-} process in DW, series 2.

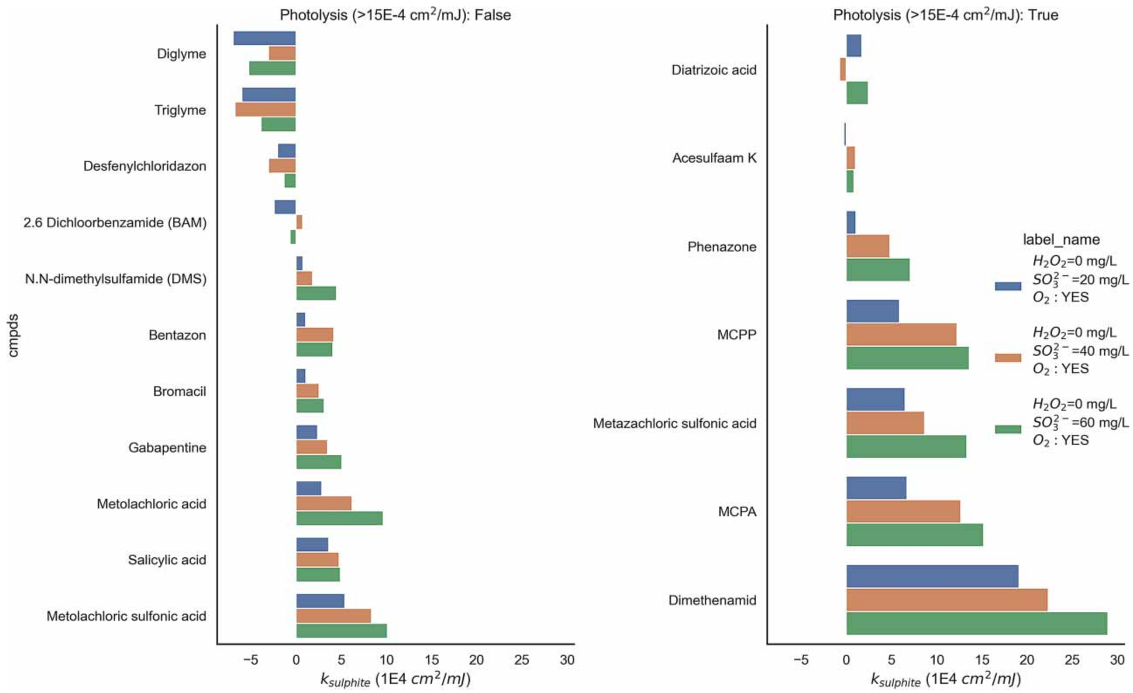


Figure 4 | $k_{sulphite}$ in DW under oxic conditions, applying MP UV-lamps.

In general, the UV/H_2O_2 process appears to be more effective than the UV/SO_3^{2-} 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 H_2O_2 concentrations: 10 mg H_2O_2/L equals 0.29 mmol/L, and every H_2O_2 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 sulphate, but as the sulphite and sulphate concentrations are three orders of magnitude higher than the micropollutants concentrations, this does not exclude the possibility that low concentrations of sulphur containing compounds may have been formed.

According to Capodaglio (2020) AORP seems less efficient than the conventional AOP, but shows a wide applicability range. The present results seem to indicate that the UV/SO_3^{2-} 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/H_2O_2 process, it may be considered to apply the UV/SO_3^{2-} 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/SO_3^{2-} 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/SO_3^{2-} 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/SO_3^{2-} is an AORP under oxic conditions. Oxygen radicals and ^{3}DOM* 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/SO_3^{2-}. In DW better results were obtained than in MQ. The conversion is affected by the presence of DOC, HCO_3^- and NO_3^-. Low concentrations of these compounds in MQ significantly enhance the degradation of OMP, possibly due to radicals like ^{3}DOM*. Increasing the nitrate concentration has a small (positive) effect on the micropollutant degradation, but increasing the TOC or HCO_3^- concentration has no or only a small negative effect, due to scavenging.

The UV/H_2O_2 process in general results in higher reaction rate constants than the UV/SO_3^{2-} process, although for some compounds, like diatrizoic acid, dimethenamid, MCPA and MCPP rate constants are similar. However, the UV/SO_3^{2-} process may be an interesting alternative. The sulphate 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/SO_3^{2-} 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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