

세륨을 이용한 전기화학적 매개 산화공정에서 농약의 분해: bench scale 연구

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**Destruction of commercial pesticides by cerium(IV) mediated electrochemical oxidation process:
A bench scale study**

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Introduction

The development of Mediated Electrochemical Oxidation (MEO) process dates back to late 1980's when the process originally intended for the dissolution of radioactive materials such as plutonium oxide in nuclear waste processing units. But later this process turned out to be an excellent treatment method for the destruction of organic pollutants and waste streams including POP's [1-4]. This process is identified as one of the most promising future technologies by UNEP. The main advantages of the MEO process are the optimum working conditions of ambient temperature (less than 100°C) and at atmospheric pressure; the products formed are only CO₂ and water; and regeneration and reuse of the oxidant, minimizing the production of secondary wastes.

In the MEO process an electrochemically generated metal ion is used as an oxidant. This mediator ion in acidic medium destructs virtually any organic material comes in contact with it completely, in a totally enclosed chamber without any harmful emissions. Usually transition and inner transition metal ions such as silver, cobalt, manganese, and cerium are used as mediator ions owing to their high redox potentials. During organic destruction metal ions are reduced to their original state and again reoxidized by the electrochemical cell thus forming a closed loop. The net result is the utilization of electrical energy for the destruction of organics. The organic compounds are completely oxidized to CO₂ and water and usually little CO are also formed. The inorganic atoms present in the wastes are converted to corresponding oxides.

The core component of the MEO system is an electrochemical cell. The electrochemical cells for metal ion oxidation with various electrode materials and cell configurations have been reported for different metal ions. Although several metal ions are available for use in MEO system cerium is preferred in our studies due to the following reasons: it possesses good oxidizing behavior due to its high redox potential ($E^\circ=1.62$ V vs SHE); the rate of water oxidation is less which is an unwanted reaction and reduces the activity of mediator ion; it does not form precipitate with chlorine containing compounds; and it can be recovered and reused without much loss.

The selection of an acid is very important and plays a key role as the coulombic efficiency of the electrochemical cell depends on the viscosity of the acid employed and hence its mass transfer coefficient. Also, the solubilizing capacity of the acid towards the metal salt is an important consideration. Sulphuric acid possesses low solubility and more over can be used only for partial oxidation of organics. Perchloric acid is explosive in nature. Hydrochloric acid can not be used because of instability of chloride ion. Therefore in this study nitric acid is employed which has low viscosity, good solubility towards cerium salts and also it is a good oxidizing agent by itself towards organics.

The objectives of the present investigation were (i) to study the destruction of various commercial pesticides in continuous addition mode; (ii) to find out the destruction efficiency for pesticides (iii) to observe the performance of the electrochemical cell for Ce(IV) regeneration under constant current mode during the organic destruction.

Experimental

Materials

Cerium(III) nitrate hexahydrate (Terio Corporation, China), and nitric acid (60%) (Sam Chun Chemicals, Korea) were used as received. The commercial grade pesticides with the following active ingredients 2,4- D (40%), Methomyl (24%), Dichlorvos (50%), Paraquat dichloride (23%), Deltamethrin (1%), Cypermethrin (5%) were used as received.

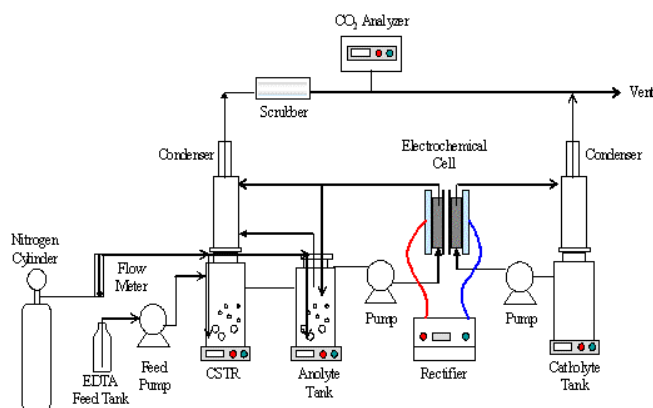


Fig. 1. Schematic diagram of the MEO set up.

