P1073

Photocatalytic Inactivation of Viruses Using Titanium Dioxide Nanoparticles

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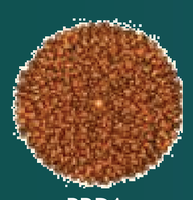
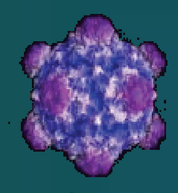
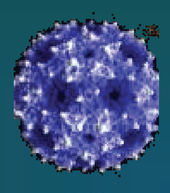
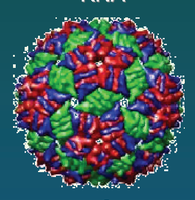
Motivation and Objectives

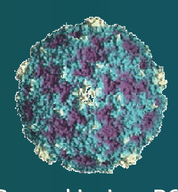
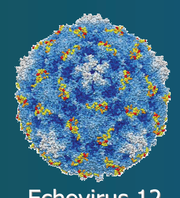
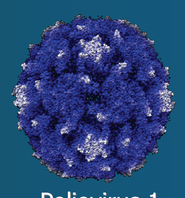
The carcinogenic potential of chlorine disinfection byproducts and recent changes in water quality regulations in the United States have led to a greater emphasis on alternative disinfection mechanisms. More specifically, the promulgation of the Long Term 2 Enhanced Surface Water Treatment Rule (LT2ESWTR) and the Stage 2 Disinfectant and Disinfection Byproducts Rule (D/DBPR) may force water utilities to implement more extensive treatment technologies to remain in full regulatory compliance. Photocatalysts, such as titanium dioxide (TiO_2) nanoparticles, have the ability to generate radical species, including hydroxyl (OH•) and superoxide radicals (O_2^-•), when irradiated by ultraviolet (UV) light. The synergistic effects of these reactive oxygen species (ROS) and UV light have the potential to destroy organic compounds and inactivate UV-resistant (adenoviruses) and chlorine-resistant (*Cryptosporidium parvum*) microbes. In this study, the efficacy of bench-scale and pilot-scale TiO_2 photocatalytic disinfection was evaluated using four bacteriophages (PRD1, phi-X174, MS2, and fr) and four human viruses (adenovirus 4, coxsackievirus B6, echovirus 12, and poliovirus 1). The bench-scale and pilot-scale experiments were performed using a collimated beam and the Photo-Cat Lab® reactor from Purifics®, respectively.

Background and Experimental Design

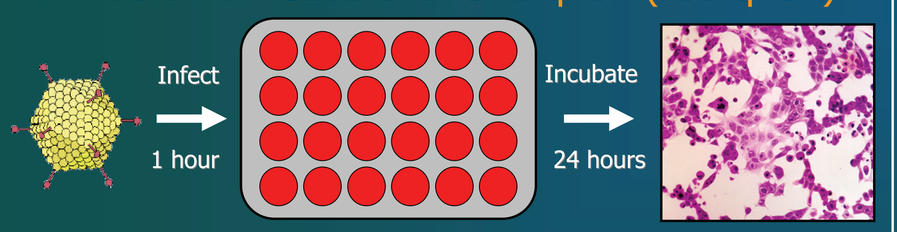
BACTERIOPHAGES – DOUBLE AGAR LAYER

Double-stranded DNA	Single-stranded DNA	Single-stranded RNA	Single-stranded RNA
			
PRD1 (*Salmonella typhimurium*)	*phi-X174* (*E. coli* 13706)	MS2 (*E. coli* 15597)	*fr* (*E. coli* 19853)

VIRUSES – ICC-qPCR

Double-stranded DNA	Single-stranded RNA	Single-stranded RNA	Single-stranded RNA
			
Adenovirus 4 (PLC)	Coxsackievirus B6 (BGM)	Echovirus 12 (BGM)	Poliovirus 1 (BGM)

INTEGRATED CELL CULTURE qPCR (ICC-qPCR)



