

Direct versus indirect electrochemical oxidation of pesticide polluted drainage water containing sodium chloride

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Introduction

Electrochemical treatment of polluted water and waste water has in several investigations showed to be effective in the oxidation of organic pollutants [1]. Electrochemical oxidation of the organophosphoric pesticide methylparathion in a sodium chloride electrolyte has in prior research been investigated showing promising results with rapid degradation and detoxification of the pesticide following first order kinetics [2,3,4]. However, the research was conducted with high pesticide concentrations in pure solutions providing optimal conditions. This research investigates into electrochemical treatment of real drainage water from a buried dump containing methylparathion, parathion and malathion and several degradation products in low concentrations, in an investigation of efficiency and determination of the responsible oxidation mechanism.

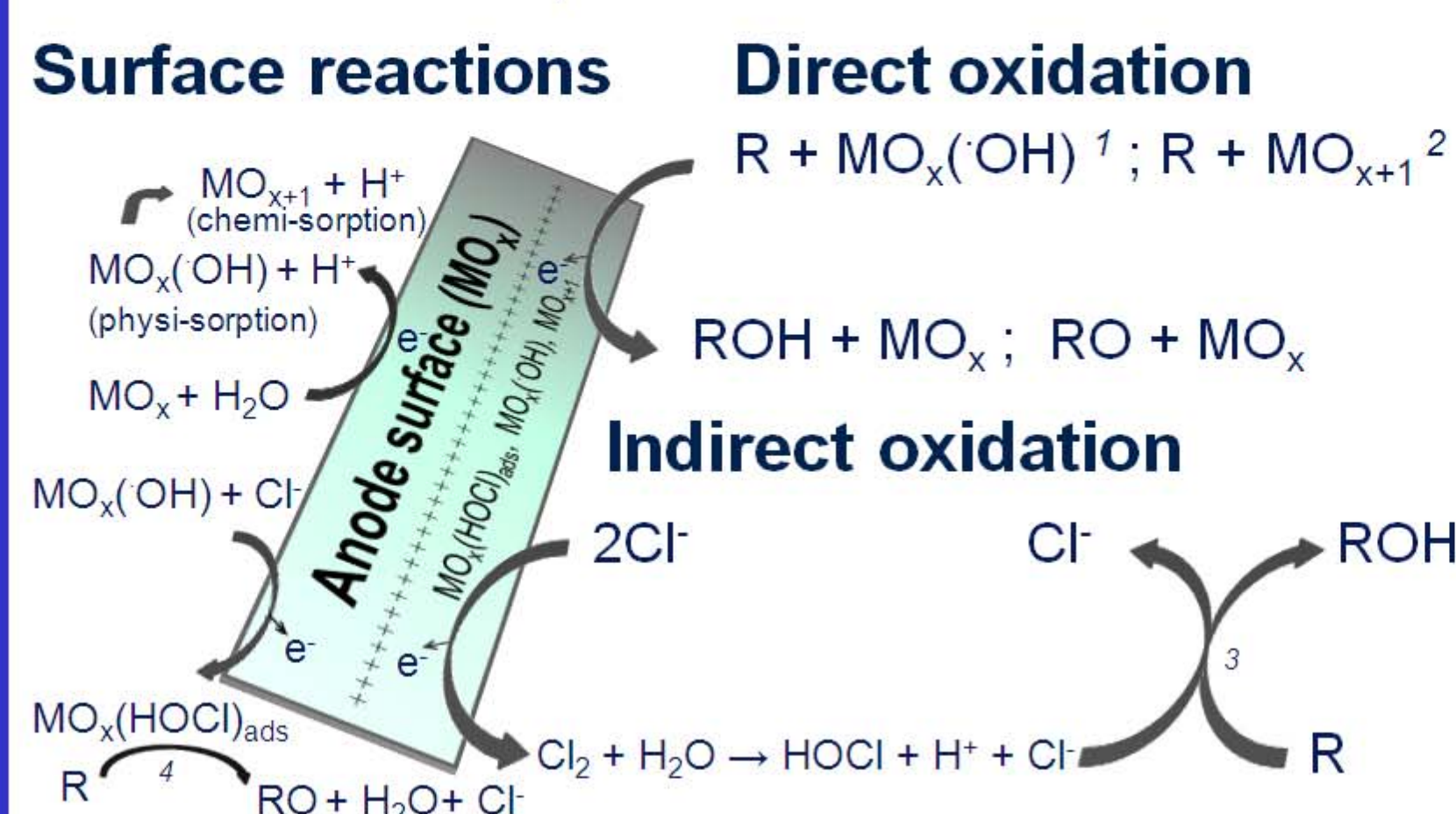


Figure 1: Electrochemical conversion/combustion of pollutants occurs directly by reaction with physio- or chemisorbed active oxygen [5], or indirectly by generation of strong oxidants with subsequent bulk oxidation of pollutants. Oxidation of pollutants by adsorbed oxychloro species has been proposed as well [6].

Objectives

The objectives of this investigation are:

- Investigation of electrochemical oxidation of real pesticide polluted water
- Investigate the main degradation mechanisms; direct or indirect oxidation?

Materials & Methods

A commercial one compartment flow through cell from WATERSAFE applied in the experimental investigation.

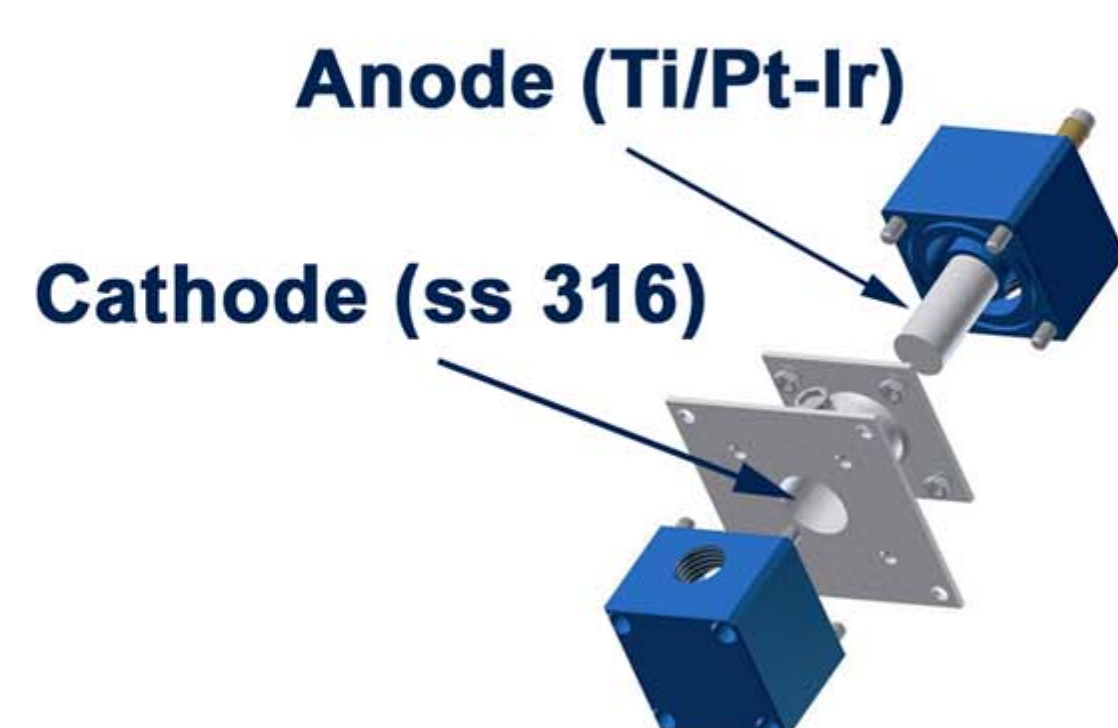


Figure 2: The electrochemical cell applied in the experimental investigation is a one compartment flow through cell with a turbulent design. The rod like anode in the center has a surface of 60.3 cm² and the reactive volume between the anode and cathode is 43.4 cm³.

Two experimental setups applied in the investigation.