Methods

A double stack electrochemical cell was constructed with two anodes and two cathodes. The anode and cathode stacks were separated by a Nafion 324 membrane [5]. The materials of anode and cathode were Pt/Ti and Ti mesh type DSA electrodes. A fluoro-polymer sheet (viton) was used as the separator between the electrodes. The electrochemical cell was operated under a constant voltage of 5 V, throughout all the experiments. The MEO process set up is shown in Fig. 1. The pesticide solutions of known concentrations were injected in to the CSTR using a syringe pump at a specific flow rates. The temperature of the system was 95°C. The changes in Ce(IV) concentration was estimated by potentiometric method using standard ferrous sulfate solution. The chemical

oxygen demand (COD) was measured by HACH procedure. The destruction was calculated based on the initial and final COD changes.

Pesticide destruction

The organic destruction experiments were carried out in a continuous stirred tank reactor (CSTR), which was attached with the electrochemical cell through the anolyte tank. The reactor and anolyte tanks were filled with 2 L of 1 M cerium(III) and 3 M nitric acid solution and Ce(III) was oxidized to Ce(IV) before starting organic addition for destruction reaction. The commercial pesticide solution (5%) was continuously fed at a fixed rate (1 ml/min.) and for a 6 hour to the CSTR by means of a peristaltic pump. The dilution of oxidant solution by the added organic was reduced by water removal using an evaporator from anolyte tank. Since the concentration of nitric acid is well below its azeotropic point the vapor condensed was richer in water with very little acid. During the experiments the liquid samples were taken and analyzed for COD. The percentage of destruction was calculated based on the initial and final COD values of the pesticides solutions.

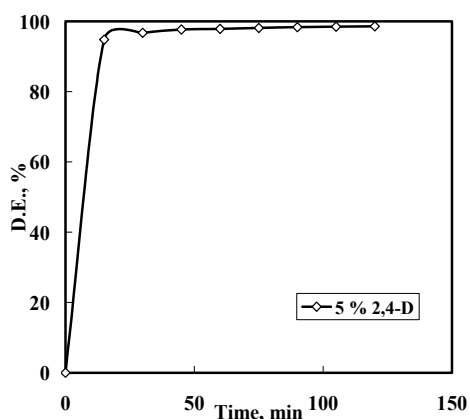


Fig. 2. Destruction efficiency vs time for the destruction of 2,4- D pesticide.

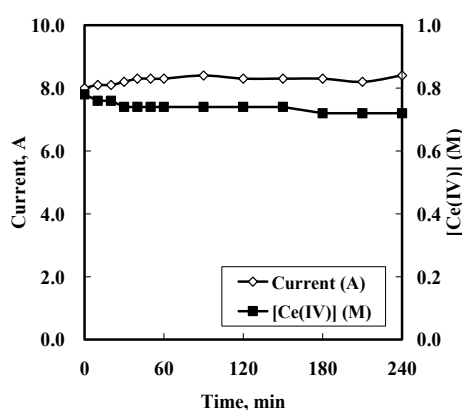


Fig. 3. Cell current and Ce(IV) concentration changes during 2,4-D destruction for 6 hours

Results and discussion

The commercial pesticide formulations like 2,4-D, Dichlorvos, Methomyl, Deltamethrin, Cypermethrin, paraquat etc., were used as the target organic materials to be destroyed by the MEO process. The plot of destruction efficiencies vs time for the pesticide 2,4-D is shown in Fig. 2. It can be seen that as soon as the pesticide solution is injected in to the system the destruction take place quickly and the residual organic measured as COD was very minimum. Therefore the destruction efficiencies increase to nearly 99% after some time and continued through out the process. The concentration level of the oxidant Ce(IV) changes in the system and the cell current changes are shown in Fig. 3. It can be seen that for the 2,4-D destruction the Ce(IV) level was maintained till the end of organic addition

showing that the cell current supplied is balanced by the organic addition. Also the cell current was seen as stable showing the stability of the Pt coated DSA electrodes of the cell for long term operation for the destruction of toxic pesticides.

Conclusions

In this study the efficiency of the MEO process for various commercial pesticides in continuous feeding mode was investigated. The commercial pesticides with active ingredients such 2,4-D, Dichlorvos, Methomyl, Deltamethrin, Cypermethrin, paraquat etc., were destructed almost completely with good destruction efficiency based on COD analyses. The level of the Ce(IV) oxidant production and the performance of the electrochemical cell were found to be good during the destruction process. The feed water was removed effectively by the evaporator. The acidity of the solution was nearly maintained in the same level. The continuous process was proven to be effective for long run operations with simultaneous water removal and oxidant regeneration.

Acknowledgement

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