



Reductive reactivity of borohydride- and dithionite-synthesized iron-based nanoparticles: A comparative study



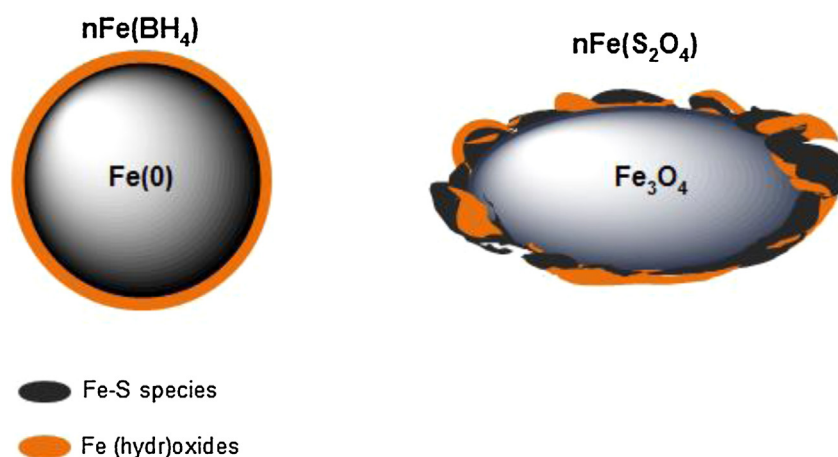
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HIGHLIGHTS

- Sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) used in synthesis of nanosized Fe particles ($\text{nFe}(\text{S}_2\text{O}_4)$).
- Particles synthesized using $\text{Na}_2\text{S}_2\text{O}_4$ mainly magnetite and small portion of $\text{Fe}(0)$.
- Particles made using $\text{Na}_2\text{S}_2\text{O}_4$ less reactive than particles made using NaBH_4 .
- Low reactivity of palladized $\text{nFe}(\text{S}_2\text{O}_4)$ due to low Pd loading and presence of Pd^{2+} .

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 30 August 2015
 Received in revised form 5 October 2015
 Accepted 6 October 2015
 Available online 20 October 2015

Keywords:

nZVI
 Pd@nZVI
 Sodium dithionite
 Sodium borohydride
 TCE degradation

ABSTRACT

In this study sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) and sodium borohydride (NaBH_4) were employed as reducing agents for the synthesis of nanosized iron-based particles. The particles formed using NaBH_4 (denoted $\text{nFe}(\text{BH}_4)$) principally contained (as expected) $\text{Fe}(0)$ according to XAS and XRD analyses while the particles synthesized using $\text{Na}_2\text{S}_2\text{O}_4$, (denoted $\text{nFe}(\text{S}_2\text{O}_4)$) were dominated by the mixed $\text{Fe}(\text{II})/\text{Fe}(\text{III})$ mineral magnetite (Fe_3O_4) though with possible presence of $\text{Fe}(0)$. The ability of both particles to reduce trichloroethylene (TCE) under analogous conditions demonstrated remarkable differences with $\text{nFe}(\text{BH}_4)$ resulting in complete reduction of 1.5 mM of TCE in 2 h while $\text{nFe}(\text{S}_2\text{O}_4)$ were unable to effect complete reduction of TCE in 120 h. Moreover, acetylene was the major reaction product formed in the presence of $\text{nFe}(\text{S}_2\text{O}_4)$ while the major reaction product formed following reaction with $\text{nFe}(\text{BH}_4)$ was ethylene, which was further reduced to ethane as the reaction proceeded. Considering that effective Pd reduction to $\text{Pd}(0)$ requires the presence of $\text{Fe}(0)$, this is consistent with our finding that $\text{Fe}(0)$ is not the dominant phase formed when employing dithionite as a reducing agent under the conditions employed in this study.

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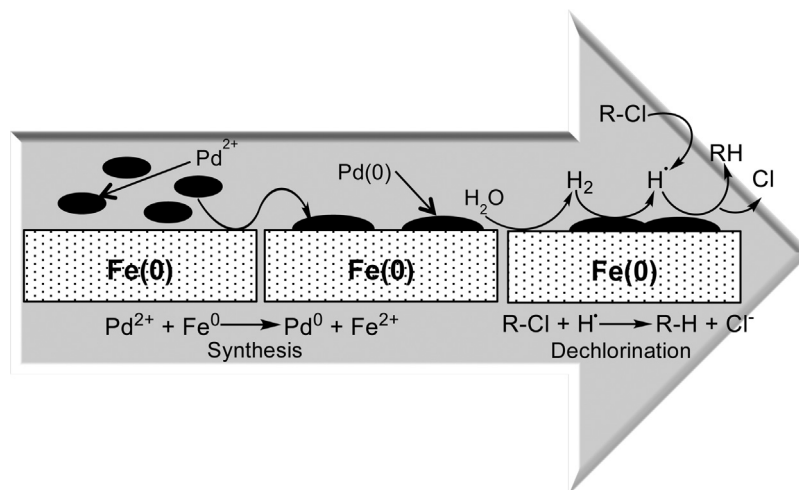
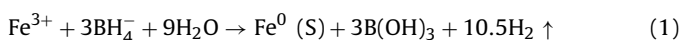


Fig. 1. Schematic description of the synthesis process for bimetallic particles (Pd@nZVI) and the mechanism for contaminant dechlorination.

