



Dual functionality of an Ag-Fe₃O₄-carbon nanotube composite material: Catalytic reduction and antibacterial activity

Bhaskar Bhaduri^a, Maya Engel^a, Tamara Polubesova^a, Wenhao Wu^b, Baoshan Xing^b, Benny Chefetz^{a,*}

^a Department of Soil and Water Sciences, Faculty of Agriculture, Food and Environment, The Hebrew University of Jerusalem, P.O. Box 12, Rehovot 7610001, Israel

^b Stockbridge School of Agriculture, University of Massachusetts, Amherst, MA 01003, United States



ARTICLE INFO

Keywords:

Silver
Characterization
Catalysis
Disinfection
Microorganism
Pollutant

ABSTRACT

Carbon-based nanomaterials have remarkable chemical and biological features. The introduction of supporting magnetic materials onto carbon-based nanoparticles has gained interest owing to their easy separation from heterogeneous systems. Herein, we report the synthesis of a novel composite comprised of single-walled carbon nanotubes, Fe₃O₄ and Ag nanoparticles with an aim to develop a bifunctional composite for water purification that maintains both high catalytic and antibacterial activities. The composite facilitated decomposition of nitrophenols and methyl orange in the presence of NaBH₄ as the reducing agent – maintaining high activity (> 90%) following three regeneration cycles. The composite's catalytic activity was unaffected by the presence of dissolved organic matter (DOM) at an environmentally relevant concentration of 5 mg CL⁻¹. DOM concentration of 50 mg CL⁻¹ slightly decreased the reduction of *p*-nitrophenol, 2-methyl-*p*-nitrophenol, and methyl orange (by ~14%, ~11%, and ~10% respectively) but significantly decreased that of *o*-nitrophenol (by 38%). The composite exhibited high antibacterial activity towards gram-negative and gram-positive bacteria even in the presence of DOM at an environmentally relevant concentration. However, the composite's efficiency decreased with increase in DOM concentration. This study demonstrates dual catalytic and antibacterial activity of a novel Ag-Fe₃O₄-single walled carbon nanotube composite material in the absence and presence of DOM, and considers its potential implementation in water/wastewater treatment applications.

1. Introduction

Past decades show that water pollution has become a major global concern. Chemicals, pathogens, and hazardous wastes are prime sources of water pollution, posing a threat to the ecosystem and human health [1]. For example, industrial waste by-products, such as nitrophenols and organic dyes, are considered highly toxic to aquatic organisms and humans [2]; they are associated with increased heart rate, jaundice and tissue necrosis [3–7]. In the environment, nitrophenols and organic dyes are highly stable and withstand natural reduction. Consequently, nitrophenols have been declared priority pollutants by the US EPA [2,8]. Pathogenic bacteria in drinking water also pose a potential health risk, especially in undeveloped countries where wastewaters are treated poorly and water regulations are frequently violated [9,10]. Pathogenic bacteria can also withstand treatment methods applied in wastewater treatment plants—pathogens have been detected in effluent waters [11].

The abundance of pollutants in water raises the need for suitable

remediation techniques. Physical, chemical, and biological approaches are used to remove toxic chemicals such as adsorption, photocatalytic degradation and catalytic reduction [2,7,12,13]. Catalytic reduction of nitrophenols to the environmentally benign aminophenols is a safe and useful approach as they benefit many industries [14]. Aminophenols are commonly used in the manufacturing of organic dyes, pharmaceuticals, wood stains, pesticides, surfactants and corrosion inhibitors in paints [14,15].

Carbon-based nanomaterials embedded with metal nanoparticles or magnetic solids (such as iron oxides) demonstrate great potential to serve as recyclable disinfectants and catalysts [16–20]. Single-walled carbon nanotubes (SWCNTs) exhibit antibacterial properties [21] that can be enhanced further by incorporating toxic Ag nanoparticles [22,23]. Ag nanoparticles loaded onto carbon micro- and nanostructures assist the catalytic reduction of *p*-nitrophenols through a redox mechanism that is dependent on Ag loading [24–26]. Umamaheswari et al. [27] showed that the catalytic reduction of methyl orange with a gold catalyst was also achieved due to the transfer of electrons

* Corresponding author.

