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Dechlorination of chlorophenols using magnesium–palladium bimetallic system

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Abstract

Ninety-four percent removal of 10 mg L^{-1} of pentachlorophenol (PCP) was achieved by treatment with 154.5 mM Mg^0 and 0.063 mM K_2PdCl_6 in the presence of 175 mM acetic acid in 1 h reaction time. Dechlorination of PCP was found to be sequential and phenol was identified as the end product along with accumulation of trace concentrations of tetra- and trichlorophenols. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) revealed that palladium in its metallic form (Pd^0) produced by reduction of Pd^{4+}, was spatially separated from magnesium granules when acid was included in the reaction. These colloidal palladium particles generated active reductive species of hydrogen and dechlorinated chlorophenols. In the absence of acid, the efficiency of dechlorination of PCP by Pd/Mg^0 system was very low and chief mechanism of removal of the compound was through sorption onto solid surfaces. Thus, it was important to include acid in the system to: (a) facilitate corrosion of Mg^0 and reduction of Pd^{4+} to Pd^0, (b) provision of protons to produce H_2, (c) retard formation of insoluble oxides and hydroxides that may deposit on the magnesium granules and sorb PCP and its partially dechlorinated products and. Application of 154.5 mM Mg^0/0.063 mM K_2PdCl_6 on PCP, 2,4,5-trichlorophenol (TCP) and 2-chlorophenol (MCP) with organic chloride equivalence showed that the rate and extent of removal increased with decrease in number of chlorine atoms on phenol.

Keywords: Chlorophenols; Dechlorination; Magnesium; Palladium; Pentachlorophenol

1. Introduction

Chlorophenols (CPs) with two or more chlorine atoms are either used as pesticides or raw material to synthesize pesticides. Pentachlorophenol (PCP) is one of such compounds that has been widely used as wood preservative and pesticide [1]. Chlorophenols including PCP have been identified as potential carcinogens [2,3]. Ecotoxicity of chlorophenols especially PCP, necessitate the development of rapid and reliable remediation techniques.

Electrochemical reduction/oxidation [4–9] and advanced chemical oxidation [10] of chlorophenols have been profusely studied in the last decade. Reductive electrochemical dechlorination of chlorophenols may be either complete [9] or partial resulting in accumulation of lower chlorinated phenols and phenol [5,6]. On the other hand, both electrochemical and chemical oxidations have been reported to yield near complete mineralization of chlorophenols [7,10].

Both aerobic and anaerobic biodegradation of chlorophenols have been studied in great depth [11–16]. While biodegradation may prove economical, requirements for specific environmental conditions (methanogenic or sulfate reducing) particularly in case of anaerobic degradation, and long acclimation and retention times in general, can restrict its field application.

Zero-valent metals and bimetallic systems have been successfully utilized to dechlorinate chlorinated organics [17–21]. Such reactions are much faster as compared to biodegradation. The main advantage of bimetallic systems is the ability to conduct reactions at room temperature and pressure without exclusion of atmospheric oxygen. Bimetallic systems make use of two metals, one in zero-valent form (with a negative reduction potential like, $Mg^0 \rightarrow Mg^{2+}$, $Fe^0 \rightarrow Fe^{2+}$, etc.) that produces molecular hydrogen when in contact with water by anodic corrosion, and the other metal with a relatively high (positive) reduction potential (such as $Pd^{4+} \rightarrow Pd^0$) as the reducing catalyst. Molecular

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hydrogen is dissociatively absorbed onto reducing catalyst to form a metal hydride (M–H), which in turn dehalogenates the target substrate.

PCP dechlorination was studied earlier by Morales et al. [19] using Mg/Pd system. The concentration of PCP used was very high (2.48 mM, ∼660 mg L^{-1}) as compared to its solubility in plain water (∼10 mg L^{-1}) and therefore solubilized in 1:1 water–2-propanol mixture (v/v). Thus the bimetal concentrations used by authors for dechlorination of 2.48 mM PCP may not be cost effective for practical application to water containing low PCP concentrations. Detection limit for PCP was reported to be 0.39 mM (104 mg L^{-1}) using GC-FID while a much more sensitive detection of PCP can be achieved using GC-ECD. It may also be noted that authors did not account for the sorption of PCP onto residual solid surfaces. This is especially important in view of the fact that reactions were conducted in the absence of acid. Dechlorination studies at low PCP concentration using low concentrations of bimetal may have their own intricate problems. Hence, we carried out all our studies using 10 mg L^{-1} of initial PCP concentration. The major objectives of our study were to: (a) evaluate Pd/Mg^0 system for its ability to dechlorinate PCP and lower CPs in aqueous phase, (b) study the role of acid in the reductive dechlorination, (c) identify the concentration of K_2PdCl_6 required for dechlorination of PCP (10 mg L^{-1}) since palladium is an expensive catalyst and (d) elucidate the mechanism of dechlorination by Mg/Pd system in the presence of acid.

