

Generation of Oxidative Radicals by Advanced Oxidation Processes (AOPs) in Wastewater Treatment: A Mechanistic, Environmental and Economic Review

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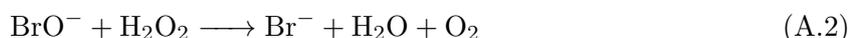
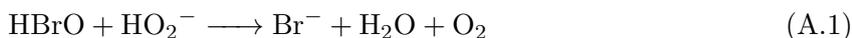
Supplementary Material

Appendix A Additional information on hydroxyl radicals

A.1 Bromate formation in ozonation

Bromate (BrO_3^-) has been extensively studied, especially in ozonation applied to drinking water treatment; since the early 1990s, it was recognised as a potential carcinogen by the International Agency for the Research on Cancer (IARC) (Pinkernell and von Gunten, 2001). Bromide (Br^-) is typically found in natural water bodies at concentrations ranging from 4 to 1000 $\mu\text{g L}^{-1}$, with 50 $\mu\text{g L}^{-1}$ being the threshold at which reactions with O_3 are triggered to form BrO_3^- (Fischbacher et al., 2015; von Gunten, 2003b). Figure A.1 depicts the complexity of this mechanism, since Br^- not only reacts with O_3 but also with $\bullet\text{OH}$ radicals, thereby forming other intermediates such as HBrO and BrO^- (Fischbacher et al., 2015; von Gunten, 2003b).

When introducing H_2O_2 in a system containing O_3 and Br^- , the impact of $\bullet\text{OH}$ radicals on BrO_3^- formation becomes negligible, as the intermediately formed HBrO/BrO^- compounds are not oxidised further towards BrO_3^- but are reduced back to Br^- at fast reaction rates (Eqs. A.1 and A.2) with the species involved in the dissociation of H_2O_2 (Eq. A.3) (Fischbacher et al., 2015; von Gunten and Oliveras, 1997).



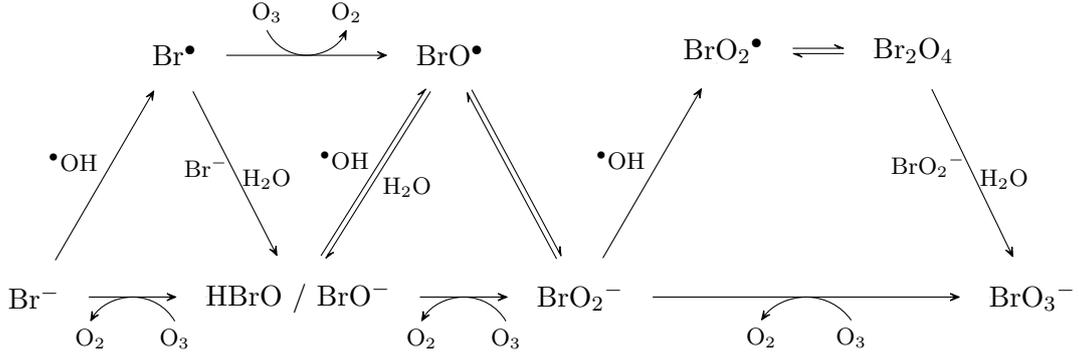
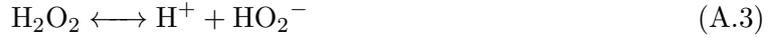


Figure A.1: Conventional pathway for bromate formation in the reaction of ozone with bromide, adapted from Fischbacher et al. (2015) (Fischbacher et al., 2015).



A.2 Halogenated byproduct formation in electrochemical AOPs

In an electrochemical cell, ClO_3^- and BrO_3^- can be generated either through a chemical or electrochemical route, as has been observed both forming after interaction with MMOs and on the surface of BDD electrodes (Jung et al., 2010; Polcaro et al., 2008). On the other hand, ClO_4^- is purely formed in electrochemical processes, especially with highly oxidising BDD anodes (Bergmann and Rollin, 2007). The occurrence of these byproducts has been observed over a wide range of applied current densities, ranging from 50 to 300 A m^{-2} . By lowering the current density, this issue would be mitigated at the expense of lower degradation performance, since the production of radicals would be reduced accordingly. Alternatively, combining electrochemical oxidation with a post-treatment such as membrane filtration, activated carbon sorption or microbial reduction has been explored, showing a strong dependency on the specific conditions of each case (e.g., presence of organic matter, NH_3 , inorganic and organic ions). In terms of material selection, electrodes such as BDD and Ti/SnO_2 are more suitable for the treatment of wastewater streams with high concentrations of fluorinated surfactants, whereas for halide-containing influents, it is best to couple the electrooxidation with activated carbon electrodes to minimise the production of toxic byproducts (Comninellis and Chen, 2010; Radjenovic and Sedlak, 2015).

