

Disinfection of wastewater with peracetic acid: a review

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Abstract

Peracetic acid is a strong disinfectant with a wide spectrum of antimicrobial activity. Due to its bactericidal, virucidal, fungicidal, and sporicidal effectiveness as demonstrated in various industries, the use of peracetic acid as a disinfectant for wastewater effluents has been drawing more attention in recent years. The desirable attributes of peracetic acid for wastewater disinfection are the ease of implementing treatment (without the need for expensive capital investment), broad spectrum of activity even in the presence of heterogeneous organic matter, absence of persistent toxic or mutagenic residuals or by-products, no quenching requirement (i.e., no dechlorination), small dependence on pH, short contact time, and effectiveness for primary and secondary effluents.

Major disadvantages associated with peracetic acid disinfection are the increases of organic content in the effluent due to acetic acid (AA) and thus in the potential microbial regrowth (acetic acid is already present in the mixture and is also formed after peracetic acid decomposition). Another drawback to the use of peracetic acid is its high cost, which is partly due to limited production capacity worldwide. However, if the demand for peracetic acid increases, especially from the wastewater industry, the future mass production capacity might also be increased, thus lowering the cost. In such a case, in addition to having environmental advantages, peracetic acid may also become cost-competitive with chlorine.

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1. Physicochemical characteristics

Peracetic acid or peroxyacetic acid (PAA) is the peroxide of acetic acid (AA). PAA is a strong oxidant and disinfectant. Its oxidation potential is larger than that of chlorine or chlorine dioxide. PAA is commercially available in the form of a quaternary equilibrium mixture containing AA, hydrogen peroxide (HP), PAA, and water as shown by the following equation (Alasri et al., 1992; Gehr et al., 2002; Block, 1991):



where

$\text{CH}_3\text{CO}_2\text{H}$ = acetic acid

$\text{CH}_3\text{CO}_3\text{H}$ = peracetic acid

H_2O_2 = hydrogen peroxide.

Although HP is also a disinfectant contributing to the disinfection power of the PAA mixture, PAA is a more potent antimicrobial agent than HP, being rapidly active at low concentrations against a wide spectrum of microorganisms (Baldry, 1983; Baldry and French, 1989b; Fraser et al., 1984). It was found that HP required much larger doses than PAA for the same level of disinfection (Wagner et al., 2002). PAA combines the active oxygen characteristics of a peroxide within an acetic acid molecule and belongs to the class of organic peroxides, which are man-made chemicals. Organic peroxides may contain peroxide radicals (oxygen–oxygen bond) that are a source of oxygen. The peroxide radical also promotes instability and combustion. Peroxides, in general, are high-energy-state compounds and, as such, can be considered thermodynamically unstable (Block, 1991).

PAA is a clear, colorless liquid with no foaming capability. It has a strong pungent acetic acid odor (acetic acid is the principal component of vinegar) and has an acidic pH of less than 2. For a 5% PAA, 20% to 24% HP, and 10% to 12% AA solution, the specific gravity is 1.10 (Solvay Interox, 2002a). For a 12% PAA solution, the freezing point is from 40.3 to 42.0 °C, and the specific gravity is 1.11 (Solvay Interox, 2002b). PAA is soluble in water in all proportions

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and in polar organic solvents. However, it is slightly soluble in aromatic solvents (Solway Interlox, 2002a).

PAA solution is produced from the reaction of acetic acid or acetic anhydride with hydrogen peroxide in the presence of sulfuric acid, which acts as a catalyst (Block, 1991). In addition, a stabilizer or a sequestering agent is employed during the production of PAA. The reaction is allowed to continue for up to 10 days in order to achieve high yields of PAA as the product.

PAA is considerably less stable than HP. A 40% PAA solution loses 1% to 2% of its active ingredients per month, while HP (for a 30% to 90% solution) loses less than 1% year⁻¹. Dilute PAA solutions are even more unstable: a 1% solution loses half its strength through hydrolysis in 6 days (Block, 1991). However, commercially available PAA solutions (10% to 15%) as used in industry are much more stable compared to higher- and lower-end strength solutions. For stability, PAA should be stored at ordinary, preferably cool, temperatures in original containers. It is unaffected by glass and most plastics. It may extract the plasticizer from some vinyl formulations used as gaskets and will attack natural and synthetic rubbers (Dychdala, 1988). Pure aluminum, stainless steel, and tin-plated iron are resistant to PAA; but plain steel, galvanized iron, copper, brass, and bronze are susceptible to reaction and corrosion (Schroder, 1984; Fraser et al., 1984).

PAA solutions exceeding 15% begin to exhibit some degree of explosiveness, instability, and reactivity (Block, 1991). Therefore, many industrial applications use PAA solutions between 10% and 15% (primarily 12%). The major advantage of this concentration is the loss of the explosive characteristic and the loss of a flashpoint. This is partially due to the reduced concentration of reactants and addition of proprietary stabilizers to reduce the hazards. The health hazards associated with 12% PAA are similar to the health hazards of the 50% hydrogen peroxide.

