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REDUCTION OF AROMATIC HYDROCARBONS BY ZERO-VALENT IRON AND PALLADIUM CATALYST

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INTRODUCTION

Permeable reactive barrier (PRB) is one of the most popular innovative technologies for remediation of contaminated groundwater and soils.[1] During the last a decade, intensive studies were carried out on developing reactive barrier materials to be used in detoxification of environmental contaminants found in subsurface.[2-8] Zero-valent iron (ZVI) is the most frequently studied as barrier materials and successfully applied on several *in situ* remediations.[9] Even ZVI has relatively low reduction potential (E^0=-0.404 V), it reduces chlorinated organic compounds such as trichloroethylene (TCE), tetrachloroethylene (PCE) and carbon tetrachloride (CT) in subsurface environments. ZVI also reduces some inorganic contaminants such as Cr(VI) and nitrate. However, it has very low reactivity for chlorinated aromatic compounds. A few studies to overcome the low reactivity of iron have been conducted including development of nano-size iron particles and bimetal systems with second metal's catalytic activity. The nano-sized iron particles dechlorinated PCE and TCE with very increased degradation rates and showed enhanced reactivity for chlorinated aromatic compounds such as PCBs.[10] Palladized iron (Pd/Fe), a bimetal, reductively dechlorinated PCE and TCE at very increased rates.[11] It also dechlorinated some chlorinated phenols and chlorinated biphenyls. Conventional or modified ZVM system has been applied to detoxify halogenated organic compounds. Another group of toxic organics, which are commonly

found in superfund sites, is non-halogenated compounds including poly-aromatic hydrocarbons (PAHs). Physical removal of the non-chlorinated aromatics using activated carbons or other sorbents could be an alternative, but the removal using sorbents has some limitations such as replacement or secondary treatment after the break-through and adverse effects of natural organic matter. If ZVMs or modified ZVM systems reduce the toxicity of non-chlorinated aromatic hydrocarbons, PRB system having relative advantages over pump and treat or bioremediation can be applied for the removal of wide range of recalcitrant organics. In this study, palladium catalysts and ZVI were simultaneously tested to remove aromatic compounds in batch reactors. A few chlorinated aromatics, chlorophenols and some non-chlorinated aromatics such as benzene, naphthalene and phenanthrene were tested. Reduction products were analyzed and reduction pathways were suggested.

EXPERIMENTAL METHODS

Materials

2-Chlorophenol (ACS grade, 99%), phenol (ACS grade, 99.5%), cyclohexanone (99%), benzene (GC grade, 99.9%), naphthalene (99%) and phenanthrene (99%) were purchased from Aldrich Chemical Co. and used as received without further purification. Hexane, methanol and acetone were all GC grade and obtained from JT&Baker. ZVI (electrolytic iron powder, particle size 100 mesh and smaller) was obtained from Fisher Scientific. Pd 5 wt. % in 10% HCl solution was obtained from Aldrich and used for Pd/Fe bimetal. Palladium catalyst, 5 wt. % on alumina pellet was purchased from Aldrich Chemical Co.

Bimetal preparation and reactor system

The preparation of bimetal followed the previous report.[4] EPA sampling vials were used as batch reactors. Samples were prepared in an anaerobic chamber. Metals, catalysts and deionized water were added into the vials. The target compounds dissolved in methanol were spiked with a microsyringe. After spiking, the vials were sealed with caps and PTFE/silicone septa. Controls were prepared identically to samples except no ZVM or no catalysts. Vials were placed on a shaker at 150 rpm.

Extraction and GC analysis

Vials were removed from the shaker for analysis at each sampling time. Hexane was added as extraction solvent into the vials and the vials were place on an orbital shaker for 20 minutes. The solvent phase was analyzed with a GC-MS equipped with a capillary column (DB-1). The removal of target compounds was monitored and daughter compounds were quantified. The daughter compounds were identified with the mass spectrum and by injection of standard solution.

RESULTS AND DISCUSSION

Reduction of 2-chlorophenol by Pd/Fe and Fe

Fe showed very low reactivity for 2-chlorophenol and about 5% of 2-CP disappeared over 17 days experiments. Pd/Fe dechlorinated 2-CP and phenol was found as product. In batch experiments, quantified phenol could not make up the removal of 2-CP in mass balance. GC-MS analyses showed cyclohexanone as another product. Quantified

cyclohexanone was added into the mass balance as shown in Figure 1. However, cyclohexanol was not found by GC/MS analysis by checking the retention time confirmed with injection of cyclohexanol standard solution. Fe and palladium catalyst combination resulted in a very increased dechlorination and reduction rate for 2-CP. This implies that Fe could supply electrons onto palladium surface through direct contact or produce hydrogen even if Fe is not chemically bonded with palladium as Pd/Fe.

