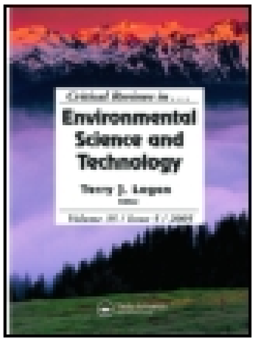

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Peracids in water treatment – a critical review

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Abstract

Peracids have gained interest in the water treatment over the last few decades. Peracetic acid (CH_3CO_3H) has already become an accepted alternative disinfectant in wastewater disinfection whereas performic acid (CHO_3H) has been studied much less, although it is also already commercially available. Peracids have also been tested for drinking water disinfection, oxidation of aqueous (micro)pollutants, sludge treatment and ballast water treatment, to name just a few examples. The purpose of this review paper is to represent comprehensive up-to-date information about the water treatment applications, aqueous reaction mechanisms, and disinfection by-product formation of peracids, namely performic, peracetic and perpropionic acids.

Keywords

peracetic acid; performic acid; disinfection; oxidation; water treatment

1. Background and physicochemical properties

Peracetic acid (PAA, CH_3CO_3H) and performic acid (PFA, HCO_3H) are industrially the most relevant peracids (or formally percarboxylic acids) since they have the highest oxidation potential [1]. Both chemicals were prepared for the first time in 1900–1910 and soon after their sterilizing and disinfecting properties were reported [2-4]. However, the interest towards the water and wastewater treatment applications emerged much later: for PAA in the late 1970's and early 1980´s and for PFA in 2000's [5-11]. One of the main drivers in this development has been the increased awareness of disinfection by-products (DBPs) resulting from the use of chlorine compounds. PFA and PAA might have also potential to replace several other industrial biocides with undesirable properties, such as formaldehyde, bromine, or isothiazoline. Furthermore, PAA and PFA have several of the qualities of an ideal disinfectant: toxicity to microorganisms, but not to higher forms of life; effectivity at ambient temperatures; stability and long shelf-life; low corrosivity; deodorizing ability; widespread availability and reasonable cost [12].

PAA and PFA are colorless liquids with characteristic pungent odors. Both are thermodynamically unstable and can decompose spontaneously or explode when highly concentrated, heated, under mechanical stress or exposed to catalytic effects of impurities [1, 13, 14]. The recommended storage temperatures are below 30 and 20°C for PAA and PFA, respectively [6, 14]. Longer carbon chain length increases stability, and thus PAA is more stable than PFA [1]. However, the O-O bond dissociation energy of PFA and PAA has been calculated to be similar: 48 kcal/mol [15]. Percarboxylic acids have typically pK_a values 3–4 units higher than the parent carboxylic acids [1]. Nonetheless, PFA and PAA are corrosive [16].

Exposure to PAA and PFA causes irritation and possibly permanent damage to the skin (cutaneous emphysema), eyes and the respiratory system. In the skin contact, 0.2% is proposed as the no-observed-effect concentration (NOEC) for short and medium length exposure [17]. When inhaled, airborne concentrations less than 0.16–0.17 ppm (0.50–0.52 mg/m^3) are considered to cause no irritation [17, 18]. However, higher concentrations are harmful and a case study suggested that PAA could cause occupational asthma [19].

The largest users of PAA on a global scale (estimated in 2013) are shown in Fig. 1. Similar numbers are not available for PFA, but it is probably used at significantly lower quantities.

The largest user, the food industry, applies PAA as a disinfectant in fresh produce washing water, clean-in-place (CIP) processes, on food processing equipment, and in pasteurizers, to name just a few examples [21, 22]. PFA is also a suitable disinfectant in low-temperature refrigerated food processing and storage rooms [23]. In healthcare, PAA is used for instance in the sterilization of endoscopes [24] and the disinfection of surfaces in hospitals [25]. In the industrial production of fine chemicals, PFA and PAA are used for epoxidation, hydroxylation and for the conversion of ketones to esters, for instance [26]. Ripin et al. [27] demonstrated that PFA can be safely used on multi-kilogram scale to oxidize thioacetate. Total chlorine free (TCF) processing of pulp uses distilled PAA (at approx. 40% concentration, stored at -6 to -10 °C) as a bleaching agent when high brightness is required [28]. PAA and PFA are also used as a biocide in paper mill process waters [29-31].

Wastewater disinfection by PAA has been reviewed a decade ago by Kitis [32]. However, no review about the use of PFA in the wastewater disinfection and about the oxidation of (micro)pollutants by PAA and PFA exists. Consequently, the purpose of this review is to present updated and extended (waste)water treatment related information regarding PAA, present the current information about PFA, and compare these two chemicals. Also, the existing scarce information about perpropionic acid (PPA) in the water treatment sector is presented.

2. Synthesis

PAA is available on the market as an equilibrium solution with acetic acid and hydrogen peroxide (H_2O_2), whereas PFA has to be always prepared on-site and preferably continuously due to instability and safety reasons [33]. The concentrations of PAA and PFA in the equilibrium solution are typically 5–15 and 8–13.5% as the active ingredient, respectively [34, 35].

The most common preparation method is by mixing the corresponding carboxylic acid and H_2O_2 according to Reaction 1 (this reaction is referred to as perhydrolysis) [1]. The exact reaction mechanisms for PAA and PFA formation are discussed by several authors [36-38]. Furthermore, the detailed kinetic analyses of Reaction 1 in the cases of PFA [33, 37, 39], PAA [36], and PPA [40] are available.

$$\text{R-COOH} + H_2O_2 \overset{H^+}{\leftrightarrow} \text{R-COOOH} + H_2O \qquad (1)$$

Leveneur et al. [33] described the energy balance of perhydrolysis and decomposition of PFA. The equilibrium constant for Reaction 1 in the case of PAA has been reported to be 2.10–2.91 1/M at room temperature (20–22°C) [41, 42]. Reaction 1 can be acid-catalyzed by sulfuric acid, ascorbic acid, boric acid or acidic ion-exchange resin, for instance [33, 43-47]. However, PFA synthesis does not necessarily require any additional catalyst, since formic acid can provide an adequate amount of hydrogen ions (formic acid-autocatalyzed synthesis of PFA) [1, 3, 37]. Higher peracid concentrations at the equilibrium can be obtained, if the molar ratio of carboxylic acid to H_2O_2 or H_2O_2 concentration is increased [1, 42]. Finally, very high concentrations of anhydrous peracids can be achieved by using for example aliphatic esters as the solvent and azeotropically removing water to drive Reaction 1 to completion [48].

Commercial solutions of PAA are stabilized with compounds, such as alkali metal polyphosphates, dipicolinic acid or quinoline derivatives [49, 50]. Furthermore, the safety hazards of peracids can be reduced by inert additives such as water, certain solvents (aliphatic and halogenated hydrocarbons, phthalate and phosphate esters, acetals), and inorganic solids (sulfates, phosphates, borates, silicates, carbonates) [1].

One of the commercially available on-site PFA production systems (Desinfix, Kemira, Finland) consists of reagent (35–50% H_2O_2 and 70–90% formic acid) storages and diaphragm pumps feeding reagents to a tubular reactor submerged in a thermostatic bath [34]. Temperature, pressure, liquid levels, and flow rates are automatically controlled and if the set threshold values are exceeded, the system automatically stops and the reactor is flushed with water [34]. Pressure relief is considered one of the most important safety controls with PFA synthesis [33]. Microreactor technology (i.e., the reactor dimensions in the range of sub-micrometer to sub-millimeter) has been studied for the production of both PFA [51-54] and PAA [45]. The main advantages of such systems are their smaller equipment size, lower levels of energy consumption, smaller amounts of waste production, and improved safety [54, 55]. Furthermore, the use of ultrasound can improve the peracid formation rate [45]. Recently, PFA was also synthesized through a plasma induced chemical reaction: the water-sealed dielectric barrier discharge of atmospheric CO_2 without catalyst and under atmospheric pressure [56, 57].

A summary of total 14 different synthesis pathways of peracids was presented by Klenk et al. [1]. However, most of those reactions are not commercially important or they produce peracids in other media than water, which might not be suitable for (waste)water treatment applications.

3. Concentration determination methods

3.1. Concentrated solutions

Redox titrations are one of the most widely used methods for the analysis of concentrated peracid solutions. These titrations are usually biphasic where H_2O_2 is first titrated, for example, with permanganate [58] or cerium(IV) sulfate [59] followed by an iodometric titration to quantify the peracid. A disadvantage of the method is the strongly acidic solution pH, in which H_2O_2 can come to equilibrium with the peracid and thus changing the composition of the solution during titration. This is avoided by working at low temperatures (< 10°C). Alternatively, the much faster reaction between iodide and peracid can be used by titrating several times with thiosulphate, then plotting the consumption of thiosulphate as a function of time and extrapolating to zero to obtain a value corresponding to the amount of peracid [60]. H_2O_2 can be also eliminated before peracid determination by the addition of a catalase enzyme [61]. Simple acid-base titration with NaOH can be used to determine both PAA and acetic acid due to their different pK_a values and when no other weak acids cause interference [62].