DEGUSSA P25 TITANIUM DIOXIDE

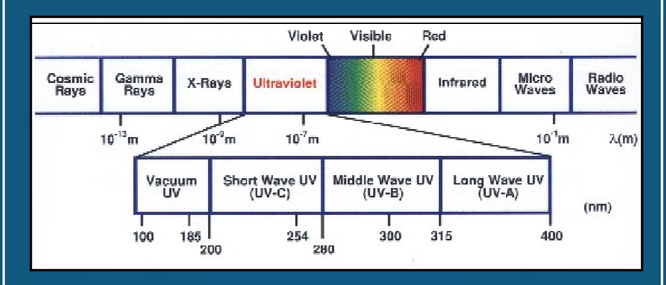
Anatase TiO_2: Efficient photocatalyst

Rutile TiO_2: Inefficient photocatalyst

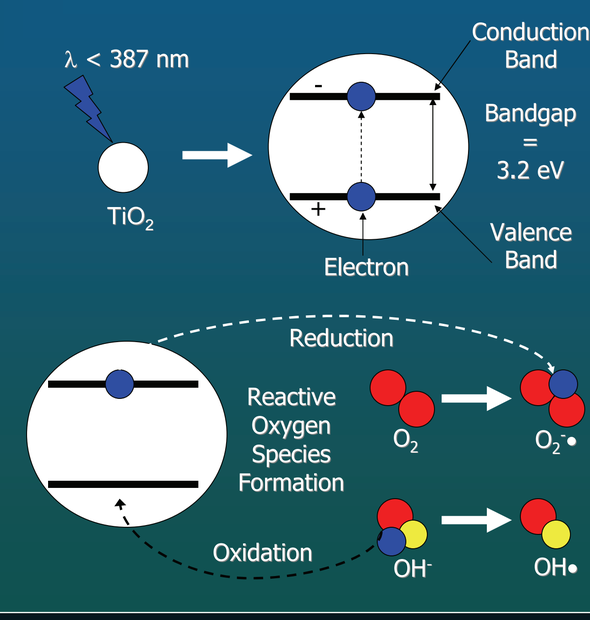
Bandgap Energy = $h\nu$ = 3.2 eV

Activation Wavelength = λ < 387 nm

LIGHT SPECTRUM

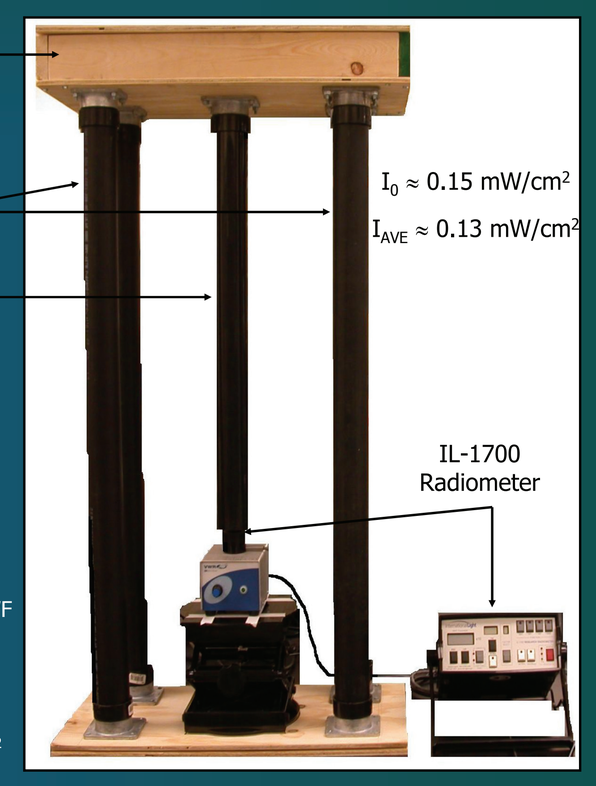


TiO_2 PHOTOCATALYSIS



COLLIMATED BEAM DESIGN

The purpose of a collimated beam is to form parallel rays of light that strike the target surface at a right angle, thereby standardizing each irradiation experiment.



