



Application of a fluidized bed reactor charged with aragonite for control of alkalinity, pH and carbon dioxide in marine recirculating aquaculture systems



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ABSTRACT

Control of alkalinity, dissolved carbon dioxide (dCO_2), and pH are critical in marine recirculating aquaculture systems (RAS) in order to maintain health and maximize growth. A small-scale prototype aragonite sand filled fluidized bed reactor was tested under varying conditions of alkalinity and dCO_2 to develop and model the response of dCO_2 across the reactor. A large-scale reactor was then incorporated into an operating marine recirculating aquaculture system to observe the reactor as the system moved toward equilibrium. The relationship between alkalinity dCO_2 , and pH across the reactor are described by multiple regression equations. The change in dCO_2 across the small-scale reactor indicated a strong likelihood that an equilibrium alkalinity would be maintained by using a fluidized bed aragonite reactor. The large-scale reactor verified this observation and established equilibrium at an alkalinity of approximately 135 mg/L as $CaCO_3$, dCO_2 of 9 mg/L, and a pH of 7.0 within 4 days that was stable during a 14 day test period. The fluidized bed aragonite reactor has the potential to simplify alkalinity and pH control, and aid in dCO_2 control in RAS design and operation. Aragonite sand, purchased in bulk, is less expensive than sodium bicarbonate and could reduce overall operating production costs.

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1. Introduction

Control of alkalinity, pH, and carbon dioxide in marine recirculating aquaculture systems is fundamental to maintaining efficiency of nitrification in the biofilter and to maintaining the health of culture animals (Timmons and Ebling, 2007). Alkalinity in the form of bicarbonate ions (HCO_3^-) is required for proper biofilter operations since it is consumed by nitrifying bacteria during the conversion of ammonia to nitrate (Timmons and Ebling, 2007). Hardness and alkalinity are often directly associated in aquaculture since both can be provided by calcium carbonate dissociation. Calcium can be associated with deleterious effects such as nephrocalcinosis (Chen et al., 2001) but is also a requirement for specific life stages (e.g., larvae) of some fish, or for proper growth of crustaceans for instance (Boyd, 1990).

Alkalinity can be adjusted in recirculating aquaculture systems (RASs) by the addition of a buffering compound such as sodium bicarbonate (Loyless and Malone, 1997; Timmons and Ebling, 2007) or by system volume replacement (Seginer et al., 2008). Dissolved carbon dioxide (dCO_2) is typically removed by using degassing towers or aeration (Moran, 2010; Summerfelt et al., 2000, 2003; Timmons and Ebling, 2007). Carbon dioxide and pH control are directly linked due to shifts in the carbonate buffering system (Boyd, 1990). The relationship between carbon dioxide, carbonic acid (H_2CO_3), bicarbonate ions (HCO_3^-), and carbonate ion (CO_3^{2-}) concentrations relative to pH in aquaculture systems is thoroughly reviewed by Boyd (1990) for ponds and Timmons and Ebling, 2007 for RASs.

Previously, a system was developed and applied to pretreatment of highly acidic waters (e.g., coal mine drainage, or acidified lake water) prior to use in fish culture systems that consists of an upflow fluidized bed of limestone sand (calcite, $CaCO_3$) (Watten et al., 2005; Sibrell et al., 2006). The build-up of dCO_2 in high density RAS operations due to respiration has the potential to acidify water within the system. The build-up is of particular concern when pure oxygen is being used since there is little stripping of dCO_2 in oxygenation systems compared to aeration systems (Summerfelt et al.,

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2000; Timmons and Ebling, 2007). In addition, the biofilter nitrification process is alkalinity consuming and adds hydrogen ions resulting in acidification of the culture water while removing its buffering capacity (Timmons and Ebling, 2007).

This study was conducted to determine whether a fluidized bed reactor similar to that applied by Watten et al. (2005) and Sibrell et al. (2006) in freshwater applications could be incorporated into a marine recirculating aquaculture system to aid in the control of pH, dCO_2 , and alkalinity. Sand composed of the aragonite form of $CaCO_2$ was selected for the reactor media rather than calcite sand due to its relatively higher dissolution rate (Chen et al., 2001). The overall performance of two pilot reactors (small-scale and large-scale) on two RASs stocked with fish was reported based on changes in water chemistry.

2. Materials and methods

2.1. Small-scale pilot reactor

A small-scale fluidized-bed pilot reactor was constructed from a 1.5 m length of clear 10.2 cm diameter PVC pipe (Schedule 40) that was fitted with a 2.5 cm diameter elbow centered in the bottom and attached using a Uniseal® bulkhead fitting. Water was pumped through the reactor with a 1/3 hp submersible pump fitted with a bypass valve to allow water flow to the reactor to be adjusted to 6.25 ± 0.03 L/min (mean \pm SE; $n = 24$) to produce a hydraulic retention time (HRT) within the fluidized aragonite bed of 1.41 ± 0.01 min (mean \pm SE; $n = 24$). The reactor was initially filled with water and aragonite sand (Aragamax™ sugar sized sand, CaribSea, Inc., Fort Pierce, Florida) added to a height of 0.4 m (0.32 m³). The aragonite sand used had a mean particulate diameter by weight of $211 \mu\text{m}$ determined by particle sieve analysis (Fig. 1). Upon initiation of flow the aragonite bed was expanded to $1.1 \text{ m} \pm 0.01 \text{ m}$ (mean \pm SE; $n = 24$). The small-scale pilot reactor was operated on a 43 m^3 marine recirculating aquaculture system (Weirich et al., 2009) with four 7.8 m^3 tanks two of which were stocked with a total of approximately 890 Florida Pompano *Trachinotus carolinus* averaging 578 g giving an overall system biomass load of 11.7 kg/m^3 . The fish were fed a ration of 2% body weight per day of a 45% protein 16% lipid commercial floating salmonid diet (Nelson and Sons, Inc., Silver Cup, Steelhead 3.5 mm) based on total biomass in the system at the initiation of tests.

