Photocatalytic Degradation of Organic Contaminants Using Catalyst-coated Fibers

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As growing water demand and increasing contamination have become issues worldwide, the water industry has moved to improve treatment and reclaim water. Instead of using other energy-intensive and expensive water treatment methods, photocatalysis uses freely available sunlight to power degradation reactions. Photocatalysis has proved promising in degrading organic pollutants in aqueous solutions because the reduction and oxidation reactions occurs at ambient conditions. Photocatalytic degradation also does not require the addition of chemical oxidants, as other advanced oxidation processes do.

Technology that uses photocatalysis can be improved by optimizing the photocatalytic reactions through different catalysts and mediums for catalyst coatings. Side-glowing optical fibers were used as a medium for the catalyst coating because light is distributed for the entire length of the fiber. The performance of these fibers was quantified for different pollutants by measuring the degradation of various test solutions. The solutions under study with organic contaminants included reverse osmosis concentrate, or the highly concentrated waste produced from reverse osmosis, and microfiltration permeate, or the effluent water from microfiltration.

When a catalyst absorbs light energy, the energy excites electrons and creates free radicals, which react with pollutants and create oxidation and reduction products. However, most photocatalysts are limited by sunlight because electron excitation only occurs with high energy UV waves, which only makes up 3% of sunlight irradiation. In order to enhance the utilization rate of solar energy and improve treatment efficiency, highly efficient catalysts must be developed. Doping, or adding an impurity to the catalyst to increase the number of charge carriers in the catalyst, is a common method of enhancing photocatalysis. Various combinations of catalysts and dopants were created and tested to develop an optimal coating for the side-glowing optical fibers. The different catalysts tested were TiO_2, $BiWO_3$, and Fe_2O_3. The different dopants added were graphite oxide, palladium, and iron.

To test the degradation rates of the fibers, each set of fibers was tested in a batch reactor, with visible or UV light irradiation. The organic dye Rhodamine B (RhB) was chosen as the model contaminant due to its complex structure and recalcitrant nature in water treatment. The highest performing group of fibers, $BiWO_3$-coated fibers, was tested for eight hours in visible light. As shown in Figure 1, the removal efficiency rates of the absorbance wavelength 553 nm of RhB ranged from 78% to 89% with different dosages of graphite oxide. However, graphite oxide increased performance by about only 10% and did not improve performance relative to the amount of graphite oxide used. This data was fitted to the Langmuir-Hinshelwood kinetics model, $r = \frac{dC}{dt} = \frac{kKC}{1+KC}$, to
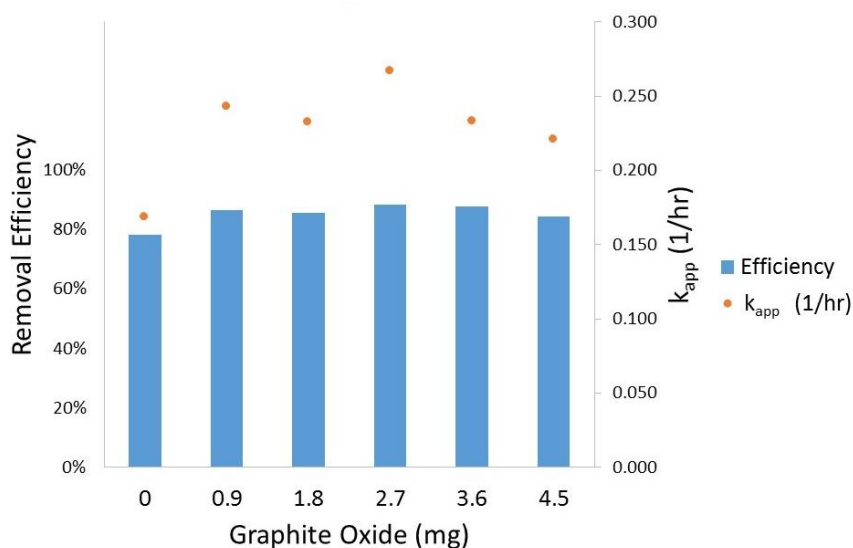

Figure 1. Removal rates and efficiency of Graphite Oxide doped $BiWO_3$

find the apparent degradation rate, $k_{app} = kK$, as plotted in Figure 1. The kinetics model was well-fitted to the experimental data, with $R^2 > 0.85$.

