Effect of Mediator on Decontamination of Chloroaromatic Compounds by Using Electrochemical Method

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Abstract

Decontamination of chloroaromatic compounds has been studied under mild conditions by a simple electrochemical reduction method in order to remove chlorine atoms completely from such compounds. Chlorobenzene was used as a model substrate to determine the optimum conditions of the dechlorination. Electrolysis of chlorobenzene in an acetonitrile solution containing tetraethylammonium perchlorate as a supporting electrolyte in a one-compartment cell fitted with a platinum cathode and a zinc anode at a constant current of 60 mA/cm² was found to be the optimum conditions in this dechlorination. However, complete dechlorination cannot be achieved by applying this conditions to dechlorinate 1,3-dichlorobenzene and 1,2,4-trichlorobenzene. Alternative method by adding naphthalene as a mediator in this system was found to solve this problem and as a result, complete dechlorination of such chloroaromatic compounds were achieved to give 100% conversion of the starting materials. This efficient and simple method could be expected and applied to dechlorinate other chloroaromatic compounds in wastewater in order to solve environmental problems.

Keywords:
Electrolysis, dechlorination, chloroaromatic, reduction, mediator.

Introduction

Chlorobenzene is the simplest aromatic organic chloride, and forms the framework of highly toxic organic chlorides, such as polychlorobiphenyl (PCB), dioxins, and furans. PCBs and other chlorinated aromatic compounds are widely distributed in soils, sludge, and estuaries. This demonstrates a need for a variety of rapid remediation method to decontaminate soils and sludge containing PCBs and to invent portable methods to destroy PCBs not yet released into the environment [1]. Several studies were carried out on specific technologies addressed to eliminate traces of these toxic chemicals by using incineration. This method is expensive and may produce undesirable by products such as polychlorinated dibenzofurans and polychlorinated dibenzoxydioxins [2]. Chlorobenzene and chlorophenols are considered to be precursors or intermediates for dioxin formation in incineration off-gases [3]. Other possible ways to dechlorinate or decompose chloroaromatics compounds has been reported such as by using sodium borohydride reductive dechlorination [4], titanium oxide-catalyzed dechlorination [5], and biodegradation technique [6]. However, these techniques require highly reactive reducing agents, long reaction times and are also expensive.

Another approach in removing chlorine molecules from such compounds so as to reduce their toxicity is by electrochemical method. Since 1970s, the electrochemical reductive approach has been suggested as a promising method for detoxification of chlorine-containing chloroaromatic hydrocarbons. In this paper, we succeeded to reduce chloroaromatics compounds under mild conditions by using a simple electrochemical method. We also found that the presence of naphthalene as a mediator will accelerate the reduction process of chloroaromatics compounds and as a result, a complete dechlorination of chlorobenzene, 1,3-dichlorobenzene and 1,2,4-trichlorobenzene have been achieved to give 100% of conversion.

Methodology

A normal one-compartment cell equipped with a magnetic stirrer was used. Electrolysis in an acetonitrile solution containing tetraethylammonium perchlorate as a supporting electrolyte in a one-compartment cell fitted with a platinum plate cathode (2x2 cm²) and a zinc plate anode (2x2 cm²) at 0°C and a constant current of 60 mA/cm² under air atmosphere was found to be the
optimum conditions of dechlorination of chlorobenzene [7]. The extent of the dechlorination was monitored by gas chromatograph.

Results and Discussions

The results of the complete dechlorination of chlorobenzene were achieved at 5 F/Mol of current passed (see Figure 1).

![Graph](image)

**Figure 1 – Dechlorination of Chlorobenzene**

The efficiency of this dechlorination method to dechlorinate 1,3-dichlorobenzene and 1,2,4-trichlorobenzene was determined at the optimum conditions. However, complete dechlorination could not be achieved by applying this condition to dechlorinate both of these compounds.

According to Kargina et al., insulating film that was produced on the surface of electrode prohibits the progress of the electrolysis [8]. Next, naphthalene which has a potential to react as a mediator to solve this problem was added [9]. As a result, naphthalene accelerates the electrolysis process and complete dechlorination of both 1,3-dichlorobenzene and 1,2,4-trichlorobenzene were achieved to give 100% conversion at 6 F/Mol and 10 F/Mol, respectively. This efficient and simple method could be expected and applied to dechlorinate other chloroaromatic compounds in wastewater in order to solve environmental problems.

Conclusion

A new electrochemical method for dechlorination of chloroaromatics compounds in the presence of naphthalene as a mediator has been developed. Naphthalene is necessary in accelerating the reduction process of dechlorination since this electrolysis process was carried out under atmosphere condition. This method can be applied to wastewater treatment.

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References