Appendix B Additional information on iodine radicals

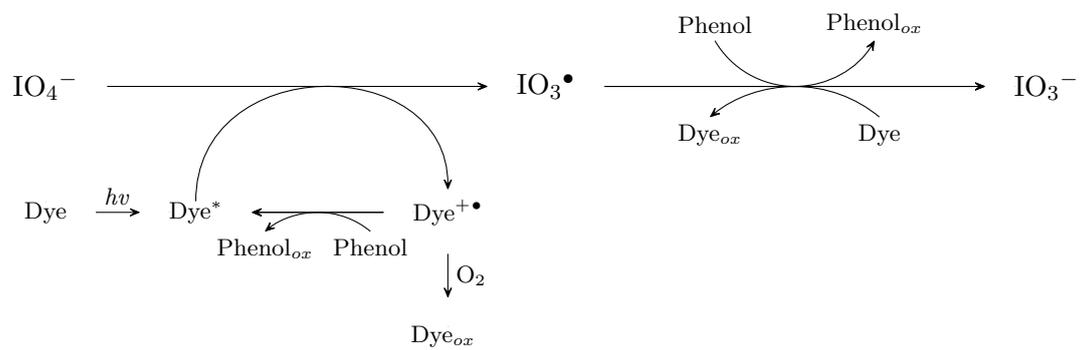


Figure B.1: The mechanism of the dye-sensitized activation of IO_4^- for the treatment of dyes, as an organic model compound, adapted from Yun et al. (2017) (Yun et al., 2017).

Table B.1: Degradation of organic compounds using various periodate activation systems.

Wastewater Matrix	Target Pollutant	Activation Method	Iodine Load	Pollution Load	Removal	Time	Remarks	Reference
Synthetic	Light green SF yellowish (LGSFY)	IO_3^-/UV	10 mM	10 mg/L	98%	10 min	- IO_2^\bullet and IO_3^\bullet played the most significant role in the decomposition	(Haddad et al., 2019)
			10 mM	20 mg/L	85%	10 min	- Compounds such as Cl^- , NO_3^- and humic acid did not affect the efficiency even at high dosage levels (up to 0.1 M)	
			0 mM	10 mg/L	36%	10 min	- SO_4^- ions significantly reduced efficiency	
			0 mM	20 mg/L	18%	10 min		
Synthetic	Phenol	IO_3^-/US	3 mM	25 mg/L	91%	90 min	- Acidic pH favored phenol degradation - CaCl_2 did not affect the efficiency	(Seid-Mohamadi et al., 2015)
Synthetic	Perfluorooctanoic acid (PFOA)	IO_3^-/US	45 mM	70.4 mg/L	95.7%	120 min	- Lower pH favored the degradation of organic compounds - Any increase in concentration of dissolved oxygen favored the generation of IO_4^\bullet and consumption of IO_3^\bullet	(Lee et al., 2016)
Synthetic	Acid Orange 7 (AO7)	Iodine-doped granular activated carbon	1 g/L I-GAC	17.5 mg/L	95%	80 min	- Formation of I_3^- and I_5^- when the catalyst is introduced into the solution promoted the interaction between I-GAC and IO_4^- , and consequently, increased the generation of IO_3^-	(Li et al., 2017)
Synthetic	Phenol	IO_4^-/MW	200 mM	100 mg/L	98.8%	30 min	- Alkaline pH promoted phenol degradation	(Mohammadi et al., 2016)
Synthetic	Furfuryl alcohol (FFA)	$\text{IO}_4^-/\text{Freezing}$	0.1 mM	2 mg/L	100%	60 min	- Efficiency increased considerably with increasing iodine concentration and decreasing pH and/or freezing temperature	(Choi et al., 2018)
Synthetic	Basic Yellow 28	Catalytic (1 g/L of TiO_2)	5 mM	100 mg/L	68%	180 min	- 1 g/L of TiO_2 at pH 3.0 was considered an efficient method to achieve a complete degradation and a considerable mineralization of the pollutants	(Gözmen et al., 2009)
	Basic Red 46			100 mg/L	76%	180 min		
	BY28 and BR46			50 mg/L	75%	180 min		
Synthetic	Phenol	ZVI (3 mM)/US	2 mM	50 mg/L	100%	90 min	- Optimum phenol degradation was achieved under acidic conditions (pH=3) - The efficiency of the methods studied was reported as $\text{US} < \text{IO}_4^- < \text{IO}_4^-/\text{ZVI} < \text{IO}_4^-/\text{US} < \text{ZVI}/\text{I}_4^-/\text{US}$	(Seid-Mohammadi et al., 2019)

