Fate of Silica Nanoparticles during Secondary Wastewater Treatment

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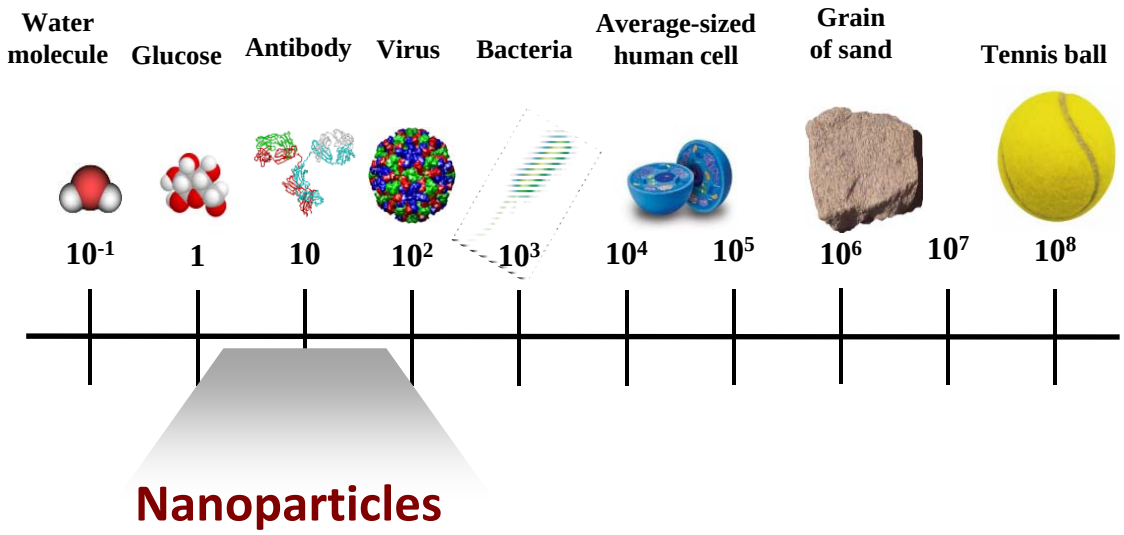
NSF/SRC Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

ARIZONA

Engineered nanoparticles

- Nanoparticles (NPs) are particles sized in less than 100 nm.



Unique Properties of NPs

- Small size
- High specific surface area
- Optical properties
- Semiconductor properties.....

Applications of SiO_2 nanoparticles

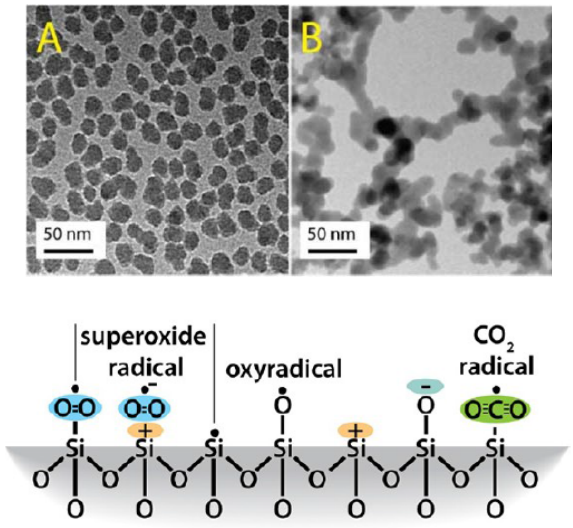
- **CMP slurries**
- Printer toners
- Biosensors

- Personal care products
- Varnishes
- Food additive

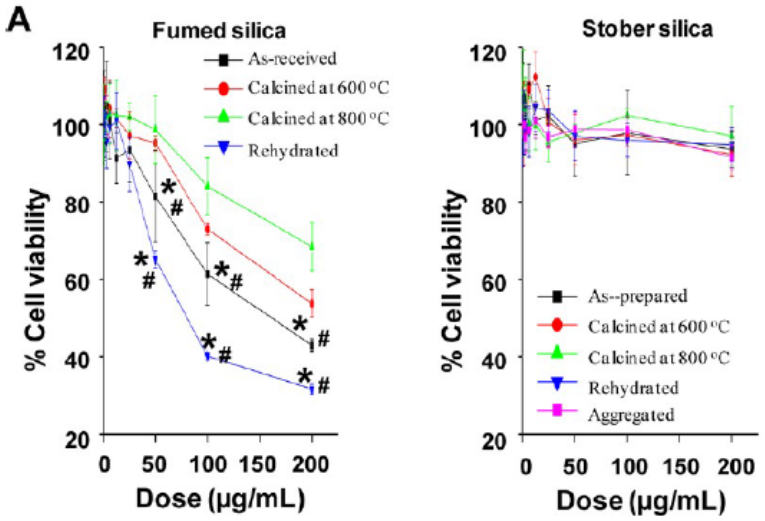
- Diagnostic and biomedical research

EHS Concerns about SiO_2 NPs

- Multiple studies indicate that some SiO_2 NPs cause toxicity.
- Recent studies suggest that fumed SiO_2 is more toxicity than colloidal SiO_2 (Zhang et al. 2012).

