Magnetic porous silica–graphene oxide hybrid composite as a potential adsorbent for aqueous removal of *p*-nitrophenol

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HIGHLIGHTS

- Magnetic porous silica–graphene oxide hybrid composites (Fe3O4@mSiO2/GO) were synthesized.
- Fe3O4@mSiO2/GO can be easily separated from solutions through an external magnetic force.
- Fe3O4@mSiO2/GO shown excellent adsorption performance for *p*-nitrophenol.

GRAPHICAL ABSTRACT
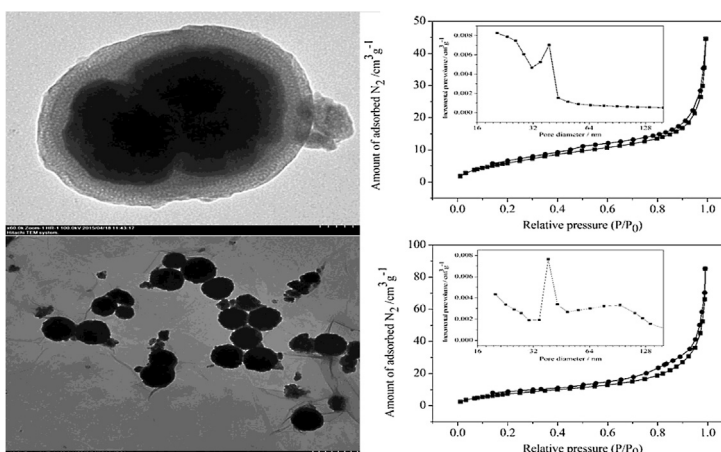
ABSTRACT

The magnetic porous silica–graphene oxide hybrid composites (Fe$_3$O$_4$@mSiO$_2$/GO) were synthesized via grafting graphene oxide sheets onto the core–shell Fe$_3$O$_4$@mSiO$_2$ nanoparticles, and their application in removing *p*-nitrophenol from aqueous solution was also investigated. The as-prepared Fe$_3$O$_4$@mSiO$_2$/GO composites were characterized by transmission electron microscopy, fourier-transform infrared spectroscopy, nitrogen adsorption–desorption isotherms and vibrating sample magnetometer. The adsorption kinetics, adsorption isotherms, adsorption thermodynamics and influence of solution pH were discussed. The experimental results indicated that the adsorption process was well fitted by the pseudo-second-order kinetic model and the Langmuir isotherm model. The maximum adsorption capacity was 1548.78 mg/g at the solution pH 8.0 and at 25 °C. The Fe$_3$O$_4$@mSiO$_2$/GO hybrid composites could be easily separated from solutions through an external magnetic force. Undoubtedly the Fe$_3$O$_4$@mSiO$_2$/GO hybrid composites might have a bright future in removing organic pollutants from wastewater.

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1. Introduction

As one of the most commonly encountered organic pollutants, *p*-nitrophenol can pose a severe threat to ecological systems and human's health. In terms of its high toxicity, eliminating it from

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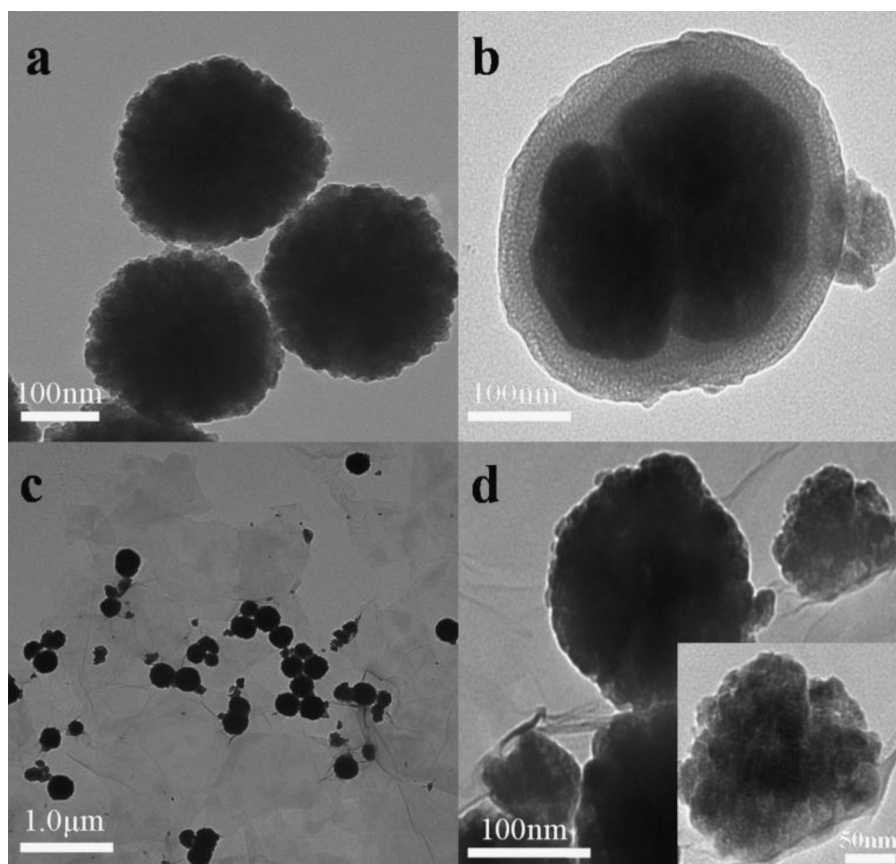 *E-mail address:* xqchen@csu.edu.cn (X. Chen).

