Fouling Prevention In Rotating Reactive Membrane Filtration

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Introduction

Current trends of water stress and scarcity worldwide necessitate the development of effective and efficient technologies for water reuse and recycle. Membrane filtration becomes an essential technique for water reuse and recycle of low-quality sources. However, biofouling and biofilm growth are major obstacles for membrane filtration because they cause dramatic losses in efficiency and system flux. By coating ceramic ultrafiltration membranes with titanium dioxide photocatalysts, we have created a multifunctional reactive membrane that resists fouling and biofilm growth by improving hydrophilicity, inactivating microorganisms, and degrading organics. Furthermore, this reactive coating has been incorporated into a rotating cylindrical geometry to take advantage of Taylor-Couette flow for enhanced biofouling prevention.

Background

TiO_2 nanoparticles can be irradiated by near-UV light to excite electrons, leaving behind positively charged holes. In the presence of water, these separated charges may react with hydroxyl groups at the surface of the TiO_2 nanoparticle to produce highly reactive hydroxyl radicals. Titanium dioxide has been demonstrated in a number of environmental applications, including use in aqueous slurries for the degradation of organic chemicals, and immobilization on a substrate for the degradation of organics in gaseous and liquid streams, usually air and water. More recently, its efficacy in the degradation of microorganisms has been shown, both in slurries and in coatings.

Anatase and rutile are the two most commonly discussed crystal phases of titanium dioxide. Anatase requires higher energy light than rutile for excitation (385 nm versus 410 nm respectively), but anatase is regarded as the more catalytically active crystalline phase due in part to its slower rates of photogenerated charge recombination. Nanoclusters containing both anatase and rutile nanoparticles have very high photocatalytic activity. Electrons within rutile are excited and then transfer to trapping sites in defects at the anatase particle surface, allowing extended periods of time for the hole to participate in photooxidation reactions, producing highly reactive oxygen species including hydroxyl radicals.

In previous work we have identified Degussa P25 titanium dioxide as a strong candidate for biofilm prevention based on its excellent bacterial cell attachment resistance and high organic degradation activity, and long-term biofilm growth prevention and reduced flux decline in experiments with Pseudomonas putida on ceramic membrane discs coated with the Degussa P25 photocatalyst. Degussa P25 is a

highly characterized commercial catalyst produced by high-temperature flame hydrolysis, with heterogeneous phase composition (15–30% rutile, remainder anatase) and particle size (primary particle size 30 nm, aggregates up to 200 nm). It is considered by many to be the “gold standard” of photocatalysts because of its high reactivity.

Taylor-Couette flow occurs between rotating cylinders when the inner cylinder angular velocity crosses a threshold value, above which instabilities create counter-rotating toroidal vortices all along the annulus (See Figure 1.) Rotating cylindrical membranes are currently used in low-pressure separation systems, especially for the separation of blood and plasma. The instabilities that occur in Taylor-Couette flow between rotating cylinders can be harnessed for the reduction of fouling along the membrane walls. We combine the chemical action of TiO_2 with the physical action of Taylor-Couette flow to create a system with robust biofouling resistance.

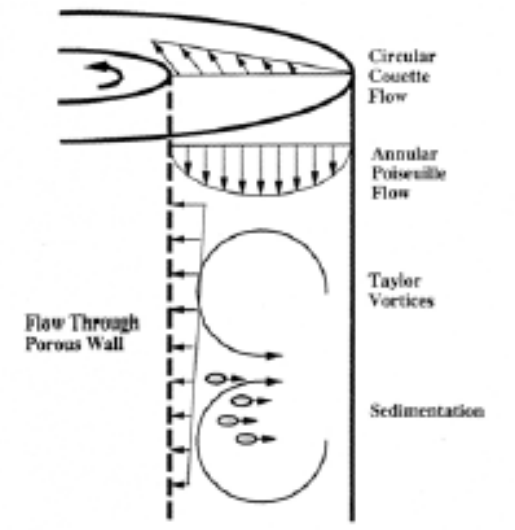

Figure 1-Flow that occurs in a rotating filter separator

Methods

Zirconia ceramic membrane discs were obtained fromSterlitech Corporation. These membranes discs have a layered structure, consisting of an alumina–titania–zirconia support material, and a zirconia pore size-controlling layer with a cut-off of 300 kDa (approximately 0.01_m pore diameter), resulting in awater flowrate of 450–600 L/hm2 at 1 bar trans-membrane pressure. The discs are 47mmin diameter and 2.5mmin thickness. They were rinsed with acetone and then rinsed thoroughly with deionized water to remove any surface impurities. Zirconia discs were coated with Degussa P25 (80% anatase, 20% rutile). To clarify the role of hydrophilicity and the role of photocatalysis at the membrane surface, a set of control discs were coated with non-catalytic rutile as well. A nanocrsytalline pure-phase rutile powder was synthesized by a low-temperature hydrothermal method using a titanium (IV) chloride precursor, as

described by Gonghu Li, et al. The high hydrophilicity and low reactivity of the rutile allows for a comparison of the hydrophilic and reactive effects of the biofilm growth prevention observed previously over the Degussa P25 coatings.

