Electrochemical degradation of PAH compounds in process water: a kinetic study on model solutions and a proof of concept study on runoff water from harbour sediment purification
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ABSTRACT
The present study has investigated the possibility to apply electrochemical oxidation in the treatment of polycyclic aromatic hydrocarbon (PAHs) pollutants in water. The reaction kinetics of naphthalene, fluoranthene, and pyrene oxidation have been studied in a batch recirculation experimental setup applying a commercial one-compartment cell of tubular design with Ti/Pt90-Ir10 anode. The rate of oxidation has been evaluated upon variations in current density, electrolyte composition and concentration. All three PAHs were degraded by direct anodic oxidation in 0.10 M Na2SO4 electrolyte, and the removal rates were significantly enhanced by a factor of two to six in 0.10 M NaCl due to contribution from the indirect hypochlorite oxidation. Second order reaction kinetics was observed for the degradation of naphthalene in all electrolytes whereas fluoranthene and pyrene followed first order kinetics. Decreased current densities from 200 to 15 mA cm$^{-2}$ in the NaCl electrolyte also decreased the removal rates, but significantly enhanced the current efficiencies of the PAH oxidation, based on a defined current efficiency constant, $k_q$. This observation is believed to be due to the suppression of the water oxidation side reaction at lower applied voltages. A proof of concept study in real polluted water demonstrated the applicability of the electrochemical oxidation technique for larger scale use, where especially the indirect chloride mediated oxidation approach was a promising technique. However, the risk and extent of by-product formation needs to be studied in greater detail.

Key words | electrochemical oxidation, polycyclic aromatic hydrocarbons (PAHs), water treatment

INTRODUCTION
The family of polycyclic aromatic hydrocarbons (PAHs) are byproducts of incomplete combustion or hydrolysis of organic materials and are widely distributed in the environment from both natural and industrial sources such as forest fires, burning of fossil fuels in diesel engines, wood stoves and power plants, tar and creosote production etc. (Douben 2003). Due to their benzene analog structures having two or more fused rings in diverse alignments, PAHs can be mutagenic, teratogenic, and carcinogenic for aquatic organisms and superior animals including man. However, a wide variety of acute toxicities are found within the structure family (Douben 2003), but even at very low concentrations the compounds pose a threat to ecological and human health and the threshold values for drinking water are in most countries in the nano gram pr. L scale. (Miljøstyrelsen 2001; USEPA 2003).
PAHs are hydrophobic compounds and their persistence in the environment is mainly due to their low water solubility and a tendency strongly to bind with clay minerals and organic matter present in soil and sediment (Panizza et al. 2000). 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 due to their highly stable physico-chemical characteristics (Alcantara et al. 2008). High concentrations of PAHs are found in several types of industrial waste water (Panizza et al. 2000), whereas natural water low in COD and polluted with low concentrations of PAHs (<1 mg L\(^{-1}\)) is an issue in removal and purification of contaminated harbor sediment. Typical, the harbor sediment is pumped ashore to inland lakes or upland sites applying five part sea water per one part sediment, and treatment of the runoff water is required before discharge to the recipient (Lund et al. 2001).

The research in PAH abatement are numerous and reportings from use of a wide range of oxidation methods have been published including biological (Kostecki & Mazierski 2008), enzymatic (Hernandez et al. 2008), chemical (Ferrarese et al. 2008), and photochemical oxidation (Plata et al. 2008), ozonation (Kommuller & Wiesmann 2003) and several advanced oxidation processes (AOPs) (Woo et al. 2007). As in most cases with recalcitrant organic pollutants, the most successful achievements reported in water treatment of PAHs were obtained with Fenton and AOP like techniques generating the powerfully oxidizing hydroxyl radicals through various combinations of oxidizing agents and UV radiation (O\(_2\)/H\(_2\)O\(_2\), UV/O\(_3\), UV/H\(_2\)O\(_2\), H\(_2\)O\(_2\)/Fe\(^{2+}\)).

