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Photo-Electrocatalysis to Mitigate the Environmental Impact of Nitrogen Compound Pollution in the Water and into the Atmosphere in Recirculating Aquaculture Systems for Trout

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Abstract

Aquaculture has rapidly expanded, surpassing capture fisheries and playing a vital role in global food security. However, this growth raises environmental concerns, especially regarding nitrogen waste accumulation in recirculating aquaculture systems (RASs). Nitrogen compounds from uneaten feed and fish excreta, mainly ammonia (NH_3) and nitrite (NO_2^-), lead to water pollution, eutrophication, and greenhouse gas emissions. This study describes the setup and the efficiency of a new photo-electrocatalytic (PEC) system in reducing nitrogen waste in a high-density RAS for rainbow trout (30 kg/m^3). The PEC system, an evolution of a pure photocatalytic system, was integrated in the units of the RAS and tested for the first time in field conditions, combining photocatalysis and electrochemical oxidation to convert toxic nitrogen species (NH_3) into less harmful nitrogen forms (NO_3^- and N_2), aiming to mitigate both water and atmospheric pollution. Over a 4-week period, water nitrogen compounds, ammonia and greenhouse gases (carbon dioxide, nitrous oxide and methane) emitted by water were continuously monitored in two groups of three tanks (PEC vs. control). Each tank was equipped as an independent RAS unit. PEC treatment led to significantly lower NH_3 concentrations (0.96 ± 0.2 mg/L vs. 1.78 ± 0.2 mg/L, $p < 0.01$), lower NO_2^- levels and higher NO_3^- levels (61.77 ± 2.14 mg/L vs. 53.10 ± 2.14 mg/L, $p < 0.01$) in water, indicating efficient nitrogen oxidation. Gaseous emissions were also reduced: NH_3 (1.49 vs. 2.64 mg/m^2/day, $p < 0.05$) and N_2O (1.44 vs. 2.88 mg/m^2/day, $p < 0.05$). These results support PEC technology as a promising solution for improving nitrogen management in intensive aquaculture. Although challenges remain in optimizing energy use and scalability, PEC offers a valuable strategy for reducing environmental impact while sustaining productivity in the aquaculture industry.

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1. Introduction

Aquaculture has undergone rapid development in recent decades, driven by the need to alleviate pressure on conventional fisheries. From 1950 to 2022, global fish production increased from 19 million to 185 million tons, with aquaculture contributing 94 million tons of this total. In 2022, aquaculture production surpassed capture fisheries for the first time (51% vs. 49%, respectively) [1], positioning itself as a vital contributor to global food security. However, this rapid growth is accompanied by significant environmental concerns, particularly related to emission of nitrogen compounds and their effects on aquatic ecosystems and atmospheric chemistry [2].

A major issue in aquaculture is the accumulation of nitrogen compounds derived from unconsumed feed and fish excreta, contributing to high concentrations of N-containing compounds, which can degrade water quality, promote eutrophication, and disrupt aquatic ecosystems by altering the ecological balance [3,4].

The environmental footprint of intensive aquaculture is further exacerbated by its relatively lower ecological efficiency compared to terrestrial livestock, particularly referring to species such as trout or sea bream, which require high protein content in aquafeed [3]. These limitations highlight the urgent need for technological innovation to enhance production efficacy while minimizing environmental impacts.

Technological progress has become increasingly important in addressing the environmental challenges associated with aquaculture, and many fisheries have been converted into closed-system technologies, which are more environmentally friendly than open-water systems [5,6]. New approaches such as integrated multi-trophic aquaculture (IMTA) and recirculating aquaculture systems (RASs) aim to minimize ecological impacts by reducing nutrient runoff and improving water quality management [7,8].

In RASs, nitrogen discharge rates typically range from 35 to 40 kg nitrogen per ton of fish production [8]. These systems are designed to optimize environmental performance through water treatment technologies that can allow up to 90% water reuse, significantly improving operational efficiency [9–11].

The wastewater generated in recirculating aquaculture systems (RASs) contains a wide range of organic and inorganic compounds produced by the reared biomass. Therefore, a series of treatments—including mechanical filtration, biological filtration, and disinfection—is required to ensure safe water reuse [12]. However, a considerable proportion of solid particles in RASs are smaller than 10 μm, and if not effectively removed, these can lead to several operational issues. Such problems include biofilter clogging, secondary ammonia production resulting from microbial degradation of retained organic matter, and negative effects on both system components and fish health [13,14]. Among system components, the biofilter plays a central role: its design (volume, surface area, porosity, and flow velocity) strongly influences treatment efficiency [15]. Nevertheless, biofilter performance can fluctuate under varying conditions such as temperature, pH, oxygen concentration, and fish biomass [10,16]. Consequently, effective nitrogen removal systems capable of maintaining nitrogenous compounds below toxic thresholds are essential to ensure both fish welfare and overall system stability [11].

In addition to conventional biofiltration, alternative and complementary water treatment technologies have been developed to enhance RAS performance [17,18]. Mechanical separation, adsorption using materials such as zeolites or activated carbon, and air stripping are commonly applied to remove suspended solids and nitrogenous compounds, though each presents inherent limitations in energy use, chemical demand, or operational complexity. Membrane technologies—including microfiltration, ultrafiltration, nanofiltration, and reverse osmosis—are increasingly adopted for their high contaminant removal efficiency and support for water reuse with minimal additives [19,20].

Advanced oxidation processes (AOPs) such as ozonation and UV/H_2O_2 are being explored for the degradation of recalcitrant organic pollutants and antibiotics, as well as for the inactivation of waterborne pathogens. However, these processes often involve high energy consumption and potential formation of by-products [21], while hybrid systems combining biological, physicochemical, and oxidative processes are increasingly recognized as efficient and sustainable approaches for managing aquaculture effluents. Among these, ozone oxidation is widely adopted, effectively breaking down organic matter and harmful microorganisms [22], though it requires precise dosing and continuous monitoring to avoid negative impacts on fish and ensure operator safety [23]. Other approaches, such as breakpoint chlorination, ion exchange, air stripping, and various chemical oxidation techniques, have also been applied, though they are often associated with high operational costs, chemical residues, and complex management requirements [24].

Among advanced oxidation processes, photocatalysis (PC) has gained increasing attention as a sustainable and effective method for aquaculture water purification. PC enables the degradation of a wide range of pollutants—including organic matter, heavy metals, ammonia, and microplastics—while also providing antimicrobial activity [25–31]. The process is based on semiconductor materials, most commonly titanium dioxide (TiO_2), which, upon light irradiation ($\geq$3.4 eV), generates reactive oxygen species (ROS) such as hydroxyl radicals (•OH) and superoxide anion radicals ($\bullet O_2^-$). These reactive intermediates promote the oxidation and mineralization of contaminants, facilitating the conversion of NH_3 into gaseous N_2 [32–34]. The fundamental mechanism can be represented by the following equations:

$$\begin{gathered}\mathrm{TiO_2} + hv \rightarrow e^-_{CB} + h^+_{VB} \\ \text{(photon absorption and charge separation)}\end{gathered} \tag{1}$$

$$\begin{gathered}h^+_{VB} + \mathrm{H_2O} \rightarrow \mathrm{OH}\bullet + \mathrm{H}^+ \\ \text{(hydroxyl radical formation)}\end{gathered} \tag{2}$$

$$\begin{gathered}e^-_{CB} + O_2 \rightarrow O_2^{\bullet -} \\ \text{(superoxide radical formation)}\end{gathered} \tag{3}$$

$$\begin{gathered}NH_3 + OH\bullet \rightarrow intermediates \rightarrow N_2 + H_2O \\ \text{(ammonia photo oxidation to nitrogen gas)}\end{gathered} \tag{4}$$

Despite its proven efficiency, conventional photocatalysis often suffers from limited charge separation and recombination of photogenerated electrons and holes, which can reduce its overall performance [35].

To overcome these limitations, photo-electrocatalysis (PEC) has emerged as an advanced hybrid technique that integrates photocatalysis with electrochemistry, enhancing electron–hole separation through the application of an external electrical bias [36]. This configuration increases the generation of reactive species and improves oxidation kinetics, particularly in chloride-rich media where reactive chlorine radicals contribute to selective NH_3 conversion [37], demonstrating high selectivity—up to 80%—for the oxidation of NH_3 to N_2, with minimal formation of NO_3^- under optimized conditions [38].

More recently, electrochemical oxidation has emerged as a promising technique for the simultaneous removal of ammonia (TAN) and microbial contaminants, particularly in saline environments [18].

The application of photocatalytic oxidation for nitrogen removal did not originally emerge from aquaculture research but from studies on livestock manure treatment. TiO_2-based photocatalysis was first proposed as an innovative approach for the abatement of ammonia in nitrogen-rich livestock effluents, demonstrating effective ammonia oxidation in a single-step process [39]. However, these studies also identified an important practical limitation: the low transparency and high suspended solids content of livestock manure markedly reduced light penetration, thereby limiting photocatalytic efficiency. This limitation suggested that aquatic environments characterized by higher water transparency could represent a much more suitable application scenario for photocatalytic technologies. Consequently, the concept was translated to recirculating aquaculture systems (RASs), where water clarity allows more efficient light utilization.

PEC aligns with the broader framework of sustainable aquaculture by offering a low-impact, cost-effective, and scalable alternative to traditional oxidation methods such as ozonation or chemical treatment. Unlike those techniques, PEC does not require the addition of oxidants or chemicals and avoids the generation of hazardous secondary waste. The integration of a TiO_2-coated mesh within existing UV disinfection units allows easy retrofitting of current RAS infrastructure, enhancing nitrogen removal efficiency while maintaining fish safety and system stability [37].