Titanium dioxide powders were applied to discs by dip-coating in a slurry of 0.1 g/L catalyst, and 0.05 g/L dioctyl sulfosuccinate surfactant in water [34]. After sonicating the slurry for 1 h, the top surface of each discwas dipped into the slurry and withdrawn by hand at a rate of about 3 cm/s. Discs were dried in a 105 ◦C oven for 2.5 h, and then heat treated in a furnace with a ramp rate of 5 ◦C/min to 450 ◦C, held there for 1 h, and then cooled slowly to room temperature. This process was repeated until 4mg of the catalyst had been deposited on the disc surface (about 5 repetitions).

Pseudomonas putida is a gram-negative, rod-shaped bacterium. It was chosen as the bacterial model because *P. putida* is commonly present throughout the environment, and readily colonizes biofilms. The American Type Culture Collection *P. putida* type strain number 12633 was grown in M9 minimal media at 25º C, maintained at the exponential growth phase in a chemostat supplied with 1 L/min sterile air, and paddle rotating at 100 rpm. It was maintained at a concentration of about 10^8 colony forming units per milliliter (CFU/mL). This solution was diluted in sterile phosphate buffered saline (PBS) to bring the solution cell concentration to approximately 10^6 CFU/mL, a bacterial cell concentration typical of fresh surface waters. This solution was fed over membranes, and confocal microscopy was used to quantify biofilm formation.

Tubular membranes were obtained from Sterlitech corporation. These had a layered structure, with an alumina-titania-zirconia support layer with large pore size on the outside, and a rutile titania inner layer bringing the pore size to 1.4 μm. These were 10 mm in outer diameter, 6 mm in inner diameter, and 250 mm long. Each tube was cut into 3 pieces, 83 mm long. Each tubular membrane was coated by dip-coating into a slurry of 10 g/L zirconia particles (< 5 um, Sigma Aldrich) to create a microfilter layer on the outer surface of the membrane. The membrane was dried at 105 C to drive off water, and then heated in a furnace at a ramp rate of 5 ° C /min up to 450 ° C, where it dwelled for one hour before being slowly cooled to room temperature. The membranes were all dipped in nanoparticle slurries to deposit the final outer layer. Half were dipped in a slurry of Degussa P25 at a concentration of 2 g/L, and half in zirconia <100 nm particles 2 g/L for control samples. These were dried and heat treated similarly, repeating the process as needed until 10 mg of active layer had been deposited on the surface. The pore size of the new membranes was confirmed through bubble point testing according to ASTM F316-03 method.

Each membrane placed into the reactor. There is a bank of 4 reactors, each illuminated by a 4-Watt UV lamp. Each tubular ceramic membrane (OD 10 mm) is surrounded by a 15 mm ID, 17 mm OD quartz tube, creating an annulus for water flow between the two. The tubular membrane is placed inside a stainless steel shaft, which is used to drive the tubular membrane at 100 rpm. A belt and gear system connects the shafts to a motor. Each tubular membrane is sealed on the upper edge to prevent water from bypassing the membrane. There is one inlet tube and two outlet tubes (permeate and retentate).

The water inlet is driven by a set of peristaltic pumps, operating at less than 30 psi transmembrane pressure. Once the membranes are positioned, the entire system is cleaned by pumping ethanol through the system for 30 minutes to sterilize surfaces.

Each day, 120 mL of chemostat outflow *pseudomonas putida* cell culture is added to 12 L of sterile 10% phosphate buffered saline solution in water, to create a synthetic water with environmentally relevant concentrations of cells (10^6 cells/mL) and organic carbon. This solution directly feeds the reactor chambers by pumping at a rate of 2 mL/min.

The pressure drop across the reactor system is measured every 4 hours to monitor fouling. The permeate and retentate flow rates are measured also every 4 hours with a graduated cylinder and stopwatch. Each day, permeate and retentate are collected for standard serial dilution plating for the determination of viable bacterial cell concentration. The test is continued for 5-10 days, until the pressure drop across the membranes becomes a limiting factor.

