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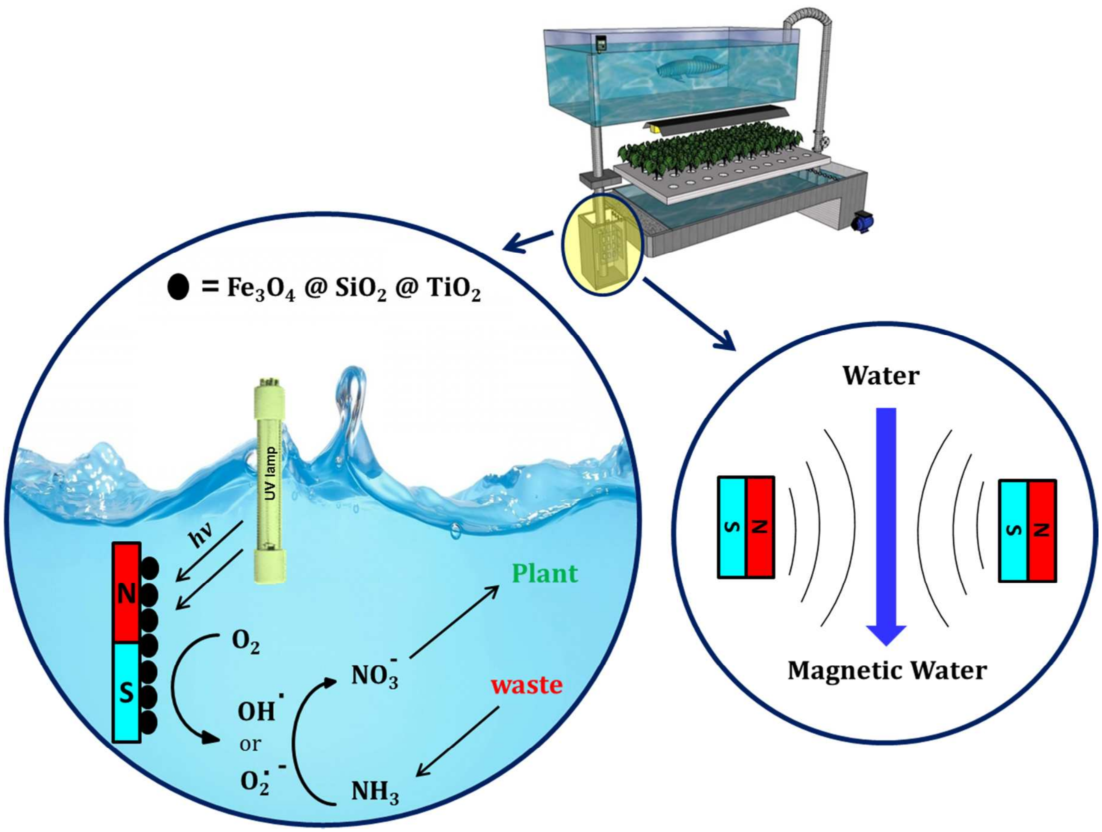

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A simple and innovative concept for a micro-aquaponic system (MAS) to valorize residual nitrogen via photocatalytic conversion was developed. Results proved that over 70% of ammonia could be oxidized to nitrates within 1.5 hours under UV irradiation and subsequently taken up by plants which experienced a remarkably superior plant growth (with results showing 1.8-1.6 times improved petiole growth) with respect to standard grown samples. The proposed methodology may pave the way to a new eco-farming paradigm aimed to maximize the value of residues to valuable end-products by combining multidisciplinary efforts and low environmental impact technologies.

1. Introduction

Aquaculture accounts for one of the most important food resources worldwide, providing ca. 50% fish food.[1] Additionally to current production, 40 million tons of aquatic food have been predicted to be produced by 2030.[1] Nitrogen transformations (NTs) comprise key biochemical processes in aquaculture systems (Figure 1a).[2, 3] With nitrogen being an extremely important component in living organisms as essential part of genetic material and protein structures.

Figure 1a illustrates how over 5% fish feed remains unconsumed in aquaculture systems[3] while 95% digested and consumed leads to a 25 % average (11-36 % range) unexploited and largely unutilised fish biomass.[4] Figures point out that over 50 % of consumed fish feed is converted to un-ionized ammonia which is partially excreted as a major product of protein metabolism. Ammonia in aquaculture is however a dangerous component due to is persistence and almost negligible volatilization[5] as imposes toxicity to fish and can inhibit growth, decreased survival as well as causing a variety of physiological dysfunctions in fish.

