



Peracetic acid degradation in freshwater aquaculture systems and possible practical implications

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ABSTRACT

Peracetic acid (PAA) is a highly reactive peroxygen compound with wide-ranging antimicrobial effects and is considered an alternative sanitizer to formaldehyde. Products containing PAA are available in solution with acetic acid and hydrogen peroxide to maintain the stability of the chemical, and it decays rapidly when applied to freshwater in aquaculture systems. The rapid decay is beneficial in an environmental context but a challenge to aquaculturists. To assess the impact of organic matter content and temperature on PAA decay, twenty-four batch experiments were set up using PAA doses ranging from 0 to 2.0 mg/l. The results revealed that increasing organic matter content significantly facilitated PAA decay, and positive temperature-decay correlations were found. Instantaneous PAA consumption above 0.2 mg/l was observed, and PAA half-lives were found to be in the order of a few minutes. The relative PAA recovery, calculated as measured PAA concentration over time compared to the PAA concentration applied, decreased with declining dose. Measurements of PAA residuals during water treatment scenarios at three different freshwater fish farms revealed moderate to substantial PAA consumption, documenting a large discrepancy between delivered quantities and realized residuals. Recent investigations of PAA application to manage parasitic diseases in aquaculture are briefly reviewed, and practical implication and guidelines are addressed.

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1. Introduction

Peracetic acid (PAA)-based products have recently gained considerable attention in the search for therapeutic aquaculture agents to replace malachite green and formaldehyde. Malachite green has been banned for more than a decade (Sudová et al., 2007; Marchand et al., 2012), and the use of formaldehyde is considered unfavorable in terms of worker safety and the potential negative environmental impact on the receiving water body (Masters, 2004; Pedersen et al., 2007). Aquaculture-related research with PAA products includes *in vitro* assessments, where promising disinfection action has been documented (Meinelt et al., 2007a,b, 2009; Straus and Meinelt, 2009; Bruzio and Buchmann, 2010; Picón-Camacho et al., 2012a). These studies have identified dose-dependent antiparasitic effects of various trade products containing mixtures of PAA on *Ichthyophthirius multifiliis* (Ich or white spot disease) and provide important information for PAA to be implemented in commercial aquaculture operations (Picón-Camacho et al., 2012b).

In vivo studies conducted as field trials have also shown beneficial efficacy of PAA on parasites (Holten et al., 2002; Rintamäki-Kinnunen et al., 2005b; Sudová et al., 2010; Jussila et al., 2011), albeit the results have not been clear (Rintamäki-Kinnunen et al., 2005a). Insufficient control of parasitic burden has also been observed, and gill damage or mortality has occurred making general guidelines difficult to define. Danish fish farmers have had mixed experiences using PAA-based products. Empirical observations range from fully effective preventive measures against the causative agent for *I. multifiliis* and other troublesome parasites, to moderately effective or ineffective; farmers have also reported compromised fish health and biofilter impairment (Pedersen and Henriksen, 2011).

The partial success of PAA-based products evaluated under practical conditions relies on several factors and circumstances. Uncertainties about PAA decay under different environmental conditions complicates residual PAA assessment and has implications on the resulting treatment regimen (PAA concentration × contact time: CT) as demonstrated by Rach et al. (1997). The active PAA concentration depends on (i) the product formulation (ranging from 2 to 40% PAA with substantial variability between and within products) and the applied dose, (ii) the stability of the product, and (iii) the PAA consumption and decay in the specific aquaculture system.

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The disinfection demand of PAA (initial consumption and decay) under aquaculture conditions is positively correlated to organic matter content of the water and existing biofilm on the surface (Pedersen et al., 2009). Therefore, there is a potential risk of discrepancy between the intended, theoretical concentration and the actual treatment concentration achieved.

The purpose of this study was to evaluate PAA decay under controlled conditions reflecting realistic situations. These experiments were made in the laboratory and included combinations of water temperature (5–20 °C), organic matter content (COD ranging from 0 to 71 mg O₂/l) and quantity of PAA applied (0–2 mg/l PAA). In addition, PAA residuals were measured at three occasions during prophylactic water treatment on three different freshwater fish farms. The results and the consequence of disinfection demand on water management practice are discussed and empirical knowledge from current studies is briefly reviewed.

2. Materials and methods

Two experiments were conducted to determine the combined effects of chemical oxygen demand (COD), temperature, and nominal concentration on the PAA decay. These experiments were designed according to a statistical surface-response method (Box et al., 2005) where fixed combinations of two independent variables (factors A and B) were arranged in a matrix in order to test combined effects on PAA decay. Furthermore, residual PAA was measured (see Section 2.3) on three commercial fish farms with prophylactic PAA water treatment. In all experiments, a PAA-based trade product (PeraquaPlus) was used, which contained 12–15% PAA and 30–35% H₂O₂ according to the manufacturer's formulation. Measurements were made on PAA only, as H₂O₂ at the levels applied (<1 up to 5 mg/l) are considered of minor importance in terms of antimicrobial effects (Pedersen et al., 2009).

