Catalytic Dechlorination of Chlorophenols in Water by Palladium/Iron

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Abstract

Three isomer chlorophenols, ortho-, meta-, and para-chlorophenol were dechlorinated by Palladium/Iron powder in water through catalytic reduction. The dechlorinated reaction is believed to take place on the surface site of the catalyst in a pseudo-first order. The reduction product for all the three isomers is phenol. The dechlorination rate increases with the increase of bulk loading of palladium due to the increase of both the surface loading of Palladium and total surface area. The molecular structure also has an effect on the dechlorination rate. For condition with 0.048% Pd/Fe, the rate constants are 0.0215, 0.0155 and 0.0112 min⁻¹ for ortho-, meta- and para-chlorophenol, respectively. Almost complete dechlorination is achieved within 5 hours.

Keywords: chlorophenol, dechlorination, Palladium/Iron, catalytic reduction

1. Introduction

Chlorophenols are usually used as the intermediates for organic synthesis, as pesticides in rice culture and as wood preservatives. Whilst they are mainly man-made compounds, chlorophenols are also the natural products of phenylurea metabolite, the products of the chlorination of phenols or the reaction of hypochlorite with phenolic acids. They are carcinogenic and also stable in water. Most chlorophenols are listed as Priority Pollutants by the US EPA [1]. Anaerobic biodegradation is a common treatment method of chlorophenols with the half-life period being more than a few days [2,3]. Advanced oxidation technologies have shown to be effective in degrading these pollutants using UV/H₂O₂ or UV/O₃ [4].

Because chlorophenols are electronegative thus they are readily to be reduced. The more the number of chlorine substituents on the aromatic ring, the more prone of chlorophenols for reduction than for oxidation [5]. Iron has been used as one kind of reagents to dechlorinating chlorinated hydrocarbons containing one to two carbon atoms and operated in field test due to its low energy consumption [6-8]. Recently, it has been found that the addition of Palladium, as a catalyst, can speed up the dechlorination. The dechlorination reaction with Pd/Fe for low molecule hydrocarbons was found to be so fast that it is suitable for treating wastewater in situ [9]. This method has been demonstrated to be effective for treatment of a variety of toxic substances such as polychlorinated biphenyls [10]. In this paper we report for the first time the results of catalytic reduction of three isomers of chlorophenol.

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2. Experimental

2.1. Chemicals

Ortho-chlorophenol (99+%), meta-chlorophenol (98+%), para-chlorophenol (99+%), Iron powder, (>200mesh, Reagent), Potassium Hexachloropalladate (99%) and Sodium sulfate anhydrous (Reagent) were supplied by Aldrich. Acetone was obtained from Fisher. Dichloromethane (DCM, HPLC) was supplied by Labscan. Sulfuric acid (H₂SO₄, 96.0%) was from Mallinckrodt.

2.2. Catalytic reductant preparation and characterization

Palladium/Iron (Pd/Fe) powder was used as the catalytic reductant. It was prepared by wet impregnation of iron powder with aqueous solution of Potassium hexachloropalladate through the following redox reaction:

The procedure is as follows. Desired amount of 5×10^{-4} g/ml potassium chloropalladate aqueous solution is added into a bottle containing iron (Fe) powder. Stir the bottle continuously until the orange-colored potassium chloropalladate solution becomes gray. Then wash the mixture twice using deionized water. Filter the mixture and dry it in the vacuum oven at 80 °C for over 12 hours.

The morphology of the reductant so formed was viewed by a Scanning Electron Microscopy (SEM, Model JSM-6300, JEOL). The surface concentration of Palladium was measured by an X-ray photoelectron spectroscopy (XPS, Model PHI 5600, Physical Electronics). The N₂-BET surface area was determined using a Coulter SA 3100 instrument. The bulk loading of Palladium was quantified by a Polarized Zeeman Graphite Atomic Absorption Spectrometer with a graphite furnace (GA-AAS, Model Z8200, Hitachi). Catalytic reductants of different Pd loading were prepared to test their efficiencies.

2.3. Experimental procedure

Batch experiment was carried out using three isomer chlorophenols as the substrates: ortho-, meta- and para-chlorophenol. Desired stock concentration was prepared using acetone as the solvent. This stock solution was stored in a refrigerator at about 5 °C. 20ml wastewater samples containing 20ppm of chlorophenols were prepared by pipetting desired amount of the stock solution and using water as solvent. The reduction reaction took place in the conical beaker with 5 g Pd/Fe pre-filled. The beaker was sealed with PEFÉ-faced screwed-cap and placed in the water bath operating at 28°C and shaking at 200rpm.

Wastewater samples were collected at a fixed time period. Exactly 15ml of the sample were withdrawn and put into a 60ml glass separating flask with one drop of 3M H₂SO₄ added in order to acidify the solution. Then the separating flask was manually shaken for 3 minutes after the addition of 10 ml of DCM. The flask was left to still until completely separated two layers appear. The solution in the bottom layer was transferred into a 10ml volumetric flask through a long-neck-glass filter covered with a layer of Sodium sulfate anhydrous. This solution is used for later on analysis.

2.4. Analytic method

The solution was analyzed using the Hewlett-Packard Gas Chromatography with

a flame ion detector (GC-FID, Model 5890) and a HP-5 capillary column (inner diameter 0.25mm x 0.25 μ m film thin and length 30m). The temperature program was as follows: initial value 70 °C, ramp at 3 °C /min to 120 °C, then at 30 °C/min to 180 °C and stay at 180 °C for 1 minutes. Highly pure grade N₂ was the carrier gas with the constant gas flow being 1.0ml/min without splitting. Temperatures of inlet and detector are fixed at 250 °C.

