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Electrochemical degradation of PAH compounds in model solutions and process water from removal of harbor sediment

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The present study has investigated the possibility to apply electrochemical oxidation in treatment of polycyclic aromatic hydrocarbons (PAHs) in water. PAHs are byproducts of incomplete combustion or hydrolysis of organic materials with recalcitrant and strong mutagenic/carcinogenic properties [1]. The family of PAH pollutants has been found widespread with high concentrations in different water bodies all over the world, and the compounds pose even at very low concentrations a great threat to ecological and human health due to their benzene analog structures. PAHs are hydrophobic compounds and their persistence in the environment is mainly due to their low water solubility [2]. Once PAHs enter into the water systems, it is difficult to remediate these by conventional methods, as PAHs are essential recalcitrant, persistent, and non-reactive in water [1].

Electrochemical oxidation of organic pollutants in contaminated water has in the recent years showed to be a versatile, non-selective, and efficient technique in the abatement of a wide range of organic pollutants [3]. The contaminated water is simply passed through electrodes in an electrochemical cell, where the organics are oxidized directly on the anode surface and/or indirectly by electrochemically generated oxidants, the removal rate and efficiency depending on several parameters as electrode material, electrolyte composition, pH etc [4].

The electrochemical oxidation of the PAHs compounds naphthalene, flouranthene, and pyrene in water has in the present work been investigated in model solutions considering variations in experimental parameters as current density, electrolyte composition, and electrolyte concentrations. The investigation has been performed in a batch recirculation experimental setup at constant temperature with a commercial cell of tubular design with Ti/Pt₉₀-Ir₁₀ anode and SS 316 cathode operated at galvanostatic conditions. The three investigated electrolytes were Na₂SO₄, NaNO₃, and NaCl, the concentration range was 0.6-1.4 M, and the current densities were 50-200 mAcm⁻².

All three of the subjected PAHs were nicely degraded during the electrochemical treatment, and all of the conducted experiments confirmed that the removal rate of the two-ring structured naphthalene was significantly faster with regards to the specific charge added, compared to the four-ring structured compounds flouranthene and pyrene. In an inert electrolyte solution (0.1 M Na₂SO₄) all three PAHs were degraded by directly electron transfer at the anode surface. The removal rate was reduced in 0.1 M NaNO₃, but significantly increased in 0.1 M NaCl, where indirectly oxidation by hypochlorite, formed by the electrolysis of chloride, showed a clear positive effect. Reducing the NaCl concentration at constants current density decreased the removal rate of all three PAHs showing the importance of the indirect oxidation mechanism. Surprisingly, a lowering of the current density increased the removal rates in all investigated electrolyte solutions, most distinct with flouranthene and pyrene. This observation is believed to be due to a higher current efficiency of the PAH oxidation at the lower applied voltages with regards to the water oxidation side reaction.

The present investigation is still ongoing, and further experiments are going to be performed; cyclic voltammetry in order to study the influence of the electrolyte composition and concentration on the oxidation potentials of the PAH compounds, and experiments clarifying the risk of formation of unwanted chloro-organic byproducts. However, the initial work has shown that the electrochemical oxidation technique has a significant potential in treating water contaminated with PAH compounds. Introductory proof of concept experiments has been performed with process water, used in the process of removing sediment from harbors, and even in very low concentrations, a wide range of PAH compounds are removed by the electrochemical treatment, to concentrations below the detection limit $(0.010 \,\mu gL^{-1})$.

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