In view of the aforementioned facts, ammonia removal in aquaculture systems is vital and currently conducted via nitrification under oxidising-conditions. Compared to ammonia, nitrates are somewhat non-toxic to fish except at very high concentration levels (> 300 ppm).[6] Nitrifying bacteria (NB) oxidize ammonia to nitrate in two steps. However, NB systems are susceptible to physical and chemical parameters including pH, temperature shifts[7] water salinity, light sensitivity,[8] dissolved oxygen levels[9] and they can be largely inhibited by chemicals. On the other hand, bacterial growth rate is very slow, making nitrification difficult.[10] An alternative solution for ammonia removal involves water exchange of un-dissolved solids and nitrates which is rather expensive and requires of large water volumes, being unfeasible in many places.[11]

Our proposed concept can be considered the basis of future sustainable eco-farming. Growing plants out of soil making use of nutrients and minerals derived from aquaculture waste (Hydroponics)[12] have associated advantages in terms of high yields, quality plants, precise and complete control of nutrition and plant diseases and shorter cultivation times as well as environment safety, being particularly useful in non-arable regions.[13] The integrated aquaponic system can also be considered as self-sustainable (with fish waste providing most of the nutrients that plants require) and requires water inputs.[14a]

2. Results and Discussions

The proposed concept comprises a designed magnetic photo-catalytic reactor (MPC reactor, 3 L) for the bio-mimetic UV-assisted photocatalytic oxidation of ammonia to nitrate (Figure 1b, step 1), an environmentally sound nano-magnetic Fe_3O_4@SiO_2@TiO_2 photocatalytic system optimized for the photo-degradation process, a fish tank (Figure 1b, step 2) containing *Oreochromis niloticus* fish and a plant tank (Figure 1b, step 3) comprising 30 strawberry shrubs (*see supporting information for full details of the system*).
Our purpose to use of the nano magnetic photocatalyst is to prevent the transition of nano particles into the fish and plant tanks via attraction onto surface of several magnetic bars. Similar magnetic systems have been used as a fixed bed photo reactor in wastewater treatment plans.[14b-d]
Nitrate concentration measurements were conducted by UV absorption spectrophotometry according to standard procedures as well as using an electrocatalytic system (Figure 2).[15] A mild aeration was kept during AOP for water saturation with oxygen. Samples taken at regular time intervals proved the oxidation of ammonia to nitrate in the MPC reactor under the investigated

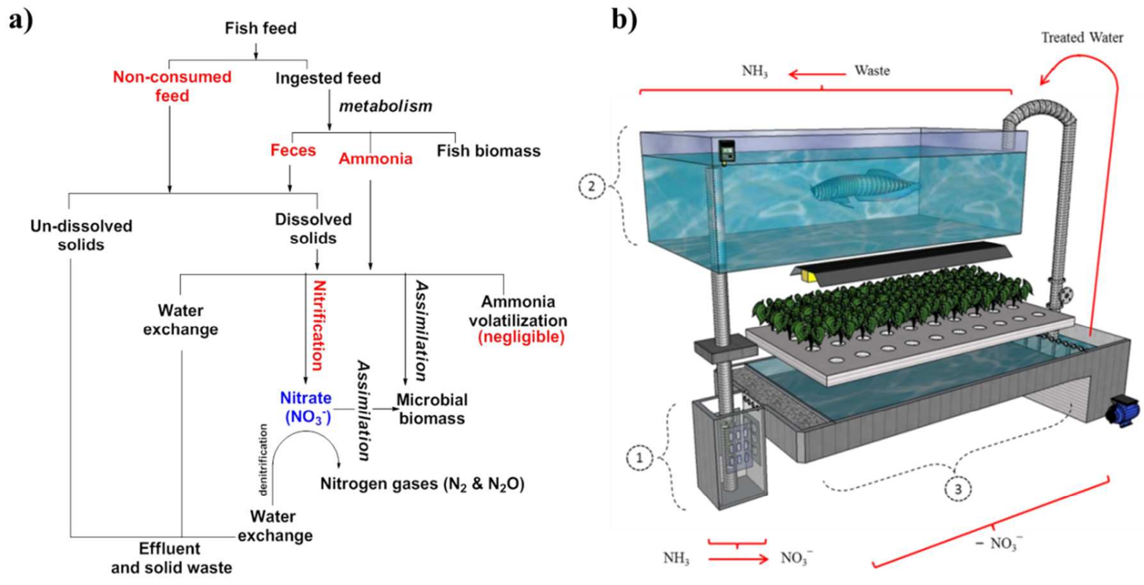


Figure 1. a) Principal of the NTs processes in aquaculture systems[2, 3]; b) Proposed waste-to wealth aquaponic concept. From fish biomass and residual nitrogen to plant growth via photo-assisted conversion. 1. MPC reactor; 2. Fish tank; 3. Plant tank.

reaction conditions. Nitrate concentration remarkably increases (in start of photo-reaction), subsequently increasing slowly in time to reach constant values between 130 to 167 ppm after several days (Figure 2, see supporting information). High initial ammonia concentration present in solution accounted for the observed rapid increase in nitrate concentration, followed by steady but continuous increase of nitrate concentration with time.

