Aquacultural Engineering xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Aquacultural Engineering

journal homepage: www.elsevier.com/locate/aqua-online

Hydrogen peroxide decomposition kinetics in aquaculture water

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ARTICLE INFO

Article history:
Received 3 July 2014
Accepted 21 December 2014
Available online xxx

Keywords:
Aquaculture
Hydrogen peroxide
Degradation
Kinetics
Enzyme inactivation
Microbial water quality

ABSTRACT

Hydrogen peroxide (HP) is used in aquaculture systems where preventive or curative water treatments occasionally are required. Use of chemical agents can be challenging in recirculating aquaculture systems (RAS) due to extended water retention time and because the agents must not damage the fish reared or the nitrifying bacteria in the biofilters at concentrations required to eliminating pathogens. This calls for quantitative insight into the fate of the disinfectant residuals during water treatment. This paper presents a kinetic model that describes the HP decomposition in aquaculture water facilitated by microbial enzyme activity. The model describes how the hydrogen peroxide removal declines and eventually stops at relatively low chemical oxygen demand (COD) concentrations. It is hypothesized that this is due to an enzyme deficit because it is destructed due to the reactive radicals created during the HP decomposition. The model assumes that the enzyme decay is controlled by an inactivation stoichiometry related to the HP decomposition. In order to make the model easily applicable, it is furthermore assumed that the COD is a proxy of the active biomass concentration of the water and thereby the enzyme activity. This was, however, not measured. The model developed successfully described the removal of HP in aquaculture water from three types of RAS and model parameters are estimated. The model and the model parameters provide new information and are valuable tools to improve HP application in RAS by addressing disinfection demand and identify efficient and safe water treatment routines.

1. Introduction

Hydrogen peroxide (HP) has shown promising results in the treatment of a number of different protozoan and fungal infections on fish (Schreier et al., 1996; Lilley and Inglis, 1997; Avendaño-Herrera et al., 2006; Heinecke and Buchmann, 2009; Giménez Papiol and Roque, 2013).

An advantage of using HP over formalin (e.g. Masters, 2004) is that HP workwise is less hazardous. HP decomposes relatively fast to oxygen and water (Block, 1991) and the break down does not include harmful disinfection by-products as is the case for other chemicals applied in aquaculture (Dawson et al., 2003), hence having the potential to be sufficiently eliminated prior to discharge and to comply with discharge regulations for land based aquaculture systems (Schmidt et al., 2006).

The studies conducted with HP have mostly concentrated on the parasite treatment efficiency and the tolerance of different fish species to HP in bath treatments (Rach et al., 2000). The treatments conducted in flow-through systems or in fish tanks have included a restricted treatment period, typically carried out using hydrogen peroxide doses of around 50–100 mg/L for 30 min to 2 h (Arndt and Wagner, 1997; Gaikowski et al., 1999; Bowker et al., 2012). This intermittent treatment procedure in freshwater systems markedly differs from short term dip baths to control sea lice where HP concentrations above 1000 mg/L are applied for a few minutes (Adams et al., 2012). Use of HP in RAS is associated with prolonged contact time and precautions regarding potential impact on biofilter performance, calling for low dose applications.

Knowledge on low dose (<20 mg/L) HP treatment efficiency and treatment regimens (contact time and active concentration) in RAS are limited and findings on potential damaging effects on aquaculture organisms and nitrifying populations in biofilters has impeded the use of HP in RAS so far (Schwartz et al., 2000; Pedersen and Pedersen, 2012). An effective and a safe threshold level for HP dose and contact time in relation to inhibition of nitrification in biofilters is complicated to assess as it depends on a number of parameters. Further research is hence needed to describe the underlying mechanisms of HP degradation and inhibition.

The decomposition of HP in a pilot scale RAS has previously been studied by Pedersen et al. (2006). HP degraded exponentially with a rate depending on the organic matter concentration measured as biochemical oxygen demand (BOD_5) of the water. It was

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http://dx.doi.org/10.1016/j.aquaeng.2014.12.004
0144-8609/

assumed that the BOD_5 reflected the microbial quality (composition and activity of microorganisms, predominately heterotrophic bacteria) and thereby the concentration of the enzyme catalase that catalyses the degradation of HP (Hosetti and Frost, 1994). Møller et al. (2009) studied HP degradation and the effect of HP treatment on nitrifying biofilms in small-scale recirculation aquaculture systems. They also observed exponential removal of HP with biofilter elements present. In both studies, HP added at dosages below 20 mg/L was completely removed within few hours. However, when using aquaculture water without biofilter elements present, Møller (2008) found incomplete HP degradation for certain conditions where the ratio of initial concentrations of HP and aquaculture water COD were above a certain value. The higher the ratio of initial HP and COD, the faster the HP decomposition levelled off and HP approached a constant concentration. This reaction behaviour, which in the following is called the "HP level off and constant concentration phenomenon", was also observed by Pedersen et al. (2009) when using a mixture of HP and peracetic acid applied at different concentrations.

The levelling off and constant concentration phenomenon has previously been observed in systems where the chlorinated aliphatic hydrocarbons trichloroethylene (TCE) and chloroform (CF) were co-metabolically transformed by a methane monooxygenase enzyme in methane oxidizing cells, methanotrophs, Alvarez-Cohen and McCarty (1991a,b,c). The removal of TCE and CF was successfully described by assuming that TCE and CF or their transformation products inactivated the monooxygenase enzyme. The concept of "transformation capacity" was introduced assuming that per unit weight of methanotrophs, only a certain amount of the contaminants (TCE or CF) can be transformed (stoichiometric inactivation). Consequently, if insufficient amounts of methanotrophs are present, only incomplete TCE or CF removal takes place which is observed by levelling off and approaching a constant concentration. Later, the transformation capacity concept and enzyme inactivation phenomenon has been applied for other monooxygenase systems carrying out co-metabolic reactions, such as ammonium oxidizing bacterial systems (Ely et al., 1997; Wahman et al., 2006).