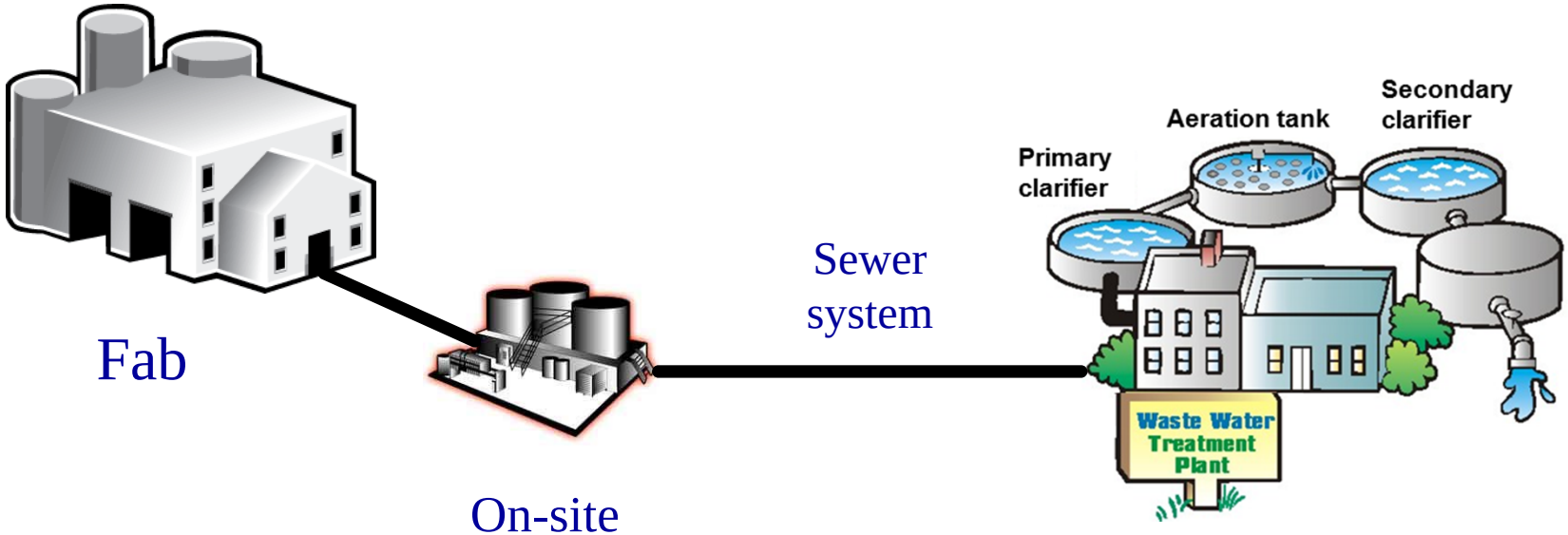


Zhang et al. 2012. J. Am. Chem. Soc. 134:15790–15804

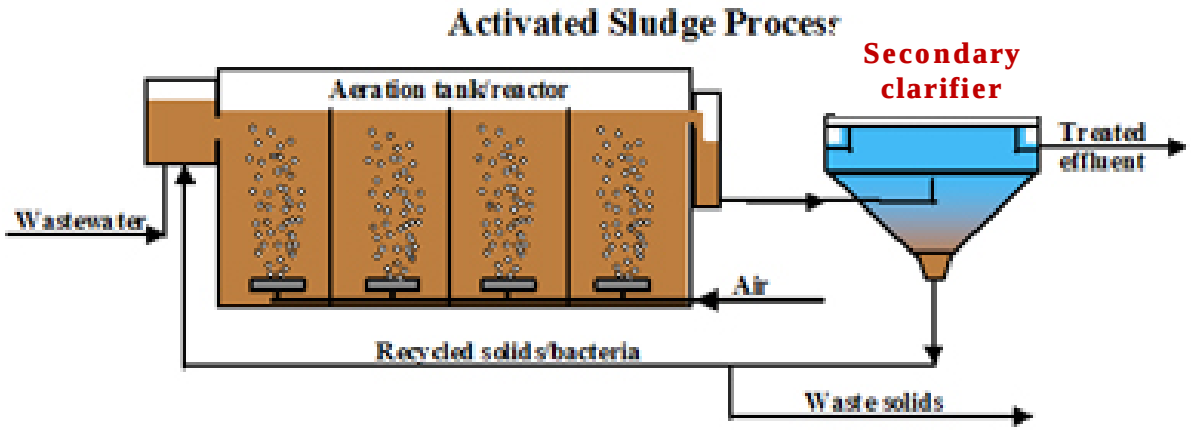


Impact of fumed SiO_2 (**A**) and colloidal SiO_2 (**B**) on viability of human bronchial epithelial cells

CMP NPs & Wastewater Treatment

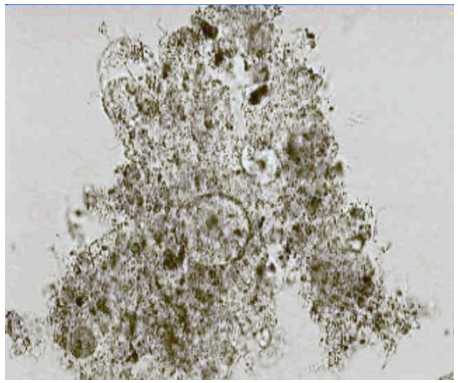


Activated Sludge (A/S) Process



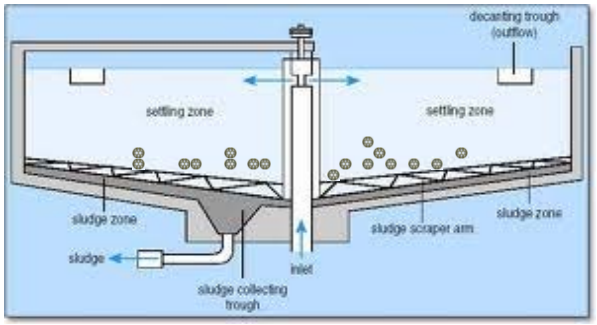
Biodegradable Organic Matter + O_2 → **Cells** + H_2O + CO_2

(biomass)

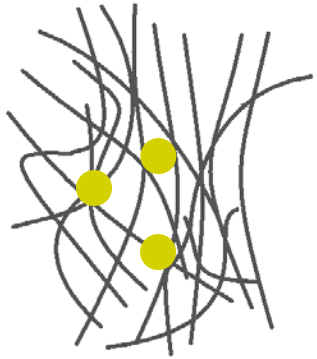


Biological wastewater treatment: Possible NP removal mechanisms

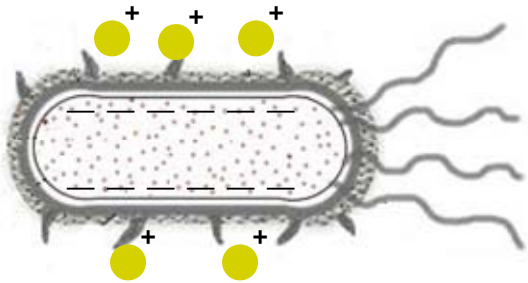
Gravity Settling



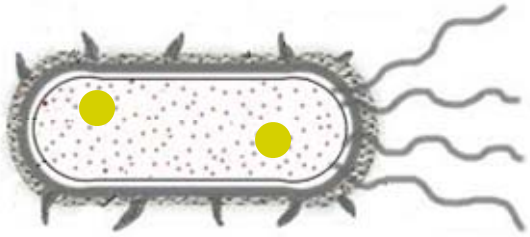
Entrapment by A/S flocs



Adsorption



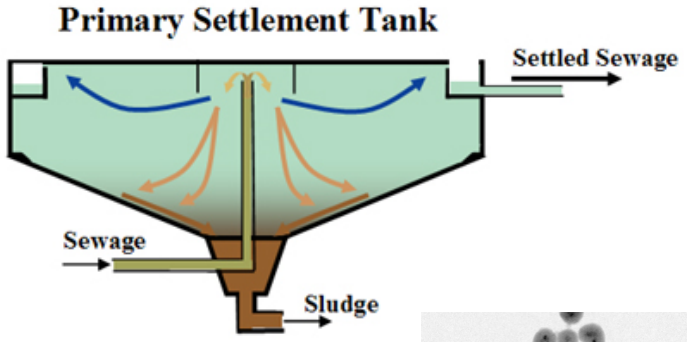
Intake (?)

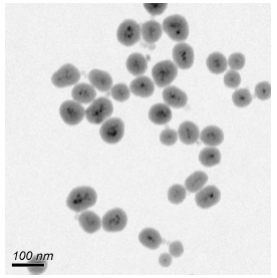


Fate of SiO_2 NP during municipal wastewater treatment

- Lack of reports on the fate of SiO_2 NP during biological wastewater treatment

- Iron oxide (core)-SiO_2 (shell) NPs not removed by **primary treatment** (settling process, prior to biological treatment). NPs coated with nonionic surfactant effectively removed (Jarvie et al, 2009).
  - **NP conc. used very high!! 2470 mg/L**





Jarvie et al. Environ. Sci. Technol. **2009,** *43,* 8622–8628

High background SiO_2 levels in wastewater can interfere with analysis of SiO_2 NPs

- Natural waters contain dissolved and suspended forms of silica
- Dissolved silica in natural waters varies from ca. **1–3 mg/L** in mountain lakes to **50–300 mg/L** in well waters in volcanic and oil production fields (Ning 2002)*
- Fluorescent SiO2 NPs valuable to study the fate of nano-SiO2 during wastewater treatment.

