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One-step biosynthesis of hybrid reduced graphene oxide/iron-based nanoparticles by *eucalyptus* extract and its removal of dye

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ABSTRACT

Green synthesis of nanomaterial using plant extract has recently attracted much scientific attention due to its simple operation and low cost. In this study, hybrid reduced graphene oxide/iron-based nanoparticles (RGO/Fe NPs) were synthesized via green route employing a one-step process with *Eucalyptus* leaf extract (EL). Hybrid RGO/Fe NPs were characterized by UV–vis spectrophotometer, Fourier transform infrared spectroscopy (FTIR), Transmission electron microscopy (TEM), Energy-dispersive spectrometer (EDS), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy (Raman). The results indicated that Fe NPs were spherical in shape, their diameter was 4–7 nm and they were uniformly dispersed on the surface of RGO. To understand the bioreduction conditions impacting on the yield of RGO/Fe NPs, testing the influence of various atmospheric conditions and the ratio of GO and ferric iron demonstrated that the content of RGO rose as the volume ratio of GO and ferric iron increased under nitrogen atmosphere. Adsorption of methylene blue (MB) using Fe NPs, RGO and hybrid RGO/Fe NPs revealed that the hybrid RGO/Fe NPs enabled superior adsorption of MB (199.4 mg/g). This suggests that RGO/Fe NPs has much potential in removing MB.

1. Introduction

Graphene is well-known for its excellent chemical, mechanical and electronic properties (Li et al., 2017). Accordingly, graphene-based nanocomposites have attracted great interest for their wide range of potential applications (Chu et al., 2016; Chettri et al., 2016). SnO_2 QDs-RGO was used to remove dyes because it has the advantage of a large surface area and excellent adsorption characteristics (Dutta et al., 2016). RGO-Pd dispersed by Bi_2MoO_6 nanoparticles was used to efficiently remove phenolic compounds in wastewater (Meng and Zhang, 2017). Also, iron-based nanoparticles (Fe NPs) have been applied in various fields such as environmental remediation and medicine (Wang et al., 2016; Shao et al., 2015). Recently, employing Fe NPs to remove contaminants in wastewater has received significant attention because of their high reactivity, good biocompatibility and natural abundance (Wang et al., 2016).

Graphene/iron-based nanoparticles (RGO/Fe NPs) have become popular in the remediation of contaminants due to their functional properties (Sun et al., 2014; Li et al., 2016). The synthesis of RGO/Fe NPs occurs through chemical reduction deposition, and solvothermal synthesis (Sun et al., 2011, 2014; Li et al., 2016; Jiang et al., 2017; Thakur and Karak, 2014). Recently, graphene supported nanoscale zero-valent iron (nZVI/rGO) has been prepared by the reduction deposition method, and served to remove U(VI) from aqueous solution, where the removal efficiency of U(VI) using nZVI/rGO (80%) was much higher than that using nZVI (8%) (Sun et al., 2014). NZVI/graphene nanosheets (NZVI/GNS) were synthesized by $NaBH_4$ reduction and they removed Cr (VI). In fact, the results confirm that the removal efficiency of Cr (VI) was approximately 1%, 40% and 70% using graphene nanosheets, NZVI, and NZVI/GNS, respectively (Li et al., 2016). This indicates that the reactivity of graphene/Fe NPs was superior to graphene or nZVI (Sun et al., 2014; Li et al., 2016).

Green synthesis of RGO/Fe NPs employing brown alga and plant extract as reducing agents have emerged as environmentally friendly, low-cost, simple and low-energy (Jiang et al., 2017; Thakur and Karak, 2014). Presently, only a few studies have been done on the green synthesis of RGO/Fe using brown alga and plant extracts (Jiang et al., 2017). RGO/Fe_3O_4 nanocomposites have been synthesized using a brown alga (*Sargassum thunbergii*) as the sole reducing agent, where the spherical-shaped Fe_3O_4 with a diameter of 7 nm were uniformly anchored on the RGO nanosheets. RGO/Fe_3O_4 composite as a photo-Fenton catalyst demonstrated rapid

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decomposition of methylene blue, and the degradation rate of MB was 96% (Jiang et al., 2017). Iron oxide/reduced graphene oxide nanohybrid (IO/RGO) has been prepared by using banana peel ash aqueous extract as the base source, and *Colocasia esculenta* leaves aqueous extract as the reducing agent, indicating the decoration of superparamagnetic IO nanoparticles on the surface of the RGO. Both organic (tetrabromobisphenol A) and metal ions (Pb^{2+} and Cd^{2+}) were effectively removed from the contaminated water (Thakur and Karak, 2014). Since biomolecules in plant leaves extract depend on the plant species, it can significantly impact on the reactivity of hybrid RGO/Fe NPs. This is due to biomolecules in plant leaves extract acting as both reduction agent and stabilizer, and involved in the bioreduction of GO to RGO and ferric iron to Fe NPs, leading to the formation of hybrid RGO/Fe NPs (Jiang et al., 2017; Thakur and Karak, 2014). However, the formation of hybrid RGO/Fe NPs due to synthesized conditions are still unclear.

