

PAA vs H₂O₂ Efficacy Comparison

The following pages are included as a simple reference to the relative efficacy of peracetic acid, which is also known as peroxyacetic acid (PAA), vs. hydrogen peroxide (HP). Other citations are available, but this particular reference is the most cited and definitive on this subject.

On the 3rd page, page 35 of the report, please read the 2nd paragraph of the subject "Case Studies". The organisms tested were E. coli, S. aureus, and Pseudomonas aeruginosa. It took 700 ppm of HP alone to achieve a 5 log reduction of E. coli with a contact time of 2 hours. When 0.75 ppm of PAA was introduced, only 100 ppm of HP was required to achieve the same results. However, when a standard PAA formulation was used, only 3 ppm of PAA was required to achieve the same 5 log reduction.

It should also be noted that "the action of hydrogen peroxide was rather slow, with bactericidal effects found even after 4 hrs. for certain organisms. On the other hand, the action of peracetic acid was almost instantaneous and, in many cases, no further change was observed after 30 minutes."

Alasri, et al's, scientific article referenced here is listed in the bibliography at the end of this file, for those who would like to do some further reading.

Disinfection of Wastewater by Hydrogen Peroxide or Peracetic Acid: Development of Procedures for Measurement of Residual Disinfectant and Application to a Physicochemically Treated Municipal Effluent

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ABSTRACT: The Montreal Urban Community Wastewater Treatment Plant (MUCWTP) located in Montreal, Quebec, Canada, uses physicochemical treatment processes prior to discharging wastewater into the St. Lawrence River via an outfall tunnel of 2 hours retention time. Although chlorination facilities exist, they are not being used, and the MUCWTP is seeking alternative methods for disinfection to achieve a 2- to 3-log fecal coliform reduction. Liquid chemical disinfectants were attractive options because of their low capital costs. This led to an investigation of the feasibility of using hydrogen peroxide or peracetic acid.

A method for measuring peroxycompounds (hydrogen peroxide or peracetic acid plus hydrogen peroxide) was developed using the peroxidase-based oxidation of 2,2'-azino-bis(3-ethylbenz-thiazoline-6-sulfuric acid) diammonium salt (ABTS) with hydrogen peroxide. The validity of the method was confirmed using effluent from the MUCWTP. Recovery was higher than 90% for peracetic acid levels as low as 1.0 mg/L. Quenching of hydrogen peroxide was achieved with 50-mg/L catalase; quenching of peracetic acid was achieved with 100 mg/L of sodium thiosulfate, followed by 50 mg/L of catalase.

Batch disinfection tests were conducted on MUCWTP effluent. Hydrogen peroxide and peracetic acid in wastewater over time could be modeled as a second-order decay, with the decay "constant" being a function of the initial concentration of peroxycompounds. This function was the same for both hydrogen peroxide and peracetic acid, possibly indicating similar decomposition pathways in wastewater matrices.

Disinfection was modeled using a modified Hom equation. Required doses of hydrogen peroxide to reach the target fecal coliform levels ranged from 106 to 285 mg/L, with the higher doses occurring when ferric chloride instead of alum was used as the coagulant. Hence, hydrogen peroxide was infeasible as a disinfectant for this application. On the other hand, the peracetic acid dose needed to achieve the target fecal coliform level was only 0.6 to 1.6 mg/L. Therefore, peracetic acid seems to be a promising disinfectant for physicochemical or primary effluent, or combined sewer overflows. *Water Environ. Res.*, 74, 33 (2002).

KEYWORDS: wastewater disinfection, peracetic acid, hydrogen peroxide, residual measurements, physicochemical effluent, second-order Hom model.

Introduction

As chlorination becomes less popular for wastewater disinfection, municipalities are seeking alternatives that are simple to operate, produce few or no byproducts, and exhibit attractive economics. The advantages of liquid chemical disinfection (compared to ozonation or UV radiation) include low capital cost, simple operation, ability to flow-pace, and rapid start-up. These characteristics are especially important for combined sewer overflows (CSOs) because disinfection is required over short periods; therefore, high capital costs would be inappropriate and flow pacing and rapid start-up are essential.