3.2. Applied and residual peracid concentrations

It is important to be able to reliably determine applied and residual concentrations of peracids from wastewater (in the mg/L range). For example, Cavallini et al. [63] and Gehr at al. [6] presented modified cerimetric-iodometric titration methods suitable for determining low concentrations of PAA and PFA.

Other commonly used methods involve spectrophotometry. Excess iodide is added; iodine is formed proportionally to the peracid concentration; and iodine reacts with N,N-diethyl-p-phenylenediamine (DPD) or a methyl-substituted form of DPD, which are determined at 530 or 565 nm, respectively [61, 63]. Also 2,2'-Azino-bis-(3-ethyl-benzthiazoline-6-sulfonate) diammonium salt (i.e., ABTS) together with peroxidase enzyme can be used to determine PAA at 405 nm after hydrogen peroxide removal with catalase [64]. In an alternative method, excess iodide is added; absorbance is measured at 352 nm every 1 s for 5 s; absorbance versus time is plotted; and the peracid concentration can be calculated by the absorbance at time zero [65].

Gas chromatography [66-68] and high performance liquid chromatography (HPLC) [69-71] have been used for the determination of very low concentrations of PAA in, for example, atmospheric samples. Electroanalytical methods of peracid determination include potentiometry and voltammetry. In one method, potentiometric determination of PAA (with the detection limit in the µM range, at approx. 0.076 mg/L) is based on the potential change in an iodide/iodine solution, in which peracid and H_2O_2 react with iodide [72]. Since the response times for PAA and H_2O_2 are a few seconds and several minutes, respectively, they can both be determined [73]. Hua et al. [74] developed a selective amperometric sensor for PAA (a linear range of 3.1 µM–1.5

mM, approx. 0.24–114 mg/L), which is based on polybenzimidazole-modified gold electrode (PBI/Au): PAA oxidizes imine to PBI N-oxide which increases the reduction current in cyclic voltammetry. Finally, simultaneous determination of H_2O_2 and PAA (with a detection limit of 0.2–0.3 mM, approx. 15–23 mg/L) was studied by a triple pulse amperometric approach involving Pt and Au electrodes [75].

PAA can also be measured on-line. For example, one commercial system involves a membrane capped two-electrode censor based on amperometry: the accuracy was reported to be ±3%, ±8%, and ±15% at 1, 0.5, and 0.25 mg/L PAA concentrations, respectively [76]. Another continuous method uses a reagent-free optical biosensor based on the determination of absorption of intermediate compounds resulting from a reaction between peroxidase and H_2O_2 or PAA: the biosensor can be used for approx. 3 months, for over 200 measurements, and it has linear range from 2×10^{-7} to 1.5×10^{-5} M (approx. 0.015–1.141 mg/L PAA), and a precision of 4% as the relative standard deviation [77].

Recently, methods to determine the residual PAA from wastewater were compared: the spectrophotometric method using DPD and catalase was recommended for 0.1–0.5 mg/L PAA concentrations and the cerimetric/iodometric titration or the DPD method were suitable for 0.5–10 mg/L PAA [63]. The iodometric titration with the catalase addition [61] could be used between 1–5 mg/L PAA, whereas the permanganometric/iodometric titration was not recommended at all [63].

4. Reactions in aqueous media: disinfection and oxidation mechanisms

The (waste)water disinfection and oxidation of aqueous (micro)pollutants by peracids are based on the formation of highly oxidative radical species, such as the hydroxyl radical (HO·), the superoxide anion ($\cdot O_2^-$), the hydroperoxyl radical ($HO_2\cdot$), acyl, and peracyl radicals [78]. These radicals are together referred to as reactive oxygen species (ROS). Also a direct reaction between peracid and the target molecule or the formation of secondary oxidants is possible [79].

In the case of PAA, the radical formation can be presented by Equations 2–8 [15, 80]. The first and the rate-determining step is the homolysis of the oxygen-oxygen bond (Reaction 2), which requires activation by a transition metal catalyst, UV irradiation, or activated carbon, for instance [81-84].

$CH_3COOOH \rightarrow CH_3COO\cdot + HO\cdot$ (2)

$CH_3COOOH + HO\cdot \rightarrow CH_3CO\cdot + O_2 + H_2O$ (3)

$CH_3COOOH + HO\cdot \rightarrow CH_3COOO\cdot + H_2O$ (4)

$CH_3COO\cdot \rightarrow \cdot CH_3 + CO_2$ (5)

$2CH_3COO\cdot \rightarrow 2\cdot CH_3\cdot + 2CO + O_2$ (6)

$\cdot CH_3 + O_2 \rightarrow CH_3OO\cdot$ (7)

$CH_3COO\cdot + HO\cdot \rightarrow CH_3COOOH$ (8)

All of the generated radicals contribute to the oxidation reactions, but HO·, peracetyl radical ($CH_3COO\cdot$), and to a lesser extent the methyl radical ($\cdot CH_3$) have been suggested to be the most important [80, 85]. However, $\cdot CH_3$ is of limited availability due to the lower reaction rate constant compared to HO· and the reaction with oxygen (Reaction 7) [78, 80]. On the other hand, organic radicals have longer half-lives than HO·, and some have argued that they are therefore more effective in antimicrobial action [86, 87]. It has also been suggested that the organic part of the peracid molecule might help to penetrate into microbial cells [88].

The diffusion of HO· is slower than its half-life and consequently it reacts with any oxidizable macromolecules, such carbohydrates, nucleic acids (mutations), lipids (lipid peroxidation) and amino acids (e.g. conversion of Phe to m-Tyr and o-Tyr) [89]. The specific reactions of PFA have not yet been reported, but it could be speculated that they proceed in a similar fashion as with PAA.

Several types of specific damage to biomolecules by peracetic acid have been described by [32] and the references therein:

- Sulfhydryl (-SH), disulfide (S-S), and double bonds in proteins, enzymes, and other biomolecules are oxidized.
- Inactivation of the catalase enzyme, which inhibits hydroxyl radical oxidation.
- Chemiosmotic function of the lipoprotein cytoplasmic membrane is disrupted.
- Protein denaturation occurs.
- Bases of the DNA molecule react adversely.

Cysteine, tryptophan, and methionine were the most vulnerable amino acids for degradation during PAA treatment when dairy proteins were exposed to oxidation [90]. Intracellular PAA has been suggested to oxidize essential enzymes [91] and this was later confirmed, as B-galactosidase activity was suppressed by PAA [92]. Peracetic acid is also able to inactivate the peroxidase enzyme [93]. Bacteria are unable to recover from the damage caused by PAA and no re-growth takes place [94]. Virus inactivation by PAA may occur by a damage to the virus surface structures, such as the protein coat of the sites needed for the infection of the host cells [88]. The rate of virus inactivation by PAA decreased when viruses were present as aggregates [95]. This was explained by the possible blockage of viral pores; a reduction of void spaces between viruses; adsorption of PAA on the viral proteins; and consumption of PAA during diffusion through the aggregate [95]. Interestingly, chloride was found to be necessary for the inactivation of MS2 coliphages by PAA [95]. Chloride has also been suggested to accelerate PAA action as a hard surface cleaner [96].

The disinfection activities of PAA or PFA are hindered, if pH is alkaline or neutral, since these peracids are present as negatively charged under those conditions (pK_a values for PFA and PAA are 7.1 [97] and 8.2 [36], respectively) [98].

H_2O_2 in the peracid equilibrium solution has a synergistic effect on the disinfection mechanism: it is an additional source of hydroxyl radicals [85]. However, hydrogen peroxide alone at applicable concentrations is a relatively ineffective disinfectant and oxidant, because catalase enzyme is able to protect microorganisms from its action [81, 88, 99, 100]. As a result, the initial inactivation of catalase by peracid is required to achieve the synergistic effect.

The factors affecting the decomposition rate of peracids are its dosed concentration, the application mode, temperature, pH, the amount of organic material, the presence of solids or transition metal ions, salinity and water hardness [61, 92, 101-105]. Furthermore, the peracid formulation, namely the peracid/H_2O_2 ratio and possible stabilizers have an effect on the decomposition rate [104]. In a concentrated solution, the decomposition of peracid occurs by three mechanisms: hydrolysis, spontaneous decomposition, and transition-metal catalyzed decomposition (Reactions 9, 10, and 11, respectively) [106-108]. The kinetics and exact reaction mechanisms of the spontaneous decomposition and hydrolysis were presented by Zhao et al. [36, 109].

$$\text{R-COOOH} + H_2O \rightarrow \text{R-COOH} + H_2O_2 \quad (9)$$

$$\text{R-COOOH} \rightarrow \text{R-COOH} + \tfrac{1}{2}O_2 \quad (10)$$

$$\text{R-COOOH} \xrightarrow{M^+} \text{R-COOH} + \tfrac{1}{2}O_2 + \text{other products} \quad (11)$$

The decomposition of PAA by Mn^{2+} with or without the presence of a chelating agent was shown to proceed via complicated redox reactions (several Mn oxidation states present) instead of a simple radical pathway [110]. Similar results were also obtained when Mn^{2+} was used as a catalyst in dye degradation by PAA [79]. Co^{2+}/Co^{3+}, on the other hand, resulted PAA to decompose to acetyl ($CH_3COO\cdot$) and peracetyl ($CH_3COOO\cdot$) radicals, whereas no hydroxyl radical formation was detected [111].

