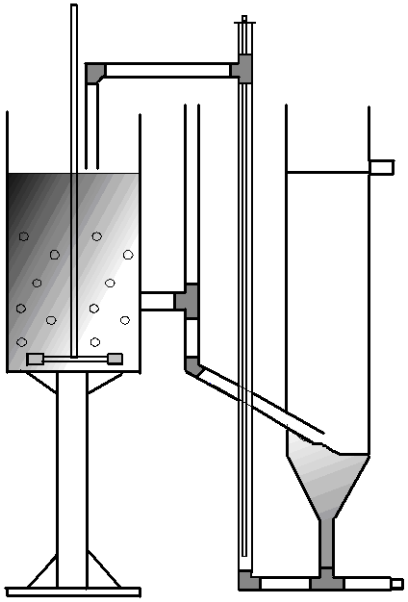
Fate of CMP Nanoparticles During Wastewater Treatment



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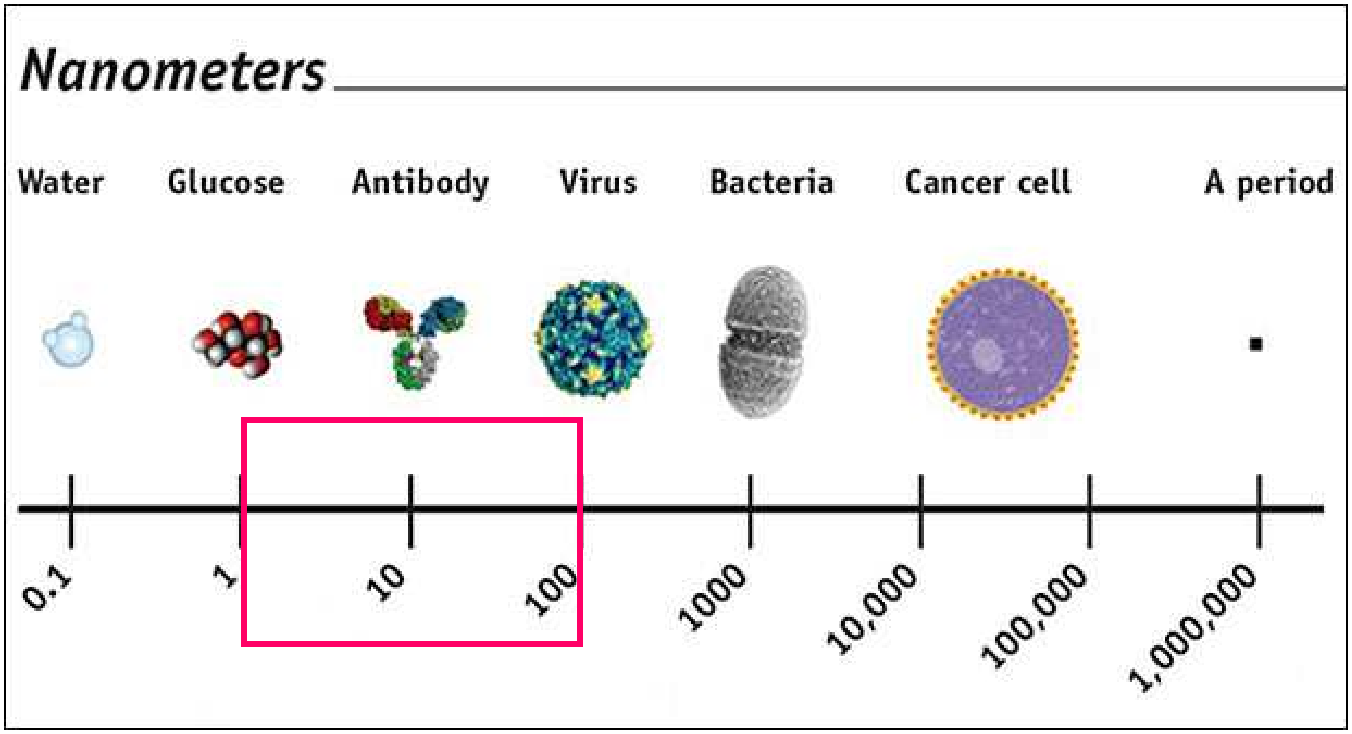
Outline

- **INTRODUCTION**
  - **Nanoparticles**
  - **Wastewater Treatment**
- **OBJECTIVES**
- **MATERIALS AND METHODS**
- **RESULTS**
- **CONCLUSIONS**

Introduction: Nanoparticle definition

Nanoparticles (**NPs**): Materials with at least one dimension of 1 to 100 nm

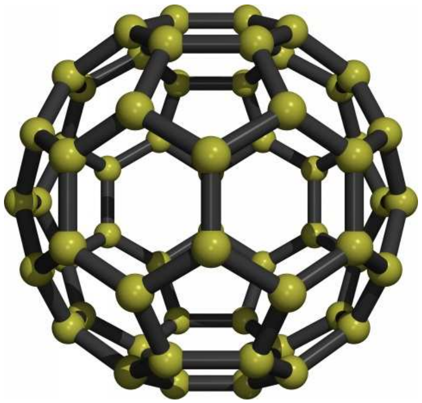


Adapted from Andrew Schneider's "Amid nanotech's dazzling promise, health risks grow", 2010

Introduction: Properties of nanoparticles

What makes nanomaterials interesting?

- **Small size:**
  Surface area, atoms exposed
- **Shape (spheres, flakes, tubes, rods, etc.):**
  Pattern of molecular bonds
- **Chemical composition:**
  Crystal structure, pollutants on surface
- **Solubility:**
  Dispersion or agglomeration



Fullerene

Quantum effects and bulk properties!!

Introduction: Properties of nanoparticles

Benefits associated to nanomaterials

- **Environmental:**
  Pollution prevention, remediation/treatment
- **Water:**
  Improve water quality
- **Energy:**
  Increase efficiency, production, and storage
- **Materials:**
  Increase selectivity in chemical reactions, replacement of toxic materials
- **Agriculture:**
  Genetic improvement of plants and animals

Introduction: Nanoparticles market

Household products containing nanomaterials:

- Sporting goods
- Food packing materials
- Stain-resistant clothing
- Healthcare products
- Cosmetics

Developed by the U.S. Air Force

Major nanomaterials consumers:

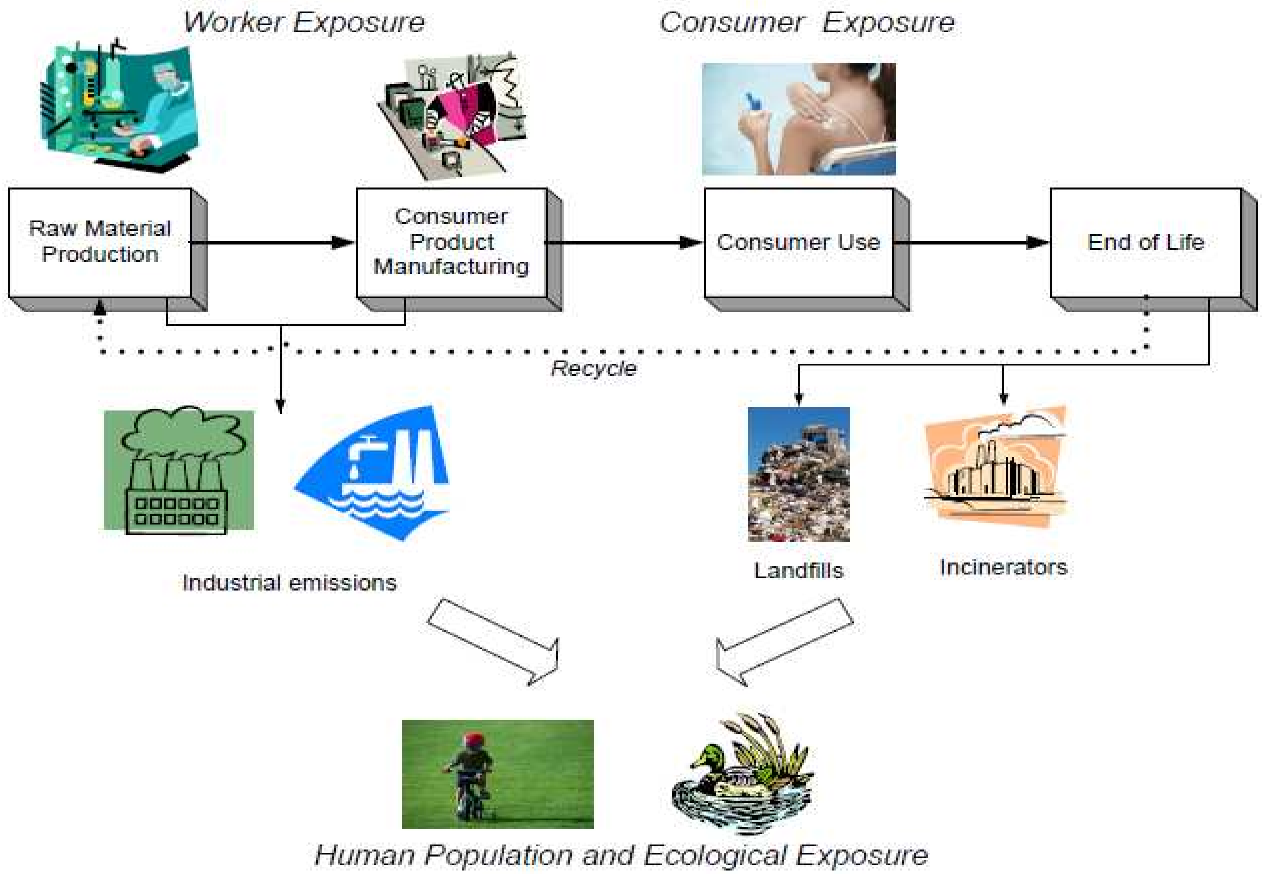
- Semiconductor industry:
  - **Chemical-mechanical planarization (CMP)**
  - **Photolithography**
- Automotive catalysts
- Magnetic recording media
- Sunscreens