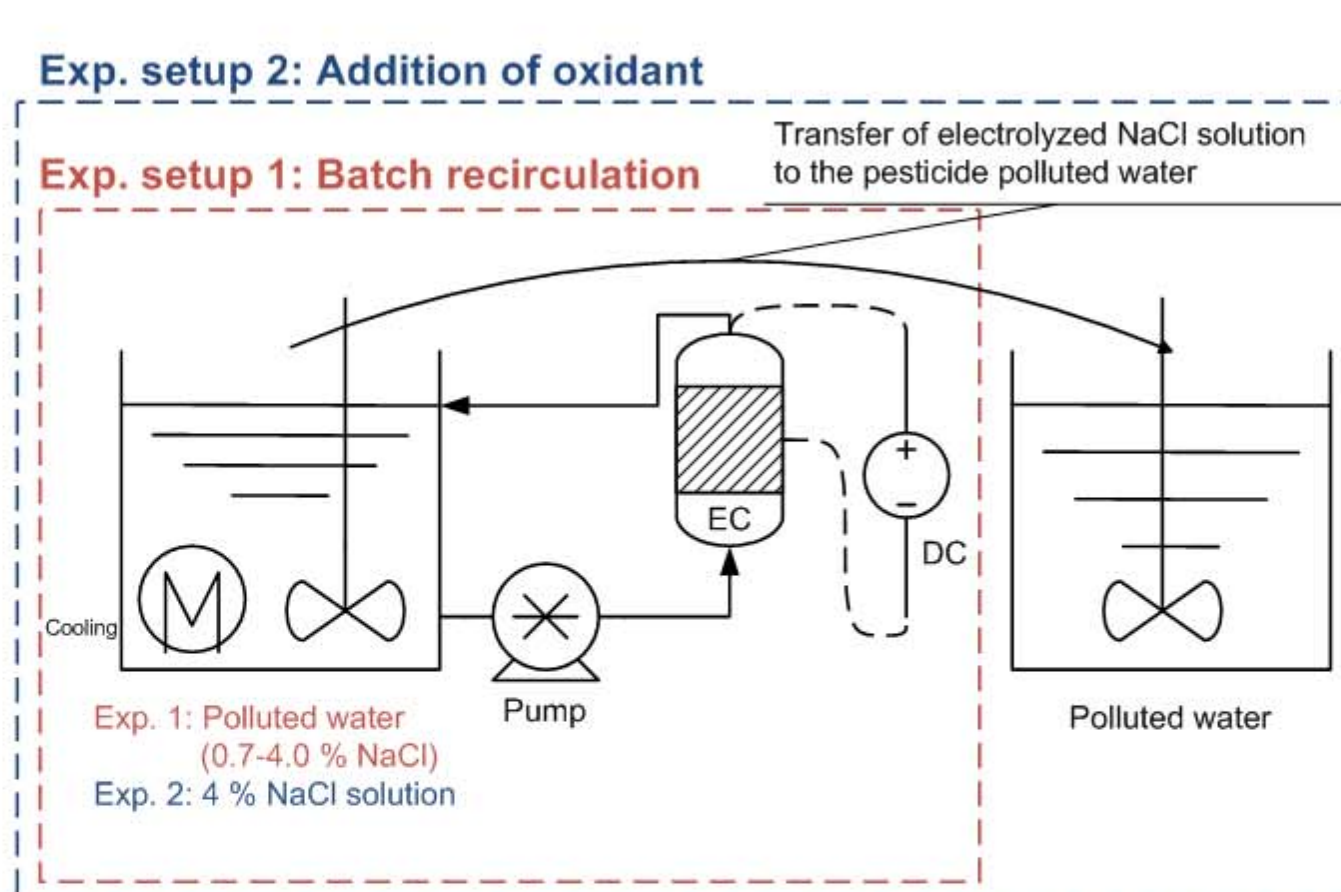


Figure 3: Two different experimental setups were applied in the investigation. First the polluted water was treated by batch recirculation by pumping through the electrochemical cell, with cooling and stirring in the tank. Second, a NaCl solution was electrolyzed in the batch recirculation setup and then added to a tank containing the polluted water.