Raffaelle 2006. http://spie.org/x8613.xml

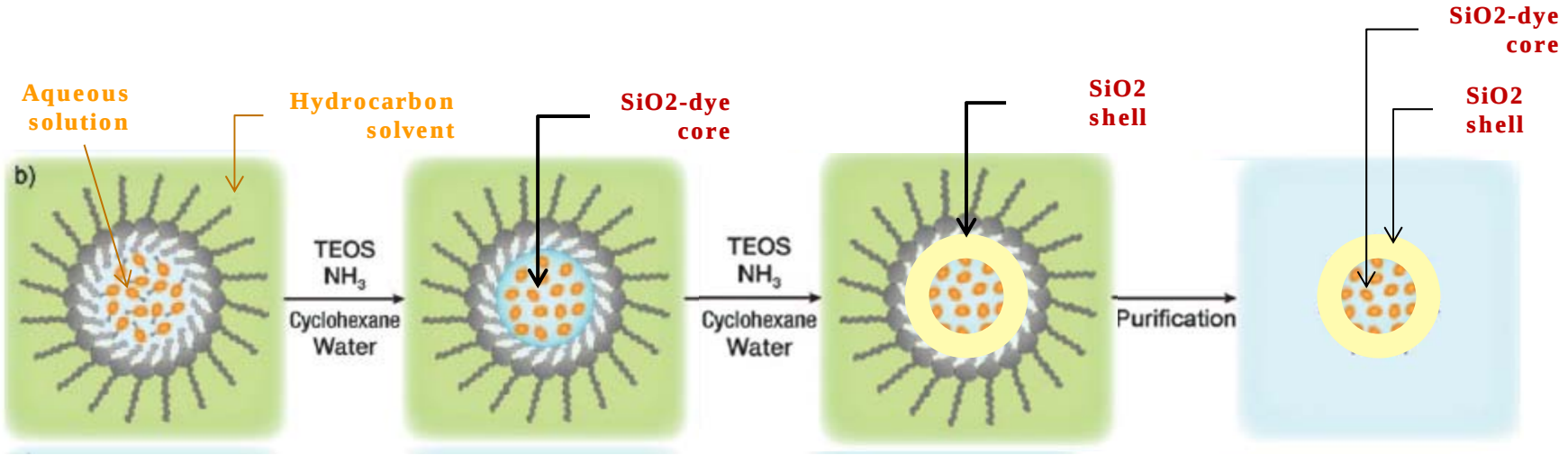
*Ning, Desalination, 151 (2002) 67–73.

Objectives

- To investigate the fate of SiO_2 NPs during conventional biological wastewater treatment.

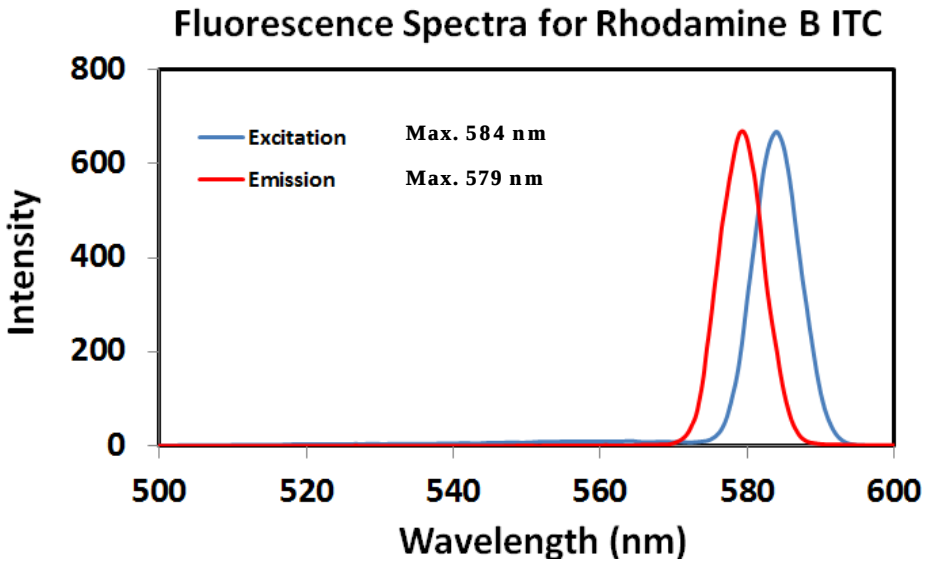
- To study the mechanisms contributing to the removal of SiO_2 NPs in the activated sludge process.

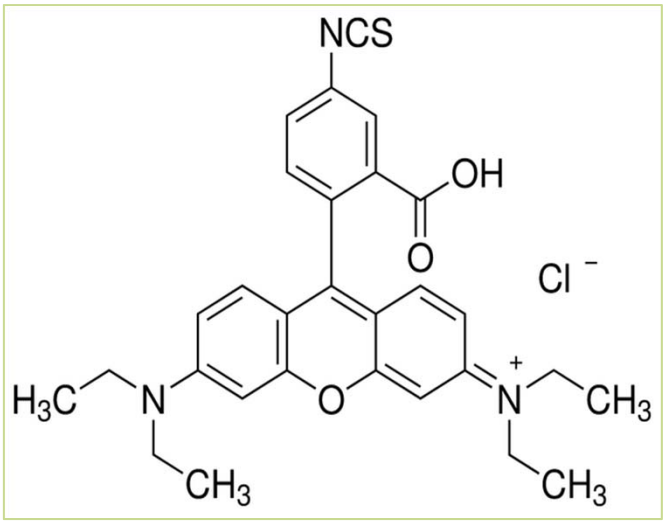
SiO_2 NP Synthesis: Water-in-Oil Microemulsion Method



