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Electrochemical degradation of thiocarbamates in NaCl solutions

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Abstract

Electrochemical degradation of thiocarbamate active ingredients was investigated in aqueous NaCl solutions. Degradation was studied with spectrophotometric methods that allowed specific light absorptions of thiocarbamates (212–220 nm), HClO (236–238 nm) and Cl_2 (225–233 nm) to be periodically or continuously measured. Measurements were also done through chromatographic analysis. The results indicate that under the reaction conditions applied, the electrochemical degradation of thiocarbamates in NaCl solutions takes place not only on the electrode but mainly in the solution phase through 'indirect' electrolysis involving the intermediates of NaCl electrolysis (Cl_2, HClO, ClO^-). This degradation process can be controlled efficiently with the help of electrochemical reaction parameters.

1. Introduction

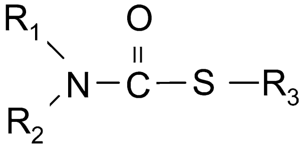
The application of electrochemical oxidation processes [1–4] in environmental protection may open up new perspectives in the handling of environmental problems which have so far been impossible to solve satisfactorily with other physical, chemical and photochemical methods. The application of electrochemical methods in pollutant degradation involves a number of difficulties, but these can be overcome.

One of the difficulties lies in the fact that current efficiency, selectivity and product composition greatly depend on electrode material [5–7]. Noble metals, especially platinum, are considered to be the most active [8]. At the same time, degradation intermediates with a blocking effect are adsorbed very easily on a platinum electrode surface [9]. Recently, successful experiments have been carried out using anodes with boron-doped diamond surfaces [10, 11].

Cell construction was also subject to experimental and theoretical investigations. New types of electrochemical reactors for wastewater treatment were studied in order to develop alternatives to conventional electrochemical reactors [12, 13].

It is advantageous [4] that both direct and indirect oxidation and reduction can be performed simply, with effective energy utilisation, in a way that can be effectively controlled and automated, in many cases without any additional material.

In certain chemical processes, wastewaters contain both organic and inorganic pollutants. Thus, for example, in the production of thiocarbamate type pesticides (where R_1, R_2, R_3 are alkyl, cycloalkyl or aryl groups), wastewater contains NaCl and organic pollutants. NaCl is produced in stoichiometric quantity from NaOH acid acceptor during synthesis. This means it is present in relatively high concentration (5–20 w/w%) in wastewater.



The purification of such wastewater is quite difficult, even with the TiO_2 photocatalytic method [14]. A satisfactory solution has not yet been found, since oxidation of organic pollutants is moderated by high Cl^- concentration, while in electrolysis, NaCl degradation is hindered by high organic material content. The effect of high chloride concentration on the electrochemical degradation process of glucose is similar, and on the basis of the obtained results, an explanation of the mediating role of chloride ions has also been proposed [15].

When NaCl solutions undergo electrolysis, NaCl and H_2O decomposition results in the formation of Cl_2 and O_2 gases, chlorine–oxygen compounds, and active redoxi particles. Oxygen and active species containing oxygen atoms may form not only on the electrode but also in the chemical reaction of chlorine and water in electrolytic solution [16]. Reaction conditions determine to what extent intermediates with chlorine and oxygen content form on the electrode or in a chemical reaction in the solution. The rate at which oxygen is produced increases with decreasing chloride concentration [17], and decreases with increasing chloride concentration. When electrolysis conditions are suitable for chlorine production, most of the oxygen and chlorine–oxygen compounds are chemically formed in the reaction of Cl_2 and H_2O in the solution.

But what happens if not only H_2O but also reactive organic material, e.g., thiocarbamate pollutants, are present in the solution and enter into reaction with chlorine? Thiocarbamate may react with other reactants containing chlorine–oxygen that have formed on the electrode, and in $Cl_2 - H_2O$ reaction in the solution. Thus thiocarbamate can compete for adsorption with H_2O and Cl^- on the electrode and may enter into electrode reaction. It can compete for Cl_2 and O_2 released on the electrode and for reactive particles containing chlorine and oxygen atoms in the solution. Electrode type, NaCl concentration, pH value, temperature, applied anode potential, and current (current density) determine the kind of processes and reactions that take place and their extent.

In NaCl solutions the electrochemical degradation of thiocarbamate parts has not been studied yet. Next, we are going to investigate how electrolysis reaction conditions affect the electrochemical degradation of thiocarbamate active ingredients themselves in NaCl solutions.

2. Experimental details

Electrochemical experiments were made in three electrode cells, each of different construction and size, and operated in batch or continuous regimes. In general, platinum mesh working and counter electrodes were used. DSA$^{®}$($RuO_2 - Ti$) was used as anode; stainless steel mesh and disc were applied as cathode; and an Ag/AgCl reference electrode was used. DC power was supplied, and cyclic voltammetry was conducted with scanning potentiostat by using EF 427 Potentiostat Electroflex (Szeged) and DC power supply TL 9158 and TR-9252/A (FOKGYEM). Cyclic voltammograms were measured at scan rates of 10, 20 and 100 mV s^{-1} in potential range of −1000 to +1300 mV at the Pt anode and in potential range of −1500 to +1500 mV vs. SCE at the $Ti - RuO_2$ Dimensional Stable Anode (DSA$^{®}$).

In several experiments, a quartz cuvette was used as the electrolysis cell with platinum wire electrodes attached to it. This way, we could directly combine electrolysis with UV spectroscopic analysis. UV spectrophotometric measurements were made with diode array spectrophotometer (HP 8452A Diode Array Spectrophotometer). The spectrophotometer can be used with 2 mm resolution in the 190–820 nm interval or with 1 mm resolution between 190 and 400 nm, and is also equipped with a thermostatable cell holder.

