Short-chain organic acids increase the reactivity of zerovalent iron nanoparticles toward polychlorinated aromatic pollutants

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HIGHLIGHTS

- Short-chain organic acids enhance iron nanoparticles to degrade pentachlorophenol.
- Oxalic acid enhances the largest degradation of PCP with NZVI.
- Oxalic acid strongly chelates ferrous ions out of NZVI particles.
- Less chlorinated byproducts are generated with oxalic acid.
- Oxalic acid is a greener treatment agent than doping metal on NZVI.

GRAPHICAL ABSTRACT
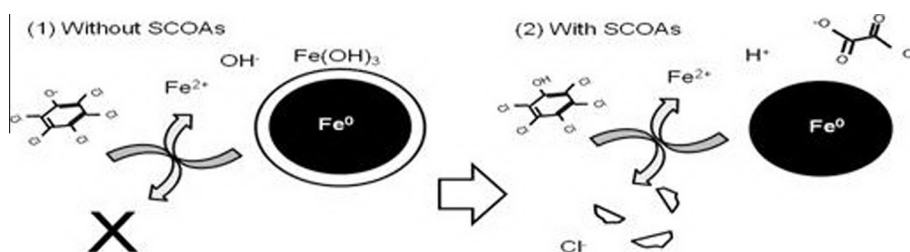
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ABSTRACT

The use of heavy metals or rare noble metal doping on nanoscale zerovalent iron (NZVI) generally enhances the treatment of hazardous chlorinated organic chemicals (COCs). To avoid the metal use, the effects of four short-chain organic acids (SCOAs) on the degradation of COCs by NZVI were evaluated. Pentachlorophenol (PCP) was the target COC because it has caused serious soil and groundwater contamination. Our results showed that PCP could not be removed by NZVI alone, and the addition of SCOAs promoted PCP degradation by NZVI in acid conditions. Oxalic acid (OA) enhanced the PCP degradation by NZVI more than the other three selected SCOAs. The formation of oxalate-iron complexes out of NZVI particles was observed, indicating that OA could strongly complex with ferrous ions produced during PCP dechlorination and decrease the formation of ferrous (hydro)oxides, which would precipitate on the NZVI surface. Consequently, less passivation layers and even fresh NZVI surfaces were obtained. A more complete PCP dechlorination and the degradation pathways were proposed according to the identification of degradation byproducts. OA led to the highest efficiency of PCP dechlorination around 89% by NZVI due to its strong complexating and pH buffering properties. This green treatment strategy, without doping secondary metals, can facilitate the decontamination of polychlorinated organic pollutants.

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1. Introduction

Iron is the fourth most abundant element in the earth's crust; therefore, it is more environmentally friendly to use zerovalent iron (ZVI) rather than other metals to degrade halogenated organic pollutants. Recently, nanoscale zerovalent iron (NZVI), which has a high specific surface area, has been shown to be more reactive than microscale ZVI (MZVI) powder [1–4]. Some green NZVI production processes and further modifications were proposed [5–8]. Due to the limited reductive power of these ZVIs, bimetallic particles have been developed by adding a second catalytic metal such as Pd, Pt, Ag, Ni, or Cu to the primary metals [9–12]. For instance, pentachlorophenol (PCP) removal, which does not seem to be possible with ZVIs alone, can be promoted by coating NZVI with Pd [13]. Bimetallic particles, such as Pd/Fe [14], Ni/Fe [15], and Cu/Fe [13], degrade PCP and other organic compounds. However, the second metals could be heavy metals, such as Ni and Cu, which could lead to second contamination in the environment. Therefore,

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the development of a greener pollution treatment technology, without the use of these heavy metals, is needed.

PCP was used extensively in the past as a wood preservative, pesticide, and herbicide, which led to serious environmental contamination. For example, one heavily PCP contaminated site in southern Taiwan needs to be remediated. The removal of PCP can be performed either by abiotic processes, such as absorption, thermal desorption, and oxidative degradation, or by biotic degradation. These treatments, however, are time-consuming or need further treatments. Although bimetallic NZVI has been developed to degrade halogenated compounds effectively [16–18], a NZVI technology without the second metals should be investigated, aiming at the development of a greener remediation method. The addition of organic acids, which are environmentally friendly agents, can be an alternative for contaminant degradation with ZVIs. Short-chain organic acids (SCOAs), which mainly originate from root exudates, plant debris, and common fermentation products, are examples of such agents. Common SCOAs in the environment are aliphatic di- and tri-carboxylic acids [19]. SCOAs are usually involved in the enhancement of mineral dissolution processes and in the industrial processes such as rust removal [20,21]. They alter chemical processes in the environment through complexation reactions with metal ions in solution and ligand exchange reactions at mineral surfaces [22–24]. The strength of complexation increases as the number of carboxylic groups in each ligand molecule increases [25]. For inorganic contaminants, the reduction of nitrate by MZVI increased in the order $H_3PO_4 <$ citric acid (CA) $< H_3BO_3 <$ oxalic acid (OA) $< H_2SO_4 <$ formic acid (FA) $<$ HCl [26]. Oxalate and citrate decreased nitrate reduction rates by blocking the ZVI reactive sites [26]. However, in the presence of oxalic and citric acids, the acceleration of Cr(VI) reduction with MZVI was observed [27], indicating that SCOAs could either promote the degradation of chlorinated compounds by ZVIs or inhibit ZVI reactivity due to iron surface complexation.

