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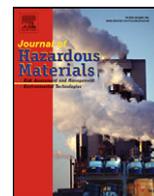
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Identification and fate of halogenated PAHs formed during electrochemical treatment of saline aqueous solutions

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ABSTRACT

Halogenations of polycyclic aromatic hydrocarbons (PAHs) comprise a serious problem, when electrochemical oxidation (EO) is applied for treatment of chloride and bromide containing polluted sea water. In this study, the possible non-polar halogenated byproducts formed were identified in a series of chemical hypochlorination experiments using GC–MS, and the analytical information from these experiments was used in the primary EO treatment tests. An electrochemical cell equipped with a Ti/Pt₉₀–Ir₁₀ anode was used in a batch recirculation setup with naphthalene, pyrene, and fluoranthene as the parent PAHs. Contrary to the chemical hypochlorination experiments, naphthalene as the most soluble compound was the only one to be halogenated in detectable amounts during EO. In a single sodium chloride electrolyte, up to 13% of the initial naphthalene was chlorinated at the peak concentration during treatment before it was subsequently removed. Even small concentrations of added bromide in a mixed electrolyte completely dominated the byproduct pattern with formation of primarily mono brominated naphthalene in peak concentrations up to 30–39% of the initial naphthalene. All of the considered byproducts were despite a more recalcitrant behavior degraded at prolonged treatment times, which need to be applied to ensure a safe discharge of the treated water.

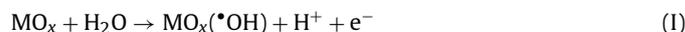
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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are one of the families of persistent organic pollutants (POPs) of concern in environmental pollution and water treatment [1]. PAHs are non-polar compounds composed of two or more fused aromatic rings, and due to their benzene analog structures PAHs are generally considered mutagenic, teratogenic, and carcinogenic for human beings, but a wide variety of acute toxicities are found within the structure family [2]. The lipophilic properties of the compounds induce low water solubilities and hence low mobilities in nature of especially the higher molecular weight PAHs (4 or more rings) that primarily are bound to soil and sediment particles. However, even in very low aqueous concentrations they pose a threat to ecological and human health, which have resulted in discharge threshold values for PAH polluted water in the nanogram per litre scale in most countries analogous to drinking water quality [3,4]. The sources of PAHs are diverse ranging from intense use of petroleum products (automobile fuel, lubricating oils, etc.) to combustion processes (fuel, wood, cigarettes, and coal burning, automobile exhaust, heat and power generation, creosote production, etc.) [5].

Treatment of PAHs in both soil and water has been reported by various methods based on biological [6], physical [7] and chemical [8] means. In water treatment, the recalcitrant nature of PAHs to participate in aqueous reactions prompts that especially advanced oxidation processes (AOPs) as ozone/UV [9], Fentons reagent [10], UV/TiO₂, [11] etc. have been used to achieve successful levels of removal. The AOPs are characterized as processes, which produce primarily hydroxyl radicals for the abatement of hardly degradable organics not suited for efficient biological treatment. One of the more recent AOPs is electrochemical oxidation (EO), where the organic pollutant during electrolysis is oxidized at the positive electrode (anode) operated at potentials above water stability [12]. EO has in a number of studies proved to be an environmentally friendly, easy-to-use, versatile, and effective method of oxidation compared to other AOPs [12–14].

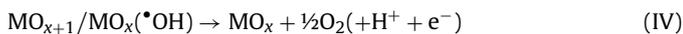
In the EO process, the organics are oxidized by a combination of two different oxygen transfer processes. In the direct electrochemical oxygen transfer process, the organics are oxidized by intermediates of oxygen evolution with the first step being the discharge of water to form adsorbed active oxygen species; physisorbed hydroxyl radicals in the case of non-active anodes (Eq. (I)) or chemisorbed active oxygen in the case of active anodes (Eq. (II)), where a stronger adsorption of the hydroxyl radicals promotes a further removal of an electron [15,16].



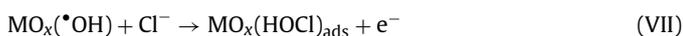
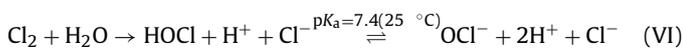
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The sorbed reactive oxygen species are then capable of partial organic oxidation (in the case of MO_{x+1}) and/or full combustion (in the case of $\text{MO}_x(\cdot\text{OH})$) (Eq. (III)). The decomposition of the active oxygen species to form molecular oxygen is the main competitive side reaction (Eq. (IV)) [16].



In the indirect mediated oxidation process, ions or other solution constituents are oxidized at the anode surface in order to produce strong oxidants capable of bulk oxidation [12]. Especially chloride has proved to be an efficient mediator in the indirect oxygen transfer process through the oxidation of chloride to hypochlorous acid/hypochlorite active chlorine species (Eqs. (V) and (VI)) or through adsorbed oxychloro-species as proposed by De Battisti and co-workers (Eqs. (VII) and (VIII)) [17].