Results

Batch recirculation treatment (Exp. setup 1)

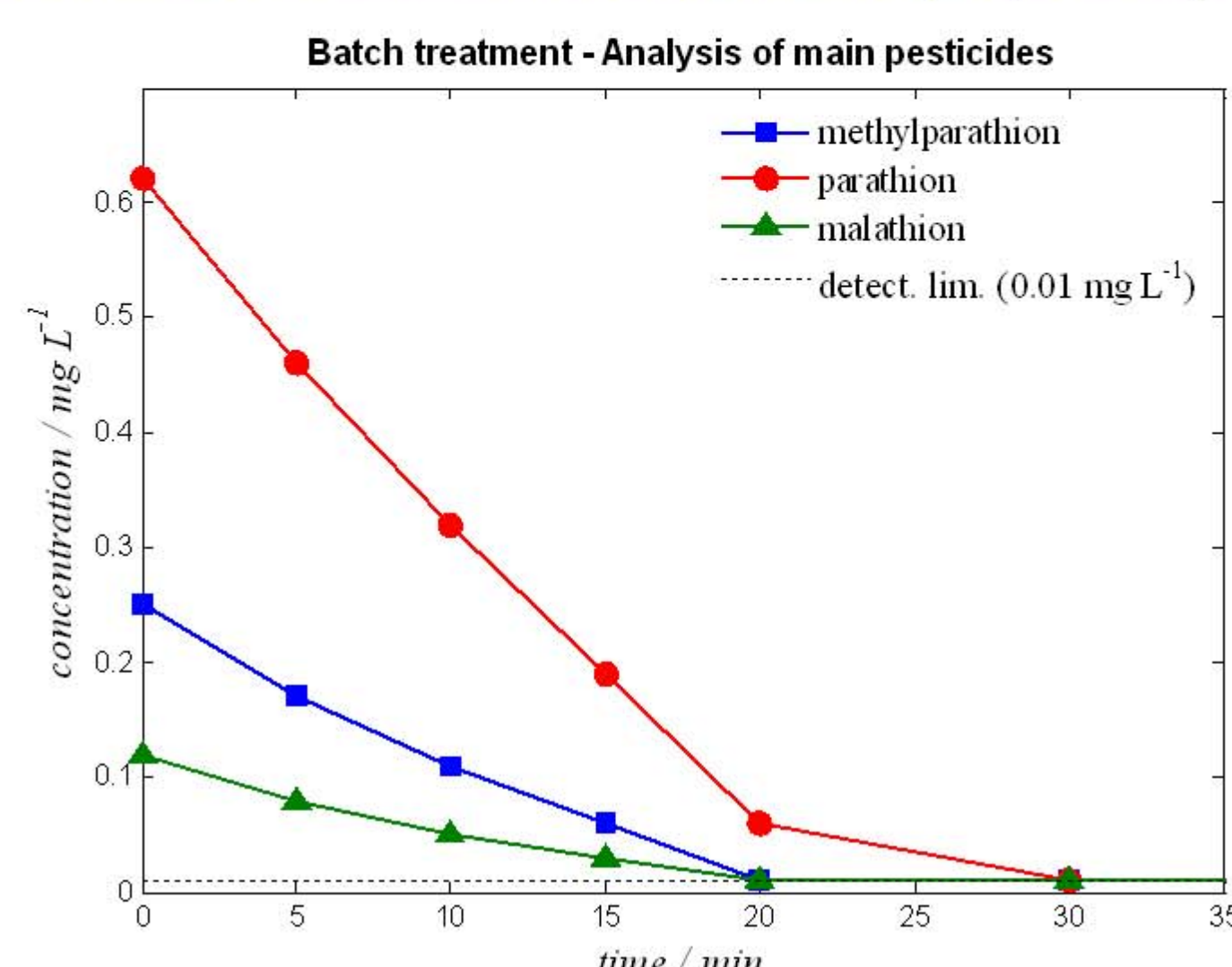


Figure 4: Results of analyses of main pesticides during batch recirculation treatment of drainage water with 0.7% NaCl at a current density of 324 mA/cm². The monitored pesticides methylparathion, parathion and malathion are degraded to the detection limit (0.01 mg/L) within 30 minutes.

