Enhanced Photocatalysis for Water Purification and Disinfection using Optical Fibers Coated with Nanocomposite Thin Films

By

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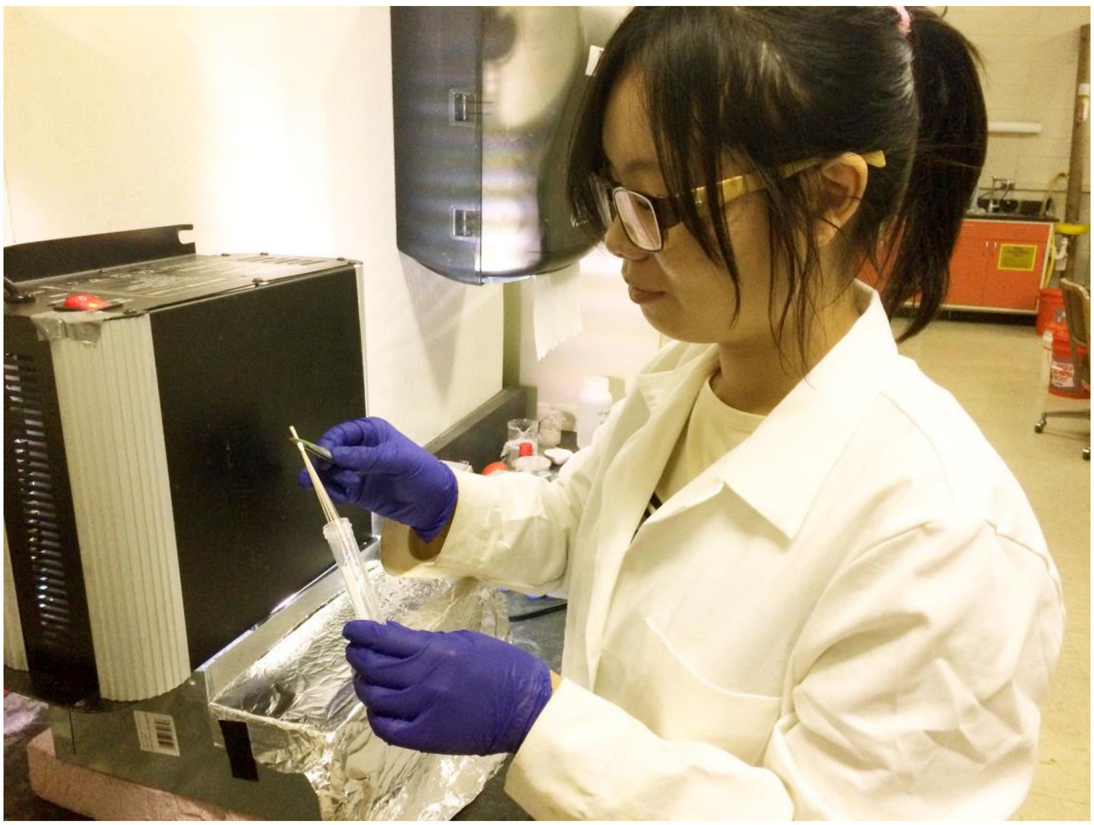

Graduate student Lu Lin prepares fibers for a photoreactor.

NM WRRI Student Water Research Grant Final Report

Student Researcher: Lu Lin
Faculty Advisor: Dr. Pei Xu

Project title: Enhanced Photocatalysis for Water Purification and Disinfection using Optical Fibers Coated with Nanocomposite Thin Films

Description of research problem and research objectives

Problem

Growing water demand and increasing contamination remain significant challenges worldwide. Current water treatment processes to remove organic contaminants such as membrane filtration, activated carbon adsorption, biological treatment, ozonation and advanced oxidation processes are typically energy and capital intensive. Photocatalysis is an attractive technology because it can use solar energy to degrade organics and inactivate pathogens [1-5]. In comparison to traditional oxidation processes, photocatalytic oxidation operates at ambient conditions without high temperature or high pressure, and many recalcitrant organic contaminants can be degraded without addition of chemical oxidants [6].

