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Electrochemical Oxidation of PAHs in Water from Harbor Sediment Purification

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Introduction

PAHs (Polycyclic Aromatic Hydrocarbons)
- One of the main POPs (Persistent Organic Pollutants), main sources are burning of fossil fuels (oil and coal), wood stove heating, cigarette smoke, production and use of tar
- Highly toxic, carcinogenic and mutagenic for human beings
- Low threshold values in drinking water: 0.005 - 0.010 µg L⁻¹
- Chemical characteristics: Lipophilic and hence low water solubility, primarily found in soil and sediment, persistent, recalcitrant, and non-reactive

Problem
Removal of sediment from harbors produce PAH-containing process water, which needs treatment before discharge to the marine recipient.

Objective
Degradation of PAHs in saline process water by means of electrochemical oxidation.

Theory
Electrochemical oxygen transfer reaction

Materials & Methods

The cell
Acetic (C₂H₄O₄)₂

The setup
Cathode (SO₂⁻)

Process water
salinity 1.1 v/v %

Model compounds
Naphthalene
Fluoranthene
Pyrene

Results & Discussion I

Tests on sediment runoff water (process water)

Electrochemical treatment approach:
- PAH removal obtained to below discharge limit (0.005 µg L⁻¹)
- Energy consumption: 32.5 kWh m⁻³

Treatment by EO generated chemical oxidant (electro-chlorination):
- Successful PAH removal obtained
- Energy consumption: 38.8 kWh m⁻³

Detailed model solution studies

Reaction kinetics & influence of current density

Results & Discussion II

Influence of electrolyte

- \( \text{Na}_2\text{SO}_4 / \text{NaNO}_3 \) (Direct oxidation)
- \( \text{M} \): anode; \( \text{R} \): PAHs
- \( \text{M} + \text{H}_2\text{O} \rightarrow \text{M}^+ \text{OH}^- + \text{H}^+ + e^- \rightarrow \text{MO} + \text{H}^+ + e^- \)
- \( \text{MO} + \text{R} \rightarrow \text{M} + \text{RO} \)
- \( \text{NaCl} \) (Indirect oxidation)
- \( \text{R} \): PAHs
- \( 2\text{Cl}^- \rightarrow \text{Cl}_2 \) + 2e⁻
- \( \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCI} + \text{Cl}^- + \text{H}^+ \)
- \( \text{HOCI} \rightarrow \text{OCl}^- + \text{H}^+ \)

Efficiency considerations

k: current efficiency constant
- Relative measure of the efficiency of the oxidation of the specific PAH at different experimental settings

Halogenated byproduct formation

Formation of unwanted chlorinated and brominated byproducts is a risk when applying electrochemical oxidation in sea water. However, the low amount of mono- and dihalogenated naphthalene products detected during the treatment where all further degraded. Byproducts of fluorenone and pyrene were not found.

Possible routes of formation
- \( \text{H OCI} + \text{Br}^- \rightarrow \text{CT}^- + \text{HOBr} \)
- \( \text{HOCI} + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_5\text{Cl} + \text{H}_2\text{O} \)
- \( \text{HOBr} + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_5\text{Br} + \text{H}_2\text{O} \)
- \( \text{HOBr} + \text{C}_2\text{H}_5\text{Br} \rightarrow \text{C}_2\text{H}_4\text{Br}_2 + \text{H}_2\text{O} \)

Conclusions
Electrochemical purification of sediment run off water:
- Needed? In deed!
- Feasible? Absolutely
- Expensive? Probably

Successful removal of PAHs was obtained by the electrochemical oxidation technique. Cost optimization is possible, which maybe will make the approach economically feasible. Halogenated byproducts are formed, but does not pose a significant risk due to subsequent degradation in the treatment process.

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