2. Antimicrobial activity

The germicidal properties of PAA were first reported by Freer and Novy (1902), who noted “the excellent disinfection and cold sterilization actions of PAA,” but it was not until years later with the development of a commercial process for the production of 90% HP, necessary for the manufacture of PAA, that it became generally available (Block, 1991). Hutchings and Xezones (1949) showed PAA to be the most active of 23 germicides tested against spores of *Bacillus thermoacidurans*. Greenspan and MacKellar (1951) found it to be bactericidal at 0.001%, fungicidal at 0.003%, and sporicidal at 0.3%. PAA was also used as a disinfectant in gnotobiotics, the production of germ-free animals (Reyniers, 1946). Even in the vapor phase, PAA demonstrated the highest kill rate at the lowest concentration when compared with a broad battery of other available disinfectants tested (Baldry, 1983). The disinfection effi-

ciency of PAA towards microorganisms can be ranked as following on a general basis: Bacteria>viruses>bacterial spores>protozoan cysts (Liberti and Notarnicola, 1999; Rudd and Hopkinson, 1989).

3. Mode of action

Although limited work has been done to probe the mode of action of PAA as an antimicrobial agent, it may be speculated that it functions much as other peroxides and oxidizing agents (Block, 1991). Its disinfectant activity is based on the release of active oxygen (Liberti and Notarnicola, 1999). It is likely that sensitive sulfhydryl and sulfur bonds in proteins, enzymes, and other metabolites are oxidized and that double bonds are reacted. It is suggested that PAA disrupts the chemiosmotic function of the lipoprotein cytoplasmic membrane and transport through dislocation or rupture of cell walls (Baldry and Fraser, 1988; Leaper, 1984). Thus, it may be that it is equally effective against outer membrane lipoproteins, facilitating its action against Gram-negative cells (Leaper, 1984). Its action as a protein denaturant may help to explain its characteristics as a sporicide and ovicide (Block, 1991). Furthermore, intracellular PAA may also oxidize essential enzymes; thus vital biochemical pathways, active transport across membranes, and intracellular solute levels are impaired (Fraser et al., 1984). It was demonstrated that PAA acts on the bases of the DNA molecule (Tutumi et al., 1973). An important advantage of PAA is that it may inactivate catalase, an enzyme known to detoxify free hydroxyl radicals (Block, 1991).

4. By-products

The decomposition products of PAA are acetic acid, hydrogen peroxide, oxygen, and water (Gehr et al., 2002; Wagner et al., 2002; Colgan and Gehr, 2001; Lefevre et al., 1992; Sanchez-Ruiz et al., 1995). There are three reactions in which PAA is consumed in an aqueous solution: spontaneous decomposition, hydrolysis, and transition-metal-catalyzed decomposition (Gehr et al., 2002; Yuan et al., 1997). The pH range of 5.5 to 8.2 would result mainly in spontaneous decomposition to acetic acid and oxygen (Gehr et al., 2002).

It has been shown that PAA produces no little toxic or mutagenic by-products after reaction with organic material present in treated wastewater effluents or surface waters used for drinking water (Baldry and Fraser, 1988; Monarca et al., 2001; Monarca et al., 2002). Monarca et al. (2001) reported that by-products isolated from river waters treated with PAA were predominantly carboxylic acids, which are not recognized as being mutagenic. Carboxylic acids are formed through the oxidation of natural organic matter in the water by PAA (Monarca et al., 2002). No halogen-containing disinfection by-products (DBPs) were observed

for PAA-treated water (Monarca et al., 2002). This is one of the most important advantages of PAA over other typically used chemical disinfectants in the treatment of wastewater or water such as gaseous chlorine, sodium hypochlorite, chlorine dioxide, or ozone. Chlorine-based disinfectants result in the formation of toxic and mutagenic halogenated by-products (chlorinated and/or brominated) after the reaction of chlorine and organic material. Furthermore, only about 50% of the total organic halides formed can be identified and quantified. Similarly, ozone produces smaller molecular weight, more polar and hydrophilic by-products (compared to the parent organics), such as carboxylic acids, aldehydes, ketones, and keto acids, which are readily biodegradable resulting in the regrowth potential in the receiving waters.

