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Effect of NaBH₄ on properties of nanoscale zero-valent iron and its catalytic activity for reduction of *p*-nitrophenol

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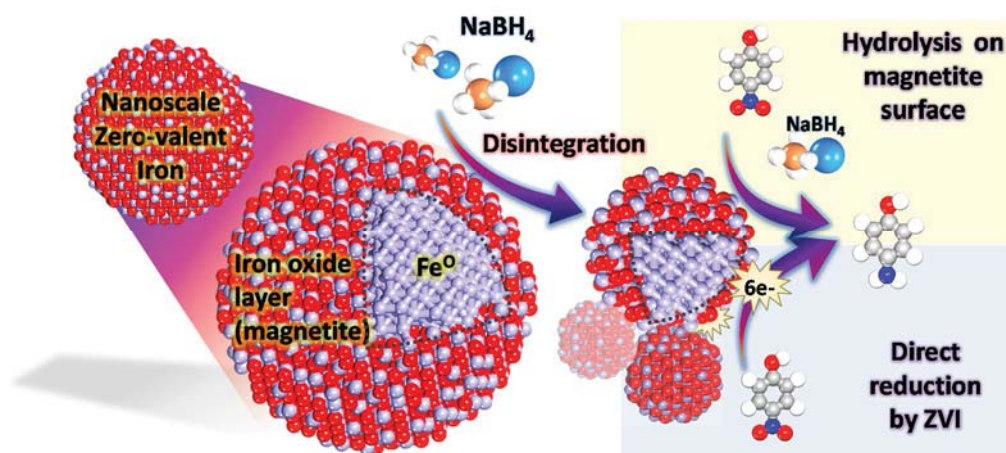
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Graphical abstract



Highlights

- NaBH_4 disintegrated NZVI to much smaller sized NZVI.
- NZVI/ NaBH_4 system showed a remarkable catalytic reduction of p-NP.
- A complete reduction of p-NP was observed during four recycling tests.
- NaBH_4 can prevent the oxidation of NZVI during the catalytic reduction process. 34
- DFT showed magnetite on NZVI also played an important role for p-NP reduction.

Abstract

The reduction of p-Nitrophenol (p-NP) to p-Aminophenol (p-AP) by nanoscale zero-valent iron 38 (NZVI)/
 NaBH_4 system in an oxygen environment was studied by means of liquid 39
 chromatography, spectroscopy (vibration and X-ray photoelectron), solid analyses 40
 (transmission electron microscopy and X-ray diffraction) and density functional theory (DFT) 41
 calculations. Addition of NaBH_4 into NZVI suspension showed the disintegration of NZVI(60- 42
 100 nm), resulting in the formation of much smaller particles (15-40 nm) due to the chemical

etching of outermost surfaces (i.e., magnetite). Interestingly, complete reduction of p-NP and high conversion efficiency of p-AP (> 98%) were observed in NZVI/NaBH₄ system even after four recycling which is quite comparable with widely used noble metallic catalysts. Surface analysis confirmed that NaBH₄ can prevent the oxidation of NZVI surface, leading to the continuous reduction of p-NP in oxygen environments. Experimental results and DFT calculations suggested that not only the formation of smaller NZVI but also thermodynamic preferences for reduction of p-NP on outermost surfaces of NZVI (i.e. magnetite) may significantly affect the reduction process of p-NP in NZVI/NaBH₄ system. These novel findings can promote the development of new NZVI technologies which can be used for wastewater reductive treatment in oxygen environments.

Keywords

Nanoscale zero-valent iron; NaBH₄; p-Nitrophenol; oxygen environment; density functional theory

1. Introduction

p-Nitrophenol (p-NP) contamination of surface and groundwater has gradually increased due to the excessive consumption of dyes, pesticides, and pharmaceuticals from industrial and agricultural activities [1]. Because it has been considered as one of the toxic organic pollutants responsible for eye and skin irritation and methemoglobinemia potentially causing cyanosis, confusion, and unconsciousness [1,2], United States Environmental Protection Agency set a guideline restricting the contaminant level of p-NP to below 10 ng/L in natural water [3]. There

is therefore an extensive effort to effectively treat the wastewater contaminated by p-NP. 69 Among many treatment technologies, catalytic reduction of p-NP to *p*-Aminophenol (p-AP) in 70 the presence of sodium borohydride (NaBH_4) has been intensively investigated [4-11]. This 71 catalytic reaction has become one of the most widely used model reactions due to the easy 72 measurement of both p-NP and p-AP by UV-vis spectroscopy and the complete conversion 73 without production of by-products [12]. Furthermore, the conversion of p-NP to p-AP has great 74 commercial relevance because p-AP is an important intermediate for the manufacture of 75 analgesic/antipyretic drugs, paracetamol, acetanilide, and aniline [13,14].

Since Pradhan et al. have reported the catalytic reduction of p-NP by Ag nanoparticle [15], various noble metallic nanoparticles (i.e., Au, Pt, and Ag) were produced by chemical and 78 biological synthesis [4,5]. These noble metals were usually immobilized on other supports (i.e., 79 carbon materials, polymers, and metal oxides) [5-10] for the effective, stable, and recyclable 80 catalysis for p-NP reduction. However, most noble metals are extremely expensive (despite of 81 its usage in low concentration) and involve potential loss of the noble metals during recycling 82 process. In addition, most synthesis methods of catalysts are usually very complicated, time- 83 consuming, and labored processes. Therefore, it is timely to develop a novel reduction process 84 of p-NP to p-AP, which could be cheap, environmental-friendly, and readily available for all.

Herein, a simple method for conversion of p-NP to p-AP by using NZVI and NaBH_4 was developed. In the past two decades, NZVI has attracted a great attention as a promising reactant 87 for reductive removal of various environmental contaminants in agricultural and industrial 88 wastewaters [16-22]. Although NZVI has shown a remarkable reduction potential in laboratory 89 and field studies, most processes performed in anoxic environments due to the rapid surface 90 oxidation of NZVI to iron oxides by oxygen. Furthermore, passivation of NZVI surface is also 91 generally observed during the reduction of contaminants even in anoxic environments [18,20].

Therefore, the surface passivation is one of the urgent problems to be overcome for wide application of NZVI to other oxygen environments.

In this work, a systematic study was performed to investigate the reduction kinetic of p-NP by NZVI with NaBH_4 in oxygen environments and its possibility to be repeatedly used in recycling tests. The impact of NaBH_4 on NZVI reactivity was evaluated by using a variety of surface analysis techniques, density functional theory (DFT) calculations, and spectrophotometric and chromatographic measurements. The driving mechanism of NaBH_4 -enhanced reductive ability of NZVI was discussed. We note that, to the best of our knowledge, this is the first study elucidating the effect of NaBH_4 on pure NZVI in oxygen environments for simultaneous contaminant degradation with production of useful organic resource.

2. Experimental and theoretical methods

2.1. Chemicals

All chemicals and solvents used in the experiment were of guaranteed analytical grade.