Adapted from Bonachi et al. 2011. Angew. Chem. Int. Ed. 50, 4056 – 4066

Synthesis of Fluorescent SiO_2 Nanoparticles

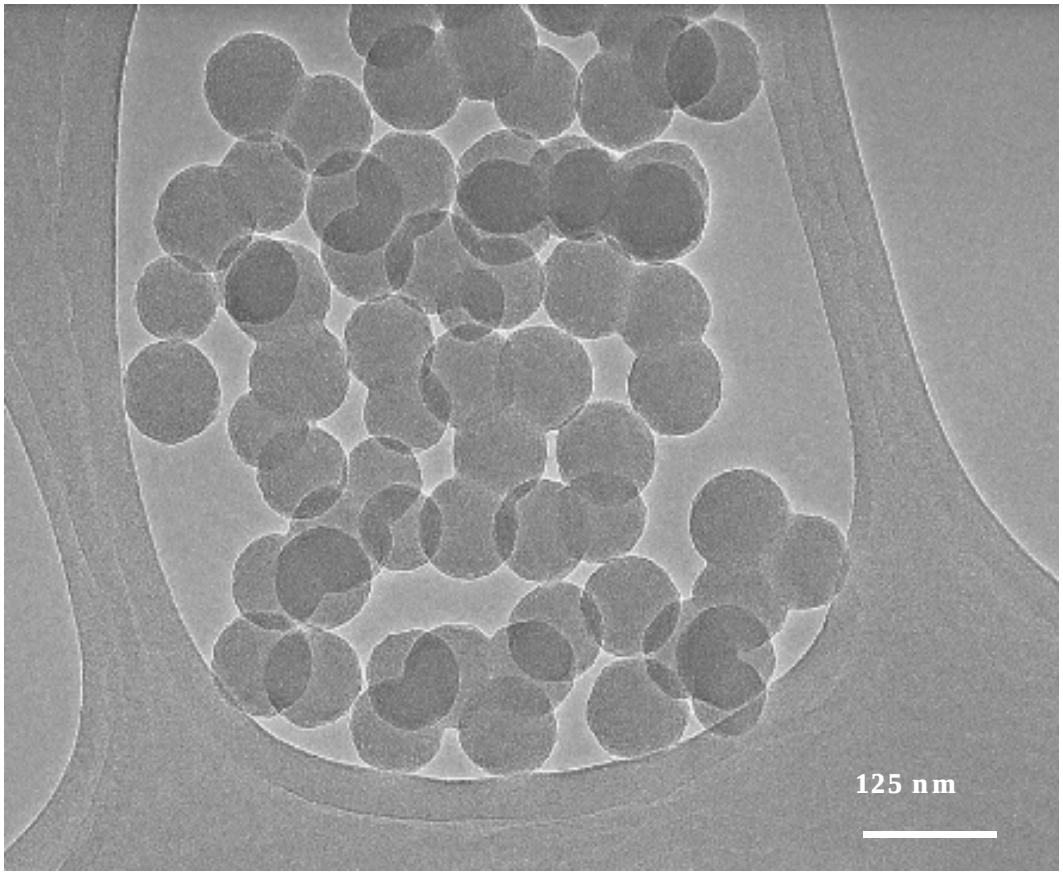




Rhodamine B isothiocyanate

Sentra et al. 2001. Anal. Chem. 73(20):4988-4993,

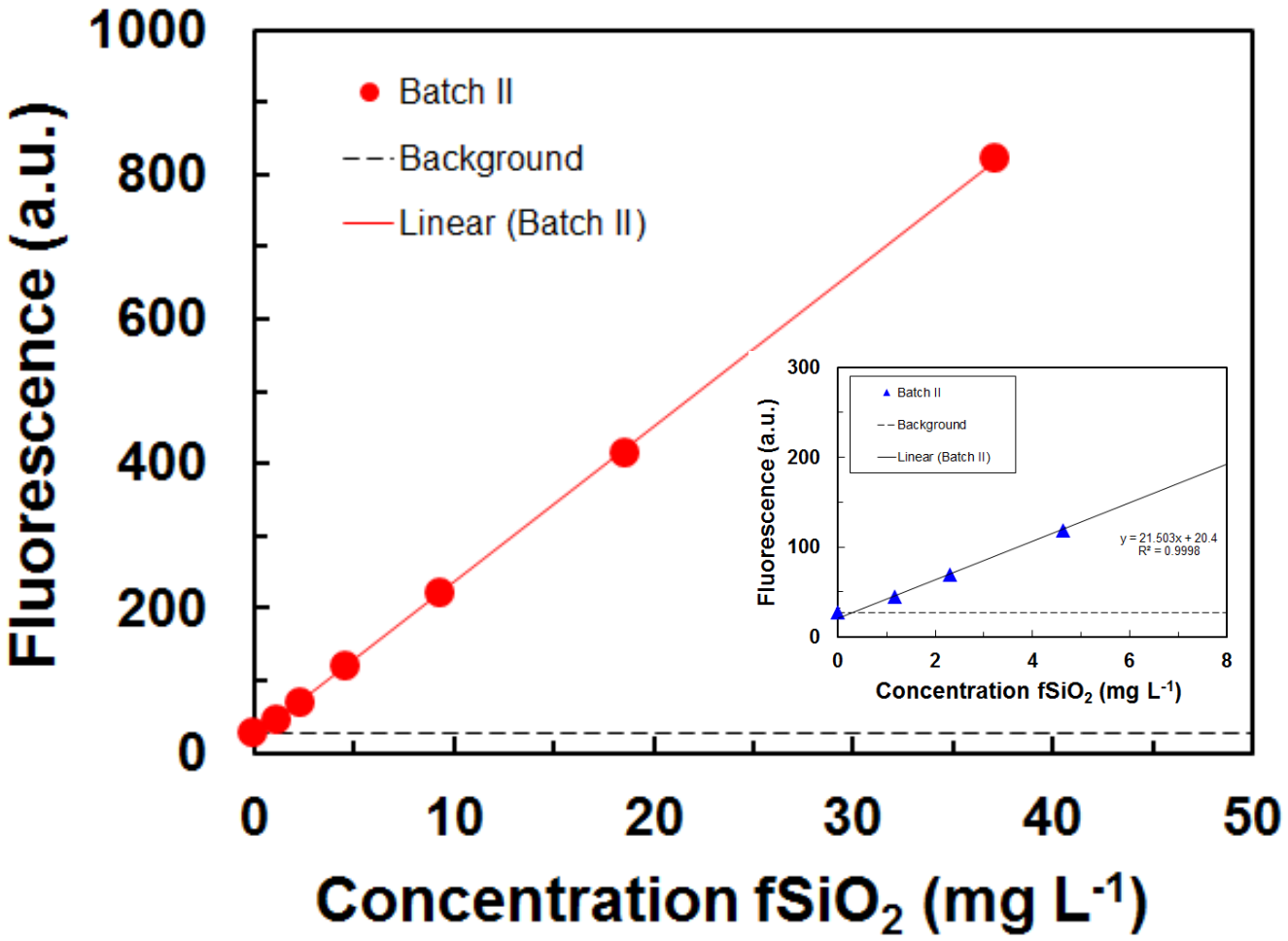
Fluorescent SiO_2 NPs: TEM



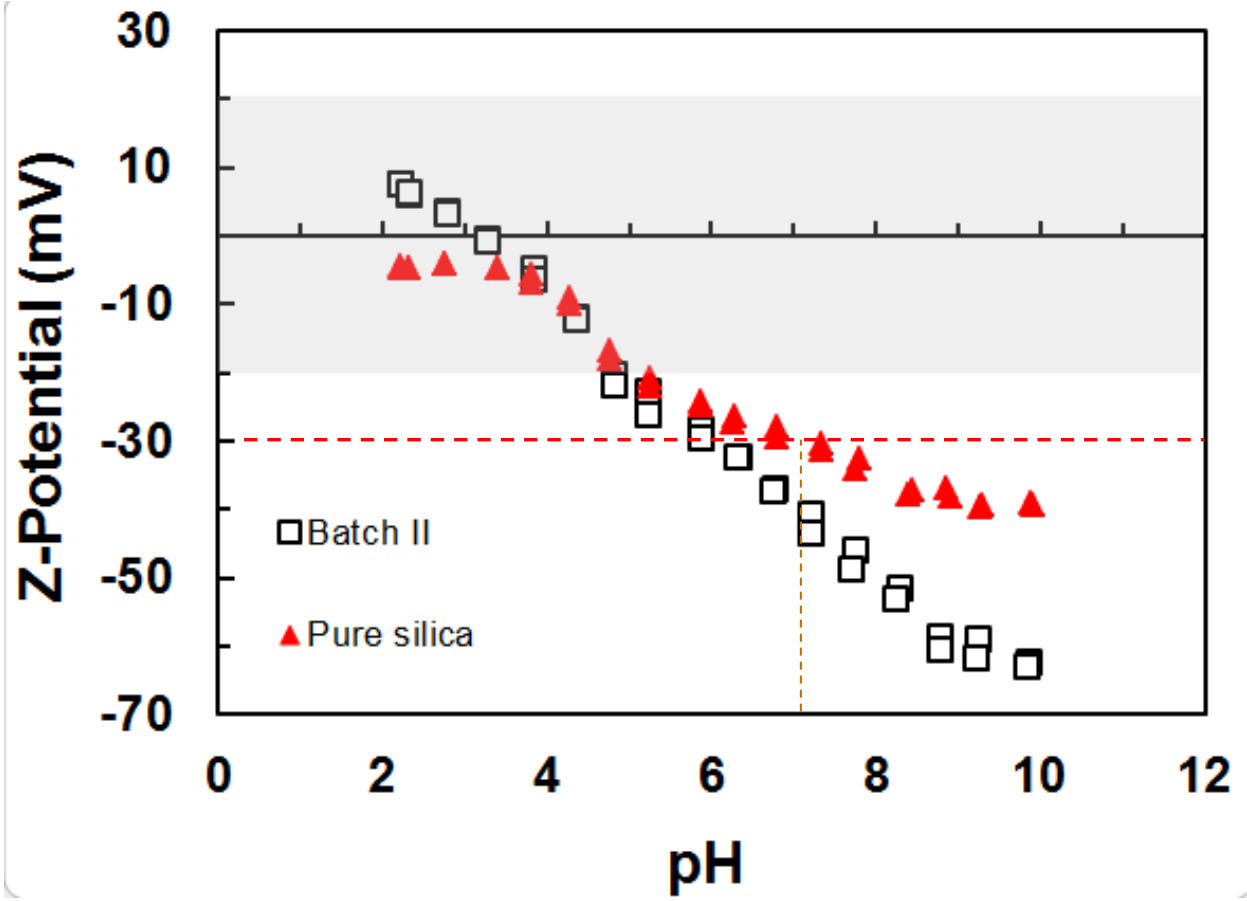
Average particle size:
88 ± 7 nm

Polydispersity:
0.315

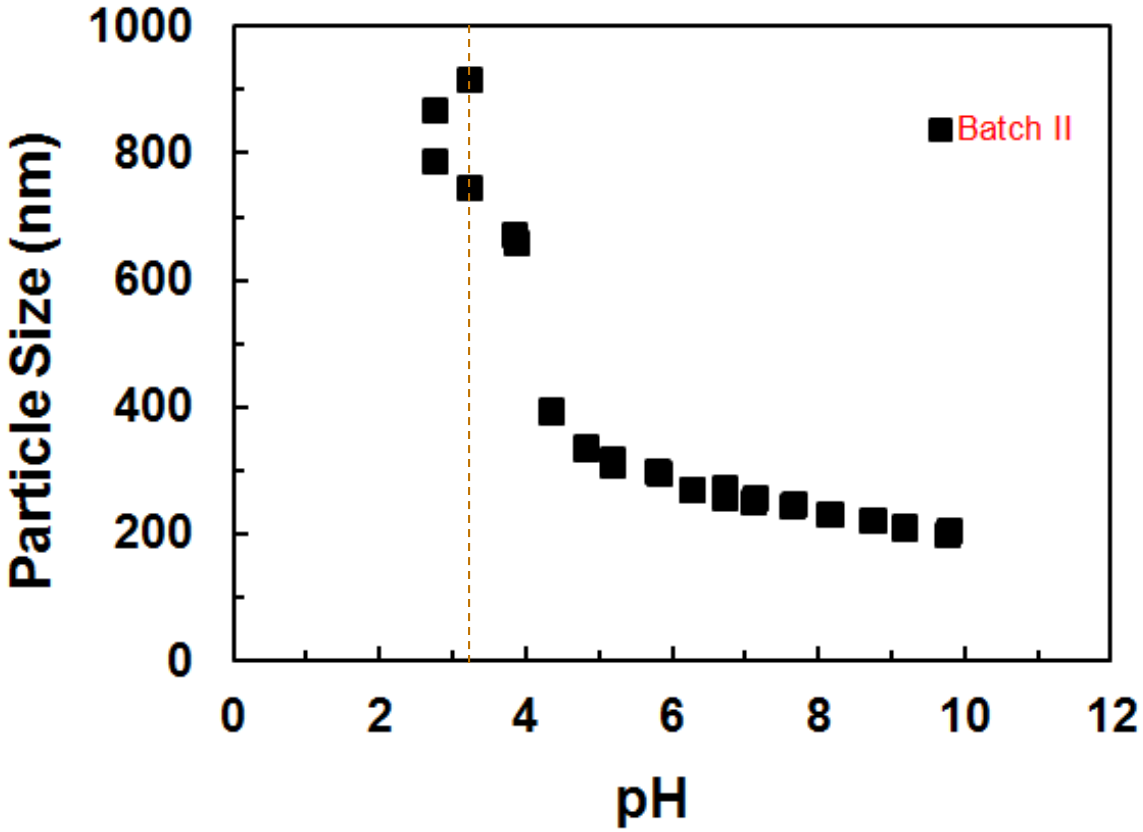
Fluorescent SiO_2 NPs: Zeta potential vs pH



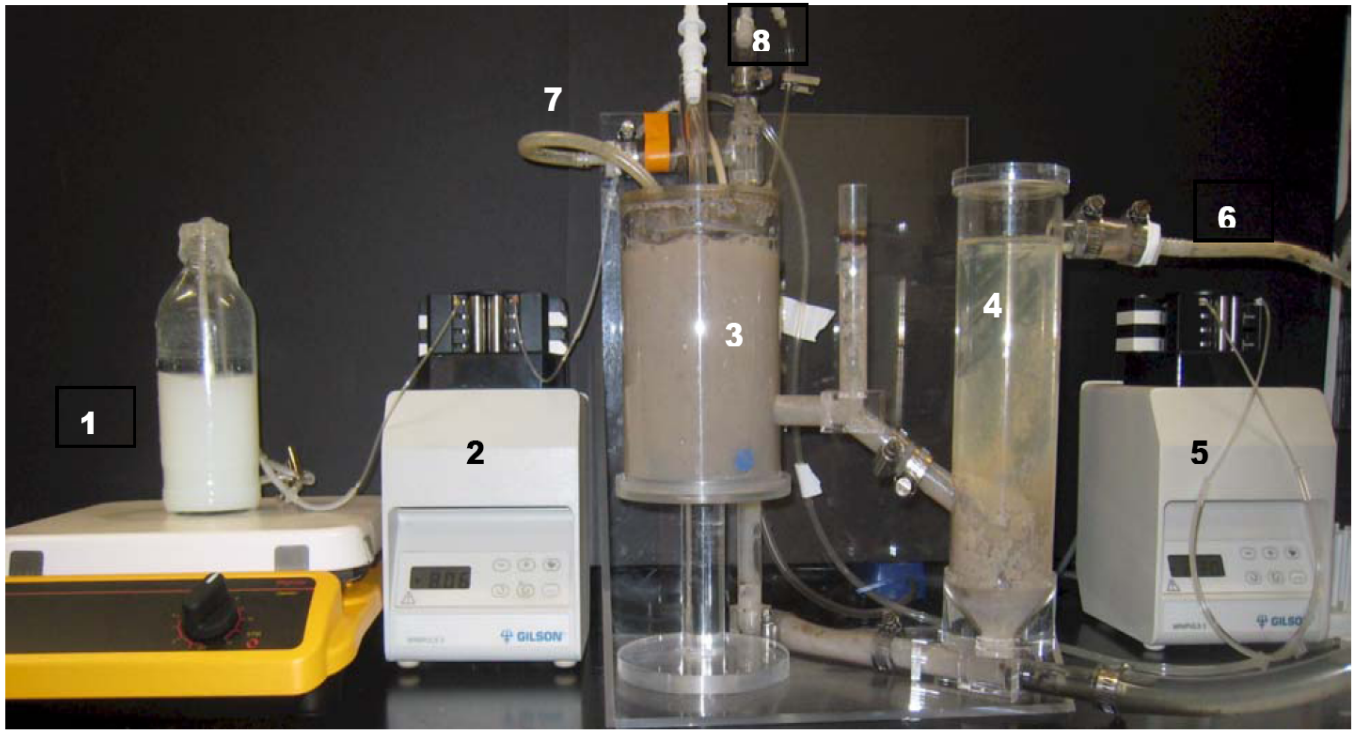
Fluorescent SiO_2 NPs: Zeta potential vs pH



Fluorescent SiO_2 NPs: Average Particle Size vs. pH



Lab-Scale Activated Sludge Bioreactor



Aeration tank:

$V_{reactor}$ = 1.19 L

HRT = 9.9 hrs

Settler:

$V_{reactor}$ = 0.6 L

Temp: 22°C

[1] NPs stock; [2] peristaltic pump feeding NPs; **[3] activated sludge bioreactor; [4] settling tank**; [5] peristaltic pump feeding wastewater; [6] effluent; [7] influent; **[8] aeration**

Synthetic Wastewater

Composition according to OECD guidelines*

Peptone	160 mg/L
Meat extract	110 mg/L
Urea	30 mg/L
K_2HPO_4	28 mg/L
NaCl	7 mg/L
$CaCl_2.2H_2O$	4 mg/L
$Mg2SO_4.7H_2O$	2 mg/L
$NaHCO_3$	150 mg/L
COD concn.	270 mg/L

F-SiO_2	7.9 ± 1.7 mg/L

* OECD GUIDELINE FOR THE TESTING OF CHEMICALS
Simulation Test - Aerobic Sewage Treatment:
303 A: Activated Sludge Units. OECD 303, January 2001

Reactor Monitoring

Influent

Effluent

BIOREACTOR SYSTEM

Organic matter

Chemical Oxygen Demand, colorimetric micro-method

Biological solids (Biomass)

Determination of volatile suspended solids (VSS)

