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$Fe@Fe_2O_3$ core-shell nanowires enhanced Fenton oxidation by accelerating the Fe(III)/Fe(II) cycles

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ABSTRACT

In this study we demonstrate $Fe@Fe_2O_3$ core–shell nanowires can improve Fenton oxidation efficiency by two times with rhodamine B as a model pollutant at $pH > 4$. Active species trapping experiments revealed that the rhodamine B oxidation enhancement was attributed to molecular oxygen activation induced by $Fe@Fe_2O_3$ core–shell nanowires. The molecular oxygen activation process could generate superoxide radicals to assist iron core for the reduction of ferric ions to accelerate the Fe(III)/Fe(II) cycles, which favored the H_2O_2 decomposition to produce more hydroxyl radicals for the rhodamine B oxidation. The combination of $Fe@Fe_2O_3$ core–shell nanowires and ferrous ions ($Fe@Fe_2O_3/Fe^{2+}$) offered a superior Fenton catalyst to decompose H_2O_2 for producing •OH. We employed benzoic acid as a probe reagent to check the generation of •OH and found the •OH generation rate of $Fe@Fe_2O_3/Fe^{2+}$ was 2–4 orders of magnitude larger than those of commonly used iron based Fenton catalysts and 38 times that of Fe^{2+}. The reusability and the stability of $Fe@Fe_2O_3$ core–shell nanowires were studied. Total organic carbon and ion chromatography analyses revealed the mineralization of rhodamine B and the releasing of nitrate ions. Gas chromatograph-mass spectrometry was used to investigate the degradation intermediates to propose the possible rhodamine B Fenton oxidation pathway in the presence of $Fe@Fe_2O_3$ nanowires. This study not only provides a new Fenton oxidation system for pollutant control, but also widen the application of molecular oxygen activation induced by nanoscale zero valent iron.

1. Introduction

Environmental pollution in the world has evoked increasing concern (Ai et al., 2005). Advanced oxidation processes (AOPs) have been widely applied for organic pollutant treatment because of their generation of strongly oxidizing hydroxyl radicals (•OH), which are highly reactive and can oxidize most organic substances rapidly and non-selectively (Andreozzi et al., 1999). Among the AOPs, Fenton reaction (Fe^{2+}/H_2O_2) is very attractive because of its high performance, simplicity of technology, and environmental friendliness of the reagents

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(Fenton, 1894). Normally, hydroxyl radicals could be generated in Fenton system via the following reactions.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {\bullet}OH + OH^- \quad k_1 = 63\ M^{-1}\ s^{-1} \tag{1}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + {\bullet}HO_2 + H^+ \quad k_2 = 2.7 \times 10^{-3}\ M^{-1}\ s^{-1} \tag{2}$$

$${\bullet}HO_2 \leftrightarrow {\bullet}O_2^- + H^+ \quad k_3 = 1.6 \times 10^{-5} M^{-1} \tag{3}$$

$${\bullet}OH + H_2O_2 \rightarrow {\bullet}HO_2 + H_2O \quad k_4 = 2.7 \times 10^{7}\ M^{-1}\ s^{-1} \tag{4}$$

$${\bullet}OH + Fe^{2+} \rightarrow Fe^{3+} + OH^- \quad k_5 = 3 \times 10^{8}\ M^{-1}\ s^{-1} \tag{5}$$

$$Fe^{3+} + {\bullet}HO_2 \rightarrow Fe^{2+} + O_2 + H^+ \quad k_6 = 2 \times 10^{3}\ M^{-1}\ s^{-1} \tag{6}$$

$$Fe^{2+} + {\bullet}HO_2 + H^+ \rightarrow Fe^{3+} + H_2O_2 \quad k_7 = 1.2 \times 10^{6}\ M^{-1}\ s^{-1} \tag{7}$$

$${\bullet}HO_2 + {\bullet}HO_2 \rightarrow H_2O_2 + O_2 \quad k_8 = 8.3 \times 10^{5}\ M^{-1}\ s^{-1} \tag{8}$$

However, the widespread application of Fenton reaction is still limited by its narrow working pH range (2.5–4), high cost of H_2O_2, and the accumulation of ferric oxide sludge (Zhang et al., 2010; Ensing et al., 2003). These drawbacks could be overcome by the strategies such as the utilization of organic chelators like ethylenediamine tetraacetate to prevent the precipitation of ferric iron (Chen et al., 2011; Wang et al., 2011), and the irradiation under UV light to accelerate the cycling of Fe(III)/Fe(II) which is called photo-Fenton system (Ma et al., 2005; Vermilyea and Voelker, 2009), as well as the development of heterogeneous Fenton systems with Fe-containing zeolites, clays supported catalyst and non-porous solids (Luo et al., 2010; Song et al., 2006; Navalon et al., 2011; Hermanek et al., 2007; Baldrian et al., 2006; Rusevova et al., 2014), and so on. Obviously, the addition of organic chelators would increase the cost, and also act as the additional •OH scavengers to lower the efficiency of contaminant oxidation, as well as might bring secondary pollution in environment application. Although abundant solar energy on the earth makes photo-Fenton system very promising, less than 5% of UV light in solar light hinders the application of photo-Fenton reaction. As for heterogeneous Fenton systems with advantages of wider working pH range and reusability of iron reagents, their oxidation efficiencies at $pH > 4$ are far from satisfactory. Therefore, it is of great importance to develop new Fenton system with high oxidation efficiency and wider working pH range.

