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 $m^{-2}$, grew at a rate identical to their established growth potential. NH$_3(aq)$ 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 CO$_2(aq)$ 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 $ 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.

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 NH$_3(aq)$ concentration of 21 $\mu$gN L$^{-1}$ was proposed as a threshold value for most marine and fresh water aquaculture species (Eddy, 2005). In order to avoid NH$_3(aq)$ 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...
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 N2(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 (NH4+) and non-ionic (NH3(aq)) species. According to Eq. (1), reduction in pH shifts TAN toward NH4+ and vice versa. Fish excrete NH3 from the gills as part of their metabolism. At the typical RAS operational pH values, NH3 is largely converted to the relatively non-toxic NH4+ species. In typical RAS practice TAN concentrations are controlled such that NH3(aq) concentration is in the range 0.05–0.27 mgN L−1 (Eshchar et al., 2006) depending on the fish species grown.

\[ \text{NH}_3 + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^- \quad \text{pK}_a = 9.24 \] (1)

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 NH3 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 mgN L−1) and a relatively low pH (pH 6.8).

Shifting to the ammonia removal angle, it is well known that NH4+ 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+, Ca2+, Mg2+), are often used for separating NH4+ 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 NH4+ concentrations in the range 1–5 mgN L−1 they showed that the practical capacity of clinoptilolite for NH4+ 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 NH4+ 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 NH4+ effectively, it is proposed to operate the pond at a relatively high TAN concentration (i.e. TAN >5 mg N L−1). In order to not exceed the NH3 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 H2SO4). Since at the close-to-neutral pH range each mole of NH3 excreted by the fish is converted to NH4+ thereby consuming one equivalent of acidity, the acid consumption rate (in equivalent units) is expected to be almost equal to the NH3 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 NH4+ 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 Ca2+). In the current approach, in order to use the regeneration solution for multiple regeneration cycles and at the same time convert NH4+ to benign N2(g), we propose to oxidize the ammonia electrochemically, using the indirect ammonia electro-oxidation approach (e.g. Vanlangendonck et al., 2005; Szpyrkowski et al., 2005; Gendel and Lahav, 2012). This complex process can be described in a somewhat typical fashion by the following stoichiometric equations (Gendel and Lahav, 2012), dominant in Cl−-rich solutions:

At the anode
\[ 2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^- \] (2)

At the cathode
\[ 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \] (3)

In the electrolyte solution
\[ 3\text{Cl}_2 + 2\text{NH}_4^+ \rightarrow N_2(g) + 6\text{Cl}^- + 8\text{H}^+ \] (4)

Overall (dominant) reaction
\[ 2\text{NH}_4^+ \rightarrow N_2(g) + 3\text{H}_2 + 2\text{H}^+ \] (5)

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 NH4+ to N2(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 N2(g) formation occurs only when the Cl2/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 N2 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 Cl2(aq). Cl2(aq) reacts with ammonium ions to form trichloramine (NCl3) as a primary product. This is in contrast with the known chloramination process, where the dominant oxidizing agent is HOCl (or OCl−) and monochloramine (NH2Cl) is the primary product of ammonia oxidation at 7<pH<8. A portion of Cl2(aq) which did not react in the near anode area reaches the bulk electrolyte solution where it undergoes hydrolysis to HOCI. Subsequently, monochloramine or and dichloramine (NHCl2) are formed by the reaction of HOCI with ammonia. NCl3 decomposes to N2 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 NH4+ ion from the zeolite (i.e. the chemical regeneration step) and the ammonia electro-oxidation step are
performed simultaneously. Such simultaneous operation necessitates low regenerant volume, as NH₄⁺ does not accumulate and its concentration remains low throughout the regeneration period. Conversely, the two regeneration steps can be carried out separately. Under such operation the column is first chemically regenerated by the brine that is passed through the column. Thereafter, the desorbed NH₄⁺ is oxidized electrochemically to N₂(g) in batch mode. This alternative requires relatively large regenerant volume, but it allows performing the electrolysis step at the low-cost electricity hours. The decision on which regeneration mode to use should be made based on local economic optimization.

According to Eq. (5) one equivalent of alkalinity is destroyed for each mole of exchanged, and subsequently oxidized, ammonium ion. To make up for both alkalinity and counter cation loss during the regeneration step, a stoichiometric mass of strong base (e.g. NaOH) should be added continuously during the electrolysis step, for maintaining the pH of the electrolyzed solution at a constant value.

Another pollutant that is excreted by the fish and is toxic to aquatic organisms is CO₂(aq). Threshold CO₂ concentrations have been reported to be 10–20 mg L⁻¹ for Salmonids and 30–50 mg L⁻¹ for Tilapia and Catfish (Eshchar et al., 2006). In aerated systems, CO₂ stripping from the water is a byproduct of the intensive air supply. On the one hand the proposed pH reduction in the fishpond shifts the carbonate system to result in higher CO₂(aq) Concentrations in the pond but on the other these conditions lead to a higher driving force for CO₂ stripping. The net result, as shown in this work for fish densities of up to 20 kg m⁻³, is that the acidification of the fishpond water to pH 6.5–6.8 with low carbonate alkalinity and thus low CO₂ concentrations can be readily achieved. Note that this conclusion is restricted to aerated aquaculture systems and does not apply to systems relying on pure O₂ supply.

1.2. Process limitations

Three operational limitations are associated with the described process: the first limitation is that the low pH maintained in the fishpond water requires intensive removal of CO₂ that can be achieved only when air is applied for oxygen supply. It is noted that modern aeration technologies make it possible to grow fish at very high densities of up to the 100 kg fish m⁻³ without need for pure oxygen supply (Mozes et al., 2005). The second limitation is associated with the IX component, which becomes inefficient at high counter cations concentrations. Accordingly, the proposed process is feasible only for fresh water RAS applications and cannot be applied in saline or seawater-fed RAS. The third limitation: since ammonium ions in the fishpond water are replaced in the proposed approach with other cations (mainly Na⁺), the method cannot be applied in very low discharge (so called “zero-discharge”) systems because as counter cations accumulate in the pond water, NH₄⁺ separation through IX becomes inefficient. However, as shown in this paper, the system operated efficiently at 5% water replacement (fish density 20 kg m⁻³), and can be theoretically shown to work also at lower exchange rates (and much higher densities).

This paper presents the results obtained when the described approach was tested at the small pilot scale, for growing tilapia for a period of 51 days. This initial work is intended to serve as proof-of-concept for the described approach, and by no means as a description of a fully developed technology. However, both the fish performance and cost estimations derived from the pilot operation showed the approach to be very promising.