It is critical to design highly efficient photocatalysts in order to enhance the utilization rate of solar energy and improve treatment efficiency. Among many different photocatalysts, TiO_2 is the most widely studied and used in various applications. TiO_2 exhibits several advantages as a photocatalyst such as strong oxidizing ability, excellent chemical stability, long durability, nontoxicity, water insolubility, superhydrophilicity, and low cost [1, 7]. When TiO_2 particles absorb the ultraviolet (UV) light with energy greater than the band gap of the metal oxide, electrons and holes are generated in the conduction and valence bands, respectively. The photogenerated holes in the valence band diffuse to the metal oxide surface and oxidize the water molecules into hydroxyl radicals (HO•), then oxidize nearby organic molecules on the metal oxide surface. Meanwhile, electrons in the conduction band react with the molecular oxygen to produce superoxide radical anions ($O_2•^-$). Solar powered TiO_2 photocatalysis has emerged as an energy neutral technique for water purification and pollution control [1, 7-12].

However, due to large band gap and low quantum yield, TiO_2 can absorb only UV light and is limited as a sunlight-driven photocatalyst [13]. Intense efforts have been undertaken to improve the light utilization efficiency of TiO_2, such as doping through incorporation or decoration with metal ions, nonmetal ions, and semiconductors [14-17].

Traditional photoreactors are mainly heterogeneous slurry systems with suspended catalysts [4, 18]. However, these photoreactors are mostly limited to laboratory study due to low light utilization efficiency, loss of photocatalysts, and difficulty and high cost for separation of photocatalyst particles from aqueous solutions [16]. Thus, an ideal photocatalytic system should be able to recover catalysts from treated water easily, and reduce the light loss from liquid absorption and catalyst particles scattering.

Several immobilized photocatalytic systems have been designed over the last few years, such as TiO_2-coated glass-beads [12], TiO_2-loaded membrane filters [4], internally illuminated monolith reactor with TiO_2 coated on the wall [19], and TiO_2-loaded zeolite [20]. However, most wastewater is not transparent and light cannot transmit through the entire water depth, thereby limiting photoreactor size. Photoreactors with catalyst-coated optical fibers can solve the light transmission problem. Optical fibers have been considered excellent media for light transmission and photocatalysts support [21-25]. Light can directly reach the photocatalysts through optical fibers instead of passing through the reaction medium, thus reducing light loss and increasing light utilization efficiency [16]. Photoreactors with catalyst-coated optical fibers have been demonstrated to improve photocatalytic activity compared to conventional photoreactors [11, 16, 26-31]. For example, the TiO_2 coating on fused-silica fibers improved the amount of photogenerated H_2O_2 along with the degradation of contaminants with regards to total organic carbon, ethylene, and dye, with no loss of catalysts [32-35]. Under a UV light source, a new water treatment system which consisted of an electrochemical oxidation unit and a photoreactor with TiO_2 coated optical fibers was able to wet-incinerate large amounts of chemical and biological contaminants in river water samples [36]. However, there is lack of systematic study investigating SOFs coated with nanocomposite photocatalyst thin films for both UV and visible light applications.

Objectives

The objective of the proposed work is to develop highly effective photocatalysts and investigate their photocatalytic performance using innovative photoreactor with optical fiber coated with nanocomposite photocatalysts for degrading organic contaminants in water, and disinfecting water under UV, visible, and natural sunlight.

Methodology

(1) ***Design, synthesize, and characterize optical fibers coated with metal oxide nanocomposite films to produce new functionalities and to improve the quantum yield.***

Polymer assisted hydrothermal deposition (PAHD) method, which has been developed by our research team, is used to coat the catalyst films onto side-glowing optical fibers (SOFs). A metal complex solution was prepared and followed by a heating process. This method provides a cost-effective and straightforward preparation of composites by a simple mixing of the solutions, precise control of the stoichiometry, and easy adjustment of film thickness.