A diode array spectrophotometer was used to follow the electrochemical reaction either in batch or in continuous regime. Part of the measurement was performed in a cuvette placed in the thermostated cell holder of the diode array spectrophotometer. Pt–Pt wire electrodes were used. The reaction mixture was stirred with a cell-stirring module (on several occasions by bubbling N_2 gas through it). Using this arrangement, continuous flow experiments were also performed, where the continuous feed and withdrawal of the reaction mixture were done with peristaltic pump. However, for most measurements, the reaction mixture of the electrolysis cell was circulated through the quartz cuvette placed in the diode array spectrophotometer, and UV absorbances were periodically measured at defined wavelengths, mostly at 214, 236, 292 and 330 nm. Electrolysis progress was measured in this way.

Parallel with the UV spectrophotometric measurements, HPLC (High Performance Liquid Chromatograph) measurements and GC (Gas Chromatograph) analyses were also performed on samples taken at appropriate intervals. For the HPLC measurements, HP 1084B and Shimadzu LC 9A chromatographs of the following parameters were used:

Column: 250 × 4, 6 mm CHROMSIL$_{18}$, 5 n; Detector: UV, 230 nm; Injection block: 7125 Rheodyne with 20 nl loop, Temperature: 45 °C. In the GC analyses, a Chrompack gas chromatograph was used under the following measurement conditions: Type of equipment: Chrompack CP 9000; Column: 3 m × 2 mm metal; Solid support: Chromosorb WHP 80–100 mesh; Liquid phase: 10 % SE-30; Detector FID, Temperature: oven 200 °C, detector 270 °C, injection block 260 °C; Sample: 0,5 nl; Attens: 7; Cht.sp.: 0,5 cm/p; Ar.rej.: 100; Pk WD: 0,04; Zero: 0,6; THRSH:5

TOC (Total Organic Carbon) content of initial and electrolysed solutions was specified with a Heraeous Liqui TOC 2001 analyser using low temperature UV-peroxidisulphate oxidation and with an Analysesystem GmbH Elementar High TOC analyser using catalytic high temperature furnace oxidation.

Chemical oxygen demand (COD) was determined using standard potassium-dichromate with $HgSO_4$ additive.

UV photolysis treatment was made in quartz tube cell. UV light was produced with commercial medium pressure mercury lamps (125–350 W).

The biodegradability of thiocarbamate active ingredients and their destruction intermediates was studied with biological oxidation method using active sludge with living bacterial strains. This method is called RBOD (Rapid Biological Oxygen Demand). It is based on measurement of oxygen concentration in the active sludge suspension mixed continuously by bubbling oxygen. When the sample containing organic waste is injected into the sludge, biodegradable organic material consumes the oxygen. The variation in oxygen concentration is proportionate to the degraded organic compound concentration. Na-acetate was used as a standard. Biodegradability was calculated as RBOD/COD in %.

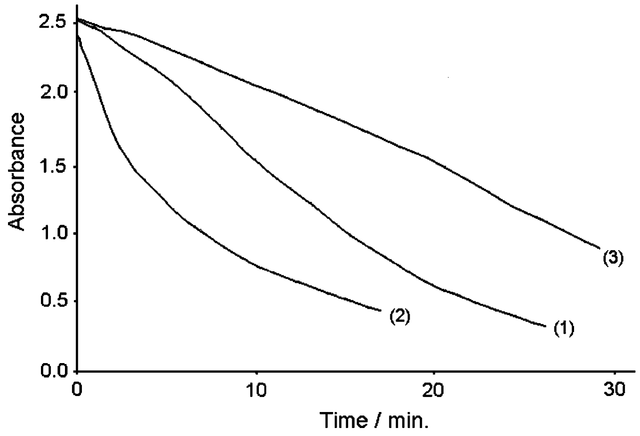


Fig. 1. Electrolytic degradation of thiocarbamates in NaCl solution. The variation in time of UV (214 nm) absorbance in the electrolysis of EPTC (1), Cycloate (2) and Molinate (3). pH = 9, Pot. = 1.3 V, Pt–Pt electrodes.

3. Results and discussion

In NaCl solutions, thiocarbamate active ingredients can be degraded with electrolysis in a one-cell reactor. Degradation rate depends on substituents (Figure 1). With such electrolysis parameters Cycloate (*S*-ethyl-*N*-cyclohexyl-*N*-ethyl-thiocarbamate) degrades more quickly than EPTC (*S*-ethyl-*N*,*N*-dipropyl-thiocarbamate) and Molinate (*S*-ethyl-*N*-hexahidro-1-*H*-azepine-carbothioate). With the help of UV absorbance measured at 212–220 nm, the tendency of the degradation process can easily be followed, but we also applied HPLC or GC analysis.

The degradation of thiocarbamates depends on electrolysis reaction parameters and on electrode types. Anode surface and material greatly influenced the process. Using Pt electrode in the cyclic voltametric investigation of EPTC, no oxidation reaction could be detected in the stability interval of the NaCl aqueous solution, that is, before Cl_2 and O_2 gas release in 0.5 M NaCl solution. If instead of a noble metal anode, a Ti–RuO_2 DSA® (Dimensional Stable Anode) electrode is applied, similar results are achieved. For a large potential range, cyclic voltamograms were typically fairly flat without any clear reaction peaks. At the same time, thiocarbamates degraded through electrolysis (Figure 1). It can be assumed that in anodic oxidation of EPTC, which depends on reaction parameters, only a small part of the degradation process takes place on the electrode surface, while a large part of the reaction process takes place either in the solution near the electrode or far from it, in the solution bulk.

3.1. *Influence of initial NaCl concentration*

NaCl concentration has a direct effect on anode potential and thus also on chlorine and oxygen evolution [17, 18]. High NaCl concentration favours chlorine evolution. Most of the oxygen is chemically formed when conditions are suitable for chlorine production, but the amount of electrochemically produced oxygen increases when conditions favour oxygen evolution [19].

