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Graphene-supported nanoscale zero-valent iron: Removal of phosphorus from aqueous solution and mechanistic study

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ABSTRACT

Excess phosphorus from non-point pollution sources is one of the key factors causing eutrophication in many lakes in China, so finding a cost-effective method to remove phosphorus from non-point pollution sources is very important for the health of the aqueous environment. Graphene was selected to support nanoscale zero-valent iron (nZVI) for phosphorus removal from synthetic rainwater runoff in this article. Compared with nZVI supported on other porous materials, graphene-supported nZVI (G-nZVI) could remove phosphorus more efficiently. The amount of nZVI in G-nZVI was an important factor in the removal of phosphorus by G-nZVI, and G-nZVI with 20 wt.% nZVI (20% G-nZVI) could remove phosphorus most efficiently. The nZVI was very stable and could disperse very well on graphene, as characterized by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). X-ray photoelectron spectroscopy (XPS), Fourier Transform infrared spectroscopy (FT-IR) and Raman spectroscopy were used to elucidate the reaction process, and the results indicated that Fe-O-P was formed after phosphorus was adsorbed by G-nZVI. The results obtained from X-ray diffraction (XRD) indicated that the reaction product between nZVI supported on graphene and phosphorus was $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ (Vivianite). It was confirmed that the specific reaction mechanism for the removal of phosphorus with nZVI or G-nZVI was mainly due to chemical reaction between nZVI and phosphorus.

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Introduction

Many freshwater lakes in China are suffering from the detrimental effects of eutrophication. The eutrophication may cause a series of problems for the lakes, such as reducing light transmission, decreasing biodiversity, and generating algal blooms (Sutcliffe and Jones, 1992). Nutrient enrichment is the main reason leading to the eutrophication in lakes (Palmer-Felgate et al., 2010). As one of the main mineral nutrients, phosphorus is an

essential and important element for all natural organisms (Ryther and Dunstan, 1971; Correll, 1998). Many structural and biochemically functional components of alga cells also need phosphorus (Dorich et al., 1984). However, if phosphorus has been over-supplied, for example, when the phosphorus concentration in lakes is higher than 0.02 mg/L, eutrophication will occur (Bennion et al., 1996; Lewis et al., 2011). As the primary limiting factor for algal growth, the role of phosphorus in the process of eutrophication had been identified several decades ago (Zhou et al., 2005).

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In many municipal wastewater treatment plants, phosphorus is removed by chemical or biological precipitation. In contrast, there is no good way to remove phosphorus from non-point pollution sources, such as urban rainwater runoff and farmland runoff. As point source pollution has been better controlled, controlling non-point source pollution becomes more and more important for most lakes in China. In order to control the eutrophication of lakes, it is essential to remove the phosphorus from non-point pollution sources. Phosphorus adsorption processes using natural sediments and pure minerals have drawn considerable attention (Lamers et al., 1998; Hongshao and Stanforth, 2001; Kim et al., 2003; Royer et al., 2006; Sibrell et al., 2009). However, there are still many challenges associated with the application of those technologies. It is necessary to find a highly efficient and low-cost process to remove phosphorus from non-point pollution sources, especially rainwater runoff or farmland runoff.

Nanoscale zero valent iron (nZVI) is one of the latest discoveries that takes advantage of the unique characteristics of small-sized particles, large surface area and high in-situ reactivity, which can provide greater reaction capability for pollutant removal than conventional microscale materials. Its potential application in environmental engineering has been known for about ten years (Ponder et al., 2000), but there are still very few reports about its engineering application (Wei et al., 2010; Su et al., 2012). nZVI has the ability to reduce oxidized pollutants (Joo et al., 2004; Zhang et al., 2009), chlorinated solvents and nitrate contaminants, etc. (Choe et al., 2000; Liou et al., 2006; Shin and Cha, 2008; Kim et al., 2010; Jiang et al., 2011). Metal ions including Cr(VI), Pb(II) and As(V) can also be removed by nZVI (Ponder et al., 2000; Kanel et al., 2005; Hoch et al., 2008; Shi et al., 2011; Zhang et al., 2011). Although nZVI has many advantages, there are still some potential limitations and challenges, including: (1) nZVI is lacking in durability, its mechanical strength is weak (Cumbal et al., 2003); (2) nZVI can be quickly transformed to iron oxides when exposed to the air (Nurmi et al., 2005), (3) it is hard to prevent nZVI particles from aggregating (Liu et al., 2007).