Electrochemical degradation or full mineralization through anodic oxidation of organic pollutants is a versatile technology applied in water treatment and included in the AOP family with the main advantage that no excess chemicals are used. Refractory and non-biocompatible organic contaminants are electrochemically oxidized in the electrochemical cell with the aim of full mineralization or conversion of the organics to small substrate molecules amendable to further biological treatment (Comninellis et al. 2008). The versatility of the electrochemical oxidation process in degradation of a wide range of organic pollutants is clearly shown in the comprehensive review by Martinez-Huitle & Ferro (2006) and the more recent review by Martinez-Huitle & Brillas (2008) concerning electrochemical degradation of organic dyes. In addition, a prior study on highly polluted ground water containing a range of organophosphoritic pesticides showed the efficiency of the electrochemical oxidation technique in the treatment of very complex contaminated matrices (Muff et al. 2009).

According to the generally accepted mechanisms, electrochemical oxidation of organics occurs through two different pathways termed direct and indirect oxidation (Comninellis et al. 2008). In direct oxidation, water is discharged at the anode active sites generating physisorbed hydroxyl radicals (M-OH) or chemisorbed active lattice oxygen in higher oxidation states (MO\(_x\)), dependent on the nature of the anode material and especially the adsorption enthalpy of the M-OH pair (Kapalka et al. 2008). A high direct oxidation power anode is the high oxygen over-voltage thin film boron doped diamond (BDD) type anodes with weak interaction between the anode surface and water molecule generating hydroxyl radicals amendable for organic oxidation, whereas the DSA and Ti/Pt anodes generate the MO\(_x\) active oxygen with lower direct oxidation power (Comninellis et al. 2008; Kapalka et al. 2008). By the indirect oxidation pathway, the low direct oxidation power anodes are efficient in generating strong chemical oxidants from ions or dissolved compounds in solution capable of bulk oxidation of the organic pollutants. A traditional and widely applied indirect oxidation mediator is hypochlorite, electrogenerated by oxidation of chloride ions which are found in significant concentrations in most polluted water (Martinez-Huitle & Ferro 2006).

Successful electrochemical degradation of a range of PAHs has been reported by different anode materials applied and high initial PAH concentrations. Treatment of waste water containing naphthalene- and anthraquinone-sulphonic acids (initial COD 1,361 mg L\(^{-1}\)) by a Ti/Pt anode showed that only a small fraction was oxidized by direct electrolysis, whereas full mineralization was obtained by addition of sodium chloride and hence indirect oxidation by hypochlorite (Panizza et al. 2000). However, indirect treatment by electrogenerated hydrogen peroxide presented residual COD and color (Panizza & Cerisola 2003). Using BDD anode in a combined biological and electrochemical oxidation of naphtalenesulfonates, complete mineralization...
was obtained in 3 h with an energy consumption of 61 kWh m$^{-3}$ (Panizza et al. 2006). Other examples are successful electrochemical treatment of sediments through soil washing in 0.5 M NaCl (Stichnothe et al. 2005) and extraction with nonionic surfactants (Alcantara et al. 2008). These reported investigations show the high potential of electrochemical oxidation in PAH abatement in water treatment, and the significant potential in using platinum based anodes when the water is saline. However, more knowledge on the influence of operating factors on the degradation kinetics and efficiency in concentration ranges transferable to PAH polluted runoff water from the sediment removal process is needed. In this study, the initial removal kinetics of three model PAH compounds have been investigated in low concentrations at varied experimental parameters as current density, electrolyte composition and concentration in slightly contaminated model solutions. The three targeted PAH compounds are the most abundantly occurring in Danish runoff water (Lund et al. 2001). From the literature study, enhancement of the degradation was expected by addition of chloride to the electrolyte, but the extent and the influence on the single PAH needed to be clarified. Finally, the electrochemical treatment was applied for remediation of a real runoff water matrix. The risk of formation of halogenated byproducts due to the presence of chloride in the saline runoff water is a matter of high concern, which will be addressed in a subsequent paper.