Appendix C Alternative radicals

C.1 Reactive Nitrogen Species (RNS)

Reactive nitrogen species (RNS) have emerged mainly under UV oxidation systems, for instance, with chloramine (NH_2Cl) as a precursor, which is a compound generated during chlorination in conventional wastewater treatment. Figure C.1 presents the mechanism of the UV/ NH_2Cl process. Briefly, Cl^\bullet and $\bullet\text{NH}_2$ radicals are produced by the photolysis of NH_2Cl . Subsequently, Cl^\bullet forms secondary radicals, such as $\bullet\text{OH}$ and $\text{Cl}_2^{\bullet-}$, involved in the degradation of organic compounds. On the other hand, $\bullet\text{NH}_2$ can react with oxygen present in the medium to generate $\text{NH}_2\text{OO}^\bullet$, which can be transformed into $\bullet\text{NO}$ to react with $\bullet\text{OH}$ or O_2 , resulting in the further formation of nitrite (NO_2^-). NO_2^\bullet is rapidly formed by the reaction of NO_2^- with $\bullet\text{OH}$ or $\text{Cl}_2^{\bullet-}$ (Wu et al., 2019).

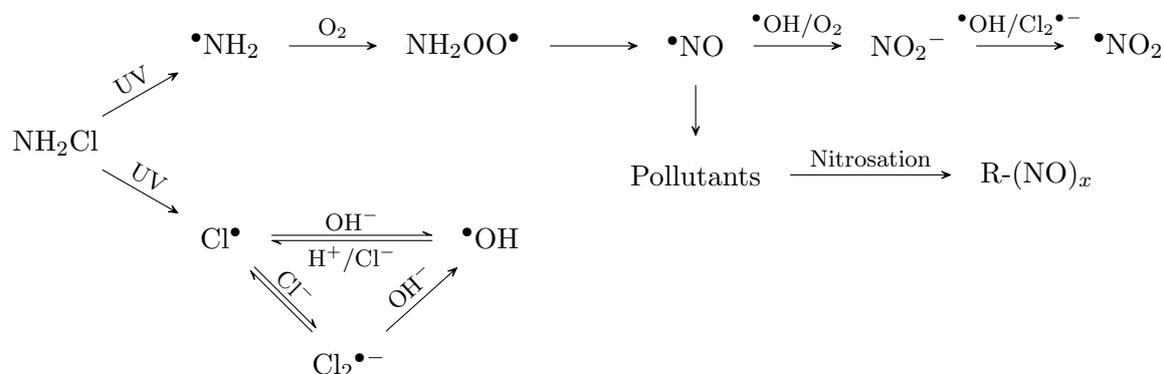


Figure C.1: Reaction mechanisms involved in the UV photolysis of NH_2Cl , adapted from Wu et al. (2019) (Wu et al., 2019).

There are a few studies published on the application of UV/RNS for the treatment of industrial effluents. For instance, the effective degradation of organic micropollutants, including triclosan, carbamazepine, sulfamethoxazole, estradiol (E2), and ethinylestradiol (EE2), under this system was reported by Wu et al. (2019) (Wu et al., 2019). They indicated that the degradation reactions involving RNS were selective for organic molecules with electron-rich moieties. As an example, $\bullet\text{NO}_2$ was able to oxidise electron-rich moieties with moderate rate constants, such as phenolic groups, anilines, phenothiazines, and thiols. Hence, the phenolic moiety on E2 and EE2 played an important role in the degradation of these compounds using the UV/ NH_2Cl process. However, it has been reported that $\bullet\text{NH}_2$ is significantly less active than $\bullet\text{Cl}$ and its daughter radicals, such as $\text{Cl}_2^{\bullet-}$ and $\bullet\text{OH}$ (Zhang et al., 2019).

There are also some other types of RNS that can be derived from nitrate (NO_3^-). Recent studies have indicated that UV irradiation of wastewater containing this ion can result in the formation of oxidative compounds, such as ONOO^- , NO_2^\bullet and $\bullet\text{OH}$ (Huang et al., 2018). Figure C.2 represents the possible reactions involving NO_3^- activation at 254 nm under mild alkaline conditions (i.e., pH 7-9) in the presence of oxygen (Huang et al., 2018). Bu et al. (2020) evaluated the UV/RNS-driven degradation of atrazine compared to that by UV photolysis and $\bullet\text{OH}$ radicals (Bu et al., 2020). They indicated that the reaction of nitrogen species with hydroxyatrazine (with electron-rich moieties) was the main route for the degradation of atrazine.

nm), the quantum yields of $\bullet\text{OH}$ generated from NO_3^- photolysis were higher than those under greater wavelengths (i.e., 300 nm): approximately 9% and 1%, respectively (Bu et al., 2020).



