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Muff, Jens; Andersen, Christian D.; Erichsen, Rasmus; Søgaard, Erik Gydesen

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Electrochemical treatment of drainage water from toxic dump of pesticides and degradation products

Jens Muff, Christian D. Andersen, Rasmus Erichsen, Erik Gydesen Soegaard*

Aalborg University, Esbjerg Institute of Technology, Niels Bohrs Vej 8, Esbjerg 6700, Denmark

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ABSTRACT

Polluted drainage water from a dump of toxic chemical waste containing organophosphoric pesticides and their natural degradation products was treated with electrochemical oxidation in order to investigate the applicability of the technique in remediation of natural complex polluted water. The dump is located adjacent to the sea in sand dunes, the natural salinity of the investigated water was 0.7 w/w% and sodium chloride served as main electrolyte. A commercial available flow cell with a tubular design, Ti/Pt₉₀–Ir₁₀ anode, and 316 SS cathode was applied, and the electrolysis experiments were conducted in a batch recirculation experimental set-up.

COD measurements showed that the overall oxidation of organic and inorganic substances followed first-order kinetics by the current densities investigated, 310–1131 mA cm⁻², and the COD removal rate increased by increased current density and to a minor extent by increased salinity up to 2.0 w/w%. Evaluation of ICE and energy consumption showed that further optimization is possible and needed. The target organic pollutants parathion, methyl-parathion, malathion, ethylaminoparathion, paraoxon, and several phosphoric triesters were all degraded during the treatment except O,O,O-triethylphosphoric acid, a compound formed during the electrochemical process with a highly stable low energy structure, rendering it recalcitrant to participate in the oxidation reaction. The degradation of the subjected organics was found to be caused by indirect oxidation by the hypochlorous/hypochlorite pair as the main oxidizing agent, produced by the anodic oxidation of chloride. The study has showed that electrochemical chloride mediated indirect oxidation is a relevant, neat and possible solution for the remediation of organophosphoric pesticide polluted natural water.

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1. Introduction

Organophosphate esters such as methyl-parathion and parathion have been used as alternatives to dichloro-diphenyl-trichloroethane (DDT) and other chlorinated hydrocarbon pesticides. However, the organophosphate esters are not rapidly degraded in natural waters. At 20 °C and pH 7.4, parathion has a hydrolytic half-life of 108 days, and its toxic metabolite, paraoxon, has a similar half-life of 144 days [1]. Various innovative technologies have been proposed for elimination of organophosphoric pesticides. Especially, degradation of methyl-parathion has been examined by photocatalysis [2,3], hydrogen peroxide [4], ultrasonic radiation [1] or hydrolysis promoted by mercury [5]. The major disadvantage of these technologies is that they are designed for decontamination of aqueous solutions with a very low pollu-

tant concentration and are not suitable for treatment of higher concentrations of pesticides.

Treatment of recalcitrant toxic wastewaters by electrochemical methods has gained more and more interest in the recent years [6–14]. In the electrochemical treatment, the organic and toxic pollutants are oxidized by direct electron transfer at the surface of the anode and by indirect oxidation via production of oxidants such as hydroxyl radicals and hypochlorite, corresponding to the models proposed by Cominellis [6,7] and De Battisti [8]. Electrochemical treatment has been successfully applied in the purification of domestic sewage [9], landfill leachate [10,11], tannery wastes [12], olive oil waste waters [13], textile dyes [14], etc. For a comprehensive review of electrochemical processes in wastewater treatment please refer to [15].

Electrochemical oxidation of organophosphoric pesticides has in prior studies been investigated with methyl-parathion as the model pollutant. In pure solution with sodium chloride as electrolyte, 80% reduction of both COD and BOD was obtained with a mean energy consumption of 8–18 kWh (kg COD)⁻¹ [16]. Furthermore, the investigation showed that methyl-parathion degradation

* Corresponding author. Tel.: +45 9940 7622; fax: +45 7545 3643.