The structure and morphology of the catalyst-coated SOFs was characterized by transmission electron microscope (TEM) and scanning electron microscope (SEM). The elements and their ionic states in the surface of catalyst films were measured by energy-dispersive X-ray spectroscopy (EDX) mounted on the SEM, and X-ray photoelectron spectroscopy. X-ray diffraction was used to analyze the crystal phase of the catalysts.

(2) ***Evaluate the photocatalytic efficiency of the nanocomposite films.***

The batch photocatalytic reactor with UV light and visible light source is shown in Figure 1. The continuous-flow experimental assembly for testing the photocatalytic reactor with natural sunlight is shown in Figure 2.

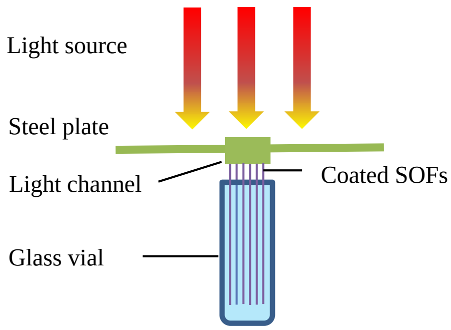

Figure 1. Batch photoreactor with catalyst-coated SOFs

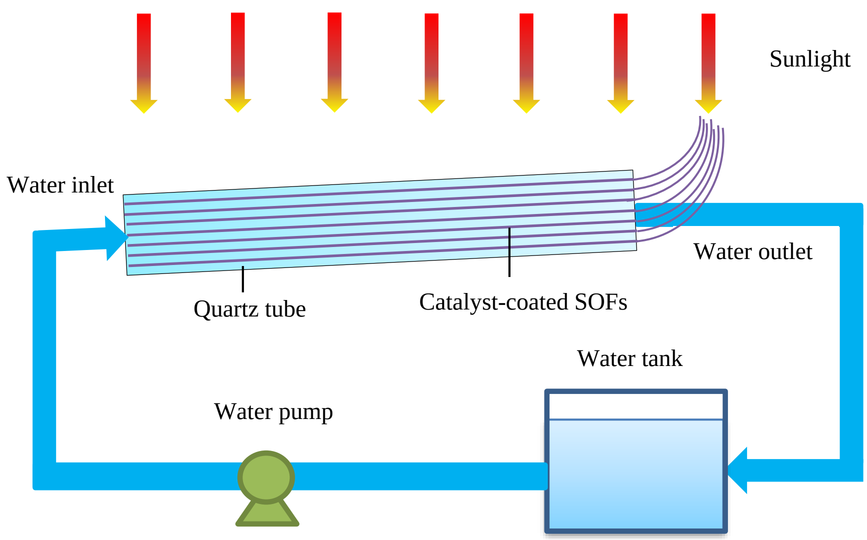

Figure 2. Continuous-flow photoreactor with catalyst-coated SOFs

Rhodamine B (RhB) was selected as the model micropollutant due to its complex structure and high recalcitrance for water treatment. Based on the results of RhB, the photocatalytic performance of environment contaminants (e.g., pharmaceuticals and disinfection by-products) in water will be further investigated. *E. coli* was used as indicators to evaluate the efficiency of photocatalysis for water purification and disinfection. Spectrophotometer and *E. coli* test kits were used for water quality analysis. In addition to the properties of the SOFs and nanocomposite films, the study also investigated the impact of different operating conditions such as water chemistry, light wavelength, and energy intensities on photocatalytic activity.

Results, conclusions, and recommendations for further research

The photocatalytic efficiencies of the catalysts coated SOFs were studied by the degradation of RhB as a representative organic contaminant [37]. The results showed that 5% Fe-TiO_2 thin films (Fe:TiO_2 molar ratio), mixture of anatase and rutile phases, achieved the highest photocatalytic activity under the irradiation of ultraviolet (UV) and visible light. The coupled adsorption and photocatalytic oxidation of RhB by the SOFs coated with photocatalyst nanocomposite thin films followed the Langmuir-Hinshelwood kinetic model, and the apparent first-order rate constants achieved 0.50 h^{-1} and 0.33 h^{-1} under UV and visible light irradiation, respectively. The Langmuir–Hinshelwood kinetic model expressed well the heterogeneous photocatalysis degrading RhB. It implies that only adsorbed molecules contributed to the photocatalytic process and the oxidation process was the controlling step.