It is assumed that H_2O adsorbed on anode surface is partly degraded in NaCl electrolysis, and degradation products react with Cl^- on the surface while adsorbed hypochlorous acid (HClO) is formed. Then the HClO may be desorbed or may react further with Cl^- with the formation of desorbed Cl_2 in an acidic or slightly acidic medium and with the formation of a chlorine-water equilibrium in the solution,

$$Cl_2 + H_2O \rightleftharpoons HClO + H^+ + Cl^- \tag{1}$$

$$Cl_2 + OH^- \rightleftharpoons HClO + Cl^- \tag{2}$$

in which besides Cl_2 and HClO, ClO^- plays an ever-increasing role parallel with the increase of pH-value.

$$HClO + OH^- \rightleftharpoons ClO^- + H_2O \tag{3}$$

ClO^- may also be formed in an electrode reaction [20]:

$$Cl^- + 2OH^- \rightarrow ClO^- + H_2O + 2e^- \tag{4}$$

NaCl electrolysis intermediates can react with thiocarbamates. On the basis of their different UV light absorbance, NaCl electrolysis intermediates, Cl_2 (325–333 nm), ClO^- (292 nm), HClO (236–238 nm) can easily be detected in the solution, and the change in concentration over time can be followed. Figure 2 shows variation in HClO, Cl_2 and ClO^- UV absorbances in electrolysis at 1 mol dm^{-3} and 5 mol dm^{-3} initial NaCl concentrations. It can be seen that at the beginning of electrolysis HClO absorbance is at its highest (238 nm) and later, as pH increases from 5.65 to 7.80, ClO^- absorbance is at its highest (292 nm).

If pH-value in starting solution is 1.0, i.e. highly acidic, then HClO formation (238 nm) is very fast and its ratio remains high in comparison with Cl_2 absorbance

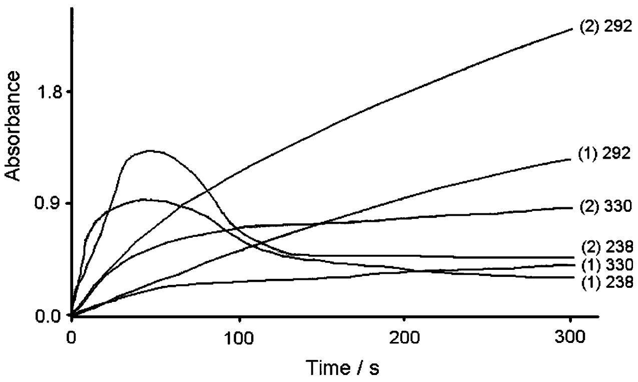


Fig. 2. Effect of initial concentration on the NaCl electrolysis. Changes of the HClO (238 nm), Cl_2 (330 nm) and ClO^- (292 nm) UV absorbances during the electrolysis of (1) 1 mol dm^{-3} and (2) 5 mol dm^{-3} NaCl solutions. Pt–Pt electrodes, $pH_0 = 5.65$, Pot. = 3.2 V, Temp.: 23 °C.

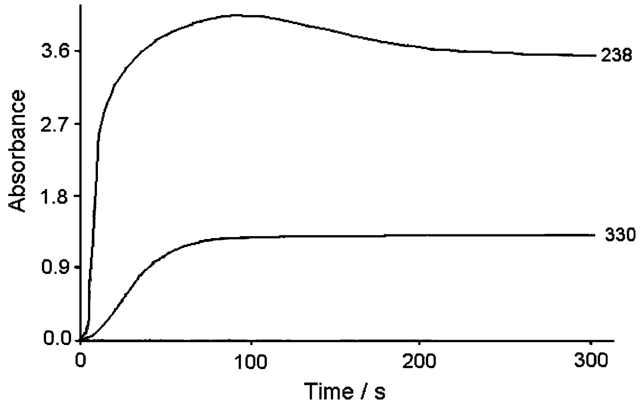


Fig. 3. Changes of UV absorbances of HClO (238 nm) and Cl_2 (330 nm) during the electrolysis of a 5 mol dm^{-3} NaCl solution in strong acidic ($pH_0 = 1.0$) solution. Pt–Pt electrodes, Pot.: 3.2 V, Temp.: 23 °C.

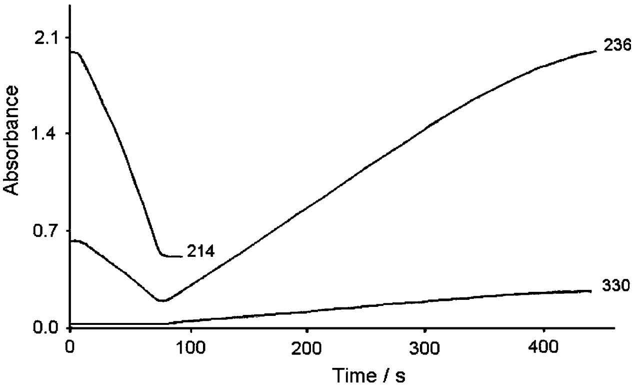


Fig. 5. Changes of UV absorbances of EPTC (214 nm), HClO (236 nm) and Cl_2 (330 nm) during the electrolysis of EPTC in 0.5 mol dm^{-3} NaCl solution. Initial EPTC concentration 50 ppm, $pH_0 = 1.5$, Pt–Pt electrodes, Pot.: 3.2 V, Temp.: 22 °C.

