

Chapter 26

Chemical oxidation processes

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26.1 INTRODUCTION

Various chemical oxidants have been widely used for many decades in water treatment, mainly for disinfection, but also to remove colour, taste and odour, as well as iron and manganese. In the last two decades, conventional oxidation with chemical oxidants and advanced oxidation processes (AOPs: use of $\cdot\text{OH}$ radicals as the main oxidants) have also come into more widespread use for removing micropollutants first from drinking water and in recent years also from wastewater effluents. The knowledge gained in these applications can be used to assess the feasibility of oxidative treatment of source-separated wastewater (greywater, urine) and the effluent from decentralized reactors.

26.1.1 Common chemical oxidants

An overview of the main chemical oxidants used in water treatment is given in Table 26.1. Ozone is the best disinfectant and can even inactivate protozoan cysts and oocysts such as *Giardia lamblia* cysts (*G. lamblia*) and *Cryptosporidium parvum* oocysts (*C. parvum*) with reasonable exposures (integral of ozone concentration over reaction time). In contrast, these microorganisms (especially *C. parvum*) require prohibitive exposures to another oxidant, namely chlorine, which may lead to high concentrations of disinfection by-products. In any case, the use of chlorine dioxide is not advised for the inactivation of protozoa. Although the novel oxidant ferrate(VI) is a good disinfectant for bacteria (Sharma 2007), it is not expected to efficiently inactivate protozoa in view of its general reactivity, which is similar to or lower than chlorine (Lee and von Gunten 2010).

Table 26.1 Oxidants used in water treatment and some of their characteristics. Rate constants for the reaction with some organic compounds are given in Figure 26.1.

Oxidant	Disinfection			Oxidation/disinfection by-products
	Virus	Bact.	Protozoa	
Ozone	+++	+++	+	Bromate, bromo-organics, AOC ⁽¹⁾ , N-nitrosodimethyl-amine (NDMA)
Chlorine	++	++	-	Cl-, Br-, I-organics, NDMA
Chlorine dioxide	++	++	+	Chlorite, chlorate
Ferrate(VI)	+	+	?	AOC ⁽¹⁾ , others?
OH radicals				AOC ⁽¹⁾

+++ Very efficient; ++ efficient; + partially efficient; inefficient; ? unknown;

⁽¹⁾ AOC; assimilable organic carbon.

Sources: Hoigné and Bader (1994), von Gunten and Hoigné (1994), Hammes *et al.* (2006), Schmidt and Brauch (2008), Krasner (2009), Sarathy and Mohseni (2009), von Gunten *et al.* (2010), Ramseier *et al.* (2011).

26.1.2 Oxidation/disinfection by-products

The possible by-products of oxidation/disinfection, which are formed from the reaction of the selected oxidants with water matrix components, are also shown in Table 26.1. The main oxidation by-product for ozone is bromate, which is potentially carcinogenic and has a drinking water standard of $10 \mu\text{g}\cdot\text{L}^{-1}$ (WHO 2004). It is formed during ozonation from bromide via a complex mechanism involving both ozone and OH radical reactions (von Gunten and Hoigné 1994). Besides the type and concentration of dissolved organic matter (DOM) and the alkalinity, the bromide concentration is the critical parameter for the extent of bromate formation. This is particularly important for oxidative urine treatment, because the bromide concentration in urine ($1.2\text{--}7.7 \text{ mg}\cdot\text{L}^{-1}$) is much higher than in typical water resources ($10\text{--}500 \mu\text{g}\cdot\text{L}^{-1}$) (von Gunten and Hoigné 1992).

