



Research paper

Preparation of Fe₃O₄-rGO via a covalent chemical combination method and its catalytic performance on p-NP bioreductionHaikun Zhang^{a,b}, Xiaoke Hu^{a,*}^a Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai 264000, China^b Key Laboratory of Industrial Ecology and Environmental Engineering, Ministry of Education, School of Environmental Science and Technology, Dalian University of Technology, Dalian 116024, China

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ABSTRACT

Magnetic amino-reduced graphene oxide was successfully fabricated via a covalent chemical combination method. Fe₃O₄ was first reacted with polyacrylic acid (Fe₃O₄-COOH) and then reacted with diethylenetriamine; finally, the amino modified Fe₃O₄ (Fe₃O₄-NH₂) was introduced as magnetic carrier and reductant to reduce graphene oxide to obtain Fe₃O₄-rGO. SEM, AFM, FTIR, XRD and XPS analyses were performed to analyze the synthesized materials. The catalytic performance of Fe₃O₄-rGO was investigated through the bioreduction of p-nitrophenol (p-NP) in the presence of *Shewanella* sp. CNZ-1. The results showed that p-NP bioreduction could be enhanced in a dose-dependent manner of Fe₃O₄-rGO. The p-NP reduction rate could achieve 0.92 mmol/(d gcell) in the presence of 25 mg/L Fe₃O₄-rGO, which was approximately 4.18-fold higher than that lacking Fe₃O₄-rGO. In addition, the experimental kinetic data of Fe₃O₄-rGO mediated p-NP bio-reduction fit well with the pseudo-first-order model ($R^2 > 0.96$). These findings indicate that Fe₃O₄-rGO could be used in designing a bioreactor for enhancing the treatment of p-NP containing wastewater.

1. Introduction

Graphene (G) has attracted much attention because of its combination of large surface area and excellent mechanical, electrical, thermal and optical properties with ultrathin thickness [1–3]. Thus far, many kinds of graphene-based materials (GBMs) have been fabricated for further extending their application areas, including materials science, electronics, optoelectronics, and electrochemical and biomedicine [2–4]. In recent years, environmental issues have attracted a lot of attention as the environmental pollution affected human beings' health enormously, the potential application of GBMs in environmental aspects have thus inspired huge interest of many researchers [5–14].

Up to now, considerable studies showed that GBMs are excellent platforms for environmental applications in the detection of nonorganic ions [5–7], biomolecules and organism [8], and the adsorption of environmental pollutants, including heavy metal ions [9–11], gas and organic pollutants [12]. Graphene could mediate the reductive transformation of a toxic compound nitrobenzene in the presence of electron donor, because the basal plane of graphene could serve as the conductor for transferring electrons from the electron donors to the electron acceptors [12]. Besides, GBMs were further proven to be capable of enhancing bioreduction of some N-substituted aromatic compounds

[12,13] and heavy metals [12,14]. Our study also proved that the bioreduced GO is of good electrical conductivity in enhancing azodye reduction in the presence of *Shewanella algae* [13]. GBMs has the potential to use in so many environmental areas, however, it's difficult to recycle these expensive materials due to that they are some materials with nano scale. To realize the efficient recycling of GBMs is the problem need to be solved before their industrial application. In this regard, magnetic materials (MMs) have been brought into sharp focus.

Decorating MMs on GBMs will impart the desirable magnetic property into GBMs, making the composite recyclable. It is believed that hybrids of G and MMs would have better performances in environmental remediation. Accordingly, the synthesis methods of magnetic GBMs need to be further improved from practical applications perspective. For example, Szabo et al. have obtained G-Fe₃O₄ hybrids by loading tris (2,20-bipyridl) Fe²⁺ ions on GO through ion exchange and subsequent calcinations [15]. Yang et al. reported that the preparation of GO-Fe₃O₄ composites could be obtained by a chemical precipitation method [16]. Cong et al. decorated reduced GO sheets with Fe₃O₄ by high temperature decomposition of the precursor Fe³⁺ acetylacetonate [17]. A number of researchers have proposed physical and chemical methods for the preparation of magnetic graphene hybrids, however, there are still drawback in practical applications: since

