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U. Leffrang[a]; U. Galla[a]; H. Schmieder[a]
[a] Forschungszentrum Karlsruhe Institut für Technische Chemie Bereich Chemisch-Physikalische Verfahren, Karlsruhe, Germany

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COMBINATION OF INDIRECT ELECTROCHEMISTRY WITH SUPERCRITICAL FLUID EXTRACTION FOR HAZARDOUS WASTE DESTRUCTION AND ORGANIC SYNTHESIS

U. Leffrang, U. Galla, H. Schmieder
Forschungszentrum Karlsruhe
Institut für Technische Chemie
Bereich Chemisch-Physikalische Verfahren
P.O. Box 3640
76021 Karlsruhe, Germany

ABSTRACT

At the Institut für Technische Chemie of the Forschungszentrum Karlsruhe a method is developed to combine indirect electrochemistry with supercritical fluid extraction. Specially two applications are investigated.

In the first case hazardous organics extracted by supercritical CO_2 from contaminated solids or aqueous effluents are destroyed by indirect electro-oxidation. A pressure cell has been constructed, where the CO_2 loaded with the organics is contacted with the electrolyte containing the oxidation agent, so that the pollutants can be destroyed by oxidation. The regeneration of the electrolyte is carried out within the pressure cell.

In the second case, with regard to synthesis, an organic reactant is dissolved in supercritical CO_2, contacted in a column with the electrolyte containing the mediator, and oxidized or reduced to the corresponding products. In an ideal case the formed product is discharged from the column by the CO_2 and can be isolated by an expansion step. The electrolyte is recycled by electrochemical regeneration outside of the pressure apparatus.

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 indirect electrooxidation process.

The same combination of supercritical fluid extraction (SFE) and mediated electrooxidation (MEO) has an application potential for synthesis of organic compounds. In an industrial scale. one limiting factor for the efficiency of the production of organic compounds is the amount of by-products. With the novel integrated method the selectivity of the desired reaction can be influenced and so the space-time yield enhanced.

This paper describes the concept of the experimental equipment. Chemical details and first results will be presented in a forthcoming paper (1).

EXPERIMENTAL METHODS

Mediated Electrooxidation (MEO)

A principal advantage of electrochemistry can be found in the ecological benefit by using a non-polluting redox species, the electrical current, so that possible emissions of additional chemicals can be avoided.

It is known from former publications that by the use of some transition metals in the highest oxidation state, organic substances can be oxidized to a useful reaction product (synthesis) (2,3) or oxidized totally to CO_2 (waste destruction) (4-6). In a procedure using indirect electrooxidation, the organic substance (pollutants or reactant) is brought in contact with an aqueous phase, where the oxidizing agent is continuously produced by anodic oxidation. The oxidant finally reacts with the organic substance to form the desired products. During reaction the redoxmediator is reduced, stays in the electrolyte and can be anodically oxidized again so that a closed cycle is formed (see Figure 1).

Most proposed mediators are the redox couples shown in Table 1 (7). Mediated electrooxidation has a wide range of applications caused by the use of different mediators. Mediators with a high standard potential (Ag, Co) are mainly used for the total oxidation in waste management (4-6). For our experiments in waste destruction,we chose Co^{3+} as oxidation agent because of the property of the Co^{3+}/Co^{2+} redox couple to be produced with great current efficiencies in electrolytic cells, which do not need a cell diaphragm (8). The behaviour of a cell diaphragm under high-pressure conditions has not yet been investigated. No insoluble cobalt chlorine compounds are known so that, when destroying chlorinated substances, no precipitations must be handled as when Ag is the mediator.

Mediators with lower standard potential (Ce, Mn, sometimes Co) are mainly used in selective organic synthesis (2,3). We chose Ce^{4+} and Co^{3+} as the oxidation agent because of the large solubility of their salts in aqueous solutions. The corrosivity of this electrolyte is similar to the case of the waste destruction. We found that all parts of the high-pressure apparatus which are in contact with the electrolyte have to be made of titanium.

The Cr^{3+}/Cr^{2+} and Ti^{3+}/Ti^{2+} redox couples have a negative standard potential and can be used for organic synthesis by reduction.