During ozonation of bromide-containing waters, bromo-organic compounds can also be formed from the reaction of the intermediate species HOBr with DOM moieties (von Gunten and Hoigné 1994, Pinkernell and von Gunten 2001). Assimilable organic carbon (AOC) represents another important class of oxidation by-products, which are formed during ozonation as well as in other oxidation processes. It consists mainly of oxygen-rich compounds such as carboxylic acids, aldehydes and ketones. These are typically easily biodegradable and can be removed by biological post-filtration (Hammes *et al.* 2006). It was recently discovered that nitrosamines such as N-nitrosodimethylamine (NDMA) can also be formed during ozonation (Schmidt and Brauch 2008, von Gunten

et al. 2010). These compounds are highly relevant because they are orders of magnitude more toxic than the generally known by-products of oxidation/disinfection (WHO 2004). The main products formed during chlorination are chloro-, bromo- and iodo-organic compounds. Since the discovery of trihalomethanes (THMs) in treated drinking waters in 1974 (Rook 1974), over 600 individual disinfection by-products (DBPs) have been identified and reported in chlorinated or chloraminated drinking water (Krasner *et al.* 2006, Richardson *et al.* 2008). Of the total organic halogen species (often expressed as adsorbable organic halogen, AOX) in chlorinated and chloraminated drinking water, only 20–40% can be attributed to identifiable species, the remainder consisting of unidentified compounds (Richardson *et al.* 2002). In chlorinated water, halogenated DBPs are formed via direct reaction with chlorine, or with the secondarily formed bromine and iodine as well as aquatic DOM to form a complex mixture of halogenated organic compounds. Substantial formation of bromo-organic compounds is expected during urine chlorination due to high bromide and DOC levels (see Table 26.2). Furthermore, substantial concentrations of inorganic and organic chloramines can be expected in this matrix, which may carry residual oxidants over to the next treatment step. The main by-products of disinfection/oxidation from the application of chlorine dioxide are chlorite and to a certain extent chlorate. The WHO recommends provisional drinking water levels of chlorite and chlorate of $0.7 \text{ mg}\cdot\text{L}^{-1}$ (WHO 2004). Chlorine dioxide only forms limited chloro-organic compounds and does not react with bromide, so that no brominated organic compounds are formed (Werdehoff and Singer 1987, Gordon *et al.* 1990, Hoigné and Bader 1994). There is only little information about the formation of disinfection/oxidation by-products from the application of ferrate. It was recently shown that significant concentrations of AOC are formed during the treatment of surface waters with ferrate(VI) (Ramseier *et al.* 2011). For AOPs, the main oxidation/disinfection by-products from the reaction of $\cdot\text{OH}$ radicals with DOM consist of oxygen-rich compounds that lead to an increase of the AOC (Sarathy and Mohseni 2009).

26.1.3 Kinetics of oxidation/disinfection processes

Figure 26.1 summarizes the second-order rate constants for the reaction of oxidants with selected functional groups of organic molecules such as activated aromatic systems (phenols, anilines), olefins and amines. The data in this figure allow an estimate of how high the second-order rate constants need to be to reach half-life times for micropollutants of for example, $<2 \text{ min}$ for a typical oxidant concentration of $1 \text{ mg}\cdot\text{L}^{-1}$ (ca. $10\text{--}20 \mu\text{mol}\cdot\text{L}^{-1}$):

$$t_{1/2} = \frac{0.69}{k_{ox,P} \cdot [ox]} \Rightarrow k_{ox,P} = \frac{0.69}{t_{1/2} \cdot [ox]} \quad (26.1)$$

$t_{1/2}$ is the half-life of micropollutant P, $[ox]$ is the concentration of the oxidant, $k_{ox,P}$ is the second-order rate constant for the reaction of the oxidant with a micropollutant. For a half-life $t_{1/2} = 120$ s, $k_{ox,P}$ is in the range of 250 to $500 \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$.

