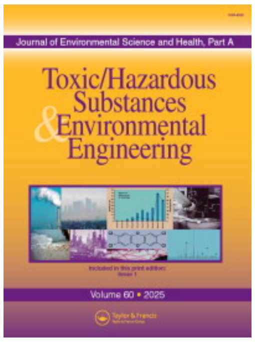

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Degradation of diclofenac using advanced oxidation processes: a review

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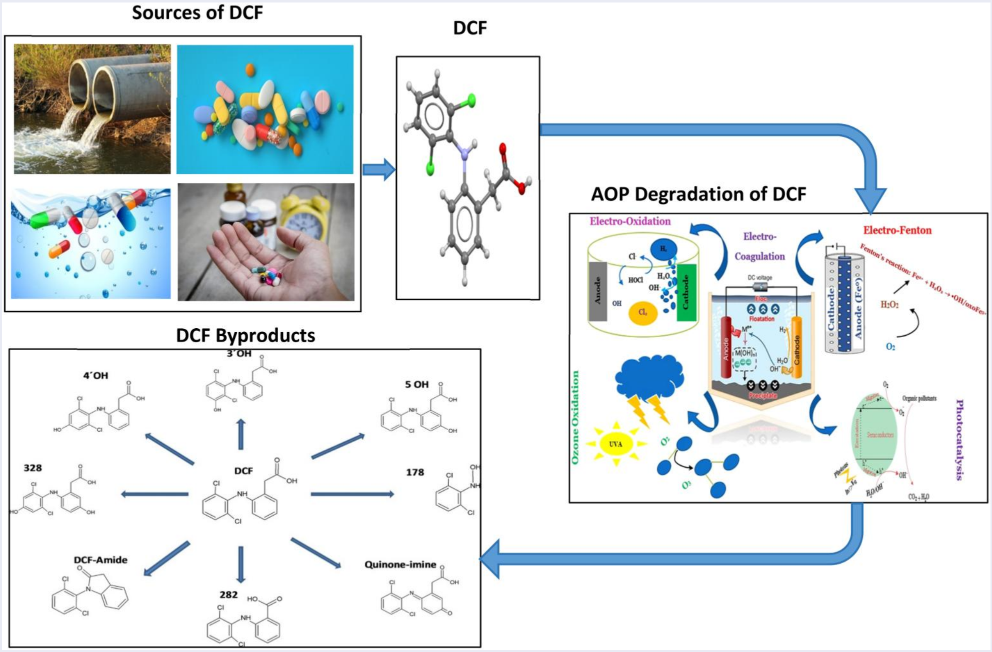
ABSTRACT

Diclofenac (DCF) is one of the emerging compounds in the environment. There are many sources of diclofenac, such as effluent of pharmaceutical industries, wastewater treatment plant effluent, and domestic wastewater. It requires advanced treatment because it cannot be removed from water and sludges using the conventional wastewater treatment process. Catalytic and free radical methods also known as advanced oxidation process (AOP) can degrade large and complex organic compounds into smaller ones. In this review, each AOP method is critically assessed for the removal of DCF in water.



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Introduction

Pharmaceuticals and Personal care products (PPCPs) are used extensively around the world and represent an environmental threat due to potential adverse impacts on human health and aqueous ecosystems.[1,2] Common pharmaceutical compounds are classified in Table 1 based on their properties and therapeutic use. DCF is one of the most common non-steroidal anti-inflammatory drugs (NSAID). It is used for the treatment of non-rheumatoid disease and painful inflammatory rheumatoid. It cannot be totally removed with the conventional wastewater treatment plants (CWWTP) as the removal efficiency is around 30%. As a result, it is detected in the effluent and influent of wastewater, surface water, and groundwater treatment plants.[7] An average concentration of DCF of 1.2 μg L^{-1} in surface water treatment plant effluent, 4.7 μg L^{-1} in wastewater treatment plant effluent, and 380 ng L^{-1} in groundwater treatment plant

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Table 1. Pharmaceutical compounds commonly detected in water (data collected from Refs.[3–6]).

Name and types	Properties	Therapeutic use
Sulfonamides, fluoroquinolones, bacteriostatic		Antibiotics
Acetaminophen diclofenac, naproxen, ibrofen	NSAIDs	Analgesic/antipyretics
Caffeine	Central nervous system (CNS) stimulant	CNS
Propranolol, atenolol	Beta blocker cholesterol and triglyceride reducers	Cardiovascular drugs
Clofibric acid, gemfibrozil	Steroid hormone's	Endocrinology treatments
Iomeprol, iopromide	Iodinated X-ray contrast media	Absorbable organic halogen compounds

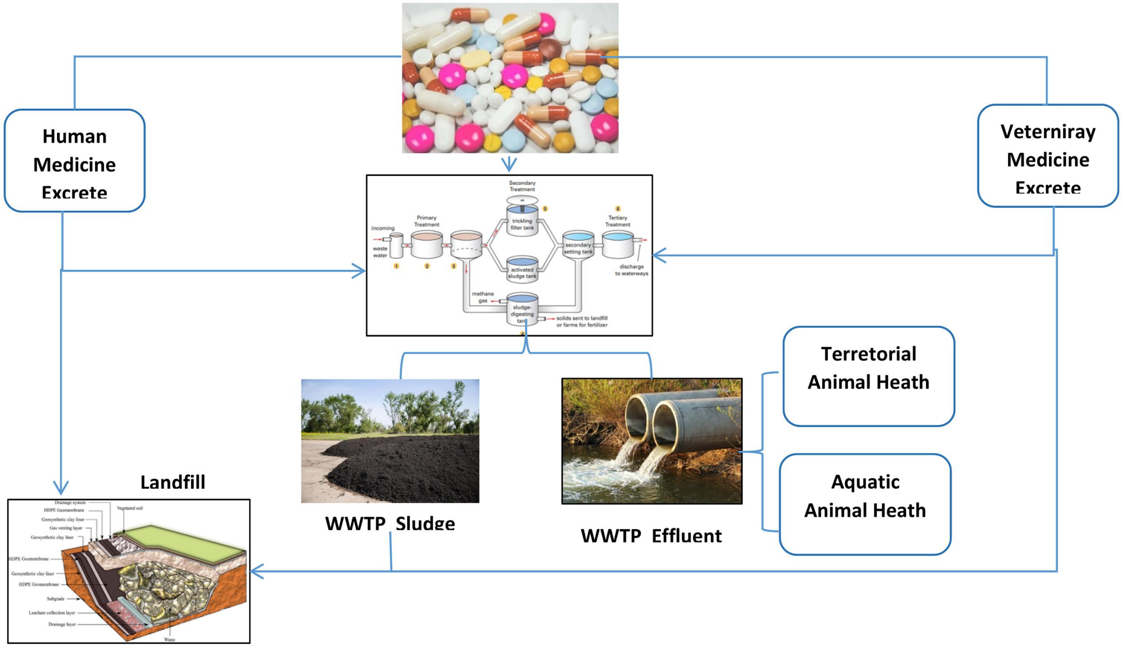

Figure 1. Sources of diclofenac.

effluent was detected.[8,9] Degradation byproducts can also be a serious threat to human health, so the removal of DCF and its byproducts is essential. Many pharmaceutical compounds are detected at ng L^{-1} level (trace level) in the aquatic environment worldwide.[10,11] Nowadays, many researchers are monitoring pharmaceutical compounds in water or wastewater. Pharmaceutical compounds enter the environment *via* many sources, such as feces or urine (active metabolic or unactive ametabolic form) from human and animals' excretion and through sewage system.[12] Surface water, ground water, and soil can become contaminated *via* manures and runoffs from cattle treated with veterinary pharmaceutical compounds.[13] The aim of this study is to review and assess the effectiveness of advanced oxidation processes (AOPs) for the removal of DCF from various aqueous systems.

