ALLIANCE™
(https://debug.globalseafood.org)

Responsible Seafood ADVOCATE

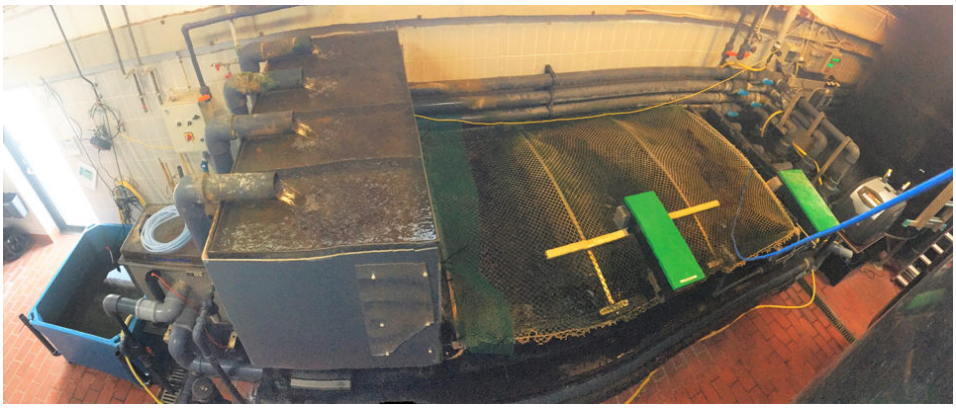
Innovation & Investment

Electrochemical treatment of RAS water

20 January 2020

By Lars-Flemming Pedersen, Ph.D. , Anna Maria Røyset Lier, M.Sc. and David Jonathan Jensen, M.Sc.

Study finds significant potential for TAN removal, disinfection



View of the pilot RAS used in the study that demonstrated the potential of the electrochemical oxidation process to improve water quality and antimicrobial activity in RAS systems.

Fish production in land-based recirculating aquaculture systems (RAS) provides a number of well-known advantages. Some of the challenges are associated with the central biological processes, nitrification and denitrification. Both types of biofiltration are subjected to rearing conditions and require constant maintenance to ensure optimal performance. As nitrification relies on biotic conditions, start-up and colonization, unforeseen events – such as improper use of chemical disinfectant, abrupt change in salinity, extreme conditions (very low temperature) or suboptimal conditions (limited oxygen or alkalinity) – may lead to an undesirable accumulation of ammonia.

Similarly, insufficient nitrate removal may occur if conditions are not met; for example, large flows and lack of (costly) easy degradable carbon sources. On top of that, potential risks of highly toxic H_2S release from anoxic zones also have to be considered.

The needs for an alternative physical, abiotic treatment technology that can replace the more sensitive biological treatment processes seem obvious. A development somehow similar to the automatization of the laborious and manual process of washing dishes using dishwasher machines.

Electrochemical water treatment

Electrochemical water disinfection is a process where electrons delivered by direct current react with ions and molecules in the water. The basic requirement for the process is a power supply and two electrodes, an anode and a cathode. Based on the electrode materials, current applied and water composition, various redox processes takes place at different rates. Different terms have been used to describe this type of **water treatment process** (https://doi.org/10.1595/147106708X329273), including Forced Redox, Electrolytic disinfection, Electrochemical disinfection, Functional water, Electrochemical oxidation process (EOP), Electrochemical active water, Electrocoagulation, and Hydroxyl radical production.

Different reactions and processes take place at both electrodes during electrolysis of water. The most common application of EOP is for **disinfection** (http://doi.org/10.1039/c3em00679d), based on electro generation of reactive oxygen species (ROS). The same technology can also be applied to oxidize complex, **slowly degradable compounds** (https://doi.org/10.1016/j.desal.2011.09.029) and **dissolved nutrient such as ammonium** (http://doi.org/10.1016/j.watres.2010.08.020). Various studies of electrochemical advanced oxidation processes for **water treatment** (https://www.sciencedirect.com/science/article/pii/S0144860914001010?via%3Dihub) of various water matrices have recently been published, including **interesting aquaculture applications** (https://doi.org/10.1016/j.aquaeng.2016.05.002).

