



Highly efficient degradation of organic pollutants using a microbially-synthesized nanocatalyst



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ABSTRACT

Magnetite is a common subsurface mineral, formed biogenically in anaerobic environments. Containing Fe(II), it is reactive towards a variety of common redox sensitive subsurface contaminants. To extend the reactivity of biomagnetite it is possible to add a coating of Pd(0) nanostructures, which is capable of sustained catalytic reactivity. Here we assess the reactivity of biogenic nano-magnetite (BnM), formed by the reduction of Fe(III) oxyhydroxide by *Geobacter sulfurreducens*, to the model organic compounds nitrobenzene (ArNO₂) and tetrachloroethylene (PCE), and compare its performance to biomagnetite functionalized with Pd(0) (Pd-BnM). The BnM and the Pd-BnM were both found to be highly reactive towards ArNO₂, quantitatively transforming it to the reduced product aniline (ArNH₂). When applied to tetrachloroethylene (PCE), the BnM was found to be poorly reactive, while the Pd-BnM rapidly dechlorinated the PCE to the benign product, ethane, at rates comparable to synthetic nano-scale catalysts. The biological synthesis route proposed is highly scalable and offers a green, environmentally benign route for the production of highly reactive nanoparticles for environmental clean-up.

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1. Introduction

The mixed-valent iron mineral magnetite (Fe(II)Fe(III)₂O₄) is widespread in the natural environment (Cornell and Schwertmann, 2003), formed via a diverse range of biotic and abiotic processes, including the bioreduction of poorly crystalline Fe(III) phases by dissimilatory iron reducing bacteria (Cutting et al., 2009; Lovley et al., 1987), the abiotic oxidation of ferrous or zero valent iron (ZVI) (Gu et al., 1999; Olowe et al., 1989) and the bio-oxidation of Fe(II) coupled to denitrification (Kappler and Straub, 2005). Early studies noted that in the absence of aqueous and sorbed Fe(II) species, magnetite is relatively un-reactive towards nitroaromatic and chlorinated compounds over timescales of hours (Elsner et al., 2004; Klausen et al., 1995). Other studies, however, have demonstrated the ability of both synthetic and biogenic magnetite to

reduce a range of environmentally relevant contaminants such as trichloroethylene (Lee and Batchelor, 2002), carbon tetrachloride (Danielsen and Hayes, 2004), nitrobenzene (Gorski and Scherer, 2009), nitramine explosives such as hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) (Gregory et al., 2004), Hg(II) (Wiatrowski et al., 2009), Cr(VI) (Cutting et al., 2010), U(VI) (Missana et al., 2003) and Tc(VII) (Lloyd et al., 2000; McBeth et al., 2011).

Ultimately the reactivity of magnetite (or other solid state reductants) appears to be governed by their ability to store (capacitance) and donate electrons from Fe(II), with Fe(II)/Fe(III) stoichiometry noted to have a profound control on reactivity (Gorski et al., 2010; Latta et al., 2012). In an attempt to overcome the limitation of a finite capacitance inherent to Fe(II)-bearing magnetite particles, composite catalysts have been fabricated by supporting nano-scale metallic palladium (Pd(0)) clusters on the surfaces of biogenic magnetite nanoparticles (Coker et al., 2010; Crean et al., 2012). These nanoparticles, synthesized using an Fe(III)-reducing bacterium, were functionalized with Pd through a one-step reduction method (Coker et al., 2010). The resulting particles consisted of a biogenic nano-magnetite (BnM) carrier

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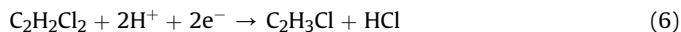
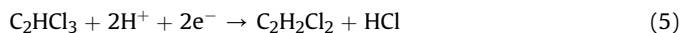
(~20 nm diameter) hosting metallic Pd particles (~5 nm) on its surface (Pd-BnM). When supplied with a suitable electron donor, typically H₂ gas, Pd(0) is able to dissociate and absorb reactive H· in to its bulk structure, available for reaction (Conrad et al., 1974; Tierney et al., 2009; Yamauchi et al., 2008). The ability to supply the reaction with fresh electron donor improves the reduction potential and longevity of particle reactivity, in comparison to the finite Fe(II) of magnetite.

A number of studies employing Pd(0) catalysts in various forms have confirmed their exceptional reactivity against a variety of pollutants (Chaplin et al., 2012). These Pd(0) particles have been deployed in a number of different forms, including as native Pd(0) particles, and more commonly on the surface of support materials including carbon, silica, alumina, oxides and metals (Henry, 1998). These supports are often employed due to beneficial effects upon reactivity, where greatly improved reaction rates have been recorded in the presence of secondary “promoter” metals, such as Au (Nutt et al., 2005). However, due to its relatively cheap cost, alumina (Al₂O₃) has gained the most attention as a support for Pd(0) during technological applications (Davie et al., 2008; McNab et al., 2000). Recently, the development of Pd(0) coatings on synthetic magnetite resulted in extremely high catalytic activities towards trichloroethylene (TCE), without the need for costly promoter metals (Hildebrand et al., 2009). The aforementioned, microbially engineered catalyst (Pd-BnM), exhibited equal or superior activity during the Heck reaction, versus colloidal Pd nanoparticles, likely due to reduced agglomeration (Coker et al., 2010). Nanoparticles synthesized via this route have been demonstrated to be effective for the treatment of other common water contaminants; Cr(VI) (Crean et al., 2012; Watts et al., 2015) and azo dyes (Coker et al., 2014).