Diclofenac

Diclofenac (2-[-2′,6′-(dichlorophenyl) amino] phenyl acetic acid), is categorized as non-steroidal anti-inflammatory drugs (NSAIDs) to relief pain in human, livestock, and domestic animals.[14] Sodium and potassium salt of DCF have different absorption time: sodium DCF has slower absorption rate to treat chronic pain while potassium DCF has a fast absorption rate for acute pain.[2] The chemical formula of sodium DCF is $C_{14}H_{10}C_{l2}NNaO_2$ and its molecular weight is 318.1 g mol^{-1}, water solubility is 2.37 mg mL^{-1} and log K_{ow} of 4.51. The chemical formula for potassium DCF is $C_{14}H_{10}Cl_2KNO_2$ with a molecular weight of 334.2 g mol^{-1}, water solubility of 2.34 mg mL^{-1} and log K_{ow} of 4.28.[7,8] DCF is primarily used to treat inflammatory diseases but is also recommended as pain relief for menstrual cramps, migraines, as well as a variety of muscle aches and pains.[15] Diclofenac causes its pharmacological effects through the inhibition of the cyclooxygenase (COX) enzyme. This enzyme is responsible for the synthesis of prostaglandins that are signaling molecules used for a wide variety of biological functions, including inflammation and the induction of pain.[16] Diclofenac binds to both COX-1 and COX-2 isoforms, preventing the conversion of arachidonic acid to pro-inflammatory prostaglandins and thereby reducing inflammation.[17] The inhibition of COX-2 results in a reduction of inflammation and pain relief, whereas inhibition of COX-1 results in an increased chance of gastrointestinal distress.[18] Diclofenac is thought to bind more favorably to COX-2 than other NSAID's resulting in it being a more commonly dispensed NSAID for inflammatory illnesses.[19]

Sources of diclofenac in water

Diclofenac enters the aquatic environment as metabolic and ametabolic form. Up to 65% of DCF is excreted when it is

Table 2. DCF concentration in worldwide waterways.

Country	Water source	DCF concentration (mg L^{-1})	References
Pakistan	River	400–1800	[23]
Germany	WWTP	1300–3300	[24]
Taiwan	Surface seawater	2	[25]
Ireland	Sea	110–550	[26]
Slovenia	River	9–282	[27]
USA	WWTP	2.5	[28]
Canada	Estuary	2–5	[29]
	WWTP	140–190	
UK	Estuary	<8–195	[30]
Spain	River	6000	[31]
	Sea	4000	
Portugal	Sea	0.18	[32]
	River	0.0032	[33,34]
	Wastewater	0.0062	[33,35,36]

taken orally. Some of the metabolites end up is sludge in wastewater treatment plants, while others are released into the environment (Fig. 1). Due to the mechanism of application, the emerging form of diclofenac entering the environment is the pure form. The excess gel is washed off and mix with the household wastewater.[20] Ordinary wastewater treatment plant (WWTP) cannot fully remove it and as a result, it ends up in the environment *via* effluent of WWTP.[21] It was placed into the emerging pollutant list under the European Water Framework Directive due to its presence and persistence in water and have adverse effects on humans and aquatic organisms.[22] DCF was detected in many regions of the world, such as Asia, America, and Europe waterways as shown in Table 2. The concentration of DCF varies from region to regions due to population densities, DCF analytical techniques and consumption rates.

DFC is the 8th best-selling pharmaceutical in the world.[37] The annually usage of DFC was estimated at around 940 tons globally and 65% of ingested DCF is eliminated through urine.[38] The major DFC effluent was generated from domestic waste, hospital, and pharmaceutical units.[38] However, it is non-biodegraded by conventional WWTPs. Low levels ($>2.00\,\mu g\ L^{-1}$) of DCF in water is detrimental to aquatic ecosystems as it damages fish tissue and alters biochemical functions. Thus, further action needs to be taken to overcome DCF pollution.[38]

Health impact of diclofenac

Diclofenac has adverse effect on humans as well as the environment. In a case study, the major cause for the death of vultures was found to be diclofenac consumption. DCF was used for the NSAID treatment of farmed cattle and when the cattle died, they were consumed by vultures.[39] The lethal dose for 50% of vultures (LD50) ranged from 98 to 225 $\mu g\ kg^{-1}$. DCF was found to be so toxic that it forced the governments to ban manufacturing of DCF in Pakistan, India, Nepal, and other countries in 2006.[40] There are several side effects of DCF in human health, such as myocardial infarction, renal failure, cardiovascular thrombotic events, stomach ulceration, and stroke.[41] The half maximal effective concentration (EC50) of DCF for bacteria was not >1 and 1–10 mg L^{-1} for invertebrate and algae.[42] The side effect in fish is a delay and reduction in hatchability.[43,44] Mammals and birds are also affected by the presence of DCF in the ecosystem, such as renal failure or increased risk of gastrointestinal problem, cardiotoxicity, neurotoxicity, nephrotoxicity, hepatotoxicity, hematotoxicity, genotoxicity, teratogenicity, and skin allergies.[45] Long exposure to DFC will leads to kidney diseases, mucosal damages, and central nervous system disorders.[46] Due to it detrimental effects, DFC has been listed as priority contaminant by the European Union since 2015 (Community Directive, 2015/495).[47]

Conventional methods for DCF removal

Adsorption is a method to remove pollutants from the liquid phase without generating toxic intermediates.[48] Various adsorbents have been used to remove DCF, such as palm kernel shells,[49] cellulose nanocrystalline (CNC) modified with polyvinylamine (PVAm) and reduced graphene oxide (rGO) cellulose aerogel (CNC-PVAm/rGO),[48] and sewage sludge-derived biochars.[50] Although it can remove high percentages of DCF and be reused several times, the adsorbent is typically landfilled once exhausted which can still cause pollution of not managed properly. More study need to be done to extend it reusability[51] and tests should also be carried out on fixed bed columns to simulate the application of adsorbent in continuous systems.[52] Table 3 lists some recent studies on the adsorption of DCF with removal percentage and mechanisms. Disadvantages of adsorption include competition of adsorption sites with other organics, saturation of adsorption sites, constant monitoring of adsorbent to know when to replace the adsorbent.

