

Virus inactivation and attachment onto TiO₂ Nanoparticles



ΠΑΝΕΠΙΣΤΗΜΙΟ
ΠΑΤΡΩΝ
UNIVERSITY OF PATRAS

Syngouna, V. I.¹, M. Bellou², A. Vandarakis², and C.V. Chrysikopoulos³

¹Department of Civil Engineering, Environmental Engineering Laboratory, University of Patras, 26504 Patras, Greece

²Environmental Microbiology Unit, Department of Public Health, University of Patras, 26504 Patras, Greece

³School of Environmental Engineering, Technical University of Crete, Chania 73100, Greece

Technical
University
of Crete



Abstract

Virus inactivation and attachment onto nanoparticles are hypothesized to influence virus fate and transport in the subsurface. Consequently, a series of static experiments were conducted at room temperature (25°C) to investigate the effect of visible light (VL) and the presence of quartz sand on virus attachment onto TiO₂ nanoparticles (NPs). Appropriate adsorption isotherms were determined. Also, the experimental virus inactivation data were satisfactorily represented by a pseudo-first order expression with time-dependent rate coefficients.

Materials and methods

➤ TiO₂ NPs Suspension preparation and characterization

Titanium dioxide powder (TiO₂, anatase, <25 nm in diameter, purity greater than 99.9%)

- TiO₂ NPs stock suspension (1000 mg/L) in Milli-Q ddH₂O
- Sonication for 30 min and determination of TiO₂ size distribution in ddH₂O after settling for 7 days: 180±31nm (ZetaSizer Nano-ZS90)
- Dillution of unsettled TiO₂ suspension in PBS solution to yield a concentration of 10mg/L
- Measured absorbance of TiO₂ NPs at 287 nm by a UV-vis spectrophotometer was converted to TiO₂ concentration

➤ Virus Suspension preparation

Model virus: Bacteriophage MS2

- F-specific
- Single-stranded RNA phage with 31% nucleic acid content
- Effective particle diameter 24 -26 nm
- Host bacterium is *E. coli* ATTC 15597-B1.
- Assay: double-layer overlay method

Theoretical considerations

➤ Virus Inactivation Calculations

The experimental data successfully described by a pseudo-first-order expression with a time-dependent rate coefficient as follows:

$$\frac{dC(t)}{dt} = -\lambda(t)C(t)$$

where C is the concentration of suspended viruses in the liquid phase, t is time, and λ is the time-dependent inactivation rate coefficient of suspended viruses described by the following expression:

$$\lambda(t) = \lambda_0 e^{-\alpha t}$$

where λ_0 is the initial inactivation rate coefficient, and α is the resistivity coefficient. The inactivation parameters λ , λ_0 and α were obtained for all the experimental log-normalized-concentration data.

Results and Discussion

➤ Virus Inactivation

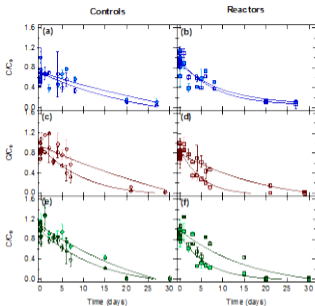


Figure 1. Effect of NPs w/o sand on MS2 inactivation under VL (open symbols) and Dark (solid symbols) batch conditions at 25°C, and simulated concentration histories (solid curves). The first row of graphs corresponds to virus initial concentration of $C_0 = 1.7 \pm 0.22 \times 10^3$ PFU/mL, the second to $C_0 = 1 \pm 0.14 \times 10^4$, and the third to $8.7 \pm 1.8 \times 10^6$ PFU/mL. The circles and squares represent experiments in Controls and in Reactors, respectively. Error bars not shown are smaller than the size of the symbol.

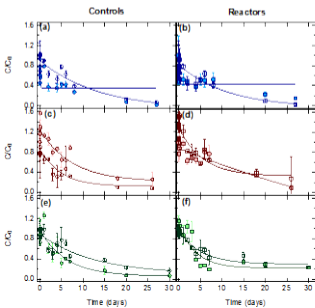


Figure 2. Effect of NPs with sand presence on MS2 inactivation under VL (open symbols), Dark (solid symbols) batch conditions at 25°C, and simulated concentration histories (solid curves). The first row of graphs corresponds to virus initial concentration of $C_0 = 1.7 \pm 0.22 \times 10^3$ PFU/mL, the second to $C_0 = 1 \pm 0.14 \times 10^4$, and the third to $8.7 \pm 1.8 \times 10^6$ PFU/mL. The circles and squares represent experiments in Controls and in Reactors, respectively. Error bars not shown are smaller than the size of the symbol.