Here the catalytic potential of biologically synthesized nano-materials for the treatment of common organic contaminants is assessed. Nitrobenzene (ArNO₂) and tetrachloroethylene (PCE) are used as model contaminant compounds, since these occur at a variety of contaminated sites, often as co-contaminants (Albright, 2011). The ArNO₂ was used to probe the reactivity of BnM, produced by incubating an Fe(III) starting phase with pre-grown cells of the Fe(III)-reducing bacterium *Geobacter sulfurreducens*. To increase the reactivity and extend its reactive lifetime the BnM was functionalized with a surface loading of Pd(0) nanoparticles, to create a biosynthesized, magnetically recoverable nano-scale catalyst (Pd-BnM). ArNO₂ is a useful probe compound as it is known to undergo reduction to aniline (ArNH₂), via the following reactions (Scherer et al., 2001):



To further compare the reactivity of the un-functionalized Fe(II) mediated reductant, BnM, compared to the catalytic, Pd-BnM, they were both also tested towards dechlorination of the relatively more recalcitrant contaminant PCE. PCE is dechlorinated via a series of potential intermediate compounds, via the idealized reactions:



The assessment of the reactivity of the particles towards PCE includes a detailed assessment of the rates and end points of degradation catalyzed by BnM and Pd-BnM, and a critical comparison of performance with a range of synthetic analogues.

2. Experimental section

2.1. Chemicals

All chemicals used in this study were of analytical grade or purer, unless otherwise stated, and used as received without further purification prior to use. All water used in the experiments was of a minimum 18.2 MΩ quality.

2.2. Biogenic nano-magnetite synthesis

BnM was prepared from a starting Fe(III) phase of 2-line ferrihydrite, prepared by alkaline hydrolysis, through addition of 10 N NaOH to a 0.66 M Fe(III)Cl₃ solution until reaching a pH of 7 (Lovley and Phillips, 1986; Schwertmann and Cornell, 2008). The precipitates were washed six times using 18.2 MΩ water, separating the precipitates by centrifuging at 17,000g for 20 min, and stored under N₂ until required. The physical and chemical properties of these biomineralization products have extensively been characterized previously (Byrne et al., 2011).

A culture of *G. sulfurreducens* was prepared according to Lloyd et al., (2003). Briefly, freshwater medium (Lovley and Phillips, 1988) was prepared, containing 20 mM acetate as the electron donor and 40 mM of fumarate as the electron acceptor, prepared under an N₂–CO₂ (80:20) atmosphere, adjusted to a pH of 7 using NaOH, determined using a Denver Instrument UB-10 bench top meter and a calibrated P Cole Parmer 5990-45 CCP probe. This medium was decanted in to serum bottles and sealed using a rubber bung and aluminum crimps, leaving a headspace of N₂–CO₂ (80:20), prior to autoclaving for sterility. An inoculum of a growing culture of *G. sulfurreducens* was added at a 10% v/v ratio. For incubation with the Fe(III) starting phases, a late log phase culture of *G. sulfurreducens* was harvested by centrifugation (Sigma 6k15), at 4920g for 20 min, and washed using a bicarbonate buffer under N₂–CO₂ (80:20) gas. This concentrated cell suspension was used to inoculate sealed serum bottles containing 10 g L⁻¹ of Fe(III) starting material (at 0.6 mg protein mL⁻¹), 20 mM Na acetate, 30 mM NaHCO₃ and 10 μM anthraquinone-2,6-disulfonate (AQDS) under an atmosphere of N₂–CO₂ (80:20) gas. These inoculated serum bottles were incubated at 30 °C in the dark until transformation to magnetite was complete. Following incubation, the resulting magnetite was magnetically separated and washed using 18.2 MΩ water and stored at 4 °C in the dark until use. The Fe concentration of the BnM slurry was determined by the acid extraction and ferrozine assay, as detailed in section 2.6.

2.3. Functionalization of biogenic nano-magnetite with Pd(0)

Biogenic nano-magnetite was used to support surface-localized Pd(0), precipitated via the method detailed in (Coker et al., 2010). Briefly, under an N₂ atmosphere an aliquot of the washed BnM slurry was added to a sterile serum bottle and crimp sealed using a rubber bung and aluminum crimps. An N₂ degassed solution of Na₂PdCl₄ was prepared, at a concentration to give a final concentration of Pd on the magnetite as 2.4 wt % Pd. This solution was then added, using an N₂ degassed syringe, to the BnM slurry while shaking prior to agitating on a roller shaker for 12 h. In order to remove excess Cl⁻ ions the resulting Pd-BnM was washed under an N₂ atmosphere, with 18.2 MΩ water. The resulting slurry was sampled and solubilized using concentrated HCl and sent for ICP-

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