1 trillion dollar market by 2015

NSF, 2001

Introduction: Potential risks

Little is known about the fate of nanoparticles in the environment and possible toxic effects on living organisms



EPA's Technology White Paper, 2007

Introduction: Potential risks

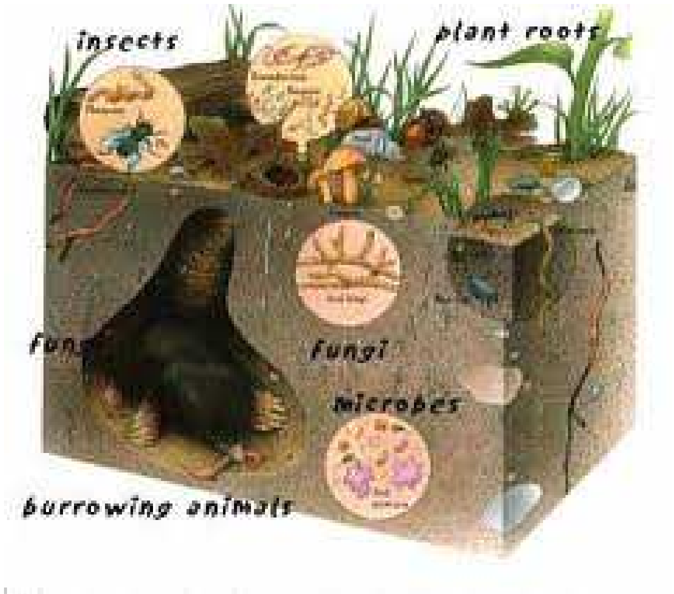
Exposure:

- Inhalation
- Ingestion
- Dermal

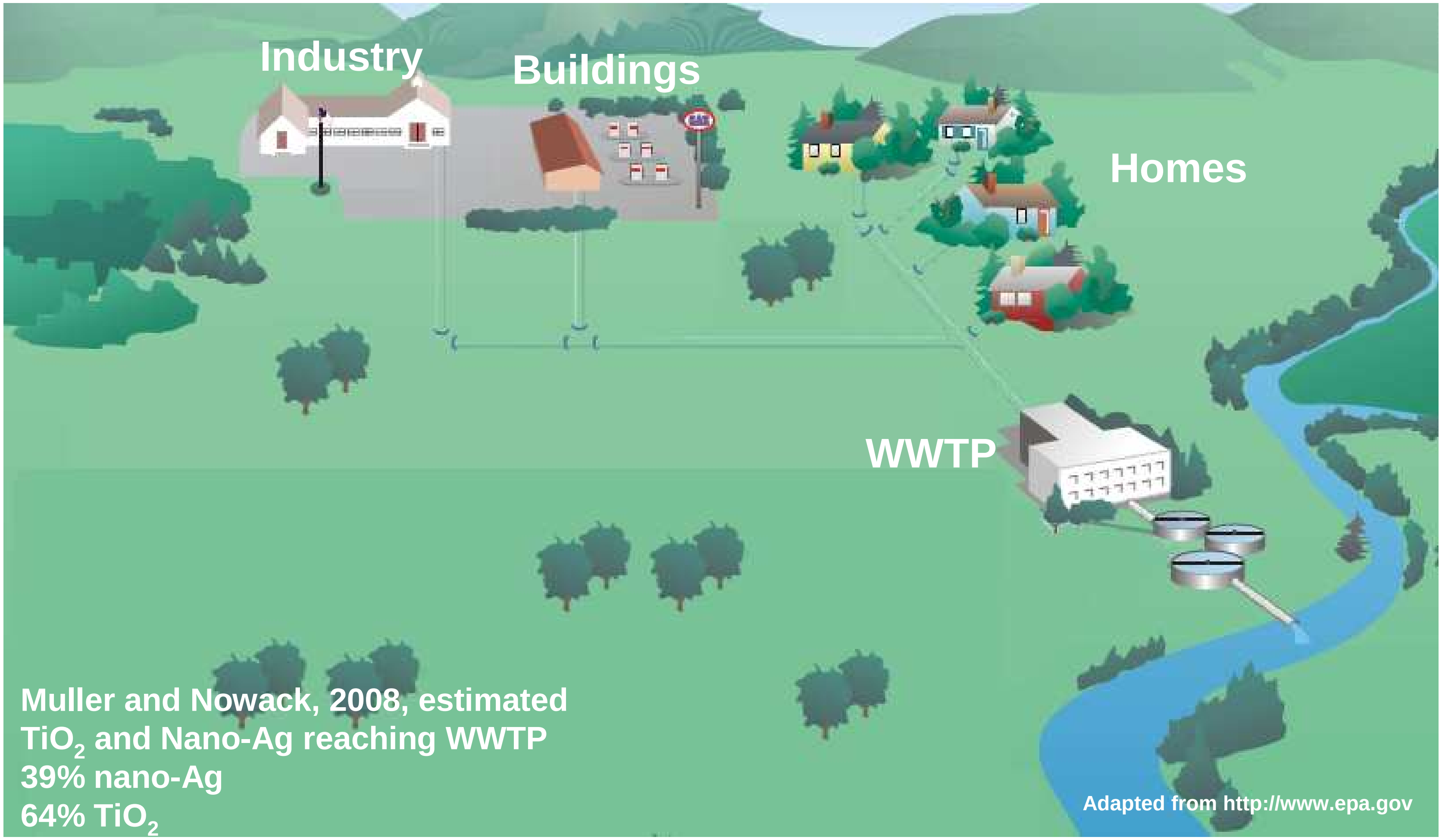
Nanoparticles	Effects
Fullerenes (C_{60})	Antibacterial; oxidative stress; may induce DNA damage in plasmids
Titanium dioxide (TiO_2)	Antibacterial; oxidative stress; may damage DNA; tissue thickening
Zinc oxide (ZnO)	Oxidative stress; may damage DNA; pulmonary adverse effects
Cerium oxide (CeO_2)	Oxidative stress; thickening of heart tissue, could bind to cell membrane of Gram-negative bacteria

Introduction: Fate of NPs in the Environment

- It is large unknown
- Agglomeration/sedimentation and partitioning onto solids are thought to control their fate in the environment
- Could travel long distances if mixed with stabilizers or attached to organic matter



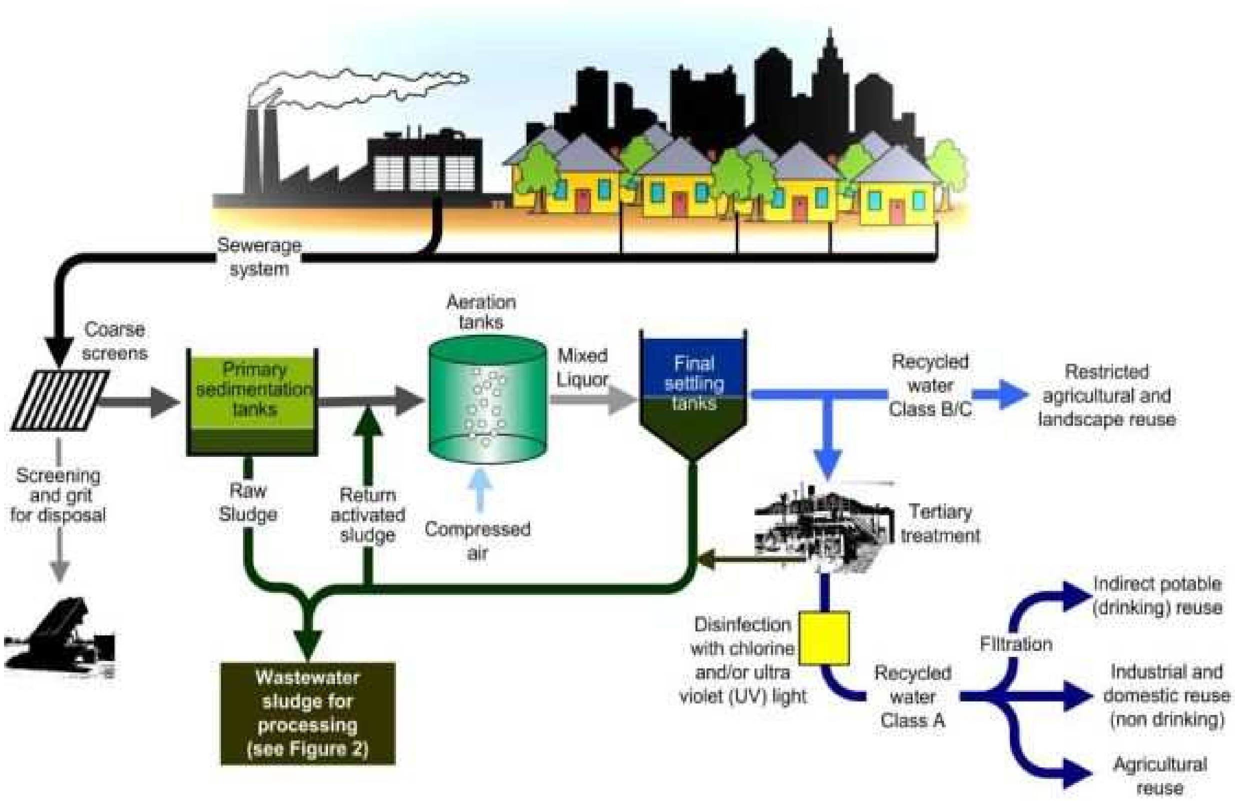
How do nanomaterials get to wastewater treatment plants (WWTP)?



