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Regular Article

Nanoparticles of magnetite anchored onto few-layer graphene: A highly efficient Fenton-like nanocomposite catalyst

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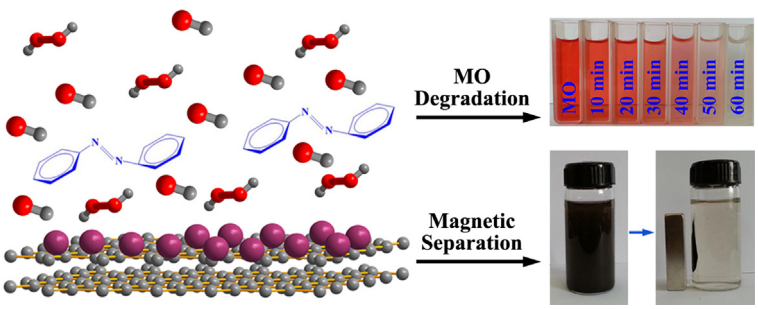
GRAPHICAL ABSTRACT



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ABSTRACT

Developing a catalyst with high efficiency and recyclability is an important issue for the heterogeneous Fenton-like systems. In this study, magnetic Fe_3O_4 and reduced graphene oxide (RGO) nanocomposites were prepared by a facile alkaline-thermal precipitation method and employed as a highly effective heterogeneous Fenton-like catalyst for methyl orange (MO) degradation. Characterization of these nanocomposites by XRD, FTIR, Raman, FESEM and TEM revealed that nanoparticles (NPs) of Fe_3O_4 were tightly anchored on the few-layer RGO sheets. The anchoring of Fe_3O_4 NPs and the reduction of GO were achieved in one pot without adding any other reducing agents. Based on the measurements of GO surface Zeta potentials, a possible anchoring mechanism of Fe_3O_4 NPs onto RGO sheets was given. The Fe_3O_4/RGO nanocomposites exhibited much higher Fenton-like catalytic efficiency for MO degradation than pure Fe_3O_4 NPs. This degradation process followed the first-order kinetics model, where k_1 and T complied with the Arrhenius equation with E_a of 12.79 kJ/mol and A of 8.20 s^{-1}. Magnetic measurements revealed that Fe_3O_4/RGO nanocomposites were ferromagnetic as indicated by the presence of magnetic hysteresis loops. The Fe_3O_4/RGO nanocomposites showed good stability and recyclability. Hydroxyl radicals, $^{\cdot}OH$ were determined as the dominant oxidative species in Fe_3O_4/RGO-H_2O_2 system and the Fenton-like mechanism for MO degradation in water was proposed and discussed.

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1. Introduction

Advanced oxidation processes (AOPs) have been widely accepted as promising approaches to treat refractory organic pollutants in wastewater due to their high degradation efficiencies.

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AOPs usually included ozonation, photocatalysis, sulfate radical-based oxidation, Fenton and Fenton-like processes, electrochemical and sonochemical oxidation [1–5]. Among these, Fenton reaction involves the *in situ* generation of highly oxidizing hydroxyl radicals (·OH) via the decomposition of H_2O_2 when catalyzed by iron ions. However, the homogeneous Fenton reagent had some limitations such as the acid working environment, the production of iron-containing sludge and the continuous loss of catalyst [6]. These limitations could be overcome by the application of heterogeneous solid catalysts where the iron ions are embedded in the structure. Therefore, some inorganic minerals and materials could work well as the heterogeneous Fenton-like catalysts because of their suitable crystal structures and chemical compositions with divalent and trivalent iron species. In recent years, magnetite (Fe_3O_4) has attracted increasing attention as a heterogeneous Fenton-like catalyst because of its low cost, non-toxicity, magnetic property and high stability. More interestingly, it is well-known from Haber-Weiss cycle of Fenton reaction (see Supplementary Information) that Fe_3O_4 could facilitate the generation of ·OH radicals in Fenton-like reaction, which is mainly ascribed to the coexistence of Fe (II) and Fe (III) in the octahedral sites of its structure. Furthermore, the smaller nanoparticles (NPs) of Fe_3O_4 have larger surface-to-volume ratio, which interact with substrate molecules and lead to higher catalytic activity [7]. Nevertheless, Fe_3O_4 NPs tend to aggregate into large granules or clusters in water, leading to the decrease of surface-to-volume ratio and consequently reduced catalytic activity. To resolve this problem, it is essential to highly disperse Fe_3O_4 NPs by anchoring onto a solid materials with large surface area, such as pillared bentonite [8], natural maifanite [9], porous silica nanofibers [10], porous carbon microspheres [11], and multiwalled carbon nanotubes [12]. Since Fe_3O_4 NPs exhibited poor adsorptive characteristics for organic substances in water [10], these supporting materials could also enhance the catalytic activity of Fe_3O_4 NPs with their synergistic adsorption capability.

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jcis.2018.07.128.