Supercritical Fluid Extraction (SFE)

Separation by supercritical fluids is characterized as well by a large ecological benefit. In our case we use the property of various gases to change their solubility for different organic substances as a function of temperature and pressure. The solubility for organic substances in CO_2 under ambient conditions is very low and increases with density. At the critical point (for CO_2: $P_c = 73$ bar; $T_c = 31$ °C; $\rho_c = 0.466$ g/cm³) and above the solvent power achieves values of "classical" solvents and is tuneable by varying pressure and temperature.

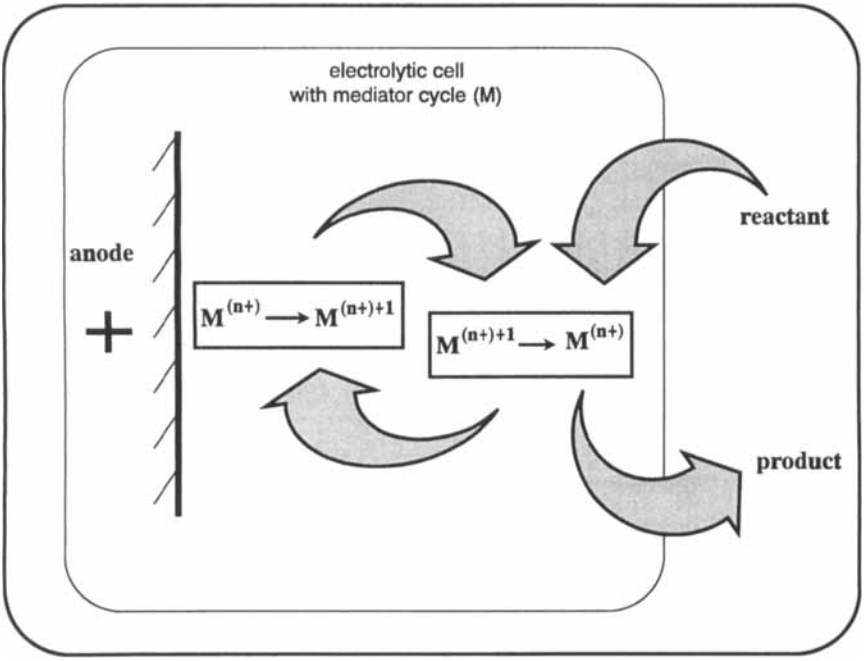

FIGURE 1. Principle of Mediated Electrooxidation

TABLE 1. VARIOUS MEDIATORS

Mediator	Standard Potential [V]
Ag^{2+} / Ag^{+}	1.98
Co^{3+} / Co^{2+}	1.81
Ce^{4+} / Ce^{3+}	1.61
Mn^{3+} / Mn^{2+}	1.51
Fe^{3+} / Fe^{2+}	0.77
Cr^{3+} / Cr^{2+}	- 0.41
Ti^{3+} / Ti^{2+}	- 0.37

Therefore, supercritical CO_2 can be used as a substitute for "classical" solvents like chlorinated hydrocarbons or hexane. The transport properties like viscosity or diffusivity are favourable (9). CO_2 is nonflammable, nontoxic, and environmentally compatible, and can be easily separated (expansion step) and recycled during the process. Supercritical CO_2 has applications for the extraction of organic pollutants out of organic-contaminated solids or liquids (10, 11) and as a solvent for organic synthesis (12).

DESCRIPTION OF THE METHOD AND APPARATUS

Combination of SFE and MEO for Synthesis

In our institute a novel method is under development to combine mediated electrooxidation and supercritical fluid extraction for synthesis of organic compounds. Figure 2 shows the principle of this combination.

With regard to an economically beneficial synthesis, an organic reactant is dissolved in supercritical CO_2 and brought in a two-phase reaction column in contact with the aqueous electrolyte. The mediator, dissolved in the electrolyte, oxidizes (or reduces) the reactant to the desired product. In an ideal case the formed product stays in the SF-CO_2 phase, leaves the column with the CO_2 and can be isolated in an expansion step. The CO_2 will again be compressed and recycled to the saturating unit. The electrolyte is recycled outside the pressure apparatus in a conventional electrolytic cell because of the use of mediators which require electrolytic cells divided by a diaphragm. Electrolysis gases and CO_2 dissolved in the electrolyte leave the apparatus from the electrolytic cell.