Although PAA is considered to decompose to harmless products and to form little to no by-products that are toxic or mutagenic, the possibility that it could form DBPs cannot be completely ignored (Crathorne et al., 1991). About 10 to 30 $\mu\text{g l}^{-1}$ of aldehydes were reported to form as transformation and/or oxidation DBP when PAA interacted with amino acids, phenols, and other aromatic substances present in treated wastewater (Crathorne et al., 1991). When phenol was used as a model compound in experimental waters with high chloride concentrations, the concentration of mono-substituted chlorophenols was increased after PAA treatment (Booth and Lester, 1995). It was demonstrated that PAA was unable to oxidize chloride to hypochlorous acid. Therefore, it was proposed that the transformation of phenol to chlorophenol occurs through the generation of free halogen radicals (from chloride, if present in high quantities as occurs in seawater), the initiation and promotion of which are dependent on the presence of other organic contaminants in the wastewater effluents. However, the electrochemistry of PAA was sufficient to oxidize bromide to hypobromous acid, subsequently forming brominated organics (Booth and Lester, 1995). In terms of toxicity, Monarca et al. (2000), contrary to their previous findings (Monarca et al., 2001, 2002), found that the *Allium cepa* test gave positive results for PAA-treated wastewater sampled in winter; however, the *Tradescantia*/MCN test gave negative results.

Although few studies suggest the formation of some DBPs (and some toxicity) from PAA, the quantity and spectrum of these DBPs are much less than those formed by chlorine or ozone. Furthermore, other oxidants, such as chlorine or ozone, also form halogen-free radicals from the background chloride or bromide ions.

5. Use for wastewater disinfection

Due to its effectiveness against bacteria and viruses as demonstrated in many industries, the use of PAA as a disinfectant for wastewater effluents has been investigated since the 1980s (Gehr et al., 2002; Baldry and Fraser, 1988; Baldry and French, 1989a; Wagner et al., 2002; Lefevre et

al., 1992; Rudd and Hopkinson, 1989; Baldry and French, 1989b; Morris, 1993; Baldry et al., 1991; Liberti et al., 2000; Sanchez-Ruiz et al., 1995; Langlais and Triballeau, 1992; Baldry et al., 1995; Stampi et al., 2001; Meyer, 1976; Lazarova et al., 1998; Bonadonna et al., 1999; Jolivet-Gougeon et al., 1996; Morris, 1993). PAA has been reported to be an efficient bactericidal (Gehr et al., 2002; Baldry, 1983; Baldry and Fraser, 1988; Baldry and French, 1989a; Wagner et al., 2002; Lefevre et al., 1992; Baldry and French, 1989b; Alasri et al., 1992), virucidal (Baldry and French, 1989a; Baldry et al., 1991; Briefman-Kline and Hull, 1960), fungicidal (Baldry, 1983), and sporicidal (Baldry, 1983; Lynwood et al., 1967) agent. The following section summarizes some relevant results (i.e., doses and contact times vs. microbial reductions) and conclusions from these studies.

As one of the pioneering studies in this area, Baldry and French (1989a) found PAA to be an effective disinfectant for secondary effluent and stated that the ease of implementing PAA treatment without expensive equipment, the broad-spectrum activity even in the presence of organic matter and the lack of environmentally undesirable by-products make PAA appear favorable for wastewater treatment (Baldry and French, 1989a; Block, 1991). Gehr et al. (2002) found that for physicochemically treated (with alum or ferric chloride) municipal primary effluents, PAA doses of 2 to 6 mg l^{-1} were required to achieve 1000 colony forming units (CFU) per 100 ml of fecal coliforms with a contact time of 60 min. For the secondary effluents, lower PAA doses of 0.6 to 4 mg l^{-1} were required to achieve 1000 CFU per 100 ml of fecal coliform. PAA consumption rates varied from 0.065 to 0.356 mM/h for the physicochemical effluents and almost all of the PAA was consumed after 120 min. For the secondary effluents, the consumption rates were lower and steadier at 0.02 to 0.05 mM/h , and only 30% of the PAA was consumed (Gehr et al., 2002).

In the studies conducted for the Montreal Urban Community Wastewater Treatment Plant in Canada, it was found that a dose of approximately 1 to 2 mg l^{-1} and 2-h contact time might be able to achieve the 10,000 CFU per 100 ml fecal coliform target in the physicochemically treated primary effluents (Colgan and Gehr, 2001). The outfall discharging the effluent was planned to be used for the contact time. A PAA dose of 5 to 10 mg l^{-1} and a contact time of 15 min was recommended to be optimal for secondary effluents, providing a reduction of more than 95% of total and fecal coliforms (Poffe et al., 1978). A PAA dose of 5 to 7 mg l^{-1} with 60 min of contact time reduced the total coliform and fecal streptococci concentrations in secondary effluents to less than 1000 per 100 ml and less than 100 per 100 ml, respectively (Lefevre et al., 1992). However, some regrowth was observed in artificial seawater. For a secondary effluent, approximately 5 mg l^{-1} PAA residual reduced total coliform and fecal coliform about 4 to 5 logs after 20 min of contact time (Morris, 1993). However, reduction was much lower for poliovirus (62%) at the same conditions. A

