



Short communication

Enhanced catalytic reduction of p-nitrophenol by nano zerovalent iron - supported metal catalysts

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ABSTRACT

Nano-sized zerovalent iron (NZVI) - supported metal catalysts were synthesized to characterize their reactivity for the reductive degradation of p-nitrophenol (PNP). Among the tested monometallic catalysts using metal promoters, Zn/NZVI showed the highest reactivity with complete reduction of PNP in 5 min ($k = 0.0263 \text{ s}^{-1}$). The addition of Pd accelerated the degradation kinetics of PNP with complete reduction in 1 min ($k = 0.095 \text{ s}^{-1}$) but promoter's presence on bimetallic catalyst surfaces simply decreased their reactivity. A proper Pd amount (1.5 wt% Pd/NZVI) showed the highest degradation rate ($k = 0.248 \text{ s}^{-1}$), while after its content increased to 10 wt% the rate was reduced by 5.8 times.

1. Introduction

Nowadays, one of the main concerns of global society is public health and environmental safety. Industrial and agricultural activities have released various organic toxic compounds, which can contaminate surface and groundwaters, thus threatening access to fresh drinking water [1]. One of the various contaminants coming from anthropogenic activities is p-nitrophenol (PNP), widely known as a toxic and carcinogenic nitroaromatic chemical compound. The primary source of industrial activities facilitating the PNP contamination is the production of rubbers, pesticides, textile, dyes, and pharmaceuticals [1–3]. It can easily intoxicate living animals and humans and lead to serious health problems such as confusion, skin and eye irritation, loss of consciousness, and even potential carcinoma [2]. Moreover, exposure to the PNP might cause a negative effect on blood cells and damage the central nervous system and other human organs [4].

Various treatment technologies, including advanced oxidation processes, thermal degradation, photodegradation, electro-coagulation, biological treatment, adsorption, and others have been used to efficiently remove PNP [1,5,6]. Although biological treatment can efficiently degrade PNP, it has several disadvantages, such as a slow start-up time and decreased efficiency at low temperatures and high PNP concentrations [7]. At the same time, purification techniques, such as

electro-coagulation, photodegradation, and adsorption, also have several drawbacks, including high cost, long operation time, and reduced efficiency [6]. Moreover, there are conventional methods available for the reduction of PNP to p-aminophenol (PAP), such as the use of hazardous Sn/HCl, or Fe/HCl, catalytic transfer hydrogenation (CTH), or molecular hydrogen (H_2) [8]. However, those methods have several disadvantages since they demand complex experimental design, high pressure, and temperature [8].

Recently, metal nanoparticles such as Au, Ag, Ni, Pt, Co, and Pd have attracted attention for the catalytic reduction of PNP due to their good initial activity [9–14]. However, the agglomeration of the nanoparticles resulting in decreased removal efficiency has been reported as a fatal defect [15]. Various immobilization techniques have been developed to prevent the agglomeration of nanoparticles using support materials such as graphene hydrogel, polystyrene beads, graphene oxide, magnetite, etc. [10,15–17]. However, no significant study has been conducted to use nanoscale zerovalent iron (NZVI) as a support material for the immobilization of metal nanoparticles to degrade PNP efficiently. In recent years, the well-known advantages of NZVI, such as high reductive capacity and economical synthesis method, made it one of the most widely studied and used environmental materials for the treatment of various surface and groundwater pollutants found in the industrial and agricultural sectors [2,7,18]. For example, NZVI has been proven to

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effectively remove diverse halogenated organic compounds, oxy-anions, and heavy metals [19]. However, NZVI has several disadvantages, such as rapid oxidation of its surface to Fe oxides, which decreases the activity of NZVI acting as a reductant. Another serious drawback of NZVI is its tendency to agglomerate due to magnetic forces, which also decreases the reactive surface and reduces the reductive efficiency of the material [1]. On the other hand, the magnetic property of NZVI allows the easy collection of NZVI-supported catalysts from the suspension system after catalytic reaction [7,18]. Hence, NZVI could be a promising support material with a great potential for the enhanced reduction of PNP.