2. Materials and methods

In order to prove the feasibility of the proposed approach, a pilot scale system was constructed and operated for 64 days. Tilapia was chosen as the proof-of-concept fish species both due to its relative tolerance to NH₃ and CO₂ concentrations and the large experience accumulated with this fish in Israel. 105 fish, with an initial average weight of 35.8 g, were grown for 51 days in a 500 L fresh-water fed container. Before stocking the fish the system was first operated for 13 days in simulation mode. A schematic of the pilot scale system is shown in Fig. 2. Technical details of all the equipment are listed in Table A.1 (Appendix A). Preliminary ion-exchange breakthrough experiments were performed in order to estimate the amount of chabazite–zeolite required for the pilot operation. The results of this step are reported in Appendix B.

2.1. Fishpond operation

The fish were grown in a 700 L tank, filled up with 500 L fresh water (T1 in Fig. 2). During the first 36 days the system was operated with 10% daily make up water exchange: in the last 15 days make up water supply was reduced to 5%. The make up (tap) water was added via a level sensor (V0 in Fig. 2) and activated carbon filters were used to remove residual chlorine from it (F1 and F2 in Fig. 2). Make up water characterization is shown in Table 1. Oxygen was supplied (also causing CO₂ stripping) by three air diffusers. Suspended solids separation was performed by continuous recirculation of the fishpond water (~12 L min⁻¹) through a 12 L coarse filter (F2 in Fig. 2), using a magnetic pump (M5 in Fig. 2). The pH value of the fishpond water was controlled at pH 6.5–6.7 by H₂SO₄ (2.35 M) dosage. The pH electrode in the fishpond was calibrated daily. Water temperature was maintained at 28 °C by a 1.2 kW heating element.

105 Tilapia fish with an average weight of 35.8(±6.6%) g were stocked in the container, making for an initial fish density of
7.5 kg m⁻³. Fish food (characterized in Table 1) was supplied by an automatic feeder for ~10 h per day. Feeding rates are shown in Fig. 4 (Section 3.1). In order to avoid formation of nitrite in the pond (which could have potentially formed due to the high TAN concentrations maintained in the water), a nitrification inhibitor, N-allylthiourea (98% Aldrich), was added dry to the fishpond once every 5 days to maintain an average concentration of 0.5 mg/l. N-allylthiourea was used because it was the only nitrification inhibitor whose acute toxicity could be found in the literature (Wood, 1953). Inhibitor addition was stopped 22 days into the experiment (see elaboration in Section 3.2).

2.1.1. Fish tank water analyses

DO, acid consumption and fish tank TAN, alkalinity, chloride, phosphate, nitrate, nitrite, Na⁺, Ca²⁺, Mg²⁺, and K⁺ concentrations were measured daily in both the fishpond and inlet water. Make up water rate was measured daily with a water meter. On top of the initial weighing, the fish were weighed three more times during the growth period: after 18 days of growth (11 fish), 36 days (89 fish) and at the end of operation, i.e. after 51 days (104 fish). At each weighing event, four randomly selected fish were examined for parasites.

2.2. Pilot ion-exchange system

Two 104 cm long, 7.0 cm diameter packed bed ion-exchange columns (empty bed volume 4 L) were applied in the pilot system (Z1 and Z2 in Fig. 2). Each column was filled with 2240 g of herschelik-sodium chabazite (CABSORB-ZS500H, GSA Resources, AZ), supplied in Na⁺ form.

Column volumes and water flow-rates were designed according to the results obtained in the preliminary ion-exchange experiments (see Appendix B). Fishpond water treatment process comprised 10 automatic operational steps controlled by a programmable logic controller and a manual electrolysis step. Fig. 3 shows the sequence of the automatic water treatment steps.

Each IX column was operated for 12 h a day versus the fishpond (Steps 1, 2, 4 and Steps 6, 7, 9 in Fig. 3 for columns Z1 and Z2, respectively). The flow rate of the treated water through the ion-exchangers was 216 mL min⁻¹ (±7.3%). During the other 12 h, the column was regenerated and subsequently put into standby mode until operation was resumed on the following day. During the IX stage (Steps 2 and 7 in Fig. 3) water from the fishpond was recirculated through the zeolite columns Z1 and Z2 by peristaltic pumps P1 and P3 (see Fig. 2), respectively. To prevent clogging of the IX columns the water was pumped through a coarse filter (F4 in Fig. 2) and two 130 μm filters (F5 and F6 in Fig. 2), which were manually washed with tap water on a daily basis. When an ion-exchange column was due for regeneration, residual water was drained from the columns back to the fish tank (Steps 5 and 10 in Fig. 3). This step lasted 7.5 min and was assisted by ~1 bar air pressure, supplied from a compressor (AC in Fig. 2).

### Table 1

<table>
<thead>
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<th>Parameter (units)</th>
<th>Value</th>
<th>Parameter (units)</th>
<th>Value</th>
</tr>
</thead>
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<td>pH</td>
<td>7.49–7.77</td>
<td>Humidity (% w/w)</td>
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</tr>
<tr>
<td>AlH₂CO₃ (mg L⁻¹)</td>
<td>96.4–132.0</td>
<td>Protein content (% w/w)</td>
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</tr>
<tr>
<td>Na⁺ (mg L⁻¹)</td>
<td>51.0–67.0</td>
<td>Lipid (% w/w)</td>
<td>9</td>
</tr>
<tr>
<td>Ca²⁺ (mg L⁻¹)</td>
<td>32.4–48.8</td>
<td>Cellulose (% w/w)</td>
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<tr>
<td>Mg²⁺ (mg L⁻¹)</td>
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<td>Ash (% w/w)</td>
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<tr>
<td>K⁺ (mg L⁻¹)</td>
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<td>Calcium (% w/w)</td>
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<tr>
<td>Cl⁻ (mg L⁻¹)</td>
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<td>Magnesium (ppm)</td>
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<tr>
<td>NO₃⁻ (mg N L⁻¹)</td>
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<td>Phosphorus (% w/w)</td>
<td>0.9</td>
</tr>
<tr>
<td>Orthophosphate (mg P L⁻¹)</td>
<td>0.007–0.025</td>
<td>Salt (% w/w)</td>
<td>1</td>
</tr>
</tbody>
</table>

Fig. 2. General scheme of the experimental pilot-scale system used in the work.
A 56 L NaCl (food grade, 99.5%) solution (T2 in Fig. 2), with an initial chloride concentration of 50 g Cl L$^{-1}$, was used to chemically regenerate the zeolite columns (Steps 2 and 7 in Fig. 3). A magnetic pump (P2 in Fig. 2) was used to recycle water (flow rate 1.72 L min$^{-1}$) between the zeolite column (Z1 or Z2 in Fig. 2) and the regenerant holding vessel. Ammonia electrooxidation and column regeneration were stopped automatically once all the ammonia was removed from the regenerant solution (Section 2.4).

