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ORGANIC WASTE DESTRUCTION BY INDIRECT ELECTROOXIDATION

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ABSTRACT

The destruction of organic model substances by indirect electrooxidation was investigated. The oxidation agent Co(III) was used because of the high redox potential of the Co(III)/Co(II) redox couple (E_0 = 1.808 V).

Experiments were performed in a batch and in a continuous electrolytic cell by using various model substances (especially phenol and different chlorophenols). Intermediate and final products of the oxidation were identified and quantified. Organic carbon is ultimately transformed to CO_2 and to small amounts of CO. The residual carbon in the process solution was determined by TOC measurement to be about 20 ppm. Organic chlorine is oxidized via chlorate to perchlorate. The remaining amount of adsorbable organic halogens (AOX) was less than 3 ppm. Based on these results, a pilot plant was constructed and is presently in operation.

INTRODUCTION

Many industrial wastewaters and landfill leachates are contaminated with organic pollutants, which are biologically persistant. Due to the low concentration levels, the removal of such effluents by incineration is not favorable. Therefore, an integrated method is under development at our institute to extract organic pollutants in a first step with supercritical fluids (especially CO_2) and to further destroy them in a second step by an electrooxidation process. The results presented in this paper are restricted to the development of the indirect (mediator) electrooxidation step.

It is known from former publications that organic substances can be destroyed by use of some transition metals in the highest oxidation state (1 - 3). In a procedure using indirect electrooxidation, the organic pollutants are dispersed or dissolved in an aqueous phase, where the oxidizing agent is continuously produced by anodic oxidation. The oxidant finally destroys the organic pollutant to CO_2. Most proposed mediators are the redox couples Ag(II)/Ag(I) and Co(III)/Co(II) (4 - 6). For our experiments, we chose Co(III) as the oxidation agent because of the high redox potential of the Co(III)/Co(II) redox couple (E_0 = 1.808 V) and its property to be produced with great current efficiencies in electrolytic cells, which do not need a cell diaphragm. No insoluble cobalt chlorine compounds are known so that no precipitations must be handled as in the case when Ag is used as mediator.

EXPERIMENTAL

The Co(II)-sulfate was dissolved in the electrolyte and oxidized continuously to Co(III) by electrooxidation. The Co(III) reacts with the organic substance, which is oxidized to CO_2. After the reduction of Co(III) to Co(II), the Co(II) can again be oxidized to Co(III). Mild reaction conditions can be used so that formation of dioxins from chlorinated phenols, corrosive gases, and flyash, known emissions from waste incineration, can be avoided.

To study the course of destruction, we chose phenol as a first model substance for detailed studies because of its known classical chemical degradation by Fenton's reagent (7) as well as by direct electrooxidation (8). Other model substances included various chlorophenols, especially 2- and 4-chlorophenol, to obtain a close proximity to real organic wastes and study the behavior of chlorine in this process.

The experiments were performed with both a batch and a continuous electrolytic cell. In the case of the batch cell, which was used for kinetic tests, a conventional electrolytic cell of 200-mL volume was used. Anode and cathode are made of platinum with the anode being 5 times larger in surface than the cathode (anode area: 60 cm^2). The electrodes are sections of a cylinder, and located concentric in the cell. Although the cell works without a diaphragm, the cathodic reduction of Co(III) is suppressed by the irreversible character of this redox couple. For Co(III) formation, current efficiencies up to 80% can be achieved. Anodic current density was kept at about 100 mA/cm². The electrolyte was 3 M sulfuric acid and on average 0.1 M cobalt(II)-sulfate. The experiments were carried out by placing the electrolyte into the cell, adding the model substance, thermostating the mixture (50°C) and starting the electrolysis. After the desired reaction time had passed, the current was switched off and samples were taken. Identification and quantification of reaction products were performed after extraction with benzene by gas chromatography/mass spectrometry (GC/MS) and gas chromatography/flame ionization detection (GC/FID). The organic acids were determined by high performance liquid chromatography (HPLC) with ultraviolet detection (UV); different chloro species appearing by destruction of chlorinated organics were measured by ion chromatography (IC) with conductivity detection (9). CO and CO_2 formation were measured by GC and by on-line infra-red (IR) equipment. Residual carbon (TOC) and the amount of adsorbable organic halogen (AOX) in the process solution completed the carbon and chlorine balances.

In tests using benzene as a model substance in the batch cell, only 40% of the initial carbon was found as CO and CO_2, although a reflux condenser in the off-gas line was used. Therefore, we equipped the continuous apparatus, which was used for establishing material balances, with a bubble column of 0.5-m length and a diameter of 0.02 m for off-gas washing with the electrolyte. With this equipment, the conversion rate for the decomposition of benzene to CO and CO_2 was improved to more than 98% of the initial carbon. This continuous apparatus is also an undivided electrolytic cell with a platinum anode (anode area: 294 cm²) as 2 annular cylinders. The cathode is made of titanium (cathode area: 62,8 cm²), and located in between the anodes. Figure 1 shows this apparatus.