Previous studies showed that a variety of metallic catalysts with the promoter and noble metals on the surface of NZVI were successfully applied to remove nitrate, trichloroethylene, and tetrabromobisphenol [18,20–24]. The type of the promoter metal highly affects the degradation kinetics of the nitrate removal [25]. Hence, promoter metals including Cu, Sn, In, and Zn on the surface of various supports were extensively tested and evaluated for the degradation of nitrates in combination with noble metals such as Pd, Pt, and Au, where Pd was the most widely and successfully used noble metal [7,25–28]. However, the combination of metal catalytic components deposited on the NZVI surface have not been used and investigated for the reductive degradation of PNP.

The present work aimed to investigate the reduction of PNP by NZVI-supported metal catalysts. First, different types of promoter metals have been tested for the enhancement of the rate of reduction of PNP. Then, more suitable promoter metals (Cu, In, Ni, Zn, Sn) have been tested along with a noble metal (Pd). Finally, the effect of significant factors such as catalyst loading, nature of chemical promoter, and noble metal loading were investigated. Based on the present results, the reaction mechanism was suggested.

2. Experimental

2.1. Synthesis of NZVI supported bimetallic catalyst

NZVI was synthesized by a well-established method [18]. 50 mL of NaBH₄ solution (0.9 M) was first prepared using deaerated and deionized water (DDIW). An exact concentration of FeCl₃·6H₂O (0.11 M) was prepared in ethanol and DDIW (1:8 v/v) and the NaBH₄ solution was added dropwise into FeCl₃·6H₂O under constant mixing for >15 min to remove the remaining H₂ gas. The suspension was sonicated for 2 min and washed with DDIW three times. The resulted suspension was used for the synthesis of bimetallic catalysts. Precursors for the promoter and noble metals were prepared by dissolving an appropriate amount of the relevant metal salt in DDIW, respectively. The solution was then added dropwise into the NZVI suspension under vigorous stirring. After addition of precursors, the suspension was stirred for 3 min to ensure reduction of metals by NZVI, and then washed with DDIW three times. The resultant slurry was used for the batch catalytic experiments.

2.2. Catalysts characterization and testing

A morphological analysis of the catalyst was conducted using Scanning Electron Microscopy (SEM) with Energy-dispersive X-ray spectroscopy (EDX, Hitachi S-4700). Dried catalysts were placed onto metal sample holders and covered with a gold film. Catalytic activity experiments were conducted in a batch reactor (20 mL amber vial), and details are provided in the ESI.

3. Results and discussion

3.1. Catalysts characterization

SEM/EDX analysis was conducted to investigate the morphological characteristics of NZVI and the dispersion of Pd particles on its surface.

Fig. S1a-b (Electronic Supporting Information, ESI) illustrates the SEM images of 1.5%Pd/NZVI particle surface with magnifications of 20 k and 100 k, respectively. Fig. S1a shows that plate-shaped NZVI particles were synthesized. During the synthesis of NZVI, an ultrasonication process was applied [29], and thereby, round-shaped NZVI particles (~50 nm) can also be seen in Fig. S1b. The results indicate a successful synthesis of nano-sized iron particles. In addition, EDX mapping of surface elements of the catalyst was carried out to investigate Pd distribution on the NZVI surface. Fig. S1c-d shows e EDX mapping images of Pd and Fe, respectively, indicating that the chemical elements were well-mixed. It is also shown that Pd particles were uniformly dispersed on the surface of NZVI support. These results suggest that the applied synthesis method of Pd/NZVI provides proper dispersion and distribution of metal catalysts on the surface of NZVI support.