Membrane separation is a more reliable physical method to remove DCF even at low concentration, but capital and operating costs are relatively high. However, fouling of the membrane caused by the accumulation of the solute on the membrane surface and the blockage of the pores reduces the water flux.[55]

Advanced oxidation processes for DCF removal

Advanced oxidation processes (AOP) produce highly reactive species (e.g. $OH^{\blacksquare}$, H_2O_2, O_3, $O^{\blacksquare}$, …) for the destruction of large molecular pollutant into smaller product in aqueous phase. In recent years, AOP has become the most suitable option because of two reasons: firstly, it has many technologies involved and secondly, it has potential application in degradation area. The main AOP methods include homogeneous and heterogeneous photocatalysis based on electrolysis, near ultraviolet or solar visible irradiation, wet air oxidation, ozonation, ultrasound, and Fenton's reagent, while less conventional but evolving processes include microwave, ferrate reagent, ionizing radiation, and pulsed plasma. While AOP are mostly used in the area of water and wastewater treatment, it also has diverse applications in soil remediation, production of ultrapure water, groundwater treatment, municipal wastewater sludge conditioning, odor control, and the organic volatile compounds treatment. Depending on the demand of treatment and the properties

Table 3. Physical studies of DCF removal.

Method	Summary of results	References
Adsorption: palm kernel shells	The maximum removal was 95% at pH 2 with palm kernel shells dose of 15 g L^{-1} and DFC dose of 50 mg L^{-1}. The best fitting model is pseudo-second order model with rate constant $(K_2) = 0.869\ min^{-1}$. The interaction *via* aromatic π–π stacking and hydrogen bonding between -OH groups of phenol and carboxylic acid groups of DCF are leading to a good adsorption efficiency despite of the low surface area of the adsorbent.	[49]
Adsorption: CNC-PVAm/rGO	CNC-PVAm/rGO had an adsorption capacity (q_{max}) of 605.87 mg g^{-1} compared to bare CNC aerogel (11.45 mg g^{-1}). The fitting model was Langmuir isotherm and pseudo-second-order kinetic models. It could be reused four times. The introduction of PVAm and rGO to the CNC-PVAm/rGO aerogel also greatly enhanced electrostatic interactions, π-π interactions, and hydrophobic effects. These enhancements significantly promoted the hydrogen bonding interactions between the DCF molecules and CNC-PVAm/rGO, thus resulting in a large improvement in the adsorption performance of the aerogel.	[48]
Adsorption: sewage sludge-derived biochars	The maximum adsorption capacity was 92.7 mg g^{-1} and the best fitting model was pseudo-second order model. The adsorption of diclofenac occurred *via* π-stacking interactions at the biochar surface mainly *via* Dubinin-Radushkevich model. Both interactions between the phenyl groups of DCF and phenol groups on biochar *via* hydrogen bonding, and non-covalent π-π stacking of aromatic groups of DCF and biochar were responsible for monolayer surface coverage. The adsorption of DCF was ascribed to Langmuir, Temkin and Dubinin-Radushkevich models and strong π–π electro-donor-acceptor interactions.	[50]
Nanofiltration membrane (NF50)	Up to 99.74% DCF removal at pH3. Only 55% when DCF is mixed with other pharmaceuticals.	[53]
Nanofiltration membrane (NF90-400)	100% removal of DCF at pH5.6–6.1.	[54]

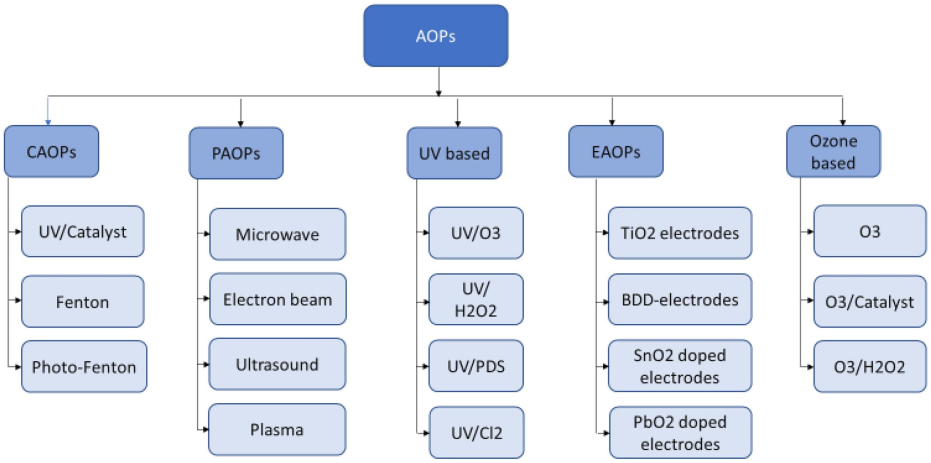

Figure 2. Broad overview of AOPs.

of the treatment objectives AOP also applied alone or coupled with biological and physicochemical processes which can lead to better efficiency. AOP can also be used to convert bio recalcitrant into biodegradable compounds.[56,57] AOPs can be classified according to Figure 2. UV/H_2O_2, ozonation, Fenton and photo-Fenton, and semiconductor photocatalysis showed its high effectiveness in removing pharmaceutically active compounds (PhACs).[41] During AOPs, oxygen free radicals are formed, such as hydroxyl radicals (·OH) which has high oxidizing power to degrade the organic compound to form carbon dioxide, water, inorganic ions, and other molecules with lower molecular weight.[42–44] This process is advantageous as it is chemical free, is low maintenance, and costs less.[44] However, the intermediates formed by AOPs can be toxic, and combined techniques are often required to enhance the removal of contaminants in water.[11]

Diclofenac removal from aqueous solutions using several methods for oxidant generation as well as activation has been widely investigated.[11] Figure 2 shows that AOP processes for DCF are categorized into UV based AOPs, Ozone based, Physical AOPs (PAOPs), Catalytic AOPs (CAOPs), and Electrochemical AOPs (EAOPs). For each category, the method, removal efficiency, media, and conditions are summarized in Tables 4–8. Many processes involve different technologies and may belong to more than one category. AOPs summarized in Figure 2 are all well-established and tested at lab scale. AOP technologies consist of two steps: the *in-situ* formation of oxidative species and the reaction with the targeted contaminant. The radical formation depends on the specific parameter and is affected by water quality and system design. Besides radicals scavenging, other parameters also play a vital role in the degradation of contaminants, such as hydrodynamics and radical mass transfer

Table 4. Diclofenac degradation through ozone based AOP.