For the experiments in the continuous apparatus experiments, the anodic current densities ranged from 20 to 70 mA/cm², and the cathodic current densities were again 5 times higher corresponding to the surface ratio. The temperatures varied between 30 and 80°C. The electrolyte used had a concentration of 3 M sulfuric acid again, but the mediator concentration of 0.5 M cobalt(II)-sulfate was higher than in the batch cell. Pure organic pollutant was added in the case of liquids and dissolved in water in the

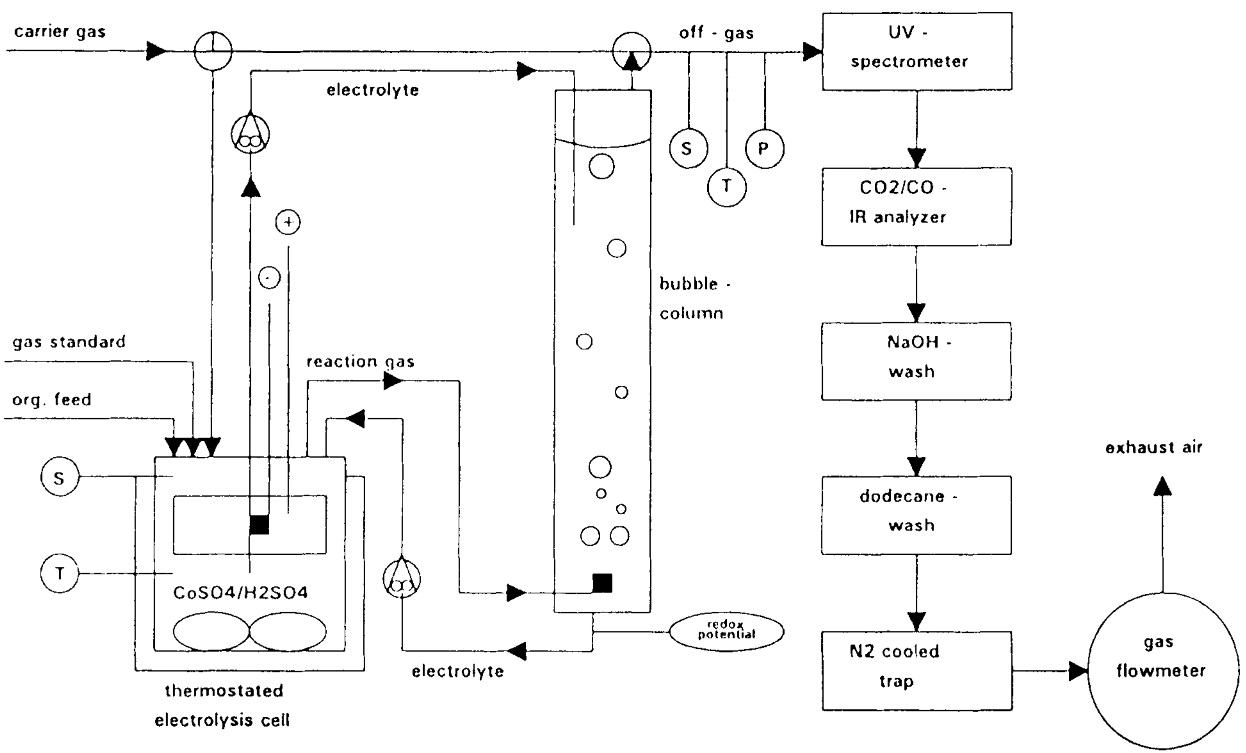


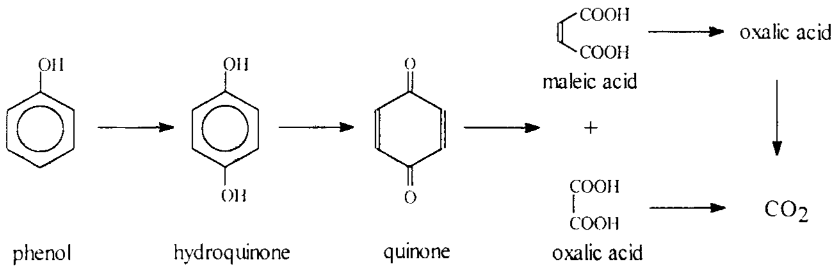
FIGURE 1. Continuous apparatus for measurement of material balances.

case of solid substances in a continuous mode controlled by the redox potential of the electrolyte. The redox potential was kept at a value of about 1.5 V (versus the Ag/AgCl reference). Additionally, the cell was equipped with wash bottles and a cooled trap to collect gaseous reaction products. The batch cell, as well as the continuous apparatus, was operated in a constant current mode. Both electrolytic cells were controlled by a PC, which was further used for visualization and recording of the measured data.