2.2. Synthesis of NZVI and iron minerals

NZVI was synthesized by reducing $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.11 M) with NaBH_4 solution (0.9 M) in anaerobic chamber (JACOMEX), modifying our previous method [18]. The precipitates in the suspension were washed three times with deaerated deionized water (DDW), prepared using ultra-pure water ($18\text{M}\Omega \cdot \text{cm}$) purged with N_2 for 4 h, by centrifuging for 5 min at 4000 rpm. NZVI was dried and stored in the anaerobic chamber. Other iron minerals were synthesized and characterized in the context of previous works (goethite ($\alpha\text{-Fe}^{\text{III}}\text{OOH}$) [23], magnetite

($\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}_2\text{O}_4$) [24] and hematite ($\alpha\text{-Fe}^{\text{III}}_2\text{O}_3$) [24]). Maghemite was purchased from Sigma-Aldrich ($\gamma\text{-Fe}^{\text{III}}_2\text{O}_3$).

2.3. Reduction of p-NP

NZVI stock suspension (105 mg/L, 1.95 mM) containing in 100 mM NaBH₄ was prepared in 119 anaerobic chamber and taken out from anaerobic chamber for reduction experiment in oxygen 120 environment. For the p-NP reduction, 2.6 mL of NaBH₄ (50 mM) was added into a quartz 121 cuvette, then 0.1 mL of NZVI stock was added into the cuvette. The aqueous NZVI suspension 122 was sonicated for 3 sec and 0.3 mL of p-NP (1 mM) was transferred into the cuvette to initiate 123 the reduction of p-NP. Total volume of reaction mixture was 3 mL with initial concentrations 124 of 3.5 mg/L NZVI(0.065 mM) and 0.1 mM p-NP. The change in p-NP concentration was 125 monitored at 400 nm wavelength by UV-vis spectrophotometer (CARY 50 probe, Varian). 126 Control test using NZVI (0.065 mM) without NaBH₄ showed no reduction of p-NP in oxygen 127 environment (data not shown). For the recycling test, the used NZVI was magnetically collected 128 at the bottom of the cuvette by removing the aqueous solution. Then, collected NZVI was 129 washed with fresh NaBH₄ solution (100 mM) twice by magnetic separation as described above. 130 Finally, 2.7 mL of NaBH₄ (50 mM) and 0.3 mL of p-NP (1 mM) were added into a quartz 131 cuvette for recycling test. To investigate the reduction of p-NP by other iron minerals, we 132 prepared the stock suspensions by mixing with NaBH₄ (100 mM) in anaerobic chamber. The 133 reduction of p-NP was performed using 10 mg/L iron minerals, 50 mM NaBH₄, and 0.1 mM p- 134 NP in an oxygen environment.

2.4. HPLC and Fe measurement

The concentration of p-NP and p-AP in aqueous solution was measured by high performance 138 liquid chromatography (HPLC) (Waters) equipped with a C18 packed column (Waters) and UV 139 detector. After finishing each reduction experiment, the aqueous sample (around 2.7 mL) was 140 collected from the cuvette and 1.7 mL of sample was filtered by 0.2-μm membrane filter for 141 HPLC and Fe measurement. Mobile phase was a mixture of 50% deionized water (DIW), 50%

acetonitrile, and 1% CH₃COOH. The p-NP and p-AP were measured at a flow rate of 1.0 mL min⁻¹ at wavelengths of 317 nm and 273 nm, respectively.

Fe loss during the reduction of p-NP and magnetic separation was measured by Ferrozine method using a UV-vis spectrophotometer (UV-1205, SHIMADZU) at the wavelength of 562 nm [25]. The membrane-filtered sample was used for measurement of dissolved Fe and 1 mL of aqueous solution remained from magnetic separation was transferred to 1 mL of 6 M HCl for measurement of total Fe by adding 10% hydroxylamine solution [26]. No significant amount of Fe was detected in membrane-filtered sample in most cases, indicating that dissolved Fe during the reduction of p-NP can be negligible in this study due to the high pH (>10) of NaBH₄ solution.

2.5. Surface characterization

The changes in particle morphology of NZVI were identified by transmission electron microscope (TEM, JEM-2100, JEOL). We prepared a variety of NZVI particles; 1) initial NZVI (oxygen free environment), 2) reacted with NaBH₄ (100 mM, oxygen free environment), 3) after the reduction of p-NP with NaBH₄ (five recycling, oxygen environment), and 4) without NaBH₄ (one reaction, oxygen environment). After the reaction, the samples were transferred to anaerobic chamber and washed by deaerated ethanol twice. We put one droplet of the diluted suspension on Cu TEM grids and analyzed the samples by TEM at an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was conducted to identify the redox states of Fe on NZVI surface using the samples prepared for TEM. The samples were dried after the reactions in anaerobic chamber for 24 h and carefully packed on XPS sampling template. Then, they were transferred to the vials containing deaerated ethanol to avoid the oxidation of NZVI during the installation of XPS template. XPS analysis was carried out using a Sigma Probe (Thermo) with a Al K α X-ray (1486.7 eV). Surface charging effects were corrected with C 1s

peak at 285 eV as a reference. We used Shirley baseline and a Gaussian-Lorentzian peak shape 168 for fitting the data. NZVI with/without NaBH₄ were also identified by X-ray diffraction (XRD) 169 (D8, BRUKER). The NZVI suspensions prepared in ethanol were used for XRD analysis. The 170 suspension were transferred to XRD holder and dried for 2 h in anaerobic chamber. Then, the 171 dried samples were treated with 1:1 (v:v) glycerol solution to avoid the oxidation of Fe(0) 172 during the analysis of XRD [20]. Attenuated total reflectance-Fourier transform infrared (ATR- 173 FTIR) spectra were recorded between 4000 and 650 cm⁻¹ on a Nicolet iS50 FT-IR spectrometer 174 system (Thermo Scientific Inc.) equipped with a MCT/A detector cooled with liquid N₂. A nine- 175 reflection diamond ATR accessory was used for acquiring spectra of the samples. One droplet 176 of p-NP (10 mM) was first put onto the diamond ATR crystal, and then followed by adding one 177 droplet of NZVI suspension (10 g/L) prepared in NaBH₄ (100 mM). ATR-FTIR spectra were 178 recorded at room temperature at a 4 cm⁻¹ resolution by averaging 100 scans.

2.6. Computational details

We performed DFT calculations to understand the reduction pathway of p-NP using the Vienna 182 Ab-initio Software Package (VASP) program [27] with the choice of Perdew-Burke-Emzerhof 183 (PBE) exchange-correlation functional [28]. According to the results obtained from our 184 experiments and other references [29], the outer shell of NZVI seemed to be covered by iron 185 oxides especially magnetite form. We thus used a slab model of magnetite that is a (4 × 4) Fe₃O₄ 186 (111) surface where bottom 1/3 layer is fixed at a lattice point to assume it as the bulk, whereas 187 the upper layers were allowed to be relaxed (Fig. S1). To avoid the interaction between slab 188 models over the periodic boundary cell, we included a vacuum slab of ~ 20 Å along the c- 189 direction of our simulation cell. Due to the limited computational cost as well as the large 190 enough simulation cell of 12 Å × 12 Å × 25 Å, only Gamma point is sampled in the reciprocal 191 space, and an energy cutoff of 450 eV is used for the plane wave basis set.