PAH compounds have been reported to be successfully electrochemically removed in chloride media even with achievement of full mineralization, with high current efficiencies and low power consumption [18]. With these findings, the EO process has a great potential for PAH treatment of saline waters such as sea water. In sediment removal and purification processes, sea water is converted into process water prior to discharge and are then subjected to strict regulation.

A major concern, when EO is applied under saline conditions, is the formation of harmful and toxic chlorinated and other halogenated organic byproducts potentially leaving the treated matrix more polluted and toxic even though the primary chemicals of concern are removed. Further on, when sea water is subjected to EO, the typically high concentrations of bromide found in sea water may add brominated PAHs to the sum of halogenated byproducts. Concerning the EO processes in low concentrated chloride media and the dedicated electro-chlorination processes, the formation and presence of substances known as disinfection byproducts (DBPs) has been subjected to a lot of attention due to the very efficient disinfection obtained with these processes and the many possible applications in the areas of drinking water treatment and water reuse [19–22]. However, the extent of substitutional halogenation of the main organic substances as the PAHs during electrochemical treatment has so far lacked attention. Only a few studies report on the influence of experimental parameters on the formation of organo-chlorine compounds [23–25]. Neto and De Andrade found that the oxide composition of dynamically stable anodes (DSAs) was insignificant with regards to the degradation rate of the herbicides in focus, but found a linear relationship between oxide composition and adsorbable organic halides (AOX) formation. Generally, the conditions favoring the chlorine production rate, high chloride concentration, high current density and most efficient chlorine evolving anode increased the AOX formation [23]. Two other chloride mediated EO studies showed volcano type AOX curves, where the organo-chlorine compounds once formed are quickly consumed before the end of electrolysis [24,25]. However, even after prolonged treatment time (14 h) a mild increase in AOX was showed by Neto and De Andrade [23], demonstrating the increased resistance of the halogenated organics towards oxidation compared to the parent compounds.

The aim of the work presented in this article was to study the extent of formation of chlorinated and brominated PAHs during electrochemical oxidation in chloride and bromide media. Naphthalene, fluoranthene, and pyrene were used as model compounds, and the potential products formed were identified in a series of chemical hypochlorination experiments applying GC–MS analysis, before EO experiments were conducted. The formation reactions of halogenated PAHs were believed mainly to be of chemical nature between active chlorine/bromine species and the PAHs. These may be influenced by the pH conditions of the media analogous to organic synthesis reactions in general, which commonly are favored by acidic conditions. Hence pH was an experimental parameter in the identification tests.

2. Experimental

2.1. Applied chemicals

All chemicals were of analytical grade purchased from Merck and Bie & Berntsen if nothing else is stated. Aqueous solutions of sodium chloride and potassium bromide were applied as electrolytes in both the identification and electrolysis experiments. Liquid 14 w/w% sodium hypochlorite (140 g L^{-1} active chlorine) obtained from VWR was used for chemical hypochlorination in the identification experiments, where acetonitrile was used as co-solvent in order to increase the solubilities of the PAHs. Hydrochloric acid was applied for pH adjustments and disodium hydrogen phosphate and sodium dihydrogen phosphate was applied as buffer system for controlled pH experiments in the EO studies. Naphthalene, fluoranthene, and pyrene were applied as model PAH compounds.

2.2. The electrochemical cell

The electrochemical cell was of tubular design and purchased by Watersafe S.A. (GR). It consisted of an inner solid titanium anode coated with and alloy of platinum and iridium in the ratio 90:10, and an outer stainless steel 316 cathode (Fig. 1). The surface area of the anode was 60.3 cm^2 and the electrode gap was 6 mm. The cell was operated under galvanostatic conditions by a Mersan (TR) power supply.

2.3. Procedures

2.3.1. Identification experiments

Identification of the halogenated PAH compounds formed during active chlorine oxidation was performed by chemical hypochlorination in batch experiments. Chloride was present in the solutions with and without bromide as co-electrolyte. Compared to common water treatment, high concentrations of sodium hypochlorite and PAHs were used in order to ensure formation of halogenated byproducts if possible.

As basis for the batch experiments, 10 mg L^{-1} of each of the PAHs naphthalene, fluoranthene, and pyrene were dissolved in a 3.33 v/v% acetonitrile/water solution with 0.10 M NaCl as electrolyte. The influence of bromide was studied by addition of 0.010 M KBr added as co-electrolyte in half of the batches. 25 mL volumes of the final solution was transferred to beakers and added 50 μL , 100 μL , 200 μL , and 500 μL sodium hypochlorite providing concentrations up to 2.75 g L^{-1} of active chlorine. The solutions were allowed reaction times of 20 min with stirring before sampling, extraction and analysis. One array of batches was kept at the resulting alkaline pH of 9–11, due to the high alkalinity of the added sodium hypochlorite. A second array was pH adjusted by drop wise addition of concentrated hydrochloric acid to pH 4.