In the present study, we pursued the same mechanistical approach of HP levelling off and constant concentration behaviour caused by inactivation of the catalase enzyme. During the decomposition of HP, radicals are produced such as strongly reactive hydroxyl radicals that can oxidize organic and inorganic matter and they can inactivate cells (Paller and Patten, 1991; Salem et al., 2000; Klimenko et al., 2009). There are few other published studies where the HP degradation in aquaculture water has been quantified without biofilters present (Tort et al., 2003; Pedersen et al., 2012). However, none of them have explained quantitatively the HP level off and constant concentration phenomenon. Therefore, the purpose of this study was to examine the degradation kinetics of HP and quantify the factors which determine the HP removal and the HP level off and constant concentration phenomenon. In particular, the effect of initial concentration of HP and the COD of the water which is assumed to positively correlate with the microbial biomass that harbour the catalase enzyme.

2. Theoretical kinetic model

This section outlines the theoretical basis for hydrogen peroxide (HP) decomposition kinetics in aquaculture water. Based on previous findings (Pedersen et al., 2006) the HP decomposition reaction rate, r_{HP}, is first order with respect to the HP concentration, C_{HP}, and the concentration of the enzyme catalase, C_E, that catalyses the HP decomposition, Eq. (1).

$$r_{HP} = -\frac{dC_{HP}}{dt} = kC_{HP}C_E \quad (1)$$

k is the HP decomposition reaction rate constant.

Furthermore, it is assumed that for each unit mass of HP being decomposed, a certain amount of catalase is inactivated (inactivation stoichiometry) due to the reactive radicals involved in the HP decomposition, Eq. (2).

$$dC_E = k_{ed}dC_{HP} \quad (2)$$

k_{ed} is the catalase enzyme inactivation yield constant (inactivation stoichiometry constant). This is the inverse of the transformation capacity applied in the modelling by Alvarez-Cohen and McCarty (1991a,b,c).

By integrating Eq. (2), C_E is obtained, Eq. (3).

$$C_E = C_{E0} - k_{ed}(C_{HP0} - C_{HP}) \quad (3)$$

C_{HP0} and C_{E0} are the initial ($t = 0$) concentrations of HP and the catalase enzyme.

By inserting (3) in (1), the HP removal is described by Eq. (4).

$$r_{HP} = -\frac{dC_{HP}}{dt} = kk_1C_{HP} + kk_{ed}C_{HP}^2 \quad (4)$$

where

$$k_1 = C_{E0} - k_{ed}C_{HP0} \quad (5)$$

after integration, and assuming batch or plug flow treatment, the concentration of HP is obtained, Eq. (6) ($k_1 \neq 0$),

$$C_{HP}^{-1} = -\frac{k_{ed}}{k_1} + \left(C_{HP0}^{-1} + \frac{k_{ed}}{k_1}\right)e^{kk_1t} \quad (6)$$

According to Eq. (5), k_1 may be positive or negative depending on C_{E0} being bigger or smaller than $k_{ed}\cdot C_{HP0}$. The C_{HP0} concentration where this transition happens is $C_{HP0,tr} = C_{E0}/k_{ed}$. For initial HP concentrations above $C_{HP0,tr}$ ($k_1 < 0$) all catalase enzyme is destructed during the HP decomposition. This state is referred to "catalase enzyme deficit". The opposite situation/state ($k_1 > 0$) is called "catalase enzyme surplus".

When catalase enzyme deficit prevails ($k_1 < 0$), the decomposition of HP gradually stops: $r_{HP} = -dC_{HP}/dt \to 0$ and a constant HP concentration, $C_{HP,c}$, is approached:

From Eq. (4), $C_{HP,c}$, is calculated,

$$C_{HP,c} = -\frac{k_1}{k_{ed}} \quad (7)$$

Based on this constant concentration, the solution for enzyme deficit, $k_1 < 0$, is

$$C_{HP}^{-1} = C_{HP,c}^{-1} + (C_{HP0}^{-1} - C_{HP,c}^{-1})\exp(kk_1t) \quad (8)$$

If k_1 is positive, complete HP decomposition takes place.

During the initial decomposition, when time t is "small" ($e^{k\cdot k1\cdot t} \sim 1 + k\cdot k_1\cdot t$), $C_{HP}{}^{-1}$ is proportional with time,

$$C_{HP}^{-1} = C_{HP0}^{-1} + kk_1(C_{HP0}^{-1} - C_{HP,c}^{-1})t \quad (9)$$

After a certain time, when the second term in Eq. (6) is dominating, the HP reduction is exponential,

$$C_{HP} = (C_{HP0}^{-1} - C_{HP,c}^{-1})^{-1}e^{-kk_1t} \quad (10)$$

For the special state/case where $k_1 = 0$, i.e. the initial HP concentration balances the initial catalase enzyme concentration, then according to Eq. (6), the HP decomposition is governed by

$$r_{HP} = -\frac{dC_{HP}}{dt} = kk_{ed}C_{HP}^2 \quad (11)$$

and the solution is

$$C_{HP}^{-1} = C_{HP0}^{-1} + kk_{ed}t \quad (12)$$

Measuring the catalase enzyme concentration in practice may be difficult or unpractical. Alternatively, a simpler, but less exact

Please cite this article in press as: Arvin, E., Pedersen, L.-F., Hydrogen peroxide decomposition kinetics in aquaculture water. Aquacult. Eng. (2015), http://dx.doi.org/10.1016/j.aquaeng.2014.12.004