From an industrial perspective, however, the objective of PEC integration is not to replace existing UV disinfection systems but to improve their environmental performance according to the principles of Best Available Techniques (BAT), as defined in the European Industrial Emissions Directive [40] and described in the BREF documents [41,42]. Within the BAT framework, technological innovation is expected to provide measurable environmental benefits while remaining technically feasible, economically sustainable, and readily applicable to existing production systems. Accordingly, technological innovation is not necessarily based on the replacement of existing infrastructure but may also consist of incremental improvements capable of enhancing environmental efficiency while facilitating industrial implementation. Consequently, the proposed PEC configuration was intentionally designed as a retrofit of a conventional UV sterilization unit through the integration of TiO_2-coated electrodes and a low-voltage DC power supply, rather than as a completely new treatment technology. This approach minimizes capital investment, preserves the hydraulic layout of commercial RASs, facilitates industrial implementation, and reflects the progressive technological improvements encouraged by BAT principles.

Beyond their impact on water bodies, nitrogen compounds and other pollutants generated in aquaculture can contribute to atmospheric pollution. Aquaculture contributes to GHG emissions through multiple pathways—including CO_2 and CH_4 released during organic matter degradation in ponds and biofilters, and N_2O generated through microbial nitrification–denitrification processes [43,44].

Ammonia volatilization can further lead to fine particulate matter formation ($PM_{2.5}$) [45], while nitrous oxide (N_2O)—a potent greenhouse gas (GHG) with a global warming potential approximately 275 times that of CO_2 [46]—is released through microbial nitrification and denitrification processes in aquaculture systems [43].

Recent studies indicate that NH_3 concentrations in the system can influence N_2O emissions, suggesting a direct link between ammonia availability, nitrification activity, and GHG production [47,48].

While studies on GHG fluxes have been conducted for ponds and open-water systems [49–51], data on RASs remain scarce. Most available assessments rely on IPCC-based estimations or simplified LCA models, which may underestimate real emissions [50,52]. The complexity of emission pathways—affected by system design, water quality, retention time, and aeration—highlights the need for more precise monitoring and mitigation strategies [53].

In addition to direct emissions, the energy demand of RASs represents another key environmental burden, with typical electricity consumption ranging from 15 to 30 kWh per kilogram of fish produced [54]. This energy requirement translates directly into indirect CO_2 emissions, depending on the energy source mix. Moreover, feed production itself accounts for over half of aquaculture's total indirect greenhouse gas (GHG) emissions [55], due to energy-intensive ingredient processing and transportation.

Despite the growing interest in photo-electrocatalytic technologies for water treatment, their application in recirculating aquaculture systems (RASs) remains largely unexplored under real farming conditions. Most previous studies have been conducted at laboratory [37] or pilot scale [56], and have mainly focused on pollutant degradation efficiency, while the broader environmental performance of PEC systems has received limited attention. In particular, there is still a lack of information regarding their ability to simultaneously improve water quality, reduce gaseous nitrogen emissions, preserve fish performance, and operate with an acceptable energy demand under commercial aquaculture conditions. This knowledge gap limits the assessment of PEC as a sustainable alternative to conventional RAS treatment technologies and hinders its potential implementation at an industrial scale.

Therefore, the present study was designed not only to evaluate the pollutant removal efficiency of a novel PEC reactor, but also to provide a comprehensive sustainability assessment of its integration into a high-density rainbow trout RAS. By simultaneously considering water quality, nitrogen transformation, atmospheric emissions, fish growth performance, nitrogen mass balance and energy consumption, this work adopts a multidisciplinary approach aimed at evaluating the overall environmental benefits of PEC technology under realistic operating conditions.

For these reasons, the present study developed and evaluated an enhanced photo-electrocatalytic (PEC) prototype integrated into a high-density (30 kg/m^3) rainbow trout RAS operating under field conditions. Unlike previous laboratory-scale investigations, this work aimed to assess the overall effectiveness and sustainability of upgrading a conventional UV disinfection unit through photo-electrocatalytic integration under commercial-like operating conditions. Specifically, the objectives were to: (i) evaluate the long-term operational stability of the PEC reactor; (ii) determine its effects on water quality and nitrogen transformation; (iii) evaluate the environmental benefits achieved by upgrading a conventional UV disinfection unit through photo-electrocatalytic integration under realistic operating conditions; (iv) quantify ammonia and greenhouse gas emissions released from the water surface; (v) assess fish growth performance and nitrogen mass balance; and (vi) evaluate the additional energy demand associated with PEC operation. By integrating environmental, biological and engineering indicators within a single experimental framework, this study provides one of the first comprehensive assessments of PEC technology for sustainable nitrogen management in recirculating aquaculture systems.

2. Materials and Methods

2.1. In Vivo Experimental Setup

The experimental study was conducted at the Spallanzani Institute in Rivolta d'Adda (LO, Italy) according to the guidelines of the European Directive (2010/63/EU) and the Italian regulations (DL 26/2014) on care and protection in animal experimentation and approved by the Animal Welfare Organization of the University of Milan (OPBA number 62_2023).

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The plant, set up by the Milan unit in collaboration with STM Aquatrade S.r.l. (Castelraimondo, MC, Italy), consisted of six identical and independent units, each serving a 500 m^3 tank for rainbow trout (*Oncorhynchus mykiss*) rearing (Figure 1). All RAS units were equipped with standard water treatment components, including mechanical filtration, biofiltration and UV sterilization. In the experimental group, the conventional UV lamp was modified to obtain a PEC reactor, resulting in three control units (UV-based) and three PEC-treated units, described in the following section.

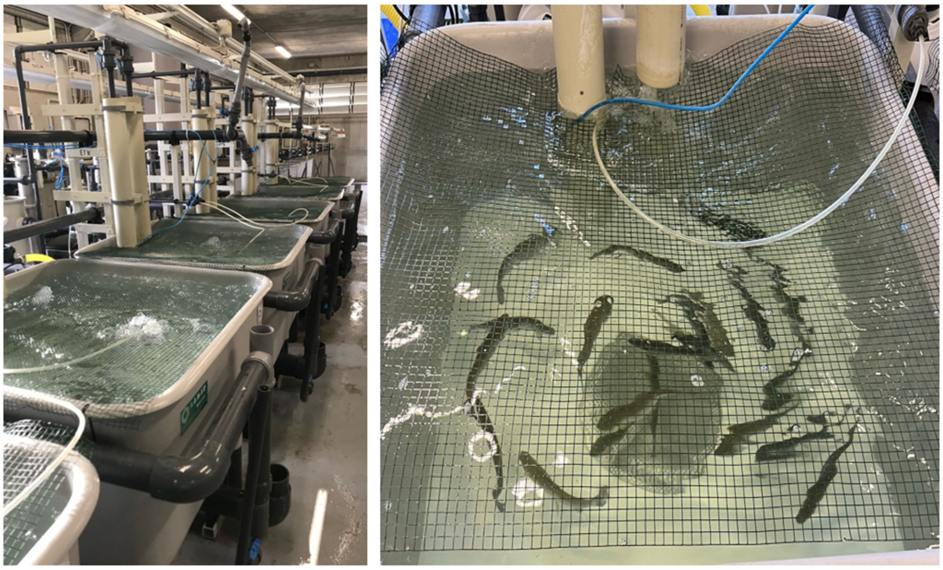

Figure 1. Lateral and front views of the experimental tanks. Water re-entered each tank via two lines: one passing through an oxygenator (longer tube, blue pipe = O_2 supply) and the other through a degasser (shorter tube). Each tank was also equipped with an aerator (white pipe = air supply).

2.2. Description of the RAS Treatment Unit

Each RAS unit operated as an independent closed-loop system directly connected to its tank, with a total recirculation rate of 500 L/h maintained by a single-phase centrifugal pump (Bering 1/4CV mono, Fluidra, Bedizzole (BS), Italy). Water entered the polypropylene bag filter (EATON Sentinel, ROTOCHIMICA Srl, Cernusco sul Naviglio, MI, Italy, Ø180 × 430 mm, pore size range 50–200 µm) by the principle of communicating vessels, allowing passive gravity-driven flow into the filter before being pumped. The mechanical filtration step removed suspended solids. Dual-level sensors installed within the filter served as safety controls to automatically shut down the pump if the water level fell below the minimum threshold or if the water level exceeded the maximum threshold to prevent dry running or overflow.

Figure 2 shows the schematic layout of the RAS treatment unit, illustrating the main hydraulic components and flow path through the system.

From the bag filter, water was moved by the pump through a pressurized biological filter housing nitrifying bacterial communities responsible for oxidizing NH_3 to NO_3^-, previously added in the bacteriological maturation phase, which lasted around 40 days. After biofiltration, water flowed into the section of the unit for water disinfection, composed of a 36 W UV-C lamp (Best UV, Aquatech, Amsterdam, The Netherlands) enclosed within a quartz sleeve (35 mm internal diameter, 900 mm length—Best UV, Aquatech, Amsterdam, The Netherlands) and housed within stainless steel (INOX 316). The three units, serving as treatment in the study, were equipped with a PEC reactor, positioned around the UV lamp in the three RAS units.

The PEC reactor was installed in the UV section of the 3 treatment units for a coaxial cylindrical setup, consisting of a central UV lamp, an anodized TiO_2-coated titanium mesh (40 mm diameter), serving as the photoanode, and a bare grade-A titanium mesh (110 mm diameter), serving as the cathode, concentrically surrounding the photoanode (Figure 3).

