Oxidation of 2,4-Dichlorophenoxyacetic acid by Electrogenerated Sulphate Radical Anion

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**Highlights**

* 2,4-D can be removed by indirect electrochemical oxidation using persulfate.
* Above 20 °C the decomposition of persulfate occurs during its electrosynthesis.
* The current efficiency decreases from 96 % to 52 % increasing j from 5 to 100 mA cm-2.
* 2,4-D disappearance follows a first-order reaction with a constant rate of 0.22 min-1.

**1. Introduction**

The use of pesticides and their release into the natural environment constitutes a direct threat for the environment and the living beings especially the human health. Consequently, the development of technics to detoxify the pesticide residues to reduce at least areas and contaminated matrix is needed. Electrochemical oxidation using a boron-doped diamond (BDD) anode allows mineralizing various organics such as pesticides. However, in the case of organochlorides, the reaction with OH may generate undesired toxic intermediates in the form of organochlorides. Costanza et al. [1] have shown that the reaction of tetrachloroethylene with sodium persulfate at 50°C leads to a complete dechlorination, without production of organochorides.

The approach chosen in this study, in view of treating obsolete pesticides solutions with low concentrations of biorefractory organic species, is to combine the following steps:

(i) the electrochemical production of peroxodisulfates using a BDD anode at low temperature and (ii) peroxodisulfate is injected into the preheated solution containing the target organic compound, the 2,4-Dichlorophenoxyacetic acid (2,4-D), for activation and reaction.

**2. Methods**

(i) Electrochemical reactor for electrosynthesis: The oxidation of sulfuric acid was performed in a two-compartment electrolytic flow cell under galvanostatic conditions [2]. The electrosynthesis was stopped after reaching a conversion rate of sulphate of 25 % corresponding to a persulfate concentration of 0.2 M.

(ii) Reactor for the coupling processes:

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|  | The treated solution containing the target compound, the 2,4-D at 0.45 mM, was stored in a thermostated, stirred tank(1) at 60 °C. The solution was pumped into a continuous thermostated, stirred tank reactor of 100 mL (2) at 60 °C, which initially contained the oxidizing solution, electrosynthesized persulfate. Various flow rates of 2,4-D solution were tested in the range of 1.66-50 mL min-1. The corresponding range of residence time for a 100 mL tank reactor is 2-60 min. A pumping device (4) placed at the outlet of the reactor (3) is used to keep the volume constant in the chemical reactor. The system working as a continuously stirred tank reactor (CSTR) at steady state under isothermal condition. |
| **Fig.1** Set-up used for the disappearance of 2,4-D by reaction with the electrogenerated peroxodisulfate**.** (1) Thermostated, stirred tank containing a 2,4-D solution; (2) pump; (3) Thermostated, stirred tank containing the electrosynthesized persulfate; (4) pump | |

**3. Results and discussion**

(i) Electrosynthesis of persulfate:

The electrosynthesis of persulfate was performed under various current densities, from 5 to 100 mA cm-2.It appears that after 180 min of electrolysis the current efficiency ranges from 98% to 48.5% for 5 to 100 mA cm-2. To explain this decreasing faradaic efficiency with the increasing current densities, different hypotheses were established. The most likely explanation is the decomposition of persulfate caused by an increasing temperature.

(ii) Degradation of 2,4-D by electrogenerated radical sulfates:

A first series of experiments were performed to study the effect of the residence time of 2,4-D in the chemical reactor on its disappearance. For a residence time of more than 10 min, the 2,4-D disappearance rate reaches more than 70 %. In parallel, the shape of the TOC disappearance correlates well with that of the target molecule 2,4-D. In addition, one can observe that a disappearance of 84% of 2,4-D corresponds to 54% of TOC removal. Unlike the reaction with hydroxyl radicals, this result shows that the reaction of the target molecule with sulfate radicals leads to the formation of intermediates.

**4. Conclusions**

Throughout this study, it has been shown that the complete disappearance of 2,4-D is possible by indirect electrochemical oxidation. This process uses the electrosynthesis of persulfate from a 2M sulfuric acid solution. The persulfate is then thermally-activated to produce sulfate radicals, which are strong and selective oxidants. These radicals react with the target molecule. The efficiency of this process depends on both of the following operating conditions:

* When the applied current density is too high, 100 mA cm-2 for a 2 M of sulfuric acid, secondary reactions occur.

- The complete disappearance of 2,4-D can be reached if the contact time with sulfate radicals is sufficient; the 2,4-D concentration profile follows a first-order reaction with an estimated constant rate of 0.22 min-1 under our operating conditions. The feasibility of the process has been demonstrated.

**References**

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[2] K. Serrano, P.A. Michaud,., C. Comninellis, A. Savall, Electrochim Acta 48 (2002) 431-436.