3.2. Catalytic activity towards PNP reduction

Kinetic experiments in a batch reactor mode were conducted to evaluate the catalytic reduction of PNP by the bimetallic 4%Zn-1.5%Pd/NZVI, and the monometallic 1.5%Pd/NZVI and 4%Zn/NZVI catalysts (Fig. 1). The reduction kinetics of PNP by bare-NZVI is also shown in Fig. 1 and compared to that obtained by the other catalysts. The control test (absence of catalyst) showed no removal of PNP throughout the experiment, indicating that no adsorption of PNP on the reactor's wall and no reduction by photolysis in the amber vial (reactor) occurred during the reaction. The reduction of PNP by bare NZVI reached 93.7% in 5 min, while a monometallic catalyst (4%Zn/NZVI) can completely degrade PNP in 3 min. The presence of promoter metal (Zn) could facilitate an electron transfer from the NZVI surface compared to the relatively slow direct electron transfer from the bare-NZVI surface, resulting in the accelerated catalytic reduction kinetics of PNP [7]. The complete reduction of PNP by 4%Zn-1.5%Pd/NZVI occurred in 1 min, and its pseudo-first-order kinetic rate constant k_1 (0.0954 s⁻¹, R² = 0.979) was found to be 3.6 and 11.8 times higher than that of 4%Zn/NZVI and bare-NZVI, respectively. Much faster reduction kinetics of PNP by the 4%Zn-1.5%Pd/NZVI solid could be originated from the additional formation of activated hydrogen on the surface of noble metal (Pd) during the facilitated electron transfer at the Zn/NZVI interface. This can rapidly and strongly degrade PNP on the Pd surface inducing much higher catalytic activity for the enhanced PNP reduction [4,30,31]. Hence, the addition of promoter and noble metal to the bare-NZVI can increase the catalytic reduction rate of PNP by facilitating electron transfer and subsequent hydrogenation [32]. In contrast, 1.5%Pd/NZVI showed the fastest reduction kinetics of PNP ($k_1 = 0.248$ s⁻¹, R² = 1), of which the kinetic rate constant k_1 is 4.1 times higher than that of 4%Zn-1.5%Pd/NZVI. It indicates how the hydrogenation occurred on the Pd surface could overwhelmingly contribute to the enhanced reductive catalysis of PNP with the fastest reduction kinetics. We show here the superiority of NZVI-supported mono noble metal (Pd) catalyst over the bimetallic one for the enhanced reduction of PNP.

The batch kinetic experimental results for the removal of PNP by the 1.5%Pd/NZVI catalytic system were compared to those obtained by other catalysts recently reported. Table S1 summarizes the kinetic rate constant for the removal of PNP by each of the catalysts under diverse experimental conditions. It can be seen that the 1.5%Pd/NZVI has the highest catalytic activity for the PNP reduction among the catalysts reported to date. Most of the previously reported catalysts for the PNP removal used passive support materials that cannot donate electrons and facilitate the electron transfer from the support, while NZVI-supported catalysts can actively donate electrons to the promoter metal or directly to the contaminant [1,15,33–35]. For instance, Chen et al. [35] investigated the performance of Au/Pd bimetallic catalyst deposited on the surface of graphene nanosheets, which did not possess any reductive capacity, and they were simply used to prevent the agglomeration of the nanoparticles. Here, NZVI-supported mono- and bimetallic catalysts showed high activity for the enhanced PNP removal. It can be concluded