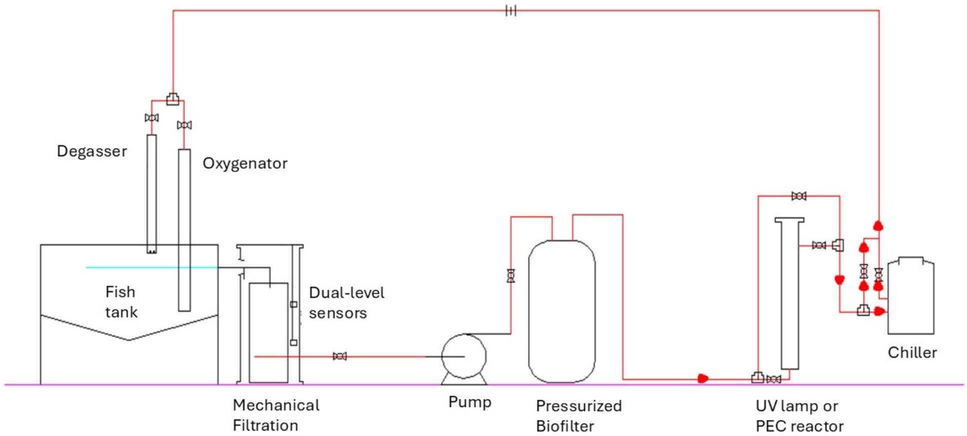

Figure 2. Schematic diagram of the recirculating aquaculture system (RAS) treatment unit showing the water flow through the main treatment components. Water is pumped from the rearing tank through the mechanical filter, where suspended solids are removed, and then passes through the pressurized biofilter for biological nitrification, followed by the disinfection unit (UV or PEC reactor) and the chiller for temperature control. The treated water subsequently flows to the degasser for CO_2 removal and to the oxygenator for O_2 enrichment before returning to the rearing tank. Red lines indicate the water flow direction.

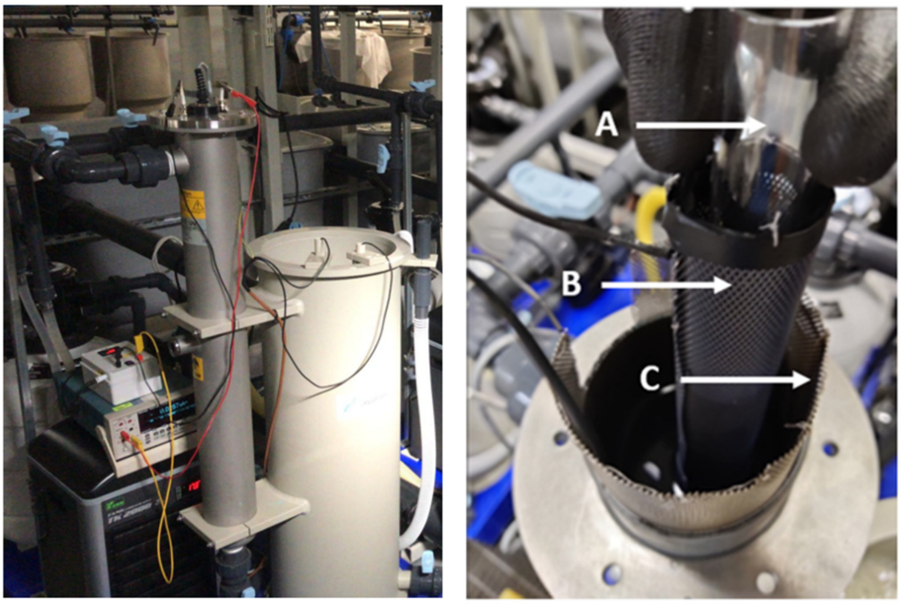

Figure 3. Photo-electrocatalytic (PEC) reactor setup. Left: external view of the customized reactor, which utilizes a modified UV sterilizer housing for photo-electrocatalytic water treatment. Right: internal coaxial arrangement highlighting (**A**) the central low-pressure UV lamp, (**B**) the anodized titanium mesh (40 mm diameter) coated with TiO_2 functioning as the photoanode, and (**C**) the surrounding grade-A titanium mesh (110 mm diameter) serving as the cathode.

The configuration was set to maximize photon absorption at the photoanode surface. The electrodes were externally connected to a DC power supply delivering a constant voltage of 4 V. According to the quartz housing and electrode assembly dimensions, the reactor's internal volume was approximately 8 L to ensure adequate hydraulic retention time (HRT) at the operational flow rate. Water entered from the reactor base to the top, guaranteeing uniform exposure and effective flow-through disinfection.

Subsequently, water passed through the chiller (TK1000, TECO refrigeration technologies, Teco S.r.l., Fornace Zarattini, RA, Italy) to maintain the optimal breeding temperature of 14.5 °C ±1.5, before flowing by gravity to the tank, through a vertical tube equipped with a degasser unit for CO_2 removal and an oxygenator to restore dissolved oxygen levels. Both gas management units were mounted above the tank on existing structural supports and operated in parallel, with flow distribution controlled by manually regulated ball valves.

Each group has a single-phase power supply (1 ph–230 V–50 Hz), and it is equipped with two panels, one dedicated to the management of the three UV sterilizers and one to the three pumps (see the Supplementary Materials). Each week, the energy consumption was recorded for both the control and PEC groups, in order to analyze differences in terms of energy consumption.

2.3. Synthesis and Characterization of the TiO_2-Based Photoanode

The photocatalytic TiO_2 coating was synthesized as a thin film directly grown by electrochemical anodization of a metal grade 1 Ti mesh (Titanium Consulting & Trading S.r.l., Milano, Italy), in order to guarantee strong adhesion and resistance of the coating. An in-house synthesis procedure was employed to prepare a thin film of a self-assembled TiO_2 nanotube array through anodization of a metal Ti mesh of 24 cm × 39 cm rolled to form a cylinder of 35 mm in diameter [57].

The employed electrochemical cell was made of a Teflon cylinder filled with Hydrofluoric acid 0.2 M + H_2O 8 M in ethylene glycol electrolyte solution, in which two coaxial Ti mesh cylinders were immersed. The outer one worked as an anode and the inner one as a cathode. The anodization was performed at 30 V for 6 h. The obtained coated mesh was finally calcined at 450 °C for 2 h.

The synthesized films were characterized by means of X-ray diffraction (XRD, Rigaku Miniflex 600, Tokyo, Japan) using Cu Kα radiation (λ = 1.5418 Å). Morphology and film thickness were investigated by field emission scanning electron microscopy (FE-SEM, Sigma Zeiss, Oberkochen, Germany). The band-gap energy was calculated from UV-vis diffuse reflectance (UV–vis DRS) spectra, recorded in the 200–800 nm wavelength range, with a Shimadzu UV-3600 Plus spectrophotometer (Kyoto, Japan) equipped with an ISR-603 integrating sphere.

2.4. Water Quality Analyses

The experimental study was conducted using fresh water, with chloride ($Cl^-_{(aq)}$) concentration adjusted to 0.28 g m^{-3}, to allow PEC and to improve its efficiency, referring to previous findings highlighting the role of $Cl^-_{(aq)}$ in UV/electro-chlorination-driven NH_3 oxidation [37]. Although reactive chlorine species (e.g., $HOCl/OCl^-$ and chloramines) were not directly quantified in the present study, previous mechanistic investigations and the high reactivity of these transient intermediates suggest that their accumulation under the adopted operating conditions is unlikely. Future studies will include their direct determination to further elucidate the reaction pathways and provide additional mechanistic insight.

A 25% mean daily water exchange was applied to the 6 tanks to guarantee trout welfare under pilot conditions and to prevent accumulation of potentially harmful metabolites due to relatively high biomass density, non-optimized biofiltration, and limited study duration.

Physical parameters, including temperature, dissolved oxygen and pH, were monitored daily using HQ Series Portable Meters (HACH®, Linate, Milano, Italy).

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Ammonia (NH_3), nitrite (NO_2^-), and nitrate (NO_3^-) concentrations were measured twice a week using LCK multiparametric tests (HACH®), with readings obtained from a Portable Lange DR1900 spectrophotometer (HACH®). Particular attention was paid to nitrogen compound kinetics for comparing control and PEC systems.

2.5. Fish Performance and Theoretical Nitrogen Mass Balance Estimation

Adult rainbow trout were reared in each tank at high density (30 kg/m^3, [58]) over a 4-week grow-out phase (130–180 g). Fish were fed a commercial high-energy diet (Power 4, Veronesi, Verona, Italy) at a fixed feeding rate of 1.5% body weight per day. Feed characteristics are presented in Table 1.

Table 1. Composition and nutritional characteristics of the commercial high-energy diet (Power 4, Veronesi) used for rainbow trout during the experimental trial.

Parameter	Unit	Value
Granulometry	(mm)	4.6–5.6
Protein	(%)	41.00
Oils and fats	(%)	30.00
Cellulose	(%)	1.30
Ash	(%)	9.90
Total carbohydrates	(%)	8.80
Phosphorous	(%)	1.10
Vit. C	(mg/kg)	150
Vit. E	(mg/kg)	150
Digestible energy	(MJ/kg)	20.95

To record fish weights and length, a group of fish was sampled weekly, and manipulation was conducted after anaesthetization with a mixture of ethyl 3-aminobenzoate and methanesulfonic acid, limiting unnecessary suffering according to the European guidelines (Directive 2010/63/EU). Stocking density was kept constant (30 kg/m^3) throughout the trial by adjusting the number of fish per tank according to biomass gain.

Growth performance was evaluated using the feed conversion ratio (FCR) and the thermal growth coefficient (TGC) [59]. The FCR was calculated as

$$FCR = \frac{feed\ distributed\ (\text{kg DM})}{Body\ weight\ gain\ (\text{kg})} \tag{5}$$

The TGC was calculated as

$$TGC = 1000 \times \left(BWfinal^{\frac{1}{3}} - BWinitial^{\frac{1}{3}}\right)/\sum d^{\circ} \tag{6}$$

where BW represents the body weight, and Σd° represents the thermal sum (mean daily temperature in °C × days of the period).

A theoretical nitrogen mass balance was estimated to provide an approximate description of nitrogen partitioning within the experimental RAS. Because the study was not originally designed as a full nitrogen budget experiment, total nitrogen pools (e.g., dissolved nitrogen, particulate nitrogen and total nitrogen in water and sludge) were not directly quantified. Therefore, nitrogen flows were estimated using measured feed intake and fish growth performance combined with literature-derived coefficients commonly adopted in aquaculture studies [15,60].

Total nitrogen input was calculated as

$$N_{\text{input}}\ (\text{kg}) = (Total\ Feed \times \%\ CP \times \%\text{N}) \tag{7}$$

where

Total feed is recorded as cumulative feed given (6.75 kg) over 30 days;

% CP is the quantity of crude protein in the feed;

N is the general percentage present in feed protein, i.e., 16%.