PAA dose of 25 mg l^{-1} provided about 5-log reductions for both *Escherichia coli* and *S. faecalis* within 5 min of contact time (Baldry and French, 1989a). The concentrations of PAA effective against bacteriophages MS2 and ϕ 174 in demineralized water were 15 and 30 mg l^{-1} , respectively, resulting in a log reduction of greater than 4 over 5 min of contact time. Poliovirus required a much higher concentration of PAA, 750 to 1500 mg l^{-1} , to produce a 4-log reduction within 15 min (Baldry and French, 1989a). An approximate 4-log total coliform reduction was achieved with a PAA dose of 5 mg l^{-1} and 60 min of contact time for secondary effluents (Arturo-Schaan et al., 1996). However, although PAA disinfection effectively reduced the total coliform and *E. coli* strain concentrations, it did not reduce the percentage of *E. coli* strains containing plasmids. The disinfection capacity of PAA was not affected by the concentration of bacteria in the secondary effluents (Poffe et al., 1978).

The reductions for heterotrophic counts were smaller than those for fecal indicators when secondary effluents were disinfected with PAA, which may be explained by the heterogeneity of the microorganisms present in heterotrophic plate counts, some of which are particularly resistant (e.g., *Bacillus* species) to disinfectants (Stampi et al., 2001).

Reductions of about 3 logs for total and fecal coliforms and fecal streptococci were achieved using 10 mg l^{-1} of PAA dose with 10 min of contact time (Lazarova et al., 1998). Much higher doses or contact times were required for virus removals, especially highly resistant viruses, such as *F*-specific bacteriophage MS2. Enzyme activity (*b*-galactosidase activity) was affected by PAA. After the application of PAA, some of the bacteria remained respiring but not cultivable and with decreasing enzyme activity (Lazarova et al., 1998). The DNA-phage and RNA-phage was reduced 5 and 2 logs, respectively, after a 25 mg l^{-1} PAA dose and 5 min of contact time (Rajala-Mustonen et al., 1997).

For tertiary effluents, PAA concentrations as low as 2 mg l^{-1} were found to provide about 2-log reduction in fecal coliform levels (Baldry and French, 1989a). On the other

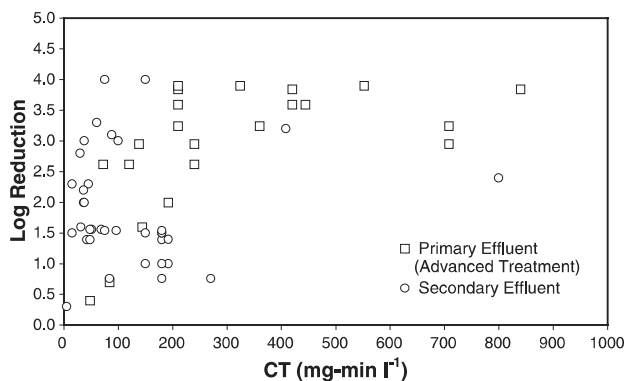


Fig. 1. Effect of CT on fecal coliform reductions in primary and secondary wastewater effluents (data obtained from: Gehr et al., 2002; Colgan and Gehr, 2001; Baldry et al., 1995; Lazarova et al., 1998; Poffe et al., 1978).

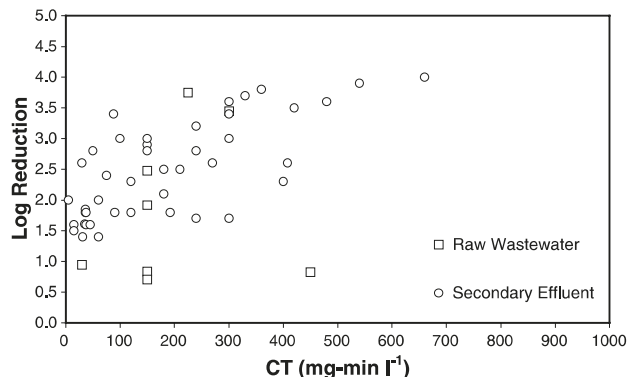


Fig. 2. Effect of CT on total coliform reductions in raw wastewaters and secondary wastewater effluents (data obtained from: Liberti and Notamicola, 1999; Lefevre et al., 1992; Sanchez-Ruiz et al., 1995; Baldry et al., 1995; Stampi et al., 2001; Lazarova et al., 1998; Arturo-Schaan et al., 1996; Poffe et al., 1978).

hand, to achieve a 2 CFU per 100 ml total coliform in tertiary effluents for unrestricted reuse in agriculture, much higher PAA doses (400 mg l^{-1} and 20 min of contact time) were required under economically unbearable conditions (Liberti et al., 2000). For a target of 1000 CFU per 100 ml fecal coliforms, however, a dose of 10 mg l^{-1} PAA with a contact time of 30 min was required (Liberti et al., 2000).