Near-neutral pH conditions (i.e., pH 6–8) have been reported as optimal for the degradation of recalcitrant organic pollutants using RNS (Zhou et al., 2020a). In addition to $\text{NO}_2\bullet$ (+1.03 V standard redox potential) and $\text{NO}\bullet$ (+0.39 V standard redox potential) being considered of moderate strength, they are also very efficient as nitrating and nitrosating agents (Zhou et al., 2020a).

Finally, special consideration should be given to the potential for increased effluent toxicity after treatment. In particular, in the presence of NO_2^- ions, nitro-products may be unexpectedly formed, which are often more toxic than the parent pollutant (Rayaroth et al., 2022). Rayaroth et al. (2022) reviewed this recurring issue across multiple AOPs, and highlighted ozonation and electrochemical treatments as solutions to minimise this risk (Rayaroth et al., 2022).

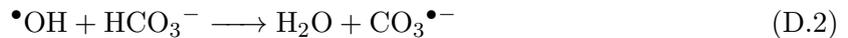
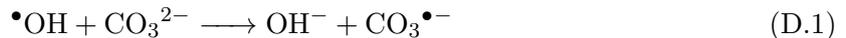
C.2 Carbonate radicals

Carbonate radicals ($\text{CO}_3\bullet^-$, +1.78 V standard redox potential) are also possible oxidation agents for the degradation of recalcitrant organic compounds (Canonica et al., 2005). They normally originate from the oxidation of carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-), which are commonly present in water and are scavengers of other radicals, such as $\bullet\text{OH}$, $\text{SO}_4\bullet^-$ and $\text{Cl}\bullet$ (Zhang et al., 2015). Compared to other radical species, $\text{CO}_3\bullet^-$ radicals are more selective, although they lead to generally slower reaction kinetics. $\text{CO}_3\bullet^-$ is an electrophilic species that tends to react with electron-rich compounds through mechanisms such as electron transfer or hydrogen abstraction (Liu et al., 2016). Examples of such organic compounds are phenol and its derivatives (10^6 – 10^8 $\text{M}^{-1}\text{s}^{-1}$), nitrogen (10^7 – 10^9 $\text{M}^{-1}\text{s}^{-1}$) and sulphur (10^6 – 10^7 $\text{M}^{-1}\text{s}^{-1}$) containing compounds, as well as indole heterocyclic nucleus containing compounds ($>10^8$ $\text{M}^{-1}\text{s}^{-1}$) (Liu et al., 2015). The effectiveness of $\text{CO}_3\bullet^-$ for the degradation of naproxen ($\text{C}_{14}\text{H}_{14}\text{O}_3$) has also been investigated in combination with different oxidation systems, such as UV/ H_2O_2 , UV/persulfate, UV/ Cl_2 and UV/ NH_2Cl (Wu et al., 2019; Zhou et al., 2020b).

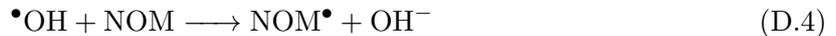
Appendix D Scavenging effects

D.1 Hydroxyl radical scavengers

Carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) ions react directly with $\bullet\text{OH}$ to form carbonate radicals ($\text{CO}_3^{\bullet-}$) under alkaline conditions (Eqs. D.1 and D.2) (von Gunten, 2003a). These reactions occur at fast reaction rates (up to $4.2 \cdot 10^8 \text{ M}^{-1}\text{s}^{-1}$ and $10 \cdot 10^6 \text{ M}^{-1}\text{s}^{-1}$ for CO_3^{2-} and HCO_3^- , respectively) and can therefore inhibit indirect oxidation pathways (Giannakis et al., 2021; Yan et al., 2019). It is estimated that CO_3^{2-} can inhibit up to 30% of the available $\bullet\text{OH}$ radicals (Devi et al., 2016).



Natural organic matter (NOM) is also a known scavenger of $\bullet\text{OH}$, which partially leads to carbon-centred radicals (NOM^\bullet) (Eqs. D.3 and D.4) that react with O_2 to further generate superoxide radicals (O_2^\bullet) (Eq. D.5) (von Gunten, 2003a). These radicals can intervene in other reaction mechanisms, such as ozonation. Nonetheless, O_2^\bullet radicals are known to be a better reducing agent than an oxidising one (Kehrer et al., 2010).



