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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 produces 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

Chlorine-mediated oxygen transfer

Materials & Methods

Cell

The cell

Anode (Cu/Cu_{2}O, Cu)

Cathode

Rationalization of experimental setup

Evaluation of experimental data

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 (0.010 µg L^{-1})
- Energy consumption: 13.2 kWh m^{-3}

Treatment by EO generated chemical oxidant (electro-chlorination):
- Successful PAH removal obtained
- Energy consumption: 0.8 kWh m^{-3}

Detailed model solution studies

Reaction kinetics & influence of current density

Results & Discussion II

Influence of electrolyte

NaSO_{4} / NaNO_{3} (Direct oxidation)

M: anode; R: PAHs

M + H_{2}O \rightarrow M^{+}OH + \cdot \Delta + \cdot \Delta \rightarrow \cdot \Delta + \cdot \Delta + \cdot \Delta

Influence of electrolyte

NaCl (Indirect oxidation)

R: PAHs

2Cl^{-} \rightarrow Cl_{2} \rightarrow Cl_{2}

Cl_{2} + H_{2}O \rightarrow HOCI + Cl^{-} + H^{+}

HOCI + OCT + R \rightarrow BO / ROH + CT

Efficiency considerations

k_{b}: current efficiency constant

Relative measure of the efficiency of the oxidation of the specific PAH at different experimental settings

k: kinetic rate constant

Comparative treatment costs and percent efficiency at different current densities for PAHs in process water

Halogenated byproduct formation

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

Possible routes of formation

HOCI + Br^{-} \rightarrow Cl^{-} + HBr

HOCI + C_{2}H_{2} \rightarrow C_{2}H_{2}Cl + H_{2}O

HBr + C_{2}H_{2}Br^{-} \rightarrow C_{2}H_{2}Br + H_{2}O

HOCI + C_{2}H_{2}Br^{-} \rightarrow C_{2}H_{2}Br + H_{2}O

Conclusions

Electrochemical purification of sediment runoff 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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