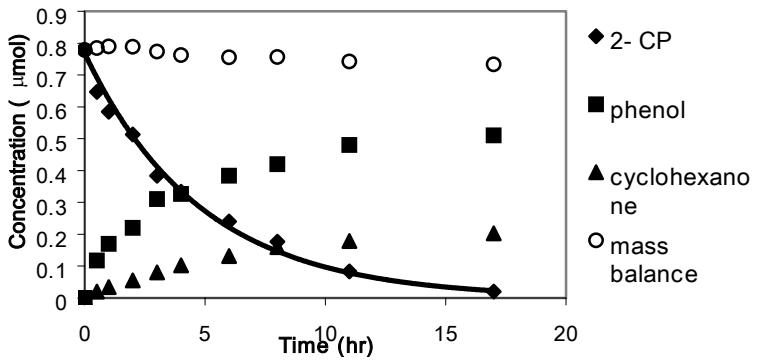

Figure 1. Dechlorination of 2-CP and reduction of benzene

<u>Reduction of benzene and biphenyl</u>

Fe and palladium catalyst combination was applied to benzene, and biphenyl and the result was shown in Figure 2. Benzene was reduced to cyclohexane, indicating that Fe/Pd catalysis system reduces the aromatic ring. Cychlohexyl benzene was found from the biphenyl reduction and 1,1'-bicyclohexyl was detected as final products. The half-life for the removal of biphenyl was about 13 hours with 1g Fe and 1g of catalyst pellets. This reaction rate is relatively fast, considering that groundwater flow rate is slow and the flow through PRB allows months of reaction time.

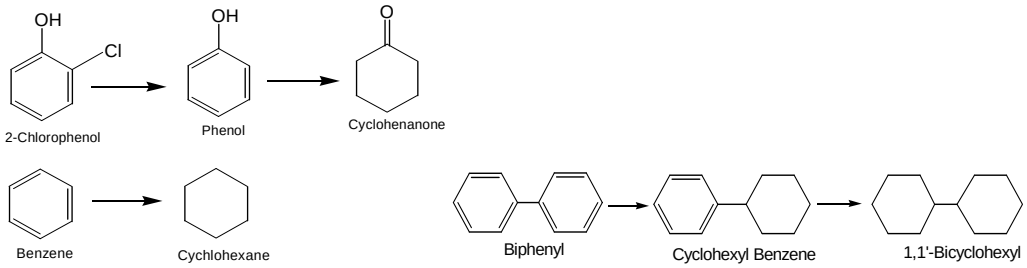

Figure 2. Reduction pathways of 2-chlorophenol and benzene with ZVI and catalysts.

Reduction of naphthalene and phenanthrene

The reduction of aromatic ring was also proved with naphthalene, as shown in Figure 3. 1,2,3,4-Tetrahydronaphthalene (one ring reduced form of naphthalene) was found as daughter product of naphthalene in Pd/Fe reactors. The reaction was further progressed to decahydronaphthalene (both ring reduced) with Fe and Pd catalyst. Both of *cis*- and *trans*-decahydronaphthalene were found as shown in Figure 3. The half-life of naphthalene was about 22 hours with 1 g of Fe and 1 g of Pd catalyst. Phenanthrene was also tested with Pd/Fe and Fe/Pd catalyst. Pd/Fe showed very slow removal rate, but Fe/Pd catalyst system showed relatively fast reaction rate. Half-life was about 30 days and the products found were 9,10-dihydrophenanthrene (the second ring reduced) and 1,2,3,4-tetrahydrophenanthrene (the first ring reduced). In general, chlorinated organic has higher toxicity comparing with non-chlorinated counter part and the compounds with aromatic rings are more toxic than those with non-aromatic same structure. Currently, PRB using plain Fe is only applicable for the removal of halogenated organic and some inorganic contaminants such as Cr(VI) and nitrate. However, from this study, it was found that Pd/Fe and Fe/Pd catalysts could dechlorinte and reduce the aromatic rings, implying that they could be an excellent alternative material for PRB, which treats not only halogenated compounds but aromatic recalcitrant contaminants.

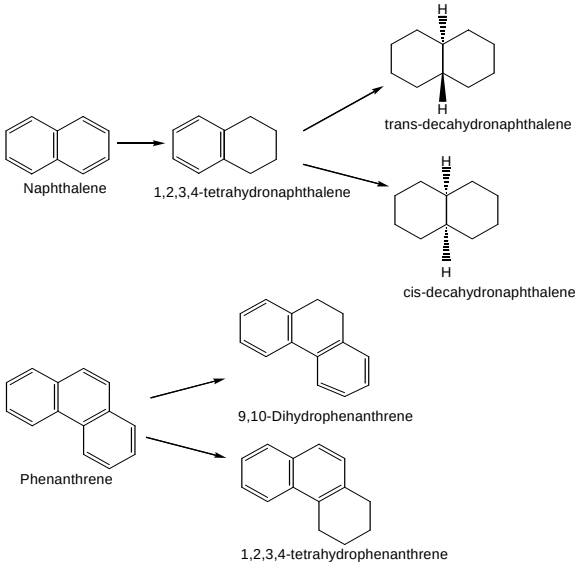

Figure 3. Reduction pathways of naphthalene and phenanthrene with ZVI and catalysts.

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