3. Results and discussion

3.1. Effect of NaBH₄ on NZVI properties.

In the absence of NaBH₄, TEM images of NZVI showed chain-like aggregates consisting of spherical shape of particles (60–100 nm) (Fig. 1a). Each individual particle was covered by 2.5–3.5 nm of iron oxide shell (Fig. 1b). It should be noted that the NZVI particles became much smaller (15–40 nm) by addition of NaBH₄ (100 mM) (Fig. 1c), but kept the same morphology (i.e., spherical shape of particles with 2.5–3.5 nm of iron oxide shell) (Fig. 1d). The formation of smaller nanoparticles by NaBH₄ could be caused by oxidative dissolution of NZVI or by chemical etching reaction on iron oxide layer. It is well-known that adsorption of borohydride on the particle surface can negatively shift in the redox potential of metallic nanoparticle, which can proceed oxidative dissolution of metals due to high susceptibility toward oxidation by oxygen [30]. Then the dissolved metal ions can be also reduced by NaBH₄ to form new nanoparticles once the oxygen level falls below a critical value, as previously observed by silver nanoparticle [30]. In the present work, the formation of smaller nanoparticles upon NaBH₄ addition was, however, observed in oxygen-free environment, ruling out the role of oxidative dissolution. Consequently, we rather suspect that chemical etching reaction may occur at magnetite surfaces which can lead to the disintegration of micro-sized magnetite into nano-sized magnetite following further by a magnetism-induced self-assembly of magnetite [31]. This mechanism seems to happen here, as magnetite is supposed to be present in the oxidized layer of NZVI. After forming of smaller NZVI particles by addition of NaBH₄ (Fig. S2a and 2b), the particles are aggregated each other again, resulting in formation of flower-like aggregates (Fig. S2c). In addition, XRD data of initial NZVI particles (Fig. 1e) revealed the presence of peaks of α -Fe (44.6° 2 θ), magnetite (57.0° 2 θ), and broad peak of iron oxides (hematite (33.5° 2 θ) and magnetite (35.3° 2 θ)). Interestingly, the broad peak of iron oxides

continuously decreased as the concentration of NaBH₄ increased from 1 to 100 mM (Fig. 1e), 218 indicating that characteristic of α -Fe seems to be stronger at higher NaBH₄ concentration due 219 probably to the formation of many smaller NZVI particles as shown in TEM images, or the 220 reduction of oxide coatings to α -Fe by NaBH₄. XPS analysis was conducted to confirm the 221 reduction of NZVI surfaces by addition of NaBH₄ (Fig. 2). The XPS spectra for Fe(2p_{3/2}) were 222 composed of four different peaks at 706.4–706.6, 709.2–709.7, 710.9–711.5, and 712.7–713.1 223 eV which were assigned to the binding energies for Fe⁰ (706.4 eV), Fe²⁺-O (709–709.5 eV), 224 and Fe³⁺-O (711–714 eV), respectively [20]. The proportion of Fe³⁺ on the NZVI surface 225 decreased from 68.1 to 57.4% upon NaBH₄ addition, while increasing in the proportion of Fe²⁺ 226 (26.9 → 32.0%) and Fe⁰ (4.9 → 10.5%) was observed (Fig. 2a and b). We also observed the 227 presence of two peaks at 187.9 and 191.7 eV (inset in Fig. 2b), which could be assigned to B in

Fe⁰-B and BO₂⁻, respectively [31]. The results from TEM, XRD, and XPS confirmed that NaBH₄ can effectively interact with NZVI leading to the disintegration of NZVI into much smaller particles and reduction of outermost surfaces to Fe²⁺ and/or Fe⁰-B.

3.2. Reduction of p-NP by NZVI with NaBH₄

The concentration of NaBH₄ (1-100 mM) used in this study was not able to reduce p-NP. On 234 the contrary, addition of p-NP into NZVI-NaBH₄ suspension showed the color change from 235 yellow to colorless in 30 min (Fig. 3a), indicating a complete reduction of p-NP. Fig. S3 shows 236 UV-vis spectra during the reduction. The initial absorption peak of p-NP is shifted from 317 to 237 400 nm after addition of NaBH₄ (pH = 10.4) due to the formation of *p*-nitrophenolate ions [10]. 238 The continuous decrease in absorption peak of the ionized p-NP at 400 nm was observed with 239 formation of new peak at 300 nm, which is known to be p-AP [14,32]. We noticed fluctuation 240 of the baseline (Fig. S3) due to H₂ production from the NaBH₄ solution ($\text{BH}_3 + 3\text{H}_2\text{O} \rightarrow \text{H}_3\text{BO}_2$

+ 3H₂) and its enhanced production by catalyst (i.e., nanoscale zero-valent iron). Indeed, a vigorous production of H₂ bubbles was observed during the reaction. However, a complete removal of p-NP was clearly observed at an identical baseline (Fig. 3b) and HPLC analysis confirmed the 98% of p-NP removal with 97% of p-AP production after 30 min (Fig. 3c, inset). The decrease in absorbance at 400 nm (Fig. 3c) was also observed due to the initial mixing of p-NP in NZVI suspension. Because the complete reduction of p-NP to p-AP needs six electrons from NZVI ($\text{HOC}_6\text{H}_4\text{NO}_2 + 6\text{e}^- + 6\text{H}^+ \rightarrow \text{HOC}_6\text{H}_4\text{NH}_2 + 2\text{H}_2\text{O}$), 0.1 mM p-NP cannot be completely reduced by 0.065 mM NZVI. Indeed, 2.8 times higher NZVI concentration (0.18 mM) without NaBH₄ was able to reduce only 0.01 mM p-NP in O₂-free environment (Fig. S4). The results suggest that addition of NaBH₄ into NZVI suspension can overwhelm theoretical reduction capacity of NZVI toward p-NP. The reduction of p-NP by NZVI was able to be described by pseudo-first-order kinetic model ($R^2 = 0.98$), as previously reported for other metallic noble catalysts (Fig. 3c) [9,10,32]. The rate constants with NaBH₄ in an oxygen environment ($k_{\text{obs-p-NP}} = 3.1 \times 10^{-1} \text{ min}^{-1}$) were approximately three orders of magnitude higher than that without NaBH₄ in an oxygen free environment ($k_{\text{obs-p-NP}} = 7.1 \times 10^{-4} \text{ min}^{-1}$), indicating that addition of NaBH₄ can significantly enhance the reduction rate of p-NP to p-AP by NZVI even in oxygen environments.

Interaction of target molecules with NZVI surfaces is a prerequisite to induce electron transfer, leading to reductive transformation of the sorbed molecules. To investigate the surface mediated reactions, *in-situ* ATR-FTIR analysis was carried out by recording the spectra of NZVI reacted with NaBH₄ and p-NP (Fig. 4). It is note-worthy that NO₂ stretch band at 1114 cm⁻¹, CH/OH bend at 1171 cm⁻¹, and CC/C-H bend at 1295 cm⁻¹ appeared at the initial stage (2 min), indicating that p-NP can be initially adsorbed on NZVI surfaces through both NO₂ and oxygen of the phenolate group [33]. However, these three main peaks continuously decreased as reaction proceeded and finally disappeared after 78 min with increase of peaks at 1240 cm⁻¹

(C-NH₂ stretch) [34]. This indicates that p-AP may be formed in the vicinity of NZVI surfaces, before being released into solution. The latter has been confirmed by checking the mass balance in aqueous solution, where conversion yield of p-NP to p-AP lied at around 95%.