E-mail address: benny.chefetz@mail.huji.ac.il (B. Chefetz).

from NaBH_4 , resulting in the formation of hydrazine derivatives. However, little information is available on the catalytic reduction of other nitrophenols such as alkyl substituted and *o*-nitrophenols, which are equally toxic and on the catalytic reduction of methyl orange by other materials. Both natural waters and wastewaters contain dissolved organic matter (DOM), a reactive heterogeneous mixture of soluble organic compounds with various aliphatic and aromatic moieties [28,29]. The presence of humic acid or natural organic matter is known to suppress the adsorption of pollutants to carbonaceous materials [30–32].

The aim of this study was to develop a bifunctional composite that maintains both high catalytic and antibacterial activity. We tested the composite's ability to reduce nitrophenols and methyl orange and to inactivate gram-positive and gram-negative bacteria. The impact of DOM on the efficiency of the composite was investigated at environmentally relevant ($5\text{--}10\text{ mg C L}^{-1}$) and high ($40\text{--}50\text{ mg C L}^{-1}$) concentrations, which are observed in wastewaters.

2. Materials and methods

2.1. Chemicals

SWCNTs (outer diameter 1–2 nm; length 5–30 nm) were supplied by Chengdu Organic Chemistry Co., Ltd. (Chengdu, China). Silver nitrate (AgNO_3 , 99.7%) was purchased from J.T. Baker Chemical Co., Phillipsburg, NJ, USA. Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 97%), ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 99.5%), sodium borohydride (NaBH_4 , > 98%) and ammonia solution (NH_4OH , 28–30%) were supplied by Aldrich Chemical Company, Inc., USA, BDH Laboratory Supplies Poole, England, Acros Organics, USA, and Merck, Germany, respectively. *p*-Nitrophenol, *o*-nitrophenol, 2-methyl-*p*-nitrophenol and methyl orange (Table S1) were purchased from Sigma-Aldrich, Israel.

2.2. Synthesis of the Ag- Fe_3O_4 -SWCNT composite

The SWCNTs were initially oxidized in HNO_3 3 M solution in a bath sonicator for 12 h, followed by their separation by vacuum filtration ($0.45\text{ }\mu\text{m}$) [20]. The oxidized SWCNTs were then washed with deionized water until the solution pH reached 7, air-dried and heated in an oven at $100\text{ }^\circ\text{C}$ for 2 h. Next, magnetic Fe_3O_4 nanoparticles were incorporated by adding 1 g oxidized SWCNTs into a 300 mL mixture of FeCl_3 and FeSO_4 (at a 2:1 ratio) [20]. The solution was vigorously stirred for 30 min, after which NH_4OH solution was added drop-wise (until pH 9), and the solution temperature was raised from room temperature to $70\text{ }^\circ\text{C}$ for 1 h before cooling down. The Fe_3O_4 -SWCNT material was then filtered by vacuum filtration ($0.45\text{ }\mu\text{m}$), washed several times with copious amount of deionized water, air-dried for 12 h and finally vacuum-dried for 24 h. Fe_3O_4 nanoparticles were also synthesized as described above in the absence of the SWCNTs. Finally, Ag nanoparticles were embedded into the Fe_3O_4 -SWCNTs. A mixture of ice-cooled 0.005 M NaBH_4 (30 mL) and 1 g of the Fe_3O_4 -SWCNTs was agitated using a magnetic stirrer for 30 min. 20 mL of 0.0025 M AgNO_3 were then added drop-wise into the solution under continuous stirring during which the colorless solution turned yellow. Stirring was continued for another 2 h after which the mixture was centrifuged for 40 min, and the product was washed with copious amount of deionized water to remove any reaction byproducts. The Ag- Fe_3O_4 -SWCNT composite was freeze-dried at $-60\text{ }^\circ\text{C}$ for 2 days (to prevent the oxidation of Ag nanoparticles) and finally stored in a desiccator until use. Ag nanoparticles were also fabricated as described above in the absence of the Fe_3O_4 -SWCNTs.