2.3. Indirect ammonia electro-oxidation unit

Desorbed ammonia was oxidized into N$_2$(g) by indirect electro-oxidation. Both the chemical regeneration and the ammonia oxidation steps were performed simultaneously (Steps 2 and 7 in Fig. 3). A flow-through, monopolar parallel plate electrolysis cell was used for electrochemical ammonia oxidation. The electrolyte solution (IX regenerant) was recirculated between the holding vessel (T2 in Fig. 2) and the electrolysis cell (EC in Fig. 2) by a magnetic pump (P4) at a flow rate of approximately 12 L min$^{-1}$, which also served for stirring the electrolyte solution during operation. The electrolysis cell was operated at 5 A, resulting in current density of 0.333 kA m$^{-2}$. The corresponding (measured) cell potential was in the range 3.1–3.2 V. The pH of the regenerant solution was controlled automatically at pH 6.5 during the electrolysis step by automatic NaOH (2.1 M) dosage.

Vanlangendonck et al. (2005) reported that at the final stage of ammonia indirect electro-oxidation, i.e. when all ammonia in the electrolyte solution had oxidized into N$_2$, the oxidation reduction potential (ORP) of the electrolyte solution increased immediately. This occurs due to the rapid development of free chlorine concentration in the electrolyte solution, in the absence of ammonia. This observation was used in this work for automatic control of the electrolysis step. An ORP electrode was connected to the analog input of a controller through the voltage, followed by operational amplifier with a voltage gain of 9.2 (both elements were based on a TL08 operational amplifier). A Schmidt trigger was applied for on–off operation of the electrolysis step. Based on the results of the simulation experiments the low trigger limit was set at 600 mV and the upper limit at 700 mV. On top of the ORP control the electrolysis step was programmed to proceed for at least one hour. This was done because a sharp increase of ORP beyond 700 mV was observed also at the very beginning of some electrochemical oxidation steps, even when a high initial TAN concentration was present in the electrolyte. Overall electrolysis duration was limited to 6 h. After the completion of the regeneration step brine was drained from the column (air-pressure assisted drainage) for 7.5 min to the regenerant tank (Steps 3 and 8 in Fig. 3). Before the regenerated column was reconnected to the fishpond in the following NH$_4^+$ adsorption cycle, residual regenerating solution had to be washed out of the column because even trace concentrations of active chlorine could be detrimental to the fish. To this end fish tank water was pumped through the IX column at the beginning of the water treatment step and was not returned to the fishpond but rather disposed of to the sewage (Steps 1 and 6 in Fig. 3). The volume of the disposed water applied for washing both columns constituted the daily make up water volume of the fishpond minus the 12 L that were used for washing the coarse filter F3 (Fig. 2). For example, during the 10% water exchange operation (i.e. 50 L of water replaced daily) each column was washed with 19 L of fish-tank water. During the simulation stage, solid precipitates were observed on the cathode surface area. This phenomenon resulted in deterioration of the observed current efficiency. To avoid this, an additional unit, aimed at acidic dissolution of the cathodic precipitates, was operated. Precipitate removal was performed manually.

**Fig. 3.** Time sequence of fishpond and water treatment operations.
every other day, by recycling (~500 mL min⁻¹) 0.25 M HCl solution (10L) between the electrolyzer and the acid tank T3 (Fig. 2) for 30 min using a peristaltic pump P6 (Fig. 2). It is noted that in industrial applications this acid rinsing would be minimized by periodic reversal of the electrodes’ polarities.

2.3.1. Electrolysis step

The duration of the electrolysis step, the rate of base consumption and concentrations of Cl⁻, NO₃⁻, K⁺, Na⁺, Ca²⁺ and Mg²⁺ in the regenerant solution were recorded daily. Detailed performance of the electrochemical stage was recorded six times during the growth period. In these experiments the following parameters were recorded as a function of time: power demand, TAN concentration, active and available chlorine concentrations, ORP and pH.

The TAN concentrations in the effluent of the IX columns at the end of the column treatment cycle were measured daily. Data regarding long term stability of the chabazite material in active chlorine solutions could not be found in the literature. In order to monitor possible zeolite breakdown, aluminum concentrations were measured (ICP) in the regenerant solution after one week, two weeks, one month and two months of process operation.

2.4. Analytical techniques

TAN concentrations were determined by the method proposed by Willis et al. (1996).

Nitrite concentration was measured using the 4500-NO₂⁻ B colorimetric method (Clesceri et al., 1998). Metal cations and total orthophosphate were determined by ICP (1CAP6300 Duo, Thermo Scientific). Chloride ion and nitrate concentrations were determined by the argenticometric and cadmium reduction methods, respectively (Clesceri et al., 1998). Free chlorine and concentration of chloramines were determined by the DPD spectrophotometric method (Clesceri et al., 1998). Alkalinity was measured by the Gran titration method (Gran, 1952). pH in the fishpond was measured daily by Titrino 718 equipped with a glass electrode (6.0228.010, Metrohm, Switzerland). The alkalinity term representative of the fishpond water is described by Eq. (6). The CO₂(aq) concentration in the pond was calculated from Eq. (7) from the knowledge of the measured alkalinity value, the total orthophosphate concentration (P₂O₅), and pH. The minute NH₃ concentrations were ignored in this calculation.

\[
\text{Alk} = \frac{[\text{HCO}_3^-] + [\text{CO}_2^{\text{aq}}] + [\text{HPO}_4^{2-}] + [\text{H}_2\text{PO}_4^-] + [\text{NH}_3] - [\text{H}_3\text{PO}_4] + [\text{OH}^+] - [\text{H}^+]}{2}\]

\[
[H_2\text{CO}_3] = 10^{-2pH} \cdot \frac{\text{Alk} - P_2 (KP_110^{-3pH} + 2KP_2KP_3 - 10^{-3pH}/10^{-3pH} + KP_110^{-2pH} + KP_210^{-pH} + KP_3) - 10^{14-pH} + 10^{-pH}}{KC_110^{-pH} + 2KC_1KC_2}
\]

where:

\[
KP_1 = 7.1 \times 10^{-3} \text{ M} \quad KP_2 = 6.3 \times 10^{-8} \text{ M} \quad KP_3 = 4.5 \times 10^{-13} \text{ M} \quad KC_1 = 4.5 \times 10^{-7} \text{ M} \quad KC_2 = 4.7 \times 10^{-11} \text{ M}
\]

3. Results and discussion

3.1. Fish performance

Fig. 4 shows average weights (and STDEV) of the fish during the growth period, as compared with the growth potential of Tilapia at 28 °C, determined using Eq. (8) (Lupatsch, 2008):

\[
W_t = [W_0^{0.453} + 0.00512 \times t^{0.69} \times \text{Temp}(28 °C) \times \text{days}]^{2.207}
\]

where \(W_t\) (g) is the fish weight after \(t\) days of growth and \(W_0\) is the initial fish weight (g).

