Electrochemical Oxidation of PAHs in Water from Harbor Sediment Purification

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REMEDIATION OF CHLORINATED AND RECALCITRANT COMPOUNDS
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Introduction

PAHs (**P**olycyclic **A**romatic **H**ydrocarbons)

- 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

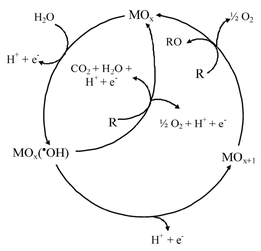
Problem

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.

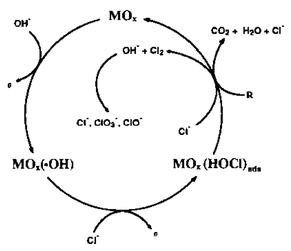
Theory



Electrochemical oxygen transfer reaction

← Scheme of the direct electrochemical oxidation of organic compounds on "active" and "nonactive" anodes. Adapted from Comninellis, C. Electrochim Acta **1994**, 39, 1857.

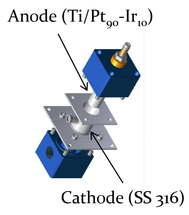
Scheme of indirect chlorine-mediated electrolysis. From Bonfatti, F; Ferro, S; Lavezzo, F; Malacarne, M; bLodi, G; De Battisti, A. J Electrochem. Soc. **2000**, 147, 592 →



Chlorine-mediated oxygen transfer

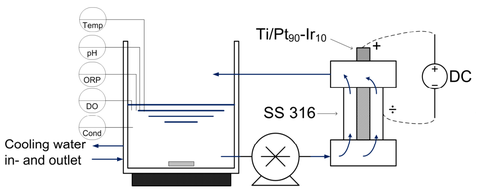
Materials & Methods

The cell



Non-active anode

The setup

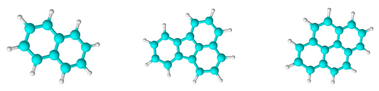


Batch recirculation experimental setup, Q = 430 L h^{-1}, V = 3 L (model solution) and 10 L (process water).

Process water

salinity 1 $^{w}/_{w}$%

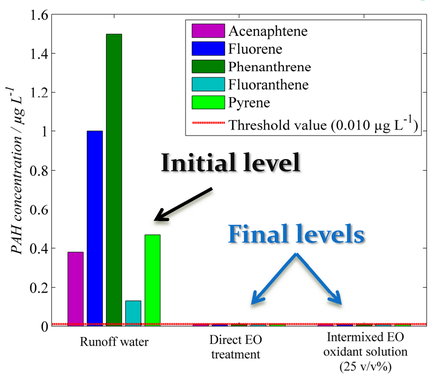
Model compounds



Naphthalene Fluoranthene Pyrene

Results & Discussion I

Tests on sediment runoff water (process water)



Electrochemical treatment of runoff water from disposal and purification of harbor sediment, which is pumped ashore to upland sites. The initial concentrations of PAHs are low, but treatment is still required to maintain the discharge limits.

Electrochemical treatment approach:

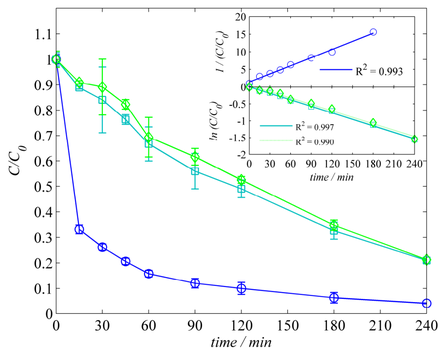
- PAH removal obtained to below discharge limit (0.010 µg L^{-1})
- Energy consumption: 13.2 kWh m^{-3}

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

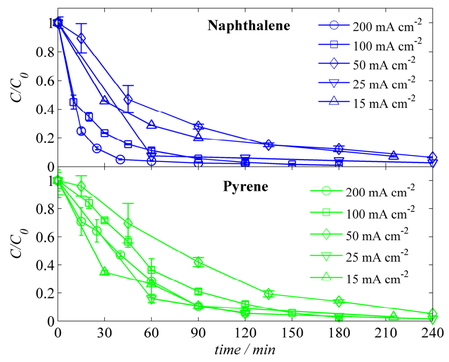
- Successful PAH removal obtained
- Energy consumption: 18.8 kWh m^{-3}

Detailed model solution studies

Reaction kinetics & influence of current density



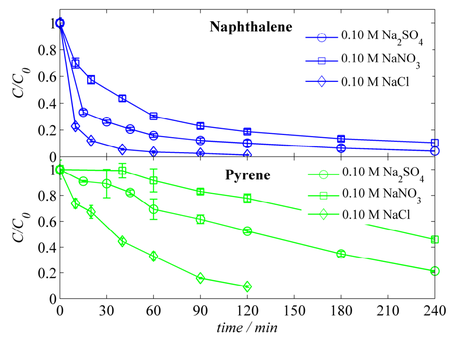
The evolution of the relative concentrations of (○) naphthalene, (□) fluoranthene, and (◊) pyrene during electrochemical oxidation in 0.10 M Na_2SO_4 electrolyte at 200 mA cm^{-2}. Subplot: The standard kinetic analysis, which showed difference in reaction kinetics.