Scheme 1 depicts a schematic representation of the proposed photocatalytic route for ammonia oxidation in the MPC reactor. The reaction is initially triggered by UV irradiation *via* conventional photocatalysis[16] in which ammonia conversion can proceed *via* interaction with valence band hole (redox potential of 2.7V)[17] or with generated radical species in the system ($OH^{\bullet}$ or $O_2^{\bullet-}$).[18] The amount of dissolved oxygen has been reported to play an important role in AOP efficiency[19] and the presence of a magnetic field in our experiments might enhance the amount of dissolved oxygen in the aqueous media as discussed later.[26]

Upon ammonia conversion into nitrate, the outlet water was transferred to the plant tank. In which the generated nitrates were consumed by the plant as nutrients (decreasing nitrate concentration). No additional nutrients were added to the plants. Last but not least, refined waters of the plant tank were eventually pumped to the fish tank and this cycle was repeated continuously. The flow-rate of water continuously circulated throughout the system was 2 m^3 h^{-1}.

Strawberry plants (*Fragaria ananassa Duch*.) were selected to evaluate petiole growth and leaf area indexes due to their susceptibility to salinity and fast reflex.[20] To compare the growth rate of petioles in strawberries from our proposed MAS with a standard hydroponic environment, a set of strawberry plants were separated and growth in Hoagland solution as a standard nutrient solution (containing 210 ppm N as well as other trace metals including K, Na, Ca, Mg, Fe, etc.).[21] All plants were under short-day (SD) conditions (10 h) at 25°C during work experiments.

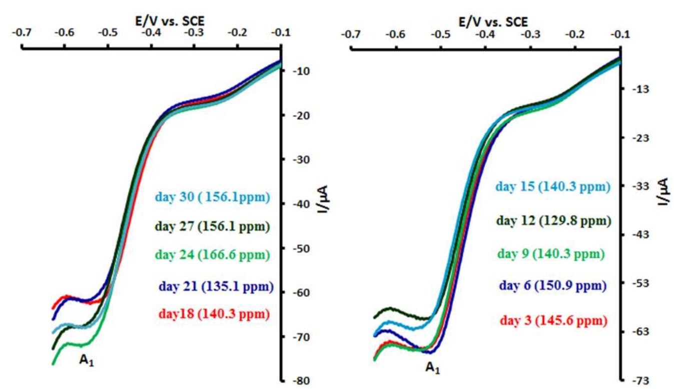
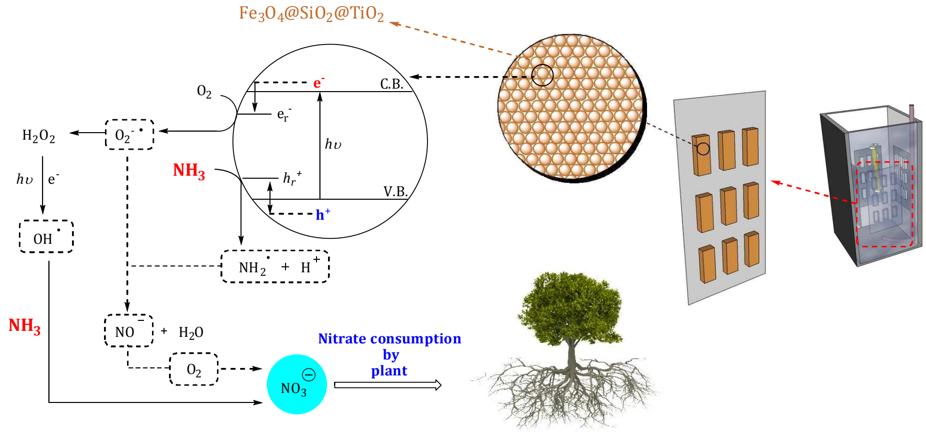


Figure 2. Linear sweep voltammograms for samples taken from MAS on the surface of a cupper modified electrode in solution containing 0.1 M Na_2SO_4 (pH = 3.0, HCl) during the 30 day period. Scan rate 100 mVs^{-1}.

Figure 3 illustrates the evolution of petiole growth of strawberry plants under MAS *vs* Hoagland solution over time. The growth was measured within 1 day intervals. Transfer of strawberry plants from soil to our new environment (MAS) resulted in significant differences in growth rate but these were only noticeable after the tenth day (see Figure 3, last two curve comparisons).



Scheme 1. A pictorial representation of the photocatalysis oxidation of ammonia. The circle symbolizes processes that may take place onto the surface of the catalyst. Two horizontal lines represent the band edges.