E-mail address: egs@aaue.dk (E.G. Soegaard).

was far more effective, when the brine solution was in the acidic range. The investigation was conducted in a laboratory scale plant using Ti/Pt as anode and SS 304 as cathode. Through a factorial experimental procedure, the electrolysis efficiency was optimized and upgraded to electro-Fenton through addition of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, and the final process resulted in a satisfactory removal of organic load with a significant improvement of the COD/BOD₅ ratio, rendering the effluent amenable to biological treatment [17]. An investigation of the degradation pathways of methyl-parathion in aqueous solution by electrochemical oxidation has showed a rapid degradation, but without full mineralization of all methyl-parathion [18]. Several intermediates were identified with oxalic, formic and acetic acids as well as tetraphosphorus trisulfide as final products [18]. However, it has not yet been clarified whether direct or chlorine mediated oxidation is the most important mechanism in the degradation of methyl-parathion. So far, both mechanisms seem to play an important role, but the fact that additional sodium chloride in the present work increased the degradation and incomplete mineralization of methyl-parathion was obtained in previous studies [18] might indicate the importance of the indirect oxidation, due to a higher selectivity of hypochlorite oxidation.

In this study, the electrochemical treatment of a complex mixture of organophosphoric pesticides and naturally occurring degradation products from the pesticides in aqueous solution was investigated. The investigated matrix was polluted drainage water, directly sampled from a dump of toxic chemical waste originating from a large-scale industrial production of pesticides. The dump was located in sand dunes adjacent to the sea. In comparison with the prior investigations of methyl-parathion degradation [16–18] in model solutions, the concentrations of the individual substances were low and the complexity of the matrix was high with regards to the presence of naturally occurring salts and impurities. However, the successful conclusions from the prior research [16–18] render electrochemical oxidation as being a promising technique in remediation of the subjected water pollution. The aim of the study was to investigate the applicability of the electrochemical oxidation technique for remediation of natural water polluted with organophosphoric pesticides, the influence of salinity and current density on the rate of COD removal, current efficiency, and energy

consumption, and to determine the importance of the indirect oxidation by hypochlorite. The latter aspect is important regarding the practical applicability of the electrochemical oxidation, since treatment of a higher capacity of water at lower cost is possible if intermixing of the drainage water and electrochemically generated oxidant is workable. Hence, the present study was conducted as a part of providing a basis for decision concerning the future remediation strategy of the polluted site.

2. Materials and methods

2.1. Applied materials and the electrochemical cell

The natural composition and characteristics of the investigated drainage water is seen in Table 1. The chemical structure of the organic compounds is seen in Table 2. The dump was located adjacent to the sea and hence a high salinity of 0.7 w/w% was initially present in the investigated drainage water. The natural conductivity is 9.51 mS cm^{-1} rendering the water amenable to electrochemical treatment. The natural pH of the drainage water was 4.2 with a high concentration of dissolved iron of 59.8 mg L^{-1} . The sodium chloride used to increase the salinity was of technical grade approved for use in foodstuff. The applied electrochemical flow cell was a laboratory scale commercially available cell from Watersafe. 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 applied cell is sketched in Fig. 1.

2.2. Experimental procedure

The electrochemical treatment of the drainage water was investigated in a water cooled batch recirculation system, see Fig. 1. The water was pumped through the cell at a flow rate of 430 L h^{-1} from a stirred tank with a volume of 25 L. The overall cell voltage was controlled by an external power supply. Prior to start of each experiment, the 25 L batch of drainage water was recirculated without applied voltage for 10 min in order to ensure homogenization and that no autocatalytic activity was found by the anode surface. During the experimental run, water was sampled from the tank for further analytical determination. The experiments were conducted at a constant temperature of 13°C if nothing else is specified. The investigated current densities range from 310 to 1131 mA cm^{-2} , the overall cell voltage from 8.0 to 20.0 V and the salinity from the natural level of 0.7 up to 4.0 w/w%. For the intermixing experiments, a 4.0 w/w% sodium chloride solution was electrolyzed for 30 min at a current density of 1131 mA cm^{-2} in order to reach an available chlorine concentration of 2 g L^{-1} . Subsequently, the oxidant solution was intermixed with drainage water in a ratio of 1:1. A similar experiment with intermixing of a pure sodium hypochlorite

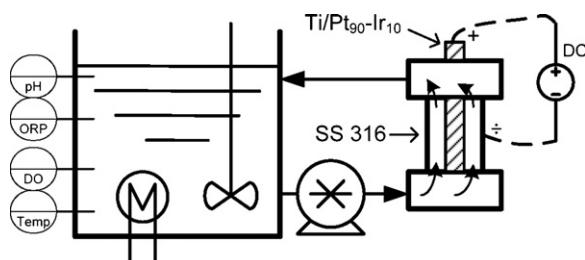


Fig. 1. Diagram of the batch recirculation experimental set-up and the applied EC cell.

Table 1
Natural composition and characteristics of the drainage water.