**MATERIALS AND METHODS**

The electrochemical cell and water characteristics

**Electrochemical cell**

The applied electrochemical flow cell was a laboratory scale commercially available one-compartment cell from Watersafe S.A. The cell has a tubular design with bottom inlet and top outlet. The applied rod-like anode was made of solid titanium coated with a 90–10% alloy of platinum and iridium, respectively, and the cathode was 316 stainless steel. The cell had a specific volume of 43 ml with an anode surface of 60.3 cm$^2$ and an electrode gap of 3 mm. The cell is sketched in Figure 1.

**Model solutions**

Naphthalene (C$_{10}$H$_{8}$), fluoranthene (C$_{16}$H$_{10}$), and pyrene (C$_{16}$H$_{10}$) were dissolved in 100 mL acetonitrile and diluted with demineralised water to a final experimental volume of 3.0 L. The initial concentrations of naphthalene, fluoranthene, and pyrene in the model solutions were in the range of 1 to 4 mg L$^{-1}$. The investigated electrolytes were sodium chloride, sodium nitrate, and sodium sulphate, added in concentrations of 0.060 to 0.140 M in the respective experiments. All of the chemicals applied were of analytical grade obtained from Merck.

**Runoff water**

In the proof of concept study, runoff water from a sediment purification process in Odense harbor, Denmark, was sampled. The runoff water was sea water processed when harbor sediment is pumped ashore to upland sites. The runoff water was low in salinity compared to normal sea water. However, the conductivity was 15.2 mS cm$^{-1}$ at 20°C and the chloride concentration was determined to 7.6 g L$^{-1}$. The organic load of the water was low with initial COD of 53 mg L$^{-1}$ and moderate levels of total nitrogen and phosphorous of 9.9 mg L$^{-1}$ and 1.1 mg L$^{-1}$, respectively. Hence, micro pollutants as PAHs are the major reason of concern. The initial pH was 8.21 and bulk oxidation and reduction potential (ORP) was 72.5 mV.

**Experimental procedure**

The experiments were conducted galvanostatic in a water cooled batch recirculation system (Figure 1). The PAH solutions were pumped through the electrochemical...
cell from a reservoir surrounded by a cooling jacket. The temperature of the model solutions was maintained at 20°C during the runs through regulation of the temperature of the cooling water, and magnetic stirring applied to avoid concentration gradient in the reservoir. The total flow in the system was maintained constant at 430 L h\(^{-1}\) in all experiments in order to ensure comparable mass transfer conditions. The investigated current densities ranged from 15–200 mA cm\(^{-2}\) and were set by control of the overall cell voltage by an external power supply. Prior to start of each experiment, the batch was recirculated without applied voltage for 10 min. in order to ensure homogenization. As a part of the introductory experiments it was ensured that no autocatalytic activity was found by the anode surface through sampling at 10 min intervals for 30 min without applied voltage. During the experimental run, water was sampled from the reservoir for analysis.

For the proof of concept study, two experimental approaches were used. In the first experiment, a 10 L batch of runoff water was directly treated by recirculation through the cell in the experimental setup (Figure 1) for 2 h at a current density of 100 mA cm\(^{-2}\) corresponding to a total added charge, \(Q\), of 1.2 Ah L\(^{-1}\). In the second experiment, an intermixing approach utilizing chemical oxidation through electro chlorination was investigated. 3.0 L 0.342 M sodium chloride solution (2.0 w/w\%) was electrolyzed for 1 h at a constant current density of 200 mA cm\(^{-2}\) in the batch recirculation setup, in order to reach an available chlorine concentration of 1.2 g L\(^{-1}\). Subsequently, 250 ml of the oxidant solution was intermixed with 750 ml runoff water to a total volume of 1.0 L and allowed a reaction time of 2 h. In the proof of concept study only initial and final samples were analyzed.