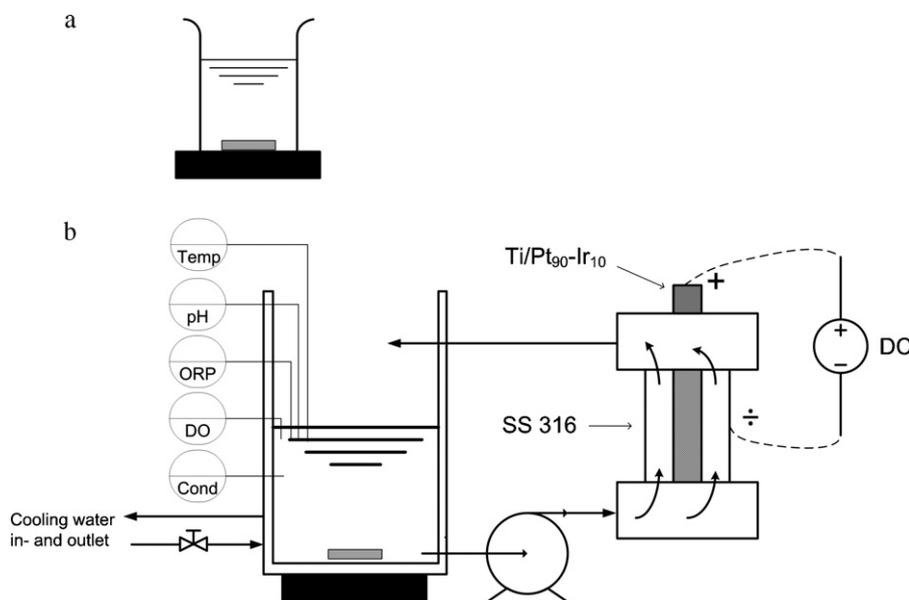


Fig. 1. (a) The batch setup consisting of a glass beaker on a magnetic stirrer used in the chemical hypochlorination experiments for identification of possible byproducts formed. (b) The batch recirculation setup used in the EO experiments.

The mixed bromide and chloride electrolyte experiments were only studied in the acidic range, since no oxidation or halogenations of the PAHs was observed in the 0.10 M NaCl experiments. Instead, experiments with different reaction times of 20 and 80 min were conducted to obtain information of the influence of prolonged time of exposure.

2.3.2. EO experiments

Similar to the identification experiments, the formation of halogenated PAHs during EO in chloride media was studied with and without the presence of bromide as co-electrolyte. Due to the very low solubilities of especially fluoranthene (0.265 mg L^{-1}) and pyrene (0.135 mg L^{-1}), excessive amounts of the three PAHs were left for dissolution under high stirring rate in the 3 L test solution for 24 h. The composition of the test solution was varied in the different experiments, but consisted of 0.10 M NaCl with and without 0.010 M and 0.0010 M KBr as co-electrolyte. 0.050 M hydrogen phosphate buffer was added to all experimental EO batches to maintain a constant pH 6. After dissolution, each batch was filtered through common filter papers for removal of undissolved PAHs before transferring to the EO setup.

The EO experiments were conducted in a batch recirculation set up (Fig. 1). The test solution was pumped from a water cooled reservoir equipped with constant stirring through the electrochemical cell at a flow rate of 430 L h^{-1} back to the reservoir. Treatment time was 4 h and sampling occurred from the reservoir regularly. All samples were immediately added sodium thiosulphate and stirred for neutralization of excessive oxidant species. The EO experiments were galvanostatically operated at a constant current intensity of 1.51 A resulting in an anodic current density of 25 mA cm^{-2} . The temperature was kept constant at $20 \pm 1^\circ \text{C}$.

2.4. Analysis

A Varian 3800 gas chromatograph (GC) with Saturn 2000 mass spectroscopy (MS) detection was applied as main analytical apparatus. 25 mL of the aqueous samples were extracted for 5 min by 2.5 mL hexane during vivid shaking before injection to the GC. Mono halogenated PAHs were identified by comparisons of retention times with analyses of pure substances, whereas di-, tri-halogenated and other possible compounds were identified

using the NIST v2.0a mass spectroscopy database incorporated in the analytical software [26]. Fluorene was used as internal standard for control of the GC sample volume injection. The information from the identification experiments was, due to the low organic concentration in the EO experiments, incorporated in a GC/MS–MS analytical method comprising the byproducts identified. The method was calibrated for mono-chloro and mono-bromo naphthalene, whereas the other byproducts were evaluated by the number of counts relative to the counts of the fluorene internal standard in the specific sample.

Analyses of the concentration of active chlorine added in the hypochlorination experiments were conducted by the common colorimetric N,N-diethyl-p-phenylenediamine (DPD) method applying a kit from Lovibond following the requirements in DS/EN ISO 7393-2. During the EO runs, the experimental conditions such as temperature, oxidation and reduction potential (ORP) and pH were measured for process monitoring applying appropriate sensors.