Parameters	Value	Parameters	Value
pH	4.2	Paraoxon	0.02 mg L^{-1}
Conductivity	9.51 mS cm^{-1}	O,O,S-trimethyl-dithiophosphoric acid	3.10 mg L^{-1}
Salinity	0.7 w/w%	O,O,S-triethyl-dithiophosphoric acid	0.27 mg L^{-1}
Dissolved iron	59.8 mg L^{-1}	O,O,S-triethyl-thiophosphoric acid	0.08 mg L^{-1}
COD	83.3 mg L^{-1}	O,O,O-triethyl-thiophosphoric acid	0.94 mg L^{-1}
Malathion	0.12 mg L^{-1}	O,O,O-triethyl-phosphoric acid	$<0.01 \text{ mg L}^{-1}$
Parathion	0.62 mg L^{-1}	O,O-diethyl-S-methyl-thiophosphoric acid	0.36 mg L^{-1}
Methyl-parathion	0.25 mg L^{-1}	O,O-diethyl-S-methyl-dithiophosphoric acid	1.30 mg L^{-1}
Ethylenimino-parathion	3.50 mg L^{-1}	O,O,S-trimethyl-dithiophosphoric acid	3.10 mg L^{-1}

Table 2

Trivial names and chemical structures of investigated compounds.

Compound	Chemical structure	Compound	Chemical structure
Parathion		O,O,S-triethyl-thiophosphoric acid	
Methyl-parathion		O,O,O-triethylphosphoric acid	
Malathion		O,O,S-trimethyl-dithiophosphoric acid	
Ethylaminoparathion		O,O,S-triethyl-dithiophosphoric acid	
Paraoxon		O,O-diethyl-S-methyl-thiophosphoric acid	
O,O,O-triethyl-thiophosphoric acid			

solution from Merck diluted to 2 g L⁻¹ of available chlorine was conducted for comparison. Samples for analytical determination of COD and specific compounds were sampled after 180 min.

2.3. Analytical methods and evaluation parameters

Parameters as oxidation and reduction potential (ORP), pH, temperature, conductivity and dissolved oxygen (DO) were monitored in the bulk solution in the tank by appropriate sensors. Analysis of the chemical oxygen demand (COD) of the sampled water was conducted by the Merck Spectroquant spectrophotometric method approved by USEPA. The concentration of available chlorine was determined by a kit from Lovibond applying the standard DPD method provided in DS/EN 7393-2. Analytical determination of the concentration of dissolved iron was performed by atomic absorption spectroscopy (AAS, PerkinElmer MHS-10). Determination of the concentration of the parent pesticides parathion, methyl-parathion, malathion and the range of degradation products in Table 1 were performed by gas chromatography with an NPD detector.

The instantaneous current efficiency (ICE) of the electrolysis was calculated from the COD concentrations using the relation [7]:

$$\text{ICE} = \frac{\text{COD}_t + \text{COD}_{t+\Delta t}}{8I\Delta t} \text{FV} \quad (1)$$

where COD_t and COD_{t+Δt} are the chemical oxygen demands at times *t* and *t* + Δ*t* (in g O₂ L⁻¹), respectively, and *I* is the current (A), *F* the Faraday constant (96487 C mol⁻¹) and *V* is the volume of the electrolyte (L). The energy consumption for removal of one kg of COD is calculated and expressed in kWh. The average cell voltage during the electrolysis was taken for calculating the energy consumption as follows [15]:

$$\text{Energy consumption} = \left(\frac{[tU]/V/1 \times 10^3]}{\Delta \text{COD}/1 \times 10^6} \right) \quad (2)$$

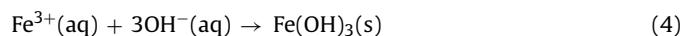
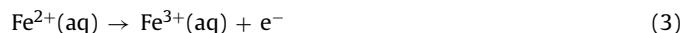
where *t* is the time of electrolysis (h), *U* is the average cell voltage (V), and ΔCOD is the difference in COD (mg L⁻¹). The rate of the

COD removal, corresponding to the degradation of organics and oxidation of inorganic substances was evaluated by modeling to the standard zero, first and second order kinetic models.

3. Results and discussion

The electrochemical oxidation of the pesticide polluted drainage water has been performed galvanostatically under different experimental conditions of salinity and current density. Due to the kinetic evaluation of the COD removal rate, the results are presented versus the time scale and not specific charge passed. However, the axes are easily transformed due to the fixed investigated water volume of 25 L. By a current density of 310 mA cm⁻², 180 min corresponds to 2.24 Ah L⁻¹.