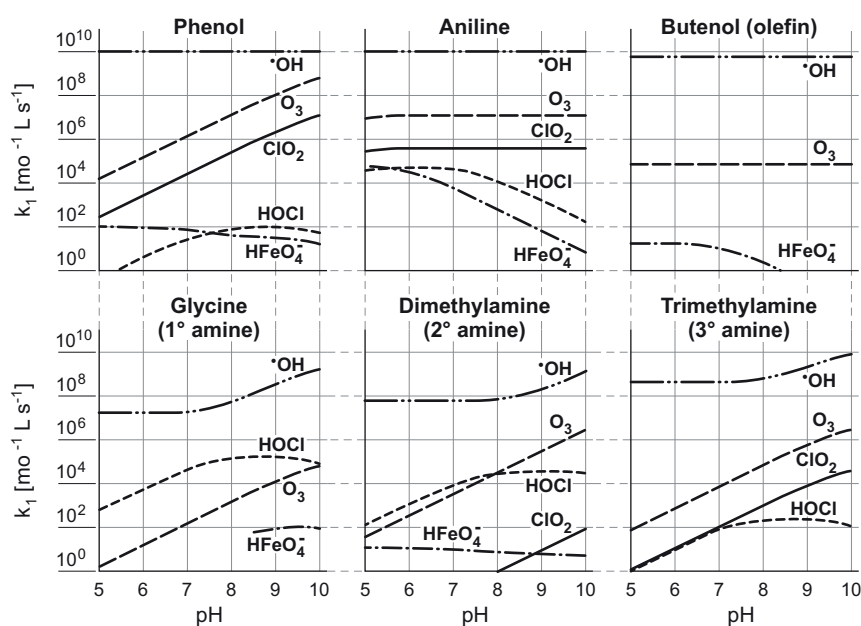


Figure 26.1 Second-order rate constants k for the reaction of oxidants ($\cdot\text{OH}$, O_3 , ClO_2 , HFeO_4^- , HOCl) with selected functional groups as a function of pH.

Source: Lee and von Gunten (2010) with permission.

To achieve significant transformation of a micropollutant at an oxidant concentration of about $1 \text{ mg} \cdot \text{L}^{-1}$, the second-order rate constants should therefore be $>250 \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$. If oxidants have short lifetimes, as is typical for loaded water matrices such as source-separated urine or greywater, the $k_{ox,P}$ -values need to be even higher to achieve significant transformation. Figure 26.1 shows that activated aromatic compounds, amines and olefins are generally reactive to ozone, activated aromatic compounds and tertiary amines to chlorine dioxide, anilines, ammonia, primary and secondary amines to chlorine, and aniline, olefins, primary and secondary amines to ferrate. Ozone has the widest range of applications for micropollutant oxidation in water treatment and ozone-based processes are consequently widely used. The rate constants for ozone and chlorine dioxide cover a range of more than ten orders of magnitude, and over about seven orders of magnitude for chlorine. The rate constants for ferrate (VI)

cover a range of only four orders of magnitude. So although the latter's reaction rate constants are relatively low, it is a much less selective oxidant and hence attractive for water treatment because it can treat a large variety of organic chemicals. Ferrate was also shown to be an excellent coagulant for precipitating phosphate from wastewater (Lee *et al.* 2009). However, since it is not produced industrially in high volumes, it is currently too expensive for application in municipal wastewater treatment.

The main oxidants in advanced oxidation processes (AOPs), namely $\cdot\text{OH}$ radicals, have to be produced in situ by various processes such as $\text{O}_3/\text{H}_2\text{O}_2$, UV/O_3 and $\text{UV}/\text{H}_2\text{O}_2$, because their lifetimes are in the μs range in water. AOPs will not be discussed in detail here but a good compilation can be found in von Sonntag (2008). As shown for drinking water and wastewater, the $\text{O}_3/\text{H}_2\text{O}_2$ process is typically more than 5–20 times more energy-efficient than the $\text{UV}/\text{H}_2\text{O}_2$ process (Katsoyiannis *et al.* 2011). Nevertheless, the latter has the advantage that no bromate and only limited concentrations of bromo-organic compounds are formed (von Gunten and Oliveras 1998). Therefore, despite the higher energy demand of the $\text{UV}/\text{H}_2\text{O}_2$ process compared to $\text{O}_3/\text{H}_2\text{O}_2$, it is better suited for water matrices containing higher bromide concentrations (e.g., urine). $\cdot\text{OH}$ radicals react with most organic compounds with rate constants in the range of 10^9 – $10^{10} \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$, which is almost diffusion-controlled. This allows the oxidation of a wide spectrum of micropollutants. Although these rate constants are extremely high compared with other oxidants, the transformation rate of micropollutants in AOPs is typically lower for a similar oxidant dose (in this case $\cdot\text{OH}$). This is because $\cdot\text{OH}$ are consumed very quickly by the water matrix components, leading to low $\cdot\text{OH}$ exposures (Lee and von Gunten 2010).