Fig. 4 shows that the fish grew from an average 35.8 g to 107.7 g in 51 days at a rate similar to the theoretical potential growth rate. The observed FCR value was 1.2 (w/w). Periodical observations proved the fish to be in excellent condition throughout the growth period. One fish out of the initial 105 died after 20 days but no other infected fish were observed during the entire experiment period. Despite not being a very long growth period, it can be stated with reasonable certainty that tilapia fish (strictly speaking, within the size range grown) were comfortable in the conditions applied in the experiment (i.e. 10 < TAN < 23 mgNL⁻¹ and pH 6.5–6.7).

3.2. Chemical characterization of fish pond water

Fig. 5 shows the concentrations of dissolved nitrogen compounds and orthophosphate that developed in the fishpond as a function of time, during the growth experiment.

The actual pH values measured in the pond during the experiment fluctuated in the range pH 6.5–6.74. Dissolved oxygen concentration was between 5.1 and 5.48 mgO₂ L⁻¹. The nitrite concentration increased to a maximum value of 0.095 mgL⁻¹ ten days into the experiment, dropped afterwards to almost zero and remained very low thereafter, in spite of the fact that addition of the nitrification inhibitor was stopped after 22 days. The low nitrite and nitrate concentrations were attributed to the very short sludge age periods of the bacteria in the tank, caused by the efficient solids filtration, which apparently caused the slow growing nitrifying bacteria to be washed out of the tank. The orthophosphate concentration increased continuously in the fish tank, reaching a value of 20.3 mgL⁻¹ after 50 days of growth. Note that phosphate removal can be, theoretically, also attained in the proposed method, via the precipitation of hydroxyapatite (Ca₁₀(PO₃)₆(OH)₂) in the fishpond, if Ca²⁺, rather than Na⁺, is applied as the predominant cation exchanged for NH₄⁺ in the IX step. To attain such conditions Ca(OH)₂ should be used instead of NaOH for alkalinity compensation in the ammonia electrooxidation step, and as a result the Ca²⁺ concentration in the pond would increase significantly, promoting hydroxyapatite precipitation, despite the relatively low pH (as can be shown from computer simulations – results not shown). In any event, phosphate removal was not attempted in the current work as NaOH was used as the strong base.

Fig. 6 depicts the change in time in the concentrations of the main cations in the fish tank: while the concentrations of Ca²⁺, K⁺ and Mg²⁺ remained very low throughout the growth period, the Na⁺ concentration went up steadily as the fish density in the pond increased, and more Na⁺ was exchanged with NH₄⁺ on a given day. Naturally, the slope of the Na⁺ concentration increase became steeper when the make up water exchange was reduced to 5%. At the end of the experiment [Na⁺] in the fishpond amounted to approximately 500 mgL⁻¹. Since the system was not maintained at steady state with respect to feed addition and fish density, the Na⁺ concentration had not leveled off, and would have increased, had the experiment been continued. The concentration of the counter cation that develops in the fishpond water under steady state conditions is a main design parameter for the IX step. For example, under the assumption of operation with fish density of 60 kg m⁻³ and 5%
water exchange, the Na⁺ concentration can be logically expected to triple, i.e. to arrive at ~1500 mg L⁻¹. Under such conditions, since the affinity of NH₄⁺ to chabazite is much higher than that of Na⁺ (Lahav and Green, 1998), the IX concept is still expected to be efficient, although IX breakthrough curves would logically be shorter and required chabazite volume, higher.

Despite the low pH maintained in the pond, the highest CO₂eq concentration recorded in the fish tank water was 7.2 mg L⁻¹, which is below the reported toxicity threshold of most aquaculture species (Eshchar et al., 2006). Overall acid consumption rate was 2.89 eq H⁺ (kg feed)⁻¹, as calculated by linearization of the cumulative acid consumption curve obtained throughout the experiment ($R^2 > 0.999$). The apparent NH₃ mass excreted by the fish was calculated backwards from the feed specific acid consumption rate (2.42 eq H⁺ per kg feed⁻¹) to be 0.034 (kg kg⁻¹).

### 3.3. Performance of the water treatment component

No. ion exchange NH₄⁺ breakthrough was observed during the entire experiment. In fact, the TAN concentration in the water coming out of the columns tended toward zero during the entire period. Aluminum concentrations measured in the regenerant solution were nil, indicating that the chabazite was stable (at least) the diluted active chlorine concentrations to which it was exposed in this work.

As described in Section 2.3, the electrolysis step was ORP controlled. Fig. 7 shows a typical regeneration/ammonia electro-oxidation step. In preliminary lab-scale indirect ammonia electro-oxidation experiments (results not shown) a sharp ORP increase was observed immediately once the ammonia oxidation had been completed. In the pilot scale process the picture was different, probably due to a certain organic matter concentration entrapped in the zeolite column during the adsorption step and released to the electrolyte solution in the regeneration step: a sharp ORP increase occurred only when the concentration of the free chlorine reached higher than between 30 and 55 mgCl₂ L⁻¹. However, since the reproducibility of the results was good, it was decided to continue controlling the electrolysis step by ORP, despite the high final Cl₂ concentration, because it was observed that most of the superfluous active chlorine produced during a given regeneration step remained almost unaffected during the delay period and was consumed for ammonia oxidation in the next electrooxidation cycle.

The consumption rates of the acid and base and the electrical power demand were averaged from linearity of the cumulative curves obtained during the whole experiment ($R^2 > 0.995$). Power and base demand measured during the electrochemical regeneration of the IX columns were 0.95 kWh (kg feed)⁻¹ and 2.38 eq OH⁻ (kg feed)⁻¹, respectively. As expected from the mass balance standpoint, the actual acid mass required in the fish tank for compensating for the alkalinity increase due to ammonia excretion (2.42 eq H⁺ (kg feed)⁻¹), was almost identical to the base consumption rate observed in the electrooxidation step.