Muller and Nowack, 2008, estimated TiO_2 and Nano-Ag reaching WWTP
39% nano-Ag
64% TiO_2

Introduction: Wastewater treatment

WWTPs remove **harmful organisms** and **pollutants**



http://www.biosolids.com.au/what-are-biosolids.php

Primary treatment

Remove large solids (rags and debris) and smaller inorganic grit

Secondary treatment

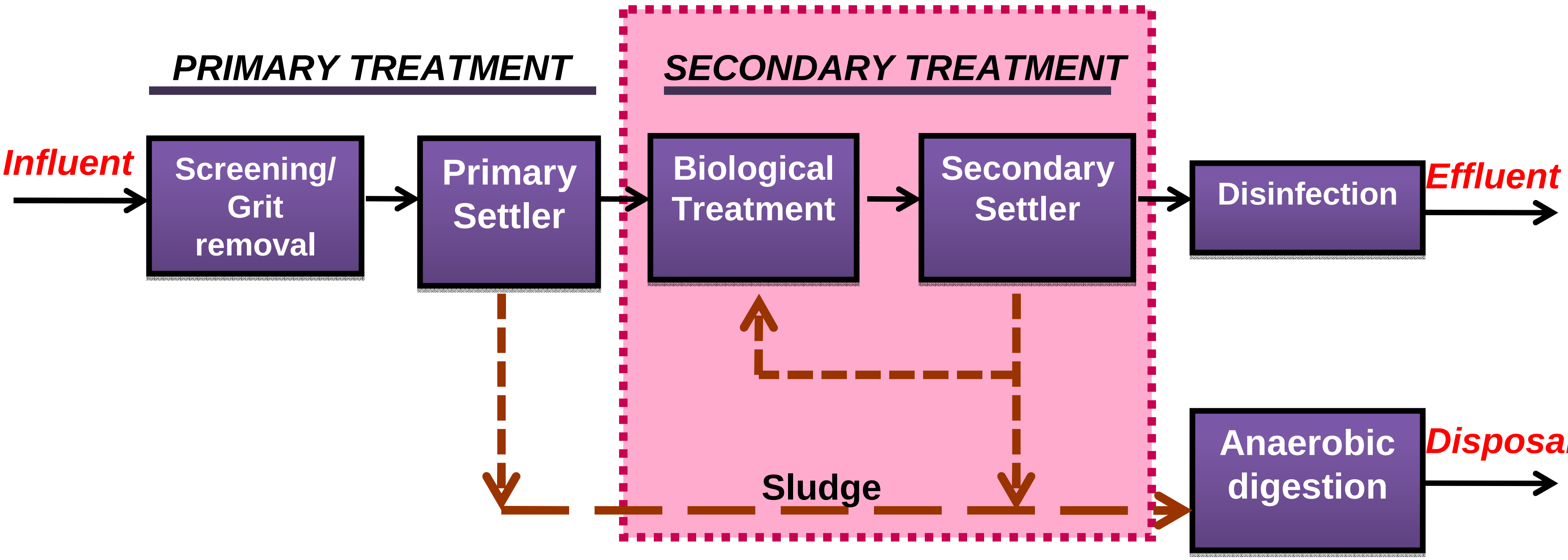
Removes organic contaminants using microorganisms to consume biodegradable organics

Tertiary treatment

Removes nutrients and may include disinfection of the effluent

Introduction: Wastewater treatment

Triangle Wastewater Treatment Plant
Durham, NC

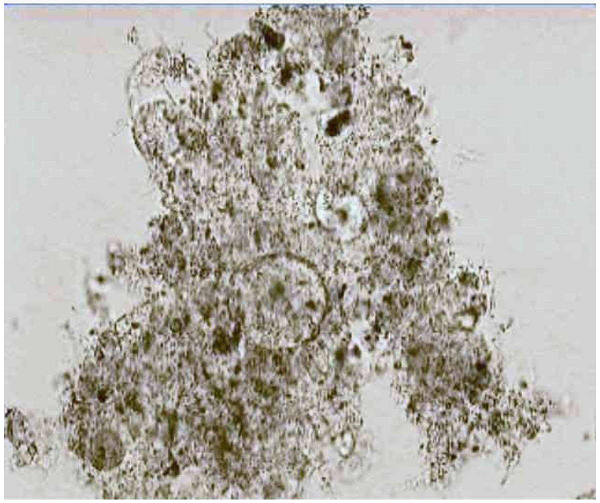


Introduction: Wastewater treatment

Returned activated sludge (RAS)

High water content

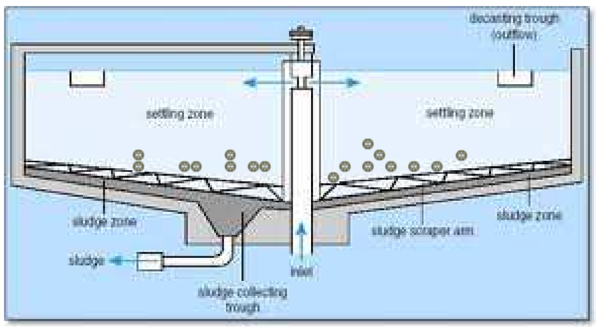
Forms flocs



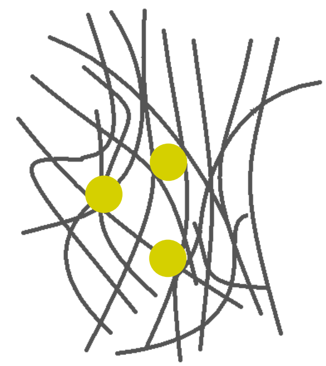
Introduction: Removal during treatment

Possible removal mechanisms

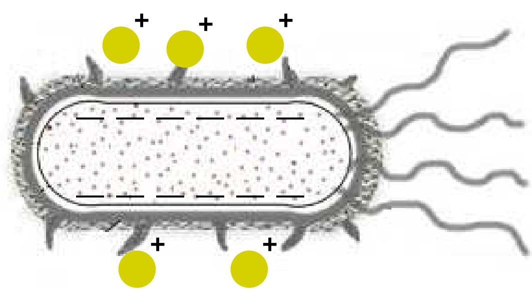
Gravity Settling



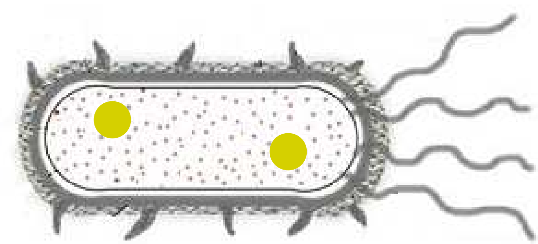
Entrapment by A/S flocs



Ad- and/or absorption



Intake



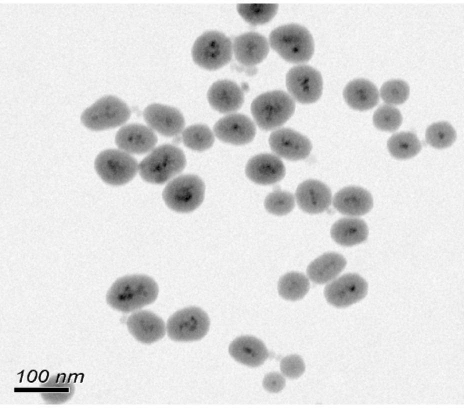
Introduction: Removal during treatment

No conclusive results have yet been obtained

- Activated sludge process attained high removal of CeO_2 from **synthetic medium** (Limbach et al. 2008)

Limbach et al, 2008

- Iron oxide (Fe_3O_4) cored SiO_2 NPs **coated with a nonionic surfactant** effectively **removed during primary treatment**. **Unfunctionalized** NPs **escaped** with the effluent (Jarvie et al, 2009).



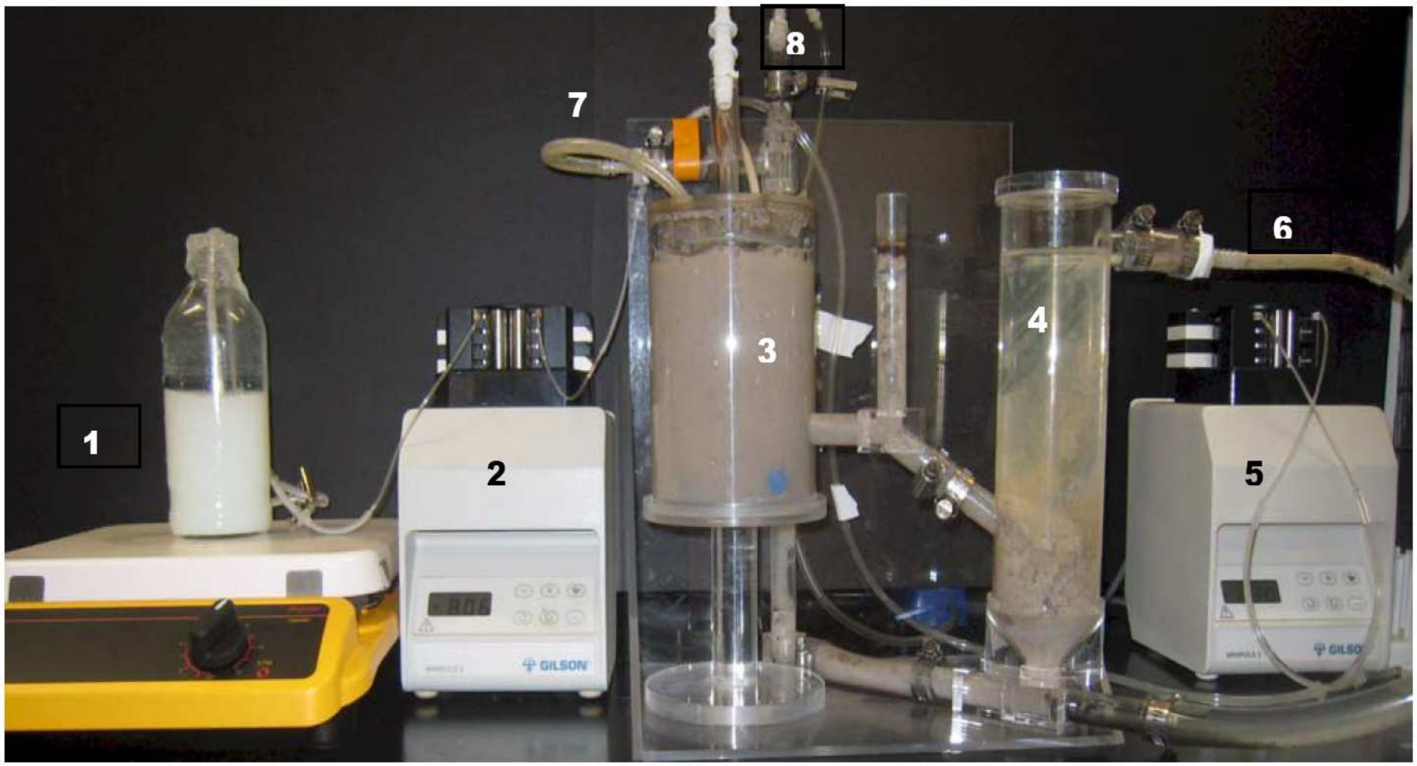
Jarvie et al, 2009

Objectives

- To investigate the removal of CeO_2 nanoparticles (NPs) in municipal wastewater during activated sludge treatment