The disinfection efficiency of PAA was also tested for raw wastewaters, which showed an ample variability (Sanchez-Ruiz et al., 1995). Factors affecting such variability were: the nature and concentration of organic matter, suspended solids concentration, initial concentration of coliforms, and, especially, the pH value. The optimal dose for raw wastewater was about 20 mg l^{-1} with a contact time of about 10 min. Higher doses or contact times did not substantially improve PAA efficiency against total coliforms (Sanchez-Ruiz et al., 1995).

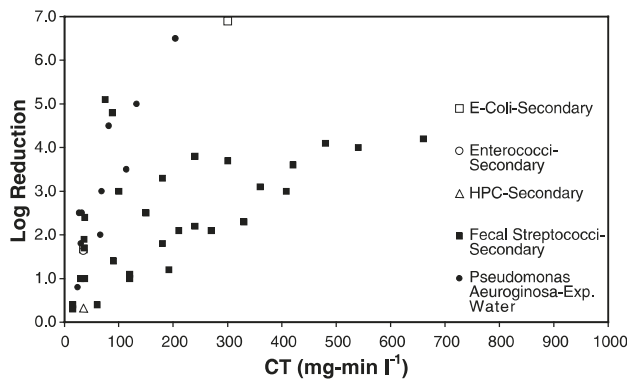


Fig. 3. Effect of CT on various bacteria reductions in secondary wastewater effluents (data obtained from: Lefevre et al., 1992; Baldry et al., 1995; Stampi et al., 2001; Lazarova et al., 1998; Lambert et al., 1999; Jolivet-Gougeon et al., 1996; Poffe et al., 1978; Exp. Water in the legend: Experimental Water).

Comparative laboratory studies of the effects of PAA, chlorine dioxide, and chlorine on indicator bacteria in secondary wastewater effluent showed PAA to be a viable alternative to these halogen biocides (Baldry and French, 1989b). PAA was dosed into secondary effluent from an activated sludge plant or from a percolating filter bed prior to tertiary lagoon treatment. Low levels of PAA greatly enhanced the natural decline in coliform levels across the lagoon, enabling much lower concentrations of bacteria to be discharged into the receiving streams (Baldry and French, 1989b). Laboratory experiments and full-scale trials in Brazil and Italy showed that PAA was a better disinfectant than sodium hypochlorite for wastewater disinfection in tropical and warm-temperature climates (Baldry et al., 1995). Its demonstrated effectiveness against *V. cholerae* suggested it should be a significant element in cholera control efforts. Approximately 5 mg l^{-1} PAA over a contact period of 10 min eliminated virtually all coliform bacteria. However, PAA was ineffective against *Clostridia* (Baldry et al., 1995).

PAA was recommended in combination with ultraviolet (UV) irradiation for wastewater disinfection (Rajala-Mustonen et al., 1997). The idea of using PAA disinfection in combination with a short UV exposure came from consideration of the fact that the retention time in UV reactors is generally limited. If it would be possible to allow wastewater to be in contact with PAA for a relatively longer time and, afterwards, to expose the wastewater to a short UV irradiation shock, a sufficient reduction in microbials could be achieved in a shorter retention time (Rajala-Mustonen et al., 1997).

To summarize the above results from literature in terms of the disinfection efficiency of PAA, values for residual concentration multiplied by contact time (CT), measured in mg min l^{-1} , vs. log reduction data were extracted from various studies for a particular microorganism and wastewater type (i.e., raw, primary, and secondary effluents). Figs. 1 and 2 show CT vs. log reduction data for fecal coliform and total coliform, respectively. Similarly, Figs. 3 and 4

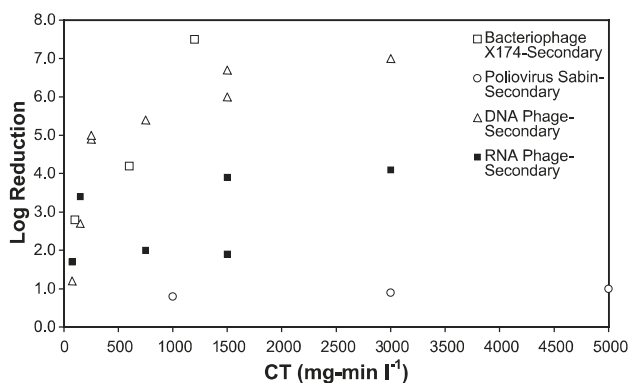


Fig. 4. Effect of CT on various virus reductions in secondary wastewater effluents (data obtained from: Lazarova et al., 1998; Rajala-Mustonen et al., 1997).

show data for various other bacteria and viruses, respectively. Due to variations in experimental conditions and wastewater characteristics between these studies, there was some significant scatter in the data, in some cases, preventing an interpretation of a good correlation.