The current efficiency recorded in the ammonia oxidation step was merely 66%, as calculated from the 3.4% (w/w) value taken in the experiment as the representative digestible nitrogen content in the fish feed. This observed efficiency is much lower than the typical current efficiencies of >85% which observed in preliminary lab-scale batch electrolysis experiments (results not shown). The reason for this low current efficiency could stem from some chlorine consumption by organic matter, as explained before and probably also by conversion of active chlorine to chlorate (ClO₃⁻) in the regenerant solution. The pH value of 6.5, which was maintained in the electrolyte during the electrolysis step, lays within the optimal pH range (pH 5–7) for chemical chlorate formation according to Eq. (9) (Tilak et al., 1981). It is thus possible that some of the
residual active chlorine, which was produced but not consumed during the electrolysis step, was converted to chloride, which does not oxidize NH₄⁺. This issue was not explored further in the course of the current work.

\[
2\text{HOCI} + \text{OCl}^- \rightarrow \text{ClO}_3^- + 2\text{HCl}
\]  

(9)

Another reason for the relatively low current efficiency measured could have stemmed from nitrate and nitrite formation (and destruction) during the ammonia electro-oxidation step (Vanlangendonck et al., 2005). [NO₃⁻] accumulated in the brine electrolyte solution during the last 17 days of growth, reaching 11.75 mgN/L. Note that this value reflects net accumulation, i.e. nitrate formation at the anode minus nitrite reduction at the cathode. However, loss of current efficiency for ammonia oxidation associated with nitrate formation could not be calculated directly from the collected data due to possible back reduction of nitrate to ammonia at the cathode (Vanlangendonck et al., 2005). The nitrite concentration in the electrolyte solution was at all times below the detection limit, obviously due to its oxidation by active chlorine.

Drainage of the brine from the IX columns after each regeneration step, as done in this work, can minimize, but not completely eliminate, the loss of sodium and chloride ions from the regenerant solution, due to the field capacity of the zeolite bed. As a result of this phenomenon, after 28 days of operation the concentrations of Na⁺ and Cl⁻ in the electrolyte solution decreased from the initial concentration of 29.9 g L⁻¹ and 44.1 g L⁻¹ to 7.14 g L⁻¹ and 13.42 g L⁻¹, respectively. From this point further 184.6 g of dry sodium chloride were added manually to the regenerant solution every other day to maintain the Na⁺ and Cl⁻ concentrations constant at ~10.93 and ~18.32 g L⁻¹, respectively.

Removal of available chlorine residuals, which remain in the IX columns after regeneration and subsequent brine drainage operations, was essential in order to prevent contact of chlorine and tank water. Fig. 8 represents the composition of the column effluents as a function of the applied volume of the fishpond water (BV), during the rinse procedure. According to Fig. 8 more than 98% of the Na⁺, Cl⁻ and available chlorine were removed from the column with the first BV of tank water applied. The concentration of available chlorine in the column effluent was lower than 0.1 mgCl₂ L⁻¹ following a rinse with two bed volumes of water.

3.4. Cost estimation

3.4.1. Operational expenses (OPEX)

Table 2 lists the operational costs assessment, which was derived directly from the data collected during the operation of the pilot plant. The main operational expenses stemmed from chemicals (acid and base) consumption and electrical power demand. As shown in Table 2, the overall OPEX of the pilot treatment system was fairly low, i.e. 28.7 $ cent per kg feed or 34 $ cent per kg fish assuming FCR of 1.2 kg feed kg fish⁻¹ (a common value for tilapia growth in Israel and also the value recorded in the present, limited, growth experiment). Assuming a higher FCR value of 1.8 kg feed kg fish⁻¹ (more appropriate for Bass growth, for example) the operational costs would become $0.52 per kg fish. Considering that this figure included an excessive cost for NaCl addition and that it was calculated based on a relatively low electro-oxidation efficiency, which could almost certainly be improved when the technology progresses to the next level, it appears that the proposed process is feasible, cost wise.

The very high NaCl consumption (0.49 kg NaCl kg feed⁻¹) observed in the pilot operation can be significantly decreased by appropriate system design that will minimize loss of salt when the column shifts between regeneration and adsorption cycles. Alternatively, cheap seawater (or another source of cheap Cl⁻-rich water) may also be used, if available, as the regenerant solution in the proposed process, thereby reducing the operational costs considerably. When a restriction exists on the discharge of Na⁺ to a receiving water body, operation should be performed with Ca²⁺ as the Na⁺ counter cation, rather than Na⁺.

Optimizing the electro-oxidation process was not attempted in this study. However it can be safely stated that the electrical power demand can be significantly reduced, as current efficiencies higher than 66% have been often reported in similar situations (Vanlangendonck et al., 2005; Gendel and Lahav, 2012). In addition, hydrogen gas, which is a valuable byproduct of the indirect ammonia electro-oxidation process, can be collected in large full-scale operations. Such practice would reduce the overall operational cost.

3.4.2. Estimation of capital expenses (CAPEX)

Estimation of the required capital investment could not be done with reasonable accuracy on the basis of the results obtained from the operation of a small pilot scale unit, such as the one operated in this study. However, a rough estimation of capital investment is presented here to show that the proposed technology is economically feasible. The two major components affecting the capital investment are the electrochemical device and the ion exchanging material and reactor. For a fish growing plant producing 100 × 10³ kg fish y⁻¹ and assuming FCR (food conversion ratio) of 1.8 kg feed kg fish⁻¹ a feeding rate of 1.8 × 10³ kg feed y⁻¹ would be required. Assuming the application of food with 4% digestible nitrogen, 7200 kg N would be released to the pond annually, i.e. 0.89 kg N would have to be removed hourly from the fishpond water (assuming a treatment system that is operated 22 h a day). Assuming that the TAN concentration in the fishpond is maintained at 15 mgN L⁻¹, 1315 m³ of fishpond water would have to be treated daily.

Further assuming that the two IX columns are operated in a sequence of 2 h for IX treatment and 2 h for regeneration, the resulting volume of treated water per cycle would be 120 m³. Since an IX column can treat 40 BV of water until NH₄⁺ breakthrough occurs, the volume of each column should be 3 m³. The overall volume of the zeolite columns will thus be 6 m³ and assuming a package density of 560 g L⁻¹ of chabazite, annual replacement of 10% (weight) and 15 years of operation, an overall 40 tons of zeolite would be required for 15 operation years. At an estimated 500 $ per ton of chabazite zeolite, the capital investment on the IX component will amount to $20,000.