High phosphate concentrations (15 mM ≈ 28 mg/L) was found to decrease the inactivation rate of viruses by PAA, which could be explained by the reported radical quenching capacity of phosphate [95].

The aqueous decomposition of PAA [61, 112-114] and PFA [16] can be generally modelled by using the first-order kinetic rate law after the frequently observed initial decay of peracids has taken place. The rate constants have varied between 0.0028–0.0396 and 0.007–0.012 1/min in the cases of PAA and PFA, respectively, depending on the water quality (Table 1). However, occasionally zero-order kinetics has also been reported for PAA with the corresponding rate constants between 0.010–0.042 mg/(L min) [16, 115]. The half-lives are in the case of PAA between 18–710 min with the shortest times reported in primary effluent and the longest in potable water [116].

5. Disinfection

5.1. Comparison of peracids to other disinfection methods

PAA and hypochlorite has been observed to have approximately similar disinfection efficiency against typical indicator bacteria (such as total and fecal coliforms or *E. coli*) [117-119], total bacteria count [120], and some more resistant microorganisms (such as *Cryptosporidium, Giardia, and Cl. perfingens*) [121]. Also in biofouling control against *M. leucophaeata* and *D. polymorpha*, PAA and hypochlorite were found to be comparable [122]. PAA was found to be more effective than hypochlorite against *V. cholera* [123]. However, fecal streptococci and coliphages were more effectively inactivated by hypochlorite than by PAA [119]. Somewhat different results were obtained by Mezzanotte et al. [124], who compared sodium hypochlorite, ozone, PAA and UV: their results suggested that the required doses and contact times in order to obtain a similar logarithmic inactivation (4–5 $\log_{10}$) of *E. coli*, fecal, or total coliforms were the lowest for ozone (3.6 mg/L, 12.8 min) followed by hypochlorite (7.5 mg/L, 18 min), whereas PAA (15 mg/L, 36 min) was the least efficient. UV disinfection was the most efficient, as it resulted in total inactivation in a few seconds using a dose of 10–20 mJ/cm^2 [124].

Ozone has been frequently reported to be more effective than PAA [124-126]. However, ozone disinfection is considered technically complex; it requires high investment costs; and the release of gaseous ozone from the disinfection unit needs to be controlled. PAA is advantageous over ozone especially when the need to disinfect is irregular. The operation and maintenance costs of ozone system (at a dose of 15 mg/L) has been calculated to be lower than with PAA (at a dose of 10 mg/L) [127].

UV has often been concluded to be more effective in terms of disinfection efficiency [124, 127]. However, the physico-chemical quality of wastewater has a strong effect on UV disinfection efficiency and consequently PAA and UV have been occasionally reported to be also more or less similar in terms of efficiency [125, 126]. For example, when disinfecting primary effluent, 1–6 mJ/cm^2 UV dose was unable to reach the fecal coliform goal of 240 MPN / 100 mL, whereas PAA (10 mg/L, 15 min) was successful [128]. The damage caused by UV to the DNA molecule can be repaired by enzymatic mechanisms known as photoreactivation and dark repair, but this is usually considered insignificant when using a UV dose higher than 60 mJ/cm^2 [129].

Chlorine dioxide has been reported to be either more effective than PAA [126] or similar [130] in terms of disinfection efficiency against typical bacterial indicators. Contradicting results were obtained by De Luca et al. [131], who concluded PAA to be preferable to chlorine dioxide, since it was less affected by organic matter, had a better disinfection efficiency, and was more economical and easier to apply. Chlorine dioxide needs to be prepared in situ, which makes the process more complicated. Furthermore, chlorine dioxide is capable of producing disinfection by-products [132].

In addition to the aforementioned disinfection methods, peracids might have potential to replace some industrially used biocides, such as formaldehyde, bromine, or isothiazoline. However, no direct comparison data in water treatment applications has been published.

5.2. Municipal wastewater effluents

5.2.1. Combined sewer overflow

Combined sewer overflow (CSO) occurs when the increased rainfall causes water levels to exceed the design capacity in sewer systems, where wastewater and rain water are transported together. The surplus effluent needs to be discharged either directly or after retention in tanks or outfall pipes and this poses potential contamination risks for the receiving water body [133]. The USEPA lists PAA as one of the potential alternative disinfectants to be used for the treatment of CSO [134]. The disinfection efficiency and decomposition kinetics of PAA (at 2–10 mg/L, a contact time of 60 mins) could be clearly improved with the pre-treatment of CSO by hydrocyclone and coagulation before PAA disinfection [135]. However, in a recent comparison study, PFA required a significantly shorter contact time than PAA: 20 and 360 mins, respectively, when a similar dose (2–5 mg/L) was used [136]. PFA was also studied in a full-scale experiment (1–8 mg/L and a contact time of 24 mins), which confirmed that the EU bathing water microbial quality was possible to be reached with the method after taking into account dilution to the receiving water body [137]. Tondera et al. [35] used PFA (at 12–24 mg/L, and with a 10-minute contact time) for CSO and obtained a 1.8–3.1 $\log_{10}$ reduction of *E. coli*, total coliform bacteria, intestinal enterococci, *Aeromonas* s, *P. aeruginosa*, and somatic coliphages, whereas *G. lamblia* and human viruses (human adenovirus, polyomavirus, norovirus, rotavirus, and enterovirus) were not inactivated. The application mode of PFA and PAA would be as continuously dosed only during the CSO event. Consequently, the irregular nature of CSO disinfection requirements might compromise the feasibility of PAA and especially PFA, since the chemicals need to be possibly stored for a long time and be still readily usable at any given moment.

5.2.2. Primary, secondary, and tertiary wastewater effluents

Primary wastewater typically contains large amounts of organic matter and suspended solids, which hinder all the disinfection processes. The required continuous PAA doses and contact times were in the ranges of 10–20 mg/L and 15–30 min, respectively, in order to reach a 2–6.5 $\log_{10}$ reduction for enteric bacteria [102, 138]. In another study, a dose of 4.5–6 mg/L of PAA with a contact time of 1 hour did not reach the 9000 CFU/100 mL target of fecal coliforms in the primary effluent [125]. PFA, on the other hand, reached a 3-$\log_{10}$ removal of fecal coliforms with a dose of 3.4 mg/L and a contact time of 45 mins in primary effluent, this clearly indicates a higher efficiency for PFA than for PAA [6]. If peracids are dosed at the beginning of the wastewater treatment process, it is important to consider their effect on biological treatment: nitrifying bacteria were only transiently disturbed by PAA at a 1.0 mg/L concentration [114]. However, higher doses might pose a risk for the functionality of biological processes.

Secondary treatment of wastewater typically includes biological treatment steps and sedimentation. Organic matter and suspended solids are subsequently reduced, which improves the peracid disinfection efficiency. After this phase, the tertiary treatment of wastewater can be implemented via sand filtration, flotation, or coagulation-flocculation. Slightly better disinfection results have been achieved in tertiary effluents when compared to secondary effluents, this is likely due to lower amounts of organics and initial bacteria amount present in the tertiary effluent

[138]. The combination of tertiary treatment and disinfection can be referred to as the multiple barrier concept, which has been shown to be the most effective approach for disinfection [126, 127]. The required doses and contact times for the disinfection of secondary effluents with PAA vary within the range of 0.6–10 mg/L and 10–60 mins, respectively (see Table 2). PAA (at 1.5 mg/L, and with a contact time of 20 mins) reduced F specific or somatic coliphages by approx. 0.5 $\log_{10}$ units in a secondary effluent [139]. It has been noticed that qPCR (quantitative polymerase chain reaction) might overestimate the survival of pathogens after PAA treatment [140]. PFA, on the other hand, typically requires 0.4–2 mg/L and 5–10 mins for secondary effluents when inactivating bacterial indicators, whereas resistant *Clostridium* and *Giardia* required larger doses [34, 141]. The PAA doses and contact times for tertiary effluents vary within the range of 1.5–15 mg/L and 10–36 mins, respectively (see Table 2). Aluminium and iron salts in combination with PAA (3 or 5 mg/L with a contact time of 5 mins) have proven to be effective in tertiary treatment: especially non-sporing bacteria (such as campylobacteria) were eliminated effectively, whereas sporing bacteria (such as clostridia) and F-specific coliphage were more resistant [142]. Furthermore, no reduction in the number of noroviruses, rotaviruses, or adenoviruses as a result of PAA treatment of tertiary effluent was observed [142]. Recently PAA disinfection was studied in combination with the sequential batch biofilter granular reactor (SBBGR) and it was found that with a dose of 1 mg/L of PAA it was possible to reach *E. coli* $<$ 10 CFU / 100 mL [143]. Furthermore, SBBGR was able to reduce the amount of antibiotic resistance genes (ARGs), whereas the PAA had no impact on ARGs [144].