Photocatalytic degradation efficiency was affected by pH and initial organic concentration. Reactivation and regeneration of the used catalysts, and long-term photoactivity testing of catalysts coated SOFs demonstrated the durability of synthesized photocatalysts for water treatment. Treatment of desalination concentrate can reduce concentrate volume for disposal, increase water recovery, and convert a waste stream to a water resource. Photocatalytic oxidation process provides a potential energy-efficient technology for desalination concentrate treatment by degrading organic contaminants in the water. High ionic strength and presence of high concentrations of chloride, bicarbonate, sparingly soluble salts, and natural organic matter in desalination concentrate may affect the photocatalytic performance. High ionic strength accelerated the photocatalytic process by reducing electrostatic repulsion between RhB molecules and catalyst. The divalent electrolyte ions in reverse osmosis (RO) concentrate increased the RhB degradation efficiency, while the presence of carbonate species and natural organic matter hindered photodegradation rates, due to photon and active species scavenging and adsorption sites competition. The overall photocatalytic efficiency was reduced in RO concentrate as compared to NaCl solution with similar ionic strength.

Disinfection experiment was conducted using outdoor continuous-flow photoreactor. *E. coli* inactivation as a function of time was monitored for up to 8 hours. Control experiment was operated in the same conditions, the inactivation rate of *E. coli* increased by 100% in the presence of catalyst-coated SOFs as compared to photolysis.

This work built a foundation for developing an innovative closed continuous-flow photoreactor for water treatment using solar energy and optimized photocatalysts. This type of photoreactor will be suitable for arid and semi-arid regions because solar resources are abundant and water resources are limited.

Beneficiaries of research

Due to high recalcitrance to conventional wastewater treatment processes, the presence of emerging contaminants (e.g., pharmaceuticals, pesticides, endocrine disrupting compounds, and disinfection by-products) in water and wastewater has become a significant challenge for many water utilities. Current water treatment technologies towards micropollutants including high-pressure membranes, advanced oxidation, ozonation and adsorption, are often energy and capital intensive. The designed photocatalytic reactor is an energy effective/neutral technology for the removal of emerging organic pollutants. Using solar energy to drive the oxidation process will significantly reduce the energy cost for the water utilities. Therefore we believe this technology will have broad applications for providing safe drinking water and water reuse. Moreover, this technology is very suitable for the areas with abundant solar energy, such as southwestern of the US, rural communities, and remote areas that do not have access to electricity and drinking water.

Presentations

Lin, L., Wang, H.Y., Luo, H.M., Xu, P. (2015). Enhanced photocatalysis using side-glowing optical fibers coated with Fe-TiO2 nanocomposite thin films. 2015 UCOWR/NIWR/CUAHSI Annual Conference. Henderson, Nevada, June 16-18, 2015.

Lu Lin, Huiyao Wang, and Pei Xu. (2015). Innovative photocatalytic water treatment using immobilized nanocomposite thin films. 12th Annual RMSAWWA/RMWEA Student Conference. May 21, 2015. Las Cruces, NM.

Lin, L., Wang, H.Y., Luo, H.M., Xu, P. (2014). Enhanced Photocatalytic Oxidation for Removal of Organic Contaminants in Water. 59th Annual NM Water Conference. Santa Fe, New Mexico, November 18-19, 2014.

Publications

Lin L, Wang H, Luo H, et al. Enhanced photocatalysis using side-glowing optical fibers coated with Fe-doped TiO_2 nanocomposite thin films. *Journal of Photochemistry and Photobiology A: Chemistry*, 2015, 307: 88-98.

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