The influence of current density on the evolution in the relative concentrations during electrolysis in 0.14 M NaCl electrolyte.

Results & Discussion II

Influence of electrolyte



The influence of electrolyte composition on the evolution in the relative concentrations during electrolysis at a constant current density of 200 mA cm^{-2}. Due to a very similar behavior of fluoranthene and pyrene, only pyrene is shown in the plot.

- Na_2SO_4 / $NaNO_3$ (Direct oxidation)

M: anode ; *R*: PAHs

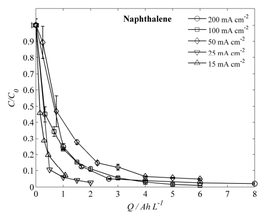
$$M + H_2O \rightarrow M(^{\bullet}OH) + H^+ + e^- \rightarrow MO + H^+ + e^-$$
$$MO + R \rightarrow M + RO$$

- NaCl (Indirect oxidation)

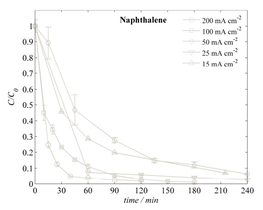
R: PAHs

$$2Cl^- \rightarrow Cl_2 + 2e^-$$
$$Cl_2 + H_2O \rightarrow HOCl + Cl^- + H^+$$
$$HOCl \rightleftharpoons OCl^- + H^+$$
$$HOCl / OCl^- + R \rightarrow RO / ROH + Cl^-$$

Efficiency considerations



Degradation of naphthalene versus the amount of charge passed through the solution, *Q* (Ah L^{-1}).



Degradation of naphthalene versus time.

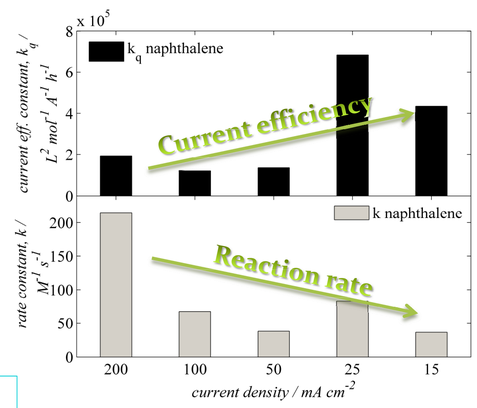
kq: current efficiency constant
Relative measure of the efficiency of the oxidation of the specific PAH at different experimental settings

$$\frac{d[Naphthalene]}{dQ} = -k_q \cdot [Naphthalene]^2$$

k: kinetic rate constant

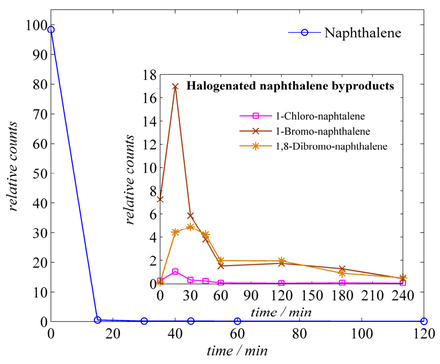
$$\frac{d[Naphthalene]}{dt} = -k \cdot [Naphthalene]^2$$

As the current density was decreased, the rate of reaction rate slowed down, but the current efficiency went up. At the low current densities, a higher yield of PAH degradation was obtained per spent ampere (lower cost), but the necessary reaction time was higher (larger reservoir dimensions).



Comparison of reaction rates and current efficiencies at different current densities for naphthalene in 0.14 M NaCl electrolytes. Naphthalene is chosen as an example, but the trends were similar for all three PAHs.

Halogenated byproduct formation



Removal of naphthalene and halogenated byproducts in 0.10 M NaCl + 0.001 M KBr (model sea water) at 25 mA cm^{-2} and pH 6.

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 fluoranthene and pyrene were not found.

- Possible routes of formation

$$HOCl + Br^- \rightleftharpoons Cl^- + HOBr$$
$$HOCl + C_8H_{10} \rightarrow C_8H_9Cl + H_2O$$
$$HOBr + C_8H_{10} \rightarrow C_8H_9Br + H_2O$$
$$HOBr + C_8H_9Br \rightarrow C_8H_8Br_2 + H_2O$$

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.

Acknowledgements

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ODENSE HAVN
watersafe.dk innovative water technologies

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