- To elucidate the mechanisms responsible for their removal from aqueous dispersions

Lab-scale secondary treatment



Aeration tank:

$V_{reactor}$ = 1.19 L
HRT = 9 to 10 hrs

Settler:

$V_{reactor}$ = 0.6 L
HRT = 5 to 6 hrs

[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

Lab-scale secondary treatment

The system was operated under two different conditions:

- **Synthetic wastewater**

  Composition according to OECD

Component	Concentration (mg/L)
Peptone	220
Meat extract	150
Urea	10
K_2HPO_4	8
$NaHCO_3$	200

- **Real wastewater**

  Primary-treated wastewater collected in a weekly basis from a local WWTP

Nanoparticle stock dispersion

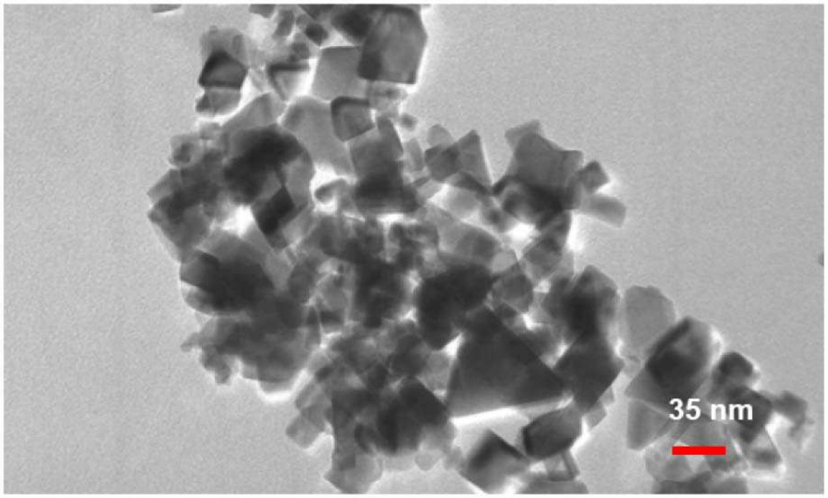
NP Stock:

CeO_2 (50nm)

Concentrated stock prepared by sonication (pH = 3.4)

Concentrated stock diluted in acidic water (pH = 3.4)

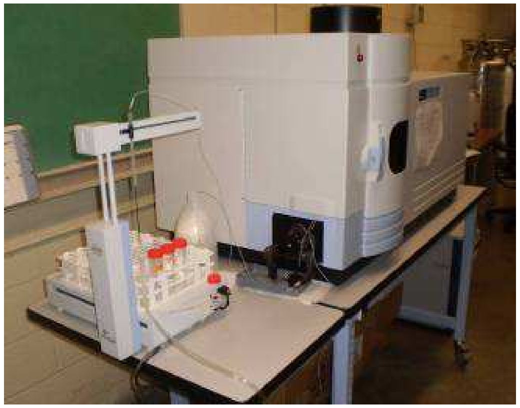
Ultrasonic processor



Transmission electron microscope image of nano-sized ceria with average particle size 50 nm

Fate of nanoparticles

Inductively coupled plasma-optical emission spectroscopy instrument (ICP-OES)



ICP- OES

- **Total Ce concentration**

Microwave-assisted digestion → Reduces interference by organic matter

- **Filtered Ce concentration (< 200 nm)**

Directly measured in ICP-OES

- **Scanning electron microscopy (SEM)**

Image the sample by scanning it with a high-energy electron beam

Reactor performance

- **Chemical oxygen demand (COD)**

Indirect measurement of the organic content

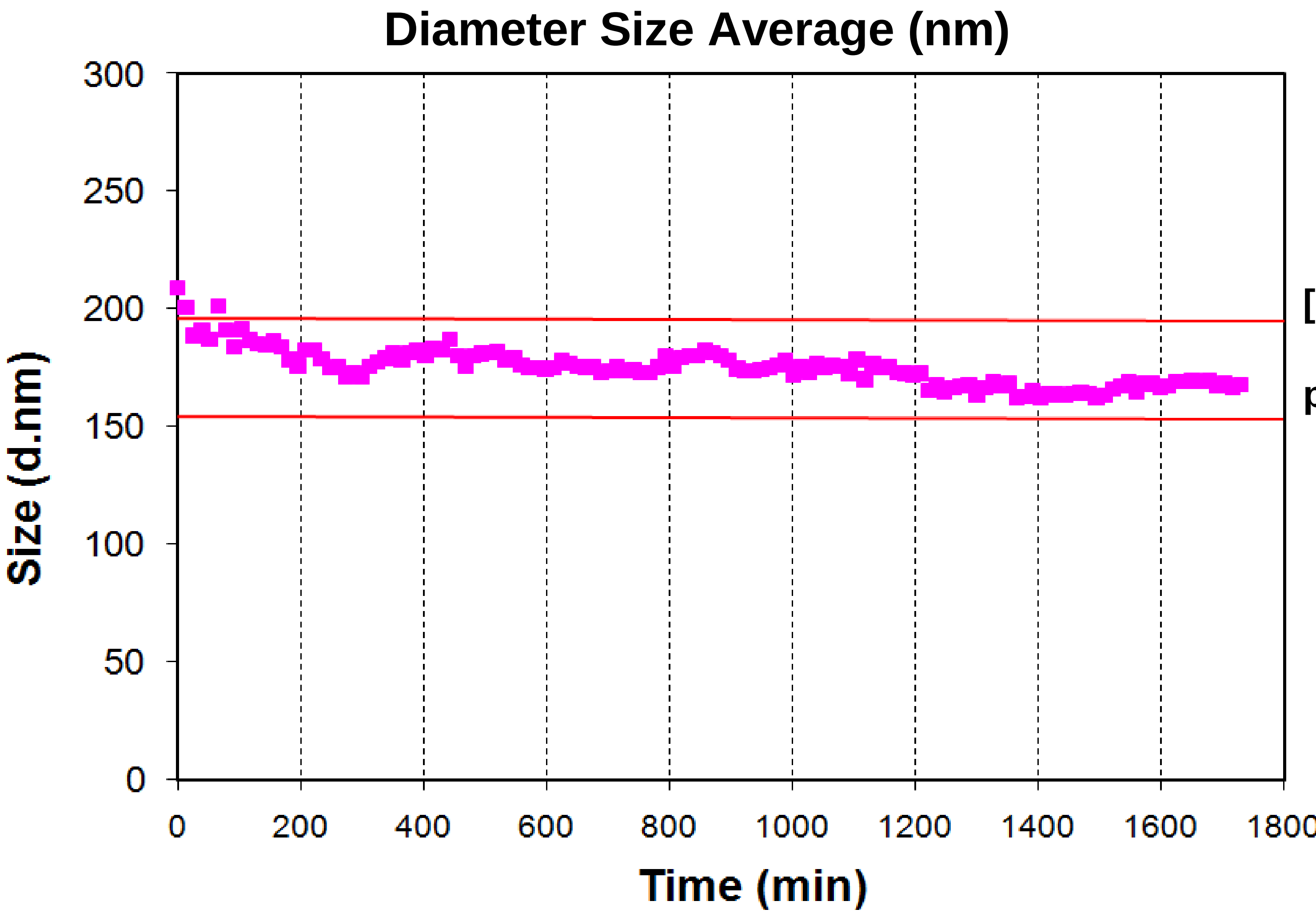
Sample + Strong oxidant —150℃→ Spectrophotometer

- **Acetic acid removal**

Measured by Gas-Chromatography with Flame Ionization Detector (GC-FID)