3.3. Recycling tests and effect of NaBH₄ concentration

The stability and recyclability of NZVI with NaBH₄ was evaluated by monitoring the reactivity of NZVI during five times of reaction cycles (Fig. 5). UV-vis analysis showed complete reduction of p-NP in 30 min during four reaction cycles (Fig. 5a). HPLC analysis also showed the removal of p-NP over 98% with the production of p-AP over 92% (Fig. 5b), thereby underscoring the excellent stability of NZVI reactivity. The very little loss of p-AP production may be caused by the adsorption of p-AP on NZVI surfaces, as it is expected based on FTIR data. Similarly to previous studies showing a continuous decrease in catalytic activity with increase in number of recycling [10,29], the reduction extent slightly decreased to 93% of p-NP removal (vs 89% of p-AP production) over 5 cycles (Fig. 5b). This slight decrease in reduction efficiency may be attributed to the loss of NZVI particles during the magnetic separation. Doong's group has also reported that the catalytic activity of Au-magnetite catalyst continued to decrease due to the loss of nanoparticles during the separation process [7,10]. Because we used an extremely small amount of NZVI (0.065 mM) for the reaction, even small loss of NZVI during the magnetic separation can significantly influence the next reaction performance. Indeed, we observed a small loss of Fe (5-8 μ M) during the magnetic separation process at each cycle (Fig. 6a). A relationship between the pseudo-first-order kinetic rate constant after the second cycle and Fe remained at each cycle was properly fitted by a linear regression ($R^2 = 0.99$) (Fig. 6b), confirming that Fe loss during the recycling test was a primary reason for decrease in NZVI reactivity. The enhancement of reduction rate constant observed between the first and the second cycle may be attributed to the higher ratio of NaBH₄: NZVI

during washing process. We prepared the NZVI stock suspension (1.95 mM) in 100 mM of 292 NaBH₄ (51:1 molar ratio of NaBH₄:NZVI), then 0.1 mL of stock suspension transferred to the 293 cuvette (0.065 mM of NZVI) for the first reduction cycle of p-NP. After second cycle, the molar 294 ratio of NaBH₄:NZVI increased to 1538:1 by washing with 100 mM of NaBH₄, which can 295 significantly enhance the reaction between NaBH₄ and NZVI. The rate constant at second cycle 296 after washing by 10 mM NaBH₄ ($k_{\text{obs-p-NP}} = 3.8 \times 10^{-1} \text{ min}^{-1}$) was 2.4 times lower than that by 297 100 mM NaBH₄ ($k_{\text{obs-p-NP}} = 9.1 \times 10^{-1} \text{ min}^{-1}$) (Fig. 6b), indicating the effect of NaBH₄ 298 concentration on NZVI reactivity. To investigate the effect of NaBH₄ concentration, lower 299 NaBH₄ concentrations (5 and 25 mM) for p-NP reduction were investigated (Fig. S5). p-NP 300 reduction in 25 mM NaBH₄ showed similar reduction kinetics as for 50 mM NaBH₄ at first 301 cycle, but lower reduction kinetics at second cycle. This may be caused by the prevention of 302 NZVI oxidation at higher NaBH₄ concentration in oxygen environments. In the case of 5 mM 303 NaBH₄, only 39% of p-NP was reduced in 60 min, which confirms that higher concentration of 304 NaBH₄ can positively act not only for enhancement of catalytic activity but also for effective 305 preservation of NZVI during the reduction of p-NP to p-AP.

TEM, XRD, and XPS analyses were carried out to compare the NZVI particles after five reaction cycles with NaBH₄ and after one reaction cycle without NaBH₄ (Fig. 7 and Fig. 2d). 308 TEM images showed that small NZVI particles were preserved even after five recycling in an 309 oxygen environment (Fig. 7a and b), and XRD diffractogram was very similar to that of NZVI 310 in 100 mM NaBH₄ before the reaction (Fig. 7e). The result from XPS also revealed that the 311 surface of NZVI was composed of approximately 7.2% of Fe⁰, 36.0% of Fe²⁺, and 56.8% of 312 Fe³⁺ (Fig. 2c). This indicates that the proportion of Fe³⁺ was very similar to that of NZVI in 100 313 mM NaBH₄ (Fig. 2b), but that of Fe²⁺ slightly increased (32.0 → 36.0%) as well as for that of 314 Fe⁰ (10.5 → 7.2%). The slight increase in Fe²⁺ after the five recycling may be induced by the 315 continuous electron transferring from Fe⁰ to p-NP, which can be re-reduced to Fe⁰-B by NaBH₄

as shown in Fig. 2b. In contrast, NZVI sample without NaBH₄ (right after first reaction) showed the presence of non-uniform platy particles (20–40 nm) and needle-shaped particles (>100 nm) in TEM images (Fig. 7c and d). These shapes may correspond to magnetite and lepidocrocite, which have been previously observed for the oxidation of NZVI by carbon tetrachloride and oxygenated water, respectively [20,35]. Consistently, XRD diffractogram revealed the presence of magnetite (30, 35.3, 57.0, and 62.3° 2 θ) and lepidocrocite (27.1, 43.5 and 46.9° 2 θ) (Fig. 7e) and XPS spectra showed a significant increase in proportion of Fe³⁺ (72%) with a disappearance of peak for Fe⁰ (Fig. 2d). Therefore, these results confirm the rapid oxidation of NZVI to Fe-oxides or Fe-oxyhydroxides during the reduction of p-NP without NaBH₄ in oxygen environments.

3.4. Borohydride-induced catalytic p-NP reduction on magnetite surface (experimental and theoretical studies).

As an attempt to elucidate the borohydride-induced catalytic p-NP reduction mechanism, the ability of four iron oxy(hydr)oxides, suspected to coat the spherical NZVI particles, to reduce p-NP in the presence of NaBH₄ was investigated (Fig. 8). First, a slight decrease in absorbance at 400 nm and its rebound to initial concentration of p-NP was observed in maghemite, hematite, and goethite suspensions as similar to p-NP alone, due to the initial mixing effect of p-NP solution (see experimental section). HPLC analysis confirmed that the removal of p-NP were 0, 2, and 8% by maghemite, hematite, and goethite, respectively, while no p-AP was detected, suggesting that the p-NP decay may be caused by its adsorption on the surface of hematite and goethite. In contrast, a significant decrease in p-NP absorbance was observed in magnetite suspension, resulting in 72% of p-NP reduction with 65% of p-AP production. However, we observed a little effect on the reduction of p-NP by magnetite at low NaBH₄ concentration (1–10 mM). It is worth noting that only magnetite showed the formation of H₂

bubbles during the reduction of p-NP, corroborating the occurrence of a chemical reaction. This 342 catalytic activity of magnetite may be attributed to the structural modifications occurred on 343 magnetite surfaces, such as generation of smaller crystals and formation of Fe⁰-B amorphous 344 alloy [31] and/or the catalytic activity of magnetite for p-NP induced by the presence of NaBH₄. 345 The former has been already shown to exhibit a catalytic activity such as dehydrogenation of 346 ethanol [36].