**Analytical methods**

Due to low initial concentrations of naphthalene, fluoranthene, and pyrene in the model solutions, the very specific fluorescent properties was utilized in the analytical procedure, where isocratic reverse phase (RP) high pressure liquid chromatography (HPLC) with fluorescence (FLU) detection was applied. A Chromspher 5 column from Chrompack was used with 56 v/v\% acetonitrile/water solution as the mobile phase. The HPLC apparatus was Perkin Elmer 250 with a Hewlett Packard 1100 fluorescence detector. In the buildup of the analytical method, the maximum excitation and emission wavelengths for each of the PAHs were determined to \(\lambda_{\text{ex,naph}} = 205\text{ nm}, \lambda_{\text{em,naph}} = 340\text{ nm}, \lambda_{\text{ex,fluor}} = 230\text{ nm}, \lambda_{\text{em,fluor}} = 460\text{ nm}, \lambda_{\text{ex,pyr}} = 230\text{ nm}, \lambda_{\text{em,pyr}} = 400\text{ nm}\). The main advantages of this analytical method were the possibility of measuring directly on the aqueous solutions and that only very small sample volumes (3 mL) were needed. This was especially important due to the focus on the kinetics in this study. In order to decrease the experimental uncertainties, true triple determination was applied. The main disadvantage of the application of the fluorescence detection was that any alteration of the electronic configuration of the PAHs will influence the characteristic emission wavelengths and decrease the detected signals. Parameters as oxidation and reduction potential (ORP), pH, temperature, conductivity and dissolved oxygen (DO) were monitored in the bulk solution in the reservoir by help of appropriate sensors. The concentration of available chlorine was determined by a kit from Lovibond applying the standard DPD method provided in DS/EN 7393-2.

**RESULTS AND DISCUSSION**

The data obtained in this study represents the initial oxidative attacks on the PAHs and not the full mineralization of the organics, where the full degradative pathway will include several intermediate species. The focuses were on determining the initial oxidation kinetics of the electrochemical system and study the influence of operating parameters on the oxidative performance. Thus, for the kinetic evaluation, the experimental batch recirculation system was treated as an assumed perfectly mixed CSTR (continuous-stirred-tank reactor) due to a high recirculation flow through the cell and high stirring rate in the reservoir. Apparent rate constants were determined through standard isothermal kinetic analysis where the reaction order was determined from degradation curves by graphical analysis and least square regression. The values of the rate constants represented the comparable performance of the system for the removal of the specific PAHs including mass transfer and electrode limitations. Based on this procedure,
the removal of the two-ring structured naphthalene and the four-ring structured fluoranthene and pyrene showed significant different reaction kinetics.

In a 0.10 M sodium sulphate supporting electrolyte, which was considered electrochemically inert by the applied Ti/Pt90-Ir10 anode material, a decrease in PAH concentrations can be attributed to direct anodic oxidation of the organic at the electrode surface. The degradation curves of fluoranthene and pyrene (Figure 2) showed similar behavior following the expected first order kinetics as the batch recirculation system was operated under mass transfer limitations. The error bars on the relative concentrations in all degradation curves represent the standard deviation of the triple determinations. On the contrary, naphthalene showed a rapid initial degradation, which was found to follow second order kinetics by the standard $C_0/C$ vs. time plot (Figure 2). This finding was found and confirmed under all the tested operating parameters, and the apparent rate constants observed for the individual PAHs are showed for comparison in Table 1. Second order dependent reaction kinetics is rarely seen in electrochemical oxidation of organics in water, and the explanation is at present time not evident. Possibly, the initial step in the naphthalene degradation involved a dimerization process, which is known to be part of the PAH formation mechanisms in combustion reactions (Siegmann & Sattler 2000).

The degradation curves found in sodium sulphate confirmed that the studied PAHs where capable of anodic oxidation. However, when the rates of oxidation were studied upon the influence of electrolyte composition, it was found that treatment in a sodium nitrate electrolyte in equal concentration and current density significantly decreased the rate of oxidation compared to the other electrolytes (Figure 3).