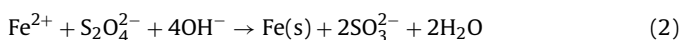
1. Introduction

Zero-valent iron (ZVI) is a powerful reducing agent ($E_0^{1/2} = -0.447\text{ V}$ vs. SHE), able to degrade a wide range of contaminants such as chlorinated hydrocarbons, polychlorinated biphenyls and inorganic elements [1,2]. Nanoscale zero-valent iron (nZVI) offers particular additional advantages due to its considerably larger surface area to volume ratio and hence enhanced surface reactivity. Its smaller particle size also allows for more efficient transport and distribution of the particles in different reaction medium, which is particularly beneficial for in situ application [3,4]. Indeed, there is a vast amount of literature that demonstrates the effectiveness of nZVI or its modified forms for the remediation of contaminated sites [5–8].

nZVI particles can be synthesized using a variety of chemical and physical methods. In the late 1990s, Wang and Zhang introduced an innovative chemical method whereby iron salts are reduced using sodium borohydride [9]. The reaction can be described as follows:



The high reactivity of the particles formed, the simplicity of this synthetic approach and the relatively small amount of materials and energy required relative to the earlier methods employed to synthesize nZVI have resulted in this method being widely applied in nZVI research [10,11]. The potential dangers associated with the generation of explosive hydrogen gas together with the high cost of borohydride however are major drawbacks. Recently it was reported that sodium dithionite, with a similarly low standard reduction potential ($E_0^{1/2} = -1.12\text{ V}$) could potentially substitute for borohydride [12] in the synthesis of ZVI via the following reaction which does not generate hydrogen gas:



To date, dithionite has been applied mainly to the treatment of iron-containing minerals, clays and sediments, in which Fe(III) can be reduced to Fe(II), thereby aiding in the degradation of environmental contaminants such as herbicides [13,14].

Another reported use of dithionite involves the regeneration of Fe(0) from aged particles, with results suggesting that sodium dithionite is able to effectively depassivate and restore the reducing capacity of oxidized nZVI particles to a similar or even more reduced state than fresh nZVI particles through a reaction with the surface passivation products [15]. The effectiveness of this strat-

egy largely depends on the dithionite loadings with an excess of dithionite suggested to induce the oxidation of the exposed Fe(0) core, resulting in the formation of less reactive Fe species such as FeS.

Dithionite has also been employed in conjunction with sodium borohydride for the synthesis of nZVI particles. The formation of an FeS shell in the presence of Na-dithionite has been found to be more favorable for TCE degradation than the formation of the iron oxide layer which forms without the addition of dithionite with the enhanced reactivity attributed to the increased roughness and conductivity of the particle surface, and the formation of more hydrophobic sites for TCE attraction [16]. In this method, the reduction of Fe(II) to Fe(0) is achieved as a result of the presence of sodium borohydride. The application of sodium dithionite as the sole reducing agent for the synthesis of nZVI particles has been reported [12] however limited information on the structure and composition of the particles formed and their reactivity is available. As such, in this study, we investigate the structure and compositions of particles formed by reduction of a ferrous salt using dithionite (only) and borohydride (only) and examine the reactivity of the resultant particles with regard to the reduction of trichloroethylene (TCE).

To improve the performance of nZVI particles for contaminant degradation [1,6], doping a second metal (such as Ni and Pd) on the surface of nZVI particles is very common. The added secondary metal ions undergo reduction and precipitate on the iron surface in their zero-valent form. The reduced form of the secondary metal serves to activate a catalytic hydrogenation reaction by inducing the transformation of hydrogen gas to atomic hydrogen, a highly reactive reducing agent which enhances the degradation of contaminants [17,18] as shown in Fig. 1. In addition to enhancing reduction, bimetallic nZVI particles are also capable of generating less hazardous byproducts containing no or lower amounts of chlorine [17,19].

Although the synthesis of bimetallic nZVI particles using borohydride has been well described, the doping of transitional metals onto dithionite-synthesized particles has not been investigated. Herein, the objectives of this work include (i) characterization of the nature and speciation of Pd-doped and undoped borohydride- and dithionite-synthesized Fe-based particles, (ii) investigation of the performance of Pd-doped and undoped Fe-based particles towards the degradation of trichloroethylene (TCE) and elucidation of the reaction products formed, and (iii) a comparison between borohydride- and dithionite-synthesized

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