6. Other environmental applications

PAA has been used or studied for various environmental applications other than use in wastewater disinfection. Some of these applications include use as a disinfectant for ion exchangers, cooling towers, combined sewer overflows (CSOs), and membrane hollow fibers. Furthermore, PAA was shown to be effective for pathogen reduction in biosolids, reduction in solid odors, and for sludge debulking. Some relevant results from these applications or studies are summarized below.

The use of a 0.2% PAA solution for 1 h was recommended to achieve complete disinfection of ion exchangers. It was found that the capacity of the respective cation and anion exchangers was not changed under the conditions used (0.2% to 1% PAA; Block, 1991). Baldry and Fraser (1988) reported onsite trials for Legionella control with 10 mg l^{-1} PAA on five cooling towers. In all cases, the organism was eradicated in 20 min. Algae was controlled with 20 mg l^{-1} PAA twice a year, but a slug dose of 30 mg l^{-1} with 10 mg l^{-1} thereafter was better when there was heavy algae accumulation (Baldry and Fraser, 1988). Levels of 300 to 500 mg l^{-1} of PAA reduced *Salmonella* levels below the limits of enumeration in all treated biosolids (Baldry and Fraser, 1988). Even at 150 mg l^{-1} , the level was reduced so that the biosolids were considered safe for distribution to pastureland in England. A dose of 250 mg l^{-1} PAA reduced *Salmonella* levels from 4600 organisms per 100 cm^3 to less than 30 organisms per 100 cm^3 during gravity thickening of surplus activated sludge (Fraser et al., 1984). PAA functions against the cestode (tapeworm) oncospheres in wastewater sludges, producing lack of motion, dark coloration, granulation, and avoids shrunken appearance (Fraser, 1987). In a digested sludge, 250 mg l^{-1} of PAA killed 99% of the embryos (Fraser, 1987). At a concentration of 1000 mg l^{-1} PAA, the hatching ability of the *Taenia saginata* ova was severely retarded (1% hatching rate) compared to controls (94% hatching rate) in raw and digested sludges (Colgan and Gehr, 2001). No active embryos were observed in sludge dosed with 1000 mg l^{-1} PAA (Colgan and Gehr, 2001). Operational use of PAA achieved up to 99% inhibition of hatching with 100% destruction in viability of beef tapeworm embryos in raw sludges (Fraser et al., 1984). Furthermore, applying PAA at the concentrations required for disinfection reduced solids odors and generated safe, readily biodegradable, nontoxic decomposition products (Colgan and Gehr, 2001; Fraser et al., 1984).

The rapid utilization of PAA in sludge and its fully biodegradable residues do not interfere with sludge humus

improvements in soil constitution through increased cohesion, better crumble structure, and, often, an increase in water retention (Fraser et al., 1984). Furthermore, rapid utilization and biodegradable decomposition products of PAA used in operational sludge disinfection means that the essential geochemical cycles performed by microorganisms in soil, which include mineralization of organic carbon, nitrogen, and sulfur, are not deleteriously affected. At operational concentrations required for disinfection, PAA does not react with ammonia (Fraser et al., 1984). PAA was also found to be cost-effective and efficient for sludge debulking, improving the settling of biomass in wastewater treatment plants (Colgan and Gehr, 2001). EPA included PAA among five disinfectants that could be used to disinfect combined sewer overflows (CSOs) (USEPA, 1999). The disinfection activity of PAA was evaluated against *Bacillus* spore isolates found on hollow fibers of stored ultrafiltration membranes and collection cultures (Alasri et al., 1993). PAA exhibited an excellent disinfection activity, with a destruction of 10^5 spores ml^{-1} after 5 min of contact time.

7. Industrial applications

PAA has been used widely as a disinfectant and sterilant in many industries, including food processing, beverage, medical, and pharmaceutical, and as a decoloring agent in textile and pulp and paper industries. The following section briefly discusses the use of PAA in these industries.

7.1. Food-processing and beverage industries

The powerful antimicrobial action of PAA at low temperatures along with the absence of toxic residuals has led to a wide range of its application in food-processing and beverage industries including meat- and poultry-processing plants, canneries, dairies, breweries, wineries, and soft drink plants, where it is indicated to be ideal for clean-in-place systems (Block, 1991; Dychdala, 1988). It is used as terminal disinfectant or sterilant for stainless steel and glass tanks, piping, tank trucks, and railroad tankers (Interox Chemicals, 1998). Its nonrinse feature, where its breakdown products in high dilution are not objectionable from the taste, odor, or toxicity standpoints, saves time and money (Block, 1991). A preparation of PAA (P-3-oxonia active) was approved by the Food and Drug Administration in the United States (FDA) in 1986, giving clearance for its ingredients as indirect food additives in sanitizing solutions. Subsequently, the EPA registration was issued and the U.S. Department of Agriculture (USDA) authorization granted (Dychdala, 1988).

