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Improvements of Pd/Fe nanoparticles by ethylenediamine disuccinic acid for 2,4-D dechlorination

Hongyi Zhou*, Junchao Xiang, Yongkang Zhao, Yong Chen

College of Environment, Zhejiang University of Technology, Hangzhou 310014, PR China

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ABSTRACT

In the current study, the reaction system of ethylenediamine disuccinic acid (EDDS, a green and biodegradable chelating agent) improved nanoscale Pd/Fe was successfully established for effective dechlorination of 2,4-dichlorophenoxyacetic acid (2,4-D). The effects of different experimental parameters including EDDS dosage, initial pH, palladium ratio and reaction temperature on 2,4-D dechlorination were investigated. The results demonstrated that higher chelating agent dosage and palladium ratio, appropriate reaction temperature (20.0–35.0 °C) and a lower initial pH were beneficial for the efficient reductive dechlorination of 2,4-D. Over 99.5% of 2,4-D removal and 97.3% of phenoxyacetic acid (PA) generation were reached within just 50 min reaction time under these experimental conditions: 20.0 mmol L^{-1} EDDS concentration, 1.0 g L^{-1} nZVI content, initial pH 5.5, palladium loading 0.50%, reaction temperature 25.0 °C and stirring speed 200 r min^{-1}. Characterization tests revealed that EDDS successfully removed the passivation layer on the nano-iron surface and thus exposed more surface active sites. In addition, EDDS chelated iron ions in the solution generated more soluble complex inhibiting the formation of inert layer on nanoscale Pd/Fe particles surface. As a result, the reactivity of nanoscale Pd/Fe was increased significantly. Findings from the present study suggested that the EDDS could be a promising substitute to enhance Pd/Fe reactivity and dechlorination efficiency.

1. Introduction

Globally, 2,4-D is recognized as a selective and efficient organic herbicide and one of the major herbicides extensively used due to its lowcost [1]. Generally, 2,4-D is resistant biodegradable, poor water-soluble and liable to accumulate in environment resulting water and soil pollution [2]. Also, 2,4-D is an endocrine disruptor with embryotoxicity, teratogenicity and neurotoxicity [3], endangering human health and environmental safety.

Zero-valent iron (ZVI) is widely used for the treatment of various organic and inorganic pollutants in wastewater containing organic compounds [4], azo dyes [5], heavy metals [6,7] and nitrates [8]. ZVI reduction technology is one of the most promising pollution control technologies received great attention in recent years. However, due to the physical and chemical properties of ZVI, the technology still has some shortcomings [9]: (1) ZVI has a small specific surface area, poor adsorption performance and low reactivity; (2) The removal efficiency over certain contaminants such as aromatic organic chlorides is low; (3) The ZVI surface is easily oxidized to iron oxides and hydroxides. In order to improve the removal efficiency of pollutants by ZVI and to promote the application of ZVI reduction technology in pollution control measures, researchers have conducted extensive studies on ZVI performance improvements.

The preparation of nano-sized zero-valent iron (nZVI) can effectively increase its specific surface area. Thereby it promotes the contact of pollutants with ZVI and accelerates the reaction rate by improving the reactivity of ZVI. However, nZVI is ineffective in treating certain pollutants, and the high surface area of nano-iron makes Fe^0 to easily oxidize and agglomerate, which reduce its reactivity and wider applications [10]. In order to solve agglomeration problem, researchers prepared nZVI composite with carbon [11], chitosan [12], silica [13], bentonite [14] and metal oxide material [15]. Nano-iron particles can be effectively distributed on the surface of the carrier to prevent the agglomeration and keep the reactivity of the nano-iron particles. Dong et al. [16] prepared nZVI/BC (biochar) to catalytically dechlorinate the trichlorethylene (TCE). Other researchers have also tried to coat nZVI with silica [17–19], iron oxide [20–22] and carbon [23] in order to prevent the oxidation of the nZVI and improve its reactivity. Mao et al. [18] synthesized SiO_2-coated iron (Fe@SiO_2) in two steps by water reduction combined with Stöber method for the removal of organic dyes. Fe@SiO_2 has better removal efficiency for organic dyes than uncoated nano-iron. Other researchers added stabilizers into the system to

* Corresponding author.
E-mail address: zhouhy@zjut.edu.cn (H. Zhou).

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keep the nano-iron dispersed in the solution, reducing the agglomeration of the nanoparticles, and increasing the contact of the reductant with the contaminants [24–26].

Loading of noble metal with a higher reduction potential onto the surface of nZVI particles forms bimetallic particles, which improves the reaction performance of nZVI [27]. When nZVI is combined with a noble metal with low reactivity, the introduced noble metal can absorb H_2 produced by iron corrosion in water [28,29], and insert it into the lattice to form strong reducing H [30]. The whole process can be summed up as the effect of inducing corrosion. The introduction of noble metal promotes corrosion reaction of nZVI surface. In this electrochemical coupling, nZVI appears as an anode because it has a negative redox potential (i.e. $E(M^{n+}/M) < E(H^+/H_2)$), and an oxidation reaction occurs to protect the noble metal. The noble metal with a positive redox potential (i.e. $E(M^{n+}/M) > E(H^+/H_2)$) is the cathode, acting as a catalyst and increasing the reduction rate. Therefore, bimetallic materials can effectively enhance the removal of contaminants by nZVI. Many noble metal materials have been shown to enhance the removal of chlorine-containing organic compounds by nZVI [31]. Meyer et al. [32] used nano-Pd/Fe bimetallic system to remove TCE. In the preparation of bimetallic reducing agents, the promotion effect of different noble metals on ZVI is different, and the catalytic activity of noble metals follows the order of Pd > Ru > Pt > Au [33]. However, although nZVI and bimetallic nanoparticles have significant advantages in the treatment of chlorine-containing organic contaminants, the formation of a passivating layer due to their extremely oxidizable surface leads to a decrease in reactivity. The complexing agent can effectively complex the iron oxides generated in the reaction process, hinder the formation of passivation layer on the iron surface, and thus effectively improve the reducibility of iron. Dong et al. [34] compared the removal of TCE by nZVI in the absence and presence of ethylenediaminetetraacetic acid (EDTA). It was found that the EDTA has a positive effect on the removal of TCE in 360 min. The presence of EDTA may inhibit the deposition of Fe^{2+}/Fe^{3+} onto the nZVI surface, thereby reducing the surface passivation of nZVI and preventing the formation of a passivating layer on the surface. Therefore, stripping off the passivation layer of ZVI is the key for the improvement of nZVI reactivity. However, due to the poor biodegradability of conventional complexing agents like EDTA, nitrilotriacetic acid (NTA) and diethylenetriaminepentaacetic acid (DTPA), they persist in environments such as water and soil with some bio-toxicity [35]. Therefore, it is imperative to explore some of their alternatives to improve the biodegradability of complexing agents.

EDDS is a good biodegradable complexing agent with strong ability to complex metal ions, which can be produced by natural materials through the role of microorganisms [36]. It can not only remove the passivation layer of ZVI surface and increase the reactive sites of the ZVI surface, but also chelate iron ions during the reaction to inhibit the formation of nano-iron surface passivation layer to maintain the ZVI reactivity and improve the removal efficiency of 2,4-D [37]. Therefore, in this study, 2,4-D as the target pollutants was dechlorinated by the highly efficient biodegradable green complexing agent EDDS improved nano Pd/Fe system. The effects of EDDS dosage, initial pH, palladium ratio and temperature on the 2,4-D reductive dechlorination were investigated. At the same time, the improvement of Pd/Fe reduction activity in the presence of EDDS was studied, and the mechanism of catalytic dechlorination was elucidated. Also, it provides a new way for the efficient catalytic dechlorination of 2,4-D by nZVI technology and vigorously promotes its practical application in environmental pollution remediation.