Sodium nitrate is in the applied system considered primarily as an inert electrolyte as well, and the decreased reaction rate is believed to be due to a decreased conductivity of the solution (9.5 mS cm$^{-1}$) compared to the sodium sulphate electrolyte (15.1 mS cm$^{-1}$) resulting in a higher

![Figure 2](https://iwaponline.com/wst/article-pdf/61/8/2043/448388/2043.pdf)

**Figure 2** The evolution of the relative concentrations of (○) naphthalene, (□) fluoranthene, and (▲) pyrene during electrochemical oxidation in 0.10 M Na$_2$SO$_4$ electrolyte at 200 mA cm$^{-2}$ current density. The error bars represent the standard deviation of the triple determinations. Subplot: The standard kinetic analysis, which showed the difference in reaction kinetics.

Table 1 The apparent rate constants found from the different experimental settings. Second order reaction kinetics was found for naphthalene and first order kinetics for fluoranthene and pyrene.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Concentration (M)</th>
<th>Current density (mA cm$^{-2}$)</th>
<th>$k$, naphthalene (M$^{-1}$ s$^{-1}$)</th>
<th>$k$, fluoranthene (s$^{-1}$)</th>
<th>$k$, pyrene (s$^{-1}$)</th>
</tr>
</thead>
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<tr>
<td>NaNO$_3$</td>
<td>0.10</td>
<td>200</td>
<td>$1.75 \times 10^1$</td>
<td>$6.50 \times 10^{-5}$</td>
<td>$6.17 \times 10^{-5}$</td>
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<td>NaNO$_3$</td>
<td>0.10</td>
<td>100</td>
<td>$3.78 \times 10^1$</td>
<td>$8.00 \times 10^{-5}$</td>
<td>$8.33 \times 10^{-5}$</td>
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<tr>
<td>NaCl</td>
<td>0.14</td>
<td>200</td>
<td>$2.15 \times 10^2$</td>
<td>$3.15 \times 10^{-4}$</td>
<td>$4.12 \times 10^{-4}$</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.14</td>
<td>100</td>
<td>$6.73 \times 10^1$</td>
<td>$2.70 \times 10^{-4}$</td>
<td>$3.67 \times 10^{-4}$</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.14</td>
<td>50</td>
<td>$3.78 \times 10^1$</td>
<td>$9.83 \times 10^{-5}$</td>
<td>$1.95 \times 10^{-4}$</td>
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<td>NaCl</td>
<td>0.14</td>
<td>25</td>
<td>$8.27 \times 10^1$</td>
<td>$1.67 \times 10^{-4}$</td>
<td>$2.82 \times 10^{-4}$</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.14</td>
<td>15</td>
<td>$3.61 \times 10^1$</td>
<td>$1.43 \times 10^{-4}$</td>
<td>$2.58 \times 10^{-4}$</td>
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<td>NaCl</td>
<td>0.10</td>
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<td>$2.29 \times 10^2$</td>
<td>$2.62 \times 10^{-4}$</td>
<td>$3.27 \times 10^{-4}$</td>
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<tr>
<td>NaCl</td>
<td>0.06</td>
<td>200</td>
<td>$6.92 \times 10^1$</td>
<td>$1.58 \times 10^{-4}$</td>
<td>$1.93 \times 10^{-4}$</td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>0.10</td>
<td>200</td>
<td>$3.61 \times 10^1$</td>
<td>$1.07 \times 10^{-4}$</td>
<td>$1.05 \times 10^{-4}$</td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>0.10</td>
<td>100</td>
<td>$2.66 \times 10^1$</td>
<td>$1.03 \times 10^{-4}$</td>
<td>$1.17 \times 10^{-4}$</td>
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</table>
ionic resistance in the cell decreasing the efficiency of the electrode reactions. When sodium chloride was applied as electrolyte, the removal rates were significantly increased for all three PAHs, hypothesized to be due to the contribution by the indirect hypochlorous acid/hypochlorite oxidation. In this way, the apparent rate constants increased by a factor of 2.4–6.3 compared to the oxidation in the inert sulphate electrolyte, most significantly for naphthalene (Table 1). The risk of the formation of halogenated organics is a matter of concern in all research whenever species of active chlorine are present as in this experiment, where it is produced due to the anodic two electron oxidation of chloride. Since fluorescence detection applied in the primary analytical technique used, the gained rate of decrease in signal with time could not for certain be attributed only to contributions from the indirect oxidation pathway, but could also include shifts in characteristic emission wavelengths due to PAH halogenations or other by-product formation. However, this was checked by reproducing the experiment in sodium chloride electrolyte and analyzing the samples by GC-MS (gas chromatography with mass spectroscopy detection). This confirmed that the PAHs where actually degraded during the runs. Minor peaks of mono-chlorinated naphthalene and pyrene showed up as intermediate byproducts, but were removed during the treatment, and were not present in amounts corresponding to the removed naphthalene and pyrene. This indicated that the observed increase in PAH removal rate most likely was caused by enhancement of the oxidative performance of the system due to the presence of chloride. Halogenated PAHs and other by-products as halogenated carboxylic acids still possess a risk, but the extent of the formation in the long run in different media are beyond the scope of this study and will be addressed in a subsequent paper.