RESULTS AND DISCUSSION

Destruction of Phenol

Two hundred miligrams of phenol was added to the batch cell, and the course of destruction was investigated by determination of intermediate and final products (CO and CO_2). Comninellis and Pulgarin (8) proposed the decomposition of phenol by direct electrooxidation by the following reaction chain:



In our experiments, we found only quinone, maleic acid, and CO_2 in significant amounts. Hydroquinone and oxalic acid were detected in very small amounts but could not be quantified because of their high reaction rates. Additionally, we could identify fumaric acid, the trans form of maleic acid. Figure 2 shows the concentrations (wt% of the added carbon) of phenol, quinone, and maleic and fumaric acids for the oxidation at 50°C and an anodic current density of 100 mA/cm^2. The electrolyte composition was 3 $\underline{M}$ H_2SO_4 and 0.1 $\underline{M}$ Co.

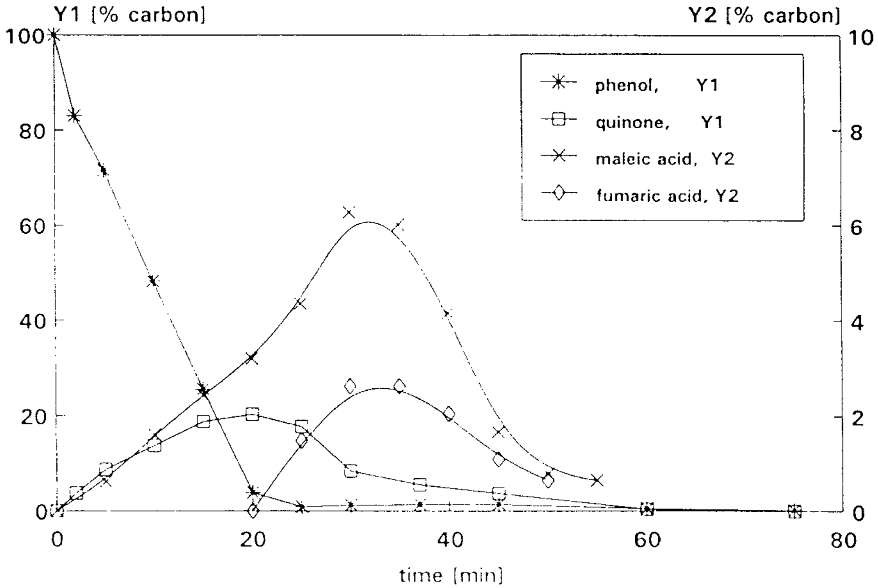


FIGURE 2. Concentrations of phenol, quinone, and maleic and fumaric acid during the decomposition of phenol as a function of reaction time.

The concentrations of the intermediates contain information about the oxidation rates of the individual intermediates and were used to build a mathematical model for the process (10). The concentrations of maleic and fumaric acids shown in Figure 2 belong to the y axis on the right side, which is expanded 10 times.

The concentration course of measured CO and CO_2 is shown in Figure 3. CO_2 and CO are added (CO_2:CO = 35:1) and normalized to 100%, which corresponds to a quantitative conversion of the added carbon to CO and CO_2. The carbon balance is given by:

$$\text{added carbon} = (CO_2 + CO) + TOC \quad .$$

During the oxidation, a brown, foamy, insoluble precipitate was formed as an intermediate, which was, however, destroyed completely at the end of oxidation. The

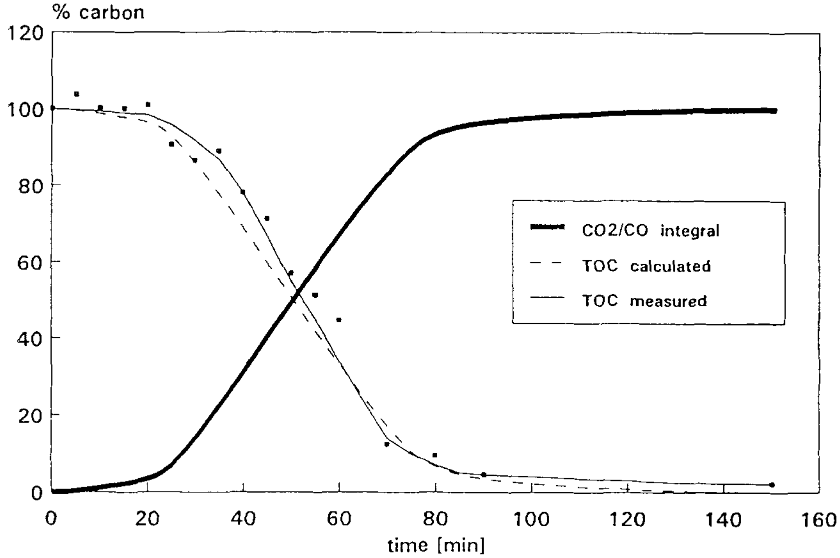
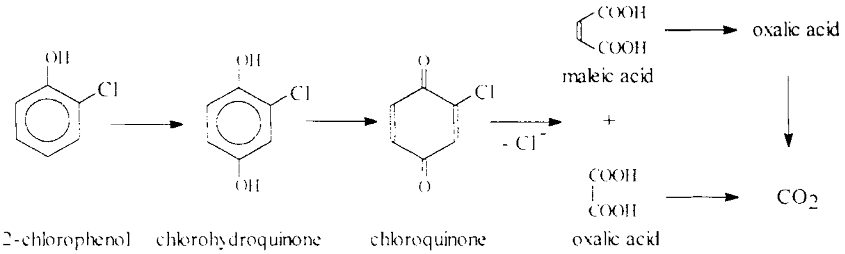