The Montreal Urban Community Wastewater Treatment Plant (MUCWTP), Quebec, Canada, the average flow of which is 29.5 m³/s or 0.9 × 10⁹ m³/a, does not disinfect its final effluent. Although the MUCWTP has chlorination facilities in place, it must replace them with a cleaner and safer technology because regulations of the provinces of Saskatchewan, Quebec, and Prince Edward Island require that all effluents discharged to waterbodies containing fish bear no materials that are toxic to the native fish population. Hence, these provinces are reluctant to allow the use of chlorine for wastewater disinfection (WEF, 1996).

In its treatment train, the MUCWTP uses physicochemical processes only, that is, primary sedimentation assisted by coagulation with alum, ferric chloride, or both and a polyelectrolyte. The effluent, therefore, still contains significant levels of suspended solids (SS), biochemical oxygen demand (BOD), and chemical oxygen demand (COD) (typically 20, 40, and 120 mg/L, respectively) and could be considered as being intermediate between a secondary effluent and a CSO. The final effluent is discharged via a 4-km underground tunnel with a 2-hour retention time at average flow into the St. Lawrence River.

Although the MUCWTP has already investigated ozonation or UV radiation as alternatives to chlorine disinfection (Gehr and Nicell, 1996), the possibility of using a liquid chemical disinfectant was attractive because of the existence of storage and dosing facilities for chlorine. Thus, some of the initial capital costs might be avoided. This was important to the MUCWTP because disinfection was only needed for 6 months in the summer each year and,

as such, a large investment in equipment that was inactive 50% of the time was unattractive. Because of high dilution levels in the St. Lawrence River, the target fecal coliform level was a relatively high 10^4 colony-forming units (cfu)/100 mL (from an initial count of 10^6 to 10^7 cfu/100 mL), which is less stringent than most jurisdictions. This high level of dilution led to a lower disinfectant dose requirement than is commonly found in the literature. Further advantages of using a liquid chemical as a disinfectant included ease of operation and low maintenance costs, the ability to flow-pace, rapid start-up and shut-down, and the use of the outfall tunnel as a contact basin, which further saved on capital costs.

Two potentially interesting chemical disinfectants that have not received widespread application for wastewater disinfection in North America are hydrogen peroxide (H_2O_2) and peracetic acid (PAA). Searches of recent literature have failed to reveal any case studies of the use of hydrogen peroxide for full-scale wastewater disinfection, although it has been used for activated-sludge bulking control (Jenkins et al., 1986). Peracetic acid has been used in several wastewater applications (most notably marine outfalls) in Europe (Baldry and French, 1989a; Lefevre et al., 1992; Liberti and Notarnicola, 1999; and Sánchez-Ruiz et al., 1995), but so far not in North America. Peracetic acid has also been studied as an alternative to chlorine bleaching in the pulp and paper industry (Yuan et al., 1997).

Because of their high chemical reactivity, both hydrogen peroxide and peracetic acid show rapid decay during disinfection. Therefore, any studies into kinetics and dosage requirements require reliable and sensitive methodologies to stop the disinfection processes as well as the ability to measure residual concentrations at low levels (less than 1 mg/L). Few such methods are available in the literature for hydrogen peroxide, and almost none are available for peracetic acid.

This study reports on methods that were developed for quenching and residuals measurement of hydrogen peroxide and peracetic acid in preparation for their use as potential disinfectants for the MUCWTP effluent. This study also examined the feasibility of disinfecting MUCWTP effluents using hydrogen peroxide or peracetic acid. The work was done on batch scale only and, therefore, must be considered preliminary particularly in the case of peracetic acid, which gave promising but somewhat inconsistent results. Because of the significant consumption of disinfectant residual during the contact period and the effect this might have on disinfection kinetics, an attempt was made to model the kinetics of disinfectant residual decay as well as bacterial inactivation under such conditions.