Finally, the potential scavenging effects of chloride ions (Cl^-) have been investigated, and divergent conclusions can be found in the literature. Some studies have reported an enhancement in the degradation of pollutants (Yang et al., 2010), while others have observed negative impacts (Chan and Chu, 2009) and even thresholds in the concentration of Cl^- ions that triggered either enhancing or inhibitory effects (Liang et al., 2006). Therefore, the exact role of Cl^- ions is not yet fully understood (Devi et al., 2016). In addition, several studies have reported the formation of refractory chlorinated byproducts of high toxicity (Chan and Chu, 2009; Yuan et al., 2011). When involved in the scavenging of $\bullet\text{OH}$ radicals, Cl^- leads to the formation of intermediate chlorine radicals (Cl^\bullet) (Eq. D.6), which afterwards can also react and generate other chlorine-based radicals (i.e., $\text{Cl}_2^{\bullet-}$, $\text{ClOH}^{\bullet-}$) and $\bullet\text{OH}$ radicals in solution (Eqs. D.7 - D.12) (Devi et al., 2016; Monteagudo et al., 2015; Yuan et al., 2011).



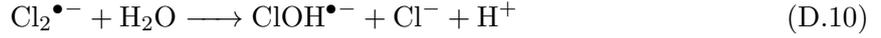


Table D.1: Reaction rates ($\text{M}^{-1}\text{s}^{-1}$) of $\bullet\text{OH}$ and $\text{HO}_2^\bullet/\text{O}_2^{\bullet-}$ radicals with scavenging compounds in aqueous media (Giannakis et al., 2021; Wang and Wang, 2020).

Scavenger	Reaction rate with $\bullet\text{OH}$	Reaction rate with $\text{HO}_2^\bullet/\text{O}_2^{\bullet-}$
CO_3^{2-}	3.2 - 4.2·10 ⁸	<4·10 ⁻²
HCO_3^-	8.5 - 10·10 ⁶	NA
Cl^-	3 - 4.3·10 ⁹	<1.4·10 ²
Br^-	1.1 - 1.9·10 ¹⁰	NA
NO_3^-	NA	NA
NO_2^-	2.5 - 14·10 ⁹	5 - 360·10 ⁶
SO_4^{2-}	NA	NA
$\text{HPO}_4^{2-}/\text{H}_2\text{PO}_4^-$	2 - 15·10 ⁴	3.5·10 ⁶
NOM	1.39·10 ⁸	NA

D.2 Sulfate radical scavengers

Despite the lower self-scavenging effect of $\text{SO}_4^{\bullet-}$ radicals, carbonates, bicarbonates and chlorides have shown scavenging effects on them (Devi et al., 2016). Both carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) ions can scavenge $\text{SO}_4^{\bullet-}$ and lead to the formation of $\text{CO}_3^{\bullet-}$ (Eqs. D.13 and D.14), which has a lower redox potential (i.e., +1.63 V) (Bennedsen et al., 2012). Since $\text{CO}_3^{\bullet-}$ radicals are formed under alkaline conditions; the higher the pH of the solution is, the more significant the scavenging effects on the overall efficiency via SR-AOPs (Asghar et al., 2015). Some studies have reported an enhancement in the degradation of pollutants in the presence of $\text{CO}_3^{\bullet-}$ (Grebel et al., 2010; Yang et al., 2010), although the general observation is that $\text{CO}_3^{\bullet-}$ radicals hinder the efficiency because they are highly selective and participate primarily in scavenging reactions (Devi et al., 2016). Regarding chloride ions (Cl^-), mixed conclusions have been reported, as previously discussed in the case of $\bullet\text{OH}$ radicals (Devi et al., 2016). Nonetheless, the reaction involving the scavenging of $\text{SO}_4^{\bullet-}$ has been reported to lead towards the formation

of Cl^\bullet radicals and SO_4^{2-} ions (Eq. D.15), from which the radicals can further react and increase the concentration of $\bullet\text{OH}$ in solution (Eqs. D.7 - D.12) (Devi et al., 2016; Fang et al., 2012; Yuan et al., 2011).

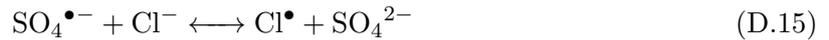
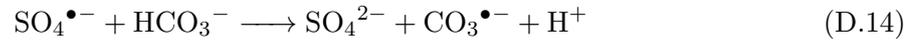


Table D.2: Reaction rates ($\text{M}^{-1}\text{s}^{-1}$) of $\text{SO}_4^{\bullet-}$ radicals with scavenging compounds in aqueous media (Giannakis et al., 2021; Wang and Wang, 2020).