The low oxidation efficiency of classical Fenton systems at $pH > 4$ is mainly attributed to the formation of insoluble ferric products, which blocks the cycling of Fe(III)/Fe(II). Moreover, the oxidation ability of •OH at high pH becomes weaker. For example, the oxidation potential of hydroxyl radicals decrease from 2.80 V at pH = 0–1.90 V at pH = 7 (Babuponnusamia and Muthukumar, 2012). As the own oxidation ability of •OH could not be changed without changing the pH value, the efficient cycling of Fe(III)/Fe(II) becomes a facile solution to enhance oxidation efficiency of Fenton systems at high pH.

Our group found that $Fe@Fe_2O_3$ core–shell nanowires, a special kind of nanoscale zero valent iron developed by us, could be used as an effective heterogeneous Fenton iron reagent to degrade dye and pentachlorophenol, and dimethyl phthalate (Ai et al., 2007a, 2007b; Luo et al., 2008; Chen et al., 2012), as well as a reductant/adsorbent to efficiently remove Cr(VI) (Ai et al., 2008). Recently, we demonstrated that $Fe@Fe_2O_3$ nanowires could induce two-electron molecular oxygen activation to generate H_2O_2 via the outward electron transfer from iron core to the iron oxide shell surface and single-electron molecular oxygen activation to produce ${\bullet}O_2^-$ ($pH > 4.8$) by the surface bound ferrous ions on the iron oxide shell (Ai et al., 2013). Obviously, the generation of H_2O_2 and ${\bullet}O_2^-$ via molecular oxygen activation by $Fe@Fe_2O_3$ nanowires might not only enhance the amount of reactive oxygen species (ROSs), but also accelerate the cycling of Fe(III)/Fe(II) at high pH, because H_2O_2 and ${\bullet}O_2^-$ can reduce ferric ions into ferrous ions ($k = 2.7 \times 10^{-3}\ M^{-1}\ s^{-1}$ for H_2O_2; $k = 5 \times 10^{7}\ M^{-1}\ s^{-1}$ for ${\bullet}O_2^-$) (Brillas et al., 2009). The rate constants for ${\bullet}O_2^-$ with Fe(III) is ~10 orders of magnitude larger than that for H_2O_2 and Fe(III), thus the reaction of Fe(III) with H_2O_2 could be neglected in the presence of ${\bullet}O_2^-$, and the generation of ${\bullet}O_2^-$ inhibited the formation of insoluble ferric products more significantly. In comparison with other nanoscale zero valent iron, $Fe@Fe_2O_3$ core–shell nanowires possess two main advantages. First, the perfect coating of Fe_2O_3 shell can protect $Fe@Fe_2O_3$ core–shell nanowires from spontaneous combustion in air, which is beneficial for the storage and the shipping as well as the usage of nanoscale zero valent iron. Second, the surface adsorbed ferrous ion on the Fe_2O_3 shell of $Fe@Fe_2O_3$ core–shell nanowires can promote the one-electron reduction process to produce more ${\bullet}O_2^-$ radicals, endowing $Fe@Fe_2O_3$ core–shell nanowires with superior molecular activation reactivity (Ai et al., 2007a, 2013). Therefore, the combination of $Fe@Fe_2O_3$ nanowires induced molecular oxygen activation process with classical Fenton system might be a perfect way to develop new Fenton system with high oxidation efficiency at $pH > 4$, but never be reported previously.

The dye pollution remediation is an important environmental issue nowadays. More than 700,000 tons of dyestuffs are produced annually, and about 10–15% of these dyes are left in effluents during the synthesis and dyeing processes. In view of dyes' poor biodegradation property and excellent visibility even at low concentrations, it is of great importance to develop high efficient methods to remove dye pollutants from wastewaters (Robinson et al., 2001; Shi et al., 2007). Rhodamine B (RhB; molecular formula: $C_{28}H_{31}ClN_2O_3$; molecular weight: 479.01 g mol^{-1}; pKa = 3.7) is a highly water-soluble synthetic dye and widely used in the industrial printing and dyeing processes. It is toxic to some aquatic organisms and also thought to be a suspected carcinogen for human beings. Unfortunately, the conventional aerobic biological treatment of RhB is not feasible because of its complex structure and persistence (structure given below). In this study, we choose RhB as a model dye pollutant to systematically investigate the influence of $Fe@Fe_2O_3$ core–shell nanowires on Fenton degradation of dye pollutants at $pH > 4$. A series of experiments are designed to reveal the roles of