5.3. Sludge

Wastewater sludge, which is nowadays frequently referred to as biosolids, can be treated with peracids to provide disinfection, pre-oxidation before digestion, and improved dewatering. The application mode of peracids in the sludge treatment could be either continuous or batch dosing. The required dose of PAA in order to remove *Salmonella* bacteria from municipal wastewater sludge was 250–500 mg/L [8, 91]. The PAA dose that is required to remove worm eggs is significantly higher: 500–6000 mg/L [155]. On the other hand, beef tapeworm (*Taenia saginata*) removal required 250–1000 mg/L of PAA [91]. Possible process phases for continuous peracid dosing in sludge treatment are gravity thickening, transportation to a treatment plant, or after digestion [91, 155, 156]. In fact, PAA (at 25 g/kg of dry solids) can also be used as a pre-oxidation agent before anaerobic digestion: solubilization of organic matter, an increase in biogas production by up to 21%, and increased formation of volatile fatty acids were observed [157]. The application of PAA for sludge treatment resulted in readily biodegradable and non-toxic products, and the process did not interfere with sludge humus improvement properties in soil constitution [32, 91]. Furthermore, pre-oxidation with PAA (0.06–0.36 g/g of total solids, 2 h mixing) was found to promote the degradation of extracellular polymeric substances, which in turn decreases sludge volume and improves dewatering [158]. Another important feature is that PAA can remove odors caused by low oxidation state sulfur compounds, such as hydrogen sulfide or mercaptans [91, 159]. However, PAA does not react with ammonia [91]. Moreover, the use of hydrogen peroxide (a component of peracid solutions) for odor abatement is quite common [160]. Finally, PAA (0.5–1%) was found to be a promising alternative for the disinfection of separated fecal matter for nutrient recycling, although the required dose was high [161].

5.4. Industrial effluents

PAA has been used as a cooling water biocide [32, 162], as it has a good potential for the removal of *Legionella pneumophila* [142, 163-165]. The continuous doses used for *Legionella* removal varied considerably (3–1000 mg/L) and re-growth after treatment was reported [142, 163-165]. A potentially effective approach for the long-term *Legionella* control could be an initial high-shock dose, with a smaller, continuous dose administered afterwards [8]. However, the high PAA doses required for Legionella removal could cause also corrosion problems due to the decreased pH [16, 163]. PAA has also been applied for the disinfection of ion-exchangers [50] and membrane hollow fibers [32]. As for other uses, both PFA and PAA have been applied to control microbial growth in paper mill process waters [30, 31], and PFA has been used for the fouling control of reverse osmosis membranes [166]. PAA is also compatible with almost all organic ultrafiltration membranes, but for example cellulose acetate and polyvinylidene fluoride can tolerate only up to 75 mg/L PAA concentrations [167].

5.5. Potable water

Peracids are not yet applied for the disinfection of surface or ground waters, although several studies on the topic exist. One reason may be the risk of biofilm formation, which increases as a result of residual carboxylic acids after peracid disinfection [168]. PAA has been recommended as a replacement for pre-chlorination, which is used at some surface water plants as the first unit process [169]. The use of PAA (doses of 0.2–1.0 mg/L) for surface water disinfection showed promising results in terms of disinfection efficiency and by-product formation [170]. Sodium hypochlorite threshold flavour and odor concentrations (0.04 and 0.23 mg/L, respectively) in potable water are much lower than with PAA (6 and 11 mg/L, respectively), this indicates that PAA disinfection has a lower tendency to produce unpleasant taste and/or odor for potable water [171]. Furthermore, a 0.8–1.6 mg/L concentration of PAA was proposed to be sufficient as a residual disinfectant [171]. PAA disinfection (at a dose of 4–5 mg/L and a contact time of 15 mins) was a promising method for the remediation of groundwater contaminated with sewage [172]. In another case, groundwater contaminated with wastewater required 2 mg/L of PAA and 10 minutes of contact time to eliminate fecal and total coliforms [173]. On the basis of the aforementioned studies, PAA seems to be a promising disinfectant for potable water and no exclusionary reasons preventing its widespread use have arisen. Currently, no studies are available about the use of PFA for potable water disinfection.

5.6. Ballast water

Ballast water of cargo and other ships has been recognized as a significant source of invasive species and non-indigenous microorganism contamination in the marine environment [174]. Consequently, ships are required to minimize the risk of invasive species and various treatment methods have been suggested [175]. One commercial system employs a hydrocyclone, a 50 µm self-cleaning filter, and dosing of PAA (150 mg/L) [176]. The role of PAA in this system is to eliminate phytoplankton and bacteria, for instance, while larger organisms are removed in the mechanical treatment [176]. PAA proved to be the most effective bactericide, but less effective against zooplankton and microalgae when compared to menadione and alkylamine-based commercial ballast water biocides [177]. Residual toxicity in the treated water was noticed after 24 hours of disinfectant application [177]. When treating saline ballast water with PAA, there is a possibility of brominated or chlorinated DBP formation, which can be minimized by the presence and a higher concentration of H_2O_2 [178]. Some commercial PAA-based ballast water treatment systems dose catalase or thiosulphate together or after PAA dosing to prevent the discharge of H_2O_2 to the aquatic environment: this practice could pose a risk to DBP formation [178].

5.7. Disinfection kinetics

The disinfection kinetics of PFA and PAA have been successfully modelled by the Hom model [179] (Reaction 12) or the S model [180] (Reaction 13), which are demand-free condition models (i.e., the disinfectant concentration is assumed to be constant during the process) [181]. A summary of the reported PFA and PAA disinfection kinetics parameters in the literature is shown in Table 3. Also the inactivation kinetics of *Staphylococcus aureus* and *Pseudomonas aeruginosa* by PAA were able to be modelled by the Hom model [182].

$$ln\frac{N_t}{N_0} = -k_H C^n t^m \tag{12}$$

where N_t is the number of microorganisms at time t (min), N_0 is the initial number of microorganisms, k_H is the rate constant (its unit depends on the value of n and m), C (mg/L) is the initial concentration of peracid, and the parameters n and m affect the curvature of the $\ln(N_t/N_0)$ vs t plot: m > 1, the survival curve displays an initial shoulder; m = n = 1, the equation simplifies to the traditional Chick-Watson model [183, 184]; m < 1, the survival curve displays a tailing-off effect. It has been suggested that the Hom model is suitable for assessing the use of peracetic acid when its dose is over 5 mg/L [113].

If the survival curve has a characteristic S shape, consisting of three distinct phases: initial resistance, exponential inactivation, and asymptotic inactivation, the process can be modelled by the S model (Equation 13) [180].

$$ln\frac{N_t}{N_0} = -\frac{k_S C^n}{1+(\frac{h}{Ct})^m} \qquad (13)$$

where k_S is the rate constant (its unit depends on the value of n) and h ((mg min)/L) is an additional model parameter. The S-model has been proposed to be especially suitable for PAA disinfection involving concentrations lower than 5 mg/L [113]. The S-model has been developed for situations where either a resistance to diffusion into the cell membrane or microbial aggregates hinder the disinfection process. At high PAA concentrations employed, the diffusion resistance has been found to be negligible [113]. In addition to the Hom and S-models, also the Monod type equation [115] or diphasic decrease kinetic models [102, 127] have been used occasionally.

Few attempts have been made to model peracid disinfection by disinfectant demand condition models (i.e., the disinfectant concentration decreases during the process). The demand condition models give a more realistic view on the disinfection and the peracid consumption is also expected to have an effect on the treatment efficacy. Falsanisi et al. [61] used the modified Haas and Joffe´s approximate expression [185]. Santoro et al. [148] concluded that the Power Law or the Hom-Power Law models could be the most suitable disinfection kinetics models taking into account the disinfectant decay.

5.8. Advanced oxidation processes for disinfection

In advanced oxidation processes (AOPs), the radical formation is enhanced either by combining two methods, such as UV/H_2O_2 or O_3/H_2O_2, or by using a catalyst, such as the Fenton oxidation (Fe^{2+}/H_2O_2) [187]. The combination of UV and peracids has synergistic effects [81, 88, 188, 189]. For instance, the synergy value for the UV/PAA treatment was 2 $\log_{10}$ units in one study (i.e., the combined efficiency was 2 $\log_{10}$ units higher than by directly summing up the individual $\log_{10}$ inactivation values) [88]. In the case of viruses, the synergy is slightly lower than with bacteria [88, 190]. Rajala-Mustonen et al. [190] allowed PAA to be in contact with wastewater for 10 mins before applying UV; they also noted that RNA phages were less effectively inactivated than DNA phages by PAA. However, from the cost parity point of view, UV/H_2O_2 and UV/PAA disinfection were claimed to be similar [188]. The advantages of UV/PAA treatment are irreversible damage to microorganisms; a lower dependency on wastewater quality than with UV; better disinfection results on a wider scale of microorganisms; a lower peracid dose and contact time is needed; a smaller UV unit is needed; and cost-competitiveness could be attractive, especially in the case of large facilities [88, 189]. The tested UV and PAA doses in the combined treatment have been in the range of 10–300 mW/cm^2 and 0.5–15 mg/L, respectively [88, 188, 189]. For a comparison, the UV doses of regular wastewater disinfection systems, according to the guidelines, are 50, 80, and 100 mW/cm^2 for membrane filtration effluent, granular medium filtration effluent, and reclaimed water systems, respectively [12].