(330 nm) all throughout electrolysis (Figure 3). Thus, in the applied experimental system, Cl_2 can be formed from HClO on the electrode, while HClO is formed mainly during Cl_2 hydrolysis in the solution (Equations (1), and (2)). This is important because the organic thiocarbamate pollutant in the solution is assumed to primarily react with HClO and with much more reactive chlorine monoxide (Cl_2O) formed from HClO in equilibrium reaction [21, 22].

$$2HClO \rightleftharpoons Cl_2O + H_2O \tag{5}$$

The investigation of the effect of stirring (Figure 4) also indicates that in the electrolytic destruction of EPTC, the decrease in absorbance measured at EPTC 220 nm is caused by the reaction of HClO (238 nm) formed on the electrode in non-stirred ranges and/or from desorbed Cl_2 in the solution, or by the reaction of Cl_2O formed from it in equilibrium (5). Since active chlorine concentration $[Cl^*] = [HClO] + [ClO^-]$ increases during electrolysis, and in the case of parallel reactions the faster reaction dominates, we find that HClO concentration decreases in mixed ranges whereas the concentration of less reactive ClO^- increases. In non-mixed ranges, where the reaction, i.e. EPTC concentration decrease, is slower, HClO amount increases quickly; its concentration soon reaches its maximum, while ClO^- concentration hardly increases.

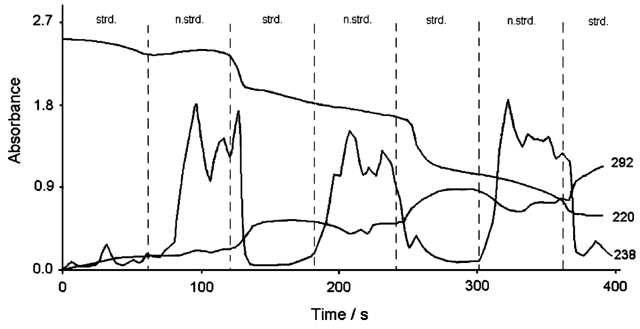


Fig. 4. Effect of stirring on the electrochemical degradation of EPTC in NaCl solution. Changes of the UV absorbances of NaCl electrolysis intermediates HClO (238 nm), ClO^- (292 nm) and of the EPTC (220 nm) in the stirred (strd.) and non-stirred (n.strd.) intervalls. EPTC initial concentration: 100 ppm, $[NaCl]_0 = 1.5$ mol dm^{-3}, $pH_0 = 5.53$, Pot.: 3.2 V, I = 0.01 A, Temp.: 23 °C.

As Figure 5 shows, while there is unreacted EPTC in the solution, HClO absorbance (236 nm) decreases during electrolysis. After EPTC has reacted, HClO absorbance begins to increase while Cl_2 (330 nm) absorbance barely increases. With these reaction parameters ClO^- (292 nm), absorbance is negligible. All this suggests that degradation intermediates formed in EPTC degradation are less reactive than EPTC 'mother compound'.

3.2. *The effect of solution pH and temperature*

The effect of pH can be concluded from what has been said so far. Solution pH influences relative rates of chlorine and oxygen evolution reactions in NaCl electrolysis. Increasing pH favours both oxygen and chlorine evolution [23, 24]. It has been proved that low pH favours chlorine evolution. At $pH = 2$ no significant oxygen evolution is found, but at $pH > 2$ oxygen evolution increases.

Under the reaction conditions used, two outcomes were noted. Without thiocarbamate organic substrate, pH increased in NaCl electrolysis (Figure 6) quickly at the beginning but later the rate of increase slowed down. On the other hand, in the presence of thiocarbamates pH did not increase at a constant rate and increase was lower (Figure 6). In the first range, pH decreased due to HCl formed from EPTC chlorine substitution. The second minimum was possibly caused by chlorine substitution of EPTC degradation intermediates.

Within freely available chlorine concentration $[Cl^*] = [HClO] + [ClO^-]$, $[HClO]/[ClO^-]$ ratio depends on pH. When pH value indicates a base solution, the predominant form of freely available chlorine is hypochlorite ion (ClO^-), while at acidic pH it is hypochlorous acid HClO (in equilibrium with Cl_2O and/or ClO_2).

If the experiment described in Figure 5 is not performed at $pH_0 = 1.5$ but at $pH_0 = 5.06$ (Figure 7), then the role of ClO^- increases. On the one hand, EPTC UV absorbance decreases more slowly than at $pH = 1.5$ (Figure 6, 22 °C). On the other hand, after EPTC runs out, ClO^-absorbance (292 nm) increases as even less reactive ClO^- reacts slowly with EPTC degradation intermediates (a part of which also get absorbed at around 214 nm). This means that if electrolytic thiocarbamate degradation is described with the

$$\mathrm{NaCl} \underset{\text{Electrolysis}}{\overset{k_1}{\rightarrow}} \mathrm{Cl}^*(= \mathrm{HClO} + \mathrm{ClO}^-) \tag{6}$$

$$\mathrm{EPTC} + \mathrm{Cl}^* \overset{k_2}{\rightarrow} \text{EPTC degradation intermediates} + \mathrm{HClO} + \mathrm{ClO}^- \tag{7}$$

$$\text{EPTC degr. intermediates} + \mathrm{Cl}^* \overset{k_3}{\rightarrow} \text{end products} + \mathrm{HClO} + \mathrm{ClO}^- \tag{8}$$

consecutive series of reactions, then, in general

$$k_1 < k_2 \text{ or } k_1 \ll k_2 \text{ and } k_1 k_3 \text{ and } k_2 \gg k_3 \tag{9}$$

and reaction rates depend on reaction parameters.

Figure 7 and Table 1 also imply that pH affects EPTC electrochemical degradation rate more than temperature does.

Electrolyte temperature influences the process rate to a lesser extent than it would be permitted by the Arrhenius-law. For example, a 10 °C increase in temperature generally increases chemical reaction rate 2–3 times (van't Hoff), while in this case a 20–26 °C increase in temperature (Table 1, Figure 7) only decreases the half-life of EPTC electrochemical degradation by half.