7.2. Medical and pharmaceutical industries

PAA has also been used in the medical and pharmaceutical industry. The Centers for Disease Control of the United States have listed it as a chemical sterilant and high-level

disinfectant (Block, 1991). Large antimicrobial spectrum, short exposure time, and nontoxic decomposition products make PAA a suitable disinfectant for medical equipment. In the preparation of pharmaceuticals, PAA permits the cold sterilization of emulsions, hydrogels, ointments, and powders. Furthermore, PAA has been used as an aerosol for the sterilization of germ-free rooms and feed for gnotobiotic animals (Block, 1991).

7.3. Textile and pulp and paper industries

Another area of use for PAA as a decoloring and/or disinfectant agent is in textile and pulp and paper industries. In Finland, the PAA mixture Desirox has been successfully used to control microbial growth in waters of the paper mill process (Maunuksela, 1995).

8. Factors affecting disinfection

8.1. Temperature

PAA can function over a wide range of temperatures. However, on a general basis, similar to other chemical disinfectants, microbial reductions increase with increasing water temperature during disinfection with PAA (Stampi et al., 2001).

8.2. pH

PAA is affected by pH with greater activity at lower pH. The biocidal form of the PAA is considered to be the undissociated acid (Colgan and Gehr, 2001). PAA has a $\text{p}K_a$ of 8.2, thus at alkaline conditions (i.e., pH above 9), the predominant species is the dissociated acid form resulting in the decreased disinfection efficiency (Baldry and French, 1989a; Sanchez-Ruiz et al., 1995; Tutumi et al., 1973). With bacteria, on a general basis, the difference in disinfection efficiency is small through pH 5 to 8, but a decrease in efficiency was demonstrated at pH 9 (Block, 1991; Baldry et al., 1991; Sanchez-Ruiz et al., 1995). For example, total coliform removals were 2 to 3 logs higher at pH 7 compared to pH 10 (Sanchez-Ruiz et al., 1995). Similarly, the activity of PAA against fecal coliforms was greater under neutral or mildly acidic conditions (Baldry and French, 1989a).

8.3. TSS and BOD

Although PAA is shown to be an effective disinfectant for primary wastewater effluents, on a general basis, it was found that the disinfection efficiency of PAA increases with decreasing total suspended solids (TSS) (Gehr et al., 2002; Colgan and Gehr, 2001; Sanchez-Ruiz et al., 1995) and biochemical oxygen demand (BOD) (Gehr et al., 2002; Colgan and Gehr, 2001; Stampi et al., 2001; Meyer, 1976; Poffe et al., 1978) of wastewater to be disinfected. The

reductions in DNA-phage and RNA-phage concentrations decreased about one to two orders of magnitude as the turbidity of wastewater rose from 2 to 10 nephelometric turbidity units (NTU) (Rajala-Mustonen et al., 1997). On the other hand, at TSS concentrations between 10 and 40 mg l⁻¹, the impact of TSS on disinfection was constant (Stampi et al., 2001). Lefevre et al. (1992) achieved good disinfection even with TSS levels over 100 mg l⁻¹.

8.4. Kinetics

Most of the reduction in microbial concentrations occurs during the first 10 min of contact time, the inactivation curve showing first-order reaction kinetics behavior (Rajala-Mustonen et al., 1997; Thurman and Gerba, 1988; Morris, 1993). The disinfection of *Staphylococcus aureus* with PAA at pH 4 appeared to approximate to log-linear kinetics (Lambert et al., 1999). The PAA disinfection of *Pseudomonas aeruginosa* had nonlinear, tailing kinetics (Lambert et al., 1999). In both cases, disinfection with PAA was much faster than with HP: 2 × 10⁶ and 1.1 × 10⁴ times faster for *S. aureus* and *P. aeruginosa*, respectively. For Gram-negative bacteria, survival curves were biphasic, whereas first-order kill kinetics behavior was found for *Bacillus subtilis* (Jolivet-Gougeon et al., 1996).

9. Safety

By their chemical nature, the peroxygen compounds are powerful oxidizers. They appear to present no danger from toxicity or other hazards when diluted in water to their effective concentration as disinfectants and sterilants (Block, 1991). However, in concentrated solution, they must be treated with caution as is the case with any strong oxidant. Peroxygen compounds should be stored in a cool place, not over 30 °C, and in the original containers provided with vents and flame resistors. Spills or leaks should be covered with weak reducing agents such as sodium thiosulfate. Organic materials and heavy metal ions of copper, iron, and manganese should be avoided because they can cause decomposition so rapid as to cause ignition and produce fires (Block, 1991).