The degree of oxidation is related to the second-order reaction rate constant and the oxidant exposure as follows:

$$-\frac{d[P]}{dt} = k_{ox,P} \cdot [P] \cdot [ox] \Rightarrow \ln \frac{[P]}{[P]_0} = k_{ox,P} \cdot [ox] \cdot t = k_{ox,P} \cdot \int [ox] dt \quad (26.2)$$

P is the microorganism or micropollutant; $k_{ox,P}$ is the second-order rate constant for the reaction of an oxidant with the microorganism/micropollutant P and $\int [ox] dt$ is the oxidant exposure.

Since the extent of disinfection and degree of transformation of micropollutants depends on the product of the rate constants and the oxidant exposures, a high rate constant does not necessarily mean a high efficiency. The achievable oxidant exposure depends greatly on the stability of an oxidant in a given water matrix and decreases in the following sequence: drinking water > municipal wastewater > greywater > source-separated urine. This effect can be partially overcome by increasing the oxidant doses in the more highly charged water

matrix. However, this has its limitations due to by-product formation and the economic feasibility of the processes. Pre-treatment of charged water matrices mainly for the removal of DOC can lead to a higher efficiency of the chemical oxidation step.

Ozone, UV, chlorine, chlorine dioxide and possibly ferrate(VI) are good candidates for the inactivation of microorganisms in all matrices (drinking water, greywater, wastewater and urine) on the basis of their disinfection efficiency. However, pre-treatment (removal of particles, ammonia, DOC etc.) may be necessary to avoid shielding of microorganisms and/or to improve the efficiency of the process. If micropollutants have to be oxidized at the same time, chlorine and chlorine dioxide become less attractive due to their high selectivity (Figure 26.1). Chlorine also leads to substantial formation of undesired halogenated compounds.

26.1.4 Transformation products and their biological activity

In the early studies on oxidation of micropollutants, the disappearance of the target compounds was of sole interest. This can be predicted from the kinetics of the oxidant-micropollutant reaction (see above). Because oxidation under typical water treatment conditions does not lead to full mineralization of the target micropollutants, interest in the transformation products and their biological effects has increased in recent years (von Sonntag and von Gunten 2012). Some recent studies have shown that ozone and $\cdot\text{OH}$ lead to stoichiometric removal of the estrogenicity of estrone, 17β -estradiol, estriol, nonylphenol, bisphenol A (Zhang *et al.* 2008) and 17α -ethinylestradiol (EE2) (Huber *et al.* 2004, Lee *et al.* 2008). Moreover, they also inhibit the activity of 12 antibacterial compounds (Lange *et al.* 2006, Dodd *et al.* 2009) and the biocide triclosan (Suarez *et al.* 2007). In the case of penicillin G and cephalexin, the primary ozone attack failed to remove the antibacterial activity completely, but the secondary attack succeeded in doing so (Dodd *et al.* 2009). So far there is only one known case of the formation of a more toxic compound from the oxidative transformation of a micropollutant: during ozonation, *N,N*-dimethylsulfamide, a non-toxic metabolite of the fungicide tolylfluanide, is transformed into *N*-nitrosodimethylamine, a potent mutagenic agent (Schmidt and Brauch 2008, von Gunten *et al.* 2010).

Numerous *in vitro* and *in vivo* studies were carried out to investigate the effect of ozonation on various biological endpoints (Cao *et al.* 2009, Escher *et al.* 2009, Petala *et al.* 2009, Macova *et al.* 2010, Reungoat *et al.* 2010, Stalter *et al.* 2010, Stalter *et al.* 2010). *In vivo* tests showed some adverse effects after ozonation/AOPs. These were mostly due to the oxidation products formed from the reaction with matrix components such as the dissolved organic material. They could typically be removed by biological filtration (Stalter *et al.* 2010).

26.2 APPLICATION OF OXIDATION PROCESSES TO SOURCE-SEPARATED WASTE STREAMS

26.2.1 General considerations

Oxidation/disinfection processes can be applied in households on the drinking water side as point-of-entry or point-of-use treatments and for treating source-separated urine, greywater and wastewater (Dodd *et al.* 2008). Oxidative treatment of faeces or blackwater does not make much sense. Both disinfection and oxidation of micropollutants can be achieved. Once the wastewater is collected, oxidation may be carried out as post-treatment of secondary wastewater effluent.