To investigate the catalytic activity of magnetite for p-NP induced by the presence of NaBH₄, DFT calculations were performed (Fig. 9 and Table S1). Although the existence of p- 349 nitrophenolate anion was observed in our experimental conditions, we used a protonated form 350 of the phenol group for DFT calculations to maintain the simulation cell neutrality without 351 including explicit solvent molecules. Considering that the reaction center locates at the opposite 352 functional group of NO₂, we expect that the deprotonation of the phenol group will barely 353 influence the relative energetics. We note that tetrahedral Fe³⁺ sites are exposed at the magnetite 354 (111) surface, which has been often investigated as a rational structure of magnetite (111) for 355 catalytic purposes in both theoretical and experimental studies [37-40]. In our systems, the 356 adsorption energy of p-NP on top of the tetrahedral Fe³⁺ site is also calculated as favorable 357 ($\Delta E_{\text{ads}} = -0.38$ eV (Table S2)), which is followed by the first nucleophilic attack of hydride (H⁻)

of NaBH₄ to the nitrogen atom with the low electronegativity, yielding NHO₂⁻ group ($\Delta E_{\text{hyd-trs}(1\text{st})} = -0.91$ eV). Then, the NHO₂⁻ group is dehydroxylated into NO group to form *p*-nitrosophenol ($\Delta E_{\text{dehydr}(1\text{st})} = -0.46$ eV downhill), which is further converted into NHO⁻ group 361 by the second hydride transfer from NaBH₄ ($\Delta E_{\text{hyd-trs}(2\text{nd})} = -1.95$ eV). The strong Brønsted 362 acidity of NHO⁻ group induces hydrolysis to form NH₂O group, producing *p*- 363 hydroxyaminophenol ($\Delta E_{\text{hydrol}} = 0.11$ eV). The third hydride transfer from NaBH₄ further 364 reduces the NH₂O group to NH₃O⁻ group ($\Delta E_{\text{hyd-trs}(2\text{nd})} = -0.39$ eV), which is followed by the 365 second dehydroxylation, eventually yielding the final product of *p*-AP ($\Delta E_{\text{dehydr}(2\text{nd})} = -2.11$ eV).

We note that our overall mechanism ($\text{HOC}_6\text{H}_4\text{NO}_2 + 3\text{NaBH}_4 + \text{H}_2\text{O} \rightarrow \text{HOC}_6\text{H}_4\text{NH}_2 + 3\text{NaOH} + 3\text{BH}_3$) is mediated by the intermediate species of *p*-nitrosophenol and *p*-hydroxyaminophenol, which is consistent with previous studies (Fig. 10) [12, 41, 42]. In addition, once BH_3 is formed, it can be further oxidized to H_3BO_3 ($\text{BH}_3 + 3\text{H}_2\text{O} \rightarrow \text{H}_3\text{BO}_3 + 3\text{H}_2$) by water in alkaline aqueous environment [43]. Therefore, we propose the entire reaction pathway for NaBH_4 induced *p*-NP reduction on magnetite surface by adding the oxidation of BH_3 ($\text{HOC}_6\text{H}_4\text{NO}_2 + 3\text{NaBH}_4 + 10\text{H}_2\text{O} \rightarrow \text{HOC}_6\text{H}_4\text{NH}_2 + 3\text{NaOH} + 3\text{H}_3\text{BO}_3 + 9\text{H}_2$). To identify the role of magnetite surface, we compared the energetics for *p*-NP to *p*-AP reduction pathway when the reaction proceeds without magnetite surface (Fig. 9 and Table S2). We found that the first and second hydride transfer steps become energetically disfavored ($\Delta E_{\text{hyd-trs}(1\text{st})} = +1.01$ eV and $\Delta E_{\text{hyd-trs}(2\text{nd})} = +0.55$ eV), indicating that reduction of *p*-NP cannot occur in NaBH_4 solution without magnetite, as it was experimentally observed. The experimental results and DFT calculations suggest that the combination of disintegration of NZVI into smaller size, formation of Fe^0 -B, and catalytic activity of magnetite may be responsible of the enhanced reduction of *p*-NP to *p*-AP.

4. Conclusions

Although NZVI technologies have been extensively studied for reduction of environmental contaminants, the rapid passivation of NZVI surface limits its application in ambient environments (21% O_2 condition). Herein, we have demonstrated that the NaBH_4 enhanced significantly the reactivity of NZVI in oxygen environments. Our surface and solution characterization and DFT calculations revealed that the NaBH_4 acts through one or combination of the following mechanisms: (i) disintegration of NZVI into much smaller particles increasing reactive surface available for NP reduction, (ii) reaction with oxides coatings in the NZVI shell leading to the formation of new surface sites with a high reductive ability and (iii) hydrolysis

of p-NP to p-AP by interaction between magnetite shell and NaBH₄. Moreover, the reduction of p-NP to p-AP in an oxygen environment was significantly enhanced by NZVI with NaBH₄ compared to NZVI without NaBH₄ in an oxygen-free environment. Therefore, NZVI-NaBH₄ system can be supposed to preserve the NZVI reactivity in contaminated systems containing naturally occurring oxidant species (e.g. O₂ and/or nitrate). The high conversion efficiency, and good reactivity/reusability are likely comparable with the widely used noble metallic catalysts (e.g., Au, Ag, and Pt). Although NaBH₄ should be carefully handled due to its production of flammable and explosive H₂ gas during the reaction with water or moist air [44], the new findings obtained from NZVI, produced by easy and cheap methods, can provide a novel possibility for mass production of p-AP from p-NP in NZVI-NaBH₄ system. These results can also help researchers and technicians for the development of novel NZVI technologies, which can apply to the reductive degradation of environmental contaminants in oxygen environments.

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Fig. 1. TEM images showing the NZVI particles without NaBH₄ (a and b) and with NaBH₄ (c and d) and (e) XRD patterns of NZVI in different concentrations of NaBH₄.

Fig. 2. XPS spectra for the narrow scan of Fe(2P_{3/2}) on the surface of (a) initial NZVI, (b) NZVI reacted with NaBH₄ (Inset: narrow scan of B(1s)), (c) NZVI after five reaction cycles with p- 497 NP in the presence of NaBH₄, and (d) NZVI after one reaction cycle with p-NP in the absence 498 of NaBH₄.

Fig. 3. (a) Color change of p-NP suspension during the reaction and NZVI separation by 501 magnetism. (b) Background compensated UV-vis spectral change in p-NP (0.1 mM) in the 502 presence of NZVI (3.5 mg/L, 0.065 mM). (c) Concentration changes of p-NP analyzed by UV- 503 vis data and the conversion efficiency after finishing the reaction (inset). The pH is highly 504 alkaline (~11) due to the addition of NaBH₄ solution.

Fig. 4. ATR-FTIR spectra during the reduction of p-NP (10 mM) by NZVI (10 g/L) with NaBH₄ (100 mM).

Fig. 5. (a) Reduction kinetics of p-NP (0.1 mM) by NZVI (3.5 mg/L, 0.065 mM) during the recycling test and (b) the conversion efficiency after finishing each cycle. The pH is highly 511 alkaline (~11) due to the addition of NaBH₄ solution.