Literature Review

***Disinfection Kinetics.** The kinetics of disinfection are typically modeled by familiar first-order kinetics, and these are applicable when there is neither a shoulder (in the early stage) nor tailing (in the later stage) of the disinfection curve. A model that does account for these effects was developed by Hom (1972) as follows:

$$\frac{dN}{dt} = -kNt^m C^n \quad (1)$$

Where

- N = microorganism concentration after time (t);
- k = microbial decay constant;
- C = residual concentration of disinfectant;

- m = a tailing or shoulder constant; if $m < 0$, tailing occurs; if $m > 0$, a shoulder occurs; and
- n = concentration constant (sometimes known as the coefficient of dilution).

If $m = 0$ and C^n is a constant, equation 1 reduces to the familiar Chick's law of first-order order kinetics. However, in tests with chlorinated effluents from stabilization ponds, Hom (1972) ascertained that the tailing or shoulder constant and the concentration constant depended on reaction time, residual chlorine concentration, and the number of surviving organisms.

To further clarify the effects of C^n not being constant, Haas and Joffe (1994) proposed the following model, assuming that the disinfectant decays at a first-order rate to an inert form:

$$\ln\left(\frac{N}{N_0}\right) = -m'kC_0^n \int_0^t \exp(-nk't)t^{m'-1} dt \quad (2)$$

Where

- $m' = m + 1$,
- N_0 = initial microorganism concentration (at time 0),
- k' = first-order residual decay constant, and
- C_0 = initial disinfectant concentration.

Haas and Joffe (1994) included an approximation method for solving (integrating) eq 2, which was exact for $m' = 1$ (or $m = 0$) but deviated increasingly as m' departed from 1 or at increasing values of time or disinfectant decay.

Sánchez-Ruiz et al. (1995) used 5% peracetic acid as a disinfectant for total coliforms from a pretreated (presumably preliminary treatment only) raw wastewater in northern Spain. They found that total coliform inactivation followed a biphasic decrease model as shown in the following equation:

$$\log\frac{N_0}{N} = I_{\max} \cdot \frac{t}{t' + t} \quad (3)$$

Where

- I_{\max} = asymptotic value of maximum inactivation, and
- t = abscissa value corresponding to $I_{\max}/2$.

For their case, the first phase of rapid kinetics was completed after 5 to 10 minutes, and little additional inactivation occurred after this time. The authors also found that for this raw wastewater (with relatively high suspended solids and COD) there was great variability in the effectiveness of peracetic acid, and that the overall extent of total coliform inactivation was less than that obtained by other researchers using secondary treated wastewater.

Byproducts. Booth and Lester (1995) conducted one of the few studies that investigated the potential for byproduct formation from peracetic acid treatment of wastewater. They focused on the possibility of chlorinated or brominated phenols resulting from the interaction of peracetic acid with chlorides, bromides (especially in discharges from seawater), and organics. Chlorophenol concentrations in the original effluents were typically much less than 100 ng/L, and although increases were measured, the concentrations never exceeded 100 ng/L, even under the most favorable reaction conditions. Therefore, although a mechanism was proposed under which the addition of peracetic acid promotes the generation of halogenated products through the formation of free chlorine or free

bromine radicals, the concentration levels produced are unlikely to pose environmental problems unless there are already significant precursor concentrations (i.e., phenols) in the effluents.

Liberti et al. (1999) used 15.5% peracetic acid in their laboratory and pilot-plant studies on activated-sludge effluents, some of which had also been pretreated with polyaluminum chloride and filtered. Possible byproducts from peracetic acid usage, namely total epoxides and 2/4/2,4 chlorophenols, were tested for but were not detected.

Concerning the potential for increasing the biodegradability of organics, Lazarova et al. (1998) found that 5 mg/L peracetic acid increases total organic carbon (TOC) by a factor of 1.5, whereas 10 mg/L tripled the TOC. In addition, the biodegradable dissolved organic carbon was multiplied by a factor of 4. Collivignarelli et al. (2000) measured an increase in COD of 5 to 6 mg/L in their effluent after the addition of 1 to 3 mg/L peracetic acid because of the presence of acetic acid. The wastewater pH decreased by approximately 0.1 units, and the oxidation-reduction potential increased by 10 to 15%.