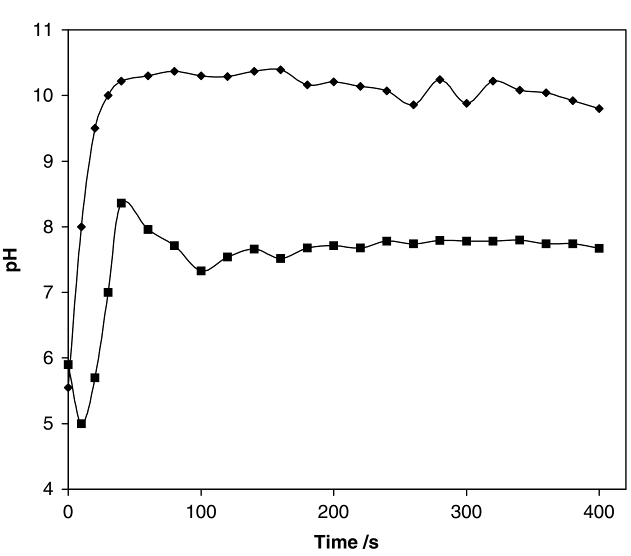


Fig. 6. Changes of the pH during the electrolytic degradation of EPTC in NaCl solution. (■) 100 ppm EPTC, (◆) without EPTC. Initial NaCl conc.: 2 mol dm^{-3},Pot.: 3,0 V, Temp.: 23 °C.

3.3. *Influence of initial thiocarbamate concentration and electrode potential*

Increasing electrolyte pH results in the chemical conversion of electrochemically produced HClO and Cl_2 to chlorine-oxygen compounds or species like ClO^- in the bulk solution.

$$2\mathrm{HClO} + 2\mathrm{OH}^- \rightarrow 2\mathrm{ClO}^- + 2\mathrm{H_2O} \tag{10}$$

$$\mathrm{Cl_2} + 2\mathrm{OH}^- \rightleftharpoons \mathrm{ClO}^- + \mathrm{Cl}^- + \mathrm{H_2O} \tag{11}$$

We may assume that with the given reaction parameters, Molinate oxidation may occur at a location near the electrode, since ClO^- absorbance, which is measured far from the electrode in reaction space, starts to increase after Molinate runs out (measured by GC analysis). Figure 8 shows that ClO^- (292 nm) formation is not linear. In the first period no or very little ClO^- is

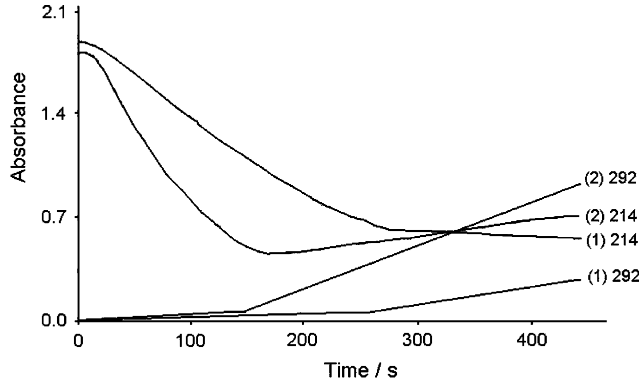


Fig. 7. Effect of temperature on the EPTC electrochemical degradation. Changes of the UV absorbances of EPTC (214 nm) and ClO^- (292 nm) in a 0.5 mol dm^{-3} NaCl solution at two different temperatures. Initial EPTC concentration: 50 ppm, Pt–Pt electrodes, Pot.: 3.2 V, I = 0.01 A, $pH_0 = 5.06$, Temperature: (1) 22 °C, (2) 48 °C.

Table 1. The dependence of half-lifes ($t_{1/2}$/s) on the initial pH and temperature in the electrochemical degradation of EPTC. Initial concentrations: $[EPTC]_0 = 45.5$ mg dm^{-3}, $[NaCl]_0 = 0.5$ mol dm^{-3}, Temp.: 22 °C

$[pH]_0$	$t_{1/2}$/s	
	22 °C	42 °C
0.56	22	
1.50	60	
5.06	185	110
9.00	220	100
11.20	428	245

released. It is suspected that Molinate traps Cl* or ClO⁻. The second period starts after Molinate runs out. In it, due to the slower reaction of degradation intermediates, more ClO⁻ is released and goes over into solution. ClO⁻ release rate increases and the increase in ClO⁻ absorbance in the solution can be measured with UV spectrophotometric method. Such a periodical ClO⁻ release has been described in the electrolysis of phenol [20].

If electrolysis in Figure 8 is performed by using higher electrode potentials (Figure 9), ClO⁻ appears earlier in the solution, which is shown by the earlier and greater increase in UV absorbance. This indicates that with such reaction parameters, reaction may take place not only in the reaction space near the electrode but also in the electrolyte.

If initial Vernolate (*S*-propyl-*N*,*N*-dipropyl-thiocarbamate) concentration is properly increased while electrolysis reaction parameters are held constant (Figure 10), then there will be no increase in ClO⁻ concentrations or it will be considerably delayed. This indicates that Vernolate has trapped HClO and/or ClO⁻ before they could diffuse into the solution (measurement point). It is a question of the extent to which the reaction takes place near the electrode or in the solution.

In NaCl electrolysis reactions taking place on and near the electrode, the decisive factors are desorption rate and the reactivity of the materials taking part in desorption equilibrium, the transport of reacting and forming materials, that is, diffusion [25–27].

As it was shown earlier, stirring influences both HClO and ClO⁻ formation and the electrolytic degradation of EPTC; thus, the reaction is diffusion-dependent and chemical reactions and transport processes together play a decisive role.

During the electrolysis of phenol in a solution containing 150 g Na_2SO_4 and 85 mM NaCl, Comninellis and Nerini [20] discovered that reaction volume near the electrode was 0.1% of total volume. In the electrochemical oxidation of thiocarbamates, due to the relatively concentrated (e.g. 0.5–5.0 mol dm^{-3}) NaCl solution we applied and to the very fast degradation process of the thiocarbamate mother compound, the reaction volume near the electrode may be of similar order. At the same time, degradation intermediates react much more slowly than the mother compound (Figures 5 and 7) so that 99.9 % of their reaction occurs in the solution phase or (electrolyte) medium. Since the slow progress of total organic material degradation is caused by these reactions, they likewise determine the electrochemical oxidation rate. All these factors indicate that electrochemical oxidation of thiocarbamates in NaCl solutions is substantially a homogeneous solution phase reaction of species generated basically in an electrochemical way. The formation of these species may be controlled through electrolysis parameters and may be harmonised with the actual concentration of the pollutants to be degraded, i.e., in the present case, with that of thiocarbamate pesticides.

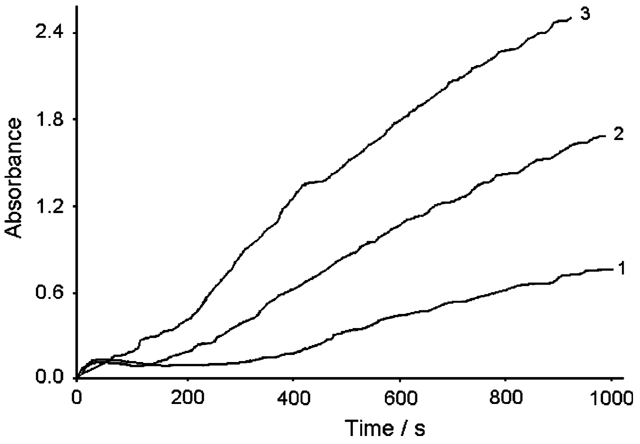


Fig. 9. Changes in the UV absorbances of OCl⁻ (292 nm) in the case of different electrode potentials in the electrochemical destruction of Vernolate. Pot.: 1 (3.19 V); 2 (3.30 V); 3 (3.40 V); Initial Vernolate conc.: 100 ppm.

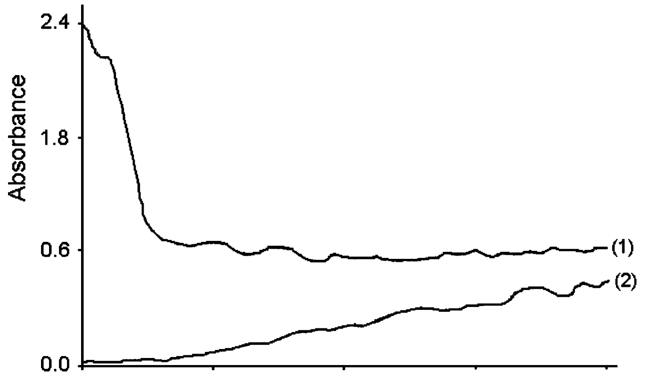


Fig. 8. Changes in the UV absorbances of (1) Molinate (214 nm) and (2) OCl⁻ (292 nm) as a function of time in the case of the electrolysis of 100 ppm Molinate dissolved in a 0.5 mol dm^{-3} NaCl solution. Pt–Pt electrode; Pot.: 3.0 V; I = 0.01 A; pH = 6.5.

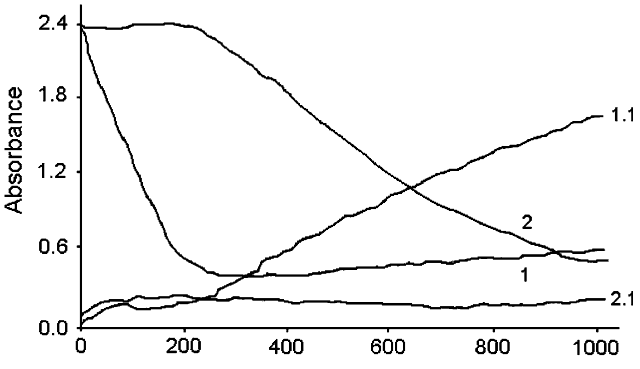


Fig. 10. Changes of the UV absorbances of Vernolate (214 nm) and OCl⁻ (292 nm) in a 0.5 mol dm^{-3} NaCl solution at two different initial Vernolate concentrations. Pt–Pt electrodes, Pot. = 3.30 V; I = 0.01 A; pH = 6.4. Initial Vernolate conc.: (1) 100 ppm; (1.1.) OCl⁻ ; (2) 200 ppm; (2.1.) OCl⁻.

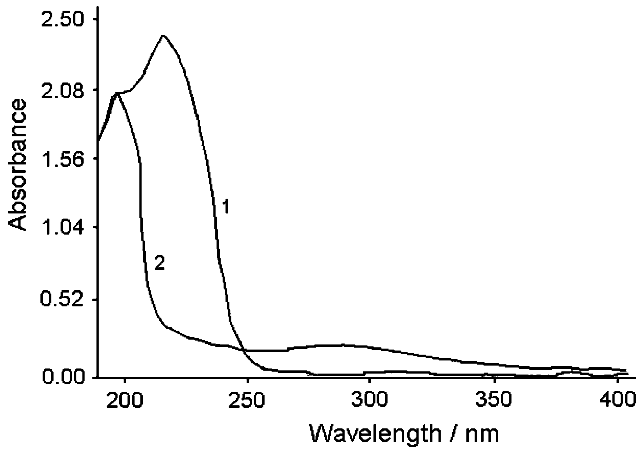


Fig. 11. Electrolytic degradation of EPTC in a continuous flow stirred electrolysis tank reactor system. The spectrum of the (1) initial and (2) treated solution. Initial EPTC concentration: 100 ppm, 0.5 mol dm^{-3}NaCl solution, pH = 6.9, Pt–Pt electrodes.

Without pre-treatment, thiocarbamate pesticide active ingredients get into rivers without being degraded or after only partial degradation in ordinary technological biological cleaning systems. The extent of biological degradation may be increased by the development of special thiocarbamate degrading bacterium stocks, but other chemicals usually have a toxic effect on these populations. However, electrochemical pre-treatment may be a solution which can all be successfully performed in a continuous reactor. Degradation process efficiency data are given in Figures 11 and 12.