AOPs	Matrix	AOP features	Summary of results	References
Fe-Cu-MCM-41/O_3	Deionized water	Fe-Cu-MCM-41/O_3	87% DCF removal in 15 min.	[58]
Fe-MCM-41/O_3	Deionized water	Dose of $O_3 = 100$ mg L^{-1}; catalytic = 1 g L^{-1}; pH = 7	76% DCF removal in 60 min.	[59]
O_3/UV	Distilled-deionized water	O_3/UV pH 5.3	100% DCF removal in 40 min.	[60]
Ozonation	Milli-Q quality water	O_3 dose 0.22 g L^{-1} pH 7	99% DCF removal in 30 min.	[61]
Ozonation/activated carbon	Deionized water	O_3/activated carbon pH = 7 RT = 15 min	95% DCF removal in 15 min.	[62]
Catalytic ozonation	Deionized water	Mixed metal oxide catalyst (SG-2101), full metal catalytic (MOLoxW 2101), Fenton type catalytic (Fe-O_3 and DELTA) Weight = 5 g DCF = 20 mg L^{-1}	100% DCF removal in 20 min.	[63]
Ozone (O_3)/activated carbons (AC)	Sewage treatment plan (STP) effluent	O_3/AC packed together in series RT = 15 and 20 min	100% DCF removal in 15 min.	[62]
O_3-catalytic	Wastewater treatment plant	Catalytic = MnO_x/Al_2O_3 with non-porous and mesoporous Al_2O_3 tested	90% DCF removal in 15 min.	[64]
O_3	Surface water	$O_3 = 1$–1.3 mg L^{-1} pH = 7.5 RT = 10–20 min	>95% DCF removal in 30 min.	[6]
O_3/fluorinated hydrocarbon	Distilled-deionized water	O_3/fluorinated = 9.52 mg L^{-1} pH = 5	100% DCF removal in 40 s.	[65]
Ozone	Distilled water	$O_3 = 36$ L h^{-1} pH = 5–6 RT = 90 min	39% DCF removal in 90 min.	[66]
Ozonation	STP effluent	AOX = 100 g L^{-1} $O_3 = 15$ mg L^{-1} pH: 7.2 RT = 18 min	>96% DCF removal in 18 min.	[67]
Ozone/OH and O_3/H_2O	Municipal treatment plant effluent	pH ~ 8 RT = 5 min	99% DCF removal in 5 min.	[68]
Polytetrafluoroethylene (PTEE) membrane/ozone	Tap water and real effluent of wastewater treatment plant	pH = 10 $O_3 = 10$, 28.5, and 45.3 g O_3/Nm^3	72% reduction of TOC, the removal of DCF was not affected by the presence of counterions. O_3 enhanced the degree of mineralization.	[45]
TiO_2/O_3	Urban wastewater samples	TiO_2/O_3 $O_2 = 50$ g Nm^{-3}	100% DCF removal in 120 min.	[69]

in surface-based AOPs. Detailed overviews of reaction principles, system design, and kinetics on AOPs are found in various book publications.[91,92]

DCF removal through ozone based AOPs

Ozone has long been used as an oxidant and disinfectant in water treatment. Recent ozone based AOP processes are listed in Table 4. As an oxidant, ozone is very selective and attacks primarily electron-rich functional groups like double bonds, amines, and activated aromatic rings (e.g. phenol). Since its reactions in real aqueous solutions often involve the formation of hydroxide radicals (OH$^{\blacksquare}$), ozonation itself is often considered an AOP or AOP-like process. OH$^{\blacksquare}$ can be formed from the reaction of ozone with hydroxide ions.[93,94] The initiation of this reaction, however, is quite slow with a second-order rate constant of 70 M^{-1} s^{-1}. In addition, radicals are formed as a side product from the reaction of ozone with organic matter (mainly phenol and amine functional groups).[95] During ozonation of secondary effluents, these reactions are the major contributors to radicals formation. Methods to actively initiate formation of radicals include the ozonation at elevated pH and the combinations O_3/H_2O_2 (also called peroxone-process), O_3/UV, and O_3/catalysts. The combination of ozonation and UV-irradiation will be discussed as a UV-based AOP in section DCF removal through UV-based AOPs. In ozone based AOPs, different mechanisms are involved, such as ozonation at elevated pH, peroxone-process (O_3/H_2O_2), and O_3/catalysts. From Table 4, it appears that DCF removal in the range 76–100% is achievable within 5–30 min. Notably, 100% DCF was removed in 40 s at pH5 in distilled water due to the rapid reaction of DCF with ozone and fluorinated hydrocarbons.[65] Another advantage of the application of ozone is that ozone can be generated on-site and as opposed to conventional chemical sanitizers, it requires neither transportation nor storage.

The pH of the solution plays an important role in catalytic ozonation as it controlled the mass transfer and decomposition of O_3. At a higher pH, the reaction mechanism follows a radical pathway and generates more OH• while at a lower pH, it follows a selective direct reaction pathway. Therefore, a higher pH of the solution is suggested to increase the decomposition of ozone into OH• which

Table 5. Diclofenac degradation through UV-based AOPs.

AOPs	Matrix	AOP features	Summary of results	References
O_3/UVA/TiO_2	Urban wastewater	$TiO_2 = 0.5–2.5\ g\ L^{-1}$ RT = 60 min	75% DCF removal in 60 min.	[9]
O_3/UV	Water	O_3/UV = 0.1 mM and 1 kGy	>90% DCF removal in 30 min.	[70]
(UV/H_2O_2)	Sewage treatment plant effluent	T-butanol Hg lamp = 254 nm Pressure = 17 W Time = 90 min	39% DCF removal in 90 min.	[66]
UV/TiO_2 UV/TiO_2/H_2O UV	Wastewater	Inlet fluid pressure = 2–4 bar pH = 4–7.5 RT = 120 min	95% DCF removal in 120 min.	[71]
UV/free chlorine (FC) by UV-B (265 mn) and UV-C (285 nm)	Synthetic wastewater	20 mg L^{-1} DCF pH 7.2; and 20 mg L^{-1} FC with the pH of 8.5	The degradation follows a pseudo first-order kinetic. DCF is completely removed, but low mineralization (20–30%) occurred and the toxicity toward tomato and radish seeds decreased.	[46]
Ce withTiO_2 nanocomposites	Deionized water	UV light Ce withTiO_2 = 25–125 mg Time = 80 min	100% DCF removal in 80 min.	[72]
O_2/UV-A/TiO_2	Aqueous solution	O_2/UV-A/TiO_2 O_3/UV-A/TiO_2 UV-A/TiO_2 pH = 5, 7, and 9	100% DCF removal in 4 min.	[73]
UV/TiO_2/H_2O_2	Synthetic wastewater	pH = 6.5 $TiO_2 = 1\ g\ L^{-1}$ DCF = 50 mg L^{-1} Time = 150 min $H_2O_2 = 10\ ml\ L^{-1}$	DFC removal = 97.71% TOC removal = 67.95%	[49]

Table 6. Diclofenac degradation using electrochemical AOPs.