2. Materials and methods

2.1. Reagents

Potassium hexachloropalladate (K_2PdCl_6, purity 99%, Sigma-Aldrich company), 2,4-D ($C_8H_6Cl_2O_3$, purity 98%, Alfa Aesar company), 2-chlorophenoxyacetic acid (2-CPA, $C_8H_7ClO_3$, purity > 98%, Alfa Aesar company), 4-chlorophenoxyacetic acid (4-CPA, $C_8H_7ClO_3$, purity > 98%, Alfa Aesar company), PA ($C_8H_8O_3$, purity 98%, Alfa Aesar company), Trisodium ethylenediamine disuccinate (EDDS, ionized, 35.0% aqueous solution, Sigma-Aldrich company). The chromatographic grade methanol was used for HPLC analysis, $FeSO_4{\cdot}7H_2O$, $NaBH_4$ and other chemicals and solvents were used in their analytical pure forms. The water used in the experiment is all deionized water.

2.2. Preparation of nanoscale Pd/Fe particles

To prepare nano Pd/Fe particle, liquid phase reduction method was adopted by reducing Fe^{2+} with $NaBH_4$. A certain concentration of $FeSO_4{\cdot}7H_2O$ solution was added into a 1000 mL three-necked flask under nitrogen protection and mechanical stirring (400 r min^{-1}). Then the reducing solution of $NaBH_4$, prepared by a 2:1 molar ratio of BH_4^- to Fe^{2+}, was added dropwisely into the flask to react with $FeSO_4{\cdot}7H_2O$ (In this experiment, 2.4892 g of $FeSO_4{\cdot}7H_2O$ and 0.6774 g of $NaBH_4$ should be weighed, and they were dissolved in 400 mL and 20 mL deionized water, respectively). After $NaBH_4$ addition was completed, the reaction was continued for about 0.5 h to ensure the formation of nZVI (Eq. (1-1)). Then 10 mL 250.0 mg L^{-1} K_2PdCl_6 solution was added into the three-necked flask to react with Fe^0 nanoparticles for about another 1.0 h to produce nano Pd/Fe bimetallic particles (Pd ratio 0.50%, Eqs. (1-2), (1-3)). The nano Pd/Fe particle was separated from the solution by external magnet field, washed by deionized water and ethanol 3 times, successively, and dried in vacuum for 5.0 h at 60 °C. Finally, the nano Pd/Fe particle was obtained, and stored in brown bottle.

$$Fe^{2+} + 2BH_4^- + 6H_2O \rightarrow Fe^0 + 2B(OH)_3 + 7H_2 \quad (1\text{-}1)$$

$$PdCl_6^{2-} + 2Fe^0 \rightarrow 2Fe^{2+} + Pd^0 + 6Cl^- \quad (1\text{-}2)$$

$$\text{Calculation formula of Pd loading: } pd(\%) = \frac{m_{pd}}{m_{Fe}} = \frac{m_{K_2PdCl_6} \times 26.2\%}{m_{Fe}} \quad (1\text{-}3)$$

2.3. Catalytic dechlorination procedures

The prepared nanoscale Pd/Fe particles were added into three-necked flask immersed in constant temperature water bath, then added 2,4-D solution under stirring to react in nitrogen gas. Meanwhile, the constant flow pump turned on and allowed the EDDS continuously drop into the flask at a rate of 20.0 mL h^{-1} (the total amount of EDDS is 0.8 mmol) [38]. At selected time intervals, take samples for subsequent analysis. To evaluate the effects of experimental conditions on 2,4-D dechlorination, the reaction was conducted at various Pd loadings, EDDS dosages, temperatures and solution pH values.

2.4. Characterizations

The nanoscale Pd/Fe particles freshly prepared and after 210 min reaction in the presence and absence of EDDS were examined by S4700 scanning electron microscope (SEM), energy dispersive spectrometer (EDS, Oxford X-MaxN), X-ray photoelectron spectrometer (XPS, Kratos AXIS Ultra DLD) and X-ray diffractometer (XRD, X'Pert PRO). SEM images were used to observe the morphology of sample particles. EDS-mapping was used to show elements distribution of Pd and Fe. XPS was used to analyze the valence state of iron by detecting binding energy. XRD pattern was used to verify the effect of chelating agent for nanoscale Pd/Fe particles by detecting Fe^0 characteristic peaks.