Luna-Pabello et al. [191] studied the use of Ag^+/PAA and Ag^+/Cu^{2+}/PAA combinations and observed disinfection synergy: for example the helminth egg (HE) requirement (≤ 1 HE/L) for agricultural reuse [192] could be reached in raw wastewater with a combination of 0.6, 1.2, and 2.0 mg/L of Ag^+, Cu^{2+}, and PAA, respectively. Supporting results were also obtained earlier by De Velásquez et al. [193]: the synergy between Ag^+/PAA was noticed in the removal of *V. cholera*, *Salmonella* s, *Shigella*, *P. aeruginosa*, helminth eggs, and fecal coliforms. Interestingly, Ag^+/PAA was more effective than Ag^+/Cu^{2+}/PAA against fecal coliforms [191]. One major advantage is that the addition of Cu and/or Ag ions decreases the required contact time [191, 193]. The proposed mechanism of the synergistic action is the oxidation of Ag and Cu to unstable and more toxic forms (such as Ag_2O, Ag_2O_2, or Cu_2O), in addition to the increased *in situ* formation of radicals [191]. It is known that the oxidized forms, such as trivalent silver, are significantly faster and more effective disinfectants than monovalent silver [194]. However, the economic feasibility of silver or copper addition together with peracids has not been evaluated. Also, the addition of soluble metals could cause secondary contamination in water bodies. Finally, bacteria are able to develop resistance against Ag and Cu, which also poses a risk [195].

5.9. Costs of disinfection

Analysis of the cost of peracid-based disinfection is not straightforward as it depends on several case-specific factors, such as the required microbial quality, the availability of chemicals and the physico-chemical properties of wastewater. The price levels of chemicals are approx. 830 €/t for on-site-produced PFA solution (9%) and 1100–1200 €/t for an equilibrium PAA (12%) solution [16]. The price of the PAA chemical is almost ten times higher than chlorine gas [118]. The cost of PAA disinfection per amount of treated municipal wastewater has been estimated to be 0.0200–0.0645 €/m^3 [16, 127, 196, 197], whereas the corresponding cost of PFA disinfection was reported to be 0.010–0.011 €/m^3 [16, 198]. The investment costs of PFA and PAA systems (e.g., chemical production unit for PFA [34], dosing equipment, and contact tanks) are estimated to be 0.05 M€ (up to 200 000 m^3/d capacity plants) and 0.015–4.4 M€ (3000 – 200 000 m^3/d capacity plants), respectively [16, 146]. According to Collivignarelli et al. [146], the investment costs of disinfection systems for biologically treated municipal wastewater are (from the highest to the lowest): UV > ozone > PAA > chlorine dioxide. In another study, the investment costs of a PAA system (including equipment, construction, electricity, automation, and overheads) were estimated to be 0.4 M€ for a 24 000 m^3/d capacity plant with an additional annual investment cost of 0.052 M€ [197]. As a result, PAA could be economically competitive, especially at relatively small wastewater treatment plants, whereas PFA becomes clearly more cost-efficient as the capacity of the plant increases [16]. If PAA is used together with UV, the cost of the combined treatment is approx. 0.031 €/m^3 (in order to reach a 6-log$_{10}$ reduction of total coliforms in secondary municipal effluent, at a PAA dose of 1 mg/L and a UV dose of 200 mJ/cm^2) [189]. Finally, PPA disinfection of tertiary wastewater was estimated to be slightly less expensive than PAA in terms of operational costs and similar in terms of investments [16].

6. Disinfection by-products and effects of peracids on physico-chemical quality of treated water

Concerns over disinfection by-product (DBP) formation began in the 1970s after the discovery of trihalomethane formation in drinking water from chlorine use [199] and since then, over 600 individual DBPs have been identified [200]. One of the major advantages of PAA over free chlorine or ozone is the lower likelihood to form DPBs [32]. PFA has been studied less systematically in terms of DBP formation, but the existing studies suggest that DBP formation is similar or even slightly lower than with PAA [136]. In the following segment, aldehydes, epoxides, halogenated DBPs, carboxylic acids, N-nitrosamines, and mutagenic or genotoxic DBPs are considered.

Aldehyde formation and subsequent decomposition was suggested to occur through the reactions of 14 and 15, respectively, when methanol is the precursor and PAA is the oxidizer [201].

$2\ CH_3COOOH + CH_3OH \rightarrow 2\ CH_3COOH + HCHO + H_2O$(14)

$2\ CH_3COOOH + HCHO \rightarrow 2\ CH_3COOH + CO_2 + H_2O$(15)

The formed aldehydes, in the case of PAA, included formaldehyde, acetaldehyde, nonanal, and decanal [120, 170, 201]. However, the aldehyde concentrations after PAA disinfection have been low or with PFA even non-detectable [34, 169, 201]. For instance, 10 mg/L of PAA was able to form a maximum 6.1 µg/L concentration of formaldehyde in surface water [169] whereas the guideline value is 900 µg/L in drinking water [202].

No formation of epoxides as a result of PAA (10 mg/L, 30 min) disinfection of wastewater took place [127], although PAA is a common epoxidation agent in the chemical industry [26]. However, epoxide and corresponding diol formation has been detected in pulp bleaching with PAA, where much harsher conditions are used [203].

The formation of halogenated DBPs occurs through the oxidation of halogenides (Cl^-, Br^-, or I^-) to hypohalous acids (HOCl, HOBr, or HOI) either by radicals [204] or peracid itself [178, 201]. Subsequently, hypohalous acids can react with dissolved organic matter to form halogenated DBPs. However, only very modest or undetectable amounts of chlorinated and brominated DBPs (e.g., chlorophenols, bromophenols, or total trihalomethanes) have been observed with PAA under typical fresh water or wastewater disinfection conditions [120, 127, 169, 170, 201]. No formation of bromate (BrO_3^-) was detected in surface or reclaimed water [169] or in saline water [205]. However, it has been found that an increase in the PAA or halogenide concentration promotes the formation of halogenated DBPs [204]. This could be encountered in the disinfection of saline ballast water, for instance [205]. PAA (150 mg/L, contact time of 5 days) in sea or brackish water was able to form $CHBr_3$ (up to 920 µg/L) and $CHBr_2Cl$ (up to 110 µg/L), whereas no formation of $CHCl_3$ or $CHBrCl_2$ was observed [205]. This is due to the much lower rate constant for the PAA reaction with chloride compared to the reaction with bromide [205]. Furthermore, H_2O_2 has an important role as a sink of HOCl, HOBr, or HOI in PAA disinfection (i.e., H_2O_2 can eliminate the formed hypohalous acids): consequently a high H_2O_2 : PAA molar ratio minimizes the formation of halogenated DBPs in these water treatment cases [178]. Ragazzo et al. [34] did not observe the formation of brominated DBPs in full scale PFA (1 mg/L, 10 min) disinfection experiments of secondary effluents (average [Br^-] = 0.4 mg/L), although brominated DBPs were reported to form in synthetic wastewater spiked with 101 mg/L of bromide. The formation of halogenated organic DBPs can be also observed with the sum parameter of adsorbable organic halogens (i.e., AOXs). Pilot scale experiments conducted with PAA indicated that no or only a slight formation of AOX took place after disinfection [119, 120].

Another study indicated that after PAA (1 mg/L, 10 min) disinfection, AOX was measured at 155 mg/L compared to 92 mg/L after PFA (1 mg/L, 10 min) use [141].

Carboxylic acid concentrations increase as a result of peracid water treatment due to the carboxylic acid present in the equilibrium solution and the decomposition of peracid to the corresponding carboxylic acid. Additionally, the oxidation of aqueous organic compounds may increase the amount of longer chain carboxylic acids. In a full scale PFA disinfection experiment, only a stoichiometric increase in the amount of formic acid was observed [34]. In contrast, the amount of octanoic, nonanoic, decanoic, lauric, myristic, hexanedioic acids was found to increase as a result of PAA treatment of surface waters, but these carboxylic acids are not considered toxic or mutagenic [170]. No exact formation mechanism of these long chain carboxylic acids has been presented so far.