Agilent 7890A GC

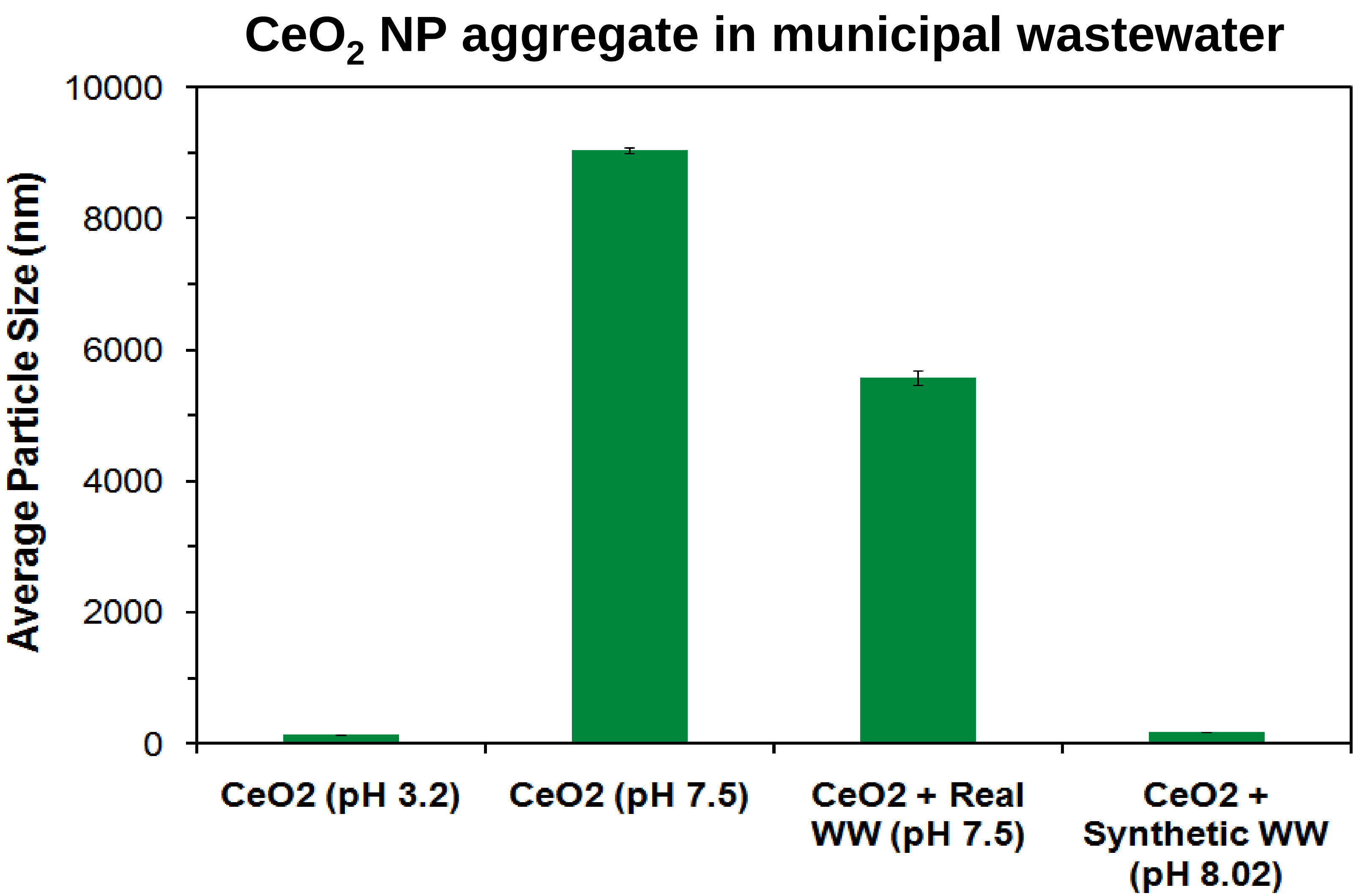
Results: Average particle size (CeO_2)



[CeO_2] = 200 ppm

pH = 3.46

Results: Stability particle size (CeO_2) in aqueous suspension

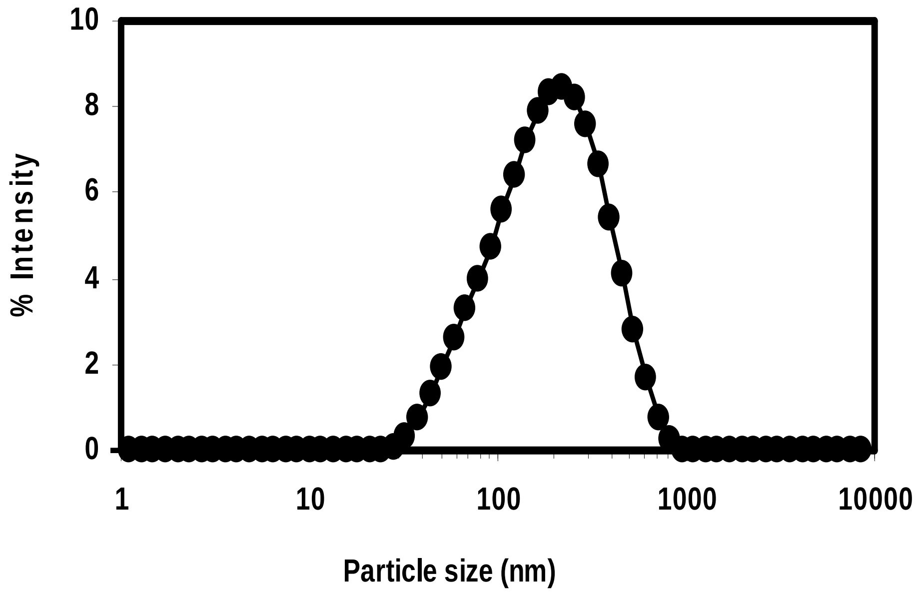


Results: Average particle size (CeO_2)

Average particle size distribution in different media

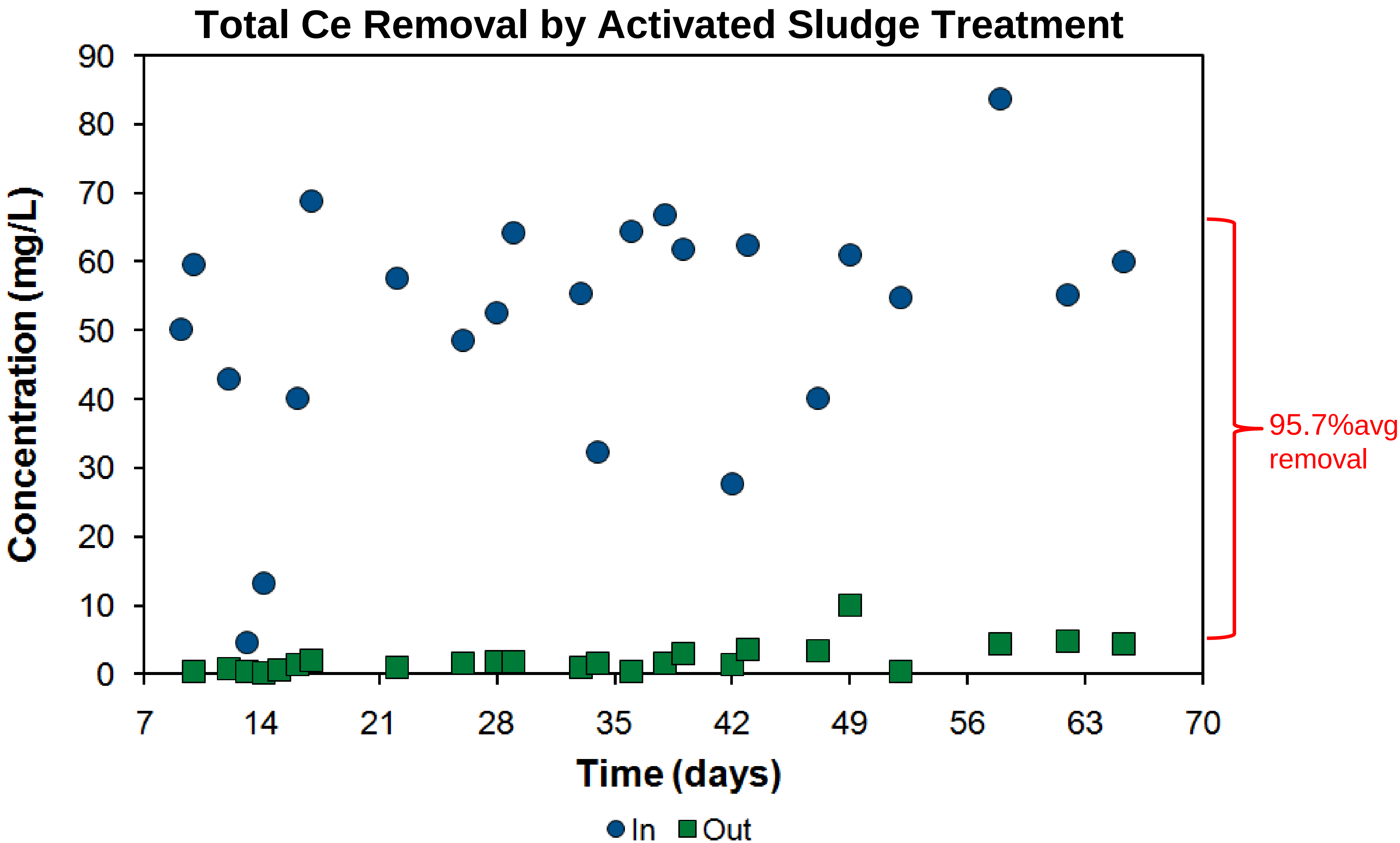
Sample	Avg Particle size (nm)	Std Dev
CeO_2 (pH 3.2)	132	1
CeO_2 (pH 7.5)	9035	46
CeO_2 + Real WW (pH 7.5)	5567	114
CeO_2 + Synthetic WW (pH 8.02)	175	6

Average particle size distribution of nano-sized CeO_2 in acidic media (pH 3.2)