Some reactions may produce by-products in addition to the desired product. In these cases a product purification has to be established, which will be a topic of further development.

Selectivity can be enhanced by changing the mediator (redox couple and electrolyte composition) and by varying the residence time. Residence time

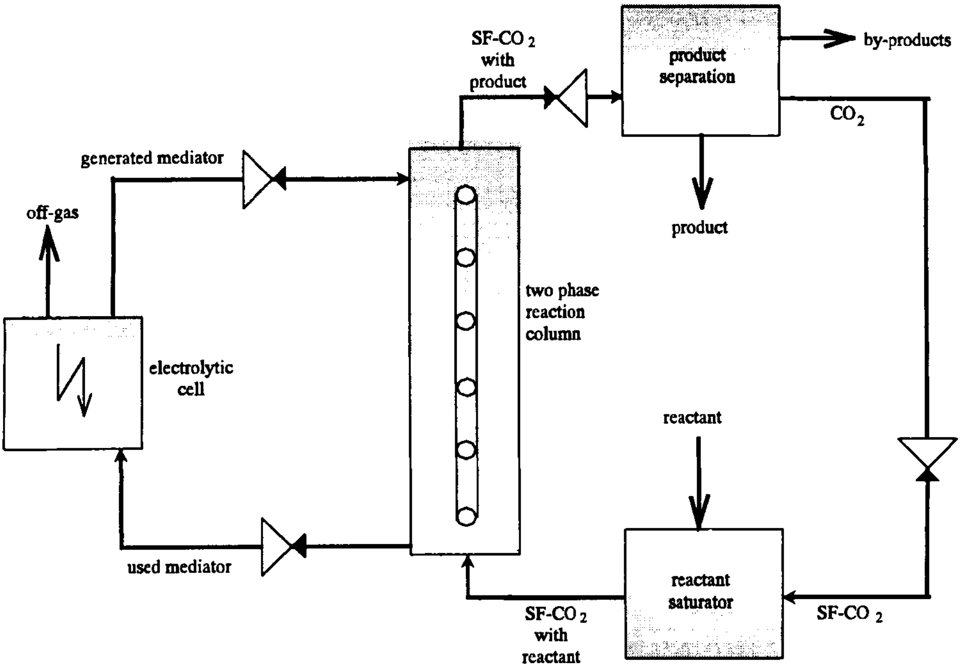

FIGURE 2. Principle of combination of SFE and MEO for synthesis

depends on the height of the column and on the reaction conditions. The apparatus can be used up to a pressure of 350 bar and a temperature up to 100°C. The mediator concentration ranges from 0.1 - 0.5 M in 0.5 - 3 M sulfuric acid. Due to the high corrosivity of the electrolyte, especially under high pressure conditions, all parts of the apparatus which are in contact with the electrolyte under high pressure are made of titanium. Figure 3 shows a P+I-scheme of the apparatus.

The closing of the CO_2-cycle is not yet realized, but will be a future topic as well.

Initial experiments show for the oxidation of toluene to benzaldehyde by cerium and naphthalene to naphthoquinone by cobalt, the principal applicability of this method.