26.2.2 Efficiency of oxidation/disinfection processes: role of water matrix components

The water quality in each compartment is decisive for the efficiency of oxidation/disinfection processes. The main parameter is the content of the organic matter, typically expressed as the DOC concentration. However, parameters such as pH, alkalinity, ammonium/ammonia, nitrite and bromide may also play an important role, depending on the chemical oxidant applied. The chloride concentration is not important because none of the oxidants can oxidize chloride to a significant extent under circumneutral pH conditions. Table 26.2 gives an overview of the water quality parameters of hydrolyzed urine, greywater, wastewater and the water resources used for drinking water production.

Table 26.2 Water quality parameters relevant for oxidation processes.

Water type	pH	DOC [–] [mg·L ⁻¹]	Alkalinity [mmol·L ⁻¹]	Tot.ammonia [mgN·L ⁻¹]	Nitrite [mg·L ⁻¹]	Bromide [µg·L ⁻¹]
Hydrol. urine	9	~2,000	~300	~4,000	<d.l. ⁽²⁾	1,200 7,700
Greywater	7 8	~35	similar to surf. water	1 17	<d.l. ⁽²⁾	similar to surface water
Wastewater effluent	7 8	~5 20	2 4	~20	<1	30 1,000
Surface water ⁽¹⁾	7 8	1 20	1 2	<0.005 to >1	low ⁽¹⁾	10 1,000
Groundwater ⁽¹⁾	7 8	<1 20	1 5	<0.005 to >1	low ⁽¹⁾	10 1,000

⁽¹⁾ Nitrite levels in waters used for drinking water production are typically very low by the time oxidants are used for controlled disinfection and oxidation;

⁽²⁾ d.l. detection limit.

Sources: Udert *et al.* (2003), Pronk *et al.* (2006), Dodd *et al.* (2008).

It can be seen that the DOC decreases dramatically from hydrolyzed urine to wastewater effluent. This is caused partially by dilution and partially by the DOC removal during activated sludge treatment. The DOC concentration in surface waters and groundwaters is typically dominated by other natural processes (soil weathering, algal growth, etc.) and is even lower. Because the oxidant demand is closely related to the DOM concentration, it is evident that waste streams with high concentrations of particulate organic substances, such as faeces, brownwater or blackwater, are not well suited for chemical oxidation treatment. However, it has to be considered that human urine represents <1% of the total flow of municipal wastewater and contains a disproportionately high fraction of many biologically active compounds (Larsen and Gujer 1996, Lienert *et al.* 2007). Therefore, it might still be a feasible option to eliminate the micropollutants from source-separated urine.

Chlorine is a special case in terms of its reactivity, because unlike the other chemical oxidants it reacts quickly with ammonia to form chloramines (Wolfe *et al.* 1984). Since these are significantly less efficient disinfectants (about 500 times less than HOCl), waters with high ammonia concentrations (e.g., hydrolyzed urine, non-nitrified wastewater) are only properly disinfected at high chlorine doses above the breakpoint (Wolfe *et al.* 1984). However, very high chlorine doses may be required, so that upstream ammonia removal (biological or physical, see Udert and Jenni and Siegrist *et al.* 2013) before chlorination may be a better solution to this problem. In the following, the effect of the DOC concentration on the oxidation efficiency is illustrated for ozonation because sufficient data are available to make such a comparison for this oxidant. Similar considerations apply to other oxidants.

26.2.3 Efficiency of oxidation/disinfection with ozone: the role of DOC concentration

Table 26.3 shows the required ozone doses for 90% elimination of two selected micropollutants during ozonation of hydrolyzed urine, electrodialed urine diluate, wastewater effluent and two surface waters. Data are given for 17 α -ethinylestradiol (EE2), a synthetic steroid estrogen, and ibuprofen (IP), an antiphlogistic. This exercise can also be done for other micropollutants as discussed by Kümmerer (2013). While EE2 reacts quickly with ozone and $\cdot\text{OH}$ (pH 7: $k_{\text{O}_3} \approx 3 \times 10^6 \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$, $k_{\text{OH}} = 9.8 \times 10^9 \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$), IP reacts mostly with $\cdot\text{OH}$, which are formed as secondary reactions from ozone decomposition (pH 7: $k_{\text{O}_3} \approx 9.6 \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$, $k_{\text{OH}} = 7.4 \times 10^9 \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$) (Huber *et al.* 2003).