Scavenger	Reaction rate with $\text{SO}_4^{\bullet-}$
CO_3^{2-}	1 - $6.1 \cdot 10^6$
HCO_3^-	1.6 - $9.1 \cdot 10^6$
Cl^-	2.3 - $660 \cdot 10^6$
Br^-	$3.5 \cdot 10^9$
NO_3^-	5 - $210 \cdot 10^4$
NO_2^-	8.8 - $9.8 \cdot 10^8$
SO_4^{2-}	NA
$\text{HPO}_4^{2-}/\text{H}_2\text{PO}_4^-$	1.2 - $16 \cdot 10^6$
NOM	$7.8 \cdot 10^7$

D.3 Chlorine radical scavengers

Table D.3: Reaction rates ($\text{M}^{-1}\text{s}^{-1}$) of $\text{Cl}^\bullet/\text{HClO}^\bullet$ with scavenging compounds in aqueous media (Giannakis et al., 2021).

Scavenger	Reaction rate with $\text{Cl}^\bullet/\text{HClO}^\bullet$
CO_3^{2-}	$5 \cdot 10^8$
HCO_3^-	2.2 - $26 \cdot 10^8$
Cl^-	$6.5 - 21 \cdot 10^9 / 1 \cdot 10^5$
Br^-	$1.2 \cdot 10^{10}$
NO_3^-	0.9 - $1.1 \cdot 10^8$
NO_2^-	4.8 - $5.2 \cdot 10^9$
SO_4^{2-}	1.5 - $2.5 \cdot 10^8$
$\text{HPO}_4^{2-}/\text{H}_2\text{PO}_4^-$	NA
NOM	$1.08 \cdot 10^8$

References

- Asghar, A., Abdul Raman, A. A., and Wan Daud, W. M. A. (2015). Advanced Oxidation Processes for in-situ production of hydrogen peroxide/hydroxyl radical for textile wastewater treatment: A review. *J. Clean. Prod.*, 87:826–838.
- Bennedsen, L. R., Muff, J., and Søgaard, E. G. (2012). Influence of chloride and carbonates on the reactivity of activated persulfate. *Chemosphere*, 86(11):1092–1097.
- Bergmann, M. H. and Rollin, J. (2007). Product and by-product formation in laboratory studies on disinfection electrolysis of water using boron-doped diamond anodes. *Catal. Today*, 124(3):198–203.
- Bu, L., Zhu, N., Li, C., Huang, Y., Kong, M., Duan, X., and Dionysiou, D. D. (2020). Susceptibility of atrazine photo-degradation in the presence of nitrate: Impact of wavelengths and significant role of reactive nitrogen species. *J. Hazard. Mater.*, 388:121760.
- Canonica, S., Kohn, T., Mac, M., Real, F. J., Wirz, J., and von Gunten, U. (2005). Photosensitizer method to determine rate constants for the reaction of carbonate radical with organic compounds. *Environ. Sci. Technol.*, 39(23):9182–9188.
- Chan, K. and Chu, W. (2009). Degradation of atrazine by cobalt-mediated activation of peroxy-monosulfate: Different cobalt counteranions in homogenous process and cobalt oxide catalysts in photolytic heterogeneous process. *Water Res.*, 43(9):2513–2521.
- Choi, Y., Yoon, H.-I., Lee, C., Vetráková, L., Heger, D., Kim, K., and Kim, J. (2018). Activation of periodate by freezing for the degradation of aqueous organic pollutants. *Environ. Sci. Technol.*, 52(9):5378–5385.
- Comninellis, C. and Chen, G. (2010). *Electrochemistry for the Environment*. Springer, New York, 1st edition.
- Devi, P., Das, U., and Dalai, A. K. (2016). In-situ chemical oxidation: Principle and applications of peroxide and persulfate treatments in wastewater systems. *Sci. Total Environ.*, 571:643–657.
- Fang, G.-D., Dionysiou, D. D., Wang, Y., Al-Abed, S. R., and Zhou, D.-M. (2012). Sulfate radical-based degradation of polychlorinated biphenyls: Effects of chloride ion and reaction kinetics. *J. Hazard. Mater.*, 227-228:394–401.
- Fischbacher, A., Löppenberg, K., von Sonntag, C., and Schmidt, T. C. (2015). A new reaction pathway for bromite to bromate in the ozonation of bromide. *Environ. Sci. Technol.*, 49(19):11714–11720.
- Giannakis, S., Lin, K. Y. A., and Ghanbari, F. (2021). A review of the recent advances on the treatment of industrial wastewaters by Sulfate Radical-based Advanced Oxidation Processes (SR-AOPs). *Chem. Eng. J.*, 406:127083.
- Grebel, J. E., Pignatello, J. J., and Mitch, W. A. (2010). Effect of halide ions and carbonates on organic contaminant degradation by hydroxyl radical-based Advanced Oxidation Processes in saline waters. *Environ. Sci. Technol.*, 44(17):6822–6828.

