Photocatalytic degradation of naphthenic acids mixtures on TiO$_2$ particles

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Outline of the Presentation

• What is Advanced Oxidation Process (AOP)
• Applications of Photocatalysis
• Photocatalysis by semiconductors
• Materials and analysis
• Results and discussions
Advanced Oxidation Process (AOP)

1 Homogeneous photolysis
(UV/H₂O₂ and UV/O₃)

O₃/H₂O₂ + UV → 3(•OH)

Dark Homogeneous oxidation:
This process DOES NOT employ UV light; it usually involves the use of Fenton’s reaction.

Fe(II) + H₂O₂ → Fe(III) + •OH + OH⁻
Advanced Oxidation Process (AOP)

1. Homogeneous photolysis (UV/H\textsubscript{2}O\textsubscript{2} and UV/O\textsubscript{3})

2. Dark Homogeneous oxidation: This process does not employ UV light; it usually involves the use of Fenton’s reaction.

3. Heterogeneous photolysis (UV/TiO\textsubscript{2}): Solid particles of TiO\textsubscript{2} absorb UV light and generate OH•

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Fig. 4. Flow Chart of a TFFBR reactor (adopted from Goslich et al. (1997)).
Band Gap for TiO₂ = 3.2 eV $\approx 400$ nm
 Proposed Mechanism

\[ \text{TiO}_2 + h^+ \rightarrow e^-_{\text{cb}} + h^+_{\text{vb}} \]

\[ e^-_{\text{cb}} + h^+_{\text{vb}} \rightarrow \text{Heat} \]

\[ e^-_{\text{cb}} \rightarrow e^-_{\text{trap}} \]

\[ h^+_{\text{vb}} \rightarrow h^+_{\text{trap}} \]

\[ H^+_{\text{trap}} + H_2O \rightarrow \cdot\text{OH}_{\text{trap}} + H^+ \]

- e – electron
- h – hole
- vb – valence band
- cb – conduction band

Fig. 4 Applications of photocatalyst
Tailings ponds adjacent to the Athabasca River hold water contaminated by naphthenic acids.

What are Naphthenic Acids?

Naphthenic acids are carboxylic acids which includes linear and/or saturated ring structures

\[ \text{C}_n\text{H}_{2n+Z}\text{O}_2 \]

n --- the carbon number
Z --- number of hydrogen atoms that are lost as the structure becomes more compact.
Materials and analysis

Naphthenic Acids
- Fluka naphthenic acids mixtures
- Syncrude tailing pond water extracts
- Model naphthenic acid (4MCHCA)

Titanium Dioxide (TiO₂): (Degussa P25), 20% rutile and 80% anatase.

Analysis
Mass Spectrometry: Loop Injection, ESI Negative ion mode for the mixtures; Selected Ion Monitoring (m/z 141.8) for the model compound
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Rutile

Anatase
Mass spectrum of naphthenic acids mixture in tailing pond water before and after the irradiation over TiO₂ under natural sunlight.

3D profile of naphthenic acids mixture in tailing pond extract before natural sunlight irradiation over TiO₂ suspension.
3D profile of naphthenic acids mixture in tailing pond extract after natural sunlight irradiation over TiO$_2$ suspension.

Comparison of relative abundance of naphthenic acids mixtures in tailing pond water before (solid line) and after (dashed line) natural sunlight irradiation over TiO$_2$ at different Z values.
Concentration change of commercial Fluka naphthenic acids mixtures under various photodegradation schemes.
Concentration change of naphthenic acids mixtures in tailing pond waters at various light sources.

Concentration change of 4MCHCA under various irradiation conditions.
Concentration changes of Naphthenic acid mixtures and model compound under various conditions

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<th>C</th>
<th>D</th>
<th>D'</th>
<th>Flu</th>
<th>Flu'</th>
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<td>1.16</td>
<td>0</td>
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C = Control; D = Dark; Flu = Fluorescent light; S = Sunlight; * = + TiO₂
MHCA = 1-Methyl-hexanecarboxylic acid

Proposed Mechanism

Scheme I (h⁺)

RCH₂COO⁻ + h⁺ →
RCH₂COO⁻ →
·RCH₂ + CO₂
RCH₂• + RCH₂• → RCH₂CH₂R

Scheme II (· OH)

· OH + RCH₂COO⁻ → RCH•COO⁻ + H₂O
Conclusions

Naphthenic acid can be degraded with TiO$_2$ under both fluorescent light and natural sunlight.

Photocatalysis with TiO$_2$ is more efficient under natural sunlight than under fluorescent light.

The degradation is much more efficient at lower |Z| values ( -Z = 0 to 6.) Compounds with higher |Z| values are too bulky to reach the surface of the catalyst so the overall catalytic efficiency is lower.

Thank you very much!