The efficiency of this process increases with decreasing DOC concentrations. This is mainly due to the competition between DOM and micropollutants for the chemical oxidant. For 90% elimination of EE2, the ozone dose varies over more

than three orders of magnitude, reflecting the difference in DOC concentration between hydrolyzed urine and the pre-treated river water used for drinking water. While this difference seems quite large, it has to be considered that the volumes of urine and wastewater differ by at least two orders of magnitude. This is reflected by the ozone dose normalized to the DOC concentration, which results in similar values for hydrolyzed urine and wastewater (within a factor of 2) for compounds with high ozone reactivity and ozone resistance. Table 26.3 also shows the absolute amount of ozone in $\text{g}\cdot\text{pers}^{-1}\cdot\text{d}^{-1}$ for the case of ibuprofen (IP). These data show that the treatment of wastewater effluent is about three times more efficient than for hydrolyzed urine, although the values become more comparable when the urine is pre-treated (e.g., by electrodialysis). Urine treatment at household level consequently seems feasible with pre-treatment, but as mentioned above, only part of the micropollutant load in the wastewater will be treated at this level. Furthermore, Table 26.3 illustrates that for compounds reacting quickly with ozone, the ozone doses involved in drinking water treatment are again significantly lower. A similar approach can be taken for disinfection processes. The ozone doses would probably lie between the values for EE2 and IP elimination.

Table 26.3 Ozone doses required ($\text{mg}\cdot\text{L}^{-1}$) for 90% elimination of 17α -ethinylestradiol (EE2) and ibuprofen (IP) in various water.

Water type	EE2		IP		
	O ₃ dose [$\text{mg}\cdot\text{L}^{-1}$]	O ₃ /DOC [$\text{g}\cdot\text{g}^{-1}$]	O ₃ dose [$\text{mg}\cdot\text{L}^{-1}$]	O ₃ /DOC [$\text{g}\cdot\text{g}^{-1}$]	O ₃ per pers. [$\text{g}\cdot\text{p}^{-1}\cdot\text{d}^{-1}$]
Hydrolyzed urine	~500	0.25	1000	0.5	1.3
Urine diluate (electrodialysis) ⁽²⁾	~150	0.375	~600	1.5	0.78
Wastewater 1 (7.7 $\text{mgDOC}\cdot\text{L}^{-1}$)	>1	>0.13	n.d. ⁽¹⁾	n.d. ⁽¹⁾	n.d. ⁽¹⁾
Wastewater 2 (5.0 $\text{mgDOC}\cdot\text{L}^{-1}$)	0.5	0.1	~4	0.8	0.4
Lake water (3.0 $\text{mgDOC}\cdot\text{L}^{-1}$)	0.1	0.03	n.d. ⁽¹⁾	n.d. ⁽¹⁾	n.d. ⁽¹⁾
River water (1.0 $\text{mgDOC}\cdot\text{L}^{-1}$)	<0.1	<0.08	>2	>2	0.28

⁽¹⁾n.d.: not determined;

⁽²⁾contained some methanol from dosing of micropollutants.

Sources: Huber *et al.* (2003), Huber *et al.* (2005), Dodd *et al.* (2008), Lee and von Gunten (2010).

26.2.4 Application of oxidation/disinfection processes to source-separated urine

On the basis of the data shown in Table 26.3 and further discussions (Dodd *et al.* 2008), it can be concluded that ozonation of source-separated urine to remove micropollutants reacting quickly with ozone is significantly more energy-intensive than the same process for wastewater, whereas the difference is smaller for ozone-resistant compounds. If the treatment of source-separated urine is combined with nutrient recovery (N, P), the overall energy requirement even becomes favourable for urine treatment (Dodd *et al.* 2008). However, micropollutants from sources other than urine cannot be treated by this approach. Disinfection of source-separated urine may be achieved for ozone doses similar to those required for IP oxidation. Significant improvement can be achieved by pre-treatment of urine, for example, by electrodialysis. For urine disinfection by chlorine, the ammonia level has to be reduced significantly before this oxidant can be considered (see above). No data is available for urine disinfection with chlorine dioxide or ferrate(VI).