FIGURE 3. CO/CO_2 formation and measured and calculated TOC value during the decomposition of phenol. The calculated TOC is obtained by the difference of added carbon and measured CO_2+CO formation.

remaining amount of organic carbon in the electrolyte after reaction was determined to be about 13 ppm, which corresponds to a 98% conversion to CO and CO_2.

Destruction of Various Chlorophenols

For the decomposition of 2-chlorophenol, a reaction behavior similar to that of phenol can be expected. A difference is the necessary dechlorination step, leading to the question as to which position of the reaction chain this step appears. As main intermediate products, chlorohydroquinone, chloroquinone, and maleic and fumaric acids could be identified. Because chloroquinone is found in considerable amounts, we assume that the cleavage of the chlorine takes place in parallel to the ring opening of the quinone body to maleic (resp. fumaric acid) and oxalic acids. This finding leads to the following reaction chain:



Similar to the destruction of phenol, a quantification was only possible for 2-chlorophenol itself, chloroquinone, and maleic acid as well as CO and CO$_2$. Figure 4 shows the concentrations of 2-chlorophenol, chloroquinone, and maleic and fumaric acids during the decomposition of 300 mg 2-chlorophenol at 50°C and 100 mA/cm^2 in wt% of added carbon. The electrolyte composition was 3 M H_2SO_4 and 0.1 M Co.

Figure 5 shows the CO/CO$_2$ formation and the measured TOC values compared with calculated TOC.

In the case of the destruction of 2-chlorophenol, the final ratio of CO$_2$ to CO was measured as 13:1. This effect, a smaller CO$_2$/CO ratio, is not understood up to now, and will be further investigated. The measured residual carbon in the process solution was 14 ppm, corresponding again to a 98% conversion of the initial carbon to CO and CO$_2$. During the reaction, a similar brown precipitate was observed as an intermediate, as in the case of the destruction of phenol. The cleaved chlorine was found as chloride, which is oxidized via chlorate to perchlorate in the electrolyte:

$$Cl^- \longrightarrow ClO_3^- \longrightarrow ClO_4^-$$

The cleavage of the C-Cl bonding could take place by an anodic dechlorination step, which is described by Beck and coworkers (11). Figure 6 shows the measured concentrations of chloride, chlorate, and perchlorate during the oxidation of 2-chlorophenol. A summation of these species yields inorganic chlorine, which is compared with the amount of organic halogen determined by AOX measurement in Figure 6.

A maximum of chloride formation is observed after 40 min. This coincides with the maximum of maleic acid and confirms the proposed reaction path. After the formation of chloride, the oxidation to chlorate and perchlorate takes place. The

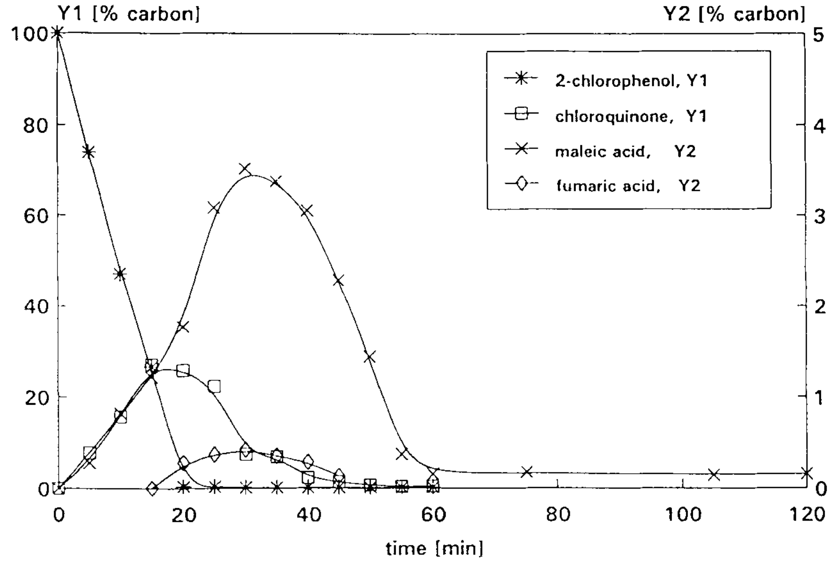


FIGURE 4. Concentrations of 2-chlorophenol, chloroquinone, and maleic and fumaric acids during the decomposition of 2-chlorophenol.