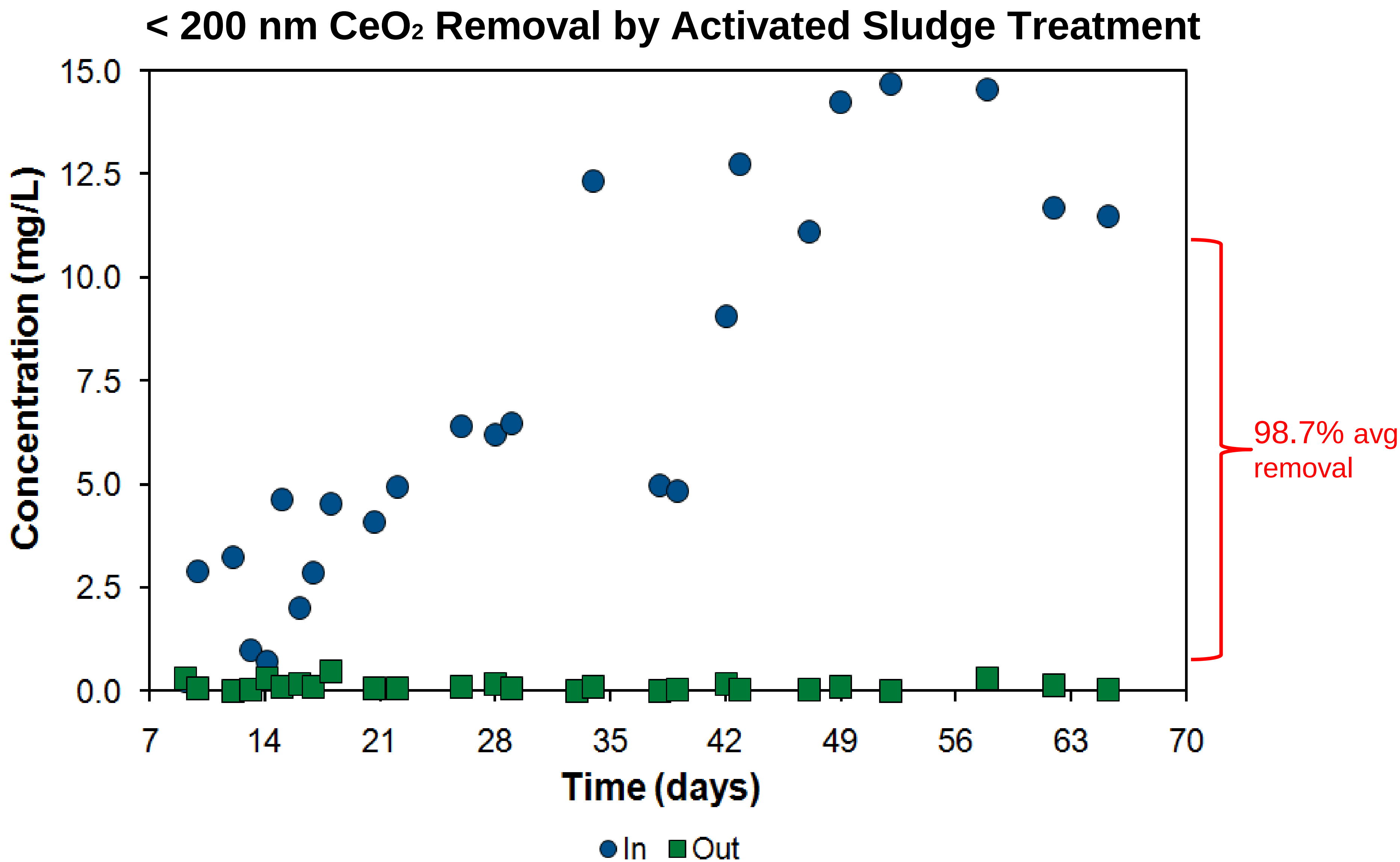


Average particle size (nm) 132 ± 1
Zeta potential (mV) 44.5 ± 1.1

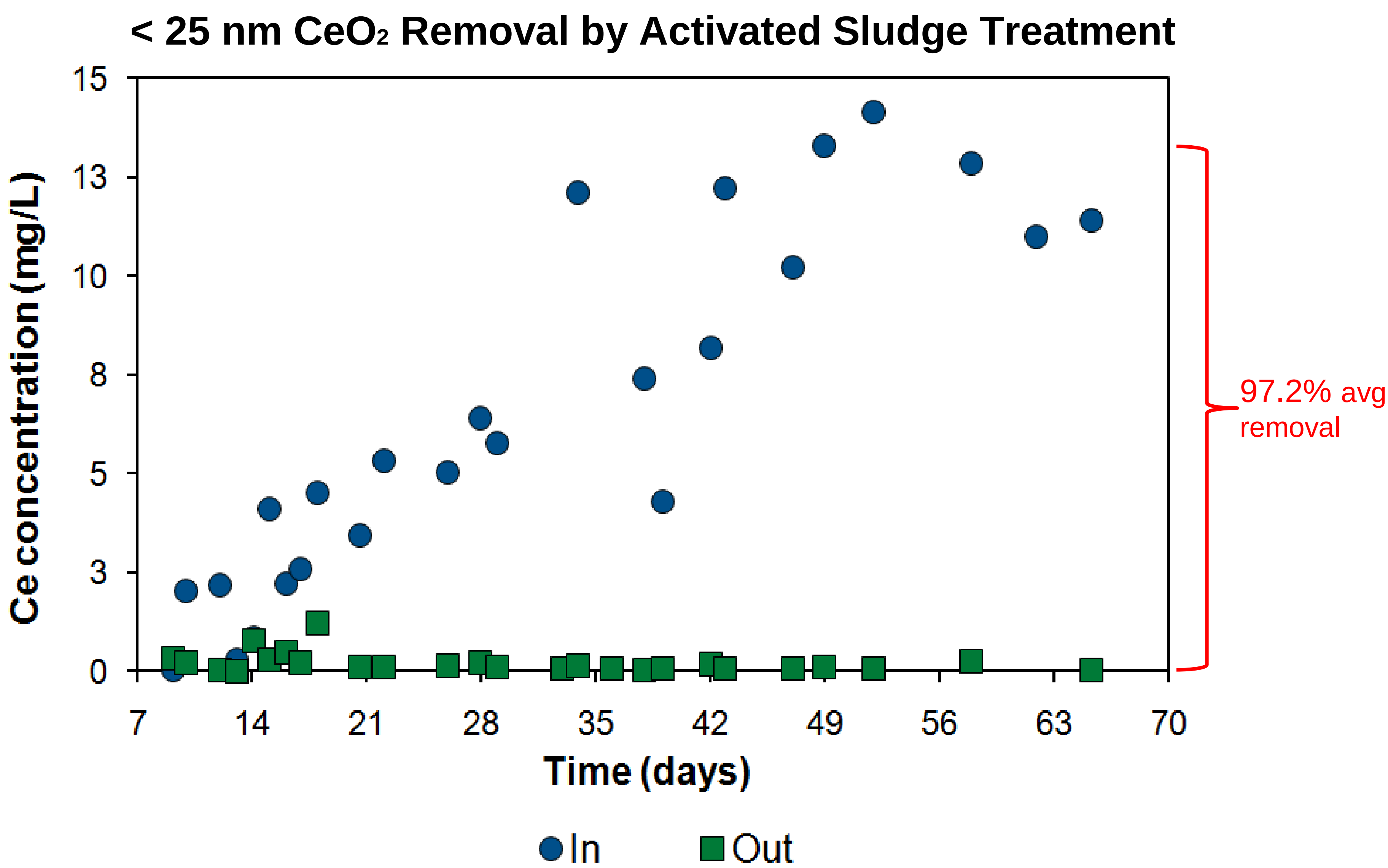
Results: Fate of CeO_2



Results: Fate of CeO_2

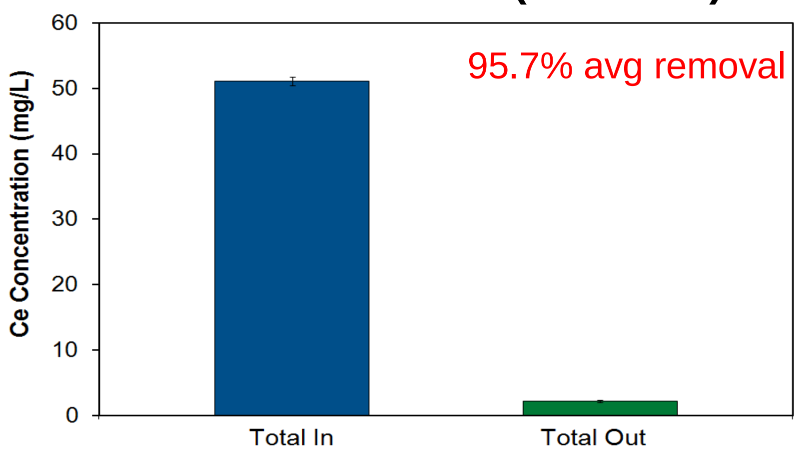


Results: Fate of CeO_2

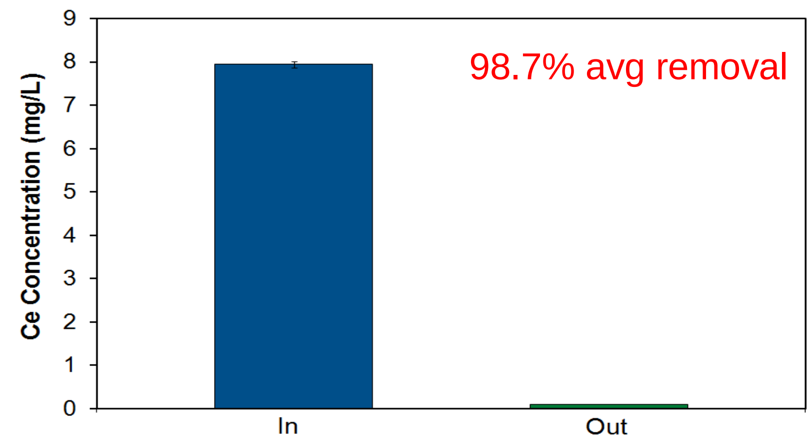


Results: Fate of CeO_2

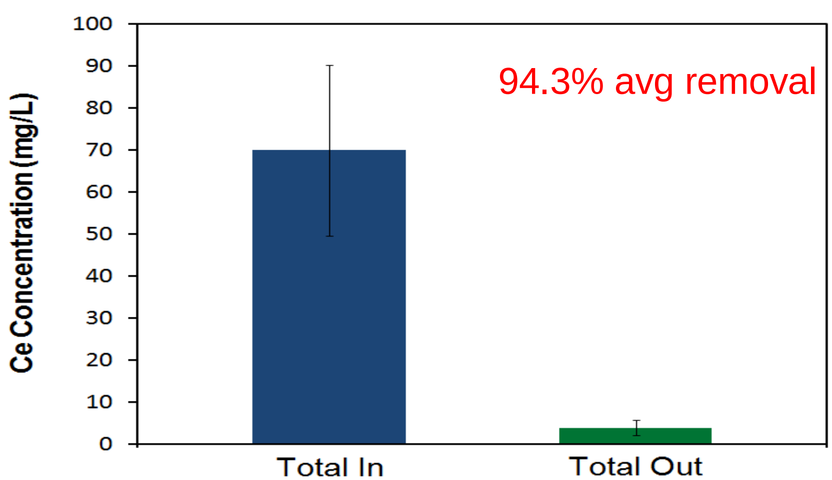
Total Ce removal (Real WW)