2.1. Experiment I: effects of COD and nominal concentration on PAA decay rate

This experiment was a central composite design with twelve separate batch experiments; four identical central-point combinations and eight different combinations (Box et al., 2005). The two independent factors were: (A) organic matter content in water measured as COD in mg/l O₂, and (B) nominal, delivered concentration of PAA in mg/l. Both factors were combined at five predefined levels with factor A at the following COD levels: 0, 10.3, 35.4, 61.2, and 70.8 mg/l O₂; and factor B, with nominal PAA concentrations at: 0, 0.29, 1.0, 1.71, and 2.0 mg/l PAA. The dependant variable was the relative PAA decay during the first 15 min after addition of the PAA. This value (PAA recovery_{15 min}) was calculated as the integral (concentration x time) of analytically measured PAA concentrations during the initial 15 min in relation to the integral with a constant PAA concentration equaling the nominal C₀.

Water for these experiments was collected from an operating experimental recirculating aquaculture system (RAS) with a feed loading of 6.2 kg/m³ as described by Pedersen et al. (2012). To each fixed combination, a water sample was taken prior to PAA addition and followed by 6–8 additional sampling measurements within the first hour after addition. The twelve experiments were conducted over a period of 3–4 days with random combinations of the two factors.

2.2. Experiment II: effects of water temperature and nominal concentration on PAA decay rate

This experiment was designed similar to Section 2.1. In this experiment, factor A was water temperature at the following

Table 1

Description of systems and conditions at three commercial Danish trout farms in connection with PAA residual measurements.

Study details	Fish farm A	Fish farm B	Fish farm C
Type of system	Pond (earthen)	Raceway (concrete)	Circular tank (concrete)
Water use	Flow-through	Recirculation	Recirculation
Rearing volume (m ³)	70	125	125
Average depth (m)	0.8	1.1	3.0
Make-up water (L/s)	5	<5	<5
Circulation flow	N/A	40	20
Fish density (kg/m ³)	<10	≥50	≥50
Water temp. (°C)	15–16	13–14	13–14
COD level (mg O ₂ /l)	21	19	24
Airlift ^a	No	Yes	Yes
Feed/day (kg)	10	50–75	50–75
PAA application ^b	~4 ml/m ³	20 ml/m ³	20 ml/m ³
Expected C ₀ ^c	0.5	2.4	2.4
PAA recovery _{15 min} (%) ^d	72	59	15
Est. half-life of PAA	23 min	~7 min	<5 min

^a Water circulation by airlift with 2–3 m depth.

^b Trade product Peraqua Plus with 12% PAA and 35% H₂O₂.

^c Expected nominal concentration of peracetic acid.

^d Percent PAA of added quantity recovered 15 min after addition.

pre-defined levels: 5.0, 7.2, 12.5, 17.8, and 20.0 °C. The temperatures were controlled with thermostatic water baths. Factor B was nominal PAA concentrations at the same levels as applied in Section 2.1. In the analysis of the twelve separate experiments, PAA recovery_{15 min} was used as the response variable of interest. Water with COD level of 70 ± 2 mg O₂/l was applied in these batch experiments.

2.3. Field experiments: PAA application in three different types of aquaculture systems

Residual PAA was measured on three occasions at commercial freshwater fish farms corresponding with prophylactic treatments using PAA during late summer. The three fish farms, a traditional flow-through system, a raceway system, and a circular tank system differed in design, fish density, feed loading, and degree of water reuse (Table 1). Samples were collected from the outlets of the rearing systems and immediately analyzed for residual PAA. The experiments were not replicated; the intention was solely to provide indication of residual PAA and order of decay in relation to the expected PAA concentration.

2.4. Chemical analysis

Residual PAA was analyzed by the DPD method according to Falsanisi et al. (2006) applying N,N-diethyl-p-phenylenediaminesulphate salt (reagent 1) and potassium iodide buffer solution (reagent 2) to form a transient color formation. Water samples were immediately analyzed for residual PAA. From a sterile-filtered (0.45 μm) water sample 2.5 ml was pipetted into a 10 mm capped cuvette into which 250 μl of reagent 1 and 250 μl of reagent 2 were added and gently mixed. The color intensity was measured on a Hach Lange 2800D spectrophotometer at λ = 550 nm 20 s after mixing with reagent 2. Concentration of PAA and hydrogen peroxide in the commercial products was analyzed by two consecutive autotitrations according to the manufacturer protocol (Brenntag, DK). Water temperature and pH was measured with a HQ40 multimeter (Hach Lange, Düsseldorf, Germany). Organic matter was measured as total COD on unfiltered water samples as described in Pedersen et al. (2012).

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