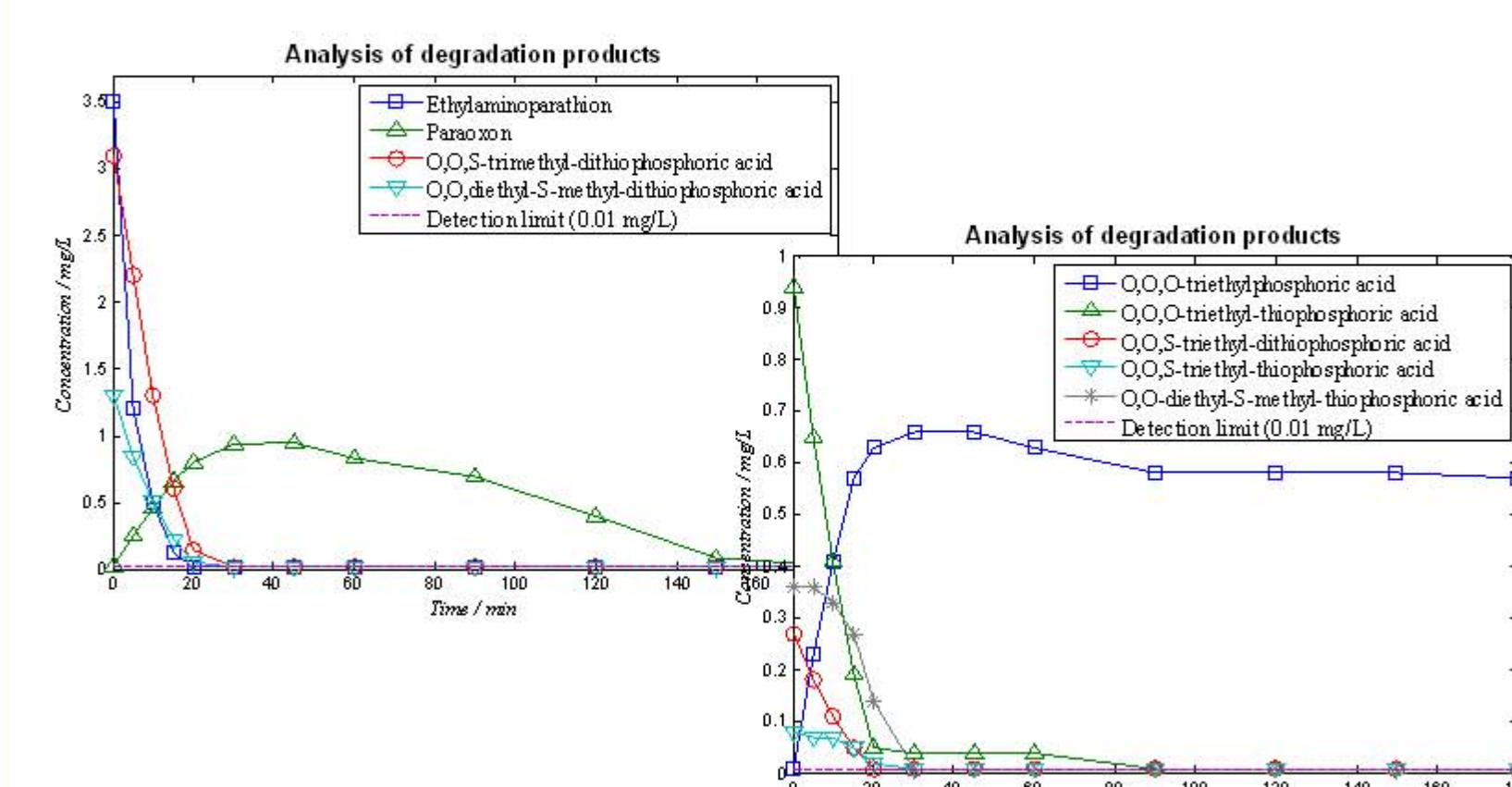


Figure 5: Results of analyses of a range of degradation products showing that all monitored substances are degraded except O,O,O-triethylphosphoric acid, a degradation product of O,O,O-triethylthiophosphoric acid. The highly toxic degradation product paraoxon is degraded to the detection limit after 160 min treatment.

- Degradation of methylparathion, parathion and malathion within 30 minutes with 324 mA/cm²
- Degradation of all degradation products except O,O,O-triethylphosphoric acid