The percentages of nitrogen retained and excreted were estimated based on reference values reported in aquaculture manuals (e.g., [15]), providing standardized assumptions for nitrogen partitioning in fish biomass and excreta.

Nitrogen retained (N_{ret}) in fish biomass was estimated using a proxy of tissue composition, assuming that fish body protein constitutes 20% of wet body weight and that nitrogen represents 16% of protein, corresponding to 0.032 kg N per kg of biomass gain (ΔW):

$$N_{ret}\left(\text{kg N kg}^{-1}\right) = \Delta W \times 0.20 \times 0.16 \quad (8)$$

Nitrogen losses were estimated by the difference between input and retained nitrogen:

$$N_{losses} = N_{input} - N_{ret} \quad (9)$$

$$\%\ N_{losses} = \frac{N_{losses}}{N_{input}} \times 100 \quad (10)$$

FCR values used for mass balance calculations represent short-term, cohort-level estimates, so they must be considered as preliminary and specific to the 30-day experimental period.

Consequently, the calculated nitrogen retention and loss values should be interpreted as theoretical estimates of nitrogen partitioning rather than as a complete experimental nitrogen mass balance with full nitrogen closure. These calculations were included to support the interpretation of treatment effects and should not be generalized beyond the experimental conditions of the present study.

2.6. Monitoring of Gases Emitted by Water

Emissions of NH_3 and GHG (CO_2, CH_4, and N_2O) from each tank were monitored twice weekly using a floating static chamber [61–64]. Emission sampling was performed in field conditions, in the morning, before feed administration, obtaining 2 replicates of 30 min sampling per tank.

The chamber consisted of an inverted rectangular box (33.5 × 27 × 20 cm) with a volume-to-area ratio (V/A) of 0.22 cm, as recommended by [65].

Floating elements were secured 5 cm inside the box edge to prevent air leakage and create an airtight seal; an internal fan ensured homogeneous gas distribution.

Gaseous concentrations were monitored using a photoacoustic gas analyzer (Innova 1512, LumaSense Technologies, Santa Clara, CA, USA), through a closed-loop circuit of Teflon tubes, with sampled air analyzed and recirculated into the chamber via the detector's outlet (Figure 4).

The chamber was positioned gently to avoid mechanical disturbance, and measurements showing outliers and irregular trend patterns were excluded from the statistical analysis.

Calculation of Emission Factors of Gases by Water

In the chamber, the concentration of each gas typically increased linearly at first, followed by a plateau as the chamber approached saturation (Figure 5).

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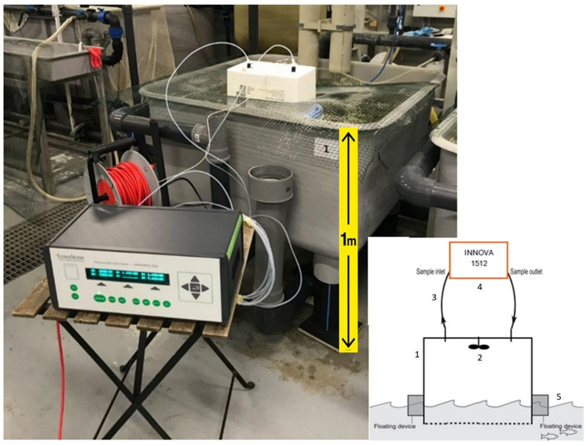


Figure 4. Measurement setup for gaseous emissions using a floating chamber coupled with a photoacoustic gas analyzer (INNOVA 1512, LumaSense Technologies, Santa Clara, CA, USA) for simultaneous detection of NH_3, CO_2, CH_4, and N_2O. The left panel shows the installation with the analyzer connected via Teflon tubing to the floating chamber positioned on the water surface. The right panel provides a schematic diagram of the sampling pathway and main components: (1) floating chamber, (2) fan, (3) sample tubing (3 mm diameter), (4) gas analyzer and (5) floating device supports.

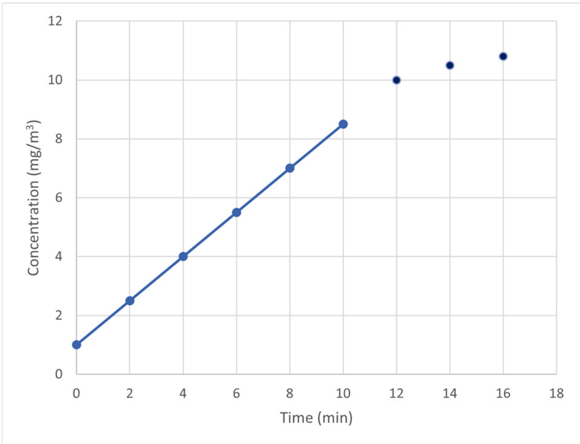


Figure 5. Typical gas accumulation curve within a static chamber: initial linear increase in gas concentration, followed by a plateau indicating saturation.

Data obtained during the 30 min of monitoring in each measuring session were submitted to a linear regression procedure (SAS 9.4, Cary, NC, USA, 2025).

The calculation of gas fluxes (emission rate) represents the relationship between concentration changes in the chamber in relation to the emitting surface [66,67].

The emission rate (mg/m^2/h), or emissivity, here defined as flux (F), was calculated according to the following equation:

$$F = \delta C/\delta t \times V/A \quad (11)$$

where

$\delta C/\delta t$ = variation in the concentration of the monitored gas in time t (mg/m^3/h), or slope of the linear regression;

V = chamber volume (m^3);

A = chamber base area (m^2).

Only linear regressions with a coefficient of determination (R^2) > 0.60 were kept for analysis to ensure the accuracy of the concentration–time relation and to minimize uncertainty in flux estimates, thereby improving the reliability and comparability of emission measurements across experimental conditions [68].

Cumulative loss values of CH_4 and N_2O were also calculated as CO_2 equivalents, for a 100 yr time horizon according to [46]—CH_4: 27 CO_2 eq; N_2O: 273 CO_2 eq.

2.7. Statistical Analysis

Descriptive statistics (mean, standard deviation, minimum, maximum—PROC MEANS, SAS 9.4, Cary, NC, USA, 2025) were used to check data in each sampling session for each investigated parameter.

The ANOVA of the parameters as nitrogen compounds and gas emission fluxes was performed using the MIXED procedure of SAS (SAS 9.4, Cary, NC, USA, 2025). The model contained the effects of treatment, time, and their interaction, the random effect of tanks nested within treatment, and residual error.

The potential correlations among the water parameters and gas emissions were investigated through Pearson correlation (PROC CORR, SAS 9.4, Cary, NC, USA, 2025).

3. Results

3.1. Characterization of the TiO_2-Based Photoanode

During the experimental study, the TiO_2 anatase crystalline structure in the PEC was characterized at the beginning, after two weeks and at the end of the monitoring period, to evaluate its persistence and adhesion to the mesh over time, by XRD analysis, which is consistent with the calcination temperature.

The anodized films resulted in a self-assembled vertically oriented nanotube array (Figure 6).

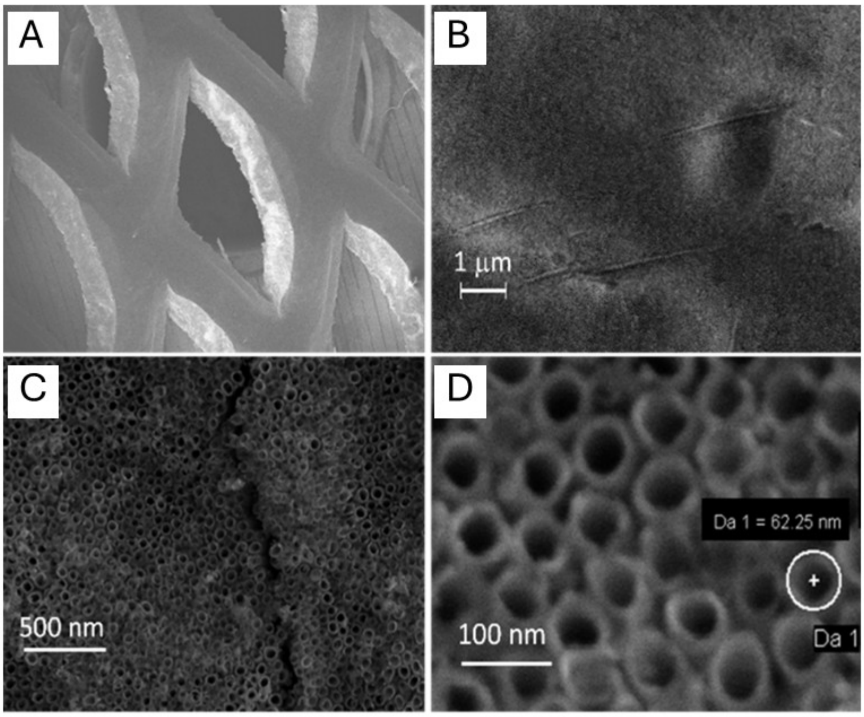


Figure 6. SEM images of the anodized titanium mesh photoanode at increasing magnification. (**A**) Low-magnification view of the anodized titanium mesh. (**B**) Cross-sectional image showing the TiO_2 nanotube layer with a thickness of approximately 1.2 μm. (**C**) Top-view SEM image of the homogeneous TiO_2 nanotube array. (**D**) High-magnification image showing the nanotube openings with an average diameter of approximately 60 nm.

The low-magnification SEM image (Figure 6A) illustrates the uniform anodization of the three-dimensional titanium mesh, while the cross-sectional view (Figure 6B) indicates a nanotube layer approximately 1.2 µm thick. Top-view images (Figure 6C,D) reveal a homogeneous and well-ordered porous morphology with nanotube openings of approximately 60 nm in diameter, confirming the successful formation of the anodic TiO_2 nanostructure.