3. Results and discussion

3.1. Identification of chlorinated PAHs

PAHs as naphthalene, fluoranthene, and pyrene have in prior research been showed to be readily oxidized through EO in chloride electrolyte [27]. However, when increasing concentrations of sodium hypochlorite were added to batches of 0.10 M NaCl and PAH solutions no significant removal was observed (Fig. 2a). Less than 25% of naphthalene as the most reactive PAH was removed at the highest active chlorine dose of 2745 mg L^{-1} . The lack of chemical reactivity implied that no byproduct peaks appeared in the mass spectroscopy spectra of the alkaline samples (pH 9–11). In this pH range hypochlorite is the predominant active chlorine species and hence did not show sufficient oxidative power to be used for PAH oxidation. On the contrary, when pH of the solutions was adjusted to acidic conditions (pH 4), all of the PAHs were to some extent oxidized even at the lowest active chlorine concentration of 279 mg L^{-1} (Fig. 2b). In this pH domain, hypochlorous acid is the main oxidative chlorine species. Differences were again seen in reactivity of the PAHs with the most soluble compound naphthalene as the most reactive and fluoranthene as the least susceptible

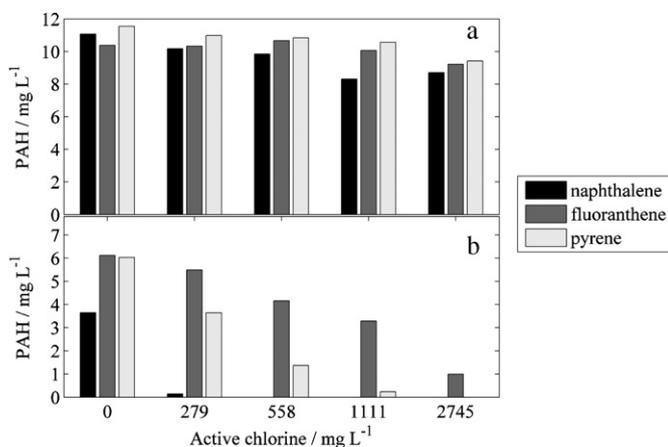


Fig. 2. The concentration of the parent PAHs after 20 min of chlorination by increasing concentrations of active chlorine, (a) alkaline conditions (pH=9–11) and (b) acidic conditions (pH=4).

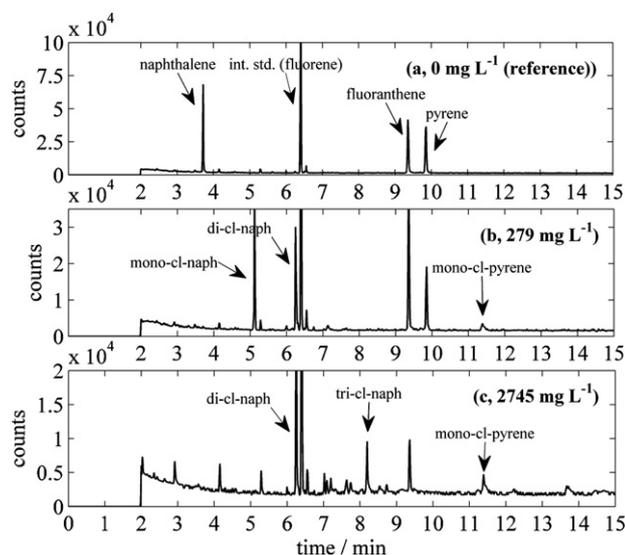


Fig. 3. Mass spectroscopy spectra of the hypochlorinated PAH solutions under acidic conditions obtained after 20 min of reaction time. (a) Reference spectra, (b) 279 mg L⁻¹, and (c) 2745 mg L⁻¹ of active chlorine.

to oxidation. Residual fluoranthene was even found at the highest active chlorine dose used.

With the observed removal of PAHs, the possibility of formation of byproducts was present. Some chlorinated PAHs were identified in the spectra of the acidic samples. At 279 mg L⁻¹, mono chlorinated naphthalene was the most significant byproduct followed by di-chloro-naphthalene and small amounts of chloropyrene (Figs. 3a and 4). When the active chlorine dose was increased in concentration, di-chloro-naphthalene became the dominant species

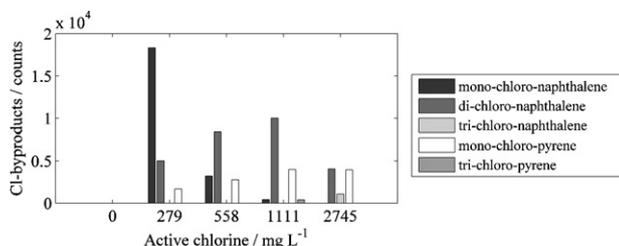


Fig. 4. The number of counts of chlorinated byproducts identified in the samples treated under acidic conditions and 20 min reaction time.

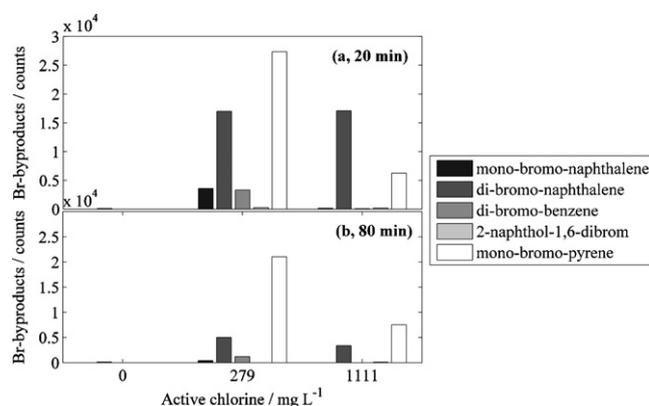


Fig. 5. The number of counts of brominated byproducts identified in the samples treated under acidic conditions at 0 mg L⁻¹ (reference), 279 mg L⁻¹, and 1111 mg L⁻¹ of active chlorine dose. Two different reaction times were investigated, (a) 20 min and (b) 80 min.

with an increase in mono chlorinated pyrene, and at 2745 mg L⁻¹ of active chlorine, naphthalene was even further chlorinated to tri-chloro-naphthalene (Figs. 3c and 4).