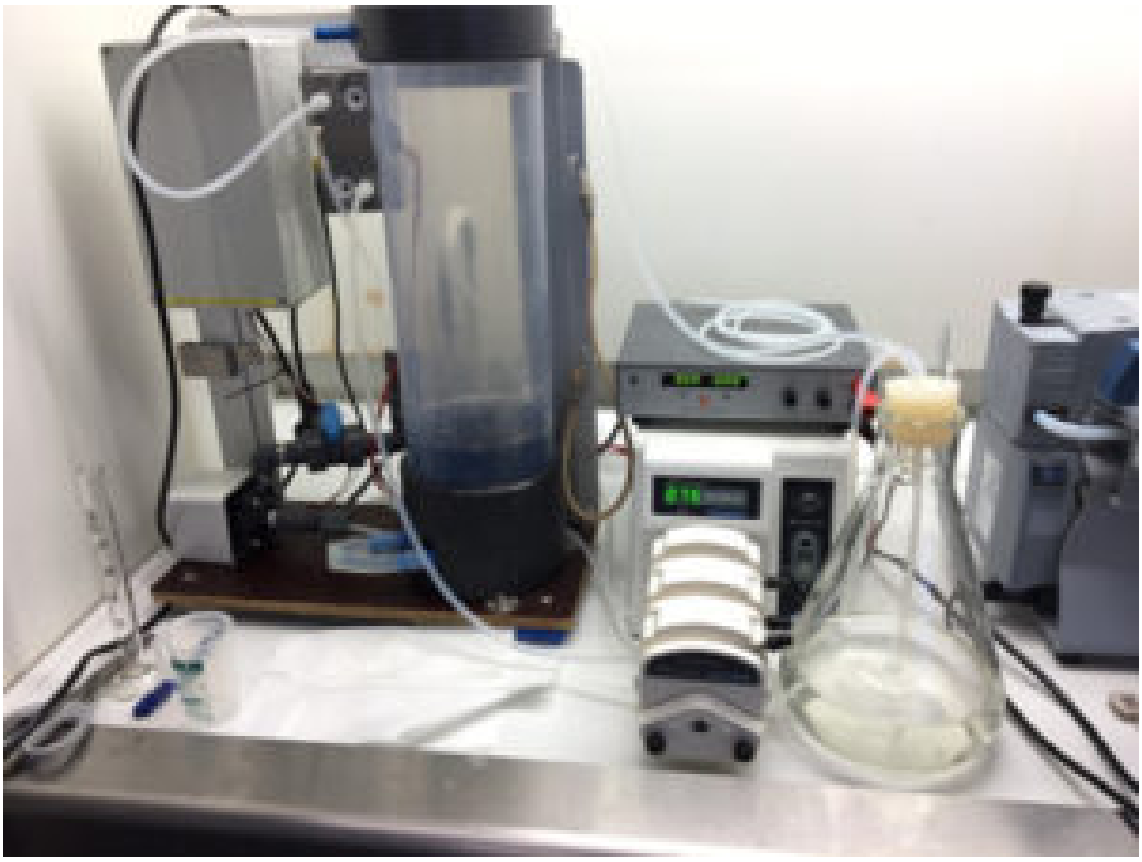
In our study, we tested EOP using micro flow cells (ElectroCell) in a bench scale setup using water from recirculating aquaculture systems (RAS). The two objectives were to test the potential of EOP to oxidize ammonium nitrogen and reduce the amount of dissolved N; and to investigate the disinfection capacity of EOP.

This study was a subtask of a work package about abiotic treatment of aquaculture discharge as part of a European innovation project, Bonus CleanAq funded by the EU and the Innovation Fund Denmark. We thank Ulla Sproegel, Brian Møller, Carine B. Jensen (DTU Aqua, Section for Aquaculture) for lab support.

