Nitrogen dynamics in cultured olive flounder (*Paralichthys Olivaceus*) using diverse developed adsorbents, including developed chitosan-hydrogel and alginate-coated zeolite

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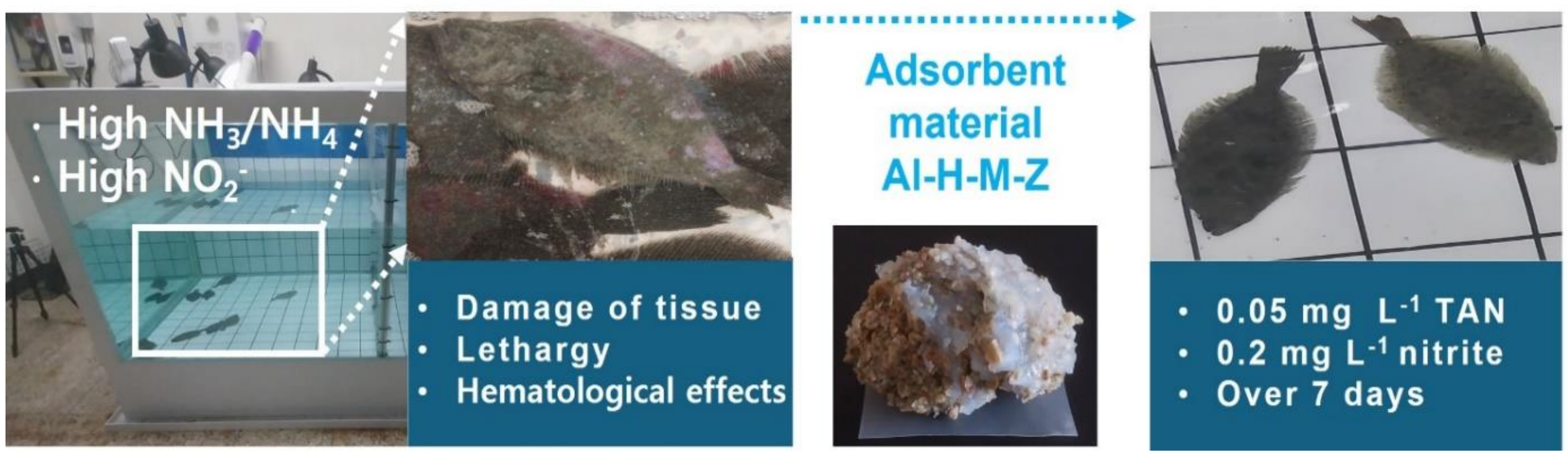
Abstract

Excess total ammonia nitrogen (TAN) and its oxidized forms, nitrite and nitrate are severe threats to marine ecosystem. This study investigates the efficacy of adsorption technologies for removing nitrogen contaminants, comparing them with a conventional method, the moving bed biofilm reactor (MBBR) in seawater condition. Commercial zeolite proved ineffective in seawater due to high salinity. However, crosslinked–hydrogels such as chitosan-based hydrogel modified with p-hydroxybenzoic acid (M-Cht-HG) and alginate-hydrogel-metal-coated zeolite (Al-H-M-Z) demonstrated notable efficacy in controlling nitrite concentrations. Notably, while Moving Bed Biofilm Reactor (MBBR) was ineffective in reducing Total Ammonia Nitrogen (TAN) below the initial concentration, both M-Cht-HG and alginate-hydrogel-metal-coated zeolite (Al-H-M-Z) achieved significant reductions in TAN concentrations, achieving 92.5% and 75.6% reductions within 24 h under seawater conditions, respectively. For actual application, Al-H-M-Z demonstrated extended adsorption effects, maintaining TAN and nitrite concentrations below 0.1 mg L^{-1} over 7 days, outperforming M-Cht-HG, which was effective for only 2 days. In terms of activation rates, MBBR required 18 h to initiate TAN and nitrite removal, whereas Al-H-M-Z needed only 12 h to effectively remove nitrogenous byproducts through adsorption.

Introduction



In this study, the adsorption effectiveness of nitrogenous contaminants was assessed using both traditional and novel materials in seawater. Chemically modified chitosan-based p-hydroxybenzoic acid hydrogel (M-Cht-HG) and alginate-hydrogel-metal-zeolite (Al-H-M-Z) were employed to remove nitrogenous contaminants, building on inventions from previous studies for actual application steps. The ammonium removal efficacy of M-Cht-HG was examined in seawater, demonstrating superior performance compared to conventional chitosan-based hydrogel (Cht-HG). Additionally, the exceptional adsorption properties of Al-H-M-Z for ammonium were substantiated through adsorption kinetics models, including Langmuir and Freundlich isotherms. The adsorption effectiveness of M-Cht-HG and Al-H-M-Z was assessed in comparison to commercial materials, such as MBBR and zeolite, through testing in an aquaculture tank.

