



Adsorptive removal of trace sulfonamide antibiotics by water-dispersible magnetic reduced graphene oxide–ferrite hybrids from wastewater



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ABSTRACT

A one-pot solvothermal synthesis method was developed to prepare reduced graphene oxide (RGO) supported ferrite hybrids using graphite oxide and metal ions (Fe^{3+}) as starting materials. The as-prepared composites were characterized by transmission electron microscopy (TEM), Fourier transform infrared spectrophotometer (FT-IR), X-ray powder diffraction pattern (XRD) and vibrating sample magnetometer (VSM). It was shown that Fe_3O_4 nanoparticles with a uniform size of ~ 35 nm were anchored on RGO nanosheets. Importantly, the obtained nanocomposites are effective adsorbents for the determination of three sulfonamides in wastewater. Several parameters affecting the extraction efficiency were optimized, including amount of adsorbent, extraction time, pH and desorption conditions. Compared with other adsorbents, the as-prepared RGO- Fe_3O_4 showed the better extraction efficiencies for the SAs due to the large surface area of RGO. A linear range from 1 to 200 ng/mL was obtained with a high correlation coefficient ($R^2 > 0.9987$), and the limits of detection for three SAs ranged from 0.43 to 0.57 ng/mL. This method was successfully applied to the analysis of SAs in environmental wastewater samples, the recoveries in different sample matrices were in the range from 89.1 and 101.7% with relative standard deviations less than 8.6%. It is believed that such composites will find wide applications in the water pretreatment area.

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1. Introduction

Graphene, a monolayer of carbon atoms densely packed into a two dimensional honeycomb crystal lattice, has recently sparked much research interest. It combines unique electronic properties and intriguing quantum effects with exceptional thermal and mechanical properties [1]. Notably, graphene is a double-sided polyaromatic scaffold with an ultrahigh specific surface area (theoretical value $2630 \text{ m}^2/\text{g}$, compared to $10 \text{ m}^2/\text{g}$ of graphite and $1315 \text{ m}^2/\text{g}$ of nanotubes) [2]. On the other hand, rapid mass transfer can be obtained due to the sufficiently large contact area

between the sorbents and the analytes, which is beneficial for rapid equilibrium [3,4], making it a promising candidate for sorption material with high loading capacity. Its large delocalized p-electron system also endows graphene a strong affinity for carbon-based ring structures, which are widely present in drugs, pollutants, and biomolecules. Graphene-based materials such as graphene and chemically modified graphene including graphene oxide have shown many applications in analytical chemistry [5–8]. Feng et al. reported the application of graphene as a sorbent for SPE and revealed the great potential of graphene in analytical process [9]. Although graphene has recently been used as the adsorbent for the preconcentration of analytes, graphene is an ultralight material, so it is usually hard to retrieve from a suspension.

To solve these problems, magnetic adsorbent has been a solution. The retrieval of the adsorbent could be realized by external magnetic field [10–13]. In this way magnetic particles were loaded

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onto graphene to fabricate magnetic graphene composite is a superior choice, which can ensure the convenient magnetic separation after adsorption. Magnetic graphene (RGO-Fe₃O₄) are of considerable interest in materials chemistry because of their unique physical properties and non-toxicity, much more convenient, efficient and economic and many interesting applications nowadays [14]. Also, it can be modified with different functional groups to prevent aggregation and extend their application. These functional groups include silica, metal oxides, polymers and so on. Up to now, graphene based Fe₃O₄ nanocomposites have become a hot topic of research and exhibit attractive application prospects in magnetic resonance imaging [15], environmental remediation [16–18], drug delivery [19,20] and photocatalyst [21,22]. An increase in the number of publications concerning the use of magnetic graphene was observed in recent years. On the basis of the advantages of graphene and Fe₃O₄, the RGO-Fe₃O₄ composites have been developed and widely applied in sample pretreatment fields.

At present, a variety of methods, such as solvothermal reaction, the reduction of GO and Fe³⁺ in a NaBH₄ solution, electrostatic interactions [3], chemical precipitation [23,24], hydrothermal reaction [25], physical adsorption [9] and covalent bonding [26,27], have been applied to prepare graphene-Fe₃O₄. Chemical methods offer potentially low cost and large scale production of graphene-based hybrid materials. In this work, an easy-to-handle approach was presented to prepare RGO-Fe₃O₄.

Antibiotics have been investigated as sources of emerging environmental contaminants. As a major class of antibiotics, sulfonamide antibiotics (SAs) are widely used for the treatment of diseases and as prophylaxis [28–30]. However, SAs cannot be effectively eliminated in conventional wastewater treatment plants because of their anionic characteristics [31]. SAs have been gained more and more concerns for the residues in the natural water system or in the water treatment facilities [32] and their potential carcinogenicity [33]. As a result, it is fundamental to develop adequate analytical methods for their determination in water samples. Nowadays, the study of nanomaterial based composites for water treatment is still at the primary stage. To design a cost effective method for the fabrication of nanomaterials is still a challenge.