Regarding the degradation of halogenated compounds with NZVI, the effect of SCOAs on PCP degradation by NZVI particles should be evaluated to propose an innovative treatment strategy. Therefore, the aims of this study were to investigate the effect of SCOAs and NZVI on PCP degradation kinetics and mechanisms; to compare the influence of the selected SCOAs on PCP degradation; and to propose a PCP dechlorination pathways by NZVI with SCOA by analyzing degradation intermediates.

2. Experimental procedure

2.1. Chemicals

PCP was purchased from Aldrich Chemical Co. (USA). Chlorophenol standard, DIN EN 12673 chlorophenols, including 19 chlorophenols, was purchased from Supelco (USA). Lactic acid (LA), tartaric acid (TA), OA, and CA were obtained from J. T. Baker (USA). The properties of these chemicals are listed in Table 1. HCl and NaOH were purchased from Riedel-de Haen. $FeCl_3$ and $NaBH_4$ were purchased from Merck (Germany). The MZVI powder, obtained from Hayashi Pure Chemical (Japan), was approximately 200 μm in diameter. NZVI was synthesized by the vigorously mixing 3 g/L $FeCl_3$ and 1 g/L $NaBH_4$ solutions [1,14,28]. The NZVI precipitate was filtered with a 0.2 μm filter and washed with pure water at least twice. All aqueous solutions were prepared in deoxygenated water purified with a Milli-Q system (18.2 MΩ cm, Millipore, USA) and purged with nitrogen gas.

2.2. Characterization of NZVI

The surface morphology and surface elemental composition of the NZVI before and after reaction were examined by scanning electron microscopy (SEM, JSM-5910 Microscope, Japan). A drop of NZVI particles was placed on an acid-washed silicon wafer and dried in an anaerobic chamber. The crystalline phase of NZVI particles was identified with X-ray diffraction (XRD, BL 13A1) at the Taiwan National Synchrotron Radiation Research Center. For the XRD analysis, the nanoparticle samples were stored in plastic bags containing their original solutions. Data points were collected over the 2θ range of 18–70° with a step size of 0.05° at room temperature.

2.3. Dechlorination experiments

The dechlorination experiments of PCP in aqueous solution were performed in 5 mL amber glass vials, capped with Teflon coated septa and aluminum caps without headspace, at room temperature. In all experiments, a 5 mg/L PCP solution was adjusted to the desired pH 3 using HCl. The aqueous PCP solution was prepared with and without SOCAs and purged with N_2 gas for 30 min prior to reaction. To start the reaction, a 1.5 g/L NZVI solution was added into the reaction vials, which were placed in a horizontal shaker at 150 rpm. After shaking in a vortex mixer, the suspension samples were taken at different time intervals, and the NZVI particulates were magnetically removed prior to chemical analysis. In order to determine the degradation of PCP, 2 mL of hexane was added to the vials followed by 0.05 mL of concentrated HCl and then shaken at 1400 rpm for 10 min. HCl was added to promote the dissolution of NZVI surfaces and protonation of chlorophenolates [29], thereby releasing adsorbed PCP and other chlorinated phenols for extraction into hexane. Furthermore, to evaluate the adsorption of PCP by NZVI, vials were extracted with a liquid–liquid method using the above acidified hexane as a solvent. At this pH condition, there was no significant adsorption of PCP on NZVI. Since there was no removal in these selected SCOAs alone, SCOAs cannot degrade or capture PCP molecules away from water.

2.4. Analyses

2.4.1. Chemical analyses

Quantitative analysis of PCP was conducted using a HPLC (Agilent 1200 series) with a reversed phase C18 column (XDB-C18, 150 mm × 4.6 mm, 5 μm) and an UV/Vis detector at 254 nm wavelength. A mixture of 0.1% phosphoric acid and methanol, in a ratio of 10:90, was used as the mobile phase at a flow rate of 1.0 mL/min. The C18-column was maintained at room temperature, and the injection volume of solution was 20 μL. The degraded byproducts were extracted by liquid–liquid extraction with an acidified acetone/hexane mixture (1:1, V/V) on a vortex orbital mixer for 5 min and quantified. Quantification was conducted using an Agilent 6890 GC with μ-electron capture detector, a flame ionization detector, and Agilent 5975B mass spectrometer. A 30-m DB-5 capillary column was used. The injector and detector temperatures were 250 °C and 320 °C, respectively. The initial temperature was 40 °C for 2 min, ramping at 40 °C min^{-1} to 100 °C with 0.5-min holding, 5 °C min^{-1} to 180 °C with a 1-min holding, and 30 °C min^{-1} to 300 °C with a 1-min final holding. The concentration of total dissolved ferrous ions was measured by a UV/Vis spectrophotometer (UNICO 2808) at 510 nm using ferrozin as an indicator [30]. The aqueous pH was measured before and after reactions with a pH meter (Jenco, model 6010), equipped with a 6 mm diameter pH electrode. After pouring the reactor contents into a centrifuge tube, the redox potential (Eh) was measured immediately with an ORP meter (Jenco, model 6010), equipped with the ORP001 probe.

2.4.2. Kinetic modeling

The degradation rates of PCP by NZVI can be described by the pseudo-first-order kinetic model: