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Fenton-like oxidation of 2,4-DCP in aqueous solution using iron-based nanoparticles as the heterogeneous catalyst

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ABSTRACT

In this report, various iron-based nanoparticles (nZVI, n-Ni/Fe, n-Pd/Fe) were used for both heterogeneous Fenton oxidation of 2,4-dichlorophenol (2,4-DCP) and reductive dechlorination of 2,4-DCP in order to understand their roles in the Fenton oxidation and the reductive degradation of 2,4-DCP. The dechlorination efficiency of 2,4-DCP using nZVI, n-Ni/Fe, n-Fe/Pd and Fe^{2+} was 6.48%, 6.80%, 15.95%, 5.02%, while Fenton oxidation efficiency of 2,4-DCP was 57.87%, 34.23%, 27.94%, 19.61% after 180 min, respectively. The new findings included a higher dechlorination using n-Fe/Pd due to Pd effective catalysis and the effective heterogeneous Fenton oxidation using nZVI depending on reductive dechlorination and heterogeneous Fenton oxidation occurs simultaneously. However, nZVI as the potential catalyst for heterogeneous Fenton was observed, and SEM, EDS and XRD demonstrate that change on the nZVI surface occurred due to the Fe^{2+} leaching, and Total Organic Carbon (TOC) (30.71%) shows that 2,4-DCP was degraded. Furthermore, the experiment indicates that the pH values and concentration of 2,4-DCP significantly impacted on the heterogeneous Fenton oxidation of 2,4-DCP and the data fits well with the pseudo first-order kinetic model, which was a diffusion-controlled reaction. Finally, a possible mechanism for degradation of 2,4-DCP was proposed.

1. Introduction

Chlorophenols have been used as preservative agents for wood, paints, vegetable fibers, leather and disinfectants. Most chlorophenols are extremely difficult to be biodegraded and it is of great concern because of its toxicity [1]. 2,4-Dichlorophenol (2,4-DCP) was one of the chlorophenols widely presented in wastewaters [1,2]. Consequently, removal of 2,4-DCP in both soil and groundwater has attracted attention. Various biological and physical chemical strategies have been investigated for the remediation of chlorophenols [2–4]. However, biological methods are limited by the toxicity of chlorophenols to microbes [5]. Physical methods such as adsorption [4] and liquid membrane [6] are not effective in removal of chlorophenols since it merely transfers the pollutants from one place to another. Chemical methods including chlorination [7] and permanganate oxidation [8] lead to form of toxic intermediate products due to incomplete oxidation. It is therefore necessary to find the effective method for the degradation of chlorophenols.

In the past few decades, advanced oxidation technologies (AOTs) represent efficient methods for degrading toxic and recalcitrant organic compounds [5,9]. Of these technologies, Fenton oxidation is one of the approaches because its reagent components are easy to handle and environmentally friendly [10,11], where the iron ion reacts hydrogen peroxide to generate highly reactive hydroxyl radicals ($^{\cdot}OH$). Although the degradation of chlorophenols with Fenton's reagent is promising, the homogeneous catalyst is usually added as ferrous salt which is rapidly consumed and consonantly the low degradation efficiency was obtained [11]. To address this issue, heterogeneous iron-supported catalysts, such as zero valent iron (ZVI) [12], goethite (α-FeOOH) [13] and Fe_3O_4 [14], were used as the Fenton-like reaction. However, the degradation of organic contaminants using these systems are so slow that additional assistants such as ultrasound or visible light irradiation and UV are needed to accelerate the reaction rate [11].

Nanoparticles are considered potentially useful for the treatment of contaminants, such as TNT [15], chlorophenols [16] and dyes [17] due to their nanoparticle size, large surface area, and high reactivity as solid catalysts [18,19]. Furthermore it has been

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shown that the dehalogenation rate of trichloroethylene (TCE) using synthesized bimetallic Pd/Fe nanoparticles was 30 times higher compared to nZVI [7,20]. Nevertheless, the chlorophenol being treated by iron-based nanoparticles cannot degrade chlorophenol completely since some of the intermediates reside as by-products, which are toxic [16,21]. Recently, nZVI has shown potential in Fenton-like system for degrading a wide range of organic contaminants in environmental remediation [22]. What is more, when nanoscale zero-valent iron particles were used as the catalyst in heterogeneous Fenton-like systems, not only was the organic pollutants rapidly degradable, also the intermediates was oxidized [20,22]. However, the mechanism of ion-based nanoparticles such as nZVI, n-Ni/Fe, n-Pd/Fe as the catalyst for the Fenton oxidation of chlorophenols are still unclear. On the other hand, ion-based nanoparticles used for the reductive degradation of chlorophenols have not been reported. These studies could help to understand the function of iron-based nanoparticles in degradation of chlorophenols by both reduction and oxidation. In addition, it is still not clear the differences of degradation chlorophenols mechanism between reduction and oxidation using these iron-based nanoparticles. For these reason, in this study, firstly, the different iron-based nanoparticles such as nZVI, n-Ni/Fe, n-Pd/Fe were used in both dechloronation and heterogeneous Fenton oxidation. Secondly, the effect of initial parameters (the value of pH, H_2O_2 dosage, nZVI addition and initial 2,4-DCP concentration) on the degradation of 2,4-DCP in the heterogeneous Fenton-like system was investigated. Thirdly, SEM, EDS and X-ray diffraction (XRD) studies provided insights into the degradation mechanism. Finally, a possible mechanism for 2,4-DCP degradation by heterogeneous Fenton-like process was proposed.