2.3. Characterization of the composite

Surface morphology and elemental composition were determined using an extra high resolution scanning electron microscope (SEM)

(Magellan TM 400 L) complemented with bright field scanning transmission electron microscopy imaging (STEM) at accelerating voltages of 5 and 30 kV, respectively. Energy dispersive X-ray (EDX) information was recorded with Oxford INCAX-sight software. Thermo-gravimetric analysis (TGA) was performed with a TGA Q500 TA instrument, New Castle, DE, USA. The extent of graphitic contents and structural defects in the prepared materials was evaluated using an Alpha confocal Raman instrument (Witec, Germany) with an Ar-ion laser at an excitation wavelength of 514 nm. Surface area and pore volume distribution were determined using a NOVA e series high speed surface area and pore size analyzer (Quantachrome, USA). Surface area of the prepared materials was evaluated using N_2 -adsorption with multi-point BET method at 77.35 K at a relative pressure (P/P_0) range of 0.05–0.3. Meso- and micropore volumes were determined using BJH desorption and t-plot methods, respectively. Surface elemental composition was evaluated using an AXIS-Ultra^{DL} X-ray electron Spectrometer (XPS) equipped with a monochromatic Al source, (Kratos Analytical Ltd, UK). Surface functional groups in the synthesized materials were recorded using a NICOLET 6700 FT-IR (Thermo Scientific, USA). Material crystallinity was determined using an X-ray diffractometer D8 Advance (Bruker AXS GmbH, Germany) with Cu $K\alpha$ radiation ($K = 1.54\text{ \AA}$). Room temperature magnetization plot of the composite material was obtained using a MPMS-3 instrument (LOT-Quantum Design GmbH, Germany). C-H-N-S elemental composition of the prepared materials was evaluated with a Flash EA 1112 CHN analyzer (Thermo Fisher Scientific Inc., Breda, The Netherlands).

2.4. DOM extraction

DOM was extracted from composted bio-solids by mixing the bio-solids with deionized water (at a 1:10 ratio) at 250 rpm for 12 h [33]. Next, the suspension was centrifuged at 12,000 g for 30 min, and the DOM extract was separated by vacuum filtration, initially through a 1 μm filter, followed by a $0.45\text{ }\mu\text{m}$ filter (Acrodisc Supor membrane, PALL Corp., Ann Arbor, MI, USA). Dissolved organic carbon (DOC) content in the fresh extract was evaluated using a total organic carbon analyzer (TOC Analyzer, Make: Shimadzu, Japan).

2.5. Catalytic reduction of pollutants by the composite

Catalytic reduction of *o*-nitrophenol, *p*-nitrophenol, 2-methyl-*p*-nitrophenol, and methyl orange with NaBH_4 (reducing agent) was performed in a 50 mL solution containing 0.1 M NaBH_4 , 0.01 M of the nitrophenols or methyl orange and 4 mg of the composite material under continuous stirring (excess NaBH_4 was present to ensure its constant availability). NaBH_4 is considered a thermally stable hydride [34] which produces sodium metaborate (NaBO_2) – used to manufacture borosilicate glasses and as a component of herbicides and antifreeze [14]. As the reaction proceeded, solution color changed from bright yellow (nitrophenols) or orange (methyl orange) to colorless, indicating reduction of the nitrophenols and methyl orange to the corresponding aminophenols and hydrazine derivative, respectively [27]. Aliquots were collected periodically (the composite was separated with an external magnet), filtered through a $0.22\text{ }\mu\text{m}$ hydrophobic syringe filter and analyzed using a UV–vis spectrometer. In the solution, the alkaline condition was produced by the presence of NaBH_4 to facilitate the formation of phenolate anions and also the alkaline environment is responsible for the bathochromic shift of the phenol's spectra. However, no such peak shift was observed for methyl orange. The characteristic peak maxima for *o*-nitrophenol, *p*-nitrophenol, 2-methyl-*p*-nitrophenol and methyl orange absorption were 415, 400, 413 and 465 nm in the presence of NaBH_4 and 350, 317, 327, and 465 nm in its absence, respectively [27,35,36]. The influence of DOM on the reduction reaction was examined at 5 and 50 mg C L^{-1} . The corresponding pH values for all systems were 10.0 ± 0.2 and 9.9 ± 0.3 in the absence and presence of DOM, respectively.

Download English Version:

<https://daneshyari.com/en/article/6663858>

Download Persian Version:

<https://daneshyari.com/article/6663858>

[Daneshyari.com](https://daneshyari.com)