The UV-Vis DRS spectrum shows the typical oscillations in the Vis-NIR region due to the interference fringes of thin coatings; the frequency of these oscillations usually increases with an increase in the film thickness, together with a decrease in the intensity. The band-gap absorption threshold is located below 380 nm (ca. 3.2 eV energy), typical of anatase.

3.2. Fish Performance and Theoretical N Mass Balance Estimation

During the 30-day trial, fish, kept at a density of 30 kg/m^3, were fed a daily diet corresponding to 1.5% of body weight, resulting in a cumulative feed intake of 6.75 kg/d. The diet, containing 41% crude protein, provided a total of 2.77 kg of protein, equivalent to 442.8 g of N, assuming a N content of 16% in protein.

Table 2 shows the growth performance of the rearing fish, with average initial weight and average final weight expressed as means and relative standard deviation.

Table 2. Growth performance of Oncorhynchus Mykiss in control and PEC systems.

Parameters	Control	PEC
Stocking density (kg/m^3)	30	30
Average initial weight (g)	130 ± 10	130 ± 10
Average final weight (g)	175 ± 10	183 ± 10
Average initial length (cm)	23.75	23.75
Average final length (cm)	25.28	25.30
Fish feed consumption (kg)	6.75	6.75
Observed FCR	1.4	1.2
TGC	1.17	1.36

Assuming an average nitrogen content of 3% of body weight gain, the N balance for fish is reported in Table 3.

Table 3. Theoretical nitrogen mass balance and growth performance of fish during the 30-day feeding trial. The table reports nitrogen intake, theoretical biomass gain, nitrogen retention and nitrogen losses (expressed as both N dissolved and N in particles) for the control and treatment groups. N.B. Values should be interpreted as approximate estimates of nitrogen partitioning under the experimental conditions and do not represent a complete experimental nitrogen mass balance with full nitrogen closure.

Group	Biomass Gain (kg)	N Intake (g)	N Retained (g)	N Lost (g)	N Losses (%)	Estimated N Dissolved (g)	Estimated N in Particles (g)
Control	4.82	442.8	143.1	299.7	67.7	260	40
PEC	5.63	442.8	166.9	275.9	62.3	239	37

3.3. Physical and Chemical Parameters of Water in the Tanks: Control vs. PEC

During the experimental study, in the PEC system, a constant voltage of 4 V was applied to drive the photo-electrocatalytic reaction, with the resulting current (amperage) shown in Figure 7. The photocurrent decreased from 300 mA to 70 mA within the first week, followed by a relatively stable plateau, suggesting an initial conditioning phase rather than continuous system degradation. A plausible explanation is the formation of limescale on the cathode surface, as observed during the inspection at the end of the trial. Indeed, during hydrogen evolution, proton reduction creates a locally alkaline environment that promotes calcium carbonate precipitation from the aquaculture water, thereby increasing the overall cell resistance. Since the measured current corresponds to the entire PEC cell, this phenomenon may reduce the operating current without necessarily indicating deactivation of the TiO_2 photoanode.

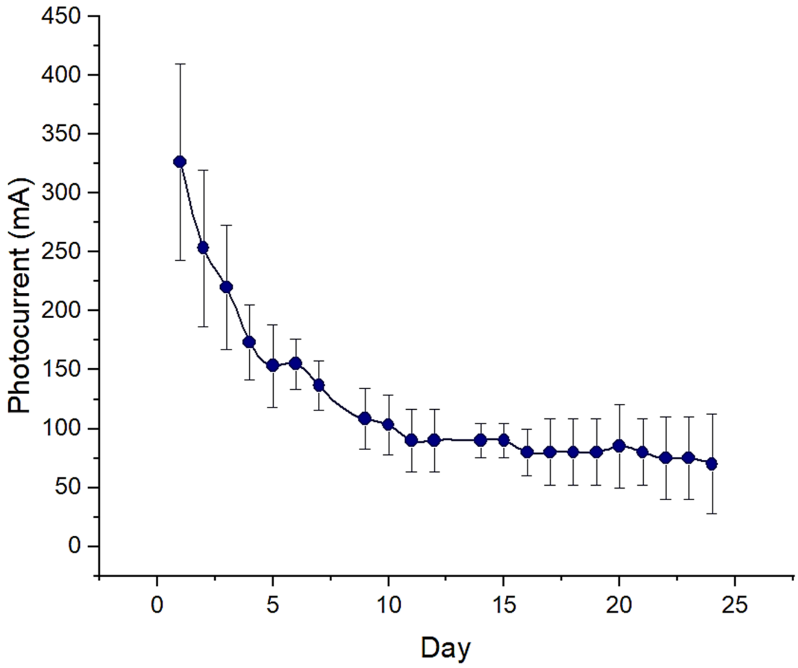


Figure 7. Temporal variation in mean values (n = 9, ±SD) of average photocurrent from PEC reactors (mA).

Table 4 shows the overall mean values and the related standard mean error (SEM) of the chemical values recorded during the trial, indicating significantly different values, with NH_3 lower in the PEC group (1.78 ± 0.2 mg/L for control vs. 0.96 ± 0.2 mg/L for PEC, $p < 0.01$). No statistical differences for overall NO_2^- in the two treatments were detected, although lower values were measured in the PEC group.

Table 4. Overall mean values and standard mean error (SEM) of NH_3, NO_2^- and NO_3^- during the 4 weeks of observation [values in the same row marked with (A, B) differ for $p < 0.01$, while those with (a, b) differ for $p < 0.05$].

	Control, LSMean	SEM	PEC, LSMean	SEM
NO_3^-	53.10 a	2.14	61.77 b	2.14
NO_2^-	2.84	0.29	2.58	0.29
NH_3	1.78 A	0.20	0.96 B	0.20

Overall NO_3^- was higher in the PEC tanks (61.77 ± 2.14 mg/L vs. 53.1 ± 2.14 mg/L, $p < 0.01$).

The measured values were analyzed to better understand the dynamics of water pollutants in the RAS units over time. Figure 8 describes the mean values and standard errors of means of physical parameters and N-containing compounds of water in the control and PEC systems during the experiment.

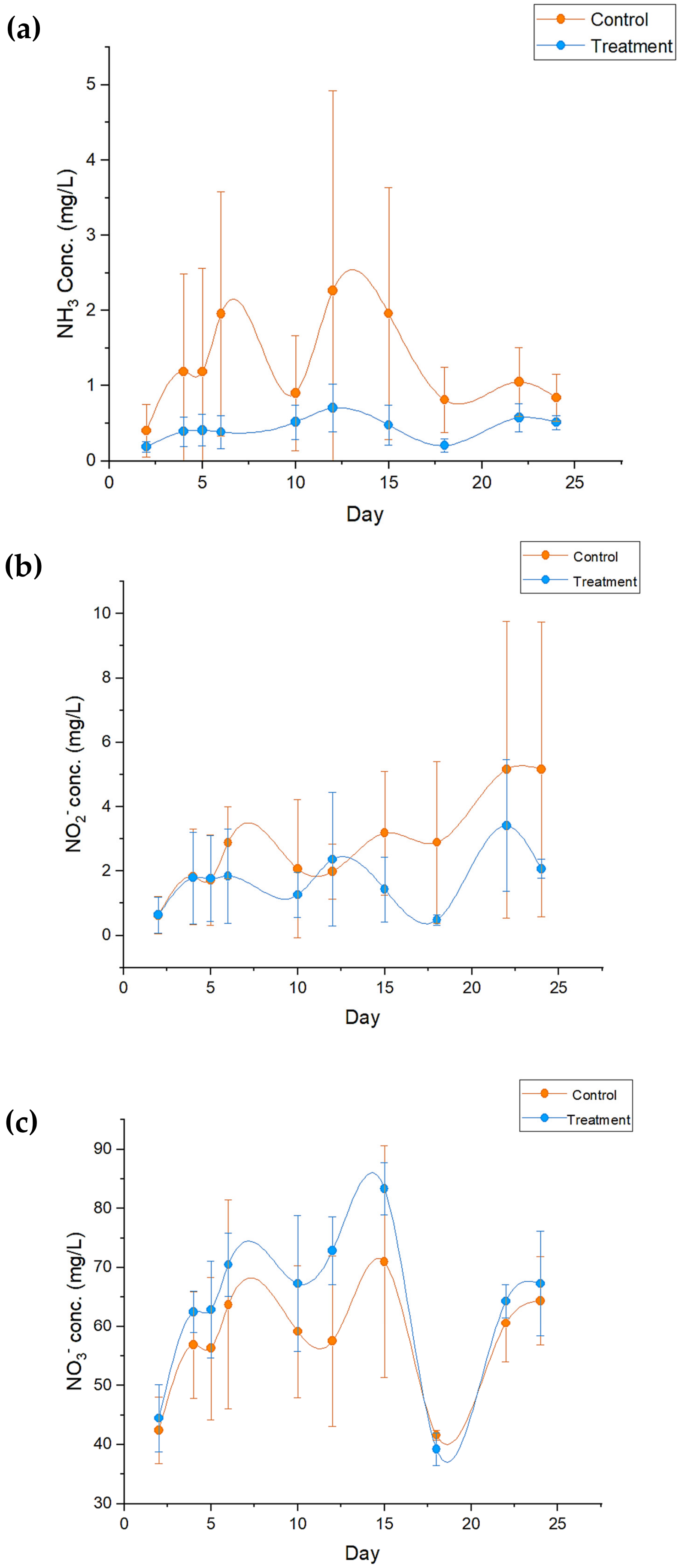
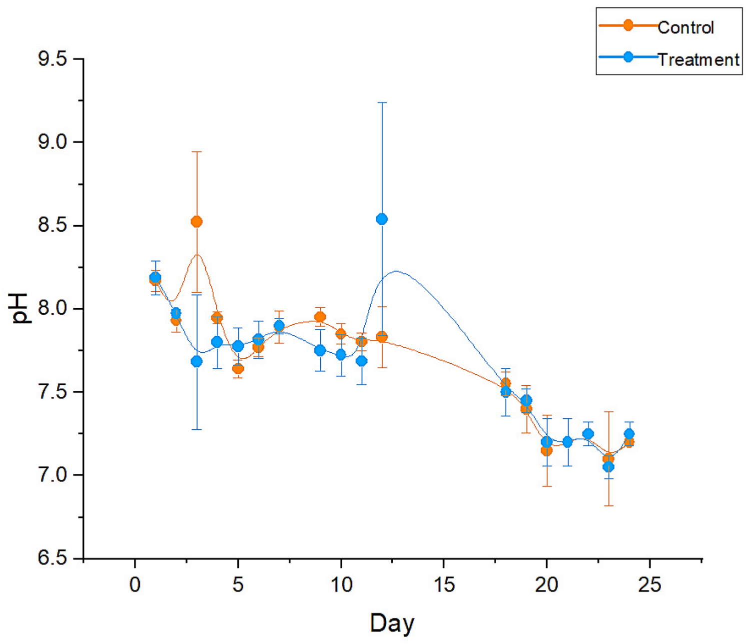