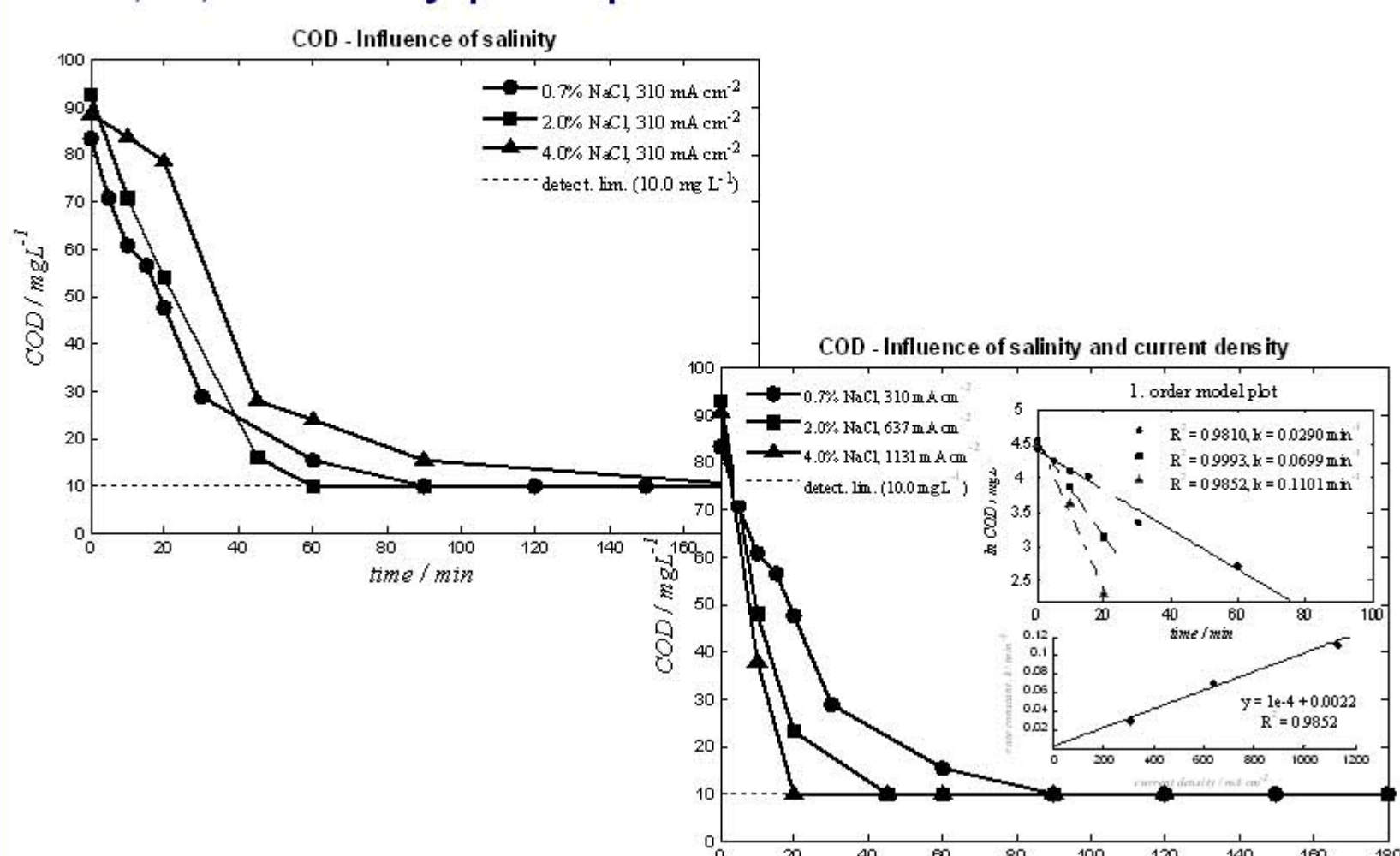


Figure 6: Degradation rate, monitored via COD measurements, increases at constant current density with addition of NaCl to a concentration of 2.0%, whereas higher concentration shows a limiting effect. Higher current efficiency enhances degradation rate to a level, where the additional energy is wasted on side reactions. A linear correlation is found between the first order rate constant and the current density.

- Addition of NaCl at constant current density increased degradation rate up to 2.0 w/w%
- Increased current density increased overall degradation rate of oxidizable substances
- Linear correlation between the first order rate constant and the current density

Treatment by addition of oxidant (Exp. setup 2)