➤ Virus attachment

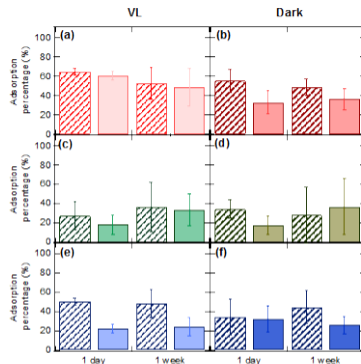


Figure 3. Percentage (%) MS2 virus attachment onto TiO_2 NPs for a period of one day and one week, w/o sand (cross shaded columns) and with the presence of sand (filled columns) under (a,c,e) VL and (b,d,f) Dark experimental conditions in PBS (pH 7.0, $I_s=2$ mM) at 25°C. The first row of graphs corresponds to virus initial concentration of $C_0 = 1.7 \pm 0.22 \times 10^3$ PFU/mL, the second to $C_0 = 1 \pm 0.14 \times 10^4$, and the third row to $8.7 \pm 1.8 \times 10^6$ PFU/mL. Error bars not shown are smaller than the size of the column.

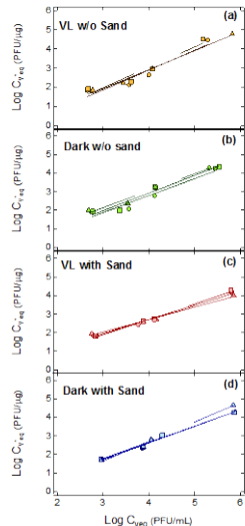


Figure 4. Freundlich isotherms for the attachment of MS2 onto TiO_2 NPs with and w/o the presence of sand under (a) VL w/o Sand, (b) Dark w/o Sand, (c) VL with Sand, and (d) Dark with Sand at pH 7.0 and 25°C.

Results and Discussion

DLVO Energy Calculations

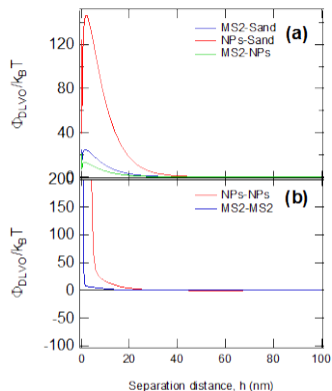


Figure 5. Predicted DLVO interaction energy profiles using (a) sphere-plate approximations for MS2 -NPs, MS2-Sand, NPs-Sand and (b) sphere-sphere for NPs-NPs, and MS2-MS2 as a function of separation distance for the experimental conditions (PBS pH 7, $I_0=2mM$).

Conclusions

- Higher inactivation rates were observed in the presence of TiO_2 NPs than in the absence of them.
- MS2 inactivation in the presence of TiO_2 NPs is generally faster without the presence of sand. This leads to the conclusion that the attachment of viruses on quartz sand grains can offer protection against virus inactivation.
- The MS2 inactivation rates were higher in ddH_2O than PBS solution. This is attributed to possible increased virus aggregation in PBS solution. Virus aggregation is known to reduce significantly inactivation.
- The experimental results of this work indicate that VL plays a significant role in virus inactivation especially in the absence of sand in ddH_2O .
- It was observed that under static batch conditions in the presence of TiO_2 NPs the attachment of viruses onto sand surfaces offers a protection against inactivation.
- The affinity of MS2 for TiO_2 NPs is greater in the presence of sand under both VL and Dark conditions.
- Lower affinity of MS2 for TiO_2 NPs was observed under VL than Dark conditions.
- The IEP of TiO_2 (anatase) NPs in ddH_2O was found to be equal to $pH_{IEP}=5.5$.
- When TiO_2 NPs approach sand grains face an energy barrier of $146.37 k_B T$, while lower energy barriers of $24.58 k_B T$ and $13.38 k_B T$ are encountered when MS2 approaches sand and TiO_2 NPs, respectively.