PAA-based disinfection (5–10 mg/L) of drinking water was shown to form no N-nitrosamines at pH 6–10 and a contact time up to 8 days with the exception of N-nitrosodi-n-propylamine, which formed at a very low concentration (< 10 ng/L) [206].

PAA disinfection (2–4.1 mg/L, 26–37 mins of contact time) did not induce genotoxicity in wastewater in the *Salmonella typhimurium* reversion (the Ames test [207]), *Allium cepa* root anaphase aberration, and *Tradescantia*/micronucleus tests [208]. However, PAA produced DNA damage during surface water disinfection as determined by the Comet assay in human white blood cells [209, 210] and in the cytokinesis-block micronucleus test [210]. The *Saccharomyce cerevisiae* D7 test showed a genotoxic response only at 5- to 10-fold doses of PAA typically used for water disinfection [209]. Furthermore, wastewater disinfection with PAA (1 mg/L, 15 mins of contact time) indicated the formation of genotoxic by-products in the Ames and *Allium cepa* chromosomal aberration tests and suppression of bacterial light emission in the *V. fischeri* bioluminescence assay [211]. The variation in mutagenicity and toxicity was explained by seasonal changes in the concentrations of precursors and water temperature [211, 212]. In another study, PFA showed no toxicological effect in *V. fischeri* assay, whereas PAA introduced some toxic effects: this was explained by the slower decomposition kinetics of PAA compared to PFA [136]. When treating surface water with PAA (1.5–3 mg/L, 90 mins of contact time), no formation of mutagenicity according to the Ames test was found and in fact the formation of *Allium cepa* chromosomal aberrations were reduced after disinfection by PAA [170]. Also Guzzella et al. [213] observed that PAA decreased the genotoxic load of surface waters. Monarca et al. [120] used a wide set of *in vivo* and *in vitro* toxicity and genotoxicity tests combined with DBP detection to evaluate PAA (1–2 mg/L, 60 mins of contact time) disinfection of surface waters: results indicated consistently lower DBP levels with PAA compared to hypochlorite or chlorine dioxide. No clastogenic/aneugenic effects or DNA damage was detected in *C. carpio* or *D. polymorpha* as a result of PAA disinfection of surface water [214, 215]. PAA (0.6–2 mg/L) disinfection of surface water induced cytochrome P450 (CYP) enzyme modulations in *C. carpio* and *D. polymorpha* biomarkers and genotoxic DBPs were observed to be excreted in the bile of *C. carpio*: therefore PAA still remained as potentially co-carcinogenic [216-218]. However, no cytotoxic effects or glutathione content variation were determined in rainbow trout hepatocytes after exposure to surface water treated with PAA, but increased reactive oxygen species (ROS) production was observed [219].

The decrease of wastewater pH as a result of PAA dosing is insignificant in the dosing area typically used for municipal wastewater disinfection [112, 152]. However, in some industrial uses, very high concentrations are required, which might in turn decrease pH significantly. For example, in one reported case 7 mg/L dose of PAA reduced pH by 0.24 and 0.18 units in secondary and tertiary effluents, respectively [138]. Another study showed that over 60 mg/L of PAA was required to decrease the pH by one unit in secondary effluent [112]. PFA (1 mg/L) caused an approximately 0.3 pH unit change at full-scale which was, however, not statistically correlated to the PFA dosing [34]. Chemical oxygen demand (COD) and total organic carbon (TOC) increase as a result of peracid dosing and it is possible to calculate the theoretical increase based on the peracid equilibrium composition [152]. COD increases of 1.94 mg/L [112], 2.8 mg/L [32], and 4.0 mg/L [152] per 1 mg/L of PAA dosing have been reported. TOC was found to triple in one study when using a 10 mg/L PAA dose [92]. However, also a decrease of COD has been observed, this was explained by oxidation of organic material [123]. Biological oxygen demand (BOD) measurement can be interfered by residual peracid, since the bacteria performing the decomposition could be eliminated and oxygen is released from peroxides during the test [152]. As a result, BOD has been reported to either decrease, stay unchanged, or increase as a result of peracid dosing [112, 123, 147, 152]. Also the COD test could be interfered, since hydrogen peroxide and possibly peracid itself reacts with the frequently used dichromate oxidizer [152, 220, 221]. The EU the urban waste water treatment directive (91/271/EEC) defines the treatment objectives for COD and BOD_5: 125 and 25 mg/L, respectively. Dissolved oxygen (DO) and the oxidation reduction potential (ORP) have been found to increase as a result of peracid dosing [112, 152]. The increase of DO has a beneficial effect for biological wastewater treatment and the removal of odors [112, 160]. The ORP change, on the other hand, could be used as a control parameter in the disinfection process by peracids [152, 222].

7. Oxidation of aqueous pollutants

Municipal and industrial wastewaters frequently contain refractory compounds, such as phenols, dyes, pesticides, organic solvents, pharmaceuticals, and halogenated aliphatic and aromatic compounds. These compounds are characterized by low biodegradability, toxicity, and some of them are endocrine disrupting chemicals (EDCs). One potential method to treat such wastewaters are advanced oxidation processes (AOPs) in which the formation of radicals is enhanced. Peracids have been used in various AOPs (Table 5). PAA has a high oxidation potential (1.96 V), which is surpassed only by ozone (2.01 V) and hydroxyl radicals (2.80 V) of the commonly used oxidizers (Table 4), whereas the oxidation potential of PFA has not yet been reported [223].

Peracids can react directly with the target compounds [26, 237-239] or form radicals (such as R-COO· and HO·) as secondary oxidizers. However, PFA and PAA have been shown to require activation in order to be effective oxidizers. One of the advantages of PAA in the oxidation is a weaker O-OH bond (38 kcal/mol) compared to H_2O_2 (51 kcal/mol), this difference could enhance the free radical formation [81]. In a different study, the O-OH bond dissociation energy for PFA and PAA was calculated to be 48 kcal/mol [15].

Table 5 shows results of studies aiming to use PFA, PAA, or PPA as an oxidizer or a source of radicals in removing organic pollutants from wastewater. The used doses have been significantly higher compared to the disinfection of wastewater: ranging from 40 to 20 000 mg/L. In fact, smaller doses of PFA or PAA were unable to degrade pharmaceutical residues [225, 226].

Another study showed that PFA alone was not able to reduce the amount or increase the biodegradability of organic matter in landfill leachate [229]. It is known that with H_2O_2, too low a concentration limits the oxidation rate, whereas too high a concentration causes ·OH radical scavenging by H_2O_2 (Reaction 16) [227].

$H_2O_2 + HO\cdot \rightarrow HO_2\cdot + H_2O$(16)

The activators with peracids have included transition metal ions (e.g., Mn^{2+}, Fe^{2+}, Cu^{2+}) as homogenous catalysts; transition metal oxides (e.g., Fe_2O_3, MnO_2) or activated carbon as heterogeneous catalysts; and UV irradiation (Table 5). Additional activators that have been studied with H_2O_2 (referred to as the iron-free Fenton-like systems) include aluminum (Al^0/Al^{3+}), cerium (Ce^{3+}/Ce^{4+}), chromium (Cr(III)/Cr(VI)), cobalt (Co^{2+}/Co^{3+}), ruthenium (Ru^x/Ru^{x+1}), and polyoxometallates [228]. Some of these may work with peracids as well.

Nadafi et al. [230] formed PAA *in situ* by dosing acetic acid and hydrogen peroxide during a dye (reactive blue 29) oxidation. A similar *in situ* formation of PAA has been used in so-called peroxy-acid process, which has been studied for polyaromatic hydrocarbons (PAHs) oxidation from lake sediments, soil, or contaminated glass bead surfaces [231-236]. The process was demonstrated to be highly successful reaching up to 100% removal of some PAHs [235]. However, the required high concentration of acetic acid drastically decreases pH, which is a major limitation [233].

The Fenton-coagulation with PAA/Fe^{2+} showed no additional benefit over H_2O_2 in the COD removal of wastewater, whereas color and turbidity were removed more effectively with PAA/Fe^{2+} than PAA alone [245]. A PAA dose (2–8 mg/L) was used together with Fe^{2+} or Fe^{3+}

for up-flow anaerobic sludge blanket (UASB) reactor effluent followed by double filtration (gravel and sand): the results showed that the combined coagulation/oxidation treatment was effective in the removal of color, increasing dissolved oxygen level and consequently enhancing BOD removal [246]. The use of PAA/Fe^{2+} was also suggested for fat-containing wastewater oxidation and flocculation [96].