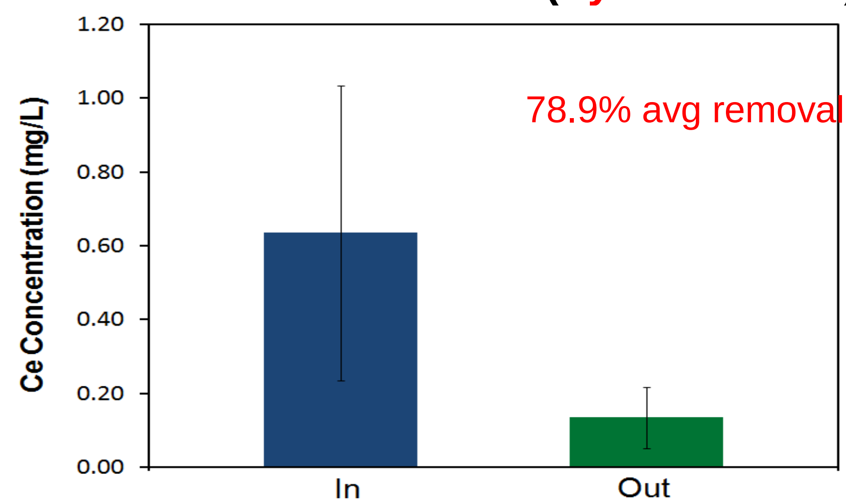
Ce < 200 nm removal (Real WW)



Total Ce removal (Synthetic WW)

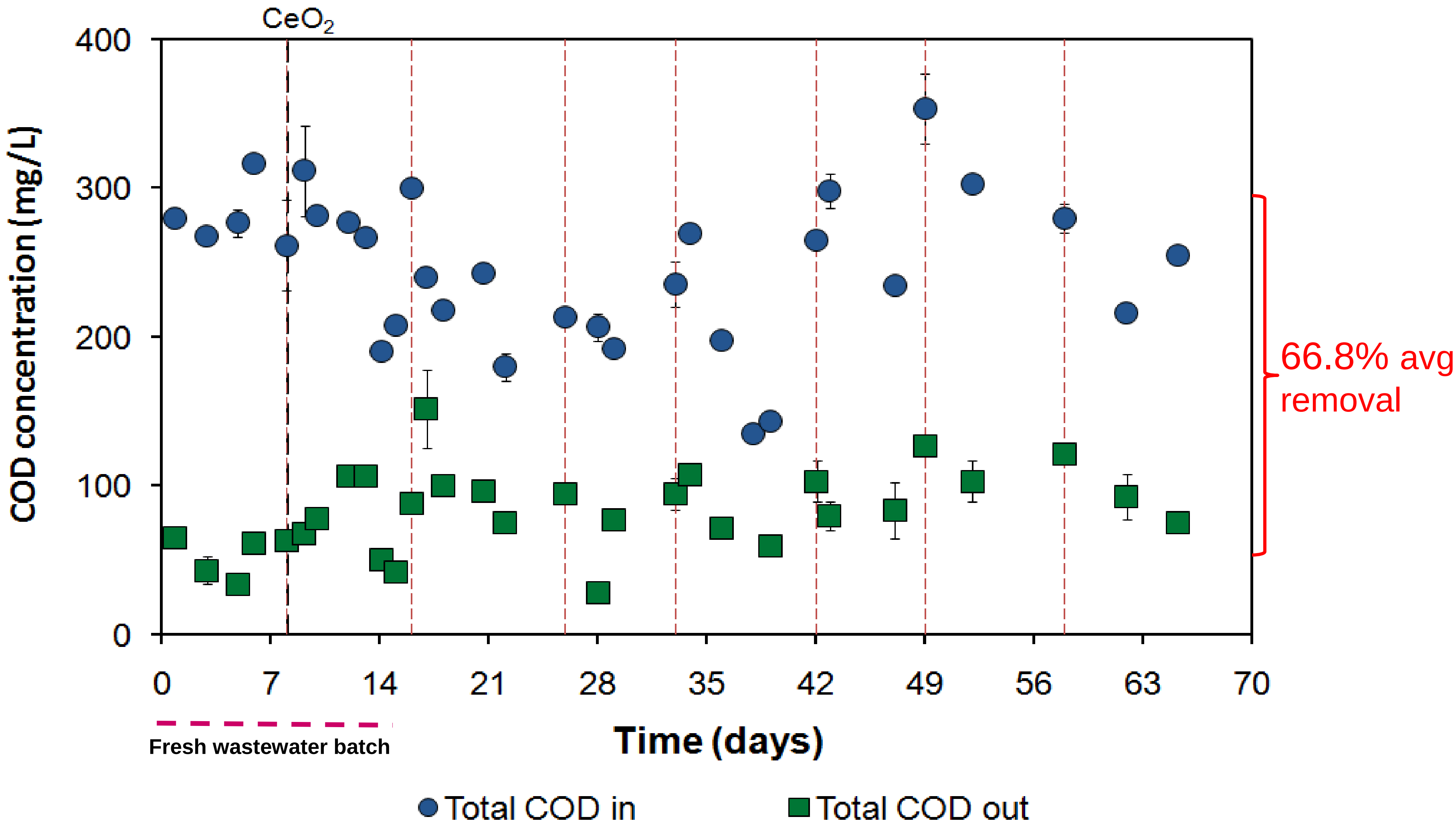


Ce < 200 nm removal (Synthetic WW)