In Fig. 2, the evolution of bulk pH, oxidation and reduction potential (ORP), and concentration of dissolved iron are presented during electrolysis at 310 mA cm⁻² and the natural salinity of 0.7 w/w%. The high initial concentration of dissolved iron showed a strong influence of both the pH and ORP of the bulk solution. The bulk ORP only slightly increased from 216 to 426 mV after 36 min of electrolysis until the concentration of dissolved iron was significantly reduced followed by a rapid ORP increment. During electrolysis, the bulk pH of the solution turned initially further acidic until the content of dissolved iron was removed and the evolution of hydrogen from the cathode and the corresponding buildup of hydroxide ions rendered a shift in the trend towards the neutral region. The decrease in dissolved iron and pH corresponds to anodic oxidation of Fe²⁺ to Fe³⁺ which subsequently reacts with hydroxide from the cathode reaction and precipitates as iron hydroxide:



The iron hydroxide was observed as reddish-brown precipitate, probably in the form of amorphous structured ferrihydrite, the most common iron oxide structure observed in dynamic water treatment systems [19]. The initial decrease in pH might be

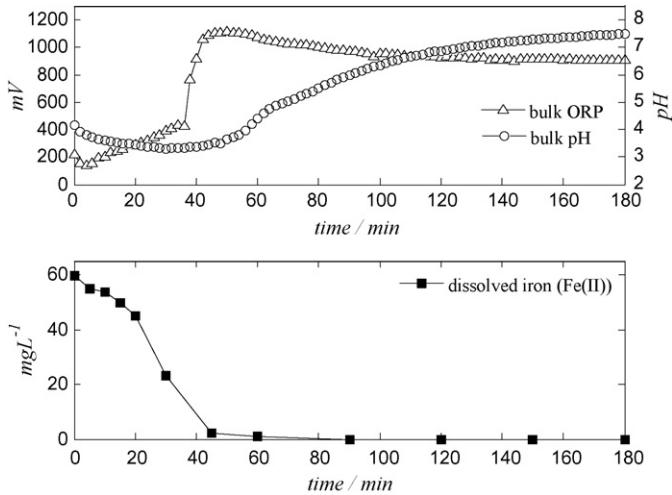


Fig. 2. Top plot: the evolution in bulk pH and oxidation–reduction potential (ORP) during electrolysis at 0.7 w/w% salinity and 310 mA cm^{-2} current density. Bottom plot: the evolution in the concentration of dissolved iron under the same conditions.

explained by a concurrent formation of different carboxylic acids as a step in the overall COD incineration process as well. The evolution in conductivity showed almost constant behavior during the experimental runs, only dependent on the initial salinity. A slightly decrease of $0.3\text{--}0.5 \text{ mS cm}^{-1}$ was observed due to the differences in molar conductivity of the hydroxide and oxonium ions and the precipitation of ironoxides as pH increased.

In Figs. 3–5, the dependencies of the COD removal rate on temperature, salinity and current density are showed. COD was under all experimental conditions removed to the detection limit within 100 min, however some differences were observed. Through standard kinetic modeling to zero, first, and second order expressions, it was found that the overall COD removal rate in the majority of experiments could be fitted to first order dependencies of the COD concentration with squared correlation coefficients, R^2 , from 0.9810 to 0.9993 (Fig. 5).

From Fig. 3 it is seen that a decrease in temperature of the bulk solution of 5°C results in 36% decrease in the apparent rate constant. The experimentally chosen temperatures are closely related to the practical use on the polluted site, since the drainage water is in this temperature range when it is sampled from the site. The

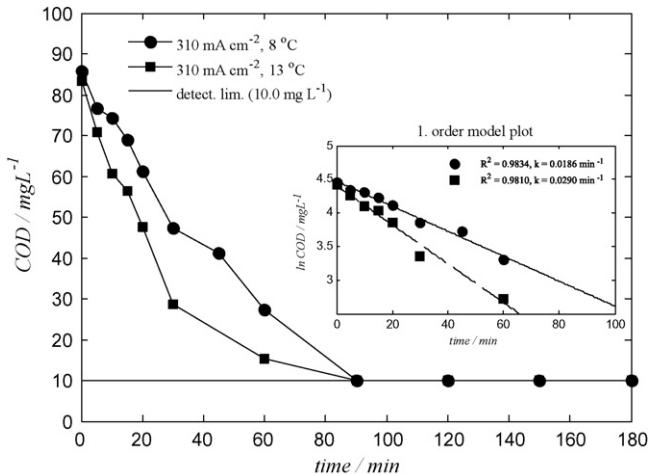


Fig. 3. Evolution in COD of the natural drainage water at 0.7 w/w% salinity during electrolysis at different temperatures.