2. Materials and methods

2.1. Chemicals

Magnesium granules (∼20 mesh), potassium carbonate, 3-chlorophenol, 2-chlorophenol, 4-chlorophenol, 3,4-dichlorophenol, 2,3-dichlorophenol, 2,5-dichlorophenol, 2,4-dichlorophenol, 2,6-dichlorophenol, 2,4,6-trichlorophenol, 2,4,5-trichlorophenol, 2,3,6-trichlorophenol, 2,3,4-trichlorophenol, 2,3,4,6-tetrachlorophenol, 2,3,5,6-tetrachlorophenol and pentachlorophenol were purchased from Sigma–Aldrich Chemical Company. Cyclohexane, phenol, 2-propanol and acetic acid were purchased from Merck India Ltd. Potassium hexachloropalladate was procured from Sigma–Aldrich Chemical Company. Methanol and acetic anhydride were purchased from S.D. FineChem Ltd., Mumbai, India. All the above listed chemicals were of high purity (≥98%) and analytical grade. Potassium carbonate was baked in furnace at 400 °C, overnight, prior to use. No pretreatment was carried out with other chemicals. Stock solutions (1000 mg L^{-1}) of all the chlorophenols were prepared in methanol and required concentrations of CPs were prepared by diluting the stock into deionized water.

2.2. Dechlorination experiment according to Morales et al.

Dechlorination experiment described by Morales et al. [19] was carried out by taking 1 g Mg^0 and 10 mg K_2PdCl_6 (concentrations equivalent to 2659 ppm) in a test tube followed by the addition of 5 mL of 2.48 mM PCP prepared in 1:1 (v/v) water:2-propanol. After initial mixing on high speed vortex mixer, the test tubes were maintained on a translatory shaker for 48 h at 30 °C. The method used for quantification of sorption of PCP and its reaction products on solid surfaces following completion of the reaction is described in Section 2.4.

2.3. Influence of acid on the kinetics and extent of dechlorination of PCP by Mg/Pd system using completely mixed batch reactor (CMBR)

Kinetics studies were carried out with 150 mL of sample volume in a 250 mL reagent bottle containing 10 mg L^{-1} of PCP in the absence or in the presence (175 mM) of acetic acid. The concentrations of Mg^0/K_2PdCl_6 were 154.5 mM/0.063 mM. Sequence of addition of reaction mixture components for all the CMBR studies was: PCP → Mg^0 → K_2PdCl_6 → acid (whenever present). Contents of the reactor were continuously mixed on magnetic stirrer at 26.5–27.5 °C through out the reaction period. Aliquots were withdrawn at various time points, derivatized and analyzed for residual PCP concentration by GC-ECD. Experiments were conducted in duplicate. Control experiments were performed under similar conditions as test experiments except that Mg^0 and K_2PdCl_6 were omitted from the reaction mixture.

2.4. Quantification of sorption of PCP and dechlorinated products

In order to quantify sorption of PCP and its reaction products on solid surfaces, supernatant was separated following reaction in a CMBR. Residual solids were washed with deionized water equivalent to three times of reaction volume. Subsequently, one reaction volume of deionized water and 175 mM acetic acid were added to dissolve the magnesium granules completely. This solution was analyzed to determine the concentration of sorbed compounds. The protocol described above was also used to quantify sorption of PCP and products following reactions conducted as per Morales et al. [19], except that concentrated HCl (1.5 mL for 5 mL reaction volume) was used to dissolve the magnesium granules completely.

2.5. Experiments using Mg^0 in combination with pre-reduced palladium (Pd^0)

A combination of Mg^0/Pd^0 granules were prepared by mixing 2 mL of water containing 2.06 M Mg^0 with 0.88 mM K_2PdCl_6 (Pd/Mg ratio ∼0.173% w/w). The contents were mixed for 30 s and allowed to incubate for 5 min for the reduction of Pd^{4+} to Pd^0. The change in the color of K_2PdCl_6 solution from orange to pale yellow was taken as an indication of completion of reduction process. Following reduction, the clear aqueous phase was discarded and Mg^0/Pd^0 particles were collected, washed using 2 mL water and dried in air at room temperature. Experiments were carried out by adding 15 mg of Mg^0/Pd^0 particles into 4 mL of solution containing 10 mg L^{-1} PCP and 175 mM acetic acid.