The retention times of the identified chlorinated products were incorporated in a GC/MS–MS method used for the EO experiments, where lower detection limits were needed since no co-solvent was used. Traces of other mixed alcoholic and chloro byproducts as 4-chloro-naphthol were found in the spectra, but not in significant amounts to be included in the study. Important to notice was that despite the very high active chlorine dose, no chlorinated fluoranthene were identified despite some removal of the parent compound. This indicated that degradation occurred rather than halogenation. Small amount of tri chlorinated naphthalene were formed, but the most dominant species, which could provide a risk in the electrochemical treatment, were the mono-chlorinated naphthalene and pyrene and di-chloro-naphthalene.

3.2. Identification of brominated PAHs

When 0.010 M KBr was added as co-electrolyte to the 0.10 M NaCl and PAH solution, brominated byproducts of the parent PAHs were formed in addition to the chlorinated. Under acidic conditions, mono- and di-brominated naphthalene together with mono-bromo-pyrene were the most predominant species identified (Fig. 5). Highest concentrations were found at the lowest active chlorine dose of 279 mg L⁻¹ after 20 min of reaction time (Fig. 5a). Increasing both the allowed reaction time up to 80 min and the active chlorine dose up to 1111 mg L⁻¹ favored a further removal of the brominated byproducts. At 279 mg L⁻¹ small amounts of di-bromo-benzene was found together with 2-naphthol-1,6-dibrom, but no tri brominated byproducts were found and once again no formation of halogenated fluoranthene species was observed.

The formation of the brominated PAHs was significant despite the much lower concentration of bromide compared to chloride (Br⁻:Cl⁻ = 1:10). It is known from chlorination of sea water that bromide ions rapidly are oxidized, when exposed to hypochlorous acid yielding hypobromous acid (second order rate constant of $2.95 \times 10^3 \text{ L mol}^{-1} \text{ s}^{-1}$ [28]) (Eq. (IX)).



Due to this reaction, the predominant oxidative agent in the mixed bromide/chloride electrolyte was most probable hypobromous acid. The chemical and physical properties of hypobromous acid are very similar to that of hypochlorous acid, with a standard reduction potential of 1.33 V just below, but still comparable, to that of hypochlorous acid ($E^0 = 1.48 \text{ V}$). The mechanisms of the chemical

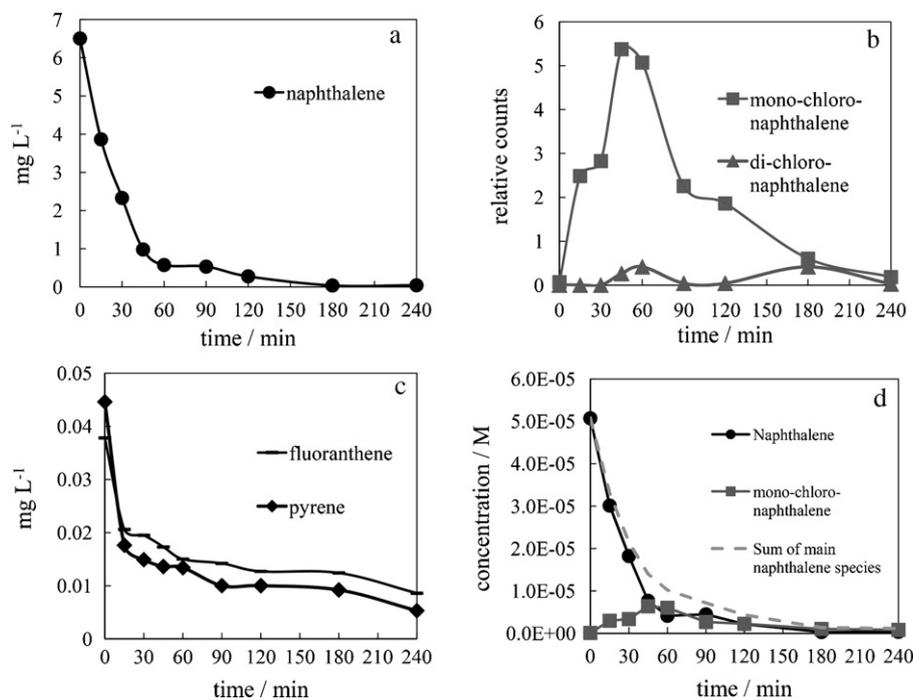


Fig. 6. The evolution of PAHs and byproducts versus time during EO in 0.10 M NaCl at 25 mA cm⁻² and pH 6. (a) The concentration of naphthalene, (b) the concentration of fluoranthene, and pyrene, (c) the number of counts of byproducts relative to the internal standard, and (d) the molar comparison of naphthalene and mono-chloro-naphthalene formation and degradation.