Correction Factors:
- Petri = 0.890
- Reflection = 0.975
- Divergence = 0.984
- Water = 0.995

Intensity Calculation:

$I_{AVE} = I_0 \times PF \times RF \times DF \times WF$

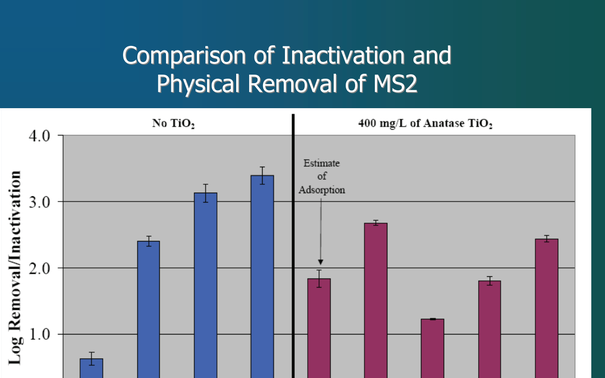
Unit = mW/cm²

Dose Calculation:

Dose = $I_{AVE} \times$ Time

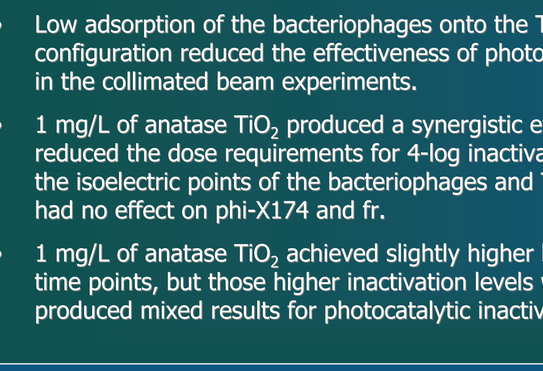
Unit = mW-s/cm² = mJ/cm²

PURIFICS® PHOTO-CAT LAB®



Bench-Scale Collimated Beam Results

Effect of TiO_2 Dose on Photocatalysis of phi-X174 (Anatase TiO_2, UV Dose = 8 mJ/cm², pH = 7.0)



Comparison of UV and Photocatalysis for 4-Log Inactivation of Bacteriophages

Virus	pH	TiO_2 dose (mg/L)	UV dose for 4-log inactivation (mJ/cm²)[a]	% Dose reduction based on UV baseline[b]
PRD1	7.0[c]	0	42	–
	7.0	1	41	2.4%
	6.0	1	34	19%
MS2	7.0	0	46	–
	6.0	1	39	15%
phi-X174	7.0	0	16	–
	7.0	1	15	6.3%
	6.0	1	16	0%
	7.0	1,000	181	N/A
fr	7.0	0	15	–
	8.0	1	15	0%

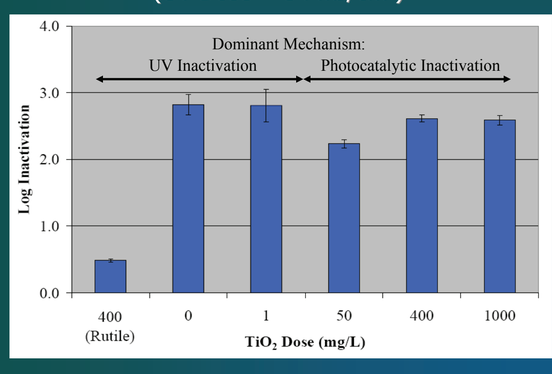
[a] Doses calculated using regression equation through triplicate points for four exposure times
[b] UV baseline denoted by a TiO_2 dose of 0 mg/L
[c] UV inactivation did not vary for each bacteriophage due to changes in pH (data not shown)