2. Materials and methods

2.1. Materials and chemicals

nZVI and bimetallic Ni/Fe nanoparticles were purchased from Hongwu Nano Material Co., Ltd. (Guangdong, China), and nZVI size ranged from 0 to 50 nm with a specific surface area of 40–60 m^2/g and a purity of >99.5%. The n-Ni/Fe particle size was ranged from 0 to 60 nm with a specific surface area of 0–50 m^2/g and Ni loading was 5 wt.%. Fe/Pd nanoparticles were synthesized using liquid-phase reduction as previous our reports [7]. The synthesized Pd/Fe nanoparticle size varied from 0 to 60 nm with a specific surface area of 40–60 m^2/g and Pd loading was 2.5 wt.%.

All chemicals used in this study were of analytical grade and were used without further purification. A solution containing 2,4-DCP was prepared by dissolving 2,4-DCP with deionized water to the desired concentration.

2.2. Batch experiments

To compare the degradation of 2,4-DCP by dechlorination and heterogeneous Fenton oxidation using iron-based nanoparticles, batch experiments were carried out using Fe^{2+}, nZVI, n-Ni/Fe, n-Pd/Fe, which was added to a 50 mL glass tube containing an aqueous solution of 100 mg/L 2,4-DCP (15 mL). These were then placed on a rotary shaker at 303 K and 250 r/min. The initial pH of the 2,4-DCP solution was adjusted by 1.0 mol/L H_2SO_4 and 1.0 mol/L NaOH. The 2,4-DCP was extracted by adding ethyl acetate as an extraction solvent to determine the 2,4-DCP concentration at 286 nm using the UV-752 spectrophotometer.

For heterogeneous Fenton oxidation of 2,4-DCP, different conditions affecting the degradation of 2,4-DCP included contact time, initial pH, initial H_2O_2 concentration, 2,4-DCP initial concentration and temperature were conducted. The pH value was detected using a pH meter (pHS-3, Shanghai, China). All organic carbon (TOC) measurements were conducted with the total organic carbon analyzer (TOC-V cph, Daojin, Japan).

2.3. Characterizations and measurements

Surface morphology and elemental composition were found using SEM, specifically a Philips-FEI XL30 ESEM-TMP (JSM 7500F, Japan) instrument. The powdered samples were first affixed onto adhesive tapes supported on metallic disks and then covered with a thin, electric conductive gold film. Then they were recorded at different magnifications at an operating voltage of 3 kV. The elemental loading on the surface of nZVI before reaction and after reaction were analyzed by INCA EDS (Oxford Instruments, UK) in conjunction with SEM.

The samples of nZVI, before and after heterogeneous Fenton reaction, were examined by an X-ray diffraction (XRD) instrument (X'Pert Pro MPD, Netherlands) with filtered Cu Kα radiation operated at 40 kV and 40 mA. Data were collected from 10° to 80° of 2θ with a step width of 0.05° and a counting time of 30 s per 0.1°.

2.4. Kinetic analyze

In most cases first-order kinetic equations with respect to the 2,4-DCP can be used for degradation [5]. Hence, the kinetics of degradation of 2,4-DCP in aqueous solution can be described according to the pseudo first-order equation as given below:

$$v = -\frac{dc}{dt} = k_1 c \tag{1}$$

$$\ln\frac{c}{c_0} = -k_1 c \tag{2}$$

where c is the concentration (mg/L) of 2,4-DCP in solution, k_1 the observed rate constant of a pseudo first-order reaction (min^{-1}) and can be calculated from the slope of the line by plotting ln (c/c_0) versus time where the correlation coefficients is high ($R^2 > 0.9$). Previous works have reported that the organic compounds degradation by Fenton system follow the pseudo first-order model well [17,21].

3. Results and discussion

3.1. Comparison of 2,4-DCP degradation using various nanomaterials

Fig. 1(a) illustrates the degradation of 2,4-DCP with the initial concentration of 100 mg/L by iron-based nanoparticles and ferrous iron to compare their dechlorination, where the removal efficiencies of 2,4-DCP by n-Pd/Fe, n-Ni/Fe, nZVI and Fe^{2+} were 15.95%, 6.80%, 6.48% and 5.02% after 180 min reaction, respectively. This indicates that the bimetallic Pd can enhance the reactivity of n-Fe/Pd, and the dechlorination rate of 2,4-DCP by n-Fe/Pd was higher than that of n-Ni/Fe and nZVI, indicating that the catalyst activity of bimetallic nanoparticle was higher than that of nZVI. This is due to the fact that the introduction of a second metal accelerates electron transfer from iron and the formation of H_2 from iron corrosion [20]. However, the removal efficiency of 2,4-DCP in the presence of n-Fe/Pd was higher than n-Fe/Ni, indicating that Pd is a more efficient catalyst than Ni and can rapidly promote the formation of abundant hydrogen radicals from the decomposition of hydrogen [20]. In addition, low removal efficiency was obtained using Fe^{2+}, which can be explained by the adsorption of 2,4-DCP onto the iron hydroxides ($Fe(OH)_2$, $Fe(OH)_3$) since Fe^{2+} in solution was easy oxide then leading to flocculation [7]. Although n-Pd/Fe did improve reductive dechlorination, the degradation efficiency