The UV spectra of the initial and treated thiocarbamate EPTC solutions in a continuously stirred flow electrolysis tank reactor show that during electrolysis the UV absorbance (at 214 nm), so that the concentration of the EPTC active ingredient decreases before the appearance of the ClO^- (292 nm). Figure 12 shows that this degradation is only a function of the cell voltage chosen in accordance with the given electrochemical reactor, the thiocarbamate fed in, and its concentration.

Therefore, in electrochemical degradation of thiocarbamate pesticide active ingredients in NaCl solutions, the rate determining reaction steps are NaCl electrolysis and NaCl electrolysis intermediate formation. Then NaCl electrolysis intermediates degrade thiocarbamate active ingredients relatively quickly (Figure 13).

But thiocarbamate abatement (Figure 13) by electrochemical pre-treatment is insufficient to guarantee that the target of organic material abatement has been achieved. After 10 min electrolysis (Figure 13), abatement of EPTC active ingredients was completed, but TOC decrease was only 25 % (w/w).

If initial TOC concentration in EPTC solution was 13.98 mg dm^{-3}, pH 3.2, pot. 1.7 V, Pt–Pt electrodes, then only 1.5 min. electrolysis time was needed for EPTC abatement; TOC concentration, measured in the 10th minute, was 9.8 mg dm^{-3}.

All these indicate that after EPTC abatement, a certain quantity of organic material (EPTC degradation intermediates) should be present in the solution.

One of these intermediates was ethane-thiol (C_2H_5SH), a very volatile sulphur-containing irritatant. Ethane-thiol was added to industrial Molinate technological wastewater ($[Molinate]_0 = 65$ mg dm^{-3}, $[Cl^-]_0 = 5$ mol dm^{-3}, pH 8) with unidentified organic impurities. Because of the

$$C_2H_5SH + NaOH = C_2H_5SNa + H_2O \qquad (12)$$

reaction, the volatility and irritation of ethane-thiol decreased. TOC of this concentrated waste-water solution was 838.5 mg dm^{-3}, COD 2900 mg dm^{-3}. Rapid Biological Oxygen Demand (RBOD) was 1071 mg dm^{-3} so Biodegradability (BD = RBOD/COD) was only 37%.

After 30 min electrolysis time (Pot.: 1.5 V, Pt–Pt mesh electrodes), Molinate active ingredients and

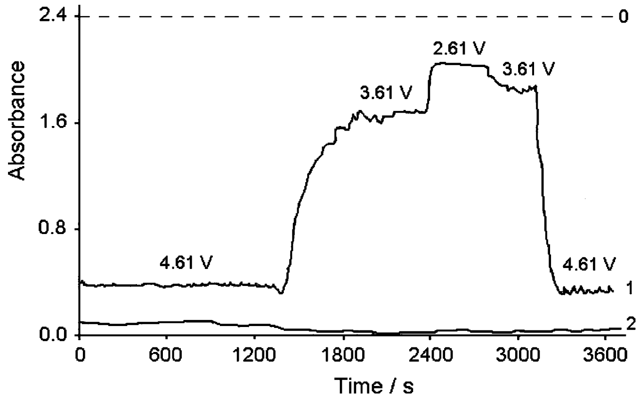


Fig. 12. Electrochemical degradation of Vernolate in a continuous flow stirred electrolysis tank reactor (CSETR). (0) Absorbance of initial Vernolate concentration: 200 ppm, 0.1 mol dm^{-3} NaCl solution, pH = 6.9, Pt–Pt electrodes. (1) Vernolate (214 nm); (2) OCl^- (292 nm).

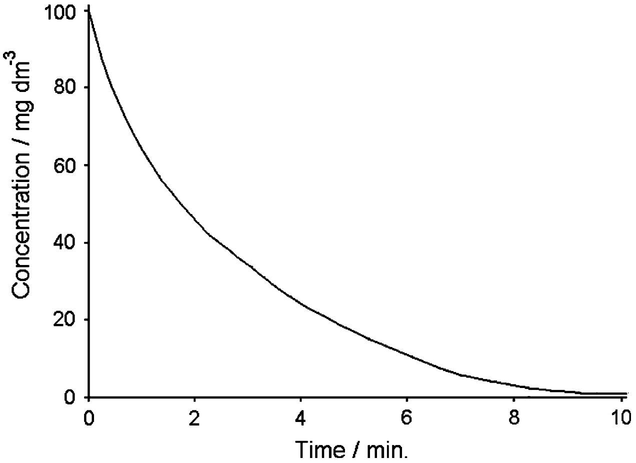


Fig. 13. Variation of EPTC conc. vs. electrolysis time in one-cell reactor measured by HPLC. Initial EPTC conc.: 100 mg dm^{-3}, $[NaCl]_0 = 0.5$ mol dm^{-3}, pH = 9.04, Pot.: 1.4 V, Pt–Pt mesh electrodes.

ethane-thiol were completely abated or removed. Among others, diethyl-disulphide ($C_2H_5SSC_2H_5$), a less volatile degradation intermediate was produced. During the next 30 min of electrolysis, diethyl-disulphide was completely degraded, but solution TOC in the 60th minute was 648.9 mg dm^{-3}.

All these examples show that after the abatement of thiocarbamate (and of several easy degradable intermediates), a certain quantity of hardly degradable organic intermediates was produced.

It is very likely that among these intermediates one or more are more toxic for the 'mother compound'. It was shown that during the electrochemical destruction of thiocarbamate pesticides, carcinogenic dialkyl-carbamoilchloride ($(R)_2NCOCl$), which is on the EPA's dangerous materials list, was formed, and tetra-alkyl-carbamide ($(R)_2NCON(R)_2$), a very persistent species was also produced. In addition to these substances, less toxic sulphur atom containing materials were also formed, including dialkyl-disulphides and dialkyl-dithiocarbonates ($(RS)_2CO$). Their production volumes and ratios were functions of NaCl electrolysis parameters.