halogenation of the PAHs are proposed to be analogous to electrophilic aromatic substitution reactions as they are known from organic synthesis chemistry. The chlorine and bromine atoms in hypochlorous and hypobromous acid are formally in the +1 chemical oxidation state, due to the sharing of a bond with the more electronegative oxygen atom. In this way they possess a partial positive charge high enough to serve as electrophiles capable of attacking the exposed π -electrons of the aromatic ring, replacing one of the hydrogen atoms in a substitution reaction leaving a water molecule [29]. The substitution reaction allows the aromatic sextet of π -electrons to be regenerated after the attack by the electrophile, hence leaving a stable halogenated byproduct. Electrophilic halogenation can also occur if molecular chlorine and bromine are present in an acidic environment with the presence of chloride and bromide ions. As example Br_2 reacts with Br^- forming a positive Br^+ ion that can act electrophilic and attacks the aromatic [29]. Traces of molecular bromine were indeed observed in the experiments, since the organic hexane phase was slightly brownish colored during extraction of the mixed electrolyte samples. Halo substituents are generally weak deactivating groups and the halogenated PAHs are hence less susceptible to further substitution and chemically reactive compared to the parent compound [29].

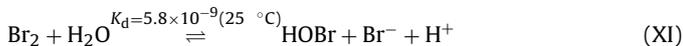
These results provided information of which halogenated PAHs typically are formed as non-polar byproducts, when aqueous chloride and bromide containing PAH solutions are chlorinated. However, the applied chlorine dose concentrations were intentionally high in order to ensure the occurrence of halogenations. During the electrochemical treatment, significantly lower steady state batch concentrations of active chlorine were present due to the low applied current density of 25 mA cm⁻². According to the performed identification experiments, this lower active chlorine concentration was expected primarily to result in the formation of mono halogenated naphthalene and pyrene formation. However, since both chloride and bromide are electrochemically active ions, other electrochemical routes of chlorination or bromination might exist, contributing to the halogenations from the pure chemical reactions.

3.3. Fate of halogenated PAHs during EO

All EO experiments were performed galvanostatically at a current density of 25 mA cm⁻², and hence the overall rate of oxidation reactions removing electrons from the solutions was the same throughout the study. At first, the extent of chlorination of the PAHs in an electro-chlorination process was investigated in a 0.10 M sodium chloride electrolyte. 0.050 M hydrogen phosphate buffer was added in order to maintain constant pH around 6, which simulated practical treatment conditions. This is in the slightly acidic part of the neutral and normal domain of sea water, but at a pH where the possibility of halogenations exists. The hydrogen phosphate ions can with the applied Ti/Pt₉₀-Ir₁₀ anode material be considered as electrochemical inactive, and without the buffer system present, pH of the solution would turn alkaline to a steady state pH of 9–10 due to the cathodic hydrogen evolution reactions. The initial concentration of naphthalene in the solutions was one order of magnitude higher than fluoranthene and pyrene, due to the much higher water solubility of this compound. However, all of the parent PAHs were degraded during the EO treatment (Fig. 6a and b). This supports prior findings [27], where the applied current density of 25 mA cm⁻² was found as the most efficient setting during galvanostatic electrolysis of a similar PAH solution.

The analysis showed a significant formation of mono chlorinated naphthalene peaking after 45 min followed by subsequent degradation with almost complete removal after 240 min (Fig. 6c). Small concentrations of di-chloro-naphthalene were detected after 60 and 180 min, but were not found after 240 min, and no further chlorination of naphthalene was seen. The four ring structured pyrene or fluoranthene was not subjected to chlorination and was left out of the figures. The lack of chlorination was probably due to the concentration of active chlorine species being too low in the bulk of the solution for chemical chlorination to occur. When compared on a molar scale, mono-chloro-naphthalene as the main byproduct comprised 13% of the initial naphthalene concentration on its high point after 45 min (Fig. 6d).

A similar experiment was performed with 0.010 M of KBr added to the 0.10 M NaCl electrolyte. Bromide is an electrochemically active ion as well as chloride and can participate in comparable EO and chemical reactions forming molecular bromine followed by disproportionation with water forming hypobromite/hypobromous acid (Eqs. (X)–(XII)).



This electrochemical route adds to the concentration of active bromine species in solution also formed from reaction (IX). One notable difference on bromine compared to chlorine is the equilibrium constant K_d of Eq. (XI), which implies that e.g. a low ionic strength water having a bromine concentration of 65 mg L^{-1} at 25°C , the concentration of molecular bromine and hypobromous acid is equal at pH 5.15 [30]. This pH is considerably higher than the similar pH of molecular chlorine and hypochlorous acid (Eq. (VI)), and molecular bromine was expected to be present in the mixed electrolyte EO experiments operated at pH 6.

The evolution of the parent PAHs during the treatment in the mixed bromide and chloride electrolyte was except a minor increase in degradation rates very similar to the curves observed in the pure chloride electrolyte, and are not showed. However, the pattern of halogenated byproducts was different with mono brominated naphthalene as the main product followed by di-bromo- and mono-chloro-naphthalene (Fig. 7a). Again, no halogenations of fluoranthene or pyrene were observed.