The electrochemical unit should be capable of oxidizing 0.89 kgN h⁻¹ which equals an active chlorine production of 11.27 kgCl₂ h⁻¹ at 60% current efficiency. The estimated cost of the electrolysis unit is $110,000 (Online electrolyzer).

The combined CAPEX of the electrolysis unit and IX material is thus $130,000. Assuming a high safety factor of 2 (to account for peripheral equipment and unknowns), an interest of 5% and a serviceable life of 15 years the annual return on the capital would be ~$25,000, i.e. ~$3 per kg TAN removed and ~$0.25 per kg fish produced.

The overall fish production cost (CAPEX and OPEX) in the new approach is estimated at $0.8 per kg fish (assuming FCR of 1.8 kg feed kg fish⁻¹).

3.5. Comparison of volumes and recirculation flow rates required in the proposed physico-chemical technology with conventional nitrification biofilters

One noticeable advantage of the proposed technology is its small volume relative to the biological systems and also the much lower recirculation flow rate required for its operation, as compared with conventional nitrifying biofilters. Table 3 lists the assumptions made for estimating the volumes and recirculation flow rates for both the proposed technology and biofiltration.
Fig. 8. Species concentrations measured in water leaving IX column during a typical rinse operation. ■ Chloride ions (g L$^{-1}$); ◆ sodium ions (g L$^{-1}$); ▲ total available chlorine (mgCl$_2$ L$^{-1}$).

Table 2
Actual operational costs, as determined from the pilot operation.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Demand</th>
<th>Price tag</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolysis power demand</td>
<td>0.95 kWh kg feed$^{-1}$</td>
<td>16.4 cent kWh$^{-1}$</td>
<td>15.6 cent kg feed$^{-1}$</td>
</tr>
<tr>
<td>Strong acid (H$_2$SO$_4$, 98%)</td>
<td>118.6 kg feed$^{-1}$</td>
<td>200 $$^{-1}$</td>
<td>24.2 $$^{-1}$</td>
</tr>
<tr>
<td>Strong base (NaOH)</td>
<td>95.29 kg feed$^{-1}$</td>
<td>400 $$^{-1}$</td>
<td>40.0 $$^{-1}$</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.49 kg feed$^{-1}$</td>
<td>150 $$^{-1}$</td>
<td>15.0 $$^{-1}$</td>
</tr>
<tr>
<td>Total cost per kg feed</td>
<td></td>
<td></td>
<td>28.7 cent kg feed$^{-1}$</td>
</tr>
<tr>
<td>Total cost per kg fish (FCR = 1.2)</td>
<td></td>
<td></td>
<td>34.5 cent kg fish$^{-1}$</td>
</tr>
</tbody>
</table>

A detailed comparison between the proposed technology and normal RAS biofiltration with respect to volume and recirculation flow rates is presented in Appendix C.

In biofilters, the highest zero-order (diffusion controlled) TAN removal rate was reported to be 0.71 (g m$^{-2}$ d$^{-1}$) (Eding et al., 2006). Plugging this value and the parameters listed in Table 3 into Eq. (C.8) (see Appendix C for elaboration) indicates that the volume required for the biofilter is 13 times higher than that required for the proposed technology (ion exchangers and electrolysis unit, combined). Additionally, Eq. (C.9) (Appendix C) reveals that the recirculation flow rate through the proposed treatment scheme is at least seven times smaller than that required for typical biofiltration practice. Moreover, TAN oxidation rate in biofilters is temperature dependent. Boller and Gudjers (1982) proposed the term $R_{10-C} = R_{T}C^{e[C(10^{-7})]}$ for linking nitrification rates with temperature in tertiary trickling filters ($K=0.044$ C$^{-1}$ and $T$ in °C). Accordingly, TAN oxidation rates in RAS operated at 10°C will be as low as 0.36 (g m$^{-2}$ d$^{-1}$). At such conditions the volume ratio between typical biofilters and the proposed system will jump to 26.

As opposed to biological processes, indirect ammonia electro-oxidation and removal of NH$_4^+$ by IX processes are both only slightly dependent on temperature. Khelifa et al. (2004) reported that electrochemical formation of active chlorine is almost similar at the range 10–40°C. McLaren and Farquhar (1973) studied the performance of clinoptilolite (a specific type of zeolite) at different operational conditions and reported no temperature dependency of NH$_4^+$ removal at the range between 2 and 12°C. Leyva-Ramos et al. (2010) reported an increase and decrease of only 13% in the maximal ammonia exchange capacity of chabazite when the temperature was increased and decreased by 10°C from an initial 25°C.

Table 3
RAS parameters applied for the comparison of the design parameters of the biological and proposed physico-chemical RAS water treatment technologies.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fishpond volume (m$^3$)</td>
<td>500</td>
</tr>
<tr>
<td>Fish density (kg fish m$^{-3}$)</td>
<td>10–100</td>
</tr>
<tr>
<td>Feeding rate (g feed kg fish$^{-1}$)</td>
<td>10</td>
</tr>
<tr>
<td>TAN load (kgN d$^{-1}$)</td>
<td>2–20</td>
</tr>
<tr>
<td>Excreted TAN (g N kg feed$^{-1}$)</td>
<td>40</td>
</tr>
<tr>
<td>Biological removal rate of TAN per biofilter surface area (g m$^{-2}$ d$^{-1}$) (after Eding et al., 2006)</td>
<td>0.36–0.71</td>
</tr>
<tr>
<td>[TAN] in the biofilter effluent (g m$^{-3}$)</td>
<td>0.5</td>
</tr>
<tr>
<td>[TAN] in biologically treated RAS (mg L$^{-1}$)</td>
<td>2.2</td>
</tr>
<tr>
<td>Specific surface area of the biofilter (m$^2$ m$^{-3}$) (Eding et al., 2006)</td>
<td>200–230</td>
</tr>
<tr>
<td>Fishpond water exchange rate (d$^{-1}$)</td>
<td>0.05</td>
</tr>
<tr>
<td>Number of IX columns</td>
<td>2</td>
</tr>
<tr>
<td>[TAN] in physico-chemically treated RAS (mg L$^{-1}$)</td>
<td>20</td>
</tr>
<tr>
<td>Retention time of IX treatment (min)</td>
<td>3</td>
</tr>
<tr>
<td>Number of BV treated by column per operation</td>
<td>40</td>
</tr>
</tbody>
</table>

