



Comparison of organic peracids in wastewater treatment: Disinfection, oxidation and corrosion



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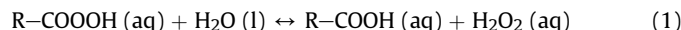
ABSTRACT

The use of organic peracids in wastewater treatment is attracting increasing interest. The common beneficial features of peracids are effective anti-microbial properties, lack of harmful disinfection by-products and high oxidation power. In this study performic (PFA), peracetic (PAA) and perpropionic acids (PPA) were synthesized and compared in laboratory batch experiments for the inactivation of *Escherichia coli* and enterococci in tertiary wastewater, oxidation of bisphenol-A and for corrosive properties. Disinfection tests revealed PFA to be a more potent disinfectant than PAA or PPA. 1.5 mg L⁻¹ dose and 2 min of contact time already resulted in 3.0 log *E. coli* and 1.2 log enterococci reduction. Operational costs of disinfection were estimated to be 0.0114, 0.0261 and 0.0207 €/m³ for PFA, PAA and PPA, respectively. Disinfection followed the first order kinetics (Hom model or S-model) with all studied peracids. However, in the bisphenol-A oxidation experiments involving Fenton-like conditions (pH = 3.5, Fe²⁺ or Cu²⁺ = 0.4 mM) peracids brought no additional improvement to traditionally used and lower cost hydrogen peroxide. Corrosion measurements showed peracids to cause only a negligible corrosion rate (<6 μm year⁻¹) on stainless steel 316L while corrosion rates on the carbon steel sample were significantly higher (<500 μm year⁻¹).

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1. Introduction

Organic peracids are peroxide compounds with an organic side chain and their structure can be generally presented with R-COOOH. They are typically available as an equilibrium solution containing peracid, hydrogen peroxide, corresponding carboxylic acid and water (Reaction (1)). Additionally small amounts of catalysts or stabilizers can be present.



Industrially the most relevant organic peracids are performic and peracetic acids (Jones, 1999). In recent years the use of organic peracids in wastewater treatment applications such as disinfection

and oxidation has attracted a great deal of interest. The main drivers have been the increased awareness of disinfection by-products resulting from traditionally used chlorine, and recalcitrant micropollutants, such as pharmaceuticals and endocrine disruptors, occurring in wastewaters.

Gehr et al. (2009) published one of the first studies about the use of performic acid (PFA), CHOOOH, for wastewater disinfection. PFA is unstable and needs to be prepared on-site shortly before use (Mattila and Aksela, 2000). There are potential safety issues in the process due to the explosive nature of PFA at elevated temperatures and concentrations. PFA has been proved to be especially effective in disinfecting primary wastewater effluents (Gehr et al., 2009) and combined sewer overflows (Chhetri et al., 2015, 2014) which can be difficult to treat with other methods. Furthermore, recent pilot and full scale experiments with secondary effluents (Ragazzo et al., 2013; Karpova et al., 2013) have indicated that a dose of 1.0–1.2 mg L⁻¹ and contact time 10 min are already sufficient to reach 2.2–4.0 log removal of fecal coliforms or *Escherichia coli*. The cost of PFA-based disinfection to reach 10 CFU/100 mL *E. coli* in

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wastewater was reported to be $0.0101 \text{ €}/\text{m}^3$ (Ragazzo et al., 2007). Eco-toxicity and disinfection by-products formation studies with PFA are still scarce but the results of Ragazzo et al. (2013) obtained under operational conditions indicated that no appreciable changes occurred in the *Vibrio fischeri* light suppression test or in the amount of volatile organic compounds after the disinfection. PFA is a strong oxidizer and it has been tested for the degradation of pharmaceuticals in primary wastewater (Gagnon et al., 2008) and refractory organic compounds in landfill leachates (Hagman et al., 2008). However, both studies showed poor removal results possibly due to rapid and non-selective reactions of PFA.

Peracetic acid (PAA), CH_3COOOH , was first proposed for wastewater disinfection over 30 years ago (Baldry, 1983; Meyer, 1976) and has been studied extensively since (Kitis, 2004). Secondary wastewater effluents require typically a $2\text{--}7 \text{ mg L}^{-1}$ dose and approximately 30 min contact time to reach 3 log reduction in total coliform number (Koivunen and Heinonen-Tanski, 2005). Biologically treated and filtered tertiary effluents can be disinfected already with a dose of $1.5\text{--}2 \text{ mg L}^{-1}$ and contact time of 10–15 min to reach the EU bathing water quality for *E. coli* (Luukkonen et al., 2014). However, the required dose and contact time strongly depend on wastewater quality (Koivunen and Heinonen-Tanski, 2005). Unlike PFA, PAA is available as a stabilized equilibrium solution thus making it technically easier to apply. The main beneficial features of PAA, which are largely similar to PFA, are the lack of harmful disinfection by-products under typically applied conditions (Dell'Erba et al., 2007; Liberti and Notarnicola, 1999; Nurizzo et al., 2005; Crebelli et al., 2005) and no significant re-growth of bacteria occurring after disinfection (Antonelli et al., 2006). The activity of PAA against microbes is proposed to be based on the formation of highly oxidizing radicals which is probably the mechanism of other peracids as well. Furthermore, it was recently shown that hydrogen peroxide has an important synergistic effect in the PAA disinfection process (Flores et al., 2014). The cost of PAA-based disinfection ($4\text{--}14 \text{ mg L}^{-1}$, 30 min contact time, tertiary wastewater effluent) has been estimated to be $0.048\text{--}0.098 \text{ €}/\text{m}^3$ depending on the required microbial quality (Nurizzo et al., 2001). The high oxidation potential of PAA, 1.959 V vs normal hydrogen electrode (Awad et al., 2004), has been applied for the degradation of phenol (Rokhina et al., 2010), organic dye (Rothbart et al., 2012) and pharmaceuticals in biologically treated wastewater (Hey et al., 2012) as well as oxidation of activated sludge as a pretreatment for anaerobic digestion (Appels et al., 2011).