The importance of the indirect oxidation in the PAH oxidation at the applied platinum based anode was expected and in accordance to earlier findings by Panizza & Cerisola (2003). However, when the chloride mediated oxidation was further investigated some irregularities in the observed trends were found (Figure 4). When the applied current density was decreased from 200–50 mA cm$^{-2}$ at constant electrolyte concentration of 0.14 M NaCl, the expected decrease in removal rates were observed, reflecting the decreased formation rate of active chlorine. However, when the current densities were decreased to 25 and 15 mA cm$^{-2}$ the removal rates reversed the trend and increased again. This observation was surprising, and a suggested explanation by the authors is a shift in the primary route of oxidation at the lower applied current densities and hence potentials. At the lower potentials, the indirect hypochlorous acid/hypochlorite oxidation may become less important since the dominating chloride oxidation is challenged by the direct MOx oxidation, which then contributes more significantly to the total oxidation even in the chloride electrolyte. However, this observation has not formerly been reported, and a full explanation is still lacking. When the change in parameter was reversed and the electrolyte concentration of sodium chloride was decreased from 0.14 to 0.06 M at constant current density of 200 mA cm$^{-2}$, the trends showed a minor decrease in removal rates (fig. not shown, see Table 1). During the experimental runs, the equilibrium between the produced hypochlorous acid and hypochlorite shifted gradually following the change in bulk pH from neutral to alkaline conditions, but even though hypochlorous acid is considered the most powerful oxidant ($E_0 = 1.48$ V) both oxychloro species were capable of oxidizing all three PAHs.

The efficiencies of electrochemical oxidation processes are most commonly evaluated based on measurements of the chemical oxidant demand (COD) of the solution at different time steps. These measurements provides the basis for calculations of recognized figures of merits of the
electrochemical process as instantaneous current efficiency (ICE), general current efficiency (GCE), electrochemical oxidation index (EOI) etc. (Martinez-Huitle & Ferro 2006). However, in the applied model solutions the total organic load was insufficient for accurate COD measurement and another approach based on a defined current efficiency constant, \( k_q \), was applied. A common approach in electrochemical oxidation studies is to evaluate the evolution in pollutant concentration with respect the specific amount of charge passed through the solution, \( Q \) \((\text{Ah} \text{L}^{-1})\), which at constant current density represents a time scale. As an analogy to the rate constant the current efficiency constant, \( k_q \), can be defined as:

\[
\frac{d[PAH]}{dQ} = -k_q[PAH]^n
\]

The current efficiency constant is a relative measure of the efficiency of the oxidation of the specific PAH compounds at the different experimental settings and hence differs from the instantaneous, general, and total current efficiency based on COD measurements commonly applied in efficiency evaluations in electrochemical oxidation literature (Martinez-Huitle & Ferro 2006).