For future industrial application, a continuous-flow reactor was developed to test the effectiveness of photocatalysis under the irradiation of natural sunlight. Based on previous studies, TiO_2 doped with iron was thus far the most effective as a photocatalyst. This photocatalyst was coated onto fibers and placed in quartz tubes, where a peristaltic pump continuously moved the solution throughout the system. Reverse osmosis (RO) concentrate and microfiltration (MF) permeate from the Scottsdale Water Campus in Arizona were used as the test solutions. The experiment was run for 15 hours in the dark to measure the extent of adsorption onto the fibers, and then for 48 hours in sunlight to measure photocatalytic degradation. Water samples were taken periodically and analyzed.

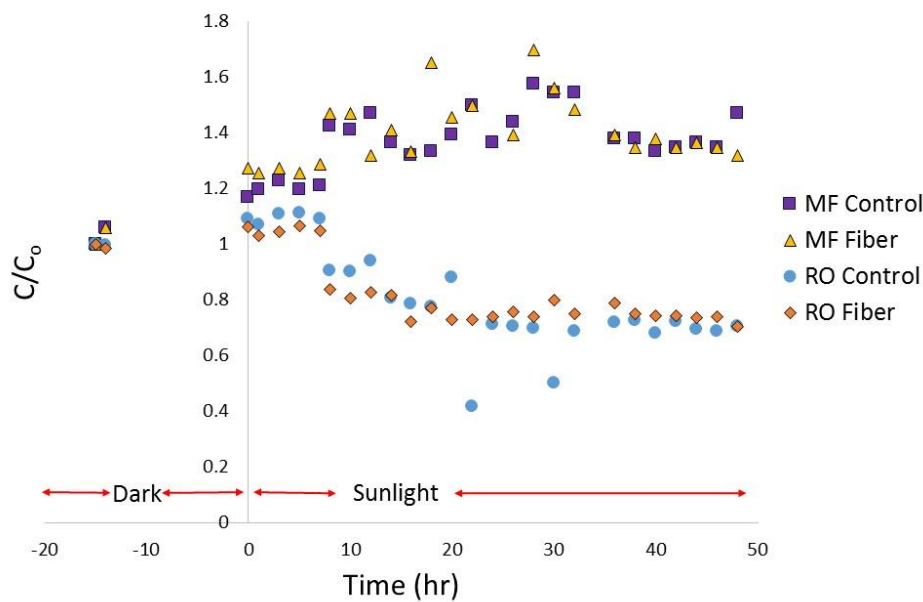The UV/Vis spectrophotometer was used to measure the absorbance of the wavelength 254 nm to see if double bonds were degrading, as shown in Figure 2. The results from UV/Vis demonstrated that the absorbance for 254 nm decreased over time for the RO concentrate in both the control and fiber. For the MF permeate, the absorbance actually increased, suggesting that more complex compounds may have degraded, such as turning triple bonds into double bonds. For both solutions under study, the data points did not show much difference between the reactors with or without the fibers.

Figure 2. Removal efficiency of photocatalytic degradation of microfiltration permeate and reverse osmosis concentrate

A fluorometer was used to create a fluorescence excitation emission matrix (FEEM) and find humic-like peaks. Both the RO concentrate and MF permeate started with two humic-like peaks. The data indicated that adsorption removed some of the organic contaminant, but had diminishing rates of removal after an hour of adsorption. For the RO concentrate, the matrices showed that the peaks degraded faster when fibers were present. However, for the MF permeate, there was little difference between reactors with or without fibers. Given that the UV/Vis absorbance data were very similar for the control and fiber for MF permeate, this data is consistent.

The research demonstrated that photocatalysis with catalyst-coated side-glowing optical fibers was effective in removing organic contaminants in aqueous solutions under both UV and visible light. Further exploration with this technology includes testing removal rates of other emerging contaminants, such as pharmaceuticals, as well as improving the technology with different mediums for the catalyst, such as glass fibers.