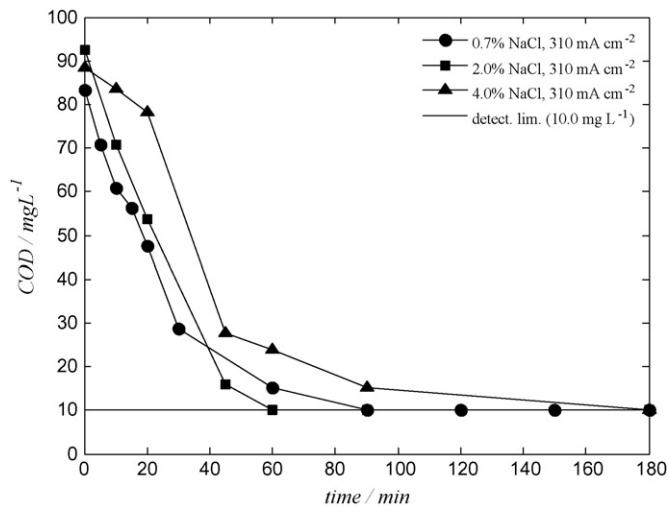


Fig. 4. Evolution in COD during electrolysis by increased salinities at constant current density of 310 mA cm^{-2} .

temperature dependence of the rate constant is explained by the Arrhenius relation between chemical rate constants and temperature, and indicated that the removal of COD mainly depended on chemical oxidation reactions rather than direct electron transfer at the anode surface, since minor temperature dependence is expected in the latter process in the investigated flow system.

An increase in salinity at a constant current density of 310 mA cm^{-2} enhanced the COD removal rate up to 2.0 w/w% probably due to an increased production of hypochlorous acid, the predominant chlorine species in the pH range investigated. However, a further increase in salinity to 4.0 w/w% showed a reverse effect on the COD removal rate, which significantly deviated from the first order reaction model. The unexplained kinetics observed at the higher sodium chloride concentration might be explained by the established competition between the lower overpotential chloride oxidation and the discharge of water generating MO_{x+1} at the anode surface. The chloride oxidation may become the main process, and as the bulk oxidation rate of COD by chlorine is slower than the surface oxidation rate by MO_{x+1} , the COD removal shows a sluggish decay. In addition, the high concentration of negatively charged chloride ions may inhibit the transport of the chloride oxidation

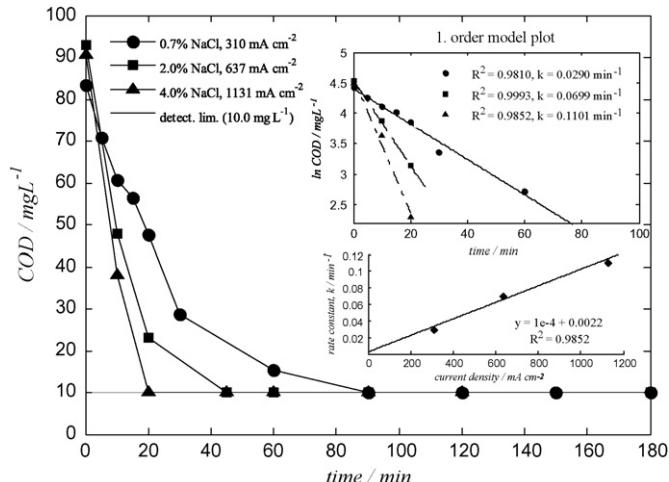


Fig. 5. Evolution in COD during electrolysis by increased salinities and current densities.