Figure 8. *Cont.*

(d)



(e)

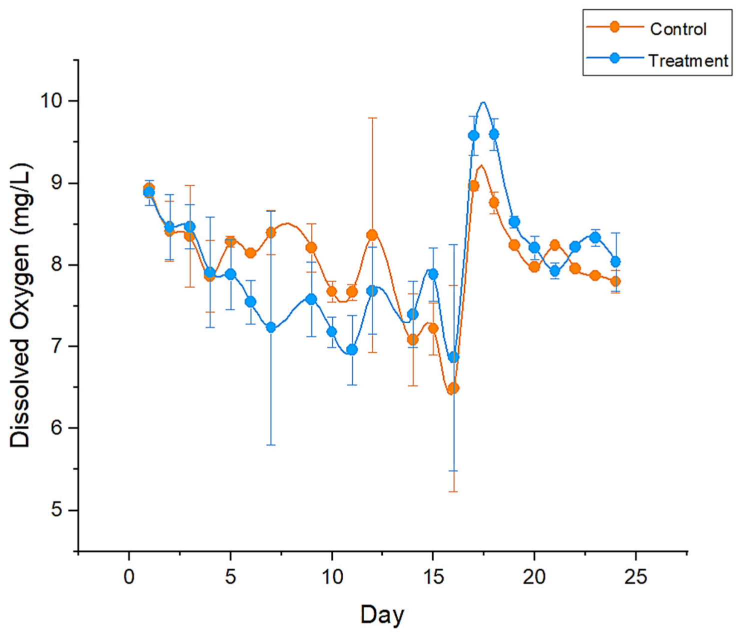


Figure 8. Temporal variation in mean values (±SD) of water quality parameters during the experimental trial for PEC-treated (blue) and control (orange) tanks. Monitored variables: (**a**) ammonia, (**b**) nitrite, (**c**) nitrate (mg/L), (**d**) pH, and (**e**) dissolved oxygen.

A beneficial effect of PEC on water quality for NH_3 (Figure 8a) and NO_2^- can be observed (Figure 8b), but not for NO_3^- (Figure 8c) Throughout the experiment, the PEC-treated systems consistently exhibited lower ammonia and nitrite concentrations compared with the control RAS. More importantly, the decrease in photocurrent shown in Figure 7 was not accompanied by any deterioration in reactor performance. These findings indicate that, under realistic aquaculture operating conditions, the measured photocurrent alone cannot be considered a direct proxy for the efficiency of ammonia conversion. Instead, the overall treatment performance results from the interplay of PEC reactions, mass transport, electrode surface processes, and the dynamic chemical composition of the circulating water. Future investigations combining electrochemical diagnostics with post-operation electrode characterization will help clarify the relationship between current evolution and long-term PEC performance.

The higher standard deviation detected for control tanks has to be related to lower general efficiency for conventional filters of the three tanks.

The pH (Figure 8d) and DO (Figure 8e) in the aquaculture tank were monitored daily; their values were similar with no differences during the observation period between the two groups. A slight decrease in pH over time in the PEC system reflected anodic oxidation reactions that consume hydroxide ions and release protons. Temperature values remained stable during the trial due to automatic continuous regulation by the chilling system.

3.4. Emission Fluxes of NH_3 and Greenhouse Gases

Figure 9 reports mean emission fluxes of NH_3 and GHGs from the water surface of control and PEC tanks.

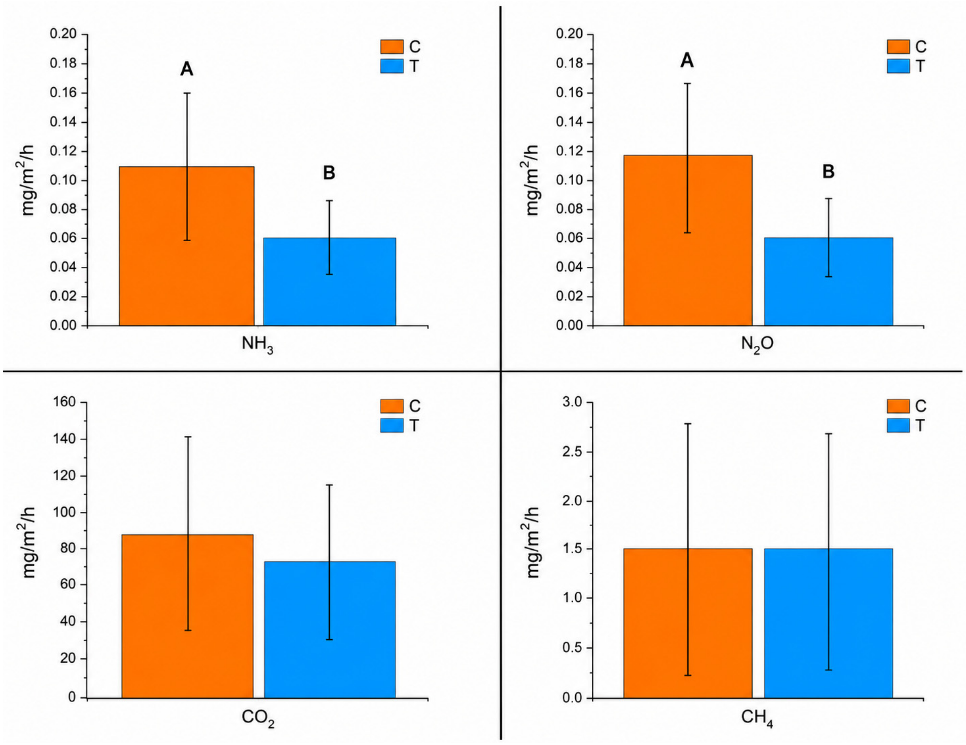


Figure 9. Fluxes of NH_3 and GHG emissions measured under field conditions using the floating chamber technique. Different letters (A, B) indicate statistically significant differences between the control and PEC groups ($p < 0.05$).

The mean emission values were higher in the control tanks than in the treated ones, with 0.11 vs. 0.062 mg/m^2/h of NH_3 ($p < 0.01$) and 0.12 vs. 0.060 mg/m^2/h of N_2O ($p < 0.05$). As regards CO_2, emissions were 87.01 ± 54.60 mg/m^2/h in the controls and 73.90 ± 44.50 mg/m^2/h in the treated tanks, suggesting a slight reduction for this GHG as well. CH_4 emissions were comparable between groups, with 1.470 ± 1.37 mg/m^2/h in the controls and 1.472 ± 1.27 mg/m^2/h in the treated ones.

The calculated GWP of the two rearing systems is expressed as CO_2 equivalents per 100 kg live weight per day, calculated according to [46], with CH_4 = 27 CO_2 eq and N_2O = 273 CO_2 eq. Control tanks showed 25.53 g CO_2 eq/100 kg LW/d, whereas PEC tanks showed 20.80 g CO_2 eq/100 kg LW/d, demonstrating the effective mitigation potential of PEC treatment on GWP.

Expressed as CO_2 equivalents, the control tanks emitted 25.53 g CO_2 eq/100 kg LW/d, and the PEC tanks emitted 20.80 g CO_2 eq/100 kg LW/d.

3.5. Correlation Among the Measured Parameters

Exploratory Pearson correlation analysis identified several relationships among water quality variables and gaseous emissions: NH_3 emissions and temperature (r = −0.985, $p < 0.01$), pH (r = −0.935, $p < 0.01$), and oxygen (r = 0.966, $p < 0.01$), and a weaker but significant association with water NH_3 concentration (r = −0.36, $p < 0.05$). Temperature was the main factor influencing N_2O emission from the water surface (r = 0.64, $p < 0.01$). The analysis showed a significant negative correlation between $NH_{3(aq)}$ and NO_3^- ($p < 0.01$). pH negatively correlated with NO_3^- ($p < 0.01$) and positively correlated with $NH_{3(aq)}$. NO_3^- showed a positive correlation with N_2O ($p < 0.01$).

3.6. Energy Demand and Operational Considerations

A comparison of the control- and treated-group RAS energy consumption was conducted, considering the energy consumption per tank per hour (Mean/Tank/h, kWh), and the energy for the PEC in the treated group, providing the cost in euros per tank per hour.

The analysis only included the additional electrical consumption associated with the PEC reactor (i.e., the electrical consumption due to the UV lamp (Aquatech, Amsterdam, The Netherlands) and the 4 V DC generated by the home-made power supply). All other RAS components, including pumps, aeration, oxygenation, degassing, chilling and mechanical filtration, were identical in the control and PEC systems and therefore excluded from the comparison, since they did not contribute to differences between treatments.

The average energy consumption per tank per hour was 0.34 kWh and 0.39 kWh for the control and PEC systems, respectively. The corresponding operational costs were estimated as 0.10 €/tank/h and 0.11 €/tank/h, based on an average electricity price of 0.30 €/kWh.

4. Discussion

This study evaluated the performance of a TiO_2-based photo-electrocatalytic (PEC) system integrated into a recirculating aquaculture setup, focusing on nitrogen compound removal efficiency, and on the potential reduction in emissions of ammonia and greenhouse gases from water into the atmosphere.