Electrochemical TAN removal

To evaluate the electrochemical removal of total ammonia nitrogen (TAN), we tested different combinations of electrodes in a bench scale setup (see image below) with freshwater and brackish water of 8 ppt salinity. Water samples – either a mix of tap water and seawater, or RAS water mixed with seawater – were spiked with NH_4Cl at a concentration equivalent to 30 ppm TAN and used in the closed setup. The setup included a volume of 1-L with a flow rate of 920 mL/min passing a micro flow cell with two electrodes with a contact area of 10 cm^2 (0.001 m^2), with an electric potential of 5 Volts and a current density of 22 mA/cm^2.

Over a period of two hours, up to 28 mg/L TAN was removed using a combination of copper cathode and boron-doped diamond (BDD) electrodes. Combinations of BDD- tin (Sn; anode and cathode, respectively) were also found to be effective (23 mg TAN/L removed), whereas BDD-BDD electrodes only showed limited TAN removal capacity.



Lab setup to test electrochemical removal of ammonium and total dissolved nitrogen.

When extrapolated to larger scales, TAN removal rates up 0.45 kg TAN per day per square meter were determined for a copper-BDD electrode. Similar rates were found in brackish RAS with a lower TAN level (3.5 ppm) – where the same cell oxidized 70 percent of the added TAN within 7 minutes and lowered the TAN concentration to 0.5 ppm, which remained stable throughout a testing period of 20 min. The electrochemical surface specific TAN removal here corresponded to approx. 0.48 kg N per day per square meter.These finding were confirmed with measures of total dissolved N, which followed the same rate of degradation. The estimated electrochemical N-removal was found to be in the range of 40 KW/kg N.

A linear reduction of ammonium and total dissolved N was found at high and low TAN concentrations (Fig. 1). The copper electrode removed ammonium at a higher rate compared to the tin electrode. At lower TAN levels, copper-BDD combinations showed an immediate and constant removal of

ammonium down to 0.5 mg N/L.

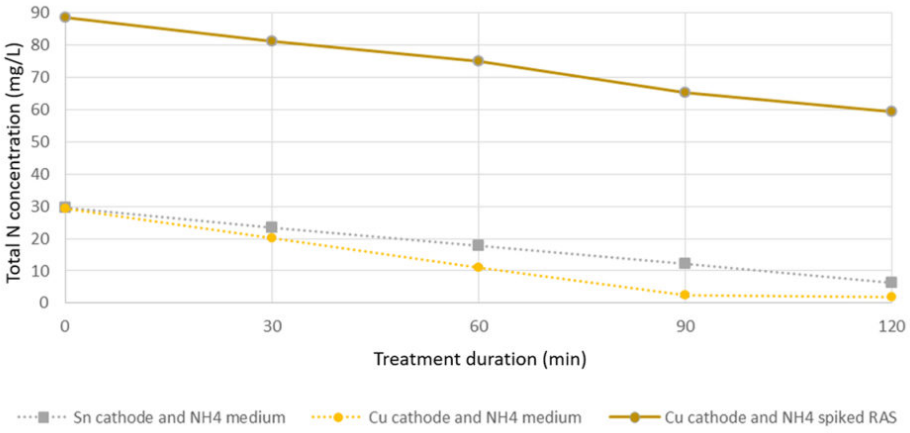


Fig. 1: Total dissolved N concentration over time during chemical oxidation treatment with a boron-doped diamond anode and tin (Sn) or copper (Cu) cathodes. The brackish water tested (8 ppt salinity) consisted of tap water and seawater spiked with 30 mg/L of NH4-N, and RAS water with an elevated nitrate level and seawater spiked with 30 mg N/L. Electrode area was 10 cm2, with 5 Volts and 0.22 A applied with a flow of 15 mL/s.