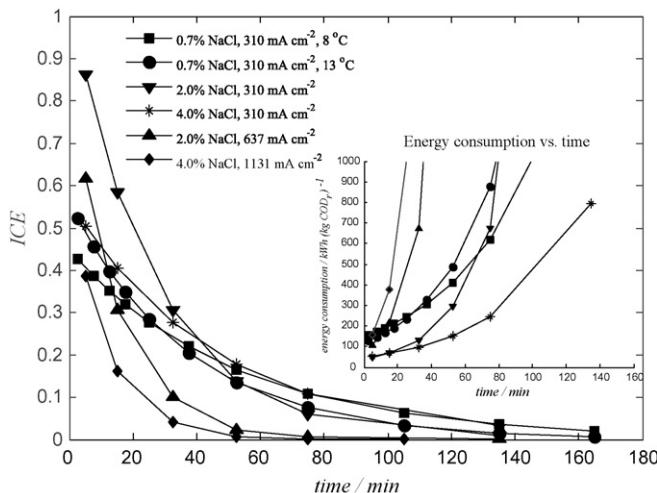


Fig. 6. Evolution in instant current efficiency (ICE) and energy consumption during electrolysis by the investigated experimental conditions.

product away from the anode, an effect enhanced by the condensation of the diffusive part of the double layer, as a result of the increased electrolyte concentration and ionic strength of the solution. In the latter case, the formed hypochlorous acid/hypochlorite might be further oxidized to chlorate and other chlorine species with only minor oxidizing capability towards COD at the present conditions. During the experiment conducted at 4.0 w/w% salinity, the overall cell voltage was reduced to 8.0 V in order to maintain constant current density, but the electrode potential was still considered well above the needed anode potential for chloride electrolysis, taken account of overpotential effects. In total, the COD removal only showed a minor dependence on the salinity at constant current density indicating that the current density acted as limiting step in the removal of COD. This indication was supported when the overall applied cell voltage was kept constant at the 19 V level at the higher salinities with only minor voltage regulations to maintain constants current densities during the experiments (Fig. 5). Due to the highly increased conductivity of the solution, the current densities increased significantly and a corresponding increase in COD removal rate was observed. In addition, the increased current density drove the electrooxidation process to a mass transfer controlled situation following first order kinetics even at 4.0 w/w% salinity. A more or less linear correlation between current density and the COD removal rate constant was found, probably due to a zero order relationship between hypochlorous acid/hypochlorite formation and current density in the electrolysis process found in prior studies (not published). This observation again indicated the importance of the indirect oxidation of the present COD by hypochlorous acid/hypochlorite. When COD was plotted with respect to the amount of specific charge (Ah L^{-1}) added to the solution during the electrolysis, the COD evolution was unaffected by the increasing current densities (plot not showed). Hence the level of COD removal only depended on the amount of charge added, an observation in agreement with prior studies of chloride mediated indirect oxidation of 2-naphthol [20].

The evaluation of the instantaneous current efficiency (ICE) of the electrochemical treatment of the drainage water with regards to the COD removal showed a rapid decrease during the electrolysis, as expected due to the first order dependence of the removal rate on the concentration of COD (Fig. 6). The highest current efficiency was found at a 2.0 w/w% salinity and by the, in the present study, low current density of 310 mA cm⁻². The rapid decrease in ICE showed that the majority of energy spent in the process went to buildup

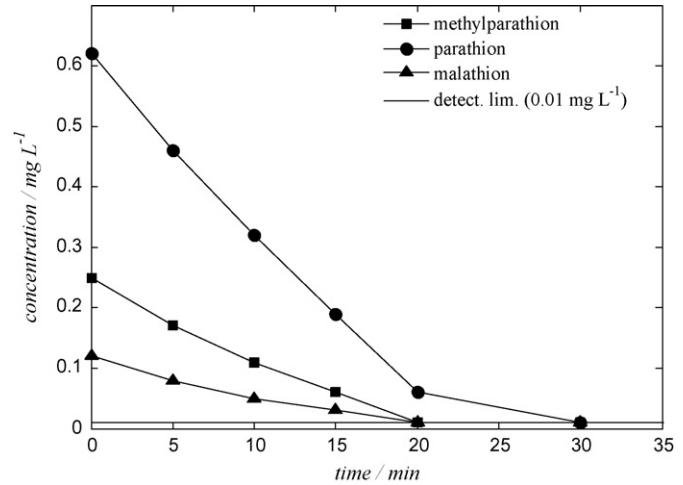


Fig. 7. Degradation of the parent pesticides methyl-parathion, parathion and malathion during electrolysis at 0.7 w/w% salinity and 310 mA cm⁻² current density.

of hypochlorous acid/hypochlorite and was wasted on side reactions, e.g. water electrolysis. Measurements of the concentration of dissolved oxygen in the bulk solution showed different trends dependent on the salinity, where oxygen was produced at 0.7 w/w% salinity and consumed at higher salinities, but no consistent pattern was observed. The evaluation of the energy consumption at the different experimental conditions showed that the high conductivity of a high bulk salinity clearly favored the energy consumption in terms of kWh (kg COD)⁻¹ reduced, but further optimization is possible and needed.