When the current efficiency constants were determined based on the data from the experimental runs in chloride electrolytes and plotted versus the applied current densities, it was found that the trends were contrary to the evolution in rate constants with all three investigated PAHs, as also indicated by the increased rate constant obtained at lower potentials. In Figure 5, a bar plot of the rate and current efficiency constants are showed for naphthalene, which is chosen as an example. Hence, as a general trend the current efficiency represented by \( k_q \) increased for the PAH oxidation as the rate of oxidation represented by \( k \) decreased with the highest efficiency in this study obtained at 25 mA cm\(^{-2}\). These observations are believed to be caused by suppression of the unwanted water oxidation side reaction at the lower applied potential, considerations supported by a measured slower increase in bulk DO concentration at the low current densities compared to oxidation at higher current density. The observation of the contradictory trends regarding reaction rate and current efficiency leads to optimization challenges when engineering the treatment system, since both high reaction rate and hence a lower need for reservoir capacity and high current efficiency are wanted.

As the final part of this study, runoff water from a sediment purification process was treated and evaluated upon capability of PAH removal. Two approaches were used; a direct treatment approach passing the water through the cell in the batch recirculation setup utilizing both the anodic oxidation in the cell and the indirect chlorine oxidation, and an electro-chlorination indirect approach.

### Figure 5
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.
where a produced active chlorine oxidant solution was added to the runoff water.

Under the applied experimental settings, both approaches resulted in satisfactory PAH removal below the detection and discharge limit of 0.010 μg L⁻¹ (Figure 6). However, the concentration of available chlorine in the indirect electro-chlorination approach was 280 mg L⁻¹ and in significant excess compared to the organic load, which lead to residual active chlorine in the effluent. Further optimization regarding the mixing ratio is then highly possible and needed which also applies to the reaction time in the direct treatment approach. The energy consumption for the direct treatment approach was 13.2 kWh m⁻³ and 18.8 kWh m⁻³ for the electro-chlorination process, which however is believed to be able of significant reduction at optimized settings.

The utilization of the indirect chloride mediated oxidation leaves a great potential for use in larger scale, since hypochlorite oxidant solutions can be produced from the runoff water itself and enable treatment of larger volumes of water through the an electro-chlorination approach.

Issues regarding the risk of chloro-organic byproduct formation during the direct and indirect treatment approaches and toxicity tests of the treated water still need to be performed before the electrochemical oxidation process is implemented in the treatment strategy. In addition, the obtained degradation curves correspond to the initial oxidation steps with subsequent loss of the characteristic fluorescent properties and the extent of mineralization is not clarified. The Ti/Pt-Ir electrode material is reported to leave residual shortlength carboxylic acids, whereas full mineralization of organics is obtained by the BDD and lead oxide electrodes (Martinez-Huitle & Brillas 2008). However, Panizza et al. 2000 reported complete mineralization of PAH by the indirect chloride mediated oxidation at Ti/Pt anode, and the electrocatalytic activity for the chlorine evolution is higher at the Ti/Pt-Ir electrodes compared to the BDD (Jeong et al. 2009), which supports the use of this electrode material for saline water and indirect chloride mediated treatment purposes, where active chlorine is capable of oxidizing the organic pollutants.

CONCLUSIONS

The kinetic study on electrochemical oxidation of naphthalene, fluoranthene, and pyrene showed second order degradation kinetics of naphthalene, whereas fluoranthene and pyrene followed the expected first order reaction kinetics under all experimental settings. Compared to oxidation in sodium sulphate electrolyte, the removal rates were decreased for all three PAHs in sodium nitrate and significantly enhanced in sodium chloride electrolyte, which is believed to be due to significant contributions from the indirect oxidation by the hypochlorous acid/hypochlorite pair. The indirect chloride mediated oxidation showed an indistinct dependence on the applied current density, but whereas the removal rates were generally decreased at lower current densities, the current efficiencies increased, which is believed to be due to suppression of the water oxidation side reaction. Treatment of real runoff water from a sediment purification process resulted in successful removal and maintenance of the 0.010 μg L⁻¹ discharge limit. However, further optimization is needed for the process to economically feasible, but the electrochemical approaches leave promising perspectives for larger scale use.
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REFERENCES