NaCl electrolysis intermediates are known to be involved in several interdependent thermodynamic equilibria [28, 29]. In the next papers we will be dealing with thiocarbamate electrochemical degradation in domains of these equilibria and with production and degradation of thiocarbamate intermediates containing N-atom and/or S-atom.

4. Conclusion

In the production of thiocarbamate pesticides, wastewater with a high NaCl concentration (8–20 w/w%) is produced. High Cl^--ion content makes it difficult to degrade organic pollutants with traditional oxidation, photooxidation, photocatalytic oxidation and biological methods.

Our experiments prove that thiocarbamates can be degraded in NaCl solutions with electrolysis. Thiocarbamate pollutants are assumed to primarily react with HClO and/or with ClO^-. The degradation rate depends to a large degree on electrolysis conditions (pH, temperature, initial concentration, electrode potential or current (current density)). Electrochemical degradation of thiocarbamate active ingredients is very fast. We assume that this reaction occurs not so much on the electrode surface but rather in the area near the electrode.

Thiocarbamate degradation intermediates react much more slowly, and they enter into reaction mainly in the solution phase far from the electrode. Thus the crucial part of the degradation process takes place in bulk solution through the reaction of intermediates formed in NaCl electrolysis. Rate determining reaction process steps are NaCl electrolysis and NaCl electrolysis intermediate formation. Then NaCl electrolysis intermediates degrade thiocarbamate active ingredients in a relatively fast reaction.

The abatement of thiocarbamate active ingredients can be carried out by electrochemical pre-treatment in a well-regulated and well-controlled way in both one-chamber batch and in a continuous electrolysis cell, but this abatement is insufficient to guarantee that the target of organic material abatement has been achieved. Toxic and persistent organic intermediates may be produced. Several kinds of such intermediates were detected in electrolyte solution. We think that in order to achieve total organic material abatement, electrolytic and solution reactions should be investigated together.

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References

1. E. Plattner and Ch. Comninellis, *in* S. Stucki (ed), 'Process Technologies for Water Treatment', (Plenum Press, New York, 1988), pp. 205 .
2. S. Stucki, R. Kötz, B. Carcer and W. Suter, *J. Appl. Electrochem.* **21** (1991) 99.
3. O.Y. Murphy, G.D. Hitchens, L. Kaba and C.E. Verostrko, *Water. Res.* **26** (1992) 443.
4. K. Rajeshwar, J.G. Ibanez and G.M. Swain, *J. App. Electrochem.* **24** (1994) 1077.
5. Ch. Comninellis and A. de Battisti, *J. Chim. Phys.* **93** (1996) 673.
6. F. Bonfatti, S. Ferro, F. Lavezzo, M. Malacarne, G. Lodi and A. de Battisti, *J. Electrochem. Soc.* **146** (1999) 2175.
7. F. Bonfatti, S. Ferro, F. Lavezzo, M. Malacarne, G. Lodi and A. de Battisti, *J. Electrochem. Soc.* **147** (2000) 592.
8. R. Beltowska-Berezinska, T. Luczak and R. Holze, *J. Appl. Electrochem.* **27** (1997) 999.
9. R. Parsons and T. VanderNoot, *J. Electroanal. Chem.* **257** (1988) 9.
10. N. Katsuki, E. Takahashi, M. Toyoda, T. Kurosu and M. Lida, *J. Electrochem. Soc.* **145** (7) (1998).
11. G. Fóti, D. Gandini, Ch. Comninellis, A. Perret and W. Haenni, *Electrochem. Solid-State Lett.* **2** (1999) 228.
12. H. Bergmann and K. Hertwig, *in* F. Lapicque, A. Storck and A.A. Wragg (eds), 'Electrochemical Engineering and Energy', (Plenum Press, New York, 1995), pp. 119.
13. H. Bergmann, K. Hertwig and F. Nieber, *Chem. Eng. Process.* **31** (1992) 195.
14. A. Vidal, Z. Dinya, F. Mogyoródy and F. Mogyoródi, *Appl. Cat B: Environ.* **21** (1999) 259.
15. F. Bonfatti, A. de Battisti, S. Ferro, G. Lodi and S. Osti, *Electrochimica. Acta.* **46** (2000) 305.
16. R.E. Connick and V.T. Chia, *J. Am. Chem. Soc.* **81** (1959) 1280.
17. N.Y. Bune, G.A. Shilaeva and V.V. Losev, *Soviet Electrochem.* **13** (1977) 10, 1317.
18. F. Hine, M. Yasuda, T. Noda, T. Yoshida and J. Okuda, *J. Electrochem. Soc.* **126** (1979) 9, 1439.
19. K. L. Hardee and L.K. Mitchell, *J. Electrochem. Soc.* **136** (1989) 11, 3314.
20. Ch. Comninellis and A. Nerini, *J. Appl. Electrochem.* **25** (1995) 23.
21. W.A. Roth, *Z. Phys. Chem. Abt. A* **145** (1929) 289.
22. C.G. Swain and R.C. De Lanson, *J. Am. Chem. Soc.* **94** (1972) 3195.

23. R.G. Érenburg, *Soviet Electrochem.* **20**(12) (1984) 1481.
24. R.G. Érenburg, L.I. Krishtalik and N.P. Rogozhina, *Soviet Electrochem.* **21**(9) (1984) 1089.
25. D.M. Novak, B.V. Tilak and B.E. Conway, *Modern Aspects of Electrochemistry* , Vol. 14 (Plenum, New York, 1980).
26. B.E. Conway, G. Ping, A. de Battisti, A. Barbieri and G. Battaglin, *J. Matter. Chem.* **1** (1991) 725.
27. C.V. Evdokimov, *Elektrohimija* **36** (2000) 254, **36** (2000) 259, **38** (2002) 355.
28. G. Zimmermann and F.C. Strong, *J. Am. Chem. Soc.* **79**(9) (1957) 2063.
29. M. Reinhard and W. Stumm, *Water Chlorination, Env. Imp. Health Effects* **3** (1980) 209.