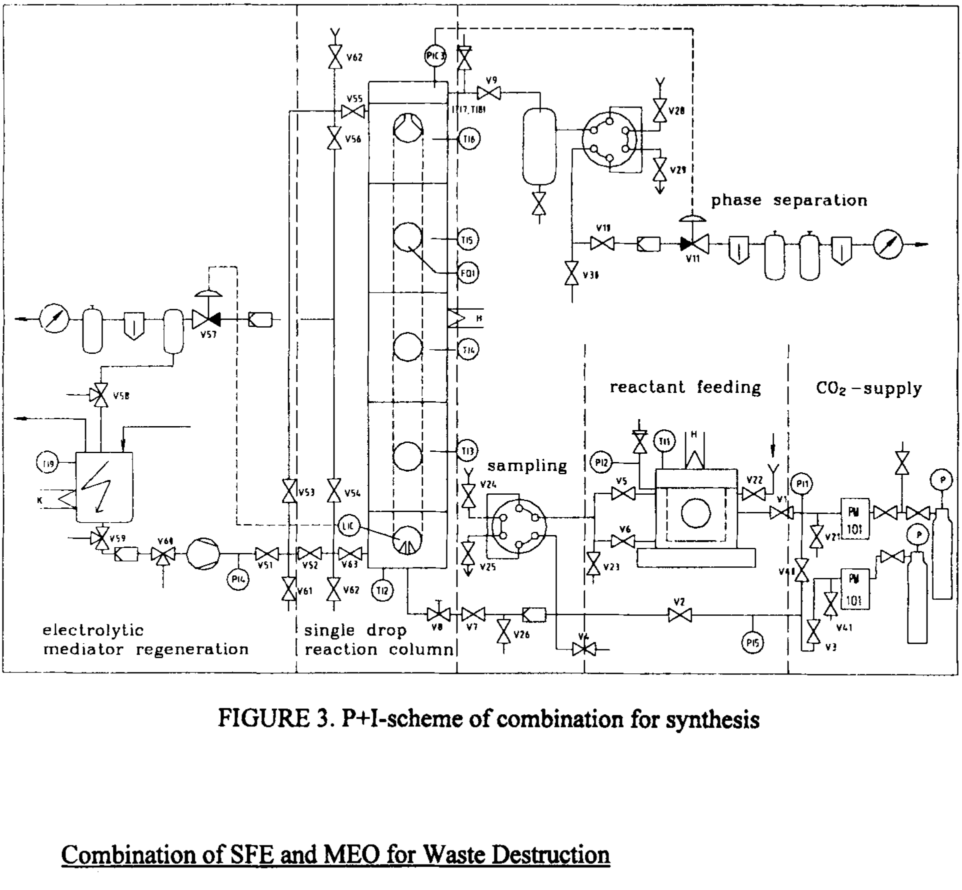

FIGURE 3. P+I-scheme of combination for synthesis

Combination of SFE and MEO for Waste Destruction

With regard to waste destruction, organic-contaminated liquids or solids can be extracted with supercritical CO_2. The organic pollutant is dissolved in the CO_2 and can be decomposed by indirect electrooxidation under the same conditions. Figure 4 shows the principle of this method.

The excess CO_2 - produced by pollutant destruction - will be separated by lowering the temperature (and, if necessary, the pressure) below the critical temperature of CO_2 to form liquid CO_2. CO, H_2 and small amounts of anodically formed O_2 are diluted by the excess CO_2 from the liquid phase in the separator. The explosion limit in the off-gas is continuously monitored. In the case of maloperation the off-gas can be diluted by air.

