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Publication date: 2010

Document Version
Early version, also known as pre-print

Link to publication from Aalborg University

Citation for published version (APA):

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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

The cell

The setup

Process water

salinity 1 g/l, %

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 (0.00 µg L⁻¹)
- Energy consumption: 12.3 kWh m⁻³

Treatment by EO generated chemical oxidant (electro-chlorination):

- Successful PAH removal obtained
- Energy consumption: 8.8 kWh m⁻³

Detailed model solution studies

Reaction kinetics & influence of current density

Results & Discussion II

Influence of electrolyte

- Na₂SO₄ / NaNO₃ (Direct oxidation)
  M: anode; R: PAHs
  M + H₂O → M⁺OH⁻ + H⁺ + e⁻ → MO + H⁺ + e⁻
  MO + R = M + RO
- NaCl (Indirect oxidation)
  R: PAHs
  2C = 2Cl⁻ + 2e⁻
  Cl⁻ + H₂O → HOCl + Cl⁻ + H⁺
  HOCl + OCT → R + RO / BOH + CT

Efficiency considerations

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

Comparison of reaction rates and percent efficiency at different current densities for naphthalene in a M NaCl electrolyte on a carbon electrodes, for the reaction Naphthalene → Carboxylic Acid

Halogenated byproduct formation

- Formation of unwanted chlorinated and brominated byproducts is a risk when applying electrochemical oxidation in seawater; however, the amount of mono- and dibrominated naphthalene products detected during the treatment was far less degraded. Byproducts of fluoranthene and pyrene were not found.

Possible routes of formation

HOCl + Br⁻ → Br + HOBr
HOCl + C₆H₆ → C₆H₅Cl + H₂O
HOBr + C₆H₆ → C₆H₅Br + H₂O
HOBr + C₆H₅Br → C₆H₅Br₂ + H₂O

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.

Acknowledgements

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