For the measurement of other parameters, samples were withdrawn from the stock using syringe and filtered with 0.45 μ m filter. A volume of 3ml of the sample was used in measuring the pH value, free Iron ion and redox-potential.

3. Result and discussion

3.1. Characterization results of the catalyst

The surface morphology of both the Fe and Pd/Fe is shown in Figure 1. The surface of Pd/Fe is a sponge-like phase with palladium dispersed on the iron surface. Atoms of C, O, Ca, Mn, Fe and Pd are detected on the catalyst's surface by XPS measurement. Because the binding energy of Pd 3d ranges from 335 to 336 eV, the chemical state of Pd is dominated by zero-valence palladium (Pd⁰). This phase facilitates the adsorption of benzene ring [11]. The surface concentration of Pd is expressed by Pd/Fe_{xps}, which can be deduced from the Pd 3d and Fe 2p line areas in XPS measurements. The total surface area of the catalyst measured by BET-N₂ varies with the Pd loading because surface area is proportional to the Pd particle size on the catalyst surface. As shown in Figure 2, with the increase of bulk loading of Pd, the surface concentration of Pd increases because of the Pd deposition on the catalyst surface. The

Figure 1. SEM image of
a) Fe powder b) Pd/Fe (0.048%)

Figure 2. Increase of catalyst surface area and Pd/Fe value with Pd bulk loading

increase of the surface area with the increase of Pd bulk loading is consistent with the information revealed from the catalyst SEM image. That is the Pd particles are dispersed on the surface rather than clustered. Such an observation would mean that the removal efficiency will increase with the Pd loading. More discussion on Pd loading will be presented subsequently.

3.2. Catalytic reduction mechanism

The dechlorination reaction is proposed as follows:

The chlorine in chlorophenol is substituted by hydrogen with phenol produced. The hydrogen atom is solely supplied by H_2O as proved by the experiment carried out in D_2O solution [12]. With the production of OH^- , the pH value of the solution should increase as indeed found in Figure 3. The increase of pH is also partially resulted from the reduction of chlorophenol and formation of phenol because the acidity of the former is stronger than the latter. Redox-potential should decrease during the reaction because chlorophenol is more prone for reduction than phenol as shown in Figure 4.

Figure 3. Variation of pH value and free Fe ion concentration with reaction time

Figure 4. Decrease of redox potential with reaction time

In the presence of dissolved oxygen at weak acidic or neutral condition, the following reaction also occurs:

With the increase of pH value, reaction (4) is favored to proceed. In connection with reaction (2), an maximum free Ferrous ion concentration is expected. Figure 5 verifies such an expectation.

Figure 5. Increase of conversion of chlorophenol to phenol with the bulk loading of Pd

The presence of Palladium speeds up the reduction reaction dramatically as shown in Figure 5. Pd can adsorb hydrogen dissociatively in addition to the adsorption of chlorophenols similar to the results found by Grittini et al. [11]. On the catalyst surface, the hydrogen produced in reaction (2) is adsorbed and dissociated into atomic H, one of the strongest reductants. Atomic H attacks chlorophenol to replace the chlorine and to form phenol and chlorine ion. Therefore, the more well-dispersed the Pd^0 , the higher the conversion.

3.3. Catalytic reduction rate constants

Figure 6 shows the history of the reduction of chlorophenols and the formation of phenol with reaction time. The amount of 0.048% Pd loading was chosen because this value has been found to be sufficient as indicated in Figure 5. Five grams of the catalyst was used in each experiment. Apparently the location of the chlorine atom on phenol plays an important role. Ortho-chlorophenol concentration drops below detectable limitation within 2 hours while it takes more than 2 hours for meta-chlorophenol and nearly 5 hours for para-chlorophenol.

Rearranging the data shown in Figure 6 and linear decrease of $\ln(C/C_0)$ with time is obtained as shown in Figure 7. This linear relationship reveals a pseudo first order reduction reaction regarding the chlorophenol concentration. The reaction rate constants (K) can be determined from Figure 7 as 0.0215, 0.0155 and 0.0112 min^{-1} respectively for ortho-, meta- and para chlorophenol with 0.048% Pd/Fe. The standard errors for the determined rate constants are 0.0010, 0.0005 and 0.0006 respectively.

Figure 6. History of reduction of chlorophenols and respective formation of phenol

Figure 7. Linear decrease of normalized chlorophenol concentration ($\ln$) with reaction time

The dependence of the reaction rate constant on the structure of substrates is not surprising. Dolfing et al. [5] have shown that the rate constant for reduction of halogenated aromatics in anaerobic estuarine sediment is proportional to the Gibbs free energy of formation ΔG_f° . ΔG_f° is one of the physical chemical parameters of compounds that reveals the difference in molecular structures. They found that the reduction reaction rate is faster for the smaller ΔG_f° compounds. While the values of ΔG_f° of ortho-, meta- and para-chlorophenol are -56.8, -56.4, -53.1 kJ/mol, respectively, the variation of the reaction rate constants obtained here are consistent with the previous analysis [5].

4. Conclusion

Dechlorination of chlorophenols using Pd/Fe takes place on the catalyst surface. The conversion rate depends on the Pd loading. The reduction reaction is found to be pseudo first order. Reaction rate constant increases with the decrease of the formation Gibbs free energy of chlorophenols, with the rate constant being 0.0215, 0.0155 and 0.0112 min^{-1} respectively for ortho-, meta- and para-chlorophenols with 0.048% Pd/Fe. Pd/Fe reduction is a fast and easy dechlorination method of chlorophenols. The present finding can be valuable for designing the in-situ treatment of chlorophenol contaminated water.

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