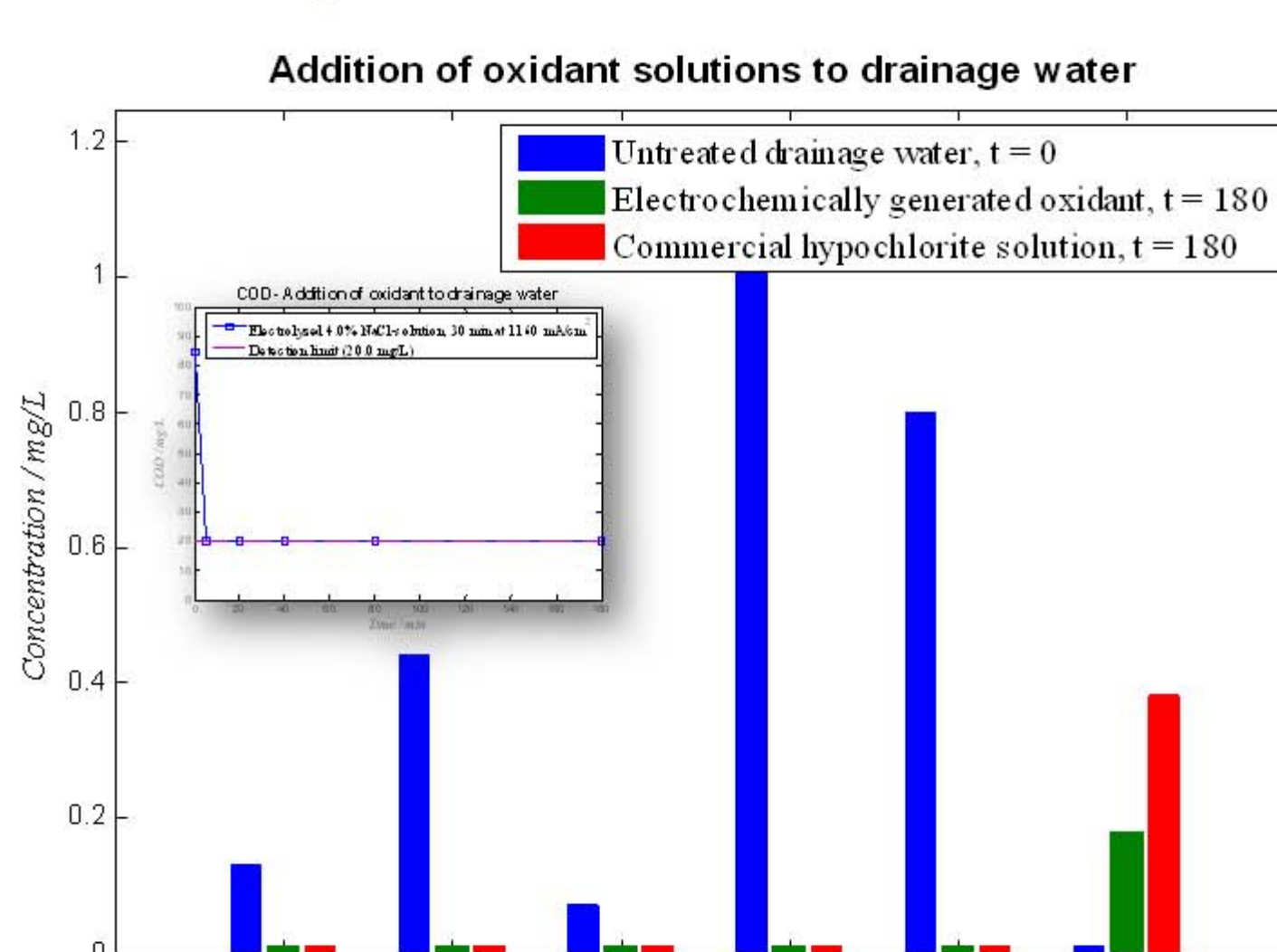


Figure 7: A 4.0% NaCl solution has been electrolyzed in the batch recirculation setup for 30 min. prior to addition to the polluted drainage water at a mixing ratio of 50:50. COD was removed to below the detection limit within 5 min after mixing, and analyses of pesticides and degradation products confirmed that all except O,O,O-triethylphosphoric acid were degraded. A similar experiment with mixing of a commercial hypochlorite solution with the polluted water showed that the degradation can be explained by hypochlorite oxidation.

- Degradation of all pesticides and degradation products except O,O,O-triethylphosphoric acid
- Addition and mixing of polluted water with a hypochlorite solution showed similar results

Discussion

The experimental results showed that degradation of the investigated organophosphoric pesticides and degradation products occurred through the indirect oxidation mechanisms mainly due to the formation of HOCl/OCl⁻.