Case Studies. The only instances of hydrogen peroxide use at reasonable doses in wastewater applications seem to be in controlling sludge bulking in the activated-sludge process (Jenkins et al., 1986). The range of dosages used is quite wide (10 mg/L) and the dosing point could be anywhere between the activated-sludge biological reactor and the final clarifier. Contact time is not listed as a variable; hydrogen peroxide is simply added at the point found to be most suitable for bulking control. Poffé et al. (1978b) reported that doses of hydrogen peroxide as high as 5500 mg/L and a contact time of 2 hours were needed to achieve adequate disinfection of the municipal wastewater that they tested.

Alasri et al. (1992) studied the inactivation of typical bacteria found in water and wastewater (*Escherichia coli*, *Staphylococcus aureus*, and *Pseudomonas aeruginosa*) with hydrogen peroxide alone and in combination with peracetic acid. High doses of hydrogen peroxide were required to achieve 5-log reductions of *E. coli* (more than 700 mg/L with contact times of 2 hours). However, when hydrogen peroxide was used with peracetic acid, the effect was synergistic: approximately 100 mg/L of hydrogen peroxide was needed in the presence of 0.75 mg/L of peracetic acid. When peracetic acid was used alone, 3 mg/L was required for the same effect. Alasri et al. (1992) also established that the action of hydrogen peroxide was rather slow, with bactericidal effects found even after 4 hours for certain organisms. On the other hand, the action of peracetic acid was almost instantaneous and, in many cases, no further change was observed after 30 minutes. The medium in which disinfection took place seemed to be a prepared broth, and there was no control reported for chemical consumption of the hydrogen peroxide or peracetic acid over time. Interestingly, the authors did not take into account the concentration of hydrogen peroxide that would be present in the peracetic acid solution itself; rather, they added hydrogen peroxide separately to each peracetic acid solution being used when synergisms were being studied.

Applications of peracetic acid for wastewater disinfection are much more widespread than hydrogen peroxide. Interest in the use of peracetic acid as a disinfectant for wastewaters began in the late 1980s with publications by Baldry, French, and their colleagues (Baldry and French, 1989a and 1989b, and Baldry et al., 1991). For many years, peracetic acid had been used as a powerful disinfectant in smaller and more confined applications (such as hospital settings) before being proposed as a suitable chemical for waste-

water disinfection. Because of the intrinsically safe nature of its components (acetic acid and hydrogen peroxide), peracetic acid is unlikely to form toxic byproducts.

Lefevre et al. (1992) assessed peracetic acid for disinfecting secondary effluents for final discharge into seawater. In addition to the need for high levels of disinfection (3- to 4-log reduction of bacterial levels), peracetic acid was chosen because of its simplicity of application, low cost, and lack of harm to the environment. The products of peracetic acid were identified as acetic acid (or vinegar), oxygen, methane, carbon dioxide, and water, none of which was considered toxic in the concentrations encountered. Lefevre et al. (1992) found that peracetic acid was insensitive to different SS concentrations in the effluent over the range of 10 to 50 mg/L, but that 100 mg/L would reduce the extent of inactivation by 1 log. On the other hand, Lazarova et al. (1998) found that SS played a major role in disinfection performance with peracetic acid. As SS increased in the range of 0 to 10 mg/L, required peracetic acid dosages also increased. However, between 10 and 40 mg/L, the effect of SS remained constant.

Lefevre et al. (1992) found that the virucidal action of peracetic acid was low, and Liberti and Notarnicola (1999) determined that, although peracetic acid was effective against total coliforms, it was ineffective toward *Giardia* and *Cryptosporidium* parasites.

In a recent report by the U.S. Environmental Protection Agency (1999), peracetic acid was included among five disinfectants for use on CSOs. Based on data for the disinfection of secondary treatment plant effluents, it was suggested that peracetic acid be strongly considered for CSO disinfection. Among the desirable attributes of peracetic acid that were listed are the absence of persistent residuals and byproducts, unaffected by pH (below a pH of 8.2) (FMC Corp., 1998), short contact time, and high effectiveness as a bactericide and virucide.