Literature concerning perpropionic acid (PPA), $\text{CH}_3\text{CH}_2\text{COOOH}$, is much more limited when compared to PAA or PFA. No published studies exist for wastewater treatment applications. However, the general disinfective properties of PPA are well known (Merka and Dvorák, 1968; Merka et al., 1965) and it has been successfully used, for example, in the decontamination of food-contact surfaces (Vimont et al., 2014). Oxidative properties of PPA have been tested for the degradation of organophosphorus and organosulfur pollutants in micellar solutions (Lion et al., 2002) and for the oxidation of NO_x and SO_2 from flue gas (Littlejohn and Chang, 1990).

Although PAA has been already studied extensively and there are several studies about wastewater disinfection with PFA, the amount of comparative studies is still limited. This applies especially for disinfection kinetics. Furthermore, no studies regarding the wastewater disinfection or oxidation capacities of PPA exist. However, one of the few comparison studies by Merka et al. (1965) indicated PFA, PAA and PPA to have a similar efficiency against *Bacillus subtilis* spores, *E. coli* and *Staphylococcus aureus*. Another pioneering study showed that PFA is a more potent sporicidal agent than PPA (Merka and Dvorák, 1968). Additionally, the virucidal efficiency of PAA and PPA was found to be similar when disinfecting food-contact surfaces (Vimont et al., 2014). Yousefzadeh et al.

(2014) on the other hand concluded PFA to be less effective than free chlorine when disinfecting sterilized active sludge effluent containing *E. coli*.

In this study PFA, PAA and PPA were compared in the disinfection of tertiary wastewater and in the oxidation of bisphenol-A (BPA) with Fenton-like reactions. BPA was selected as a model compound as it is a well-known endocrine disruptor which is widely used as a plasticizer and as a plastic monomer (Vandenberg et al., 2007). Elevated concentrations of BPA can be encountered in industrial effluents while it is present as a micropollutant in municipal wastewaters and drinking waters. Furthermore, uniform corrosion caused by peracids for two steel alloys was evaluated by electrochemical measurements in the concentrations typically used in wastewater applications since no data of this kind are available.

2. Experimental

2.1. Water samples

A chemically–biologically treated and filtered tertiary wastewater sample from The Taskila municipal wastewater treatment plant (Oulu, Finland) was used in the disinfection and peracid decomposition experiments. Additionally, tap water was used in the peracid decomposition experiments.

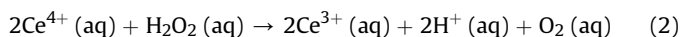
Metal concentrations of water samples were determined by an optical emission spectrometer (Perkin Elmer Optima 5300 DV) while conductivity and pH were measured with a Hach HQ40d meter. Chemical oxygen demand (COD_{Cr}), total nitrogen and phosphate were determined using a Hach Lange DR 2800 photometer and cuvette tests LCK314, LCK138 and LCK349, respectively. Seven day biological oxygen demand with allylthiourea addition ($\text{BOD}_{7, \text{atu}}$) was determined with the OxiTop manometric respirometric method.

2.2. Preparation of peracids

Peracids were prepared by mixing 10 mL of carboxylic acid with 0.94 mL of 95–97% (w/w) sulfuric acid (Baker) in a round-bottom flask placed in an ice-bath. 10 mL of 30% (w/w) hydrogen peroxide (Merck) was then slowly added. Contents of the flask were mixed with a magnetic stirrer (250 rpm) for 90 min and the flask was moved to the refrigerator. The carboxylic acids used in the synthesis were 98–100% formic acid (Merck), 99–100% acetic acid (Baker) and 99% propionic acid (Merck). The commercial peracetic acid (Desirox 12:20) sample was received from Solvay.

2.3. Concentration measurements of peracids

Concentrations of prepared peracids were measured with a two-stage cerimetric–iodometric titration method (Greenspan and Mackellar, 1948). Gehr et al. (2009) presented a modification involving the addition of molybdate catalyst before iodometric titration. 0.1 mL of peracid was weighed and placed in an Erlenmeyer flask containing 10 mL 5% (w/w) sulfuric acid (Baker). The Erlenmeyer flask was kept in an ice bath to maintain the temperature under 10 °C . Three drops of ferroin indicator (Riedel) was added and the contents of the Erlenmeyer were titrated with 0.1 M ceric sulfate (Merck). The volume used was recorded as V_{T1} . A color change from orange to light blue occurred at the equivalence point. Ce^{4+} reacts with hydrogen peroxide according to the Reaction (2).



5 mL of 10% potassium iodide (Merck) solution, three drops of molybdate (Merck) solution and 1 mL of starch (Merck) indicator

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