The 40% solution of PAA has a lethal dose for 50% kill (LD₅₀) to rats of 1540 mg kg⁻¹ (Block, 1991; National Institute of Safety and Health, 1974). For a 4% formulation, a value of 3400 mg kg⁻¹ was given, which compares favorably to other common sanitizers (Dychdala, 1988). In another study, PAA was tested on skin, and it was stated that 0.4% to 0.8% PAA can be used directly as a body disinfectant for swine (Block, 1991; Busch and Werner, 1974). According to the work of Bock et al. (1975), PAA is a potent tumor promoter and a weak carcinogen. At 3% and 1%, PAA was a tumor promoter, but not at 0.3%. With 2% PAA in water, 10% of the animals developed skin tumors in 6 months; none did in the following 6 months (Block, 1991;

Bock et al., 1975). Using the Ames' test, PAA was not mutagenic (Yamaguchi and Yamashita, 1980).

10. Negative aspects

Major disadvantages associated with PAA disinfection are the increase of organic content in the effluent, the potential microbial regrowth due to remaining acetic acid (AA is also a product of decomposed PAA), and the lower efficiency against some viruses and parasites (e.g., *Giardia lamblia* cysts and *Cryptosporidium parvum* oocysts) (Baldry and Fraser, 1988; Liberti and Notamicola, 1999; Lefevre et al., 1992; Lazarova et al., 1998). The increase in organic content in treated wastewater is due to acetic acid, which is already present in a PAA mixture and formed after PAA decomposition. For example, for a 5 mg l⁻¹ PAA dose, 13 mg l⁻¹ acetic acid would be formed (assuming the theoretical stoichiometry of PAA decomposition), resulting in a chemical oxygen demand (COD) of about 14 mg l⁻¹. As acetic acid is readily biodegradable, this additional food source may result in microbial regrowth if there is no residual PAA left in the effluents. Lazarova et al. (1998) concluded that PAA may not be an appropriate technology for wastewater disinfection because of the considerable increase in effluent organic load. In another study and under laboratory conditions, total coliform populations exposed to PAA were lower, but presented slightly higher T₉₀ values (time required to reduce the microbial concentration by 90%) than those not previously exposed, suggesting the possible regrowth potential due to biodegradable acetic acid supply by PAA decomposition (Sanchez-Ruiz et al., 1995).

11. Cost

Currently, the major drawback for the use of PAA in wastewater disinfection is its high cost, which is partly due to limited production capacity worldwide. The cost in Europe is about US\$3 gal⁻¹ (US\$0.80 l⁻¹) for 12% PAA solution, approximately four to five times the cost of sodium hypochlorite. As there is no mass production of PAA, especially in the United States, chemical manufacturers cannot quote prices comfortably for large demands such as for wastewater treatment plants.

12. Conclusions

Peracetic acid is a strong disinfectant with a wide spectrum of antimicrobial activity. It has been used in many industries including food processing, beverage, medical, pharmaceutical, textile, and pulp and paper. Due to its bactericidal, virucidal, fungicidal, and sporicidal effectiveness as demonstrated in these industries, the use of PAA as a disinfectant for wastewater effluents is drawing more atten-

tion recently. PAA has been tested and used for wastewater disinfection in England, Finland, Italy, Brazil, and Canada.

The desirable attributes of PAA for wastewater disinfection are the ease of implementing treatment (without the need for expensive capital investment), the broad spectrum of activity even in the presence of heterogeneous organic matter, the absence of persistent toxic or mutagenic residuals or by-products, the no quenching requirement (i.e., no dechlorination), the small dependence on pH, the short contact time, and the effectiveness for primary and secondary effluents. The application of environmentally benign PAA disinfection might be attractive to utilities that do not disinfect year round and to those that would appreciate the low-capital investment. Disinfection with PAA also might be advantageous for wastewater treatment plants having long effluent discharge pipelines (e.g., marine outfalls) because the contact time in these outfalls might be used for disinfection, eliminating the need for costly contact basins.

PAA has also been used or studied for various other environmental applications including use as a disinfectant for ion exchangers, cooling towers, and stored membrane hollow fibers. PAA was shown to be effective for pathogen reduction in biosolids, reduction in solid odors, and sludge debulking. It could also be beneficial for applications such as supplementation of ultraviolet (UV) systems, during storm conditions, and for combined sewer overflow (CSO) disinfection, which requires treatment availability at very short notice and for short periods of time. EPA included PAA among five disinfectants that could be used to disinfect CSOs.

Major disadvantages associated with PAA disinfection are the increases of organic content in the effluent due to acetic acid and thus in the potential for microbial regrowth (acetic acid is already present in PAA mixtures and is also formed after PAA decomposition). Another drawback to the use of PAA is its high cost, which is partly due to limited production capacity worldwide. The cost in Europe is about US\$3 gal⁻¹ (US\$0.80 l⁻¹) for 12% PAA solution, approximately four to five times the cost of sodium hypochlorite in United States. However, if the demand for PAA increases, especially from the wastewater industry, mass production capacity might also be increased in the future, thus lowering the cost. In such a case, in addition to having environmental advantages, PAA may also become cost-competitive with chlorine. Thus, PAA might replace chlorine-based disinfectants in wastewater treatment processes.

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