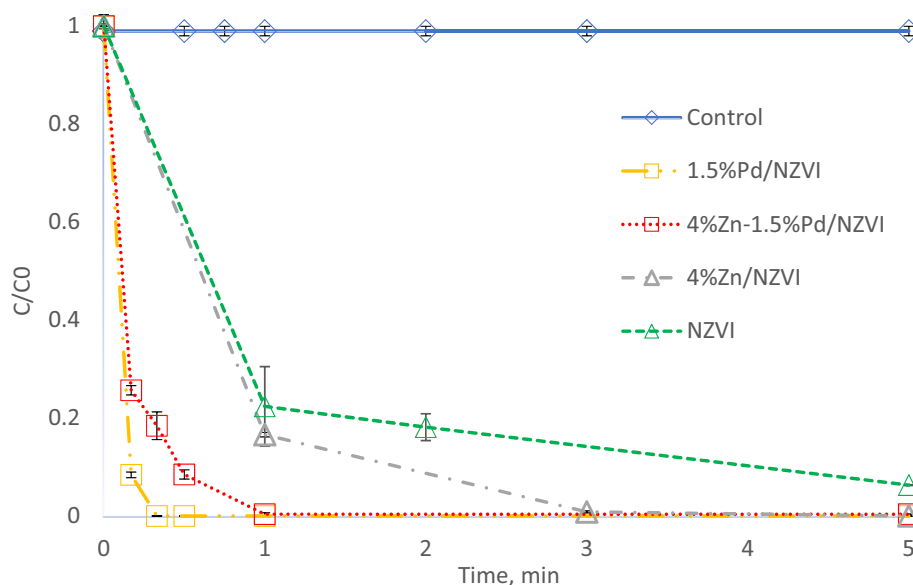


Fig. 1. Catalytic reduction of PNP by bare NZVI and NZVI-supported metal catalysts.

that the synthesized Pd/NZVI catalyst appears as one of the most promising nanocatalysts for the enhanced PNP removal.

3.3. Evaluation of environmental factors on the catalytic reduction of PNP

NZVI-supported monometallic catalysts with different promoter metals including Cu, Sn, Zn, Ni, and In were tested for the reduction of PNP. 4%Zn/NZVI showed the fastest reduction kinetics; hence, it was selected for further experimental studies. An increase in the catalyst loading resulted in the saturation point of its catalytic reactivity at a concentration of 500 mg/L. Monometallic Pd/NZVI catalyst showed a faster reduction kinetics than bimetallic Zn-Pd/NZVI since Zn particles could block available reactive surface sites of Pd. However, an increase in Pd loading of Pd/NZVI catalyst led to a decreased reduction kinetics of the catalyst. The details of the section are provided in the ESI.

3.4. Reaction mechanism of PNP reduction on Pd/NZVI

Fig. 2 shows the variation of UV–Vis spectra during the reduction of PNP by Pd/NZVI. Once PNP was added to a weak basic aqueous solution (pH ~7.5), it could be easily deprotonated to form p-nitrophenolate. The catalytic reduction is initiated by the addition of Pd/NZVI. As the catalytic reaction proceeds, the peak at 400 nm corresponding to p-nitrophenolate is decreased, while a peak at 300 nm corresponding to p-aminophenol (PAP) is increased [2]. It indicates that the main reduction product of the catalytic reduction of PNP by Pd/NZVI is PAP.

The catalytic reduction of PNP to PAP on the surface of Pd/NZVI can be explained via two main reduction pathways: (i) direct reduction of PNP to PAP via electron transfer from the reactive NZVI support in the form of Fe(II) and Fe(0) (Eqs. (1), (2)) and (ii) indirect reduction (hydrogenation) via reactive H_{ads} generated on the Pd surface (Eqs. (2)–(4)) [4,7,31].