AOPs	Matrix	AOP features	Summary of results	References
Carbon nanotubes-polytetrafluorethylene electrode (CNTs-PTFE)	Aqueous phase	CNTs-PTFE charged as cathode (negative) = 27 mg L^{-1} Degradation time = 60 min Current = 100 mA	100% DCF removal in 60 min.	[74]
Hydroxyapatite and TiO_2 (HApTi)	Aqueous phase	HApTi = 0.2 g DCF = 4 g L^{-1} RT = 24 h	95% DCF removal in 24 h.	[75]
TiO_2–SnO_2	Wastewater	DCF concentration = 20 mg L^{-1} TiO_2–SnO_2 = 0.8 g L^{-1} pH = 5	100% DCF removal in 300 min.	[76]
Sonication/TiO_2, SiO_2, SnO_2 TiO_2/SiO_2	Distilled water	TiO_2, SiO_2, SnO_2 TiO_2/SiO_2 Sonication = 216, 617, and 850 Hz, 90 W Diclofenac = 50–100 mg L^{-1} Time = 60 min	90% DCF removal in 60 min.	[21]
Titanium-coated with RuO_2-IrO_2-TiO_2) as anode and stainless steel as cathode and a biochar particulate electrode (1–2 mm)	Treated wastewater samples	Biochar TN 1–2 mm = 30.0 mg An inter-electrode distance of 7.5 cm pH value = 7 Current density = 7 mA cm^{-2}	90% of 10 mg L^{-1} was removed.	[47]

enhances the degradation of refractory organics,[96] and it also results in higher TOC removal at higher pH levels.[97] The production of hydroxyl radicals as a result of ozone decomposition is significant at neutral pH for ozonation only.[96] At increased pH, more hydroxyl radicals would be generated by ozone decomposition due to the presence of a large quantity of hydroxide ions for homogeneous catalytic ozonation. The pH of treated water influences direct ozonation efficiency since dissociated target organic compounds might have significantly different kO_3 values.[98] Furthermore, the abundance of hydroxide ions directly influences the $OH^\blacksquare$ generation and therefore indirect ozonation. If the water to be treated has a pH > 8, ozonation applied as an AOP might be a promising process, if the precipitation of calcium carbonate is not of concern.

In the peroxone process, ozone reacts with the peroxide anion (HO_2) to form OH precursors, which are subsequently reacting to $OH^\blacksquare$. Residual H_2O_2 might have to be destroyed before discharging the treated water to the receiving aqueous environment. The optimum molar ratio for the peroxone process is $H_2O_2/O_3 = 0.5\ mol\ mol^{-1}$.[99,100] Typical ozone doses in the peroxone process are 1–20 mg L^{-1}. Peroxide can also be formed from reactions of ozone with the water matrix but its contribution to overall $OH^\blacksquare$ formation during wastewater ozonation is not significant.[101] O_3/H_2O_2 is a well-established process in drinking water

Table 7. Diclofenac degradation through catalytic AOPs.

AOPs	Matrix	AOP features	Summary of results	References
UV/TiO_2	W	DCF = 0.005–0.15 mmol L^{-1} TiO_2 Aeroxide P25 (hybrid photocatalysis-DCMD) = 0.05–0.4 g L^{-1} Germicidal lamp for 4 h	85% DCF removal in high concentration at 4 h.	[77]
UV/TiO_2/H_2O_2 and UV, UV/TiO_2	WW	Inlet fluid pressure = 3 bar, pH = 4	95% DCF removal in 120 min.	[71]
UVA/TiO_2/O_2	WWTP effluent	UV lamps = 0, 1, 2, 4, 6, 8, 16, 32 TiO_2 = 50 ppm RT = 40 min	70% DCF removal in 40 min.	[78]
UVA/TiO_2/O	WWTP effluent	Lamp = black light, 25 W, 300–420 nm. RT = 2 h TiO_2 = 0.8 g L^{-1}	85% DCF removal in 2 h.	[79]
Simulated solar radiation/TiO_2/O_2	WWTP effluent	TiO_2 dose = 0.1 g L^{-1} Photon flux = 6.9 Einstein s^{-1} (290–400 nm) Solarbox = (0.078 L) 1 kW Xe-OP lamp	99% DCF removal in 120 min.	[80]
Simulated solar radiation/TiO_2/O_2	WWTP effluent	Xenon arc lam > 290 nm TiO_2 = 104–500 mg L^{-1}	97% DCF removal in 120 min.	[81]
Solar photocatalysis	WWTP effluent	UV/TiO_2 UV/Fenton RT = 100 min	>90% DCF removal in 100 min.	[82]
Fe^{3+}/H_2O_2/LP UV	DW	DCF = 20 mg L^{-1} Fe^{3+}/H_2O_2/LP pH = 2.8 UV = 254 nm	100% DCF removal in 50 min.	[83]
Fe^{2+}/H_2O_2/Sunlight	DW	DCF = 50 mg L^{-1} Sun light/Fe^{2+}/H_2O_2 pH = 6.5	100% DCF removal in 60 min.	[84]
Fe^{2+}/H_2O_2/Sunlight	Synthetic fresh water	DCF = 50 mg L^{-1} Sunlight/Fe^{2+}/H_2O_2 pH = 7.2	100% DCF removal in 100 min.	[82]
UV-A/FeZSM5/H_2O_2	Synthetic water	DCF = 0.1 mM H_2O_2 = 50 mM $FeZSM_5$ = 2.0 mM pH = 4	The presence of UV-A activated FEZSM5 to convert DCF and extended the mineralization. It improved the biodegradability and the toxicity has been reduced after 2 h. Low Iron leaching indicated that the used catalyst was able to retain its function after several runs.	[48]
Peroxy mono sulfate (PMS)/cobalt (II)	WWTP effluent	H_2O_2 or ozone = 250–500 μM Co^{2+} or Fe^{2+} = 250–500 μM	83% DCF removal in 2 min.	[85]
Photo catalyst	WW	Reduced graphene oxide-Ag-BiOI synthetic by using UV light with thermal strategy in 80 min.	100% DCF removal in 80 min.	[86]
Photo catalyst	W	TiO_2 pH 6.5 RT = 360 min	100% DCF removal in 360 min.	[87]

W: water; WW: wastewater; WWTP: wastewater treatment plant.