- Gözmen, B., Turabik, M., and Hesenov, A. (2009). Photocatalytic degradation of Basic Red 46 and Basic Yellow 28 in single and binary mixture by UV/TiO₂/periodate system. *J. Hazard. Mater.*, 164(2):1487–1495.
- Haddad, A., Merouani, S., Hannachi, C., Hamdaoui, O., and Hamrouni, B. (2019). Intensification of light green SF yellowish (LGSFY) photodegradation in water by iodate ions: Iodine radicals implication in the degradation process and impacts of water matrix components. *Sci. Total Environ.*, 652:1219–1227.
- Huang, Y., Kong, M., Westerman, D., Xu, E. G., Coffin, S., Cochran, K. H., Liu, Y., Richardson, S. D., Schlenk, D., and Dionysiou, D. D. (2018). Effects of HCO₃⁻ on degradation of toxic contaminants of emerging concern by UV/NO₃⁻. *Environ. Sci. Technol.*, 52(21):12697–12707.
- Jung, Y. J., Baek, K. W., Oh, B. S., and Kang, J.-W. (2010). An investigation of the formation of chlorate and perchlorate during electrolysis using Pt/Ti electrodes: The effects of pH and reactive oxygen species and the results of kinetic studies. *Water Res.*, 44(18):5345–5355.
- Kehrer, J., Robertson, J., and Smith, C. (2010). 1.14 - Free Radicals and Reactive Oxygen Species. In McQueen, C. A., editor, *Comprehensive Toxicology*, pages 277–307. Elsevier, Oxford, 2nd edition.
- Lee, Y.-C., Chen, M.-J., Huang, C.-P., Kuo, J., and Lo, S.-L. (2016). Efficient sonochemical degradation of perfluorooctanoic acid using periodate. *Ultrason. Sonochem.*, 31:499–505.
- Li, X., Liu, X., Lin, C., Qi, C., Zhang, H., and Ma, J. (2017). Enhanced activation of periodate by iodine-doped granular activated carbon for organic contaminant degradation. *Chemosphere*, 181:609–618.
- Liang, C., Wang, Z.-S., and Mohanty, N. (2006). Influences of carbonate and chloride ions on persulfate oxidation of trichloroethylene at 20 °C. *Sci. Total Environ.*, 370(2):271–277.
- Liu, Y., He, X., Duan, X., Fu, Y., and Dionysiou, D. D. (2015). Photochemical degradation of oxytetracycline: Influence of pH and role of carbonate radical. *Chem. Eng. J.*, 276:113–121.
- Liu, Y., He, X., Duan, X., Fu, Y., Fatta-Kassinos, D., and Dionysiou, D. D. (2016). Significant role of UV and carbonate radical on the degradation of oxytetracycline in UV-AOPs: Kinetics and mechanism. *Water Res.*, 95:195–204.
- Mohammadi, A. S., Asgari, G., Poormohammadi, A., and Ahmadian, M. (2016). Oxidation of phenol from synthetic wastewater by a novel Advanced Oxidation Process: Microwave-assisted periodate. *J. Sci. Ind. Res. (India)*, 75(4):267–272.
- Monteagudo, J., Durán, A., González, R., and Expósito, A. (2015). In situ chemical oxidation of carbamazepine solutions using persulfate simultaneously activated by heat energy, UV light, Fe²⁺ ions, and H₂O₂. *Appl. Catal. B-Environ.*, 176-177:120–129.
- Pinkernell, U. and von Gunten, U. (2001). Bromate minimization during ozonation - Mechanistic considerations. *Environ. Sci. Technol.*, 35(12):2525–2531.
- Polcaro, A. M., Vacca, A., Mascia, M., and Ferrara, F. (2008). Product and by-product formation in electrolysis of dilute chloride solutions. *J. Appl. Electrochem.*, 38:979–984.
- Radjenovic, J. and Sedlak, D. L. (2015). Challenges and opportunities for electrochemical processes as next-generation technologies for the treatment of contaminated water. *Environ. Sci. Technol.*, 49(19):11292–11302.