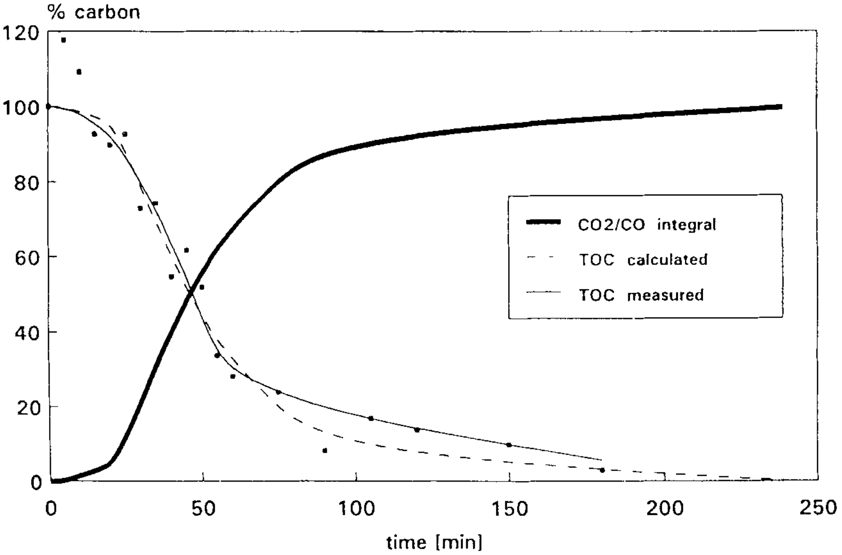


FIGURE 5. CO/CO_2 formation, and measured and calculated TOC values during the decomposition of 2-chlorophenol

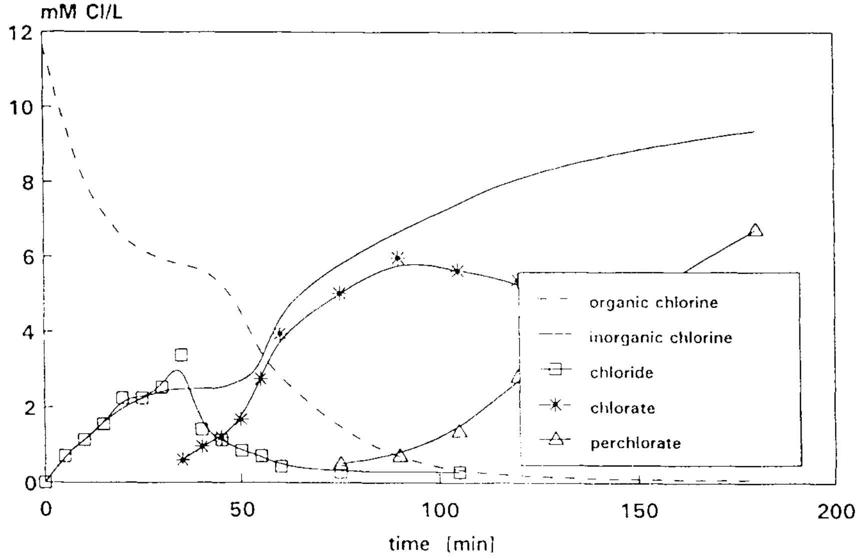
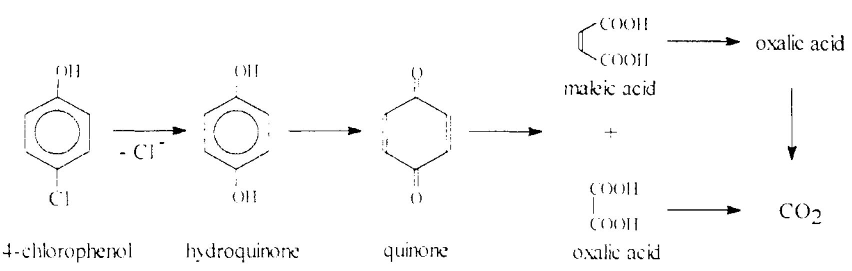


FIGURE 6. Concentrations of various chlorospecies and the AOX values during the oxidation of 2-chlorophenol.

remaining amount of adsorbable organic halogen was measured as less than 3 ppm after the end of reaction, corresponding to 1 % of the initial chlorine.

For the case of 4-chlorophenol, we found as intermediates hydroquinone, quinone, and maleic and oxalic acids. We therefore conclude that the dechlorination step takes place earlier than in the case of 2-chlorophenol.