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the Fe₃O₄ nano particles are attached to the graphene only by physical absorption or electrostatic interaction, they may easily deviate from the graphene during application. Up to now, to the best of our knowledge, limited reports have managed to fabricate magnetic graphene hybrids by covalent chemical combination method, which can bind MMs and GO tightly [18]. Thus, we developed a covalent chemical combination method for preparing Fe₃O₄/Graphene nanocomposite (Fe₃O₄-rGO) in this study.

In addition, nitroaromatic compounds and their derivatives (NCDs) exhibit serious mutagenic and carcinogenic effects toward humans and wildlife and have been listed as a priority pollutant [19]. In most cases, biotreatment constitutes the primary mechanism for NCDs removal due to its eco-friendliness and low cost. Thus, p-nitrophenol (p-NP) was selected as a typical contaminant, the catalytic performance of Fe₃O₄-rGO on p-NP bioreduction was investigated in the presence of an electrochemical active bacterium, *Shewanella* sp. CNZ-1. The purpose of this study is to develop a recyclable GBM via a stable and controllable method and to investigate its catalytic effect on p-NP bioreduction by strain CNZ-1. During this process, the reaction kinetic of p-NP reduction was analyzed by zero-order and pseudo-first-order model, respectively.

2. Materials and methods

2.1. Chemicals

p-NP was purchased from Tokyo Chemical Industry Co., Ltd (Tokyo, Japan). 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) was purchased from Shanghai Macklin Biochemical Co., Ltd (China). GO was purchased from Nonoon Technologies Co., Ltd (China). All other reagents used in this study were of the highest analytical grade.

2.2. Cultivation of bacteria strain

Strain *Shewanella* sp. CNZ-1 (GenBank accession number KX384589), a member of electrochemical active bacteria, was selected in this study. CNZ-1 was grown aerobically in Luria-Bertani (LB) broth (5 g/L yeast extract, 10 g/L peptone, and 10 g/L NaCl) in an orbital shaker operating with a speed of 150 rpm at 30 °C. p-NP reduction experiments were conducted in mineral salt medium (MSM) containing 2 g/L sodium lactate, 1.0 g/L (NH₄)₂SO₄, 0.8 g/L Na₂HPO₄, 0.2 g/L KH₂PO₄, 0.2 g/L MgSO₄·7H₂O, 0.1 g/L CaCl₂·2H₂O, 20 g/L NaCl (pH 7.2). All the p-NP reduction experiments were conducted in dark to avoid photolysis.

2.3. Preparation of Fe₃O₄-rGO and its characterisation

First, Fe₃O₄-COOH was synthesized according to the method described as follows [20]: 1.0 g Fe₃O₄ nanoparticles and 20 mL buffer solution (BS, including 3 mM phosphoric acid and 100 mM NaCl) were mixed in a 250 mL flask. Then, 5 mL EDC solution (2.5 wt%, with the treatment of light avoidance) was added. After 20 min sonication, 25 mL polyacrylic acid (6 wt%) were added and reacted for 2 h at 25 °C. The as-prepared product (Fe₃O₄-COOH) was washed twice with deionized water. The Fe₃O₄-COOH was separated by magnet for further study.

Second, Fe₃O₄-rGO was prepared by the following steps: (i) 1.0 g Fe₃O₄-COOH, 45 mL BS and 5 mL EDC solution were first mixed by water bath sonication for 20 min at 25 °C; Then, 5 mL diethylenetriamine were added to the mixture in a 250 mL flask; The flask was placed in a water bath at 98 °C and stirred for ~6 h; The product (Fe₃O₄-NH₂) was cooled to room temperature and washed twice with deionized water. (ii) 0.1 g graphene oxide was dissolved in 90 mL BS and 10 mL EDC solution by water bath sonication for 1 h. Sequentially 1.0 g Fe₃O₄-NH₂ was added in above solution with a 250 mL round-bottom flask; The flask was placed in a water bath at 98 °C and stirred

for ~24 h; The products (Fe₃O₄-rGO) were cooled to room temperature, washed with deionized water, and separated by magnet. Finally, Fe₃O₄-rGO was dried in a vacuum freeze drying equipment for the following experiments.