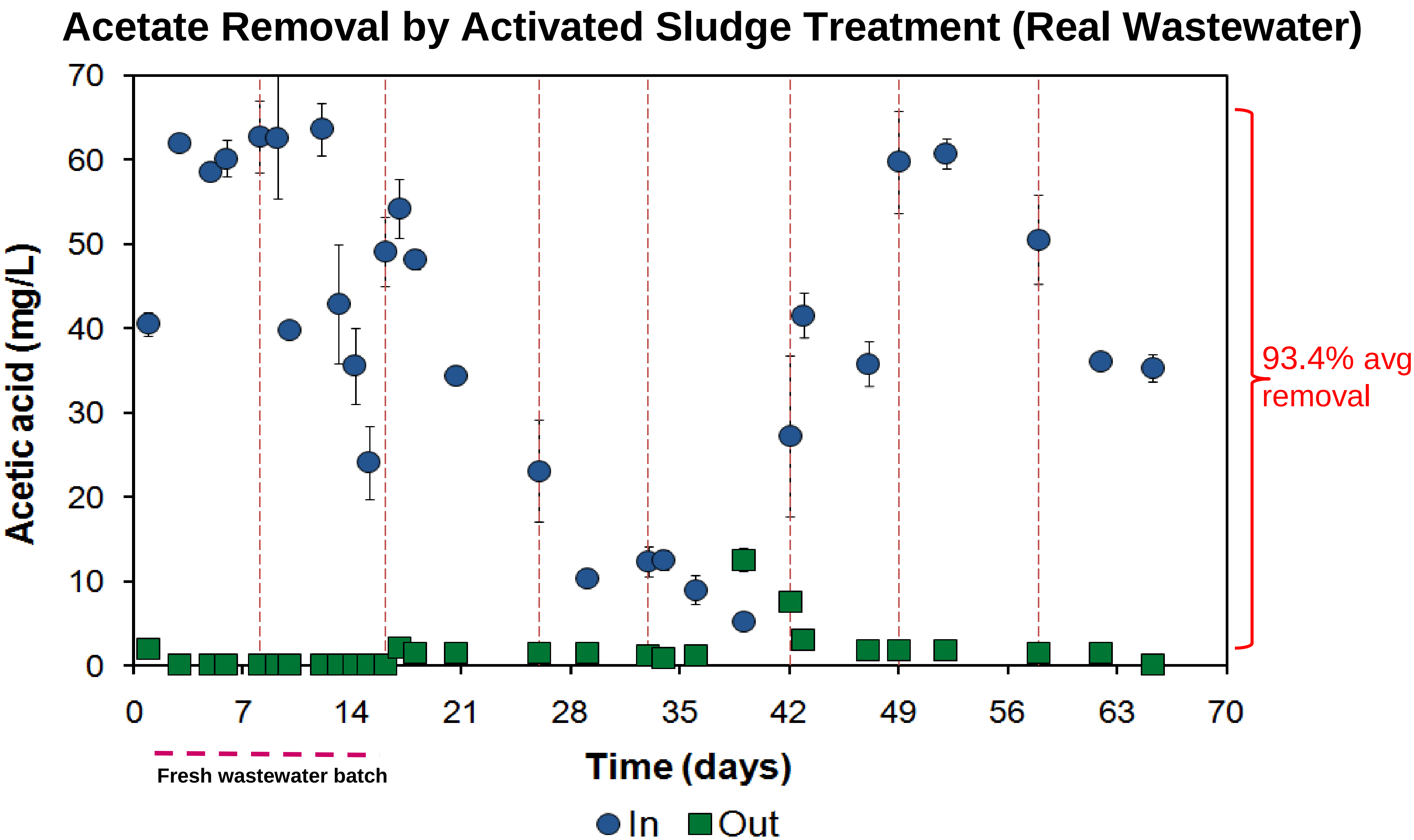


Results: Reactor performance

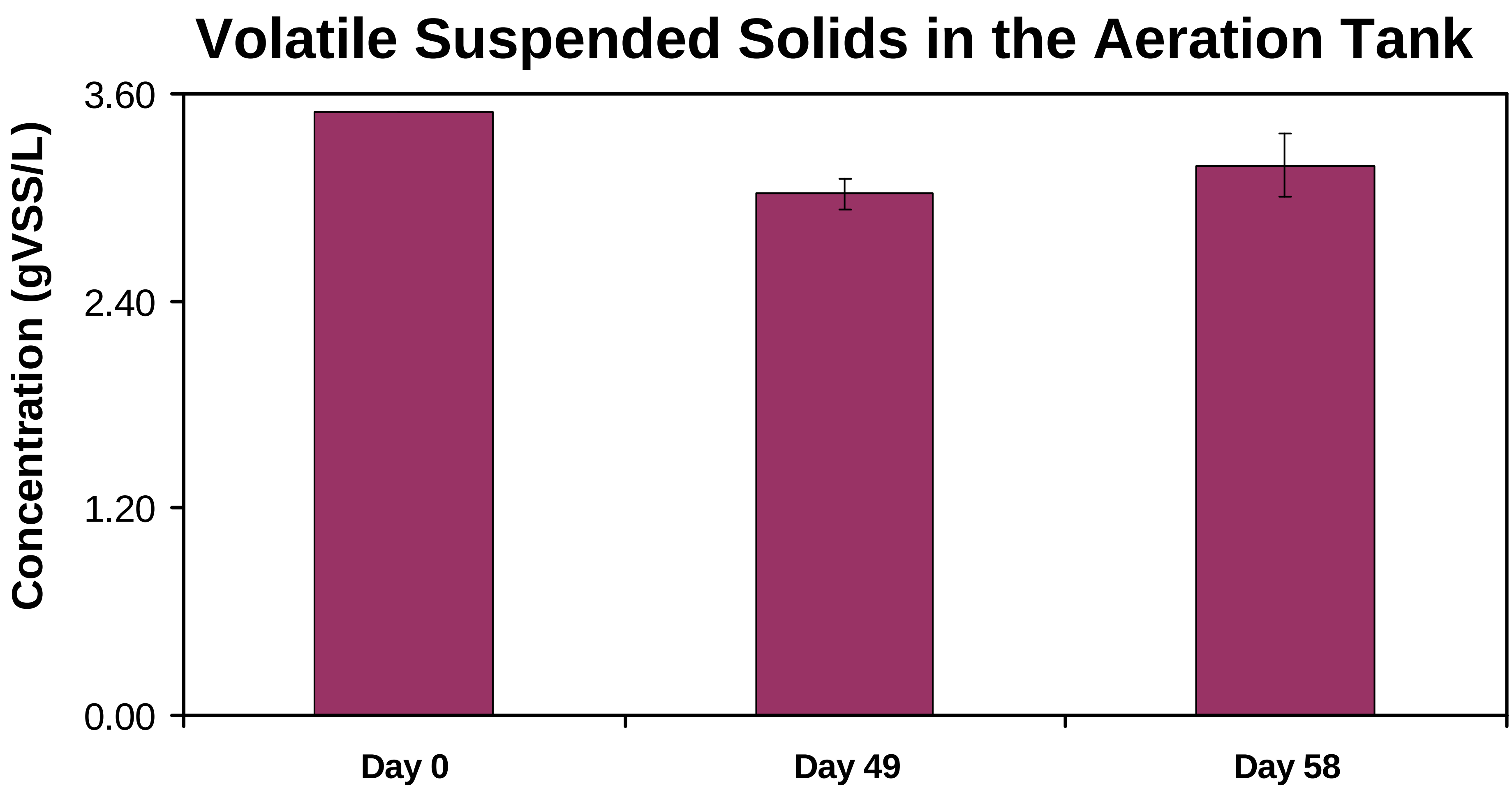
Removal of Organic Matter by Activated Sludge Treatment (Real Wastewater)



Results: Fate of CeO_2

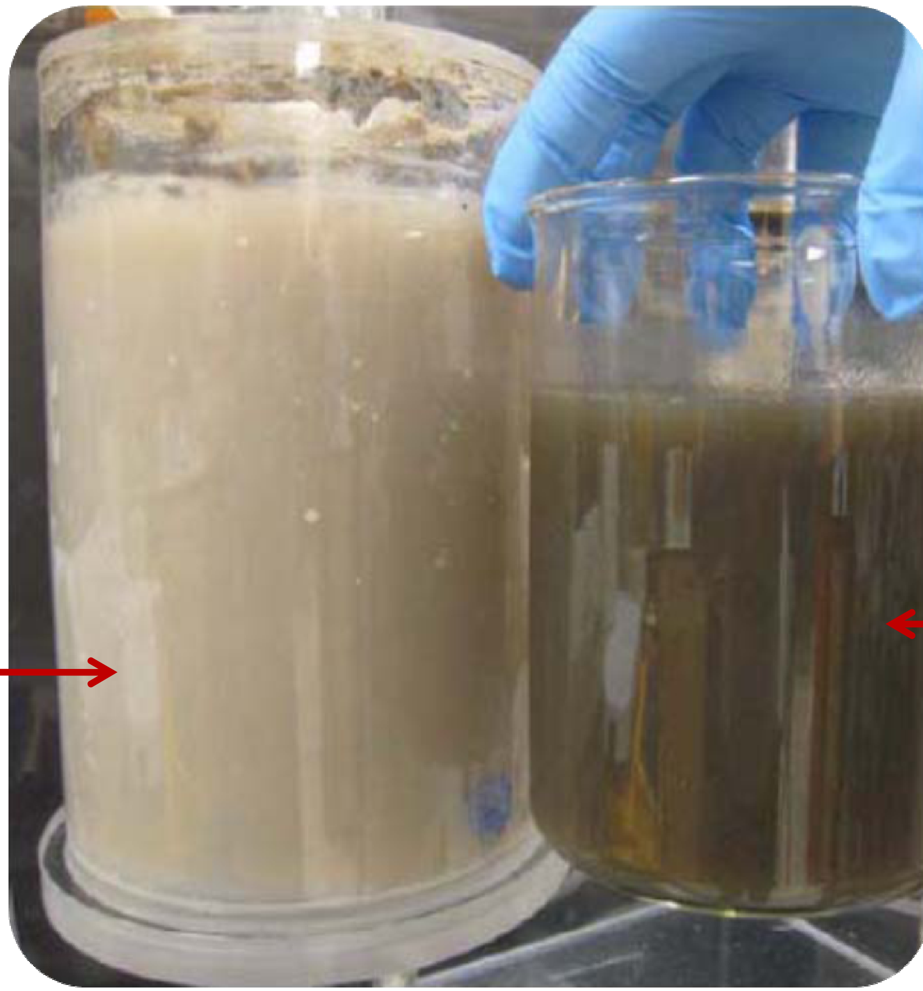


Results: Reactor performance



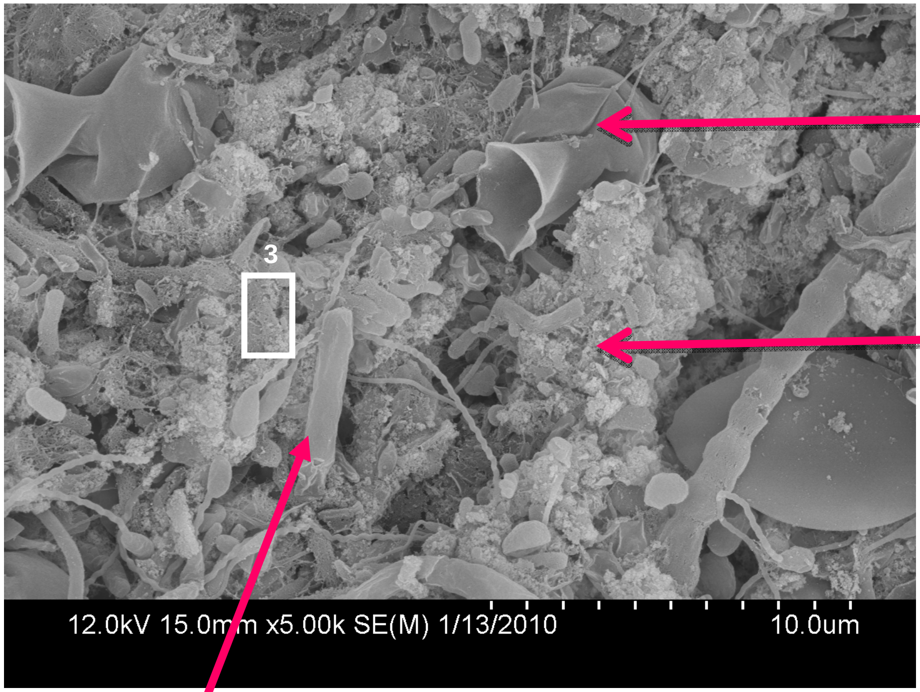
Results: CeO_2 + sludge

Bioreactor



Original sludge
(t= 0 day)

Results: CeO_2 + sludge

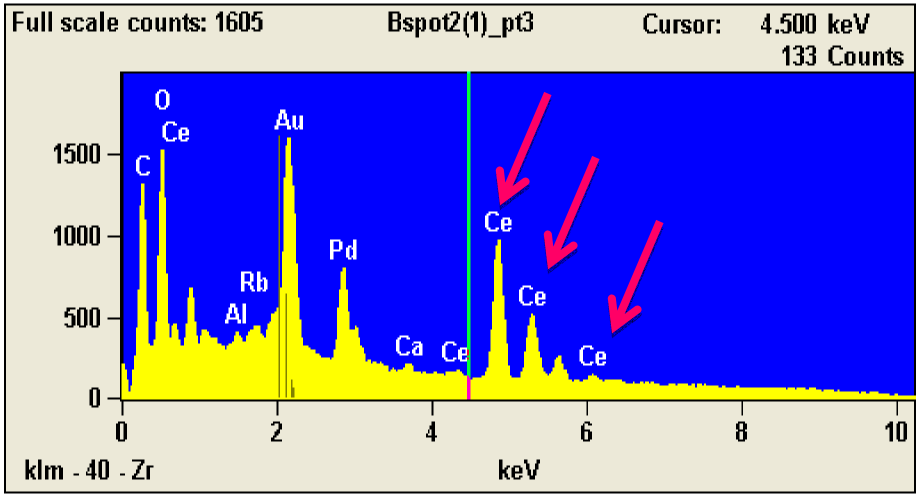


Protozoa

Sample from Bioreactor

Extracellular material

Bacteria



Element microanalysis by energy dispersive X-ray spectroscopy (EDS)

Conclusions

- CeO_2 is highly removed during secondary treatment. Only a small fraction of the NPs (< 5%) detected in the effluent.
- Neutral pH values promote agglomeration of NPs dramatically increasing their average particle size compared to the size in a pH 3 solution.
- CeO_2 did not cause microbial inhibition, as demonstrated by the continuous removal COD and acetate.

Ongoing Work

- Fate of aluminum oxide (Al_2O_3) NPs in municipal wastewater during activated sludge treatment.

Acknowledgments

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