4. Conclusions

- A new ion exchange/electrochemical regeneration process was introduced and successfully applied at the pilot scale for continuous oxidation of ammonia from RAS water to N$_2$(g) in one reaction step.
- The suggested process has low sensitivity to temperature, does not require long startup and recovery periods, and can be switched on and off at will.
• Tilapia fish grew from 35.8 g to 107.1 g at a rate similar to their potential growth rate under conditions of TAN concentration of up to 23 mgN L⁻¹ and pH 6.5–6.7.
• Nitrite and nitrate concentrations recorded in the pond water were very low (<0.1 mgN L⁻¹), with and without addition of a nitrification inhibitor.
• The volume of the required ammonia oxidizers (ion exchange and electrolysis reactors, combined) is at least 13 times lower than the volume of typical RAS nitrification biofilters.
• The required recirculation flow rate through the ion exchange reactors is 7 times lower than the equivalent recirculation rate typically applied for typical RAS biofilter operation.
• The system converts ammonia directly to the benign N₂(g) in one oxidation step.
• The low biomass concentration maintained in the pond in the proposed process has the potential to reduce fish disease and off-flavor development.
• The process was shown feasible from both the operational and economic standpoints.

Acknowledgement

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Appendix A.

See Table A.1.

Appendix B.

B.1. Preliminary ion-exchange experiments used for IX columns pilot design

NH₄⁺ breakthrough curves were obtained using a 300 mL packed-bed ion-exchange column made of a transparent PVC pipe (length 33 cm; internal diameter 3.4 cm). The column was filled with 180 g (dried at 100°C) of chabazite. Three breakthrough curves (applied hydraulic retention time = 6 min) were recorded: two curves using RAS water as background and one with tap water. Cationic composition of RAS and tap water were: (mg L⁻¹): [Ca²⁺] = 112; [Mg²⁺] = 51.7; [Na⁺] = 194.4; [K⁺] = 26.45 and [Ca²⁺] = 82.6; [Mg²⁺] = 36.2; [Na⁺] = 101.8; [K⁺] = 4.9, respectively. TAN concentrations in RAS water breakthrough curves were adjusted to 15 and 30 mgN L⁻¹ by addition of (NH₄)₂SO₄; pH values were adjusted to 7.2 and 6.8, respectively, with H₂SO₄ (1.8 M). TAN concentration and pH in the tap water experiment were adjusted to 29.7 mgN L⁻¹ and pH 6.8. The water leaving the ion-exchange column was collected in a stirred vessel and the (cumulative) TAN concentration measured throughout each experiment.

NH₄⁺ breakthrough curves are shown in Fig. B.1. Arbitrary cumulative ammonia breakthrough concentration of 2 mgN L⁻¹ was chosen. This value was attained (for water containing 15 and 30 mgN L⁻¹) after 93 and 60 BV, respectively. In the tap water experiment (29.7 mgN L⁻¹) 2 mg L⁻¹ in the effluent were attained after 98 BV. The pilot scale fishpond water treatment system was designed based on these results.

The following assumptions were applied for the design of the treatment process:

• Maximal fish density: 22 kg m⁻³.
• Maximal feed load: 2.3 g fish⁻¹ d⁻¹.

<table>
<thead>
<tr>
<th>Table A.1</th>
<th>List and parameters of the equipment used in the pilot scale studies.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equipment description (in Fig. 2)</td>
<td>Parameters/model/manufacturer</td>
</tr>
<tr>
<td>Fishpond (T1)</td>
<td>700L Box pallet type 1120 solid, Dolev Plastic Products</td>
</tr>
<tr>
<td>Regenerant holding vessel (T2)</td>
<td>60 L Plastic drum HDPE, Pachman Packaging Ltd.</td>
</tr>
<tr>
<td>Acid tank for electrodes treatment (T3)</td>
<td>16 L Plastic Jerrycan HDPE, S 18L, Pachman Packaging Ltd.</td>
</tr>
<tr>
<td>Automatic ball valves (0)</td>
<td>1/2&quot;, 24VAC. Sogit Ltd.</td>
</tr>
<tr>
<td>Automatic ball valves (V1–V9)</td>
<td>PVC, OM-1.24 PVC coil, 1/2&quot;, Sun Yeh Electrical Ind. Co. Ltd.</td>
</tr>
<tr>
<td>Manual ball valves (V10–V14)</td>
<td>PVC, 1/2&quot; 11151005, Plsson Ltd.</td>
</tr>
<tr>
<td>Peristaltic pump (P1, P2, P3)</td>
<td>Drive: 6–600 rpm, 7553-75, Cole-Palmer</td>
</tr>
<tr>
<td>Head: 77200-62, Cole-Palmer</td>
<td>Tubing: 06404-24 Noprene, Masterflex</td>
</tr>
<tr>
<td>Magnetic pump (P6, P5)</td>
<td>NH-50FX-Z, Pan World Co.Ltd.</td>
</tr>
<tr>
<td>130 μm filter (F1, F5, F6)</td>
<td>3/4&quot; Tagline plastic filter, Amlad Water Systems</td>
</tr>
<tr>
<td>Activated carbon filter (F2)</td>
<td>5&quot;, Granular activated carbon, Naga WaterCare</td>
</tr>
<tr>
<td>Coarse filter (F3, F4)</td>
<td>1.5I and 12 I, Two layers of plastic screen ~0.5 mm mesh, Self made</td>
</tr>
<tr>
<td>Drainage air compressor (AC)</td>
<td>250 PSI portable 12VDC. Unknown manufacturer.</td>
</tr>
<tr>
<td>Ion-exchange columns (Z1, Z2)</td>
<td>PVC, length-105 cm</td>
</tr>
<tr>
<td></td>
<td>Internal diameter: 7.04 cm, Unknown manufacturer. Self made assembly</td>
</tr>
<tr>
<td>Electrolysis cell (EC)</td>
<td>Klrogen M10, Monopolar, parallel plate</td>
</tr>
<tr>
<td></td>
<td>5 electrodes, 15 2.5 0.5 cm cm Anode: Ti/precious metal oxide coating</td>
</tr>
<tr>
<td></td>
<td>Cathode: Ti/precious metal oxide coating</td>
</tr>
<tr>
<td></td>
<td>Titanium Tantalum Products Ltd.</td>
</tr>
<tr>
<td>DC power supply</td>
<td>HCS-3402. 1–30 VDC, 20 A. Manson.</td>
</tr>
<tr>
<td>Base addition pump (Regenerant)</td>
<td>Dosing pump, Gala1000, ProMinent Glass electrode. ECTC252101B, Eutech Instruments</td>
</tr>
<tr>
<td>pH sensor (Regenerant)</td>
<td>Alpha pH190, Thermo Scientific.</td>
</tr>
<tr>
<td>Fishpond/pH sensor</td>
<td>Dosing pump. Pulsatron C-plus. Pulsofeder Inc.</td>
</tr>
<tr>
<td>Fishpond (regenerant)</td>
<td>DN82. Syrelec</td>
</tr>
<tr>
<td>Acid addition pump (Fishpond)</td>
<td>NA610, Suzhou Newasia Technologies Inc.</td>
</tr>
<tr>
<td>Fishpond water level sensor</td>
<td>1.2KW. Titanium body. Unknown manufacturer.</td>
</tr>
<tr>
<td>Temperature controller (Fishpond)</td>
<td>6.045.100, Metrowh</td>
</tr>
<tr>
<td>ORP sensor (regenerant)</td>
<td>Millennium 3 custom, XD26, 24VDC, Crouzet.</td>
</tr>
</tbody>
</table>