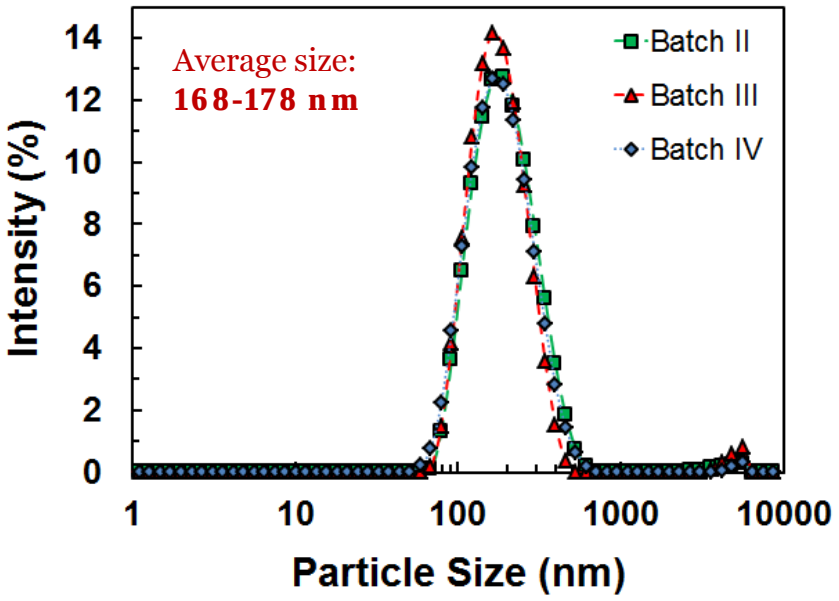
SiO_2

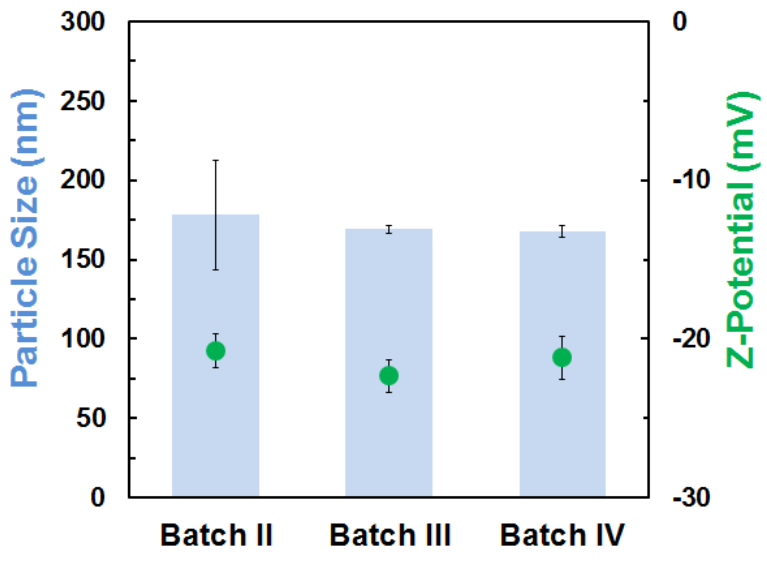
- Fluorescence measurement

pH

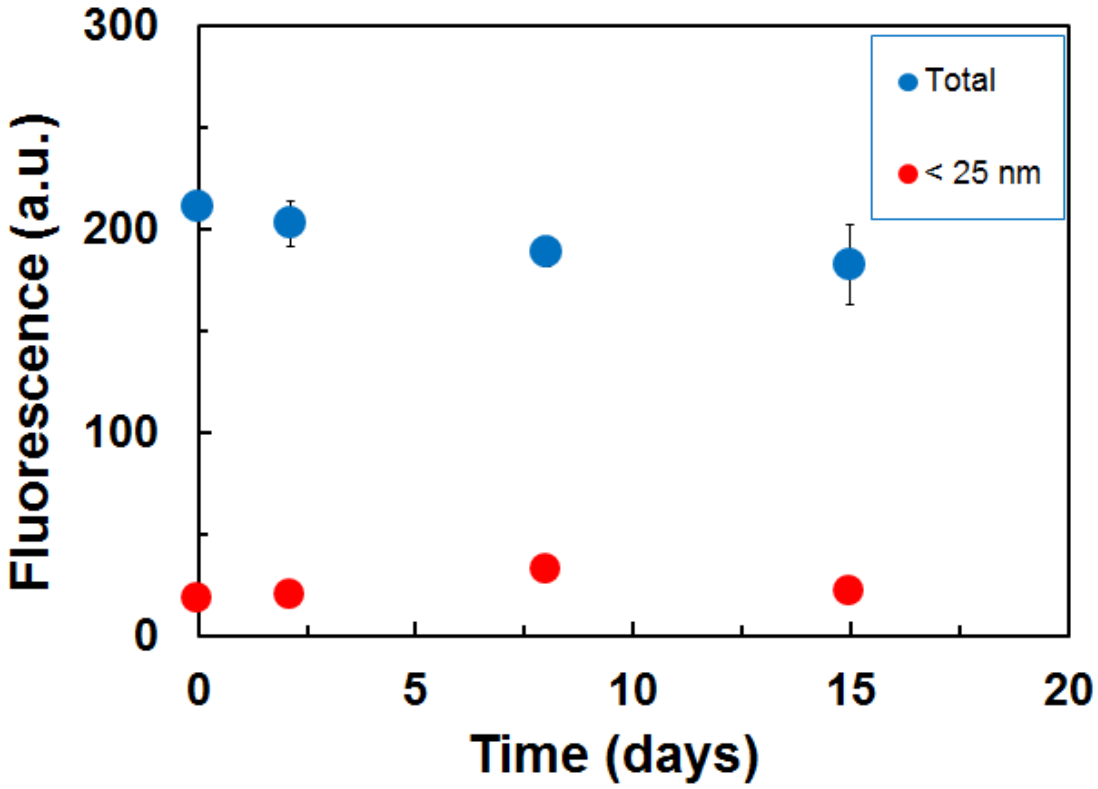
Particle size and zeta potential of SiO_2 NPs in wastewater

PSD & Zeta Potential (DLS)