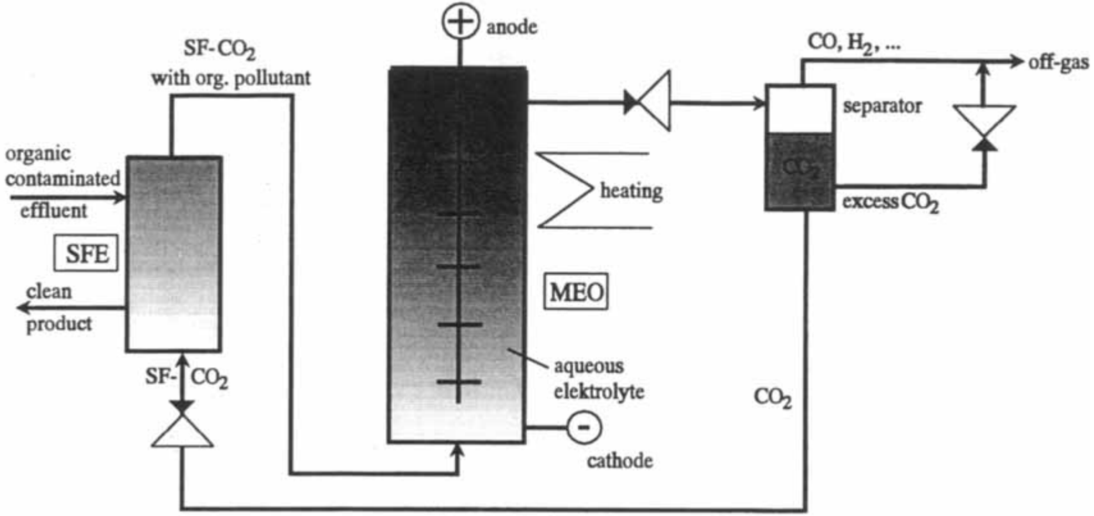

FIGURE 4. Principle of combination of SFE and MEO for waste destruction

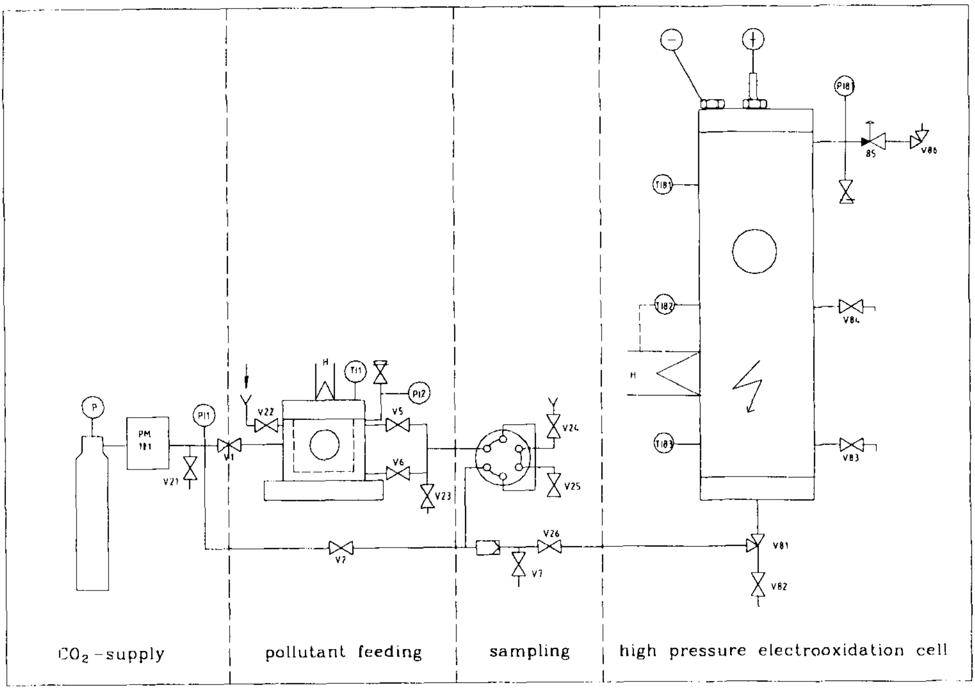

FIGURE 5. P+I-scheme of combination for waste destruction

The apparatus is designed for a pressure up to 350 bar and a temperature up to 100 °C. The electrolyte composition is 0.5 M cobaltsulphate in 3 M sulfuric acid.

In the high-pressure electrolytic cell the casing is used as the cathode, a platinated central bar with additional sieve plates as the anode. The current density ranges up to 100 mA/cm^2, the cell voltage ranges from 3 - 5 V. Electrochemical regeneration of the mediator is performed inside of the pressure apparatus because no diaphragm is needed for the oxidation of cobalt. The complete unit becomes very compact and the side reaction (water oxidation by Co^{3+} with formation of O_2) can be suppressed. Figure 5 shows the P+I-scheme of this apparatus.

At the moment SFE is simulated by a saturating unit, where organic model substances can be dissolved in supercritical CO_2 and decomposed in the high-pressure electrolytic cell by the mediator. CO_2 recycling has not been established yet.

SUMMARY

A novel combination of two non-polluting engineering processes has been demonstrated: mediated electrooxidation (MEO) and supercritical fluid extraction (SFE). The combination has potential for application to waste destruction and organic synthesis. A small apparatus has been constructed for each application. In the case of organic synthesis the electrolyte recycling is performed outside of the pressure apparatus, in the case of waste destruction inside of the apparatus.

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