In the aquaculture sector, pure photocatalysis was applied for the first time by Randazzo et al. [69], with positive results in mitigating nitrogen compounds in Zebrafish culture, demonstrating that photocatalytic oxidation can act as a sustainable water remediation system. In 2022, a PEC system was tested in a small-scale experiment in trout by [56], with encouraging results in improving water quality parameters.

In this study, no significant differences were observed in environmental parameters, such as temperature and dissolved oxygen, between treatments, confirming that the PEC integration did not compromise rearing conditions and health of fish in the PEC group.

In the present study, the 6-day-long transient accumulation of ammonia and formation of nitrite, reported in our preliminary study, were not observed, probably due to the proper maturation of the biofilters prior to introducing animals into the tanks.

The PEC treatment achieved a clear reduction in NH_3 concentration in water (1.78 ± 0.2 mg/L vs. 0.96 ± 0.2 mg/L, $p < 0.01$), together with a lower NO_2^- accumulation and a moderate rise in NO_3^- levels (53.10 ± 2.14 mg/L vs. 61.77 ± 2.14 mg/L, $p < 0.01$). These trends indicate a more complete oxidation of reduced nitrogen species, consistent with the mechanism of PEC-driven nitrification. NO_2^- is a transient and toxic intermediate, while NO_3^-, although less harmful to fish, is relevant for eutrophication risk when discharged [14]. The modest NO_3^- increase therefore reflects improved oxidative capacity without reaching toxic thresholds for rainbow trout [70]. The PEC unit significantly

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improved NH_3 removal in water compared with the control, demonstrating its potential as an advanced oxidation technology for sustainable aquaculture.

Despite these positive results, the practical significance of PEC technology should be evaluated in comparison with currently available ammonia removal strategies in recirculating aquaculture systems (RASs). Biological nitrification–denitrification remains the dominant full-scale technology because of its relatively low capital and operating costs, low energy demand, and extensive validation under commercial conditions [71,72]. However, biological processes are inherently dependent on microbial stability and environmental conditions, making them vulnerable to startup periods, operational disturbances, and fluctuations in water quality [71]. In contrast, advanced oxidation approaches such as electrochemical oxidation and photo-electrocatalysis provide faster ammonia conversion rates and do not require microbial acclimation, potentially offering greater operational flexibility under intensive production conditions [18,73].

Photocatalytic (PC) processes have previously shown promise for total ammonia nitrogen (TAN) removal from aquaculture wastewater without affecting fish health [69]. However, the efficiency of conventional PC is often limited by rapid electron–hole recombination [35]. PEC addresses this limitation by coupling photocatalysis with electrochemical bias, which enhances charge separation and pollutant oxidation rates [36,74,75].

These findings are consistent with those reported by [56], where a similar technology applied on a smaller scale (50 L/tanks) and for a shorter duration resulted in comparable trends—lower nitrite concentrations in the treated group (5.51 mg/L vs. 3.21 mg/L, mboxemphp < 0.05) and higher nitrate accumulation—reinforcing the scalability of the observed pattern.

The nitrogen removal performance observed in the present study is consistent with the growing body of evidence showing that advanced oxidation systems can achieve ammonia removal efficiencies comparable to, or in some cases exceeding, conventional biological treatments. Electrochemical oxidation systems operating in saline aquaculture waters have reported near-complete total ammonia nitrogen (TAN) removal under controlled conditions [76], while recent PEC-based systems achieved ammonia-N removal efficiencies approaching 95–100% in laboratory-scale reactors [77,78]. Nevertheless, most of these studies were conducted under simplified experimental conditions, whereas evidence from integrated RAS environments remains limited [37,79]. Therefore, the present study contributes novel evidence supporting the applicability of PEC technology under realistic aquaculture operating conditions.

From an electrochemical standpoint, the applied voltage (4 V) ensured efficient oxidation despite a gradual decline in current density over time (from 300 mA to 70 mA) at the end of the rearing phase, likely due to substrate depletion and partial electrode passivation. Nevertheless, nitrogen oxidation remained effective throughout the trial, confirming the operational stability of the system. The literature indicates that PEC application can reduce electron–hole recombination by up to 70% and double degradation rate constants under optimized conditions [36,74,75].

Besides improving nitrogen oxidation, the biological safety of PEC integration represents a key prerequisite for its practical application in aquaculture. Complementary studies performed extended the welfare assessment beyond conventional production parameters by evaluating sensitive histological and physiological endpoints in rainbow trout exposed to the PEC system. No adverse effects were detected on fish growth performance, condition factor, skeletal morphology, muscle structure or bone mineralization during the experimental period [80], while corneal histology indicated better preservation of epithelial integrity and lower oxidative damage in fish reared under PEC conditions, suggesting improved tolerance to water quality fluctuations [81]. Collectively, these findings support the short-term biocompatibility of the proposed PEC configuration under the operating conditions tested.

Although the present study was not designed to elucidate the detailed reaction mechanism, the observed reduction in ammonia accumulation is consistent with previously proposed PEC pathways involving the simultaneous generation of hydroxyl radicals and reactive chlorine species through the reaction with photogenerated holes in the semiconductor valence band: Under UV irradiation of TiO_2 at 4 V, chloride ions may be oxidized by holes to transient active chlorine species (Cl_2 and ClO^-) that react with ammonia to form chloramine intermediates, which are subsequently converted into molecular nitrogen under UV irradiation. At the same time, hydroxyl radicals generated at the illuminated TiO_2 surface may contribute to the oxidation of nitrogen-containing intermediates to nitrites and nitrates. Because these reactive species are characterized by very short lifetimes, they are expected to react rapidly within the reactor rather than accumulate in the bulk solution. The lower ammonia and nitrite concentrations observed in the PEC-treated systems may also have indirectly benefited the biological filtration process by reducing fluctuations in nitrogen loading. Therefore, although no evidence of adverse biological effects was observed during the 4-week trial, future studies should combine detailed chemical characterization of oxidative by-products with chronic welfare assessment under commercial operating conditions to fully establish the toxicological profile of PEC technology.

Regarding the PEC efficiency in reducing N-atmospheric environmental impact, PEC treatment substantially reduced gaseous nitrogen emissions. Both NH_3 and N_2O fluxes at the air–water interface were significantly lower in PEC tanks (0.062 mg/m^2/h and 0.060 mg/m^2/h, respectively), corresponding to a 45% reduction relative to controls. Expressed on a daily basis, average NH_3 and N_2O emission fluxes were 1.49 and 1.44 mg/m^2/day in PEC tanks, compared with 2.64 and 2.88 mg/m^2/day in control tanks. The reduction in these two important gases is likely to depend on the limited ammonia volatilization and inhibition of nitrification–denitrification sequences that generate N_2O [82]. Although no previous studies have quantified these fluxes in trout RASs, our values fall within the expected range for intensive aquaculture [83].

Total gaseous nitrogen losses in aquaculture systems typically range from 22% to 36% of total nitrogen input [82,84–87]; in comparison, ammonia volatilization represents about 12–13% of total nitrogen losses in catfish ponds [88], with reported fluxes of 0.45–0.49 mg/m^2/h in catfish–rice and shrimp–rice systems [89]. Ammonia volatilization depends on the NH_4^+/NH_3 equilibrium, which is strongly influenced by environmental conditions such as pH and temperature [90].

Previous studies have reported N_2O fluxes ranging from 0.01074 to 0.0548 mg/m^2/h in shrimp and fishpond systems, including crab–fish co-culture ponds [48,50,90–92], while values up to 2.47 mg/m^2/day have been observed in marine shrimp culture [85]. The present results thus fall within the expected range for intensive aquaculture, supporting the view that RASs, despite their efficiency, can be important sources of gaseous nitrogen emissions.

Beyond nitrogenous gases, the analysis of GHG emissions revealed that the PEC system also influenced the fluxes of CO_2 and CH_4. Mean CO_2 emissions were 73.90 $\pm$ 44.50 mg/m^2/h in the PEC tanks and 87.01 $\pm$ 54.60 mg/m^2/h in the controls, indicating a slight reduction in carbon dioxide release in the presence of the catalytic reactor. These emissions are consistent with values reported for intensive aquaculture ponds (57–98 mg/m^2/h; [90,91]) and primarily reflect fish respiration and organic matter mineralization. Conversely, CH_4 fluxes were very similar between treatments (1.472 $\pm$ 1.27 vs. 1.470 $\pm$ 1.37 mg/m^2/h), suggesting that methanogenesis was not directly affected by PEC operation. Methane emission in recirculating systems is mainly linked to anaerobic microenvironments and organic sediment accumulation [63,93]. The comparable CH_4 fluxes observed in both groups likely indicate limited anoxic sediment formation under the experimental conditions.

Overall, when expressed in CO_2 equivalents, total GHG emissions decreased from 25.53 to 20.80 g CO_2 eq/100 kg LW/d in the high-density trial, highlighting the potential of PEC to mitigate the carbon footprint of RASs through enhanced nitrogen oxidation and a lower buildup of organic matter in sediments.

The exploratory correlation analysis identified several significant associations between water quality parameters and gaseous emissions. However, these relationships should be interpreted with caution because they were derived from a relatively limited dataset collected under controlled pilot-scale conditions and therefore do not necessarily imply causal mechanisms.

The strong associations observed between NH_3 emissions and temperature ($r = -0.985$, $p < 0.01$), pH ($r = -0.935$, $p < 0.01$), and dissolved oxygen ($r = 0.966$, $p < 0.01$), together with the weaker correlation with dissolved NH_3 ($r = -0.36$, $p < 0.05$), likely reflect the combined effects of the PEC treatment and the temporal evolution of the system rather than the independent influence of each environmental variable. Although ammonia volatilization is generally expected to increase with increasing temperature and pH through the NH_4^+/NH_3 equilibrium, temperature, pH and dissolved oxygen remained within relatively narrow operating ranges throughout the trial. Under these conditions, the observed correlations may have been driven by treatment-related covariance and by simultaneous changes in nitrogen transformation processes rather than by direct physicochemical effects.