treatment and water reuse applications (e.g. Windhoek, Namibia). However, recent studies have shown that the benefits of its application in wastewater are limited due to high competition reactions and already efficient radical formation with ozone alone.[102] Catalytic ozonation is distinguished between homogeneous and heterogeneous catalytic ozonation, depending on the water solubility of the catalyst. Homogeneous catalytic ozonation can be described as a three-step catalytic cycle as approached by Pines and Reckhow using Co(II) as a catalyst and oxalic acid: (1) formation of Co(II)-oxalate complex, (2) oxidation by ozone to Co(III)-oxalate complex, and (3) decomposition of Co(III)-oxalate complex forming an oxalate radical and Co(II).[103] Heterogeneous catalytic ozonation mechanisms are mediated by metal oxides (e.g., TiO_2, Al_2O_3, MnO_2) and result in more complex reaction paths based on multiple-phase transport mechanisms and respective reactions as described in detail by Beltran.[104] Most studies in Table 4 were carried out in distilled water achieving high percentage removals, but 90–100% removal is also possible within 15 min in real wastewater suggesting a minimal impact of organics and inorganics on DCF destruction by ozone. Some studies in Table 4 also show the high removal of DCF (96–99% in 5–18 min) even at pH 7–8 in real wastewater.[67,68] Both homogeneous and heterogeneous catalytic ozonation have shown their potential for water treatment at laboratory scale mainly based on lower ozone demand compared to ozonation alone.[105,106] However, full-scale application is limited due to catalyst recovery and a lack of understanding of the catalytic ozonation mechanisms.[107] Some studies report the use of activated carbon as a catalyst in catalytic ozonation.[108] However, $OH^{\blacksquare}$ production in this process is based on the reaction of ozone with pyrol groups present on the activated carbon surface indicating that it acts as a radical

Table 8. Diclofenac degradation through physical AOPs.

AOPs	Matrix	AOP features	Summary of results	References
Ultrasonic persulfate (US/PS)	WWTP effluent	pH = 6 Temperature = 30 °C PS = 120 mg L^{-1} RT = 240 min	97% DCF removal in 240 min.	[88]
O_3/US	Wastewater	O_3/US(Ultrasound)/Fe	90% DCF removal in 10 min.	[89]
Electroenzymatic system	Aqueous phase	Graphene-hemin hybrid used as photocatalytic Time = 11 h	96% DCF removal in 11 h.	[90]
Pulsed corona plasma	Water	High positive voltages of 80 kV are applied with 20 Hz frequency plasma corona was generated. pH = 3	>80% DCF removal in 15 min.	[71]

promoter rather than a catalyst, which needs to be continuously renewed to maintain efficient radical generation.[109] Another disadvantage of ozone is the need for the detection and destruction of ozone for the safety of personnel in various processing plants as exposure to ozone may cause irritation to the eyes, nose, and throat whereas high ozone levels (up to 95 mg L^{-1}) can even have fatal effects on humans.

DCF removal through UV-based AOPs

UV-based AOPs comprise processes based on UV-irradiation (mostly UV-C) and the combination of UV-light with different radical promoters.[110] Diclofenac degradation using UV-based AOPs are reviewed in Table 5. UV radiation applied for advanced oxidation are usually >200 mJ cm^{-2} and therefore exceed UV-dose requirements for 4-log inactivation of most pathogens including UV-resistant organisms (e.g. adenovirus).[111] UV-irradiation sources usually consist of either low- (LP) or medium-pressure (MP) mercury lamps with mono- or polychromatic emission spectra, respectively. Recently, UV-light emitting diode (LED) light sources with specific wavelength distributions have been investigated and summarized for disinfection purposes.[112] The principal advantages of LEDs compared to conventional medium and low-pressure lamps are the elimination of mercury, unique peak emission wavelengths, compact size, and therefore flexible application design as well as a short startup phase. However, despite the prediction of future UV-LED wall plug efficiencies of about 75% in 2020,[113] current diodes emit UV radiation at efficiencies of <10%.[114] This results in electric energy per order reduction of pollutant (E_{EO}) values for LED systems that are not yet competitive with conventional UV-systems.[115] The most frequently applied UV-based AOP is the combination with H_2O_2. Other radical promoters, such as persulfate (to form sulfate radicals) and chlorine (hydroxyl radicals and radical chlorine species) are also being investigated. Besides established oxidants, Keen et al. investigated the applicability of nitrate in combination with MP-lamps as an alternative UV-based AOP.[116] However, to the best of our knowledge, no E_{EO} values are available for this process. The combination of UV-irradiation and H_2O_2 leads to the photolytic cleavage of H_2O_2 into two $OH^{\blacksquare}$. However, the molar absorption coefficient of H_2O_2 is relatively low with $\varepsilon = 18.6\ M^{-1}cm^{-1}$ at $\lambda = 254$ nm resulting in an H_2O_2 turnover of >10%. If LP UV lamps are used, high concentrations of H_2O_2 are required to generate sufficient $OH^{\blacksquare}$ ($[H_2O_2]$ 5–20 mg L^{-1}) leading to the necessity of removing residual H_2O_2 in a subsequent step. Applied H_2O_2-doses are mainly set based on economic aspects.[116] However, at higher concentrations, scavenging of OH with H_2O_2 ($k_{OH,\ H2O2} = 2.7 \times 10^7\ M^{-1}\ s^{-1}$) also affect the radical yield.[117] UV/H_2O_2 for TOC removal has been examined widely throughout peer-reviewed journal articles at laboratory-scale[116,118,119] for water qualities ranging from ultrapure water to landfill leachate.[120] First full-scale applications are already established for potable water reuse[121] and surface water treatment applications.[122] UV/H_2O_2 is not established for advanced wastewater treatment mainly because of low UV-transmittance and high scavenging capacity of secondary or tertiary treated wastewater effluents but is used in some potable reuse treatment trains employing integrated membrane systems (ultrafiltration/reverse osmosis)[123] based on its negligible disinfection by-products formation potential. In the UV/O_3 process, UV irradiation ($\lambda < 300$ nm) results in a cleavage of dissolved ozone, followed by a fast reaction of atomic oxygen with water to form a thermally excited H_2O_2. Subsequently, the excited peroxide decomposes into two OH.[93] Ozone has a molar extinction coefficient of $\varepsilon = 3{,}300\ M^{-1}cm^{-1}$ at $\lambda = 254$ nm, which is significantly higher than that of H_2O_2 at this particular wavelength. However, due to recombination, only a small proportion of generated H_2O_2 decomposes to $OH^{\blacksquare}$ resulting in a free $OH^{\blacksquare}$ quantum yield of only 0.1.[103] Furthermore, both UV lamps and ozone generator need large amounts of electrical energy, resulting in relatively high energy demands for the combination of UV and ozone. Direct oxidation by the combination of ozonation and photolysis covers a wide range of TOC reactivity and leads to the main advantage of this process. However, low energy efficiency of radical generation might explain that to the best of our knowledge, no published data on full-scale UV/O_3 application are available.

No significant effect of pH is observed in the only UV system, indicating that although the deprotonation of DCF could occur when pH changed, the degradation of DCF by UV had nothing to do with whether DCF was deprotonation, which was due to the same UV absorbance for DCF under 254 nm at pH 3–11.[124] However, the k_{obs} of DCF in

UV system was only 0.065 min^{-1}. The optimal pH for DCF degradation in UV/peracetic acid (PAA) system was 8.5. The removal of DCF was enhanced gradually with increasing PAA dose. Since NO_3^- is a photosensitive substance which can generate $HO^{\cdot}$ under UV irradiation, its existence promoted the degradation of DCF. The presence of CO_3^{2-} could slightly improve DCF degradation, which might be due to the role of generated carbonate radicals. Cl^-, SO_4^{2-}, and Fe^{3+} had little effect on DCF removal, while Cu^{2+} could enhance DCF degradation because of its catalytic ability for PAA decomposition. An inhibition effect on DCF removal was observed in the presence of DOM, and it was more obvious at higher concentration of DOM. Disadvantage of UV-based methods is the low total organic carbon (TOC) removal.