To overcome these shortcomings, technologies have been developed using some materials as mechanical supports to enhance the dispersion of nZVI particles. Many studies have been carried out on the use of porous materials to support nZVI, e.g., nZVI particles supported on resin were used to remove CrO_4^{2-} and Pb^{2+} in aqueous solution, the resin supported 22.6 wt.% of nZVI and the results showed that the adsorption rates for CrO_4^{2-} and Pb^{2+} were up to 30 times higher than the adsorption rates using iron filings or powder (Joo et al., 2004). Kaolinite was selected as the supporting material loaded with 20 wt.% nZVI (K-nZVI) (Zhang et al., 2011), and it could remove Pb^{2+} from aqueous solution as its concentration was very high, and the removal efficiency was 96.7%; but when using bare nZVI as the adsorption material, the removal efficiency for Pb^{2+} was only 16.8% (Zhang et al., 2011). Bentonite-supported nanoscale zero-valent iron (B-nZVI) containing 40 wt.% nZVI was used to remove some metal pollutants, and the removal efficiencies for Cr, Pb and Cu were higher than 90% (Shi et al., 2011).

In the above reports, some three-dimensional porous materials were used as the supporting materials for nZVI due to their good characteristics, such as relatively high specific surface area, large numbers of active sites, etc. However, a typical two-dimensional material, graphene, was used to support nZVI in this paper, and its capability and mechanism for phosphorus removal from aqueous solutions was investigated. After the character of graphene was first reported in 2004 (Novoselov et al., 2004), there have been increasing studies focused on its properties and applications. Due to the strictly two-dimensional structure, graphene has some extraordinary properties, such as low resistivity, and high mobility of charge carriers (Stankovich et al., 2006; Geim and Novoselov, 2007). Graphene can be used as a good supporting material because it is very stable and it has very large specific surface area. Compared with other supports, graphene exhibited very good iron dispersion and stabilization, leading to excellent efficient phosphorus removal.

1. Materials and methods

1.1. Materials and chemicals

The chemical reagents used (NaBH_4 , HCl, NaOH, KH_2PO_4 , $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) were reagent grade and obtained from Sinopharm Chemical Reagent. The activated carbon, 13X molecular sieve, diatomite and activated alumina were purchased from Sinopharm Chemical Reagent. The nZVI material was synthesized as follows: 1.0 mol/L sodium borohydride (NaBH_4) aqueous solution was added into a N_2 gas-purged 0.5 mol/L $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ aqueous solution at 25°C with magnetic stirring as described by Wang and Zhang (1997). When the NaBH_4 solution was added, the mixture was continuously stirred for 20 min. The prepared materials were separated from the liquid phase via vacuum filtration, and the black solid was dried under vacuum at 70°C overnight (Zhang et al., 2011). All iron materials were stored in N_2 -purged desiccators.

The graphitic oxide was synthesized by oxidation of purified natural graphite flakes according to Hummer's method (Hummers and Offeman, 1958). Graphene sheets were prepared by Li's method (Li et al., 2008).

The graphene-supported nZVI (G-nZVI) material was prepared using the following method: 2.5 mL of 0.5 mol/L $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ aqueous solution was dropped into 0.5 g graphene at 25°C until the graphene turned to jelly. The jelly was dried in the oven for 10 min. The last two steps were repeated until the mass content of iron became a specific proportion in the mixture, such as 7%, 12%, 20%, 40%, 50%, and 60%. Then, 50 mL of 1.0 mol/L NaBH_4 aqueous solution was dropped into the series of mixtures at 25°C with magnetic stirring under N_2 protection. The dropping rate was 20–30 drops per minute. After the NaBH_4 solution was added, the mixture was continuously stirred for 20 min. The prepared materials were separated from the liquid phase via vacuum filtration and the resulting black solid was vacuum-dried at 70°C overnight. Other materials (activated carbon, 13X molecular sieve, diatomite and activated alumina) used to support nZVI were loaded with nZVI by the same method as used for the synthesis of the G-nZVI material.

1.2. Characterization

X-ray diffraction (XRD) patterns of G-nZVI and nZVI samples were measured on a Bruker D8 Advance diffractometer with a high-power Cu-K α X-ray source (generator tension = 40 kV, current = 40 mA). Continuous scans from 5° to 90° of 2 θ were collected at a scan rate of about 6° of 2 θ /min.

The G-nZVI and nZVI materials were characterized by X-ray photoelectron spectroscopy (XPS) using a Physical Electronics Quantum instrument (VG ESCALAB 250, England). The binding energy of the spectra was calibrated with the C 1s peak of adventitious carbons at 284.6 eV.

The Fourier Transform infrared spectroscopy (FT-IR) detection of G-nZVI and nZVI used a Nicolet 6700 spectrometer (Thermo Corp., USA). The sample was prepared by mixing 1 wt.% specimen with 100 mg of KBr powder. The mixture was pressed into a sheer slice. Then, the average over 9 scans was collected for each measurement with a resolution of 4 cm^{-1} , and the scan range was from 4000 to 400 cm^{-1} .

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