Innovative Photoelectrocatalytic filter for Recirculating Aquaculture Systems

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Significance and Relevance

This work aims to study an innovative photoelectroncatalytic (PEC) water treatment in recirculating aquaculture system (RAS) for fish farming alternative to the conventional biological filters used so far. This novel filter exploits the UV-electrochlorine advance oxidation process and has been tested *in vivo* in order to study the effectiveness and the biocompatibility of this technology in presence of living fishes (rainbow trout). This PEC reactor also has the advantage of being easily implemented within the existing UV sterilizer, thus reducing overall operating costs.

Preferred and 2nd choice for the topic: Water treatment, Photocatalysis and Photoelectrocatalytic approaches, solar energy utilization.
Preferred presentation: Oral only

Introduction and Motivations

Ammonia poses a threat to biodiversity in aquatic environments, having toxic effects on fish and animals living in freshwater and seawater[1]. Land-based aquaculture uses recirculating aquaculture systems, which take advantage of biological filters to oxidise ammonia to nitrite ion NO_2^- and the much less toxic nitrate ion NO_3^-. Periodical replacement of water leads to the emission in the environment of large amounts of nitrogen rich wastewater, contributing to eutrophication in fresh and seawater. It's possible to couple a semiconductor to the already present Hg-UV lamp setups in fish farming plants, to construct a photoelectrochemical reactor which exploits the UV-electrochlorine advanced oxidation process. The semiconductor coated anode illuminated by the lamp oxidizes chloride ions naturally present in fresh- (or sea-) water, the generated highly reactive chlorine species oxidize the ammonia released by fish and convert it into NO_3^- and the more inert N_2.[2]

Materials and Methods

Synthesis of the photoanode material is achieved through an easily scalable anodization procedure yielding highly active thin film of TiO_2 arranged in self-assembled vertical nanotubes arrays from metal Ti metal substrate.[3] Ti mesh tubes of 4 cm diameter and 39 cm long are anodized in an electrolyte solution of 0.2 M HF, 8 M H_2O in ethylene glycol at 30 V for 1.5-6 h. Finally, the meshes are rinsed and sonicated in absolute ethanol, following calcination at 450°C for 2 h with heating ramp of 10 °C min^{-1}. Preliminary tests were performed in a 1.08 L glass lab scale reactor (fig. 1). A metal Ti mesh tube surrounding the TiO_2 coated photoanode is used as counterelectrode, water is recirculated by a rotary pump from a 2.5 L tank. Ammonia degradation tests are run on 5 mmol L^{-1} KCl and 100 ppm NH_3 solutions at 4 V potential bias. Periodical analysis of NH_4^+, NO_2^- and NO_3^- by ion chromatography allows to trace ammonia conversion and selectivity towards the NO_2^- and NO_3^- N_2 products. *In vivo* tests have been performed with six individual tanks (three control and three treated groups), with a recirculating flow rate set at ca. 120 L/h. A total of 375 g of juvenile rainbow trout (around 60 individuals/tank, 16

°C, 10 L/14 D photoperiod), at 7.5 kg/m3 density and fed twice daily (0.7% body weight) was distributed in each tank at the beginning of the test.

Results and Discussion

Anodization of the Ti metal meshes in presence of HF yields a TiO_2 thin film layer arranged in a vertical nanotube array as shown in the SEM image in fig. 1. The film composition is anatase, and show very high photoactivity in the UV range at $\lambda < 380$ nm. Ammonia concentration linearly decreases overtime while NO_2^- accumulates over the first 2 hours and is then further consumed, NO_3^- concentration increases during the whole experiment as ammonia is converted. The concentration profiles are typical of consecutive reactions where NO_2^- is the first intermediate and is then consumed to make the NO_2^- end product. Selectivity toward nitrate only reaches up to 50% of the total ammonia converted, and the remaining nitrogen is converted to N_2. Optimization of the synthesis procedure by changing the anodization time from 1.5 h to 6 h allows to increase the photocurrent and increase the overall PEC performance of the reactor.

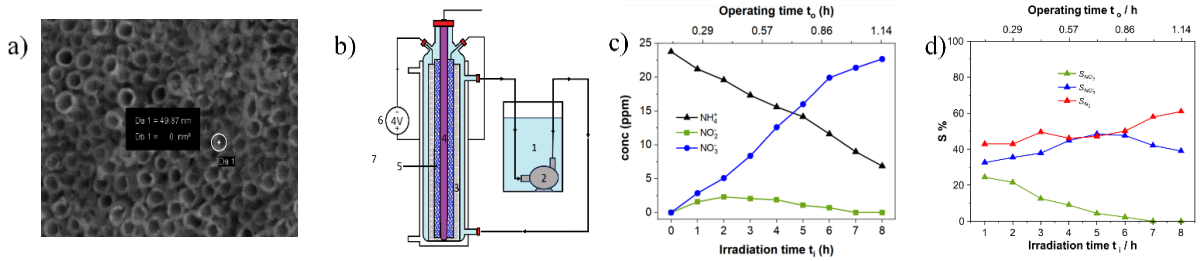

Figure 1 SEM image of the anodized Ti mesh (a), lab-scale PEC setup (b), variation of NH_3 (black), NO_2^- (green), and NO_3^- (blue) concentration (c) and selectivity to NO_2^- (green), NO_3^- (blue), N_2 (red) (d) during the PEC experiment in KCl 5 mM.

By contrast, only a slight X_{NH3} (ca. 10 %) is observed in K_2SO_4 electrolyte solution. These results suggest that chlorine has a crucial role in the ammonia PEC oxidation process: photo-generated holes on the photoanode surface can oxidize Cl^- to $Cl^\bullet$ (electro-induced process), which is a reactive radical able to oxidize ammonia through the formation of different chloramines intermediates.

The in-vivo tests confirmed the photocatalytic performances obtained in lab scale and the histological analysis made on the fishes did not revealed any pathological alteration in the gills and liver of both groups. The superoxide dismutase (sod1), glutathione reductase (GR), glutathione peroxidase (GPx1), and Tumor necrosis factor (TNFa) gene expressions were significantly higher in the control group than in the PEC-treated group, while the Heat shock protein 70 (Hsp70) expression did not show any difference in the two groups. These results indicate that the use of PEC filters has a positive effect on water quality, compared to the use of conventional biological filters, inducing a high level of welfare in rainbow trout.

References

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