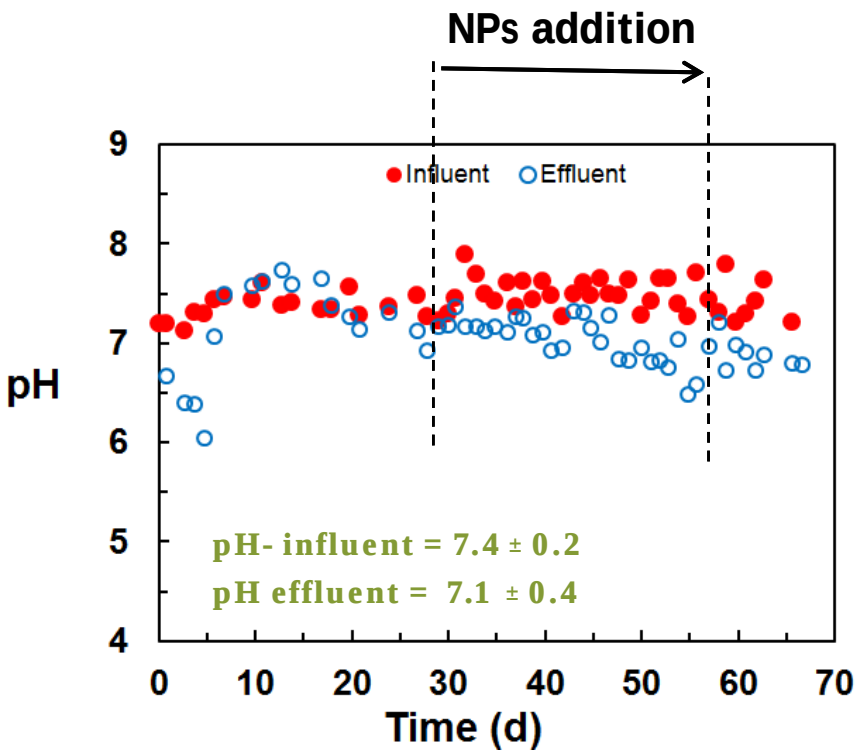


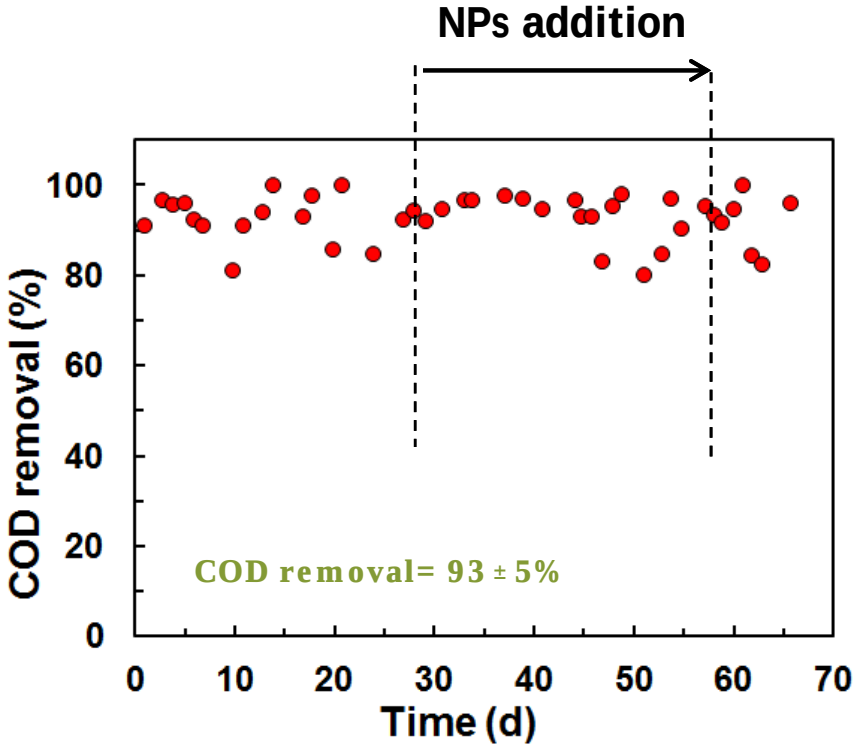


Fluorescent SiO_2 NPs: Leaching behavior in wastewater

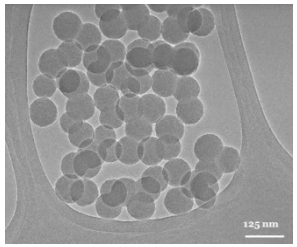


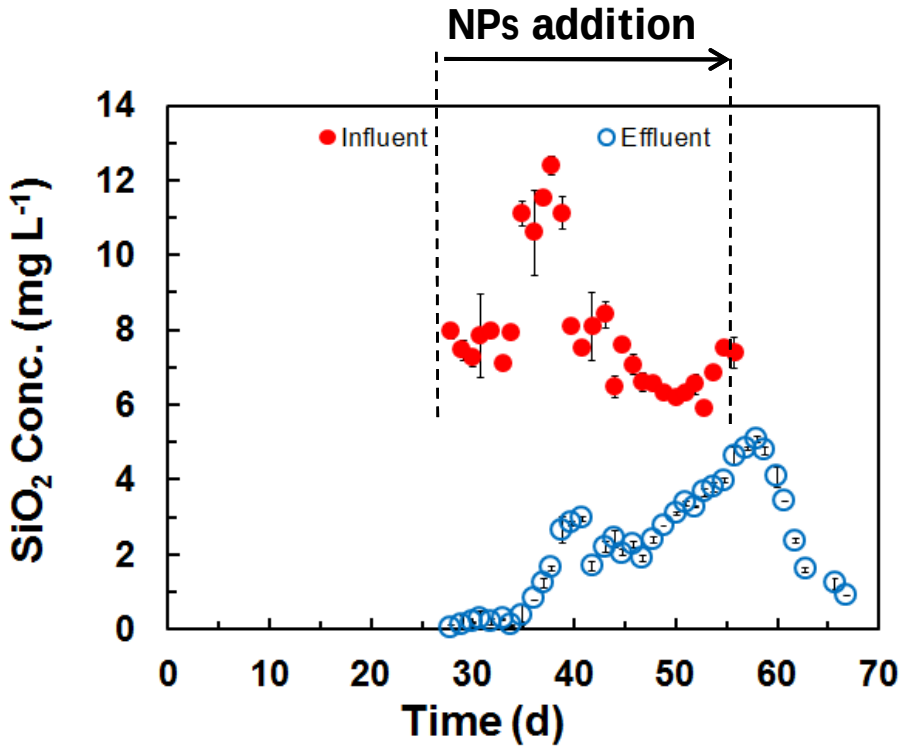
Operation and Performance of the Activated Sludge Process

