



A novel approach for ammonia removal from fresh-water recirculated aquaculture systems, comprising ion exchange and electrochemical regeneration

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ABSTRACT

A new physico-chemical process for ammonia removal from fresh-water recirculated aquaculture systems (RASs) is introduced. The method is based on separating NH_4^+ from RAS water through an ion-exchange resin, which is subsequently regenerated by simultaneous chemical desorption and indirect electrochemical ammonia oxidation. Approach advantages include (1) only slight temperature dependence and no dependence on bacterial predators and chemical toxins; (2) no startup period is required and the system can be switched on and off at will; and (3) the fish are grown in much lower bacterial concentration, making the potential for both disease and off-flavor, lower. A small pilot scale RAS was operated for 51 d for proving the concept. The system was stocked by 105 tilapia fish (initial weight 35.8 g). The fish, which were maintained at high TAN (total ammonia nitrogen) concentrations (10–23 mgN L^{-1}) and fish density of up to 20 kg m^{-3} , grew at a rate identical to their established growth potential. $\text{NH}_3(\text{aq})$ concentrations in the fish tank were maintained lower than the assumed toxicity threshold (0.1 mgN L^{-1}) by operating the pond water at low pH (6.5–6.7). The low pH resulted in efficient CO_2 air stripping, and low resultant $\text{CO}_2(\text{aq})$ concentrations (<7 mg L^{-1}). Due to efficient solids removal, no nitrification was observed in the fish tank and measured nitrite and nitrate concentrations were very low. The system was operated successfully, first at 10% and then at 5% daily makeup water exchange rate. The normalized operational costs, calculated based on data derived from the pilot operation, amounted to 28.7 \$ cent per kg fish feed. The volume of the proposed process was calculated to be ~13 times smaller than that of a typical RAS biofilter. The results show the process to be highly feasible from both the operational and economical standpoints.

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1. Introduction

Recirculated Aquaculture Systems (RASs) are the future of the aquaculture industry. Despite being more capital-intensive than traditional approaches, RAS has major advantages such as lower water and area requirements, year-round production, temperature control and mitigation of environmental effects. RAS is species-adaptable, allowing operators to follow market trends for seafood preference. RAS is also a “point” pollution source, enabling efficient solids waste treatment and nutrients removal, which allows reducing the impact on the environment at a reasonable cost.

The high fish densities practiced in RAS require efficient gas-transfer systems to dissolve oxygen into the culture water and strip carbon dioxide out of it. Additionally, since NH_3 is toxic to most fish species it has to be constantly removed. A maximum $\text{NH}_3(\text{aq})$ concentration of 21 $\mu\text{gN L}^{-1}$ was proposed as a threshold value for most marine and fresh water aquaculture species (Eddy,

2005). In order to avoid $\text{NH}_3(\text{aq})$ accumulation, a nitrification unit is invariably employed in RAS to reduce the total ammonia nitrogen (TAN) to concentrations typically below 2–3 mg L^{-1} (warm-water fish). Most RAS configurations do not include a nitrate removal unit (denitrification), and hence, typically, the nitrate concentration in the system and effluents is set only by the make-up water exchange rate (except for minor uncontrolled denitrification, which invariably occurs in the system). Intensive nitrate removal is feasible only if a dedicated denitrification reactor is operated, as is the case in certain low discharge systems (Singer et al., 2008) and where strict environmental regulations are enforced (Klas et al., 2006). Nevertheless, the increasing demand for releasing aquaculture effluents to receiving waters with low total dissolved nitrogen concentrations, will, in all likelihood, lead to a need for the inclusion of nitrate removal systems in RAS in the near future.

The reliance of RAS on conventional biological processes for nitrogen species removal, despite being an established procedure, has disadvantages: nitrifying bacteria are autotrophic organisms with long doubling times and a low biomass yield. As such they are sensitive to low temperatures (especially relevant in the growth of cold water fish, e.g. juvenile salmonids), their start-up periods

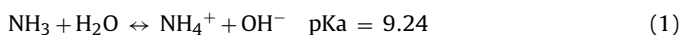
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are long, and when system failure occurs the bacterial population requires a long period to recover. Moreover, when a denitrification system is employed and its effluent is recycled back into the system, turbidity, caused by both organic matter and bacteria loads may develop in the pond, increasing the potential for disease outbreak and the development of off-flavor in the fish.

The incentive for the development of a new, physico-chemical technology for RAS water treatment stems from the drawbacks associated with the biological treatment sequence, in particular in cold places and where the excreted ammonia is required to be transformed all the way to benign $N_{2(g)}$. The goal of the current paper is to introduce a reliable and cost effective physico-chemical process, which has the potential to replace the widespread biological nitrogen-species removal techniques.

1.1. Description of the proposed physico-chemical operational approach

Ammonia in aqueous solution acts as a weak-acid, comprising ionic (NH_4^+) and non-ionic ($NH_{3(aq)}$) species. According to Eq. (1), reduction in pH shifts TAN toward NH_4^+ and vice versa. Fish excrete NH_3 from the gills as part of their metabolism. At the typical RAS operational pH values, NH_3 is largely converted to the relatively non-toxic NH_4^+ species. In typical RAS practice TAN concentrations are controlled such that $NH_{3(aq)}$ concentration is in the range 0.05–0.27 mgNL⁻¹ (Eshchar et al., 2006) depending on the fish species grown.