Fig. 1. TEM images of Fe_3O_4 (a), $Fe_3O_4@mSiO_2$ (b) and $Fe_3O_4@mSiO_2/GO$ (c and d).

wastewater becomes necessary [1]. Currently, various techniques have been developed and employed to remove p-nitrophenol from the environment, such as electrochemical treatment [2], photodegradation [3], biodegradation [4], membrane filtration [5] and adsorption [6]. Up to now, adsorption technique has drawn considerable attention due to its favorable properties such as high capacity, simplicity of operation and cost-effective [7]. Therefore, adsorption has become one of the best choices for the removal of p-nitrophenol.

The selection of a suitable adsorbent is the key factor while using the adsorption method. Nowadays, different kinds of materials were developed to purify sewage, such as nanomaterials [8], organoclays [9], activated carbon [10–12] and graphene oxide [13,14]. Among those materials, graphene oxide (GO) is identified as a superb adsorbent. The abundant oxygen-containing functional groups on the surface of GO and the large surface area of GO play vital roles in the adsorption process. Those oxygen-containing functional groups between layers make it easy to bind with the objects to be adsorbed through intermolecular forces. And the large surface area of GO would provide abundant adsorption site on the surface of GO.

However, GO suffers from two serious weaknesses. Firstly, the layers of GO would be easily aggregated, leading to the reduction of surface area and decrease of adsorption capacity. Secondly, GO was water soluble and hard to be reused. Therefore, it is necessary to modify the GO with other materials. It is well-known that magnetic nanoparticles have gained rapid development since they emerged because of their excellent biocompatibility [15] and superparamagnetism [16]. Specially, the magnetic core–shell structured materials have also received widespread applications in preconcentration [17], cell separation [18], chemosensor [19] and adsorption [20]. Porous silica materials possess high surface area, large pore vol-

ume, accessible surface functionalization [21,22], making them ideal shell materials which are promising for applications in many fields [23–25]. In addition, it should be noted that the introduction of magnetic Fe_3O_4 nanoparticles make it possible to rapidly separate the adsorbents from wastewater with an external magnetic field. Furthermore, the porous silica could be applied to enhance the adsorption capacity. Based on this, the GO composites would be promising materials in removing aqueous organic pollutions [26–28].

In this work, preparation of magnetic $Fe_3O_4@mSiO_2/GO$ composites and the application of the composites in removing of p-nitrophenol from aqueous solutions are reported. The core/shell-like magnetic nanostructure ($Fe_3O_4@mSiO_2$) was firstly synthesized, followed by grafting GO sheets onto the surface of $Fe_3O_4@mSiO_2$ nanospheres. Factors affecting the adsorption such as contact time, pH of solution were systematically studied. Additionally, the adsorption kinetics, isotherms, and thermodynamics of adsorption were discussed in detail, and the experimental results indicated that the resultant products had a favorable adsorption performance.

2. Experimental

2.1. Reagents and chemicals

Flake graphite with high purity 100 mesh was supplied by Nanjing XFNano Material Tech Co., Ltd. 1-Ethyl-3-(3-dimethylaminoprophy) carbondiimidehy drochloride (EDC) and n-hydroxylsuccinimide (NHS) were Sigma–Aldrich products. Tetraethyl orthosilicate(TEOS), cetyltrimethyl ammonium bromide (CTAB), p-nitrophenol, ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), polyethylene glycol (PEG 6000) were purchased from Sinopharm