An interesting alternative to $OH^{\blacksquare}$ based AOPs is UV/SO_4—which generates primarily sulfate radicals ($SO_4^{\blacksquare}$) for the oxidation of organic contaminants in water.[125] Sulfate radicals have a strong oxidizing power and are more selective oxidants than $OH^{\blacksquare}$.[126] Peroxydisulfate (PDS, $S_2O_8^{2-}$) is homolytically cleaved by UV-C activation. The quantum yield of $S_2O_8^{2-}$ is larger than H_2O_2 (1.4 compared to 1.0) and molar absorption for $S_2O_8^{2-}$ is slightly higher as well (22 and 18.6 $M^{-1}\,cm^{-1}$, respectively) resulting in a higher generation of radicals using PDS as oxidizing agent.[127] Peroxymonosulfate (PMS, HSO_5^-) is activated by UV radiation into SO_4^- and $OH^{\blacksquare}$ with a quantum yield of 0.52 at pH 7.[128] Several studies have investigated the mechanisms and application of UV/PMS.[129] However, based on its lower quantum yield, high commercial pricing, and low availability of E_{EO} values, it was not considered in this review. Recent research has shown the advantages of UV/SO_4^- compared to UV/H_2O_2 in laboratory-scale experiments.[130,131] However, based on more selective reactivity of sulfate radicals, results reveal a higher sensitivity to water matrix changes and dissolved organic matter composition compared to UV/H_2O_2.[132] Depending on the respective target compound and water matrix, SO_4^- based AOPs can be an interesting alternative to $OH^{\blacksquare}$-based processes. However, UV/PDS has a higher formation potential of disinfection by-products in comparison to UV/H_2O_2.

UV/Cl_2 is another promising AOP, where UV-activated chlorine forms radical species, i.e. Cl, Cl_2, and $OH^{\blacksquare}$ which then oxidize target compounds.[133] Disinfectant, such as chlorine used in drinking water treatment plants can also react with DCF. A second-order reaction (first-order relative to DCF concentration and first-order relative to free chlorine concentration) was reported with rate constant of $1.51 \times 10^3\,M^{-1}\ s^{-1}$ and $3.89 \pm 1.17\,M^{-1}\ s^{-1}$ at pH 7 for chlorine and chlorine dioxide, respectively.[12,134] Cl is a more selective oxidant than $OH^{\blacksquare}$ since it reacts favorably with electron-rich contaminants.[135] However, in the UV/Cl_2 AOP, the two oxidants mainly used are hypochlorite and chlorine dioxide.[135–138] The pH dependency of HOCl/OCl^- speciation needs to be considered since it influences the molar absorption coefficient significantly. UV/Cl_2 is especially favorable for waters with lower pH values, such as reverse osmosis permeate.[133] Research has mainly been conducted on laboratory-scale systems degrading organic indicator compounds.[135–138] Studies in Table 5 show that 75–95% DCF degradation can be achieved within 10–60 min by UV-based AOPs in real wastewater which appears less efficient than ozone-based processes. Coupling ozone with UV does not seem to enhance the ozone performance. Coupling UV and free chlorine could remove all DCF in minutes,[46] but there was limited DOC removal due to the formation of stable dimers, which was confirmed by the yellowish color formed after each photolysis process and deserves additional attention as further treatment might need to be implemented to remove them. The process was relatively cheap with 0.6 kWh required to reduce the concentration DCF by one order of magnitude (90% removal) in 1 m^3 of water.

DCF removal through electrochemical AOPs

Electrochemical AOPs for water treatment applications were recently reviewed in detail by Chaplin.[139] The major electrode types commonly used in this process are doped SnO_2,[140] PbO_2,[141,142] RuO_2,[143] boron-doped diamond (BDD),[144] and sub-stoichiometric and doped-TiO_2.[145,146] Diclofenac degradation using Electrochemical AOPs are summarized in Table 6. However, BDD-electrodes are the most applied eAOP method due to their relatively low production costs compared to other electrodes and high stability of the diamond layer under anodic polarization.[139]

The electrochemical oxidative treatment of contaminated water with BDD electrodes can generate $OH^{\blacksquare}$ directly *via* O_2 evolution from water oxidation.[147] As diamond is a nonconductor it is doped with boron to use it as an electrode material that is deposited onto a carrier material, such as niobium, tantalum, or silicon by chemical vapor deposition.[148] The radicals are generated without the addition of further chemicals. Therefore, BDD-electrode treatment has attracted interest as an eco-friendly and efficient method for the removal of various pollutants. However, since $OH^{\blacksquare}$ generation occurs directly on the electrode surface, the reactivity range of $OH^{\blacksquare}$ is limited to about 1 mm,[149] and diffusive transport through the boundary layer at the electrode surface is the limiting factor of high oxidation efficiencies. For eAOP processes, hydrodynamic parameters therefore have to be considered, as energy used to pump water, might account for the greatest share of energy consumption in this process. This applies especially if low current densities are used to achieve higher $OH^{\blacksquare}$ formation efficiency prolonging overall treatment duration and pumping energy requirements. Apart from the oxidation of TOCs in water treatment, BDD electrodes were investigated for disinfection purposes as well as for the removal of chemical oxygen demand (COD).[150,151] Besides the generation of $OH^{\blacksquare}$, secondary oxidants, which enhance elimination reactions and disinfection in the bulk solution, can be produced.[151] A limiting factor for the applicability of BDD is unintentional formation of halogenated disinfection by-products.[152–154] Nevertheless, several full-scale eAOP systems for COD removal are already in operation.[155]