![Fig. B.1. NH₄⁺ breakthrough curves](image-url)
The design TAN load on the water treatment system was assumed to be 9.7 g N·d⁻¹. In order to achieve a TAN concentration of 30 mg N·L⁻¹ in the fishpond at the highest TAN load, each column was designed to treat ~160 L of fish tank water during 12 h of operation, assuming 100% TAN removal efficiency. Consequently, the flow rate of the water through the column was calculated to be 220 mL·min⁻¹. The cationic composition that would develop in the fish tank water in the fish growth experiment could not be predicted a priori with reasonable accuracy. Therefore, it was arbitrarily decided that within the 12 h of the water treatment stage each column would accept a maximum volume of 40 BV of fishpond water. These considerations ultimately led to the design of two IX columns, each with a volume of 4 L.

Appendix C.

Fig. C.1 shows the general schematic of the RAS operated with the biological/iod-exchange water treatment methods. The term “Filter unit” in Fig. C.1 stands for either the biofilter or the ion-exchangers, respectively.

Eqs. (C.1) and (C.2) are mass balances of TAN round the biofilter and the fishpond, respectively.

\[
\begin{align*}
Q_{T-BIO} \cdot C_{TAN-BIO} &= C_{EFF-BIO} \cdot Q_{T-BIO} + R \cdot V_{BIO} \cdot S \\
L_{TAN} &= Q_{T-BIO} \cdot C_{TAN-BIO} - C_{EFF-BIO} \cdot Q_R
\end{align*}
\]

(C.1) \hspace{1cm} (C.2)

The volume of the biofilter (Eq. (C.3)) and the recirculation flow rate thereof (Eq. (C.4)) can be calculated from the combining Eqs. (C.1) and (C.2):

\[
\begin{align*}
V_{BIO} &= \left( \frac{V}{R_S} \right) \left( L_{TAN} - C_{EFF-BIO} \cdot W_{ER} \right) \\
Q_{T-BIO} &= V \cdot \left( \frac{L_{TAN} - C_{EFF-BIO} \cdot W_{ER}}{C_{TAN-BIO} - C_{EFF-BIO}} \right)
\end{align*}
\]

(C.3) \hspace{1cm} (C.4)

where \( Q_{T-BIO} \) – flow rate of the filter influent (m³·d⁻¹); \( C_{TAN-BIO} \) – TAN concentration in the fishpond (g·m⁻³ as N); \( C_{EFF-BIO} \) – TAN concentration in the biofilter effluent (g·m⁻³ as N); \( R \) – biological removal rate of TAN relative to filter surface (g·m⁻²·d⁻¹); \( S \) – specific surface area of the biofilter (m²·m⁻³); \( L_{TAN} \) – TAN load on the fishpond (g·d⁻¹ as N); \( V \) – volume of the fishpond water (m³); \( V_{BIO} \) – volume of the biofilter (m³); and \( W_{ER} \) – fishpond water exchange rate (1·d⁻¹).

At least two IX columns have to be operated (in series) in order to maintain the TAN concentration in the fish tank roughly constant. Besides the number of IX columns the volume of proposed method depends on the TAN concentration maintained in the fishpond, the number of tank water BV passed through a single IX column, and the retention time of the water in the IX column. If the TAN concentration in the IX effluent is neglected, the water flow rate through the IX column becomes (Eq. (C.5)):

\[
Q_{T-PC} = \frac{L_{TAN}}{V_{C_{TAN-PC}}}
\]

(C.5)

Consequently, the volume of a single IX column is:

\[
V_{IX} = R_T \cdot L_{TAN} \cdot \frac{V}{C_{TAN-PC}}
\]

(C.6)

where \( V_{IX} \), \( R_T \) and \( C_{TAN-PC} \) stand for empty bed volume of a single IX column (m³), water retention time in the IX column (d) and TAN concentration maintained in the fishpond (g·m⁻³), respectively.

For a process operated with two IX columns, the overall volume of the system (\( V_{PC} \)) comprises the volume of the columns and the volume of the regeneration solution that can be assumed to be equal to three empty bed volumes of a single column. Thus, the overall volume of the IX treatment system becomes:

\[
V_{PC} = 3V_{IX} = 3 \cdot R_T \cdot V \cdot \frac{L_{TAN}}{C_{TAN-PC}}
\]

(C.7)

Finally, Eq. (C.8) describes the maximal ratio between the volume of a bio-trickling filter (\( V_{BIO} \)) and the volume of the proposed physico-chemical process (\( V_{PC} \)):

\[
V_{BIO} = \left( \frac{C_{TAN-PC}}{R \cdot S} \right) \cdot \left( \frac{L_{TAN} - C_{EFF-BIO} \cdot W_{ER}}{C_{EFF-BIO} - C_{EFF-BIO}} \right)
\]

(C.8)

The ratio of the flow rates applied in biologically treated RAS vs. the proposed method was derived from combining Eqs. (C.4) and (C.5):

\[
\frac{Q_{T-BIO}}{Q_{T-PC}} = \frac{\left( \frac{L_{TAN} - C_{EFF-BIO} \cdot W_{ER}}{C_{EFF-BIO}} \right)}{\left( \frac{C_{TAN-BIO} - C_{EFF-BIO}}{C_{EFF-BIO}} \right)}
\]

(C.9)

References