Material and Methods

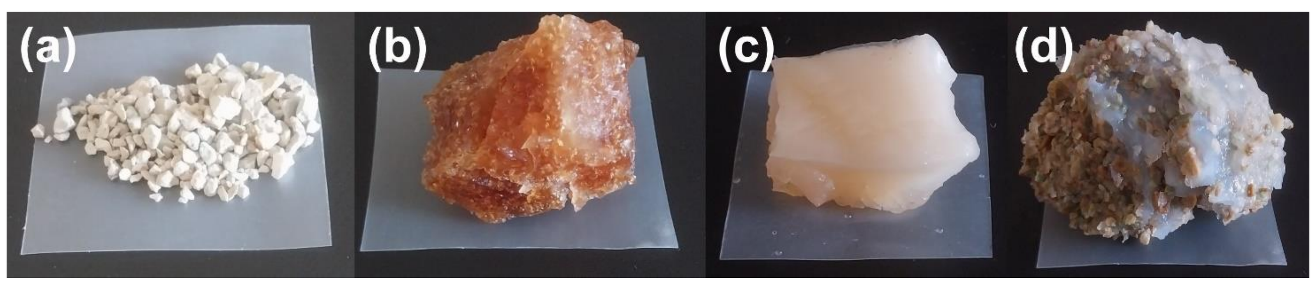


Fig. 1. Developed adsorbent materials: commercial zeolite (a), Cht-HG (b), M-Cht-HG (c), and Al-H-M-Z (d).

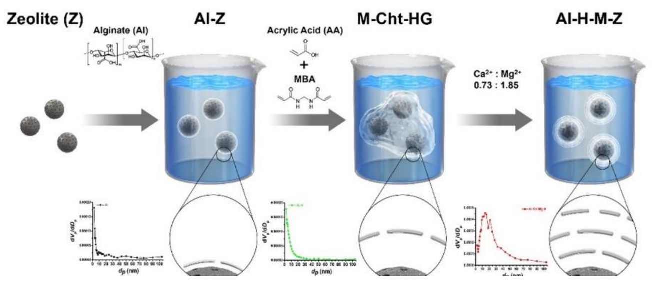


Fig. 2. Coating process of Al-H-M-Z, including alginate coating (Al-Z), hydrogel functionalization composed of acrylic acid and MBA (Al-H-Z), and multilayered coating zeolite (Al-H-M-Z) showing different surface area and pore diameters.

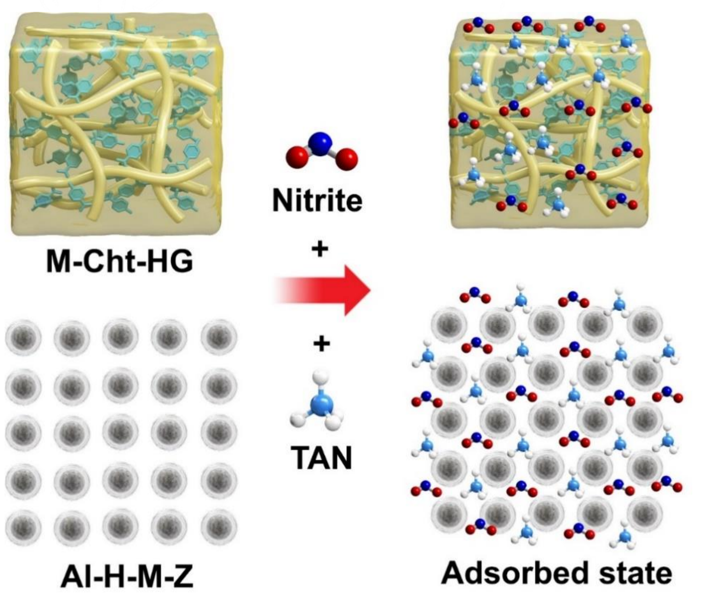


Fig. 3. Illustration of synthesized M-Cht-HG and Al-H-M-Z adsorbents, demonstrating their expanded surface areas which adsorb TAN and nitrite.

The effectiveness of various adsorbents—zeolite, Cht-HG, M-Cht-HG, and Al-H-M-Z—was compared to that of commercial MBBR in terms of their capacity to remove high concentrations (over 100 mg L^{-1}) of artificial nitrogen byproducts (TAN, nitrite, and nitrate). The removal efficiency (*Re*) was calculated using the following formula:

$$Re = \frac{Influent\ (mg\ L^{-1}) - Effluent\ (mg\ L^{-1})}{Influent\ (mg\ L^{-1})}$$

Additionally, the first-order kinetics model was used to describe the pollutant removal rate, expressed by the decomposition coefficient rate (*k*), with the equation:

$$\frac{C_{out}}{C_{in}} = e^{-kt}$$

where C_{in} (mg L^{-1}) denotes the influent pollutant concentration, C_{out} (mg L^{-1}) denotes the effluent pollutant concentration, and t represents the hydraulic residence time (HRT) within a 24-h period.