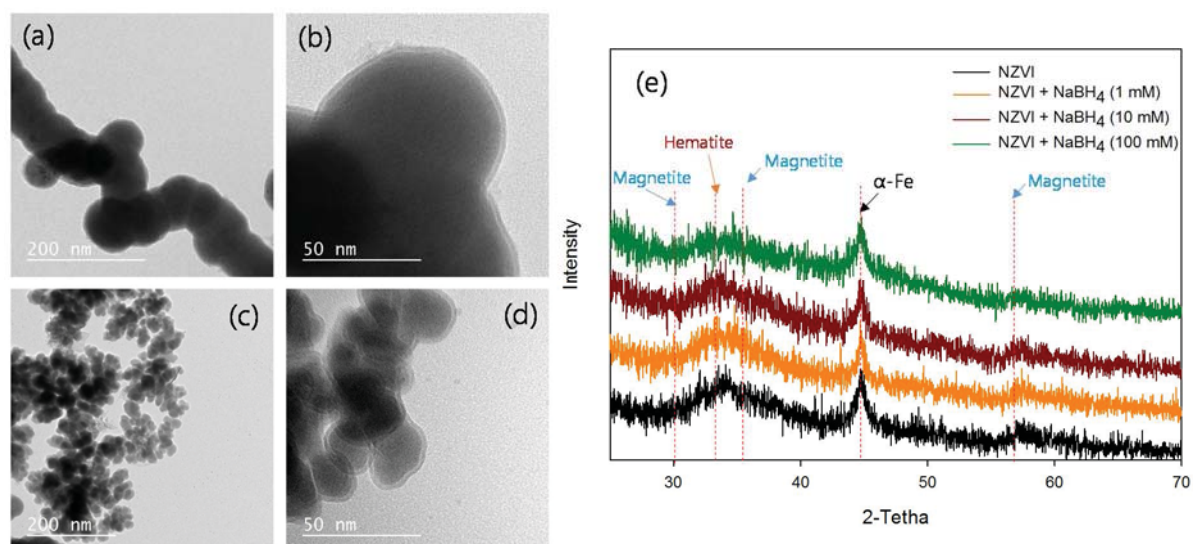
Fig. 6. (a) Fe loss during the separation process and (b) change in $k_{\text{obs-p-NP}}$ with respect to the Fe(0) concentration remained at each cycle.

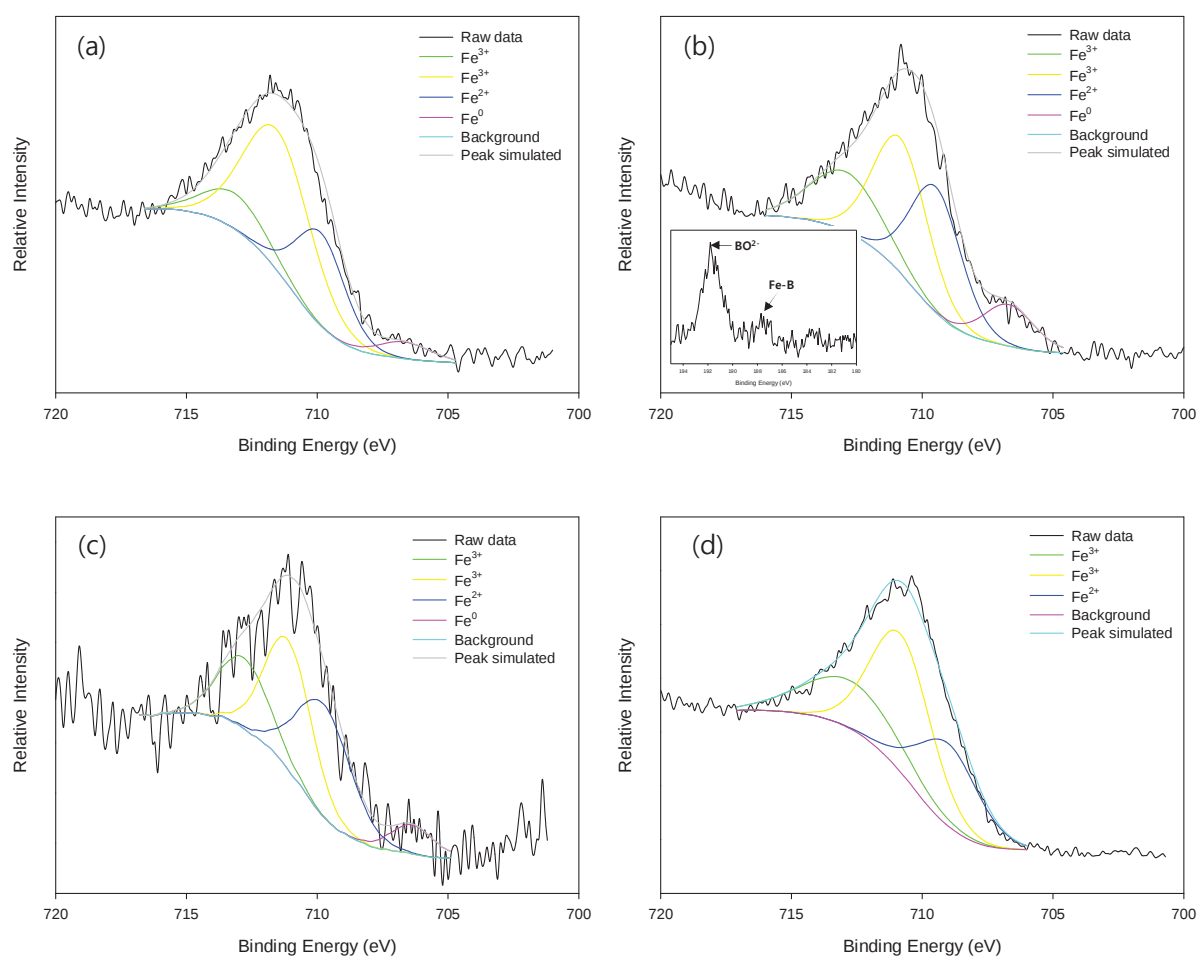
Fig. 7. TEM images showing the NZVI particles after five reaction cycles with p-NP in the presence of NaBH₄ (a and b) and after one reaction cycle in the absence of NaBH₄ (c and d) and (e) their XRD patterns

Fig. 8. Removal kinetics of p-NP by Fe minerals (maghemite, hematite, goethite, and magnetite) and (b) their conversion efficiencies

Fig. 9. Hydrolysis mechanism of p-NP to p-AP on magnetite surface based on the DFT calculations. Black lines show the energetics with magnetite (111) surface, while the energetics without magnetite surface are shown as grey lines.

Fig. 10. Reaction mechanism proposed by this study for p-NP reduction to p-AP on magnetite surface by NaBH₄.