When in action, mass transport to the reactive anode surface in the electrochemical cell is controlled by convective diffusion due to the forced convection provided by the pump in the recirculation system. Additionally, ions are transported to the surface by migration in the electric field.

Mass transport analysis (Simple approach via dimensionless numbers)

Exp. conditions: $Q = 439 \text{ L/h}$, $T = 13^\circ\text{C}$, $C_{\text{NaCl}} = 0.0833 \text{ M}$, $C_{\text{parathion}} = 2.13 \cdot 10^{-6} \text{ M}$

Mass flux to surface due to convection and diffusion:

$$N_{\text{Re}} = \frac{v_{\text{Re}} \cdot d_h}{\eta_{\text{water}}} = 825$$

$$N_{\text{Sc-Cl}^-} = \frac{\eta_{\text{water}}}{D_{\text{Cl}^-}} = 1.95 \cdot 10^{-6} \text{ s}$$

$$N_{\text{Sh-Cl}^-} = 1.85 \cdot N_{\text{Re}}^{1/3} \cdot N_{\text{Sc-Cl}^-}^{1/3} \cdot \left(\frac{d_h}{L}\right)^{1/3}$$

$$(Av. N_{\text{Sh}} \text{ for laminar flow between parallel plates [7]})$$

$$k_{\text{m-Cl}^-} = \frac{N_{\text{Sh-Cl}^-} \cdot D_{\text{Cl}^-}}{d_h} \Rightarrow k_{\text{m-Cl}^-} = 2.24 \cdot 10^{-5} \text{ m/s and } k_{\text{m-P}} = 7.16 \cdot 10^{-6} \text{ m/s}$$

$$I_{\text{Cl}^-} = k_{\text{m-Cl}^-} \cdot (C_{\text{bulk}} - C_{\text{surf}}) \Rightarrow I_{\text{Cl}^-} = 1.87 \cdot 10^{-3} \text{ mol/(s} \cdot \text{m}^2)$$

$$I_{\text{P}} = 1.52 \cdot 10^{-9} \text{ mol/(s} \cdot \text{m}^2)$$

Mass flux to surface due to electromigration ($U = 14 \text{ V}$):

$$I_{\text{mig}} = u \cdot C_{\text{bulk}} \cdot \frac{U}{d_h} \Rightarrow I_{\text{Cl}^- \text{ mig}} = 3.07 \cdot 10^{-2} \text{ mol/(s} \cdot \text{m}^2)$$

Model of direct surface oxidation of parathion: (Fractional conversion in plug flow reactor [7])

$$X_{\text{PFR}} = 1 - e^{-\left(\frac{k_{\text{m-P}} \cdot A_{\text{surf}}}{V_{\text{reactor}}}\right) \tau_{\text{retention}}}$$

$$(\text{Single pass})$$

$$X_{\text{PFR,R}} = 1 - e^{-\left(X_{\text{PFR}} \cdot \frac{\tau}{\tau_{\text{residence}}}\right)}$$

$$(\text{Batch recirculation})$$

$$C_{\text{P}}(t) = C_{\text{P,bulk}} \cdot (1 - X_{\text{PFR,R}})$$

Figure 8: A model of the direct oxidation of parathion at the surface is developed from expressions for fractional conversion in a plug flow reactor in batch recirculation mode, when the mass transfer coefficient is considered as the limiting step. The model shows that direct oxidation can not explain the observed experimental degradation rate of parathion ($t_{1/2} = 3483 \text{ min}$), hence providing evidence for indirect electrochemical oxidation as responsible mechanism.

- Higher diffusion coefficient of chloride results in a higher mass transfer coefficient compared to parathion
- The high bulk concentration of chloride makes the total mass flux of parathion insignificant compared to chloride
- Migration in the electric field provides a considerably contribution to the total mass flux of chloride

The method of addition of electrolyzed oxidant provides opportunities to treat higher capacities of polluted water.

Conclusion

- Electrochemical treatment of pesticide polluted water is an effective technique, degrading all monitored pesticides and degradation products except O,O,O-triethylphosphoric acid
- Degradation occur through indirect mechanisms mainly due to oxidation by hypochlorite
- Addition of electrolyzed sodium chloride solution in treatment of pesticide polluted water is a promising technique directly transferable to remediation of pesticide polluted soil

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