- Rayaroth, M. P., Aravindakumar, C. T., Shah, N. S., and Boczkaj, G. (2022). Advanced oxidation processes (AOPs) based wastewater treatment - unexpected nitration side reactions - a serious environmental issue: A review. *Chem. Eng. J.*, 430:133002.
- Seid-Mohamadi, A., Asgari, G., Shokoohi, R., and Adabi, S. (2015). Phenol disgrace via periodate in integrating by using supersonic radiation. *J. Med. Life*, 8(3):233–237.
- Seid-Mohammadi, A., Asgari, G., Shokoohi, R., Baziar, M., Mirzaei, N., Adabi, S., and Partoei, K. (2019). Degradation of phenol using US/Periodate/nZVI system from aqueous solutions. *Glob. Nest J.*, 21(3):360–357.
- von Gunten, U. (2003a). Ozonation of drinking water: Part I. Oxidation kinetics and product formation. *Water Res.*, 37(7):1443–1467.
- von Gunten, U. (2003b). Ozonation of drinking water: Part II. Disinfection and by-product formation in presence of bromide, iodide or chlorine. *Water Res.*, 37(7):1469–1487.
- von Gunten, U. and Oliveras, Y. (1997). Kinetics of the reaction between hydrogen peroxide and hypobromous acid: Implication on water treatment and natural systems. *Water Res.*, 31(4):900–906.
- Wang, J. and Wang, S. (2020). Reactive species in advanced oxidation processes: Formation, identification and reaction mechanism. *Chem. Eng. J.*, 401:126158.
- Wu, Y., Bu, L., Duan, X., Zhu, S., Kong, M., Zhu, N., and Zhou, S. (2020). Mini review on the roles of nitrate/nitrite in advanced oxidation processes: Radicals transformation and products formation. *J. Clean. Prod.*, 273:123065.
- Wu, Z., Chen, C., Zhu, B.-Z., Huang, C.-H., An, T., Meng, F., and Fang, J. (2019). Reactive Nitrogen Species are also involved in the transformation of micropollutants by the UV/Monochloramine process. *Environ. Sci. Technol.*, 53(19):11142–11152.
- Yan, S., Liu, Y., Lian, L., Li, R., Ma, J., Zhou, H., and Song, W. (2019). Photochemical formation of carbonate radical and its reaction with dissolved organic matters. *Water Res.*, 161:288–296.
- Yang, S., Wang, P., Yang, X., Shan, L., Zhang, W., Shao, X., and Niu, R. (2010). Degradation efficiencies of azo dye Acid Orange 7 by the interaction of heat, UV and anions with common oxidants: Persulfate, peroxymonosulfate and hydrogen peroxide. *J. Hazard. Mater.*, 179(1):552–558.
- Yuan, R., Ramjaun, S. N., Wang, Z., and Liu, J. (2011). Effects of chloride ion on degradation of Acid Orange 7 by sulfate radical-based Advanced Oxidation Process: Implications for formation of chlorinated aromatic compounds. *J. Hazard. Mater.*, 196:173–179.
- Yun, E.-T., Yoo, H.-Y., Kim, W., Kim, H.-E., Kang, G., Lee, H., Lee, S., Park, T., Lee, C., Kim, J.-H., and Lee, J. (2017). Visible-light-induced activation of periodate that mimics dye-sensitization of TiO₂: Simultaneous decolorization of dyes and production of oxidizing radicals. *Appl. Catal. B-Environ.*, 203:475–484.
- Zhang, G., He, X., Nadagouda, M. N., E. O’Shea, K., and Dionysiou, D. D. (2015). The effect of basic pH and carbonate ion on the mechanism of photocatalytic destruction of cylindrospermopsin. *Water Res.*, 73:353–361.

- Zhang, Z., Chuang, Y.-H., Huang, N., and Mitch, W. A. (2019). Predicting the contribution of Chloramines to contaminant decay during Ultraviolet/Hydrogen Peroxide Advanced Oxidation Process treatment for potable reuse. *Environ. Sci. Technol.*, 53(8):4416–4425.
- Zhou, S., Li, L., Wu, Y., Zhu, S., Zhu, N., Bu, L., and Dionysiou, D. D. (2020a). UV365 induced elimination of contaminants of emerging concern in the presence of residual nitrite: Roles of reactive nitrogen species. *Water Res.*, 178:115829.
- Zhou, Y., Chen, C., Guo, K., Wu, Z., Wang, L., Hua, Z., and Fang, J. (2020b). Kinetics and pathways of the degradation of PPCPs by carbonate radicals in advanced oxidation processes. *Water Res.*, 185:116231.