**Fig. 1**

**Fig. 2**

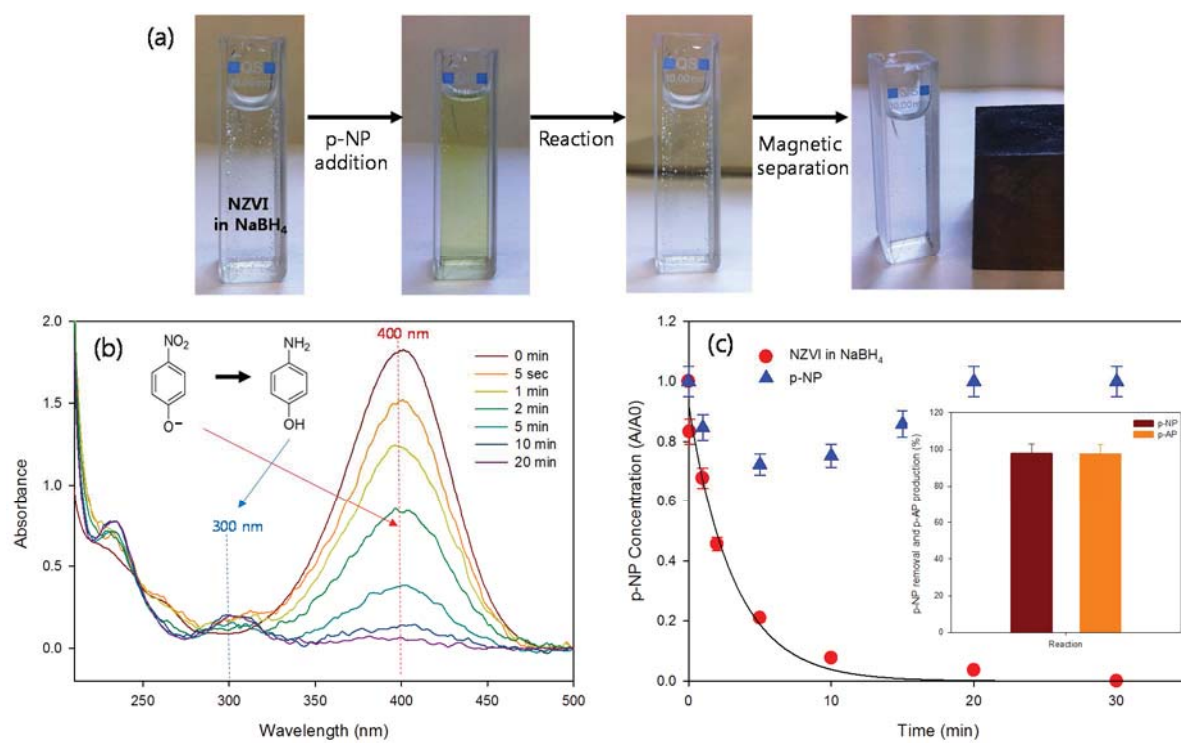
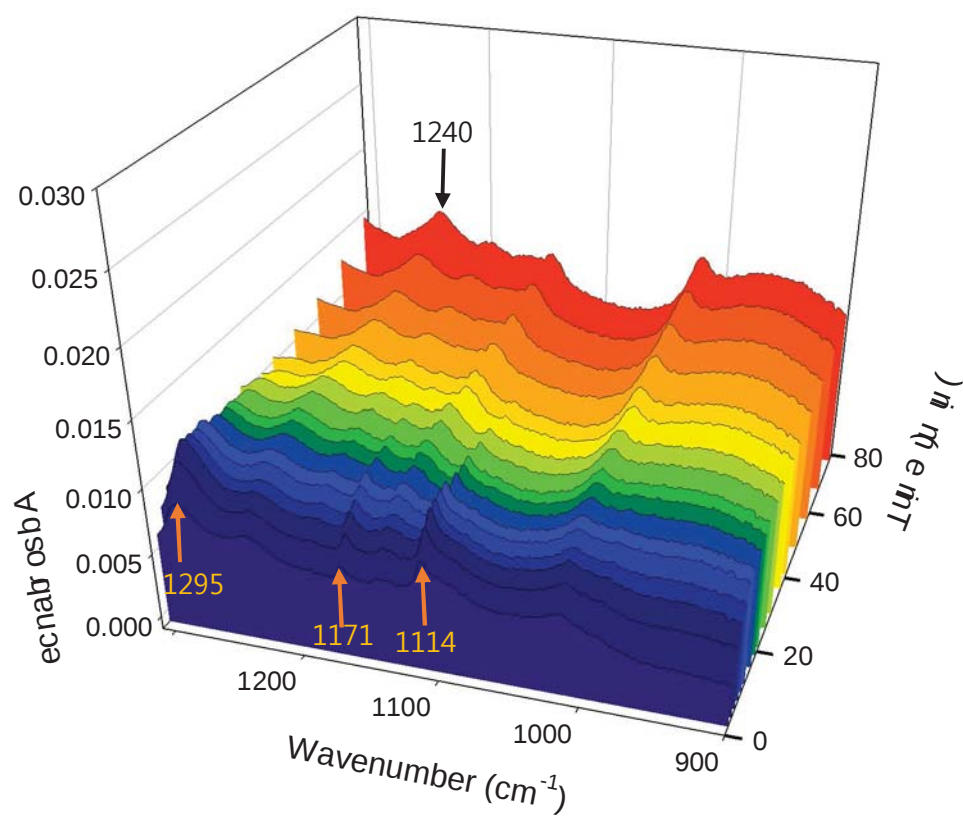