Results

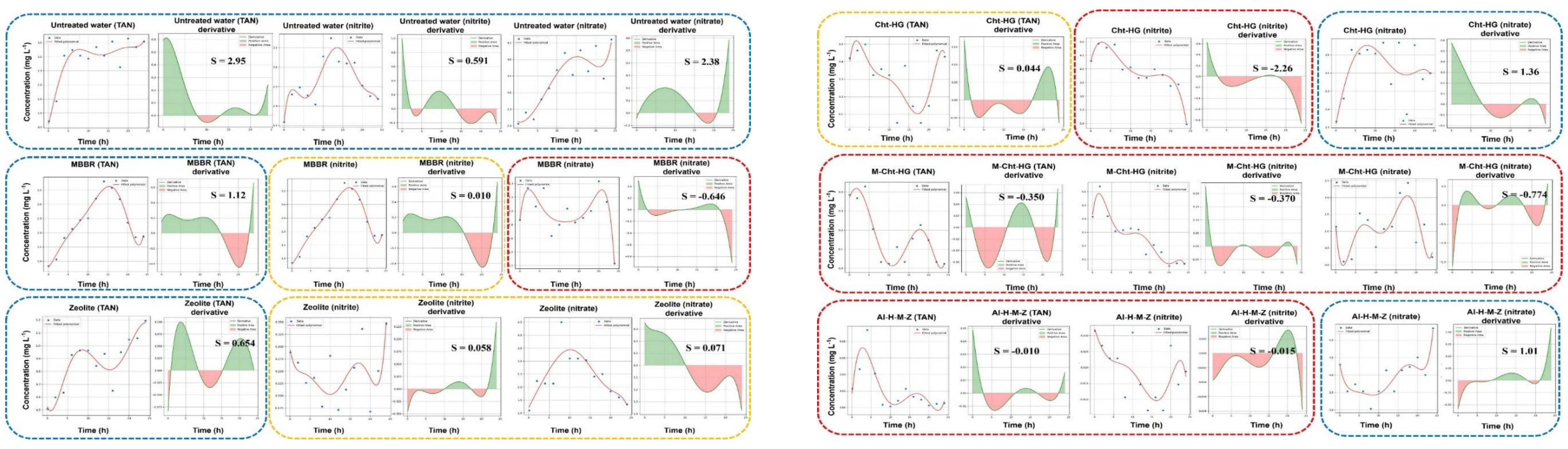


Fig. 4 Optimized nitrogen dynamics model utilizing a 6th-order polynomial function to analyze the behavior of TAN, nitrite, and nitrate in a fish tank under various conditions including untreated water, MBBR, zeolite, Cht-HG, M-Cht-HG, and Al-H-M-Z treatments. Derived functions, from 0 to 24 h, yielded aggregated values reflecting increases and decreases, denoted as S, and are estimated using the extent of the derivative functions. The S values are colored blue (S > 0), yellow (S ≈ 0), and red (S < 0).

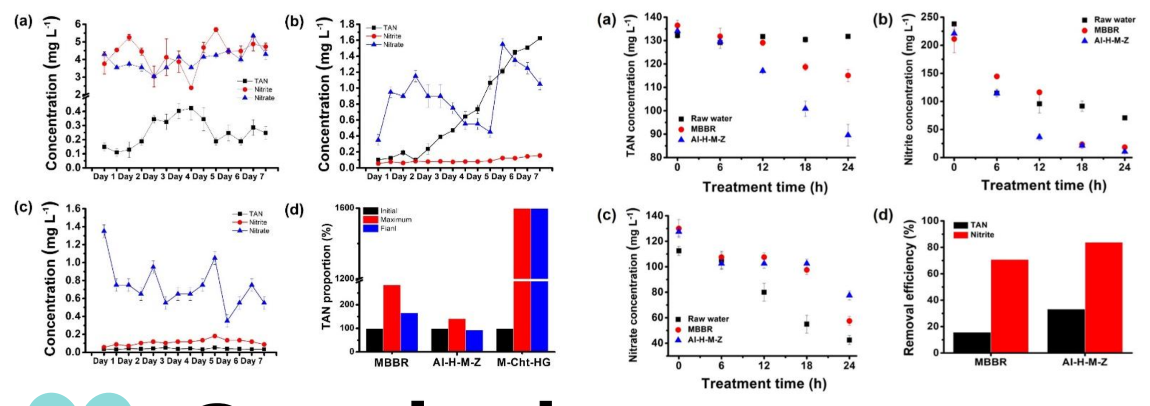


Fig. 5 Long-term applicability for 7 d using MBBR (a), M-Cht-HG (b), and Al-H-M-Z (c), with fluidity measurements of TAN (■), nitrite (●), and nitrate (▲). Long-term TAN dynamics comparison using MBBR, Al-H-M-Z, and M-Cht-HG (d).