The results of the analysis of the concentration of the specific organophosphoric pesticides and degradation product during the electrochemical treatment at 310 mA cm⁻² and 0.7 w/w% are seen in Figs. 7–9. The parent pesticides methyl-parathion, parathion, and malathion were readily degraded within 30 min whereas paraoxon, a toxic degradation product of parathion not present in measurable amounts in the natural drainage water was formed during the oxidation of parathion. It was eliminated after 180 min. The decrease in concentration was observed once the parent compound parathion was removed from solution. Other degradation products as ethylaminoparathion and O,O,S-trimethyl-dithiophosphoric acid initially present in highest concentrations

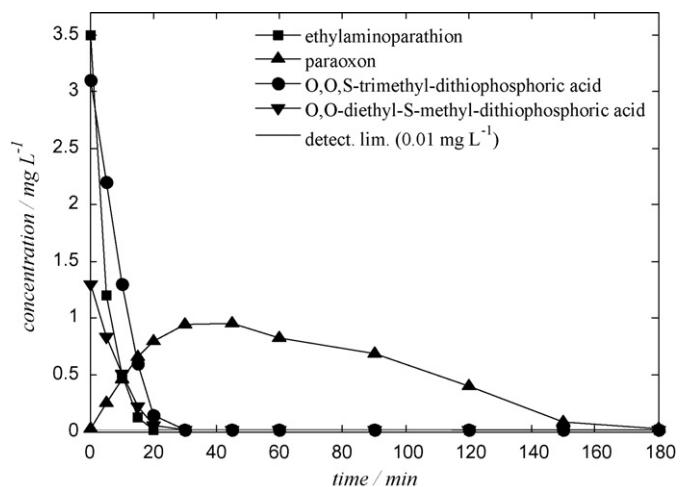


Fig. 8. Evolution of ethylaminoparathion, paraoxon and two phosphate triesters during electrolysis at 0.7 w/w% salinity and 310 mA cm⁻² current density.

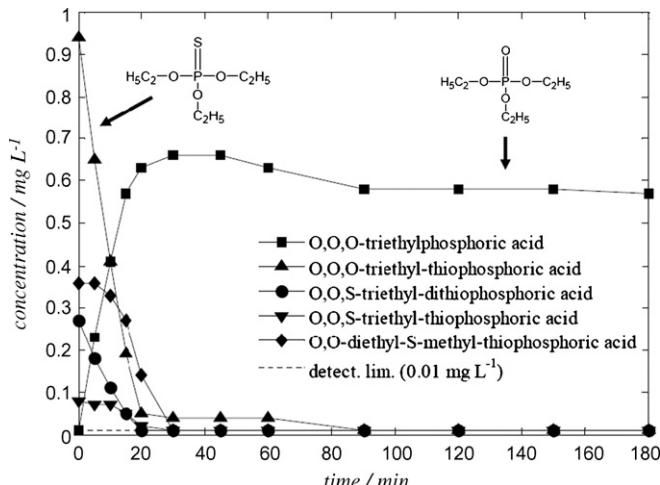


Fig. 9. Evolution of a range of phosphate triesters during electrolysis at 0.7 w/w% salinity and 310 mA cm^{-2} current density.

(3.1–3.5 mg L^{-1}) of the organics monitored in the drainage water were readily degraded as well (Fig. 8).

A single triester showed a more recalcitrant behavior. O,O,O-triethylphosphoric acid was formed during the electrolysis as the double bonded sulfur atom on O,O,O-triethyl-thiophosphoric acid was substituted with oxygen, a process which apparently formed a more stable triester that were not significantly affected by either the hypochlorous acid/hypochlorite oxidation or direct oxidation at the anode surface. 79% of O,O,O-triethyl-thiophosphoric acid was oxidized to O,O,O-triethylphosphoric acid, the last part is expected to be converted to O,O-diethyl-thiophosphoric acid and ethanol by hydrolysis. O,O,S-triethyl-thiophosphoric acid, a compound with similar side chains and structure, but with sulfur forming one of the ester bonds, was oxidized during the process without obstacles. The influence of the presence of the sulfur atom in the considered triester compounds on the stability and the reactivity towards oxidation reactions was investigated by quantum mechanical computational calculations of the internal energies of the molecules in vacuum. It was found that the length of all phosphorous oxygen bonds in the triester was shortened due to the change from a polarisable sulphur atom to a double bonded and hard oxygen atom which also has a shorter bond length to the phosphorous atom. The result of this change is a more stable molecule and probably therefore also a molecule more recalcitrant to the oxidation process (Fig. 9).