8. Perpropionic acid

Perpropionic acid (PPA, CH_3CH_2COOOH) is the next member of the aliphatic series starting with PFA and PAA. Studies concerning the environmental use of PPA are clearly more limited than with PAA or PFA. PPA was prepared for the first time already in the early 1900´s [249]. The safe preparation of PPA should employ a molar ratio of H_2O_2 to propionic acid of more than 3.5:1, temperature up to 60°C, a H_2O_2 to water ratio up to 0.8, and a catalyst (such as H_2SO_4) concentration 10–40 weight-% [250]. The disinfecting properties of PPA are well known [251, 252]. PPA was recently studied in the decontamination of food-contact surfaces [253]. Luukkonen et al. [16] compared PFA, PAA, and PPA for the disinfection of tertiary wastewater in laboratory-scale: the order of efficiency was found to be similar as by Merka et al. [252]: PFA > PAA ≈ PPA. In the Fe^{3+} or Cu^{2+} catalyzed oxidation of bisphenol A from aqueous solution, PPA was again comparable to PAA and more efficient than PFA [16]. These results are in agreement with Swern [3], who reported that PPA is analogous to PAA in physical and chemical properties, but more stable and less explosive. However, one of the main disadvantages of PPA in water treatment is the larger introduction of organic carbon to the treated effluent compared to PFA or PAA. The oxidation properties of PPA have been utilized in the degradation of organosulfur and organophosphorus pollutants in micellar solutions [248] and for the oxidation of NO_X and SO_2 from flue gases [247], while it has also been used as an epoxidation agent [254].

9. Conclusions

In 2013, the amount of PAA used in water treatment on a global scale was approximately 29.01 kt and this is estimated to steadily increase. This illustrates that PAA has become an accepted alternative oxidant/disinfectant chemical, especially in wastewater disinfection. At the moment, there are significantly less published studies available about the (waste)water treatment uses of PFA, but the existing studies point out that it is at least as useful as PAA. Furthermore, based on the very limited available literature about the third aliphatic peracid, PPA, it appears to be as effective as a biocide as PAA. However, PPA is not commercially used for water treatment at the moment.

One major difference between PFA and PAA is that PFA has to be prepared on-site due to its instability, whereas PAA is supplied as a ready-to-use solution. This makes the use of PFA more complicated, as it requires typically three chemicals (i.e., formic acid, hydrogen peroxide, sulfuric acid) and meticulous process controls (such as the reaction temperature). Consequently, the use of PFA is associated with more safety hazards than the use of PAA. However, the commercially available PFA-producing systems can utilize modern microreactor technology, for instance, to overcome the main safety issues.

In disinfection of combined sewer overflows and primary, secondary, or tertiary municipal wastewater effluents, PFA has proven to require lower doses of chemicals and/or contact time than PAA to yield a similar result. In terms of operational and investment costs, PAA-based disinfection of municipal wastewaters has been estimated to be more economical at small wastewater treatment plants, whereas PFA becomes clearly more cost-efficient as the capacity of the plant increases. Both chemicals have also been used in various industrial water treatment applications. Finally, PAA has been also studied for wastewater sludge, potable water, and ballast water disinfection, where PFA might not be as feasible. The disinfection properties of these chemicals can be improved in advanced oxidation processes using UV or transition metal catalysts as activators.

Current literature indicates that the formation of disinfection by-products by PAA disinfection, such as aldehydes, epoxides, halogenated DBPs, carboxylic acids and N-nitrosamines is either non-existing or insignificant in terms of the reported by-product concentrations. Although PFA has been studied much less systematically than PAA at the moment, the existing studies suggest PFA to cause possibly even less disinfection by-products than PAA. However, recent studies about mutagenic or genotoxic disinfection by-products, involving biomarkers, indicate that the co-carcinogenic effects of PAA cannot be completely ruled out.

Peracids have also been used for the oxidation of various refractory micropollutants present in wastewaters, such as dyes or pharmaceuticals. The activation of peracid by catalysts or UV is essential in their oxidation. However, the existing studies suggest that peracids are not very efficient in these uses and the needed doses can often be very high. Beyond wastewater treatment, PAA has proven to be rather effective in oxidizing polyaromatic hydrocarbons from contaminated lake sediments and soils in the so-called peroxy-acid process.

To conclude from the above numerous examples, peracids (especially PFA and PAA) possess many advantages over e.g. chlorine in the harmful by-product formation, smell and odor threshold etc. The only major concern that has been reported in the above (and other) studies is the relative cost of the PAA/PFA treatment. However, with the proprietary dosing, measurement, and control technology currently readily available, this issue could also become a moot point in most applications of PAA. A final note regarding PAA deals with the fact that unlike chlorine, there are multiple components and different equilibrium compositions present in various commercial PAA formulations and therefore any results presented in the literature would be different from one case to another.

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Table 1. The aqueous decomposition kinetics of peracids reported in the literature.

Peracid	Dose [mg/L]	Water matrix	Order	k_α	D [mg/L]	$t_{½}$ [min]	Reference
PFA	15	Tap water	1st	0.007	0	99	[16]
PFA	15	Tertiary effl.	1st	0.012	0	58	[16]
PAA	21–28	Primary effl.	1st	0.0396	19.41	18	[61]
PAA	10	Secondary effl.	1st	0.0088	-	79	[112]
PAA	1.5–8.5	Secondary effl.	1st	0.0028	0.44	248	[61]
PAA	1–15	Secondary effl.	1st	0.007	0.415	99	[113]
PAA	1–15	Secondary effl.	1st	0.009	0.785	77	[113]
PAA	4–8	Secondary effl.	0	0.016	0.8	100–225	[115]
PAA	15	Tertiary effl.	0	0.036	1.424	189	[16]
PAA	15	Tertiary effl.	0	0.042	0.925	168	[16]
PAA	1–15	Tap water	1st	0.007	-	100	[113]
PAA	15	Tap water	0	0.010	0.810	710	[16]
PAA	15	Tap water	0	0.016	0	469	[16]
PPA	15	Tap water	0	0.023	1.886	285	[16]
PPA	15	Tertiary effl.	1st	0.003	1.903	231	[16]

α=0 or 1

Table 2. Examples of the required continuous PFA and PAA doses for secondary and tertiary effluents.

Secondary effluents					
Peracid	Continuous dose [mg/L]	Contact time [min]	Target organism	Result	Ref.
PFA	0.4–0.5	10	EC, E	1 log$_{10}$ reduction	[141]
PFA	1.7–2.2	10	FSC	1 log$_{10}$ reduction	[141]
PFA	2	5	FC, E, S	approx. 0.5–2 log$_{10}$ reduction	[141]
PAA	0.6–1.6	120	FC	2–3 log$_{10}$ reduction	[99]
PAA	0.6–4	60	FC	1000 CFU/100 mL	[145]
PAA	1	15–20	TC	20000 MPN/100 mL	[146]
PAA	1	15–20	FC	12000 MPN/100 mL	[146]
PAA	1	15–20	FS	2000 MPN/100 mL	[146]
PAA	1.5	20	FSC, SC	0.5 log$_{10}$ reduction	[139]
PAA	1.5–2	20	EC	5000 CFU/100 mL	[130, 139, 147]
PAA	2–7	27	TC, E	3 log$_{10}$ reduction	[138]
PAA	4	10	EC	2 log$_{10}$ reduction	[148]
PAA	5	20	TC, FC	4–5 log$_{10}$ reduction	[149]
PAA	5–7	60	TC	1000 CFU/100 mL	[150]
PAA	5–7	60	FS	100 CFU/100 mL	[150]
PAA	5–10	10–50	EC	10 CFU/100 mL	[113, 115]
PAA	5–10	15	TC, FC	> 95% reduction	[151]
PAA	10	10	TC, FC, FS	3 log$_{10}$ reduction	[92]
Tertiary effluents					
Peracid	Continuous dose [mg/L]	Contact time [min]	Target organism	Result / required reduction	Reference
PAA	1.5–2	10–15	EC	500 CFU/100	[152]

				mL	
PAA	2–15	12–36	FC	0.5–4.5 reduction	[94]
PAA	10	30	TC	1000 CFU/100 mL	[153]
PAA	10	30	FC	1000 CFU/100 mL	[127, 154]
PAA	15	36	EC	4 $\log_{10}$ reduction	[124]
PAA	400	20	TC	2 CFU/100 mL	[153]

FC = fecal coliforms, FSC = F specific coliphages, SC = somatic coliphages, EC = *E. coli*, TC = total coliforms, E = enterococci, FS = fecal streptococci, S = *Salmonella* spp.

Table 3. Comparison of obtained peracid disinfection kinetics parameters in the literature.