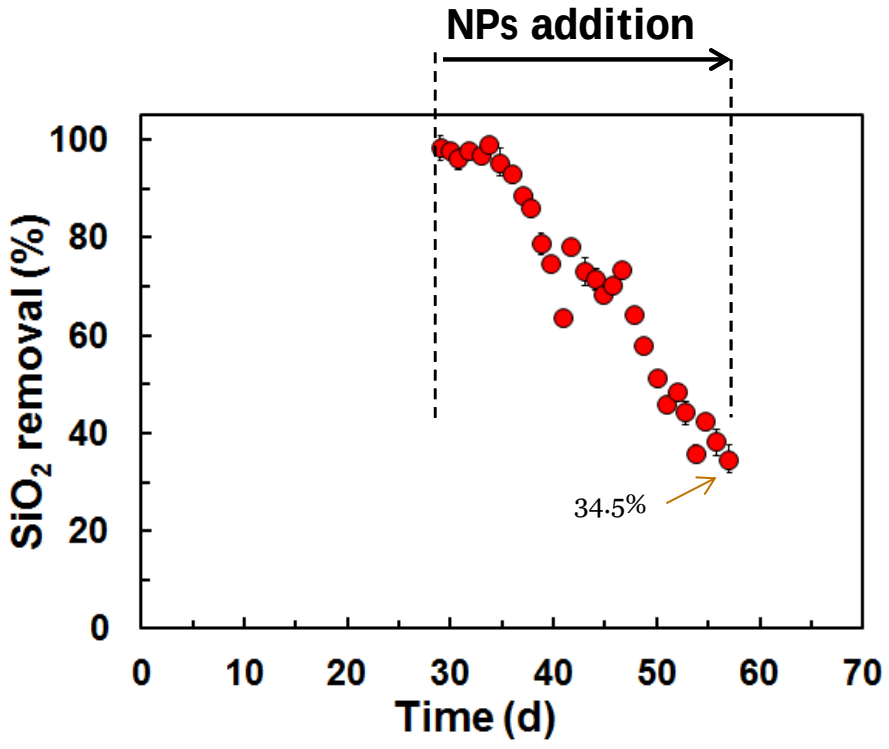




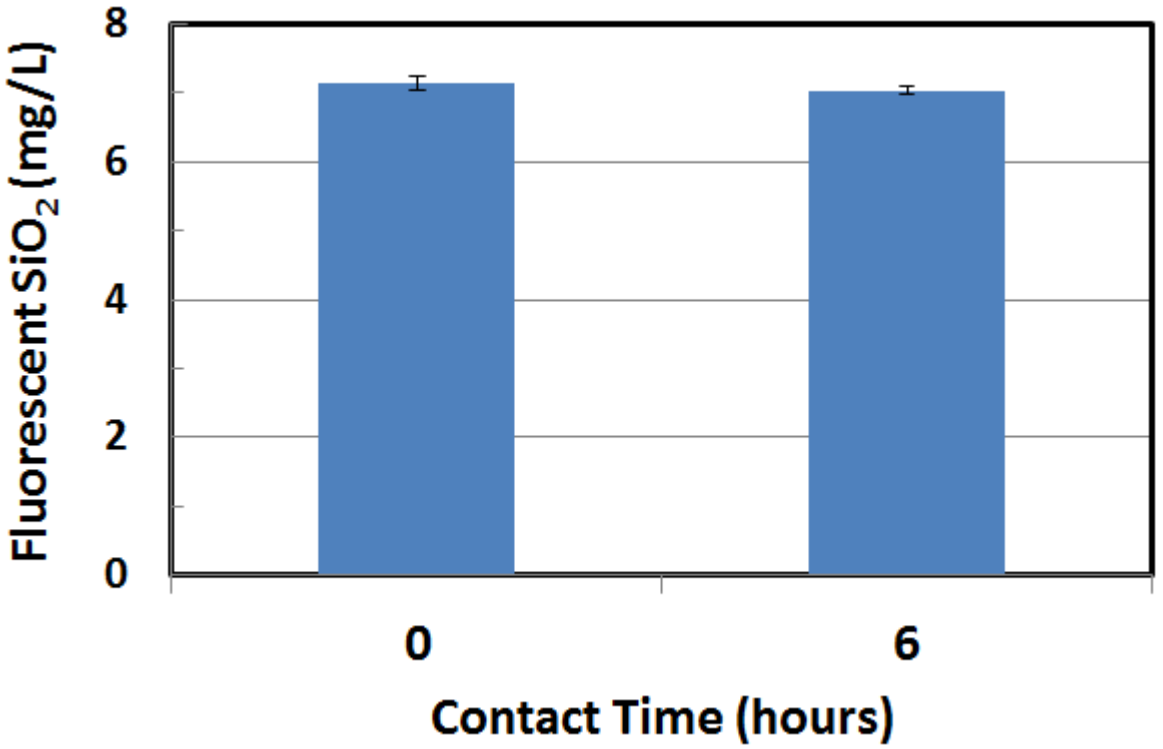
Removal of SiO_2 NPs by Activated Sludge Treatment



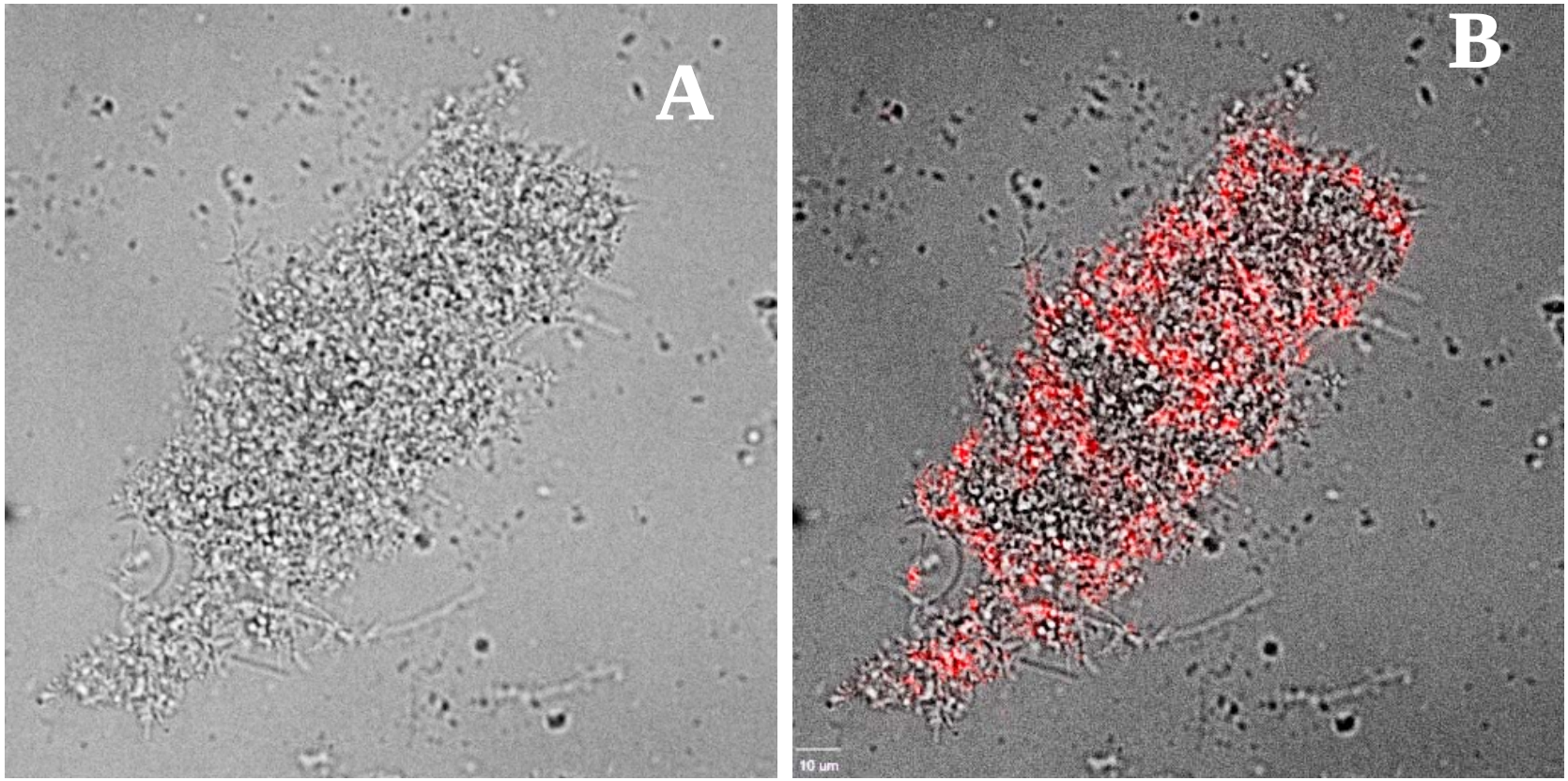




Suspension of fluorescent SiO_2 NPs stable in the synthetic OECD wastewater



Association of SiO_2 with Activated Sludge



Bright-field (A) and epifluorescence (B) images of activated sludge biomass.

Conclusions

- Continuous-flow bioreactor studies demonstrated that biological treatment (*i.e*. activated sludge) has a limited ability to remove SiO_2 NPs from the synthetic wastewater used.

- Removal of SiO_2 NPs was mainly due to NP association with the biomass. The suspension of fluorescent SiO_2 NPs was stable in the synthetic wastewater used in this study.

- SiO_2 did not cause microbial inhibition, as demonstrated by the high COD removal efficiency.

Future plans

- Investigate the fate of CMP NPs and III/V species (In, Ga, As) in CMP effluents during wastewater treatment.

Acknowledgments

- Dr. Lila Otero, Chao Zeng
- Dr. Farhang Shadman & Dr. Jim A. Field
- Dr. C. Aspinwall and Isen A. Calderon

- ERC support

Related Publications

- Gonzalez-Estrella J, Puyol D, Sierra-Alvarez R, Field JA. 2014. Role of biogenic sulfide in attenuating zinc oxide and copper nanoparticle toxicity to acetoclastic methanogenesis. (*Under review*).
- Otero-González L, Field JA, Sierra-Álvarez R. 2014. Inhibition of anaerobic wastewater treatment after long-term exposure to low levels of CuO nanoparticles. *Water Res.* **58**:160-168.
- Gonzalez-Estrella J, R. Sierra-Alvarez, JA Field. 2013. Toxicity assessment of inorganic nanoparticles to acetoclastic and hydrogenotrophic methanogenic activity in anaerobic granular sludge. *J. Hazard. Mater*. **260**:278-285.
- Otero-González L, Field JA, Sierra-Alvarez R. 2014. Fate and long-term inhibitory impact of ZnO nanoparticles during high-rate anaerobic wastewater treatment. *J. Environ. Management*. **135**:110-117.
- Gomez-Rivera F, JA Field, D Brown, R Sierra-Alvarez. 2012. Fate of cerium dioxide (CeO_2) nanoparticles in municipal wastewater during activated sludge treatment. *Bioresource Technol.* **108**:300-304.
- Rottman J, F Shadman, R Sierra-Alvarez. 2012. Interactions of inorganic oxide nanoparticles with sewage biosolids. *Water Sci. Technol*. **66**:1821-1827.

Thank you!