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Synthesis and application of rGO/CoFe₂O₄ composite for catalytic degradation of methylene blue on heterogeneous Fenton-like oxidation

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ABSTRACT

A high-specific surface-area, monodisperse and highly active magnetic composite reduced graphene oxide rGO/CoFe₂O₄ were synthesized using one-pot solvothermal reaction. Concretely, Fe(acac)₃ and CoCl₂•6H₂O used as starting materials were grown on graphene oxide at 200 °C to prepare rGO/CoFe₂O₄ composite. Graphene oxide was reduced to graphene, and CoFe₂O₄ microspheres were simultaneously generated on the carbon basal planes under the conditions generated in the solvothermal system. The morphology and structure of the prepared nanocomposite were characterized by transmission electron microscopy (TEM), N₂ adsorption-desorption isotherms, X-ray photoelectron spectroscopy (XPS), vibration sample magnetometer (VSM), and X-ray diffraction (XRD), respectively. Moreover, the heterogeneous catalytic activity and degradation ability were investigated by degrading methylene blue (MB) experiment of Fenton-like reaction. The satisfactory results demonstrated that the rGO/CoFe₂O₄ showed excellent catalytic degradation ability toward MB than CoFe₂O₄ in water phase, thereby suggesting that rGO played an important role in rGO/CoFe₂O₄ for the decomposition of MB. Optimal degradation was achieved (nearly 100% within 15 min) using initial concentrations of 3.0 mmol/l H₂O₂, 5.0 mmol/l NH₂OH and 20 mg/l MB. In addition, the nanocomposite can serve as an effective catalyst for decomposition aromatic amines in industrial effluent sample, which indicated its potential for practical applications in water pollutant removal and environmental cleanup.

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1. Introduction

Methylene blue (MB) is one of the thiazin dyes [1]. It is widely used in textile, paper, plastics, leather, food, and cosmetic industries. With rapid development of textile and dye industry, more and more important commercial dyes are discharged into water bodies through different means. More than 100,000 commercially available dyes and over 7 × 10⁵ tons of dyestuff are produced annually [2–4]. The concern about MB has increased because it can cause burning pain of eye and may be responsible for permanent injury to eyes of human and animals even at low doses. Upon

inhalation, it can give rise to short periods of rapid or difficult breathing. If ingested, a burning sensation is felt. Meanwhile, nausea, vomiting, profuse sweating, mental confusion and methemoglobinemia may ensue [5–7]. Since its ubiquitous nature in dyeing industry and toxicity, MB has been included in monitoring study of environmental water through many techniques [8]. Thus far, a large number of methods have been available for removal of MB, including biological degradation [9], ion exchange [10], ultrafiltration [11], nanofiltration [12], adsorption [13], advanced chemical oxidation [14] and photocatalytic degradation [15–18]. Biological degradation and adsorption are by far most widely used methods for removing MB from wastewaters. Because of poor biodegradability of MB, both of them cannot completely degrade and mineralize the pollutants from wastewater. Hence, it was need to prepare material with a highly degradation ability for MB removal.

Recently, advanced oxidation process (AOPs) have been proposed as offering promise for wastewater treatment as AOPs are very powerful way to destroy structures of a wide range of tough organic contaminants. Moreover, AOPs can generate hydroxyl radical (•OH) which is a nonspecific oxidant. Generally, hydrogen

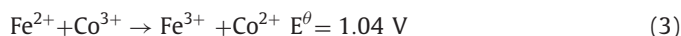
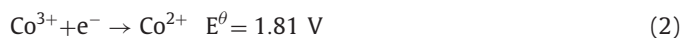
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peroxide (H_2O_2) is often applied to produce $\bullet\text{OH}$ in combination with UV light [19], ozone [20] or iron salts. Hydroxyl radicals have strong oxidizing ability and the oxidation potential reaches 2.8 V, which can react with most organic contaminants at near diffusion-limited rates [21–23]. Among AOPs, Fenton system is an attractive technique for effective decolorization and degradation of dyes because of low cost, the lack of toxicity of the reagents (Fe^{2+} and H_2O_2), the absence of mass transfer limitation due to its homogeneous catalytic nature, and the simplicity of the technology [24]. However, disadvantages also exist for the applications of the homogeneous Fenton process, such as the requirement of strong acidity (pH 3.0), the formation of a considerable amount of ferric hydroxide sludge in the process of Fenton treatment, and the requirements of further separation and disposal for the resulting sludge [25,26]. To overcome above disadvantages of the homogeneous Fenton process, heterogeneous Fenton-like systems using iron-based catalyst have been recently developed. Magnetic nanoparticles in heterogeneous Fenton system have been the focus of research because of ferromagnetism, an external magnetic field enable to separate catalyst from system. Organic pollutants could partially be degraded in the Fe_3O_4 MNPs– H_2O_2 system [27–29]. In previous reports, CoFe_2O_4 MNPs were used as an efficient heterogeneous catalyst to degrade organic pollutants in aqueous solution by Fenton-like reaction [30,31]. The high activity has been discussed in terms of thermodynamically favorable reduction of Co^{3+} by Fe^{2+} through an electron transfer within the semiconductor oxide (Eq. (1)–(3)).