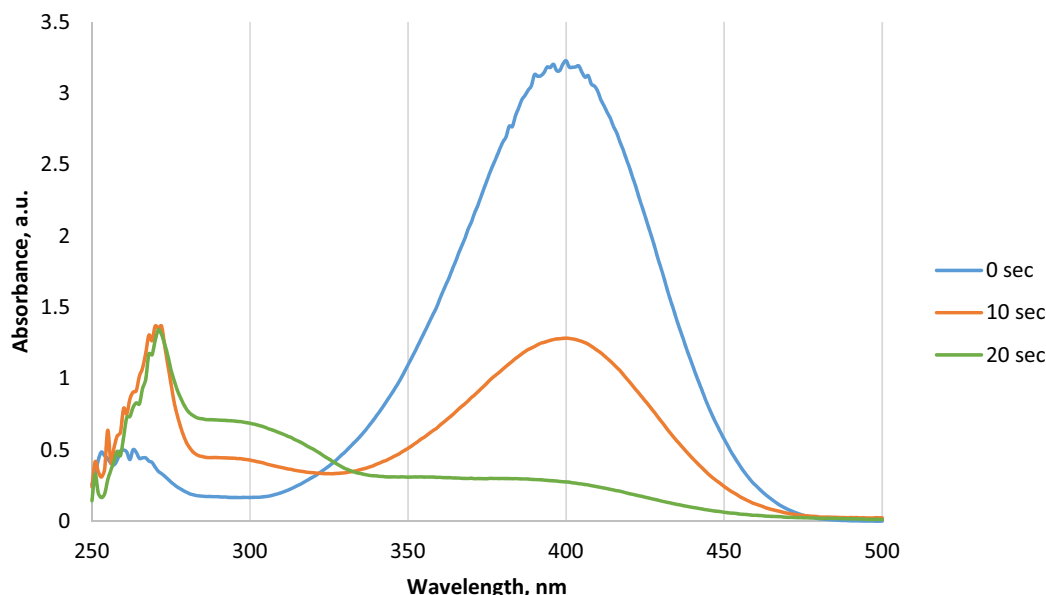
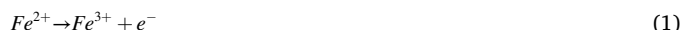
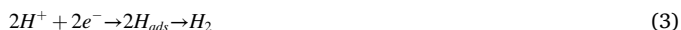


Fig. 2. Variation of UV–Vis spectra of aqueous samples during the catalytic reduction of PNP (50 mg/L) by the 1.5%Pd/NZVI catalyst.



The surface of NZVI could be oxidized to Fe(II) oxides with the generation of electrons until its surface reached complete passivation by Fe(III) oxides. They could further react with aqueous H^+ forming the reactive H_{ads} adsorbed species on the Pd surface that is the main overwhelming driving force to vigorously reduce PNP to PAP in the mono-metallic system (Eq. (3)). Pd particles were able to continuously activate H_2 to the reactive H_{ads} species on their surface (Eq. (4)), leading to the enhanced PNP reduction kinetics by the continuous catalytic reduction system of PNP. Lai et al. [31] demonstrated that the generation of H_{ads} was the main reducing power in the reductive degradation of PNP by Fe/Cu catalyst. It could not completely reduce the PNP under high pH conditions since low H^+ concentration limited the generation of H_{ads} [31]. Moreover, since the addition of promoter metal and its loading increase have deteriorated the catalytic reduction kinetics of PNP, we can conclude that the indirect reduction of PNP via hydrogenation pathway with the reactive H_{ads} species played the main role in the reaction mechanism of the catalytic PNP reduction.

4. Conclusions

The study provided insights on the proper synthesis of NZVI-supported metal catalysts for the enhanced catalytic reduction of PNP. The effect of significant factors such as catalyst loading, promoter type and loading, and noble metal loading on the performance of catalytic PNP reduction were evaluated for the optimal operation of the batch catalytic system. Monometallic catalyst with a noble metal (1.5%Pd/NZVI) showed the fastest PNP reduction kinetics ($k_1 = 0.248 \text{ s}^{-1}$, $R^2 = 1$) among the catalysts reported to date, while bimetallic catalyst (4%Zn-1.5%Pd/NZVI) has shown much faster PNP reduction kinetics ($k_1 = 0.095 \text{ s}^{-1}$, $R^2 = 0.979$) than the Pd monometallic catalysts with different promoters. The optimal catalyst loading was observed at 500 mg/L for the enhanced catalytic reduction of PNP. Indirect reductive transformation of PNP to PAP via hydrogenation with reactive H_{ads} on Pd surface was suggested as the main reduction pathway since 1.5%Pd/NZVI has shown the highest rate for the catalytic reduction of PNP to PAP. The type and content of noble metal influencing the catalytic activity for an application to practical water treatment systems need to be carefully selected and evaluated by considering its role and behavior in the catalytic reduction of PNP. The limitations of this study are the absence of activity tests under different pHs of the suspensions and the absence of stability test of the catalyst during repeated cycles, which will be both our near-future research tasks.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.catcom.2021.106337>.

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