Because of the low concentrations, hydroquinone and oxalic acid could only be identified but not quantified. Figure 7 shows the concentrations of 4-chlorophenol

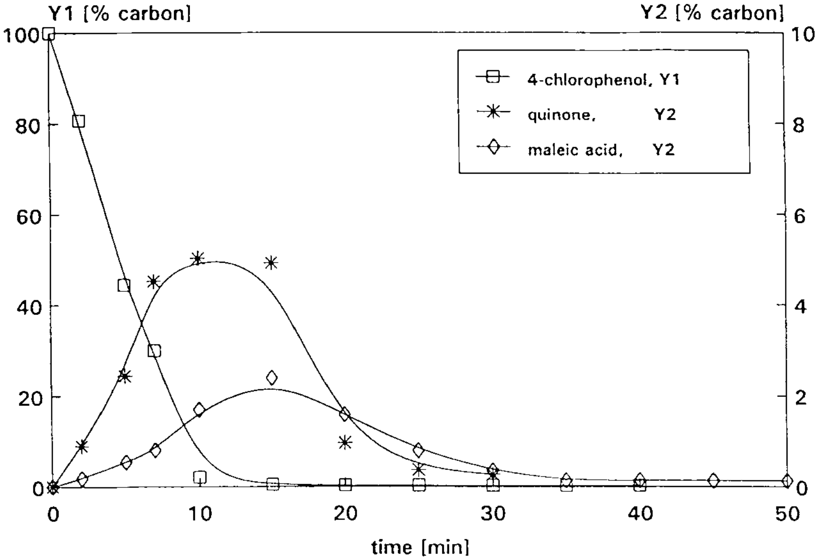


FIGURE 7. Concentrations of 4-chlorophenol, quinone, and maleic acid during the decomposition of 4-chlorophenol.

itself, quinone, and maleic acid during the decomposition of 300 mg 4-chlorophenol at 50°C and 100 mA/cm². The electrolyte composition was 3 M H_2SO_4 and 0.1 M Co.

Figure 8 shows the TOC value calculated from CO/CO_2 formation compared to the measured TOC values.

In the case of the destruction of 4-chlorophenol, the measured final ratio of CO_2 to CO was 10:1. The residual carbon in the electrolyte was 7 ppm, corresponding to a 99% conversion of the initial carbon. Figure 9 shows the concentrations of chloride, chlorate, and perchlorate during the oxidation of 4-chlorophenol. The total inorganic amount and the amount of organic halogen, determined by AOX measurement, are shown in Figure 9.

The maximum chloride formation is found after a 15-min reaction time, earlier than in the case of 2-chlorophenol. This leads to the assumption that 4-chlorophenol is converted in the first step to hydroquinone with a Cl substitution by OH.

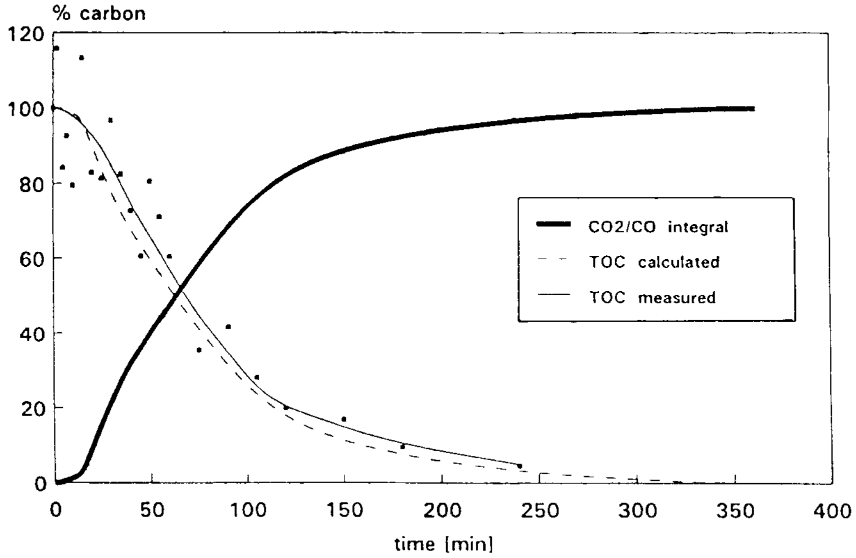


FIGURE 8. CO/CO$_2$ formation, and measured and calculated TOC values during the decomposition of 4-chlorophenol.

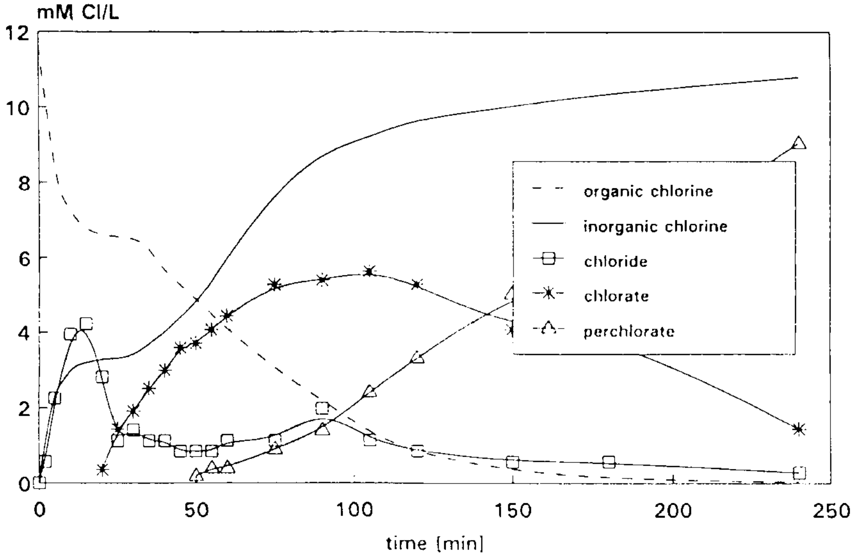


FIGURE 9. Concentrations of various chlorospecies and the AOX values during the oxidation of 4-chlorophenol.