Graphene is an important allotrope of carbon in the form of two-dimensional structure composed of hexagonally close packed network of carbons [13]. Graphene exhibits unique and superior properties including extraordinarily high carrier mobility, superlative mechanical strength, excellent thermal and electrical conductivities, large specific surface area etc. [14]. These properties impart graphene and its derivatives with the potential to serve as platform of nanocatalysts with enhanced catalytic behavior [15]. Not surprisingly, graphene and its derivatives have been developed as the carriers for magnetic Fe_3O_4 NPs to catalyze H_2O_2 and propagate the Fenton circular reaction. For instance, graphene oxide (GO), a graphene derivative was used as the carrier of Fe_3O_4 NPs and a chemical precipitation route was used for anchoring of Fe_3O_4 NPs onto GO sheets. The obtained Fe_3O_4/GO nanocomposites exhibited high degradation efficiency of isatin, which was mainly attributed to the synergistic functionalities of Fe_3O_4 NPs and GO sheets [16]. Zubir et al. showed that, in heterogeneous Fenton-like reaction, Fe_3O_4/GO nanocomposites could show 20% higher degradation efficiency of Acid Orange 7 than pristine Fe_3O_4 NPs [17]. Later, they found that GO was a sacrificial agent in this process because of the oxidation of C=C domains accompanied by electron transfer to Fe_3O_4 [18]. Moreover, after the attack of highly reactive radicals (e. g. ·OH and $\cdot SO_4^-$), the overall oxygen-containing groups on GO sheets dramatically declined and sheet-like GO was decomposed into many smaller-size flakes and low-molecular-weight molecules suggesting that the chemical stability of GO in AOPs should be carefully assessed [19]. Therefore, reduced graphene oxide (RGO) was proposed as a support for Fe_3O_4 NPs. The Fe_3O_4/RGO nanocomposites were synthesized and employed as heterogeneous Fenton-like catalysts for the oxidation of methylene blue in a broad operating pH range of 5 to 9. The H_2O_2-activating ability of Fe_3O_4/RGO with 10.0 wt% RGO was found to be six times higher than that of pure Fe_3O_4 NPs [20]. Furthermore, the Fe_3O_4/RGO nanocomposites could work as novel catalytic materials with excellent photo-Fenton catalytic properties [21–23]. However, with regard to these previously reported Fe_3O_4/RGO nanocomposites, an additional preparation procedure was required for the reduction of GO with toxic and costly reducing agents such as hydrazine hydrate [20] and sargassum thunbergii [21]. So, it is still a challenge to obtain Fe_3O_4/RGO nanocomposites using a facile one-pot route. In addition, more studies are needed to further understand the kinetics and mechanism of Fenton-like reaction catalyzed by Fe_3O_4/RGO.

Here, we developed a facile alkaline-thermal precipitation method for *in situ* anchoring of Fe_3O_4 NPs onto RGO sheets. In this strategy, the anchoring of Fe_3O_4 NPs and the reduction of GO were simultaneously realized in one pot without adding any other reducing agents. Then, the resulting Fe_3O_4/RGO nanocomposites were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy (Raman), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM) and BET surface area analysis. In addition, the surface Zeta potential (ξ) of GO was measured. Based on these tests and analyses, the anchoring mechanism of Fe_3O_4 NPs onto RGO sheets was proposed. The Fenton-like efficiency of Fe_3O_4/RGO nanocomposites was evaluated using an azo dye, Methyl Orange (MO) as the target pollutant. The various factors affecting dye degradation, kinetics and mechanism of Fe_3O_4/RGO-H_2O_2 Fenton-like system were discussed. The magnetic property of Fe_3O_4/RGO catalyst was detected by vibrating sample magnetometer (VSM) and its stability and recyclability were investigated as well.

2. Materials and methods

2.1. Preparation of Fe_3O_4/RGO

A modified Hummers method previously reported in the literature [24] was employed for the preparation of GO using natural flakes of graphite powder (carbon content greater than 99.5%) as the raw material. Fe_3O_4/RGO nanocomposites were prepared by a facile alkaline-thermal precipitation method. In a typical procedure, 0.2 g GO was treated by ultrasonication for its complete exfoliation in 200 mL deionized water. Then, based on RGO content in the composites (5, 10, 15, 20, and 25 mass ratio (wt.%) in this study), a certain amount of ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) was added into the GO solution while ultrasonicating the mixture. After $FeSO_4 \cdot 7H_2O$ was completely dissolved, the conical flask with the mixed solution was transferred into a water-bath and heated to a set temperature (55, 65, 75, 85, or 95 °C) with mechanical stirring. Afterwards, 100 mL solution of NaOH and $NaNO_3$ with a mass ratio of 2:1 was added dropwise and then the resulting black suspension solution was kept at the set temperature for some time (1, 2, 3, 4, or 5 h) with vigorous stirring during the whole period. The specific amounts of $FeSO_4 \cdot 7H_2O$, NaOH and $NaNO_3$ are listed in Table S1 (See Supplementary Information). After cooling to room temperature, the black precipitate was separated by a magnet and alternately washed with deionized water and anhydrous alcohol until the filtrate reached neutral pH. After drying at 60 °C in a vacuum oven overnight, Fe_3O_4/RGO nanocomposites were obtained. The Fe_3O_4/RGO nanocomposites with 5, 10, 15, 20 and 25 wt% RGO content were labeled as FG-5G, FG-10G, FG-15G, FG-20G and FG-25G, respectively. The composites with 10 wt % RGO prepared at 55, 65, 75, 85 or 95 °C in a temperature-controlled water-bath and were labeled as FG-55 T, FG-65 T,

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