Short-term Chronic Toxicity of Photocatalytic Nanoparticles to Bacteria, Algae, and Zooplankton

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EPA Nanotechnology and the Environment: Applications and Implications
STAR Progress Review Workshop II, August 18-20, 2004, Philadelphia
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“The creation, processing, characterization and utilization of materials, devices, and systems with dimensions on the order of 0.1 to 100 nanometers, exhibiting novel and significantly enhanced physical, chemical, and biological properties, functions, phenomena, and processes due to their nanoscale size.”

The Periodic Table of Nanoparticles

Objectives

(1) To determine the acute toxicity of photocatalytic nanoparticles to a mixed bacterial culture,
(2) To determine the short-term chronic toxicity of photocatalytic nanoparticles to pure bacterial culture, daphnia and green algae,
(3) To determine the short-term chronic toxicity of copper(II) to green algae in the presence of photocatalytic nanoparticles, and
(4) To determine the short-term chronic toxicity of chlorinated phenols to pure bacteria culture, and daphnia in the presence of photocatalytic nanoparticles.
Particle Characteristics

• **Size**
  - procaryotic cells: 0.3 – 2 mm (or 300 – 2000 nm)
  - eucaryotic cells: 2 – 20 mm (or 2000 – 20000 nm)
  - nano-particles: 0.1 – 100 nm

• **Surface charge**

• **Chemical composition**

• **Photocatalysis**
Particle Size

- Turbidity
- Solubility
- Collision

\[ \tau \propto \frac{d^6}{\lambda^4} \]

\[ K_{so} = K_{so}^0 e^{-\frac{12\gamma}{3\rho RTd}} \]

\[ \beta_{kj} = 2\pi(d_j + d_k)(D_j + D_k) \]

\[ D = \frac{\kappa T}{6\pi \eta r} \]

(Sadar 1996)

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Surface Charge

Surface charge of typical nanoparticles and biological substances (Stumm and Morgan, 1996)

Effect of particle size on the surface charge of nano-$\text{TiO}_2$ particles
Photocatalyst

- Photocatalyst materials:
  - GaP: 2.2 eV
  - Si: 1.1 eV
  - CdS: 2.4 eV
  - CdSe: 1.7 eV
  - TiO$_2$: 3.0 eV
  - ZnO: 3.2 eV
  - MoS$_2$: 1.75 eV
  - SnO$_2$: 3.5 eV

- Band positions:
  - Valance band
  - Conduction band

- Types of photocatalysts:
  - R type
  - OR type
  - O type

- Reaction:
  - UV light excites TiO$_2$ to produce electron-hole pairs:
    - $\text{TiO}_2 \rightarrow \text{TiO}_2^-$ (electron)
    - $\text{TiO}_2 \rightarrow \text{TiO}_2^{(h^+)}$ (Hole)

- Oxidation products:
  - $\text{O}_2$ (Oxygen)
  - $\text{H}_2\text{O}$ (Water)
  - $\text{OH}^-$ (Hydroxide)

- Decomposition of water by oxidation:
  - $\text{H}_2\text{O} \rightarrow \text{OH}^-$ (Decompose by Oxidation)
Test Organisms

- **Bacterial:** E. coli; mixed cultures (Microcat-XR)
- **Green algae:** *Selenastrum capricornutum*; algal assemblies
- **Zooplankton:** *Ceriodaphnia dubia*
Testing Conditions

- **Photocatalysts:**
  - IR-sensitive: CdSe, MoS$_2$
  - Visible light-sensitive: GaP, CdS
  - UV-sensitive: TiO$_2$; ZnO; SnO$_2$
- **Soluble toxic chemicals:**
  - Cu(II)
  - Chlorinated HCs
Toxicity Observation

- **Bacteria:**
  - Metabolic activities: Respiration (oxygen demand, biokinetics constant)
  - Die-off
  - Lipid peroxidation: Malondialdehyde (MDA)
  - DNA sequencing
  - TEM, SEM

- **Algae:**
  - Cell density
  - Chlorophyll
  - TEM, SEM

- **Zooplankton:**
  - Survival
  - Reproduction
  - SEM, TEM

**Point estimation techniques**
- LC50; IC25; IC50; EC50

**Statistical analysis** (Fisher, Dunnett, Steel)
- LEOC ; NEOC

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Expected Results

• Determine the IC50, LC50, LEOC, NEOC values of selected testing organisms in the presence of selected photocatalytic nanoparticles.

• Understand the mechanism of the ecotoxicity of nano-particles: particle size, chemical composition, surface charges and photocatalysis.

• Understand the ecotoxicity of chemical hazards as affected by potocatalytic nanoparticles.