In addition, another chemical reduced GO (NH₂-rGO) was used as control to describe the property changes of Fe₃O₄-rGO during above modification. The chemical reduced rGO was obtained by following steps: (i) 0.1 g graphene oxide was dispersed in 100 mL deionized water (pH = 10 adjusted by adding ammonia); (ii) 3 mL diethylenetriamine as a reducing agent was added into the mixed solution after it was heated to 98 °C using water bath; (iii) The products (NH₂-rGO) was separated and washed with deionized water after 6 h of reaction.

Scanning electron microscope (SEM, Hitachi S-4800, Japan), Atomic Force Microscope (AFM, Veeco DI 3100, U.S.A.), Fourier transform infrared spectroscopy (FTIR, Jasco FT/IR-4100, Japan), X-ray diffraction patterns (XRD, RIGAKU 18 KW, Japan) and X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, England) were used to investigate the morphology and chemical compositional changes on the surface of the Fe₃O₄ nano particles, GO, NH₂-rGO and Fe₃O₄-rGO. The magnetization curves of the Fe₃O₄ and Fe₃O₄-rGO were examined using a vibrating sample magnetometer (VSM, Lake Shore 7410, USA).

2.4. Enhanced p-NP bioreduction by Fe₃O₄/graphene nanocomposite

For bioreduction assays, strain CNZ-1 was first cultured overnight in LB in a rotary incubator shaker at 150 rpm, 30 °C. Then, the CNZ-1 cells were harvested by centrifugation (10,000 rpm, 5 min) and washed twice with a sterile phosphate buffer solution (PBS, 10 mM, pH 7.0). At last, the cell pellets were resuspended with MSM and held in an anaerobic chamber. The experimental systems utilised 135 mL serum bottles containing 0.1 mM p-NP and 100 mL deoxygenated sterile MSM. The CNZ-1 cells were added into the systems at a final concentration of 0.1 g L⁻¹. After cell inoculation, samples were periodically taken with a sterile needle and a syringe for the analysis of p-NP. Repeated batch operations were carried out to investigate the stability and persistence of Fe₃O₄-rGO. All treatments and controls were run in triplicate.

2.5. Analytical methods

The samples were first treated by centrifugation (12,000 rpm, 2 min) and the supernatant was used for further analysis. The P-NP concentration was determined by UV-vis spectrophotometer at its characteristic absorption peaks. For reduction products analysis, the supernatant was filtrated using 0.22 μm filter membrane and then directly injected into the mass spectrometer (mobile phase: methanol at 1.0 mL/min). The reduction rate of p-NP was calculated using Eq. (1) [14] as follows:

$$\text{Reduction rate} = \frac{C_i - C_t}{mt} \quad (1)$$

Where C_i (mg/L) and C_t (mg/L) are the initial and residual P-NP at time zero and t, respectively; m (g cell/L) is the dry weight of the cells; t (h) is the reaction time.

A zero-order model was applied to describe the kinetics of P-NP bioreduction. The zero-order rate constant k₁ (mol L⁻¹ d⁻¹) was determined according to the following Eq. (2), where t (h), C₀ (mg/L) and C_t (mg/L) are the reaction time, the initial and residual P-NP at time zero and t, respectively.

$$C_0 - C_t = k_1 t \quad (2)$$

A pseudo-first-order model was used to describe the kinetics of P-NP bioreduction. The first-order rate constant k₂ (d⁻¹) was determined according to the following Eq. (3), where t (h), C₀ (mg/L) and C_t (mg/L) are the reaction time, the initial and residual P-NP at time zero and t, respectively.

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