The importance of the indirect oxidation of the subjected organics by hypochlorous acid/hypochlorite was evident when an electrochemically generated oxidant solution right after electrolysis was intermixed in 1:1 ratio with the untreated drainage water in a separate container. By a concentration of 2 g L^{-1} of available chlorine in the electrolyzed oxidant, the concentration of 1 g L^{-1} in the water/oxidant mixture was sufficient to obtain resulting degradation levels similar to the ones from the batch recirculation experiments (Fig. 10). Compared with results obtained by intermixing of a pure sodium hypochlorite solution of equal concentration of available chlorine and the subjected water, the main oxidizing agent was identified to the hypochlorous acid/hypochlorite pair. However, one difference noticed was a higher amount of the recalcitrant triester O,O,O-triethylphosphoric acid formed when sodium hypochlorite alone constituted the applied oxidant solution. This observation indicated that other oxidants generated in the electrochemical process might be capable of oxidizing smaller amounts of the triester, also indicated by the minor decrease in concentration of the triester found in the batch experiments before the steady state level was obtained.

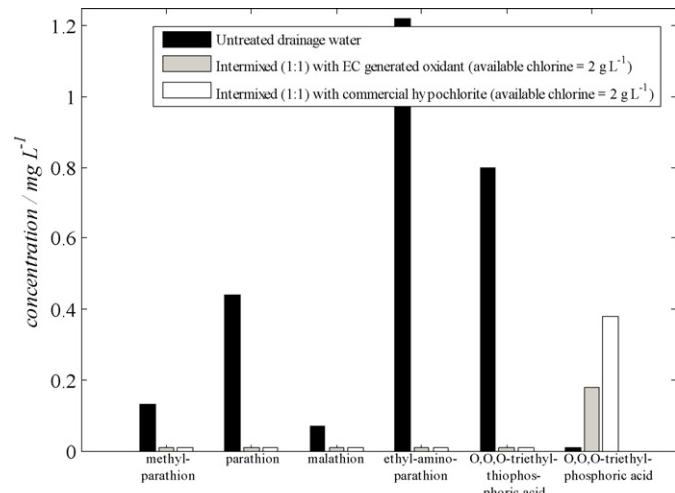


Fig. 10. Initial and final concentrations of methyl-parathion, parathion, malathion, ethylaminoparathion, O,O,O-triethylthiophosphoric acid and O,O,O-triethylphosphoric acid after intermixing in 1:1 ratio of EC generated oxidant and sodium hypochlorite solution respectively with drainage water.

The fact that the organophosphoric pesticides are oxidized due to the chloride mediated indirect electrochemical oxidation process is of significant practical use, since the required oxidant solution can be generated on site from the adjacent sea water and transportation of chemicals can be limited. The results obtained in the study also suggest possibilities for applying the electrochemical generated oxidant solution for remediation of the polluted soil by injection into the formation. However, this application requires more intensive pilot scale studies to be performed prior to practical use.

4. Conclusion

In this paper, the electrochemical treatment of drainage water sampled from a dump of toxic chemical waste and polluted with organophosphoric pesticides and several naturally occurring degradation products was investigated under different experimental conditions. Electrolysis performed in a batch recirculation setup has showed that the present COD was efficiently depleted within time scales of practical use and the removal rate increased with increased current density and to a minor extent by increased salinity up to 2.0 w/w%. An evaluation on the basis of the evolution in the instantaneous current efficiency and energy consumption showed that optimal conditions was 2.0 w/w% salinity and 310 mA cm^{-2} , but further optimization is possible and indeed needed for the process to be of practical use.

The subjected pesticides parathion, methyl-parathion, malathion and degradation products ethylaminoparathion, paraoxon and several triesters were all degraded during the electrolysis except O,O,O-triethylphosphoric acid due to a highly stable low energy structure surrounding the central phosphorous atom, rendering it recalcitrant towards oxidation. The degradation of the subjected organics was found to be caused by chloride mediated indirect oxidation by the hypochlorous/hypochlorite pair as the main oxidizing agent. The study has showed that electrochemical chloride mediated indirect oxidation is a relevant, neat and possible solution for the remediation of organophosphoric pesticide polluted natural water.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.electacta.2008.09.032.

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