26.2.5 Application of oxidation/disinfection processes to greywater

There is not much if any information on applying oxidation processes to greywater. The main purpose of these processes is disinfection and decoloration. Oxidation of undesired micropollutants can also be an issue. On the basis of the water matrix composition of greywater shown in Table 26.2 and the ozone doses shown in Table 26.3, ozone doses of the order of 3.5–35 mg·L⁻¹ can be expected for the inactivation of bacteria (Zimmermann *et al.* 2011). Decoloration is an important factor with regard to aesthetics, especially if greywater is reused for toilet flushing, for instance. An 80% removal of true colour (455 nm) was achieved for two wastewaters for an O₃/DOC (w/w) ratio of 0.6–0.8 (Wert *et al.* 2009). This is in a similar range of ozone doses as for disinfection and transformation of ozone-resistant micropollutants. So if greywater is optimized for colour removal, efficient inactivation of its bacteria can be expected. Since greywater has a significantly lower DOC concentration than urine, other disinfectants such as chlorine or chlorine dioxide may also be feasible for inactivating microorganisms. Disinfection may require pre-treatment for particle removal to avoid reduced efficiency due to the association of microorganisms with particles.

26.2.6 Application of oxidation/disinfection processes to effluents of biological reactors

There is a wealth of information on ozone application to secondary wastewater effluents (von Sonntag and von Gunten 2012). These results are well transferrable to biological reactors. It has been shown in laboratory tests (ferrate, ozone; Huber

et al. 2003, Lee *et al.* 2009, Wert *et al.* 2009, Lee and von Gunten 2010), at pilot-scale (ozone; Ternes *et al.* 2003, Huber *et al.* 2005) and in full-scale operation (ozone; Hollender *et al.* 2009, Reungoat *et al.* 2010, Zimmermann *et al.* 2011) that micropollutants can be efficiently removed from secondary wastewater effluents by oxidative processes with ozone (ferrate). Furthermore, a high degree of inactivation of microorganisms can be achieved with the same ozone doses (Zimmermann *et al.* 2011). Compared to household treatment, this also allows micropollutants derived from sources other than households to be oxidized (e.g., hospitals, industries, etc.).

26.3 CONCLUSIONS

Several chemical oxidants are available for oxidative water treatment in the urban water cycle. Depending on the location of the oxidation process, micropollutants from different sources can be treated. Typically, pre-treatment steps are necessary (particle removal, removal of DOC, ammonia and nitrite) to increase the lifetime of the oxidants and the overall efficiency of the processes. Ozone, OH radicals and possibly ferrate are the oxidants with the best overall performance for the elimination of micropollutants on the basis of their reaction kinetics, oxidant stability and by-product formation. It has been shown that ozonation can be used for disinfection and removal of micropollutants from source-separated urine, greywater, and for wastewater effluent polishing. Chlorine is not well suited for micropollutant removal, but can be used for disinfection. Pre-treatment for ammonia removal is then necessary to avoid the formation of less efficient chloramines.

Micropollutants are typically not mineralized in oxidative water treatment and the toxicity of the transformation products is a major concern. *In vivo* tests have shown that ozonation leads to reduced toxicity, and the same applies to *in vitro* test systems in combination with biological filtration or other separation steps. Only a few cases of the formation of more toxic products are known so far. More information is needed to fully assess this issue.

Oxidation/disinfection by-products are formed from the reaction of chemical oxidants with water matrix components. Bromide plays an important role here, since it can be oxidized to bromine by chlorine and ozone. This results in the formation of bromo-organic compounds during chlorination, whereas both bromo-organic compounds and bromate can be formed during ozonation. Higher concentrations of these toxicologically relevant compounds can be expected to occur with increasing bromide levels.

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