Graphene is an interesting two-dimensional carbon allotrope that has been paid close attention extensively because of its unique structure and physicochemical properties [32]. High surface area and low diffusion resistance make it an ideal candidate for catalytic supporting materials [33]. Yao et al. reported a method to prepare magnetic composites consisting of CoFe_2O_4 on graphene. The catalysts aided the degradation of phenol via oxidation with oxone through a Fenton reaction [34]. However, the capability to boost the degradation rate of heterogeneous Fenton reaction is restricted, thereby enhancing activity and efficiency are still a challenge.

The accumulation and precipitation of Fe^{3+} were the biggest challenges for application of the Fenton system, which could further result in the decline of reaction rates. Hydroxylamine (NH_2OH) was adopted as a common reductive chemical to reduce Fe^{3+} in many applications such as total iron determination. Our previous researches have demonstrated that NH_2OH can effectively improve the rate of heterogeneous Fenton-like reaction [35–37]. Furthermore, an efficient method for integrating NH_2OH as a reductant with graphene oxide as a supporter with to improve the degradation rate of heterogeneous Fenton reaction has not been reported in the previous literatures.

The present work reports the preparation of $\text{rGO}/\text{CoFe}_2\text{O}_4$ by a simple solvothermal method. The obtained nanocomposites were characterized by TEM, FT-IR, XPS, XRD, BET and VSM. The catalytic capability was estimated by degrading MB in a heterogeneous Fenton-like system. The stability and reusability of the catalyst in the decomposition MB was determined. Compared with CoFe_2O_4 , the catalytic activity, recycling and stability of $\text{rGO}/\text{CoFe}_2\text{O}_4$ were significantly improved. In addition, it can be applied to degrade aniline amines in industrial effluent sample, which indicated that it can serve as an efficient material for practical applications in water pollutant removal and environmental cleanup.

2. Experimental

2.1. Chemicals and materials

The graphene oxide was prepared by Hummer's method and was purchased from Nanjing XFNANO Materials Tech Co., Ltd. (99%, Nanjing, China). Iron acetylacetonate and cobalt dichloride hexahydrate were obtained from Sigma–Aldrich (99.9%, AR, United Kingdom). The H_2O_2 was purchased from Guangfu Chemical Co. Ltd. (30%, Tianjin, China). Methylene blue, Sodium acetate anhydrous and sodium hydroxide were obtained from Tianjin Guangfu Fine Chemical Research Institute (AR, Tianjin, China). Hydroxylamine hydrochloride was purchased from Sinopharm Chemical Reagent Co. Ltd (AR, Shanghai). Ethylene glycol, ethanol amine and ethanol were purchased from Rionlon Pharmaceutical Chemical Co. Ltd (AR, Tianjin, China).

2.2. Preparation of magnetic materials

2.2.1. Preparation of CoFe_2O_4 MNPs

The CoFe_2O_4 MNPs were synthesized via a modified one-pot polyol method according to a report by Mohapatra et al. [38]. Anhydrous $\text{Fe}(\text{acac})_3$ (1.483 g, 4.2 mmol), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.576 g, 2.1 mmol) and sodium acetate anhydrous (0.5 g) were dissolved in a 45 ml ethylene glycol/ethanol amine mixture solution (v:v = 2:1) under vigorous stirring for 1 h until dispersion evenly. The resulting mixture was transferred into a Teflon-lined stainless steel autoclave (50 ml) and heated to 200 °C for 10 h. After cooling to room temperature, the solid product was collected using a magnet. Then the resultant product was washed with ethanol by Soxhlet extraction and dried under vacuum at 50 °C for 12 h.

2.2.2. Preparation of $\text{rGO}/\text{CoFe}_2\text{O}_4$ nanocomposite

The synthesis of nanocomposite was similar to that of magnetic nanoparticles. In a typical experiment, graphene oxide (0.5 g), anhydrous $\text{Fe}(\text{acac})_3$ (1.483 g, 4.2 mmol), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.576 g, 2.1 mmol) and sodium acetate anhydrous (0.5 g) were mixed in 30 ml ethylene glycol and 15 ml ethanol amine. After stirring for 1 h under sonication, the resulting mixture was transferred to a Teflon-lined stainless steel autoclave (50 ml) and heated to 200 °C for 10 h. After cooling to room temperature, the solid product was collected using a magnet. Then the resultant product was washed with ethanol by Soxhlet extraction, and dried under vacuum at 50 °C for 12 h.

2.3. Instrumentation

The morphology of prepared $\text{rGO}/\text{CoFe}_2\text{O}_4$ composite and CoFe_2O_4 MNPs were characterized by a transmission electron microscope (TEM, Tecnai G² F30). Powder X-ray diffraction (XRD, Rigaku D/MAX-2400 X-ray diffractometer with Ni-filtered $\text{Cu K}\alpha$ radiation) was used to qualitative the structure of them. X-ray photoelectron spectroscopy (XPS) verified the composition and the change of iron ion valence state before and after reaction. The N_2 adsorption–desorption isotherm was measured at liquid nitrogen temperature (76 K) using a Micromeritics ASAP 2010 M instrument. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method. Magnetic properties were characterized by a vibrating sample magnetometer (VSM, LAKESHORE-7304) at room temperature. UV–visible spectroscopy (TU-1810 PC) was used to measure the concentration of MB. The pH of the solutions was detected by pH meter (HI 9025, HANNA instruments made in Romania).

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