Key results from several case studies are summarized in Table 1. From approximately 10 years of studies on peracetic acid disinfection, it is evident that the range of dosages (1 to 500 mg/L) and contact times (< 1 to 120 minutes) is too broad to be able to draw generalizations. However, the following trends may be ascertained:

- Inactivation is a function of dose as well as contact time (i.e., the typical concentration \times contact time concept as applied to other chemical disinfectants, such as chlorine, is valid) (Lefevre et al., 1992).
- The DNA phages are much easier to inactivate than the RNA phages (Rajala-Mustonen et al., 1997), and bacteria are much easier to inactivate than phages (Lazarova et al., 1998).
- Lower pH values are desirable (Baldry et al., 1991, and Sánchez-Ruiz et al., 1995).
- No studies are available for inactivation of bacteria (such as fecal coliforms) in physicochemically treated effluents, although a typical concentration \times contact time combination for activated-sludge effluent and 3-log reduction might be a peracetic acid dose of 5 to 10 mg/L and a contact time of 30 to 60 minutes.

Chemistry, Properties, and Analytical Methods. *Hydrogen Peroxide.* Although almost pure (98%) hydrogen peroxide exists, it is commercially available as a water solution in a wide range of concentrations (Snell and Ettore, 1971). The reactions of hydrogen peroxide can be classified into four categories: decomposition into oxygen gas and water reduction-oxidation reactions, peroxide

Table 10—Chemical and 5-day biochemical oxygen demand following 1.5 mg/L peracetic acid addition and 2-hour contact time (February 17, 2000).

Sample ^a	Raw		Raw-	Disinfected-
	Raw	Disinfected	quenched	quenched
BOD ₅ ± SD (mg/L)	92 ± 2	99 ± 3	139 ± 3	147 ± 3
COD ± SD (mg/L)	169 ± 7	193 ± 9	219 ± 2	245 ± 6

^a SD = standard deviation.

Based on a typical unit cost of (U.S.) \$4/kg of the 15% peracetic acid product for a 6-month per year disinfection period and a dose of 1 mg/L, the annual chemical cost for a flowrate of 29.5 m³/s would be \$12 million for disinfection with peracetic acid.

Conclusions

Methods were developed for quenching the activity of hydrogen peroxide and peracetic acid disinfectants as well as measuring low levels of residuals of hydrogen peroxide and peracetic acid in wastewater matrices after specific contact times. It was then possible to model and calibrate the decay of hydrogen peroxide and peracetic acid and the kinetics of inactivation of fecal coliforms under decreasing concentrations of these disinfectants. The decay of hydrogen peroxide and peracetic acid was found to be second order with respect to the total concentration of peroxycompounds. The decay constant itself depended on the initial chemical concentration, the inverse (negative) power relationship suggesting that lower concentrations would decay less rapidly. Free-swimming microorganisms are always the first to be inactivated; those that are attached will succumb only after the disinfectant has been able to diffuse through any protective layers. Thus, the slow decay of the peroxyresiduals might be advantageous in cases where long contact times are available, such as in the present case with the MUCWTP.

To reach the target fecal coliform level of 10 000 cfu/100 mL, batch tests showed that doses of hydrogen peroxide greater than 100 mg/L would be required, even for a 2-hour contact time. This is clearly uneconomical. On the other hand, peracetic acid doses of 1.6 mg/L or less would be adequate to reach the same target level. This shows that although hydrogen peroxide and peracetic acid can both be considered peroxycompounds, their mode of action on bacteria is different. Furthermore, because peracetic acid will decompose to hydrogen peroxide and the two will also coexist, it is likely, as already suggested by other authors, that there is a strong synergistic effect.

Thus, in agreement with many other studies conducted on European wastewaters (Table 1), peracetic acid has been shown to be capable of disinfecting municipal wastewaters at reasonably low doses. Although the target fecal coliform level in the present study, at 10 000 cfu/100 mL, is much higher than typically required, physicochemical effluents of the type used in this study usually require higher disinfectant doses than effluents from biological treatment plants. Thus, a dose of 1.0 to 1.6 mg/L can be regarded as an encouraging indication that peracetic acid may become a cost-effective alternative to chlorine, UV radiation, or ozone for wastewater disinfection in North America. This dose is, in fact, lower than most of the doses reported in Table 1, which may, in

part, be the result of the lenient target fecal coliform level. Further studies are underway to assess the dosage levels needed for biologically treated effluents.

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