Here, we report a novel magnetic composite based on GO synthesized *in situ* at low temperatures (<100 °C). In a solvothermal strategy of the mixture of iron(III) and GO in alkaline condition and the reduction of GO by the addition of hydrazine hydrate could proceed simultaneously. The as-prepared RGO-Fe₃O₄ can also be dispersed in water due to the retained hydrophilic moieties, which were applied for the first time as a novel adsorbent for the enrichment of three sulfonamide antibiotics (SAs) from water samples. Coupling this MSPE technique with HPLC separation and detection, a highly simple and sensitive analytical method to determine SAs in environmental water samples was established.

2. Materials and methods

2.1. Chemicals and materials

Graphite powder was obtained from the Nanjing XFANO Materials Tech Co. Ltd. (Nanjing, China). Iron(III/II) chloride (99.9+ %) and hydrazine hydrate (99%) were purchased from Sinopharm Chemical Reagent Co. Ltd, China. Sulphuric acid (H₂SO₄, 98%), phosphoric acid (H₃PO₄), hydrochloric acid (HCl), Ammonia solution, H₂O₂ (30%), KMnO₄, sodium acetate (NaAc) and acetone were purchased from Aladdin. Gradient grade ACN, MeOH for LC and acetic acid were purchased from Merck (Germany).

Analytical standards of sulfadiazine (SDZ), sulfamerazine (SMR), sulfamethoxazole (SMX) were provided by Sigma-Aldrich Co. LLC (USA) and their chemical structures are shown in Fig. S1. The stock

solutions (1 mg mL⁻¹) of the analytes were prepared in methanol and stored in the dark at 4 °C.

The primary and final sewage effluent samples were taken from Hospital of Nanjing Medical University (Nanjing, China). The lake water sample was collected from Xuanwu Lake (Nanjing, China). The tap water sample came from our laboratory. All water samples were collected randomly and stored at 4 °C. The spiked water samples were made by adding certain amounts of SAs standard solution to the real water samples of fixed volume and stored at room temperature.

2.2. Instrumentation

The TEM image was performed on a FEI Tecnai G2 F20 transmission electron microscope. Phase identification was done by the X-ray powder diffraction pattern (XRD), using X'TRA X-ray diffractometer with Cu K α irradiation at $c = 1.540562$. FT-IR spectrum was collected by using a 8400s FTIR spectrometer in KBr pellet at room temperature (Shimadzu Corporation, Japan). The magnetic properties were studied using an LDJ 9600-1 vibrating sample magnetometer (VSM) operating at room temperature with applied fields of up to 10 kOe. Deionized water was acquired from Milli-Q50SP Reagent system (Millipore Corporation, MA, USA).

2.3. Synthesis of graphene oxide (GO)

GO was fabricated according to the method previously reported in the literature with minor modifications [34]. The details of synthesis steps were described in Supporting information.

2.4. Synthesis of magnetite graphene (RGO-Fe₃O₄) composites

Fig. 1 displays the synthetic scheme of RGO-Fe₃O₄ composites prepared in this work. Typically, 0.3 g GO was dispersed in 220 mL of deionized water and ultrasonicated for 2 h to produce a suspension of GO sheets. The mixed solution of 5.3 g FeCl₃·6H₂O and 1.99 g FeCl₂·4H₂O (Fe³⁺ and Fe²⁺ with a mole ratio of 2:1) was added slowly to the GO solution at RT. 30% Ammonia solution was added to this solution until the pH = 10. The temperature of solution raised to 90 °C and 5 mL of hydrazine hydrate was added. After that, the mixture was transferred into a 50 mL Teflon-lined stainless-steel autoclave and maintained at 190 °C for a certain period of time to ensure complete reduction of GO, and then cooled naturally to room temperature. The black solution was filtered, washed with water and ethanol several times, and finally dried in vacuum at 70 °C to obtain the RGO-Fe₃O₄ composites.

2.5. MSPE procedure

The extraction procedure was similar to our previous work with minor modification [35–37]. 20 mg of sorbent (RGO-Fe₃O₄) was added into 5 mL spiked water sample by ultrasonating to form a homogeneous suspension. Then 5 mL phosphate buffer solution (PBS, 0.02 M) were added to adjust the suited pH. Subsequently, the mixture was homogenized and the extraction was performed under an oscillator for 15 min. Then, the magnetic adsorbent was collected using an external magnet and supernatant solution was decanted. Desorption of the target analytes was accomplished by washing the sorbent with 1.5 mL acetonitrile containing 5% ammonium (0.5 mL + 1.0 mL). The collected sorbents adsorbing the target analytes were eluted with 1.5 mL acetonitrile containing 5% ammonium to desorb the analytes. Then evaporated to dryness under a mild nitrogen stream. The residue was dissolved in 0.5 mL methanol and 10 μ L of the eluate was injected into the HPLC system for analysis.

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