Peak concentrations of all byproducts were observed within 15–30 min, indicating that the bromination reactions were faster than the reactions leading to chlorination observed in Fig. 6. The presence of bromide suppressed the chlorination of naphthalene as compared to EO in pure chloride electrolyte, may be due to the fast reaction of active chlorine with bromide before the chlorination reactions occurred. Calibration of di-bromo-naphthalene was not possible. However, if equal sensitivity of mono- and di-bromated naphthalene in the MS detector was assumed, the concentration of di-bromo-naphthalene corresponded to 10% of the mono-bromo-naphthalene as measured in relative counts. In addition, di-bromo-naphthalene showed as expected a higher resistance to oxidation, demanding higher treatment times for complete removal. Comparisons based on counts were however made with caution and were avoided where possible. Important to notice was that the brominated naphthalene species once formed in fact were degraded like the chlorinated naphthalene during the EO. At its peak level after 15 min, the concentration of the primary byproduct mono-bromo-naphthalene corresponded to as high as 39% of the initial naphthalene concentration that was completely removed already after 30 min (Fig. 7b). This removal was faster than compared to the pure chloride electrolyte, but was caused both by the added oxidation from hypobromous acid and the bromination reactions. However, the initial concentration of naphthalene in this experiment was due to insufficient dissolution only half compared to the electro-chlorination experiment, and hence a direct comparison of amounts is difficult.

0.010 M of KBr is high compared to natural waters. In order to study the extent of halogenation under conditions comparable to sea water, the concentration of bromide in the electrolyte was decreased ten-fold to 0.0010 M KBr in addition to the 0.10 M NaCl ($\text{Br}^-:\text{Cl}^- = 1:100$), corresponding to $80 \text{ mg Br}^- \text{ L}^{-1}$ in solution (typical sea water 65 mg L^{-1} [30]). The halogenated species found and their fates during the EO treatment were similar to the pattern already observed (Fig. 8a). Trace amounts of di-bromo-benzene was detected after 15 min, but was removed to below the detection limit

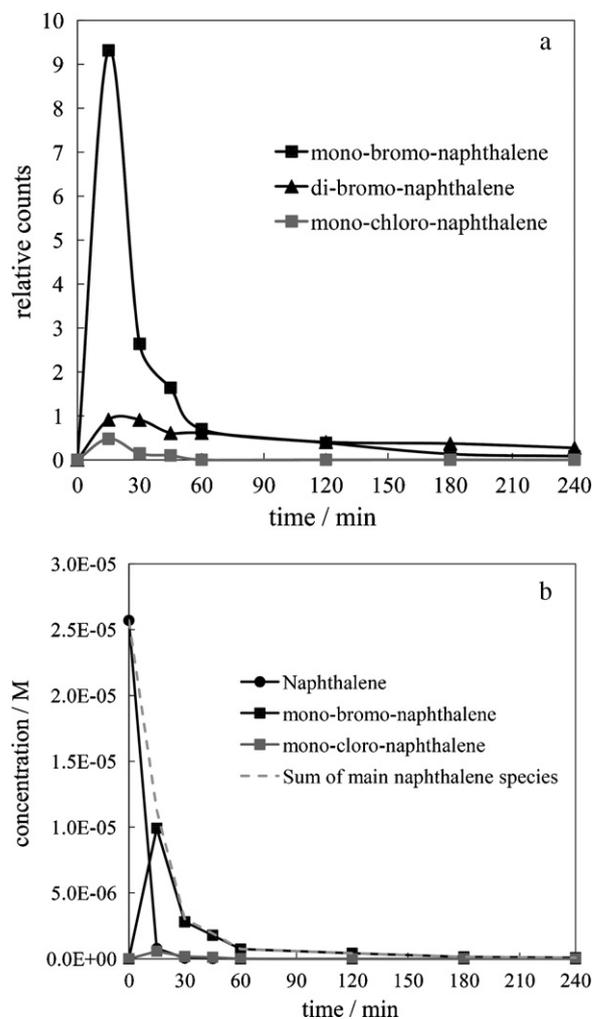


Fig. 7. The evolution in (a) brominated and chlorinated byproducts during EO in mixed 0.010 M KBr and 0.10 M NaCl electrolyte at 25 mA cm^{-2} and pH 6. (b) The molar comparison of naphthalene and mono halogenated naphthalene concentrations during the EO treatment.

already in the next taken sample and are not included in the figure. The amount of di-bromo-naphthalene peaked after 30 min of treatment time. Based on the measure of relative counts and appropriate assumptions it corresponded to 29% of the mono-bromo-naphthalene, considerable more than formerly observed 10%. The reason of the almost doubled scale of relative counts of byproducts compared to the 0.010 M bromide experiment was an increased initial concentration of parent naphthalene up to $6 \times 10^{-5} \text{ M}$ (Fig. 8b), resulting in an increased absolute byproduct formation. Even at this lower bromide concentration compared to the chloride content, bromide was still in far excess compared to the total organics present. The possible concentrations of active bromine species formed were as showed sufficient to result in formation of brominated organics, still greatly exceeding the formation reactions of chlorinated organics that were significantly suppressed.