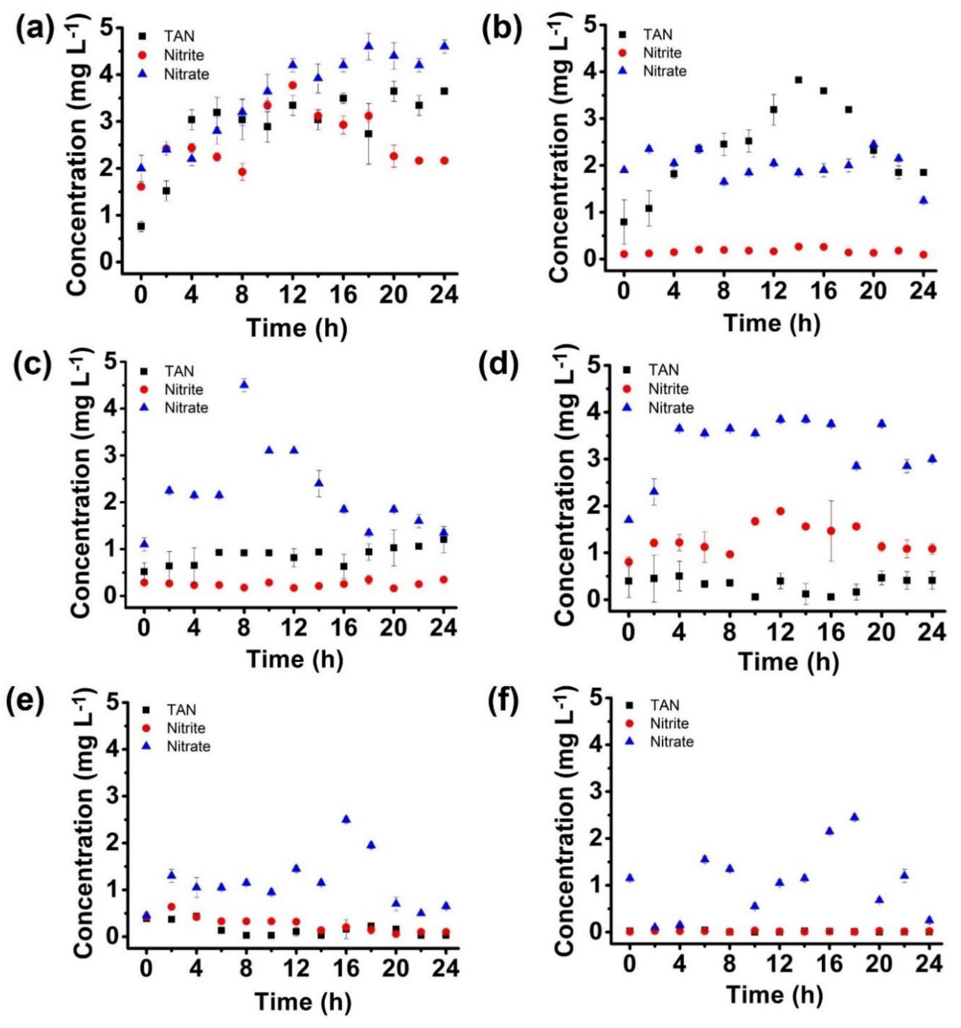


Fig. 6. Nitrogen dynamics of TAN, nitrite, and nitrate under various treatments for 24 h: untreated water (a), MBBR (b), commercial zeolite (c), Cht-HG (d), M-Cht-HG (e), and Al-H-M-Z (f). Different nitrogenous byproducts are symbolized as a black square (■), red circle (●), and blue triangle (▲) in TAN, nitrite, and nitrate, respectively.

Conclusion

In this study, nitrogenous contamination from fish excrement was treated and investigated using various developed adsorbents (Cht-HG, M-Cht-HG, and Al-H-M-Z) in nitrogen dynamics experiments. These materials were compared with a commercial biofiltration medium, the MBBR, to validate their performance. Al-H-M-Z emerged as the most effective material for removing TAN and nitrite in both short- and long-term applications within an aquaculture system. Additionally, Al-H-M-Z exhibited faster activation times for removing TAN and nitrite compared to MBBR. Notably, homogeneous adsorbents, such as zeolite or hydrogel alone, displayed limitations in their physicochemical properties. In contrast, the hydrogel-zeolite complex demonstrated more efficient and robust removal efficiency, making it well-suited for practical applications in aquaculture systems.