Peracid	Dose [mg/L]	Contact time [min]	Wastewater matrix	Indicator organism	Hom model				S-model				Reference
					k	n	m		k	n	m	h	
PFA	2–10	30	Tap water	EC	4.25	0.35	0.35		-	-	-	-	[44]
PFA	6–15	30	ASL	EC	0.54	0.48	0.87		-	-	-	-	[44]
PFA	1.5	60	TE	EC	3.151	1.894	0.042		15.100	0.050	0.080	30.316	[16]
PAA	1.5	60	TE	EC	-	-	-		5.077	0.060	0.829	25.356	[16]
PAA	2–25	6–54	TE	EC	-	-	-		3.182	0.069	1.128	26.173	[186]
PAA	2–25	6–54	TE	EC	-	-	-		3.12	0.07	1.13	24.10	[124]
PAA	2	55	SE	EC	-	-	-		2.651	-0.445	1.968	15.561	[113]
PAA	1–8	30	SE	EC	0.008	0.92	n/a		-	-	-	-	[148]
PPA	1.5	60	TE	EC	-	-	-		6.509	0.030	0.912	17.086	[16]
PAA	2–25	6–54	TE	TC	-	-	-		2.830	0.146	0.916	65.326	[186]
PAA	2–25	6–54	TE	TC					2.83	0.15	0.92	65.33	[124]
PAA	1–8	30	SE	TC	0.159	0.59	0.53		-	-	-	-	[148]
PAA	2–25	6–54	TE	FC	-	-	-		2.70	0.13	0.91	50.58	[124]
PAA	1–8	30	SE	FC	0.0469	2.88	n/a[a]		-	-	-	-	[148]
PAA	1–2	55	SE	FC	0.087	0.538	0.646		-	-	-	-	[113]
PAA	5–15	55	SE	FC	0.260	0.430	0.4153		-	-	-	-	[113]
PFA	1.5	60	TE	E	-	-	-		6.164	0.094	1.439	4.164	[16]
PAA	1.5	60	TE	E	-	-	-		2.392	0.101	5.557	41.694	[16]
PPA	1.5	60	TE	E	-	-	-		2.195	0.100	2.138	26.285	[16]

SE = secondary effluent, TE = tertiaray effluent, SBS = synthetic bacterial suspension, ASL = active sludge effluent, EC = E. coli, TC = total coliforms, FC = fecal coliforms, E = enterococci, n/a = not available

Table 4. Oxidation potentials and half-reactions of oxidizers commonly used in water treatment applications [223, 224].

Oxidant	Half-Reaction	E° [V]
Hydroxyl radical (·OH)	$\cdot OH + e^- \leftrightarrow OH^-$	2.02
Ozone (O_3)	$O_3 + 2H^+ + 2e^- \leftrightarrow O_2 + H_2O$	2.076
Peracetic acid (CH_3CO_3H)	$CH_3CO_3H + 2\ H^+ + 2\ e^- \rightarrow CH_3CO_2H + H_2O$	1.960 [a]
Hydrogen peroxide (H_2O_2)	$H_2O_2 + 2H^+ + 2e^- \leftrightarrow 2H_2O$	1.776
Permanganate (MnO_4-)	$MnO_4^- + 4H^+ + 3e^- \leftrightarrow MnO_2 + 2H_2O$	1.679
	$MnO_4^- + 8H^+ + 5e^- \leftrightarrow Mn^{2+} + 4H_2O$	1.507
Chlorine gas (Cl_2)	$Cl_2(g) + 2e^- \leftrightarrow 2Cl^-$	1.358
Hypochloric acid (HOCl)	$HOCl + H^+ + 2e^- \leftrightarrow Cl^- + H_2O$	1.482
Chlorine dioxide (ClO_2)	$ClO_2 + H^+ + e^- \leftrightarrow HClO_2$	1.277
	$HClO_2 + 3\ H^+ + e^- \leftrightarrow Cl^- + 2\ H_2O$	1.570

[a] = reported as 1.762 V vs Ag/AgCl in [223].

Table 5. Oxidation of aqueous pollutants with PFA or PAA. All studies were conducted with synthetic wastewater unless stated otherwise.

Pollutant	C_0 [mg/L]	Max. removal [%]	Oxidizer	Activator	Optimum conditions					Ref.
					Activator dose [g/L]	pH	Oxidizer dose [mg/L]	t [min]	T [°C]	
4-chlorophenol	51.4	98	PAA	UV	-	9.5	3040	1	r.t.	[240]
4-chlorophenol	51.4–150	95	PAA	UV [a]	-	9.5	2040	30	r.t.	[241]
Dichlorophenol	100	70	PAA	Fe_2O_3 montmorillonite	1	n.r.	20000	210	25	[242]
Chlorophenols (industrial wastewater)	142	97	PAA	UV [a]	-	11	4035	30	n.r.	[243]
Phenol	98.8	89	PAA	MnO_2 + ultrasound	1	≈ 7	50	120	22	[244]
Phenol	n.r.	80	PAA	MnO_2	0.7	n.r.	50	120	n.r.	[80]
Bisphenol-A	60	64	PFA	Fe^{2+} or Cu^{2+}	0.02	3.5	40	10	r.t.	[16]
Bisphenol-A	60	100	PAA	Fe^{2+} or Cu^{2+}	0.02	3.5	40	10	r.t.	[16]
Dye (Reactive Brilliant Red X-3B)	30.8	92.5	PAA	Activated carbon fibers	2	7	380	40	25	[84]
Dye (Reactive Blue 29)	30	30	PAA	-	-	2.5–3	344:344:0.16 [b]	60	45	[230]
Dye (Orange II)	17.5	n.r.	PAA	Mn^{2+}	0.001-0.0001	9.4	38–3802	n.r.	25	[79]
Pharmaceut	0.04	0–90	PAA	-	-	6.7	15–50	108	n.r	[22

icals (municipal wastewater)[c]	0	[e]				– 7.0		0	.	6]
Pharmaceuticals (primary-treated municipal wastewater)[d]	43–2556 * 10^{-6}	< 8	PFA	-	-	8.1–8.2	6	18	n.r.	[225]

[a] = optimum UV input 250 W;

[b] = mole ratio of acetic acid (50 %) to hydrogen peroxide (30 %) to Reactive Blue 29;

[c] = diclofenac, ibuprofen, clofibric acid, naproxen, gemfibrozil, and mefenamic acid;

[d] = salicylic acid, clofibric acid, ibuprofen, 2-hydroxy-ibuprofen, naproxen, triclosan, carbamazepine, and diclofenac; [e] = depending on the pharmaceutical; r.t. = room temperature; n.r. = not reported.

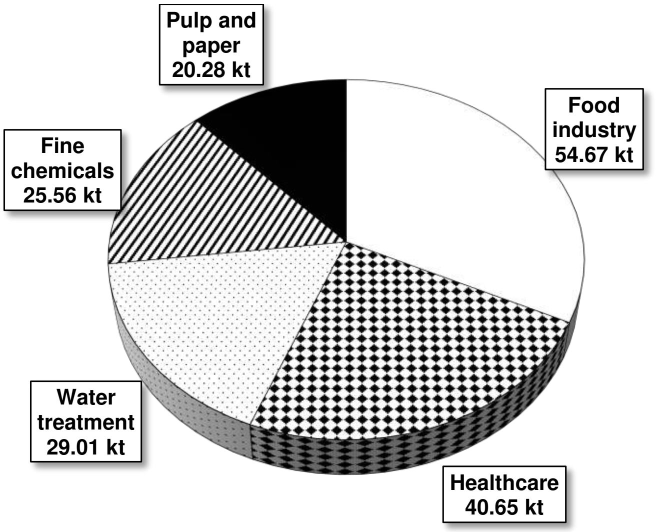

Fig. 1. Largest user segments of PAA in 2013 on a global scale [20].

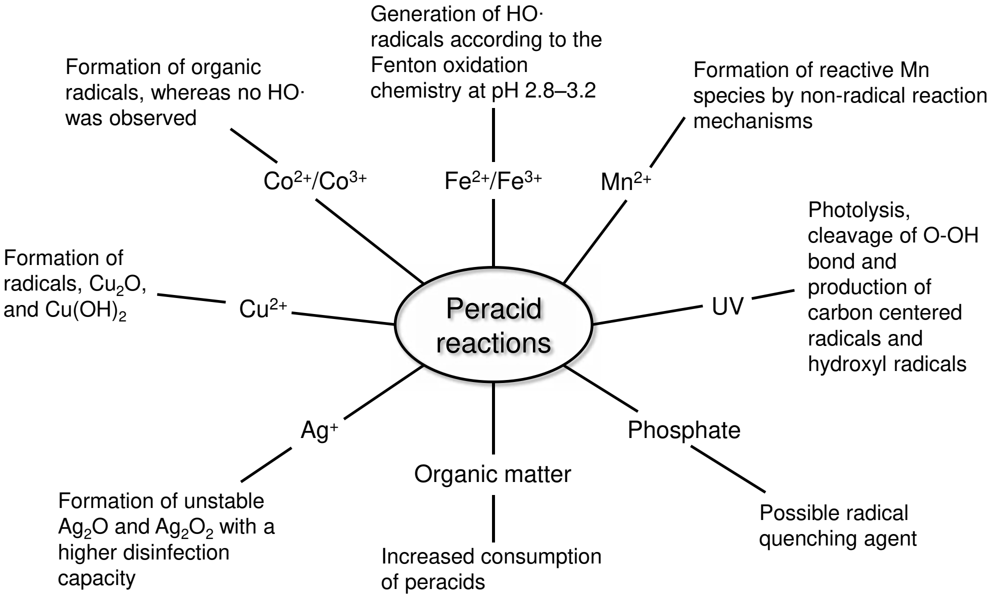

Fig. 2. Reactions of peracids with various aqueous species and UV.