Based on Eq. (1), one can readily calculate the maximal TAN concentrations that can be maintained in RAS as a function of pH, assuming a given, fish-specific NH_3 threshold concentration. From the practical standpoint, Eshchar et al. (2006) showed that relatively sensitive fish fingerlings (*Sparus aurata*) can be grown unharmed at high TAN concentrations (20 mgNL⁻¹) and a relatively low pH (pH 6.8).

Shifting to the ammonia removal angle, it is well known that NH_4^+ can be effectively separated from fresh water by ion-exchange (IX). For example, natural zeolites, having a high affinity toward a wide range of cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+}), are often used for separating NH_4^+ from wastewater (e.g. Lahav and Green, 1998). With regard to aquaculture, Dryden and Weatherley (1989) reported that clinoptilolite (a common natural zeolite) can be applied for continuously removing TAN from RAS. Working with NH_4^+ concentrations in the range 1–5 mgNL⁻¹ they showed that the practical capacity of clinoptilolite for NH_4^+ increased almost proportionally with the ammonium ion concentration. This observation means that, for given concentrations of competing cations, a proportionally lower zeolite mass is required when the NH_4^+ concentration is higher. The new approach presented in this work, which is shown schematically in Fig. 1, relies (with respect to the TAN removal component) on the observations of Eshchar et al. (2006), coupled with the method proposed by Dryden and Weatherley (1989).

Referring to Fig. 1: In order to remove NH_4^+ effectively, it is proposed to operate the pond at a relatively high TAN concentration (i.e. TAN >5 mgNL⁻¹). In order to not exceed the NH_3 design threshold concentration, the pH value in the fishpond should be maintained at a relatively low value by controlled addition of strong acid (either HCl or H_2SO_4). Since at the close-to-neutral pH range each mole of NH_3 excreted by the fish is converted to NH_4^+ thereby consuming one equivalent of acidity, the acid consumption rate (in equivalent units) is expected to be almost equal to the NH_3 flux (acid consumption is also affected, to a much lesser degree, by the makeup water alkalinity influx). The TAN concentration in the fishpond water is maintained constant by continuous

removal of NH_4^+ from the water, carried out by passing the water through an ammonium-specific ion-exchange resin (from the zeolite group). Once the ion-exchange capacity of the operative column is exhausted, it should undergo regeneration, and the flow from the fishpond is transferred to another, fresh column, i.e. the fish are grown at pseudo steady state conditions with respect to both the TAN concentration and pH.

The typical regeneration sequence of cation exchange resins is performed by passing through it water with high counter cation concentration (typically Na^+ , less often Ca^{2+}). In the current approach, in order to use the regeneration solution for multiple regeneration cycles and at the same time convert NH_4^+ to benign $N_{2(g)}$, we propose to oxidize the ammonia electrochemically, using the indirect ammonia electro-oxidation approach (e.g. Vanlangendonck et al., 2005; Szpyrkowicz et al., 2005; Gendel and Lahav, 2012). This complex process can be described in a somewhat simple fashion by the following stoichiometric equations (Gendel and Lahav, 2012), dominant in Cl^- -rich solutions:

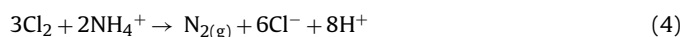
At the anode



At the cathode



In the electrolyte solution



Overall (dominant) reaction



The rate of ammonia electro-oxidation has been reported to be pseudo-zero order and first order with respect to the TAN and chloride ions concentrations, respectively (Liu et al., 2009). In spite of the similarity in the overall stoichiometric reaction (Eq. (4)) the mechanism of the electrochemical ammonia oxidation process is completely different from that observed in classic breakpoint chlorination (Gendel and Lahav, 2012). The conversion of NH_4^+ to $N_{2(g)}$ in the latter process (at the range $7 < pH < 8$) when $HOCl/OCl^-$ is the active chlorine source, proceeds almost completely via the conversion of TAN into chloramines species, and $N_{2(g)}$ formation occurs only when the Cl_2/TAN molar ratio exceeds unity. In contrast, in the indirect ammonia electro-oxidation process carried out at batch mode, very low concentrations of chloramine species are observed, and N_2 formation occurs from the very beginning of the oxidation. The difference between the two processes has been attributed to the particular conditions prevailing in the near anode (i.e. $pH < 2$, high $[Cl^-]$) and near cathode ($pH > 12$) zones (Gendel and Lahav, 2012). In this study the primary oxidizing agent in the near anode zone was found to be $Cl_{2(aq)}$. $Cl_{2(aq)}$ reacts with ammonium ions to form trichloramine (NCl_3) as a primary product. This is in contrast with the known chloramination process, where the dominant oxidizing agent is $HOCl$ (or OCl^-) and monochloramine (NH_2Cl) is the primary product of ammonia oxidation at $7 < pH < 8$. A portion of $Cl_{2(aq)}$ which did not react in the near anode area reaches the bulk electrolyte solution where it undergoes hydrolysis to $HOCl$. Subsequently, monochloramine or/and dichloramine ($NHCl_2$) are formed by the reaction of $HOCl$ with ammonia. NCl_3 decomposes to N_2 both in the bulk electrolyte solution and in the near cathode area via a reaction with hydroxide ions and ammonia. In batch mode electro-oxidation mono- and dichloramine are converted to trichloramine upon their return to the near anode area. For elaboration on the mechanism the reader is referred to Gendel and Lahav (2012).

As shown in Fig. 1, during the regeneration step, both the extraction of the NH_4^+ ion from the zeolite (i.e. the chemical regeneration step) and the ammonia electro-oxidation step are

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