It was anticipated that the plants may not show an adequate growth trend within the first 10 days (as compared to those grown on Hoagland solution) due to the shock generated by the plants transfer (from soil to the hydroponic solution).

Gratifyingly, growth trend of petioles for plants under MAS (slope 6.181) was promisingly superior to that under Hoagland solution (slope of 5.763), even during the first 10 day period of changing environment.

Nevertheless, further growth dates, in which plants were able to reach an equilibrium and natural conditions, clearly demonstrating a remarkably different growth trend for plants with slopes almost twice as better (1.8-1.6 times) as compared to standard growth plants under Hoagland solution (Figure 3). Furthermore, experiments aimed to measure leaf area growth in plans further confirmed a steady increase in leaf area within 32 days (See supporting information). More importantly, the fish were observed to have a normal growth during the process time, all surviving after 30 days, confirming the usefulness of the proposed concept.

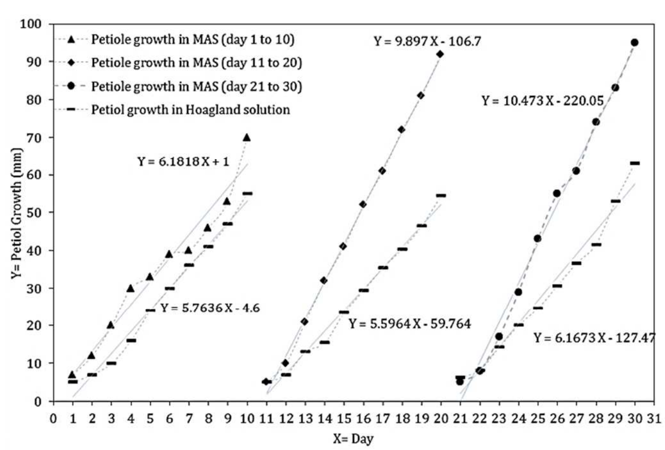


Figure 3. The growth trend of petioles of strawberry plants in MAS and Hoagland solution.

Observations regarding petiole growth and the effectiveness of the system were in fact way over expectations, particularly related to the exclusive production of nitrates from ammonia in the system, so we were prompted to further investigate potential effects of the magnetic system (as super strong magnets were applied to the MPC reactor during the photo-conversion step). Detailed investigations in terms of physical properties of water (including surface tension, viscosity and amount of dissolved oxygen) and parameters intrinsically related to the proposed MAS (e.g. conductivity, pH measurements and monitoring of growth) seemed to indicate that the presence of the magnetic field altered the physical properties of the water in the aquaponic system, in good agreement with previous reports.[22-28] Results comparing water collected after the process and 72 h after the process proved that surface tension and viscosity increased in magnetized water during MAS (see supporting information data and Figures) being potentially interesting to decrease water evaporation. Furthermore, UV-irradiation also rendered as in principle could be expected a higher conductive water (see supporting information) but most importantly the quantity of dissolved oxygen was slightly superior (9 ppm) in magnetized water as compared to the same water 72 h after the experiment (7 ppm, see supporting information). pH was observed to remain constant (around 7) all the way through the process.

Based on these findings, we cannot rule out a relevant involvement and role of magnetized water in the unexpectedly observed superior growth of strawberry plants under the proposed MAS with respect to a conventional nutrient system.

3. Conclusions

An innovative concept based on an integrated residual nitrogen photo-conversion to nitrates with a micro-aquaponic system to grow plants has been proposed for the first time (Figure 4). The proposed concept remarkably predates biological nitrification providing an unprecedented more controllable, non-sensitive and and effective alternative methodology for a sustainable valorization of residual nitrogen making use of a simple, efficient and cheap continuous system.

Figure 4. The actual structure of MAS from different directions

Nitrates (130-167 ppm) were efficiently produced upon ammonia photo-conversion using magnetic nanoparticles of Fe_3O_4@SiO_2@TiO_2 and efficiently taken up by strawberry plants under hydroponic conditions leading to significantly improved plant growth as compared to plants grown under hydroponic conditions with typical nutrients.

The developed approach is envisaged to set up the basis of sustainable farming and potentially a major re-thinking in eco-farming strategies aimed to maximize the value of residues to valuable products by combining multidisciplinary efforts and low environmental impact technologies.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Details for MPC Reactor and the MAS; Analysis of MPC; Nitrate concentration measurement in the MAS; Leaf area index, Surface tension, Viscosity, Dissolved oxygen, Conductivity and pH measurements. Catalyst preparation; TEM images, Energy-dispersive X-ray spectroscopy (EDX) and XRD pattern of the Fe_3O_4@SiO_2@TiO_2 nanoparticles. See DOI: 10.1039/b000000x/

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