UV and Photocatalytic Inactivation of Adenovirus 4 (Anatase TiO_2, TiO_2 Dose = 1 mg/L)

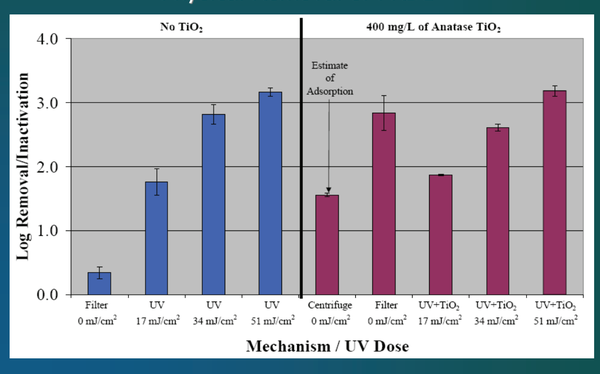
UV and Photocatalytic Inactivation of Enteroviruses (Anatase TiO_2, TiO_2 Dose = 1 mg/L, pH = 7.0)

Pilot-Scale Photo-Cat Lab Results

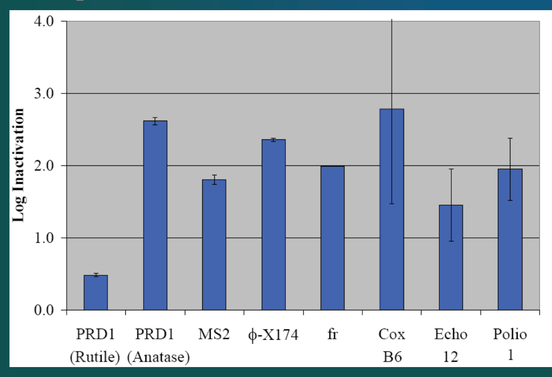
Effect of TiO_2 Dose on Photocatalysis of PRD1 (UV Dose = 34 mJ/cm²)



Comparison of Inactivation and Physical Removal of PRD1



Photocatalytic Inactivation of Viruses (TiO_2 Dose = 400 mg/L, UV Dose = 34 mJ/cm²)



Comparison of Inactivation and Physical Removal of MS2

Significant Observations

- Low adsorption of the bacteriophages onto the TiO_2 nanoparticles (data not shown) and an inefficient reactor configuration reduced the effectiveness of photocatalysis, particularly for high TiO_2 doses (100 – 1,000 mg/L), in the collimated beam experiments.
- 1 mg/L of anatase TiO_2 produced a synergistic effect between UV inactivation and TiO_2 photocatalysis, which reduced the dose requirements for 4-log inactivation of some of the bacteriophages. Changes in pH based on the isoelectric points of the bacteriophages and TiO_2 enhanced the synergistic effect for PRD1 and MS2 but had no effect on phi-X174 and fr.
- 1 mg/L of anatase TiO_2 achieved slightly higher levels of inactivation for some adenovirus and enterovirus time points, but those higher inactivation levels were generally statistically insignificant. Changes in pH produced mixed results for photocatalytic inactivation of adenovirus 4.
- The annular reactor configuration and improved mixing in the Photo-Cat Lab significantly increased adsorption of the bacteriophages onto the TiO_2 nanoparticles, thereby increasing the effectiveness of photocatalysis even at high TiO_2 doses (400 – 1,000 mg/L).
- Rutile TiO_2 achieves very low levels of inactivation due to decreased quantum yields, light scattering, and absorption. This control indicates that photocatalysis is the dominant mechanism for high TiO_2 doses.
- The "dynamic" membrane filter provides a higher level of bacteriophage removal in the presence of TiO_2.
- UV irradiation is slightly more effective than TiO_2 photocatalysis with respect to virus inactivation, but the potential for simultaneous photocatalytic inactivation and destruction of organic compounds, including disinfection byproduct precursors, provides an additional benefit that is generally impractical with UV irradiation alone.

Acknowledgements

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