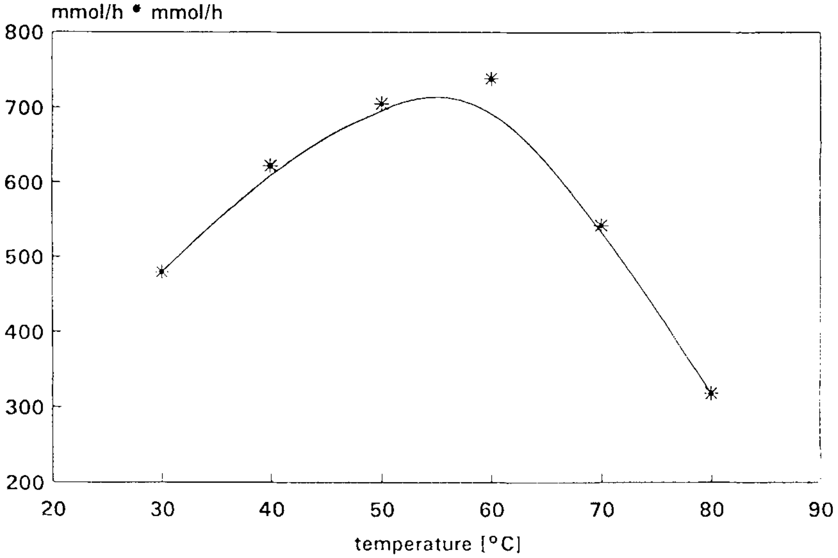


FIGURE 10. Decomposition rate of phenol as a function of temperature.

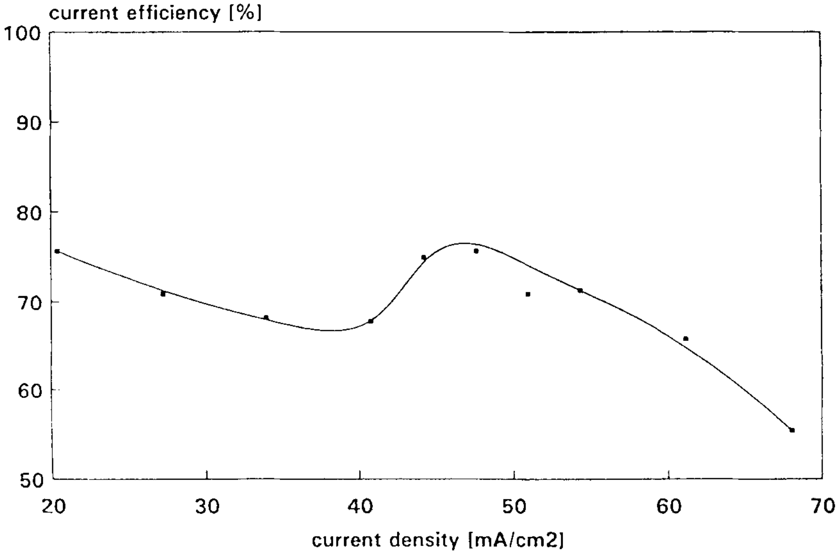


FIGURE 11. Optimization of current density.