DCF removal through catalytic based AOPs

The combination of ferrous iron (Fe(II)) and H_2O_2 at acidic conditions results in $OH^{\blacksquare}$ formation which is known as the Fenton reaction. Iron acts as a catalyst with maximum catalytic activity at $pH = 3$, particularly due to the precipitation of ferric oxyhydroxide at higher pH value.[156] Excess addition of H_2O_2 leads to the reduction of Fe(III) to Fe(II).[157] By substitution of iron oxides by other transition metals, enhanced TOC removal performance can be achieved.[158–160] To prevent iron precipitation, the Fenton process is restricted to acidic conditions. Therefore, alternative iron-free Fenton-like processes have recently been investigated as summarized by Bokare and Choi.[161] The main advantages of the Fenton process are operation at low-costs[162] and possibility of easy magnetic separation of residual iron. The Fenton process is therefore established in several industrial full-scale applications.[163] The use of photo-active catalysts for oxidation processes in water treatment has been investigated intensively over the last decades (Photocatalytic AOPs).[164–166] Although there are numerous catalysts with photocatalytic properties (i.e., TiO_2, WO_3, or ZnO), research has mainly concentrated on two types of reactions based on the solubility of the catalyst:homogeneous photo-Fenton processes:

$$Fe(OH)^{2+} + hv \rightarrow Fe^{2+} + {}^{\blacksquare}OH$$

heterogeneous photocatalysis based on semiconductors (TiO_2):

$$TiO_2 + hv \rightarrow (e^- + h^+)$$

$$h^+ + OH_{ad}{}^- \rightarrow {}^{\blacksquare}OH_{ad}$$

UV and visible light (wavelength: 180–400 nm) accelerate the Fenton process by photoreduction of Fe(III), however, the quantum yield for this reaction is relatively low.[156] Hence, it is directly coupled with the Fenton process. Photo-Fenton processes with an organic ligand (e.g. ferrioxalate) have a higher quantum yield and thus a higher efficiency due to the high UV absorption of Fe(III)-polycarboxylates. Additionally, the ferrioxalate complex can absorb radiation up to a wavelength of $\lambda < 550$ nm, making it suitable for solar-driven AOPs.[167] A recent review of photo-Fenton applications for wastewater treatment is given by Rahim Pouran et al.[168] In TiO_2-based photocatalysis, a semiconductor material is irradiated by UV light ($\lambda < 400$ nm). It is usually investigated as suspended colloidal particles or immobilized on different substrates. If photons with sufficient energy hit the photocatalyst surface, an electron is excited to the conduction band, leaving a positively charged hole (hþ) in the valence band. These species can cause oxidative or reductive transformations of water constituents, either directly on the semiconductor surface or *via* radical reactions. A sufficient amount of dissolved oxygen is necessary for the latter reactions. The combination of oxidation and reduction mechanisms is specific for photocatalysis, whereas other AOPs are based only on $OH^{\blacksquare}$ reactions. Diclofenac degradation studies through catalytic AOPs are summarized in Table 7. Unfortunately, the quantum yield of TiO_2 photocatalysis for oxidation and reduction of contaminants is usually very low (~0.04) due to the fast recombination of electron-hole pairs.[169] The addition of an electron donor (e.g. citric acid) may lead to the "filling" of positive holes and increased reduction rates from the negative electrons in the conduction band.[170,171] Advantages of TiO_2 photocatalysis for TOC removal include low costs of the catalyst itself and easy commercial availability in various crystalline forms and particle characteristics. Furthermore, the catalyst is nontoxic and photochemically stable. The limitation of heterogeneous photo-catalysis application at full-scale is mainly based on two factors: (1) separation of colloidal catalyst from the water suspension after treatment and (2) mass transfer limitations to the surface of the immobilized catalyst on a substrate.[172] Despite strong research efforts in the field of photocatalysis, the process is rarely applied in industrial or municipal water treatment facilities because of the low quantum yield for $OH^{\blacksquare}$ production.

DCF removal through physical AOPs

Electrohydraulic discharge (Plasma) is defined as liquid-phase electrical discharge in reactors and these have been investigated as AOPs in water treatment.[173,174] Strong electric fields applied within the water (electrohydraulic discharge) or between water and gas phase (nonthermal plasma) initiate both chemical and physical processes. Diclofenac degradation studies through physical AOPs are summarized in Table 8. Besides the direct oxidation of contaminants in water, various oxidizing radicals or active species, UV radiation, and shock waves are formed during the discharge, which can promote oxidation.[175] Sonication of water by ultrasound (US) (20–500 kHz) leads to the formation and collapse of micro-bubbles from acoustical wave which induces compression and implosion. These bubbles implode violently after reaching a critical resonance size and generate transient high temperatures (>5,000 K), high pressures (>1,000 bar), and highly reactive radicals. Destruction of water contaminants occurs by thermal decomposition and various radical reactions Cavitation *via* ultrasound exhibits low interference from water matrix and less heat transfer compared to UV irradiation. A comprehensive review of sonochemical methods is provided by Pang et al.[176] Sonochemical processes have proven to oxidize various contaminants at laboratory-scale.[177,178] However, the application of ultrasound is highly energy intensive and results in a very low electrical efficiency in comparison to other technologies.[178,179] Therefore, the coupling of ultrasound with UV-irradiation (sonophotolysis), oxidants (O_3, H_2O_2), or catalysts (TiO_2) (sonocatalysis) or both (sonophotocatalysis) has received increased attention. These hybrid processes can yield additional advantages. However, major improvement of energy efficiency is often achieved due to the higher efficiency of the coupled additional processes (e.g. UV/H_2O_2 in $US/UV/H_2O_2$).[178] The application of highly energetic radiation in the microwave range (300 MHz–300 GHz) has been investigated for the oxidation of water contaminants. Microwaves have been used in combination with oxidants

(H_2O_2) or catalysts (TiO_2, GAC) to assist in the destruction of organic pollutants.[180–182] Microwaves can enhance reaction rates and induce selective heating of the contaminants through internal molecule vibration. Additionally, microwaves can generate UV radiation *via* an electrodeless discharge lamp for combined MW/UV reactors. Unfortunately, most of the applied microwave energy is converted into heat. Beside the low electrical efficiency (E_{EO} not readily available in literature), cooling devices have to be employed to prevent treated water from overheating. The utilization of ionizing radiation from an electron beam source (0.01–10 MeV) for water treatment has been tested since the 1980s. The accelerated electrons penetrate the water surface and result in the formation of electronically excited species in the water, including various ionic species and free radicals. The maximum penetration depth of the accelerated electrons is directly proportional to the energy of the incident electrons (e.g. 7 mm, reported by Nickelsen).[183] Therefore, water is irradiated in a thin film or as a sprayed aerosol. This process exhibits a high oxidizing power and little interference by the water matrix and the electrical efficiency is within the feasibility range ($E_{EO} < 3\,\text{kWh m}^{-3}$).[184] Due to the high capital costs for an electron accelerator (usually >1 million US-$), the related risk potential from X-rays, and hence the necessary security measures, further development of the electron beam process does not seem profitable.

Conclusions

In this study, a critical review of different AOPs techniques was undertaken including a mechanistic discussion of process principles and specific byproduct formation. Processes used for diclofenac removal from aqueous solutions include ozone based AOP, UV based AOP, electrochemical based AOP, catalytic based AOP and Physical based AOP. Physical based AOP, such as ultrasound, microwave, or plasma have high capital and operating costs. The Ozone AOP method has degradation efficiency up to 100%. The degradation efficiency of UV based AOP can reach up to 95%. Due to the selectivity and efficiency, ozone base AOPs with or without catalyst is considered best for diclofenac removal, as it requires minimum amount of energy. Combination of catalytic UV and ozone also seems to be promising technique. Further research should also look at the degradation of DCF by-products along with DCF degradation as little is known about by-products toxicity.

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