In contrast, no significant correlations were observed between N_2O emissions and dissolved oxygen or NO_2^- concentration, suggesting that N_2O production was likely regulated by additional biological processes beyond the individual physicochemical variables measured in this study. Conversely, the positive association between NO_3^- and N_2O is consistent with the close coupling between nitrification and nitrogen oxide production, although this relationship should also be interpreted as exploratory. Reduced N_2O fluxes observed in PEC tanks may still contribute to improved control of nitrification intermediates and lower substrate availability for denitrification [47,48].

Correlation analysis also identified associations between water physicochemical parameters and greenhouse gas emissions. Dissolved oxygen was positively correlated with CH_4 and negatively correlated with CO_2, while positive trends were observed between NO_3^- and CH_4 emissions and between CH_4 and N_2O fluxes. These relationships may reflect the coexistence of aerobic and anaerobic microenvironments within biofilms and localized sediment deposits in RASs [94]. However, given the limited number of observations and the complexity of microbial carbon and nitrogen cycling, these correlations should be regarded as hypothesis-generating rather than definitive evidence of coupled biogeochemical processes. Further studies including microbial community analyses and larger datasets will be necessary to clarify these interactions.

Integration of gas fluxes with feed and biomass data revealed that a larger proportion of input nitrogen was retained in fish biomass under PEC treatment (37.7%) than in the control group (32.3%), consistent with the improved feed conversion ratio (FCR = 1.2 vs. 1.4), associated with greater nutrient retention efficiency and reduced excretory nitrogen losses [95].

Nitrogen retention values, for both groups, aligned with those reported for intensive systems (25–57%) [59,96,97]. Enhanced nitrogen use efficiency (NUE) in the PEC group likely stems from reduced reactive nitrogen losses and improved water quality, both of which support better fish metabolism. Although interspecies comparisons must be made cautiously, our retention rates exceed those reported for carp–lettuce aquaponic systems [60], reflecting trout's higher protein assimilation capacity. Measured NH_3 and

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N_2O volatilization accounted for less than 0.03% of feed nitrogen input, consistent with or lower than previous estimates [98,99], confirming that gaseous losses represent a minor yet environmentally relevant fraction of the nitrogen budget.

Regarding energy performance, the average electricity consumption remained comparable between treatments. The PEC-equipped tanks consumed 0.39 kW/tank/h compared to 0.34 kW/tank/h in the controls, corresponding to 0.026 and 0.0227 kWh/kg of fish produced, respectively. The modest increase in energy demand (about 15%) is largely offset by the efficiency gain in nitrogen oxidation and lower gaseous emissions. These results confirm that the integration of PEC technology does not substantially raise operational costs while offering environmental benefits, aligning with reported energy ranges for RASs of 2.9–81.5 kWh/kg fish produced [55,100].

Energy consumption and operating costs remain among the principal barriers limiting the large-scale adoption of advanced oxidation technologies for ammonia control [101,102]. Compared with biological biofiltration, PEC systems require both electrical input and electrode maintenance, potentially increasing operational complexity. However, unlike many physicochemical ammonia removal approaches, including ion exchange, membrane separation, and chemical precipitation, PEC simultaneously promotes pollutant oxidation and water disinfection without the need for chemical regenerants or extensive waste streams [79,101]. The relatively modest increase in electricity consumption observed in the present study suggests that PEC may represent a viable complementary technology, particularly in situations where compact footprint, rapid treatment, or enhanced biosecurity is desirable.

Unlike most previous studies investigating photocatalytic or photo-electrocatalytic technologies in aquaculture, which primarily focused on water quality parameters and nitrogen removal efficiency [56,69], the present work also quantified NH_3, N_2O, CO_2 and CH_4 fluxes at the air–water interface. This broader assessment provides new evidence regarding the environmental implications of PEC integration in recirculating aquaculture systems, demonstrating not only improved nitrogen transformation within the water column but also a measurable reduction in atmospheric emissions. Considering the increasing attention toward the environmental footprint of aquaculture production, these findings suggest that PEC technology may contribute simultaneously to water treatment and greenhouse gas mitigation strategies within intensive RASs.

Although the present study focused on operational energy consumption, other economic aspects should also be considered before commercial implementation. Because the PEC reactor was obtained by modifying an existing UV disinfection unit through the addition of TiO_2-coated titanium meshes and a low-voltage (4 V) DC power supply, installation costs are expected to be limited compared with the replacement of entire treatment units. Routine maintenance requirements are also expected to remain similar to those of conventional UV systems, with the additional need for periodic inspection and cleaning of the photo-electrodes to prevent fouling.

Consequently, a complete economic evaluation, including capital investment, maintenance costs, electrode lifetime and return on investment, was beyond the scope of the present study and should be addressed through long-term commercial-scale trials.

One practical advantage of the proposed PEC configuration is that it can be retrofitted into existing UV sterilization units without major modifications of the hydraulic layout of the RAS. This substantially reduces the investment required compared with installing dedicated oxidation systems.

Some methodological limitations should be acknowledged. The relatively high water-exchange rate (25%) used in this pilot-scale RAS, although necessary for trout health welfare, limits comparability with commercial systems, where water renewal is generally kept to a minimum and adjusted according to fish biomass (expressed in liters per kilogram of fish produced) to optimize water quality and system efficiency [103]. Furthermore, the short duration of the experimental cycle, which did not reach steady-state growth benchmarks, means that nitrogen retention should be interpreted as a transient indicator.

In addition, the nitrogen budget presented in this study should be regarded as a theoretical estimation rather than a fully validated nitrogen mass balance. Since total nitrogen pools in water, suspended solids, fish biomass and discharged effluents were not directly quantified, nitrogen retention and losses were estimated from measured feed intake and fish growth using literature-derived coefficients commonly adopted in aquaculture studies [15,59]. Although this approach does not allow complete nitrogen closure and introduces a degree of uncertainty, it provides a useful approximation of nitrogen partitioning under experimental conditions.

The elevated water renewal may also have facilitated removal of fine suspended solids (<10 μm), which otherwise could contribute to ammonia regeneration and biofilter clogging [13,104]. In this context, granular media filters and foam fractionators—known for their high efficiency in removing this particle size fraction [104]—could be integrated to further enhance PEC performance. Therefore, future studies should include direct quantification of total nitrogen pools in water, solids and biomass to achieve a fully validated nitrogen mass balance. Longer experimental periods, improved particle filtration and monitoring of phosphorus and particulate nitrogen fractions would also provide a more comprehensive characterization of nutrient cycling within the RAS.

In general, the physicochemical and emission data consistently indicate that PEC promotes a more oxidizing environment, leading to lower reactive nitrogen losses and better control of GHG production: integrating PEC technology into RASs demonstrated clear potential for enhanced nitrogen control, lower gaseous emissions, and improved nutrient utilization efficiency without compromising water quality or fish health. These results position PEC as a promising complementary technology for ammonia management in intensive aquaculture. While biological biofiltration remains the most established and economically favorable solution for full-scale RASs, PEC offers several potential advantages, including rapid ammonia oxidation, reduced gaseous nitrogen emissions, compact reactor design, and the possibility of simultaneous water disinfection. Further research should focus on long-term operation, cost–benefit assessment, catalyst durability, and validation under commercial-scale conditions before widespread implementation can be recommended.

5. Conclusions

The present study demonstrated that photo-electrocatalytic (PEC) treatment can effectively enhance water quality in recirculating aquaculture systems (RASs) by reducing NH_3 and NO_2^- accumulation and mitigating gaseous nitrogen emissions (NH_3 and N_2O) at the air–water interface. These findings support the potential of PEC as a promising advanced oxidation process to improve nitrogen management and environmental performance in intensive aquaculture.

Addressing the increasing demand for environmentally responsible aquaculture, technologies like PEC can directly contribute to United Nations Sustainable Development Goals (SDGs)—notably SDG 6 (Clean Water and Sanitation), SDG 12 (Responsible Consumption and Production), and SDG 14 (Life Below Water)—by improving water quality, reducing nutrient discharge, and promoting circular water use within intensive fish production systems.

However, this work should be regarded as a preliminary proof of concept, and further research is needed to assess its long-term feasibility and performance at larger scales. The present findings suggest that further improvements could be achieved through electrode optimization or catalyst doping to enhance light absorption and long-term activity. Although the reduced NH_3 and N_2O emissions together with improved nitrogen removal may translate into economic benefits through better water quality management and potentially improved fish performance, the present study did not quantify these benefits economically. Therefore, calculation of return on investment was beyond the scope of this work and should be further investigated in future long-term studies.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/su18147333/s1, Figure S1. Electrical supply and control panels serving the six recirculating aquaculture tanks. On the left: the main electrical control panels for the PEC treatment unit and associated UV lamp system; on the right: the pump control panel and instrumentation for water quality management. These units provide power, operational control, and safety management for the treatment processes used in the experimental setup.

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Abbreviations

The following abbreviations are used in this manuscript:

IMTA	Integrated Multi-Trophic Aquaculture
RAS	Recirculating Aquaculture System
AOPs	Advanced Oxidation Processes
PC	Photocatalysis
PEC	Photo-Electrocatalysis
ROS	Reactive Oxygen Species
UV	Ultraviolet
GHG	Greenhouse Gas
LCA	Life Cycle Assessment
OPBA	Animal Welfare Body
UV-C	Ultraviolet C
DC	Direct Current

HRT	Hydraulic Retention Time
FE-SEM	Field Emission Scanning Electron Microscopy
XRD	X-Ray Diffraction
UV-vis DRS	Ultraviolet–Visible Diffuse Reflectance Spectroscopy
LCK	Cuvette Test Kits (HACH)
FCR	Feed Conversion Ratio
TGC	Thermal Growth Coefficient
BW	Body Weight
CP	Crude Protein
DM	Dry Matter
DO	Dissolved Oxygen
V/A	Volume-to-Area Ratio
GWP	Global Warming Potential
LW	Live Weight
NUE	Nitrogen Use Efficiency

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