The recirculating system consisted of two propeller washed bead filters (Aquaculture Systems Technology, LLC, New Orleans,

LA.) filled with 0.7 m^3 of floating plastic bead media. The submersible pump supplying the reactor was alternately installed in the side box of one of the two 7.8 m^3 culture test tanks each fitted with the Cornell style dual drain system. One of the two tests tanks, Tank 1, was stocked with 41 kg/m^3 of pompano ($n = 590$; average weight 540 g), the other, Tank 2, was not stocked with fish allowing for comparison of two different influent dCO_2 concentrations during the trials.

Reactor performance was determined in each of the two tanks empirically by manipulating total alkalinity of the entire system by controlling additions of sodium bicarbonate. Four individual trials were conducted over the course of several weeks during which the total alkalinity of the system was targeted at 70, 100, 130, and 200 mg/L as $CaCO_3$ (Table 1). At each alkalinity level the influent and effluent water from the reactor was sampled three times from each tank to determine alkalinity, pH, and dCO_2 . Alkalinity was measured by titration using the bromocresol green-methyl red indicator under the assumption that the primary contributor to alkalinity under the conditions of the tests was bicarbonate (HACH® method 10244, Hach Company, Loveland, CO). A handheld pH meter that was calibrated against 7.00 and 10.01 pH buffers each day prior to use was employed for pH measurement (YSI EcoSense pH100, Yellow Springs Instruments, Inc., Yellow Springs, OH). Water flow rate out of the reactor was measured and adjusted prior to each trial and after each sample was collected using a timer and calibrated 20L bucket. Dissolved carbon dioxide was measured by the method of Moran (2010) that was verified periodically using a head space unit and a CO_2 infra-red gas analyzer (GD-444, CEA Instruments, Inc., Westwood, NJ) (Pfeiffer et al., 2011). Salinity was measured by conductivity (YSI Model 30 SCT meter, Yellow Springs Instruments, Inc.). The system was operated at a salinity of 8.3 ± 0.04 g/L (mean \pm SE; $n = 24$) and temperature of 28.3 ± 0.02 °C (mean \pm SE; $n = 24$) during all four trials.

During a separate test run changes in Ca^{++} , K^+ , Mg^{++} , Na^+ , P^+ , Mn^{++} , Zn^{++} cations as the water passed through the aragonite reactor were measured by inductively coupled plasma (ICP) spectrometry using an Optima 2100-DV ICP-optical emission spectrometry spectrometer (PerkinElmer, Shelton, CT). The reactor was run for several minutes influent water was collected and after an appropriate amount of time passed for the associated water to have passed completely through the reactor a sample of effluent water was collected. The test conditions of the small-scale aragonite reactor during sample collection for this ion analysis were: salinity = 8.2 g/L, alkalinity = 126 mg/L, influent pH = 6.5, influent $dCO_2 = 34$ mg/L, and HRT = 1.25 min.

Multiple regression analysis was used to establish the relative change in hydrogen ion concentration ($\% \Delta [H^+]$), and in alkalinity in mg/L as $CaCO_3$ ($\% \Delta [ALK]$), or the percent change in dCO_2 across the reactor (SAS 9.2, SAS Institute Cary, NC). Graphical representations of the predictive models were developed using GraphPad Prism 4.03 for Windows (GraphPad Software, Inc., La Jolla, CA). The relative change in H^+ was calculated by assuming that hydrogen ion activity was equivalent to H^+ concentration and therefore, $\% \Delta [H^+] = ((10(-pHe) - 10(-pHi)) / 10(-pHi)) \times 100\%$, where pHi is the influent pH, and pHe is the effluent pH.

2.2. Large-scale pilot reactor

A 0.6 m diameter CycloBio® (Pentair Aquatic Ecosystems, Apopka, FL) fluidized sand bed biofilter operated with a water level of 2.3 m was used as the vessel for the large-scale pilot reactor (reactor vessel volume = 0.67 m^3) (Summerfelt, 2006). The reactor vessel was filled with water, and then aragonite sand (0.12 m^3) was added to the filter to a compacted bed depth of 0.41 m. Water was pumped into the reactor with a 0.5 hp submersible pump fitted with

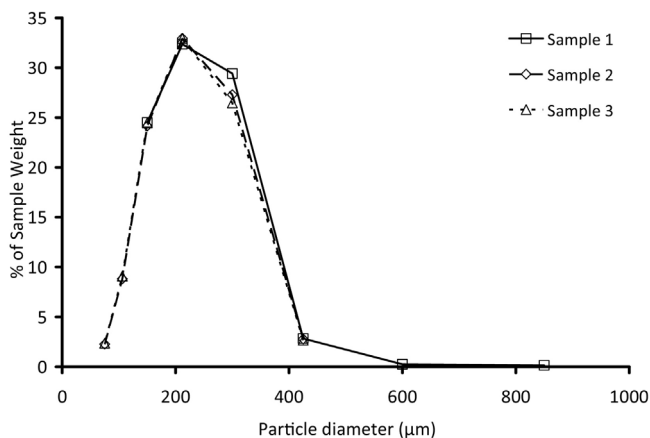


Fig. 1. Particle size distribution of aragonite sand (Aragamax™ sugar sized sand, CaribSea, Inc., Fort Pierce, FL) used in both the small-scale and large-scale aragonite reactors.

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