Eucalyptus has been widely planted for timber production due to its fast growth, high tolerance and high yield (Pourmortazavi et al., 2015). Since *eucalyptus* leaf extract contains abundant acids (caffeic, chlorogenic, etc.), flavonoids, alkaloids, and minor amounts of other organic compounds, the use of *eucalyptus* leaves to produce valuable nanoparticles is a sustainable technology. Consequently, the extracts that serve as reducing and capping regents for nanoparticles synthesis (e.g. Ag, Au, Fe and Fe/Ni NPs) exhibit many advantages such as being environmentally friendly and cost effective. For these reasons they have attracted much interest in this field (Pourmortazavi et al., 2015; Pinto et al., 2017; Weng et al., 2017; Zhuang et al., 2015). This has been confirmed by our previous work on green synthesis of Fe NPs and bioreduction of GO to RGO (Li et al., 2017; Weng et al., 2017; Zhuang et al., 2015). We hypothesize that the one-step synthesis of hybrid RGO/Fe NPs using *eucalyptus* leaf extract is possible. Although the main challenge frequently encountered in the green synthesis of RGO/Fe is to control the formation of RGO/Fe NPs, efforts will be devoted to such issues by controlling the formation factors. These include such things as reaction atmosphere and the volume ratios of GO and ferric iron.

In this study, *eucalyptus* leaf extract was used to green synthesize hybrid RGO/Fe NPs, where the schematic for the formation of hybrid reduced graphene oxide/iron-based nanoparticles is illustrated in Fig. 1. Specifically, it is used to remove methylene blue (MB) from aqueous solution. The main objectives of this study are: (1) identification of RGO, Fe NPs and RGO/Fe NPs using UV–vis spectra; (2) characterizing the hybrid RGO/Fe NPs; (3) conditions impacting on the yield of RGO/Fe NPs; and (4) testing the removal efficiency of MB using Fe NPs, RGO and RGO/Fe NPs.

2. Experimental

2.1. Materials and chemicals

Graphite powder was supplied by Aladdin Reagent Co. Ltd., Shanghai, China. Potassium permanganate, concentrated sulfuric acid, anhydrous ethanol, hydrogen peroxide, ferric chloride, methylene blue, sodium acetate and other reagents used were all analytical grade. These were purchased from Guangdong Guanghua Sci-Tech Co., Ltd., another Chinese company. Distilled water was used in all the experiments. *Eucalyptus* leaves were provided by a local farm in Minhou in April 2017 (Fuzhou, China).

2.2. Green synthesis of hybrid RGO/Fe NPs using eucalyptus leaf extract

The GO used in this study was prepared from graphite powder employing a modified Hummers method and the *eucalyptus* leaf extracts were prepared as described in our previous report (Li et al., 2017). Green synthesis of hybrid RGO/Fe NPs was done using *eucalyptus* leaf extract via a one-step process. 50 mg of GO was dispersed in 100 mL distilled water under ultrasonic conditions for 60 min and then 50 mL of 0.1 mol/L $FeCl_3$ was mixed for 60 min. Then the *eucalyptus* leaf extract was added to the mixed solution at 80 °C for 480 min. The black suspension was separated from the mixed solution by filtration, washed with ethanol and double distilled water three times, respectively. Finally, the obtained black powder was dried in a vacuum freeze dryer to obtain hybrid RGO/Fe NPs.

To understand the bioreduction conditions impacting on the yield of hybrid RGO/Fe NPs, the influence of various atmospheric conditions and the volume ratios of GO and ferric iron were investigated. The volume ratios of GO (0.5 g/L) and ferric iron (0.1 mol/L) were 2:1, 1:1, 1:2 and 1:10, respectively; nitrogen atmosphere, air atmosphere and oxygen atmosphere served as reaction atmospheres.

2.3. Characterization

The synthesized nanoparticles were dissolved in double distilled water and dispersed evenly using the ultrasonic method. Then this solution was placed in a cuvette and its absorbance was recorded with a UV–vis reflective spectrophotometer (UV1902, Phoenix, Shanghai, China). Specifically, the wavelength ranged from 190 to 770 nm under normal pressure and ambient temperature.

Fourier transform infrared (FTIR) spectra were recorded in KBr pellets by a MATTSON 1000 Model FTIR spectrophotometer. Transmission electron microscopy (TEM) observations were done on Tecnai G2 20 equipped with an X-ray energy dispersive spectroscopy (EDX; model EDAX, AMETEK). X-ray photoelectron spectroscopy (ESCALAB 250, X-ray photoelectron spectrometer) was used to investigate the surface chemical and valence states, especially Fe and C elements of hybrid RGO/Fe NPs. Raman spectra were determined in the spectral range 500–3000 cm^{-1} using 532 nm excitation source on a LabRAM HR-800 high resolution Raman spectrometer. Nitrogen adsorption and desorption isotherms were collected by multi-point Brunauer-Emmett-Teller (BET Autosorb-IQ) measurements under 77 K. Finally, an analysis was undertaken of the hybrid RGO/Fe NPs which were prepared via the volume ratio of GO (0.5 g/L) and ferric iron (0.1 mol/L) as 1:1 or 1:10 under air atmosphere.

2.4. Adsorption testing

The adsorption activities of Fe NPs, RGO and hybrid RGO/Fe NPs were evaluated by adsorption of MB in aqueous solution, where the volume ratio of GO (0.5 g/L) and ferric iron (0.1 mol/L) was 1:1 under air atmosphere. 0.2 g of materials was added into 200 mL MB aqueous solution (200 mg/L) and the suspension was mechanically and continuously stirred under 303 K. Following the given adsorption time intervals, 5 mL mixed suspension was sampled and then centrifuged at 9000 rpm. Then the supernatant was analyzed using UV–vis spectroscopy with absorption spectra at 665 nm to obtain the residual concentration of MB.

Both the adsorption amount and removal rate were calculated as shown below in Eqs. (1) and (2) (Ai et al., 2011; Weng et al., 2017):

$$Q_t = \frac{(C_0 - C_t) \times V}{m} \tag{1}$$