On the concentration scale, mono-bromo-naphthalene at its 15 min peak concentration comprised 30% and mono-chloro-naphthalene 2% of the initial naphthalene concentration (Fig. 8b). The decrease in percentage of mono-bromo-naphthalene formation compared to Fig. 7b is explained by the observed increase in di-bromo-naphthalene formation.

When EO is to be considered for treatment of saline water, the presence of bromide has a significant effect on the formation of halogenated byproducts, which needs to be considered.

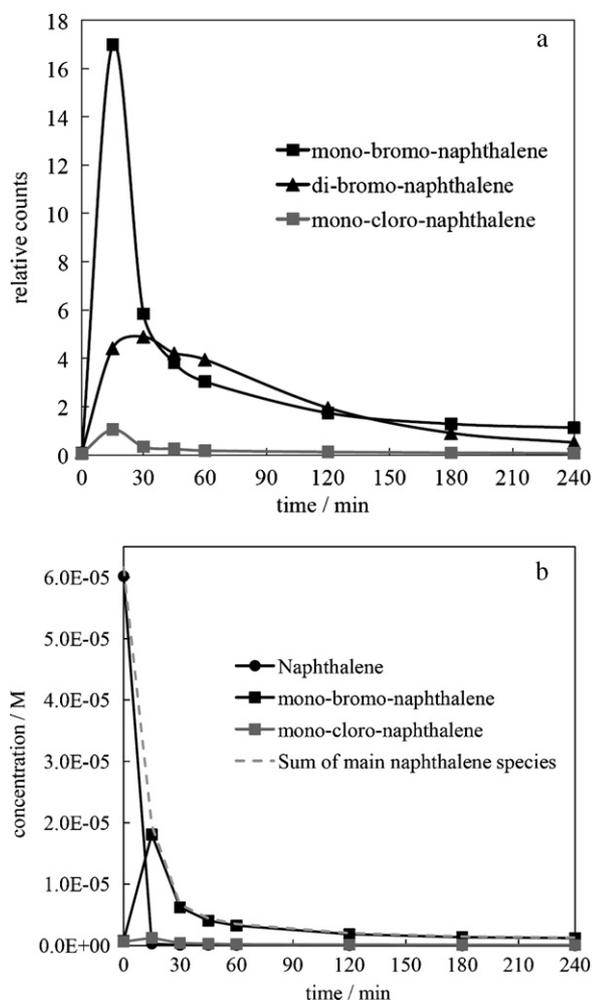


Fig. 8. The evolution in (a) brominated and chlorinated byproducts during EO in mixed 0.0010 M KBr and 0.10 M NaCl electrolyte at 25 mA cm⁻² and pH 6. (b) Comparison of the concentration development of the main naphthalene species during the EO treatment.

Not specifically due to the electrochemical reactions, but rather to the chemical actions of active chlorine producing hypobromous acid available for the electrophilic substitution reactions. Chlorination of PAHs seems not to be a considerably threat as long as bromide is present, but up to 10% of mono chlorinated products was observed in the single sodium chloride electrolyte. This needs to be taken into account as well when treating bromide free waters. Mono halogenated naphthalene species were the main byproducts found with minor concentrations of di-bromo-naphthalene. No tri halogenated species were observed during EO as in the identification experiments, where it required very high active chlorine concentrations. This is believed to be due the low current density applied keeping the concentrations of active halogen species low. Interestingly, differences were observed among the three different PAHs. The inert chemical properties of fluoranthene and pyrene did not, despite removal from solution, result in halogenation of the compounds during EO. Naphthalene was due to the higher solubility and chemical reactivity halogenated during the EO treatment, but the byproducts were further degraded and solutions to the issue may be a matter of treatment time adjustment. This study was conducted under slightly acidic pH conditions favorable for halogenations, and increased pH may be another important parameter for the suppression of halogenation reactions as indicated in the identification experiments. Another issue not treated in this study is the formation of halogenated polar oxidation byproducts

as minor carboxylic acids and alcohols. These compounds cannot be detected with the applied GC–MS apparatus, but their production can be significant and will be investigated further in coming experiments.

4. Conclusions

The experimental work of this study has revealed halogenation of the parent organics to be a matter of consideration, when treating PAH rich seawater by electrochemical oxidation. Differences were seen among the PAHs, and naphthalene as the most soluble compound was the only one to be halogenated in detectable amounts. In a single sodium chloride electrolyte, up to 13% of the initial naphthalene was chlorinated at the peak concentration during treatment before it subsequently was removed. However, even small concentrations of added bromide in the electrolyte suppressed the formation of chlorinated byproducts for an exchange with primarily mono and di brominated naphthalene in peak concentrations up to 30–39% of the initial naphthalene. All of the considered byproducts were despite a more recalcitrant behavior degraded subsequent to formation. This means that considering the removal of the PAHs in question by EO, treatment times need to be prolonged to ensure a safe discharge of the treated water, with an acceptable low level of halogenated byproducts.

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