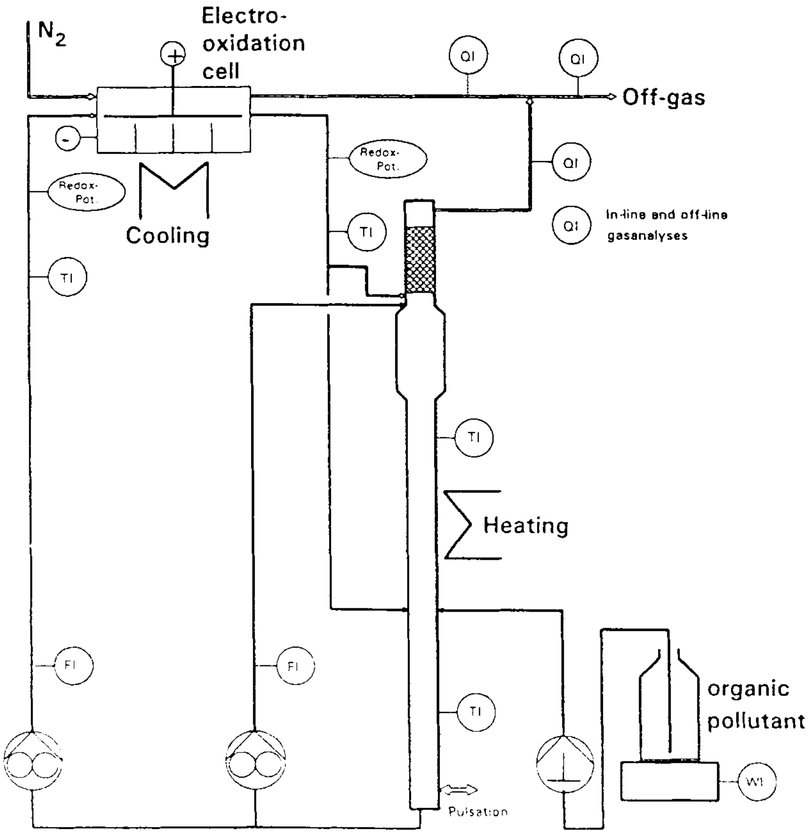


FIGURE 12. Flowsheet of electrooxidation pilot plant.

Results with the Continuous Cell

The main purpose of these experiments was the empirical selection of optimum temperature and current density. The stability of Co(III) decreases with increasing temperature by oxidation of water as shown in preliminary experiments. On the other hand, a higher temperature increases the reaction rate of Co(III) with the organic material. In the experiments, an aqueous solution of phenol (0.708 M) was used. The solution was metered at a constant current density of 34 mA/cm^2 and a controlled cell potential (kept always over 1.5 V) to the electrolyte at different temperatures, and the

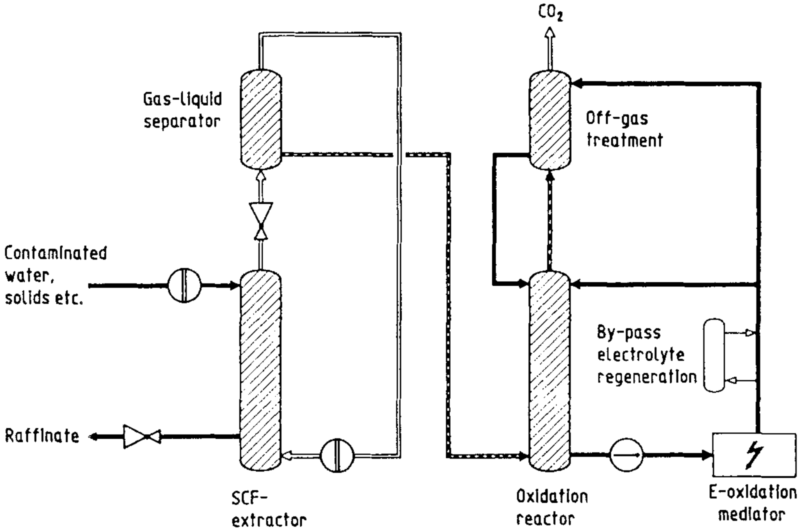


FIGURE 13. Effluent decontamination by combination of supercritical extraction and indirect electrooxidation.

concentrations of phenol and formed CO and CO_2 were measured. Figure 10 shows the results of these experiments.

Figure 10 shows that a maximum of the conversion rate appears at temperatures between 50 and 60°C.

The optimal current density for the reaction was determined by variation of current. From the amount of decomposed phenol and current input, the current efficiencies were calculated (750.4 Ah/mol phenol correspond to 100% theoretical current efficiency). Figure 11 shows the results.

A maximum current efficiency of 75% is reached at an anodic current density of about 45 mA/cm^2.

Outlook

Based on the results of the laboratory experiments described above, a small pilot plant was built with a pulsed sieve plate column as the reactor. The column has a length of 4 m and is designed for a throughput of 0.25 mol carbon/h. Figure 12 shows a simple flowsheet of this pilot plant which is presently in operation.

With real effluents, the pollutants are dissolved or dispersed in aqueous solutions, as in the case of industrial wastewaters or landfill leachates. Before these pollutants can be destroyed by indirect electrooxidation, they must be enriched. A possible technical application could be the combination of mediated electrooxidation with supercritical CO_2 extraction, which is another R/D topic in our institute. By such an integrated process, the organic pollutant will be extracted from the contaminated effluent with supercritical CO_2, and then, after separation, the pollutant can be destroyed by indirect electrooxidation (Figure 13).

Summary

Indirect electrooxidation is a suitable method to destroy organic pollutants under mild conditions. In this work, indirect electrooxidation was investigated with the redox couple Co(III)/Co(II) and selected aromatic model substances (phenol, 2-and 4-chlorophenol). All these model substances could be destroyed totally to CO_2 with a small amount of CO. The residual carbon in the electrolyte was, at maximum, 14 ppm, corresponding to a conversion rate of at least 98% of the added substance. For the decomposition of phenol, we found the highest conversion rate for the tested laboratory-scale cells occured at a reaction temperature of 60°C and with a current density of 45 mA/cm^2. The maximum overall current efficiency was 75%.

The indirect mediator oxidation has an application potential for the degradation of pollutants coming from aqueous effluents or contaminated solids. For the separation of such pollutants, we are investigating supercritical fluid extraction. The objective of these activities is the integration of these process steps into a pollutant separation/degradation process.

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