Results

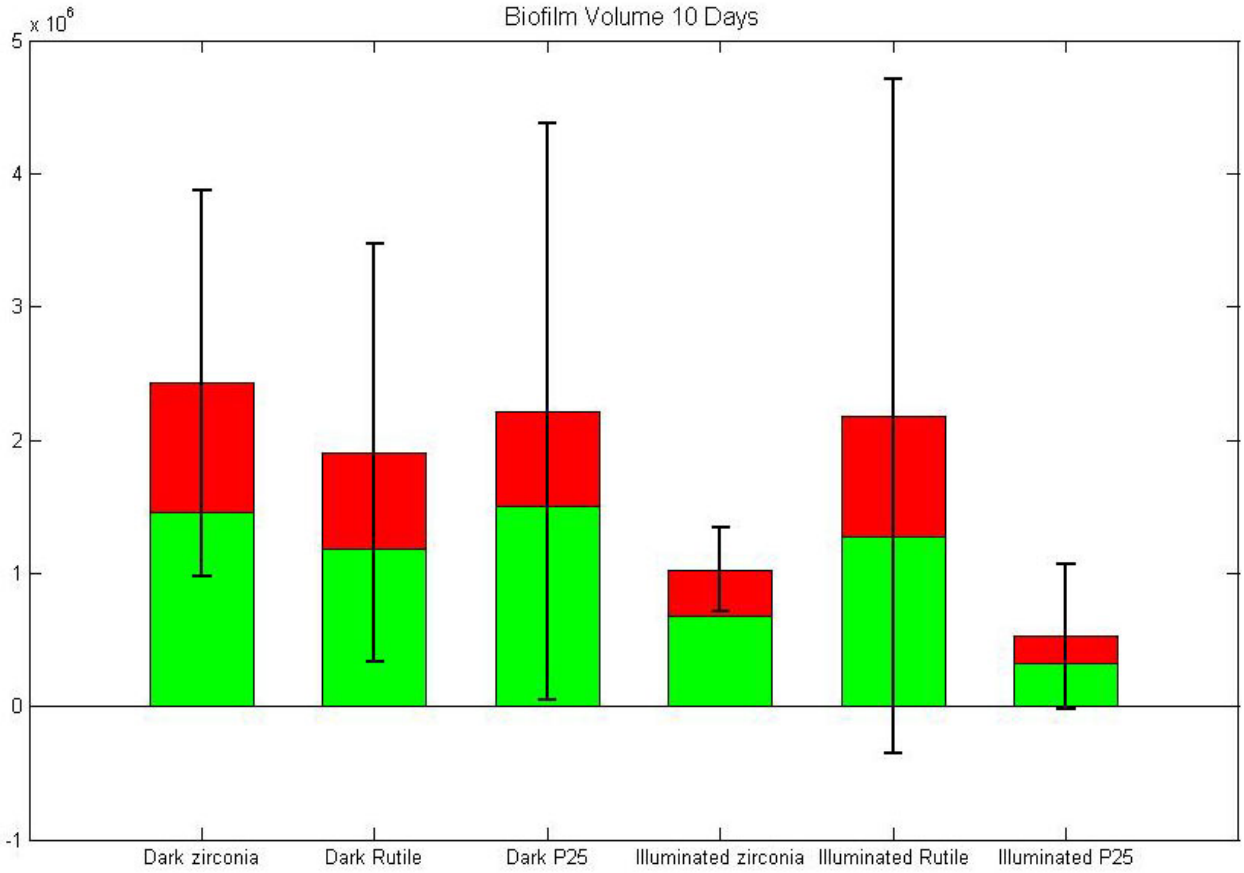

Figure 2

In this study, we confirmed previous results, finding a 90% confidence interval that the illuminated Degussa P25 samples had significantly less biofilm growth than the dark zirconia samples. Furthermore, the results show that there is less biofilm growth over the illuminated Degussa P25 samples than on the illuminated rutile samples (82% confidence interval). This shows that the combination of hydrophilic and photolytic effects over titanium dioxide catalysts are not sufficient to control biofilms, but that the photocatalytic effects observed in P25 are important for biofilm prevention.

Within the rotating reactor system, a control sample with no catalyst, no illumination, and no rotation was found to have significant biofouling within 7 days. I will report the latest results from this experimental setup, including preliminary results on the overall flux decline and biofilm growth reduction.