Fig. 3

**Fig. 4**

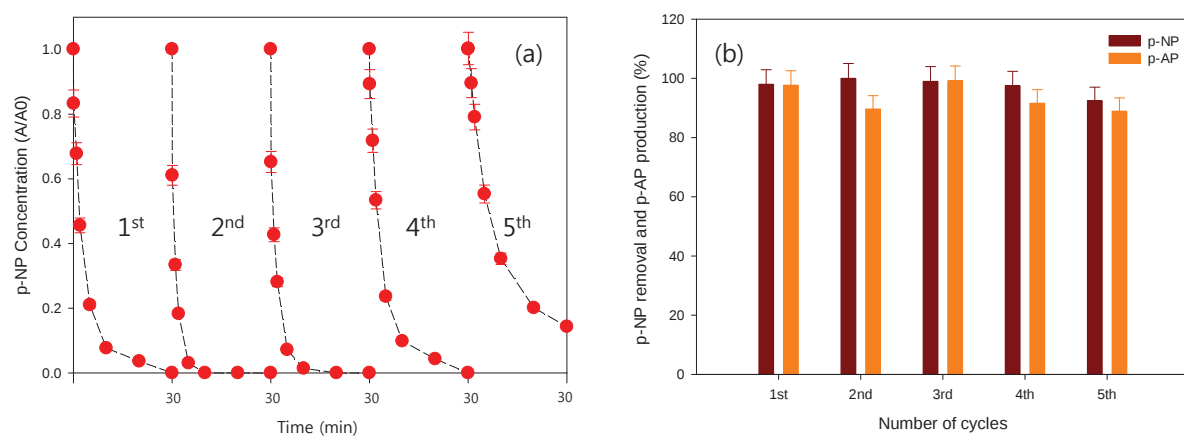


Fig. 5

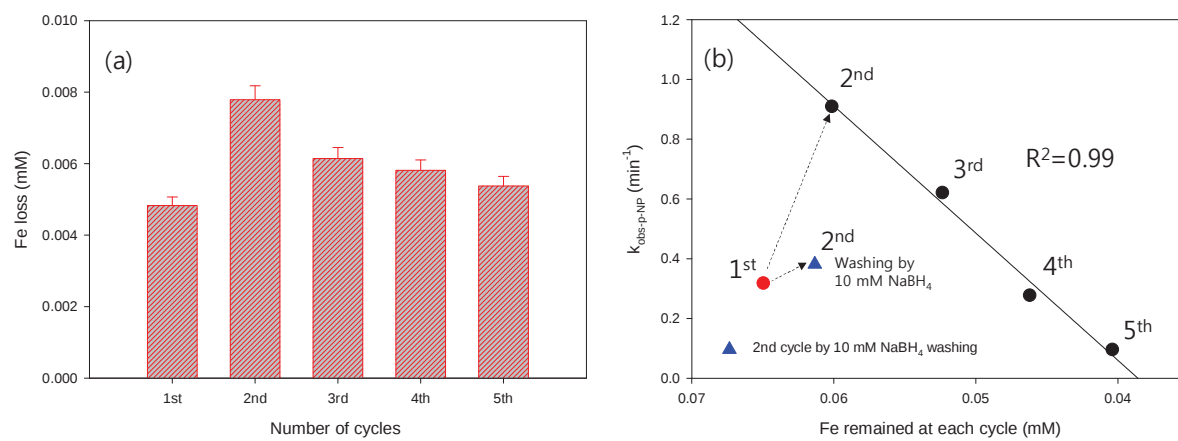


Fig. 6

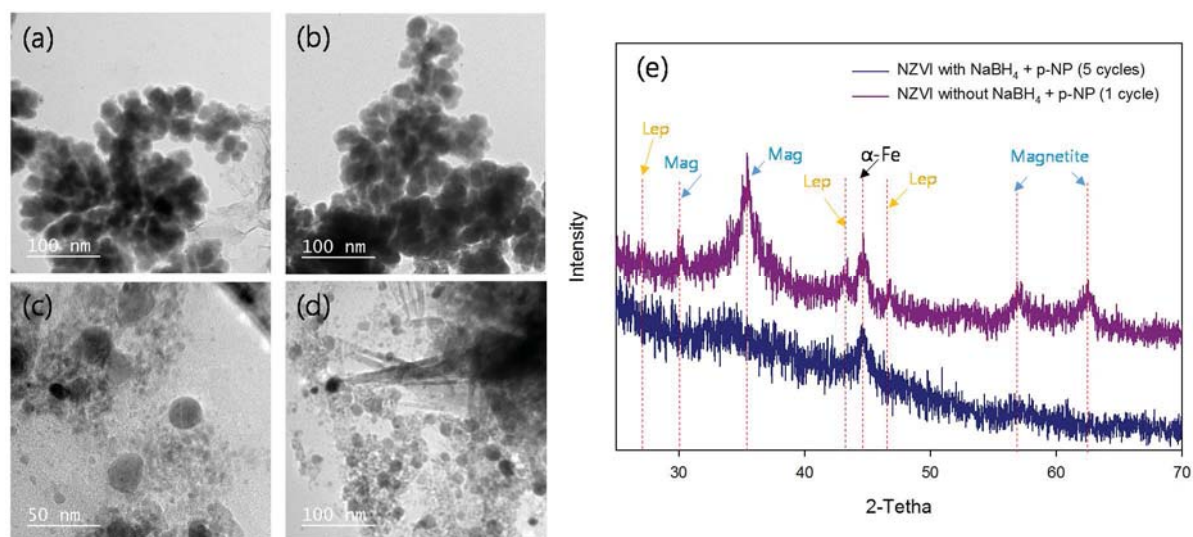


Fig. 7

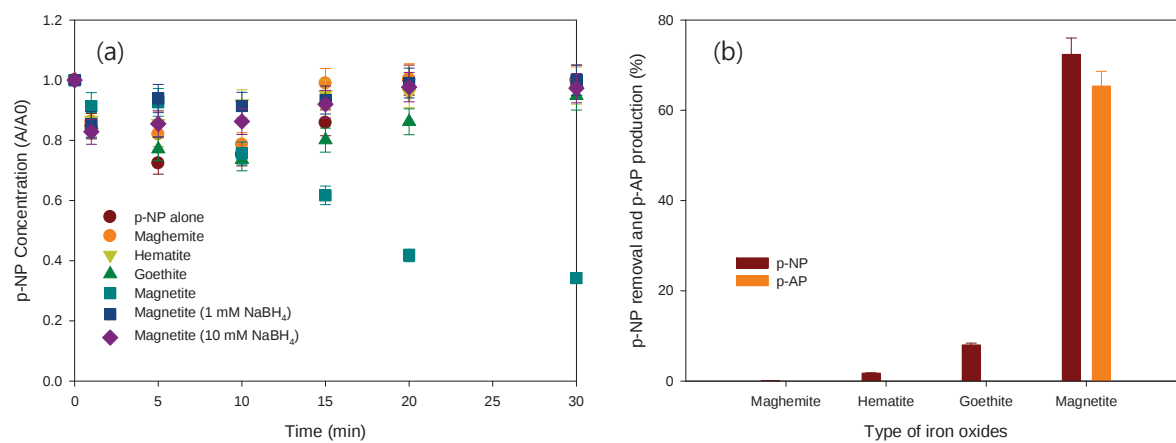


Fig. 8.

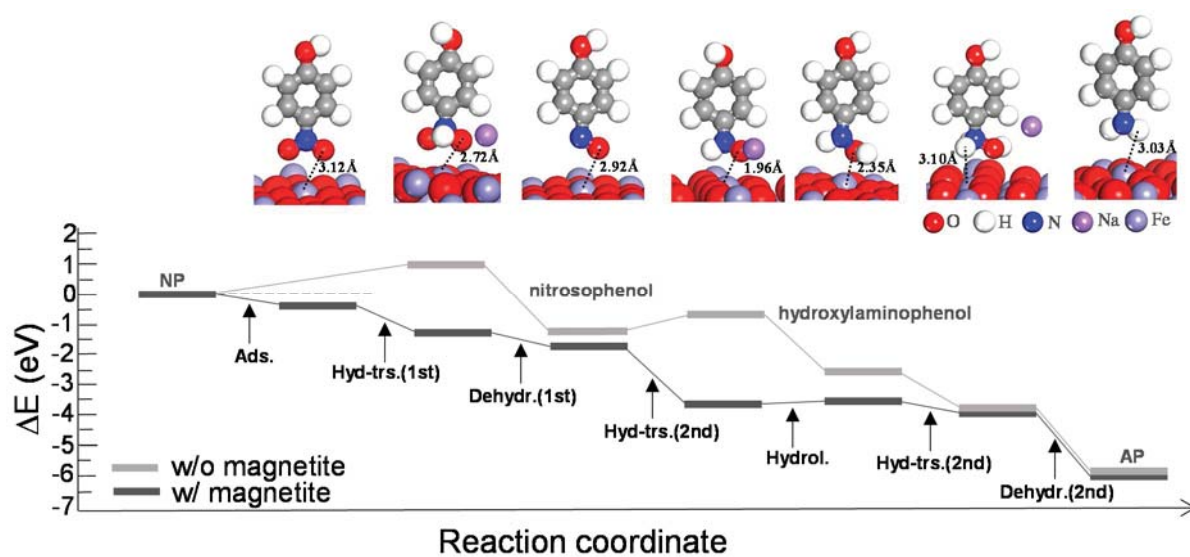
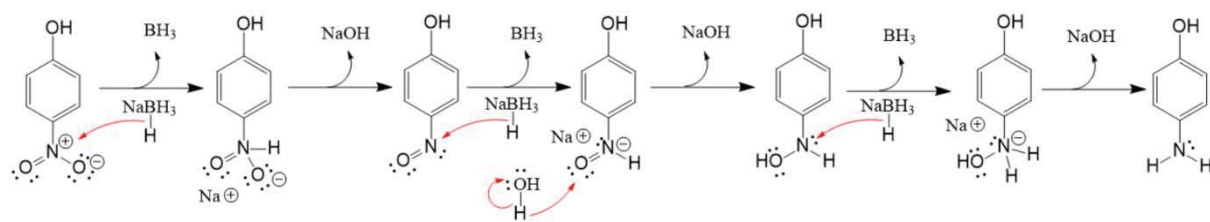


Fig. 9

**Fig. 10.**