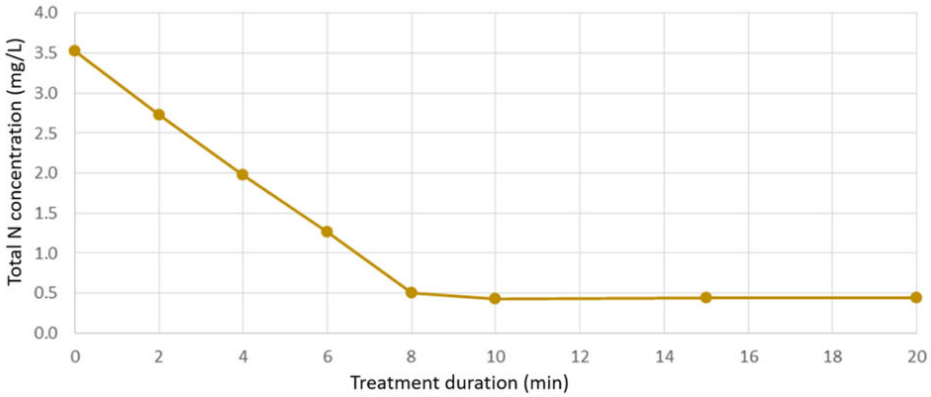


Fig. 2: Concentration of total dissolved nitrogen in the aquaculture water sample spiked with NH4Cl prior to electrochemical treatment. Volume was 1000 mL; anode = BDD; cathode = Copper; applied with 5 Volts.

Electrochemical disinfection

The potential disinfection capacity of a flow-cell with combined BDD-BDD electrodes was tested in freshwater and in brackish RAS water. Furthermore, an ozonizer treatment device called “Doctor Chihiro” was also evaluated in batch scale experiments. The water samples originated from a pilot scale freshwater RAS and from a commercial saltwater RAS or mixtures hereof. The studies did not quantify the composition of radicals and oxidants formed during electrochemical oxidation but

measured the total amount of oxidants (also referred to as total residual oxidants, TRO) as chlorine (Cl_2) equivalent. Here, we found linear positive correlations between current density, salinity and exposure time on the formation of oxidants.

In addition, the electrochemical disinfection efficacies were evaluated by use of new microbial assays quantifying the bacterial activity in the water. The microbial activity in the water was tested on RAS water samples prior to, during and after electrochemical treatment. The degrees of bacterial inhibition were proportional to the oxidants produced at the batch experiments and showed that a 1,000-fold reduction (Log3) could be achieved within 5 minutes of electrochemical oxidation (Fig. 3).

Fig. 3: Electrochemical disinfection of brackish RAS water. Water samples were sampled at different exposure times and the microbial activity in the water was measured by a microbial assay, BactiQuant®.

Potential use in aquaculture

Summarizing our overall findings, it is possible to remove total ammonia nitrogen (TAN) by electrochemistry, and reactive oxygen species (ROS) were found to be formed in freshwater, and particularly in brackish water, with high antimicrobial effect. The study did not address quantification of the oxidants formed, so the toxic effects on fish and the safety issues need more attention before further upscale and potential implementation.

Provided these issues can be effectively addressed, electrochemical oxidation may be a future alternative treatment technique that can be considered, for example, during live fish transport where ammonia excretion and accumulation is critical and water volumes are low. Furthermore, the electrochemical oxidation process (EOP) can potentially reduce the start-up time required for (very) cold water RAS facilities, where biofilter maturation can require months before nitrification is established.

EOP can potentially be applied for disinfection of aquaculture systems. In situations where severe disinfection (sterilization) is required to eradicate pathogens or if cleaning between batches is needed (all-in all-out), the EOP can produce potent oxidants that can be circulated within the RAS and hence disinfect microorganisms in the water and on surfaces, including biofilms.

Authors

LARS-FLEMMING PEDERSEN, PH.D.

Corresponding author
Technical University of Denmark
DTU Aqua, Section for Aquaculture
The North Sea Research Centre
P.O. Box 101, DK-9850 Hirtshals, Denmark

lfp@aqua.dtu.dk (mailto:lfp@aqua.dtu.dk)

ANNA MARIA RØYSET LIER, M.SC.

University of Life Sciences
Faculty of Chemistry, Biotechnology and Food Science
Ås, Norway

DAVID JONATHAN JENSEN, M.SC.

Technical University of Denmark
DTU Aqua, Section for Aquaculture
The North Sea Research Centre
P.O. Box 101, DK-9850 Hirtshals, Denmark