Facile and highly efficient removal of trace Gd(III) by adsorption of colloidal graphene oxide suspensions sealed in dialysis bag

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HIGHLIGHTS

- Loading GO suspensions into dialysis bag for sorption of Gd(III) avoids re-pollution.
- GO shows higher adsorption capacity for Gd(III) than any other currently reported.
- Effects of pH, ionic strength and temperature on GO sorption for Gd(III) were studied.
- Gd(III)-saturated GO has high desorption rate in nitric acid aqueous solution.
- The thermodynamics and kinetics models of Gd(III) sorption on GO were studied.

GRAPHICAL ABSTRACT

Schematic diagram of Gd(III) adsorption and desorption on GO nanosheets in colloidal suspensions sealed by dialysis membrane.
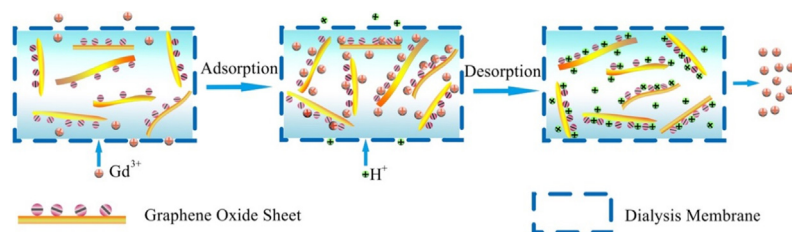
ABSTRACT

A facile, highly efficient and second-pollution-free strategy to remove trace Gd(III) from aqueous solutions by adsorption of colloidal graphene oxide (GO) suspensions in dialysis bag has been developed. The effects of pH, ionic strength and temperature on Gd(III) adsorption, and the pH-dependent desorption were investigated. The maximum adsorption capacity of Gd(III) on GO at pH = 5.9 ± 0.1 and T = 303 K was 286.86 mg g^{-1}, higher than any other currently reported. The Gd(III)-saturated GO suspension could resume colloidal state in 0.1 M HNO$_3$ with desorption rate of 85.00% in the fifth adsorption–desorption cycle. Gd(III) adsorption rate on GO was dependent more on pH and ionic strength than on temperature. The abundant oxygen-containing functional groups such as carboxyl and hydroxyl played a vital role on adsorption. The thermodynamics and kinetics investigations revealed that the adsorption of Gd(III) on GO was an endothermic, spontaneous and monolayer absorption process, which well fitted the pseudo-second-order model. GO could be a promising adsorbent applied in the enrichment and removal of lanthanides from aqueous solutions. More significantly, the combination of colloidal GO suspension with dialysis membrane facilely solves the re-pollution of the treated solutions due to the great difficulties in separation and recovery of GO.

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1. Introduction

With more and more widespread use of rare earths (RE) in a variety of fields, drastically growing RE have been released into the environment and exposed to humans over the past three decades [1]. Aqueous Gd(III) ion, even at trace level, is believed to be a risk

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for human beings for example, About 100 μM Gd(III) may cause proliferation of human cervical carcinoma cells–HeLa cells [2] and destroy the human primary peripheral lymphocytes, pneumonocyte, etc. [3]. Due to its high toxicity, highly efficient enrichment of Gd(III) as well as its removal from aqueous solutions is of extreme importance. Numerous techniques for removal of RE ions from water have been proposed, including adsorption [4,5], ion exchange [6], membrane separation [7], etc. Among these methods, adsorption technique turns out to be a favorable and feasible approach for separation of trace RE ions owing to its simplicity, low cost and high efficiency. In the past years, such adsorbents as brown marine Alga [8], γ-Al$_2$O$_3$ [9], pseudomonas fluorescens cells [9], and by-pass cement dust [10], etc. were used to remove RE ions from water.

In the recent years, graphene, chemically modified graphene and graphene-based nanocomposites promise potential applications in environmental clearup due to a range of unique and prominent properties [11]. As graphene oxide is the most common chemically modified graphene with a range of abundant oxygen-containing functional groups, and can be readily prepared by the modified Hummers method using flake graphite as raw material on a large scale and at a low cost [12,13], GO is most likely to be practically applied in the removal of metal ions from large volume of aqueous solution as an ideal adsorbent. It was reported that few layered GO had a higher adsorption capacity than any of today's nanomaterials in the removal of Pb(II) [14], Cd(II) [15], Co(II) [15], Cu(II) [16], U(VI) [17], Eu(III) [18] and Th(IV) [19] from aqueous solutions. In order to further improve their adsorption for metal ion, various graphene-based nanocomposites have been fabricated by chemical modification of GO or combination of nanoparticles with GO [20–22]. As graphene-based adsorbents are well dispersed in water and form a stable colloid when used in removal of hazardous metal ions and organic pollutants from waste water, a great challenge restricting their application in real work has been confronting us, i.e. difficulty in their recovery and separation from aqueous suspensions after the adsorption process, which may result in the re-pollution of the treated solutions by adsorbents and increase the cost of industrial applications. To overcome the separation problems derived from using GO as adsorbents, many efforts have been focused on fabrication of magnetite/reduced GO nanocomposites by combining graphene with magnetite nanoparticles magnetite nanoparticles on the graphene due to the convenient magnetic separation [23–26]. However, the attachment of magnetite nanoparticles on graphene certainly leads to reduced absorption capacity per weight unit owing to adding dead weight [23]. Moreover, the massive application of functional hybrids of graphene oxide–magnetic nanoparticles in removal of organic ion and inorganic pollutants is still limited due to their synthetic complexity and high cost, and especially in strongly acidic solutions, there are greater difficulties owing to the easy dissolution of magnetic nanoparticles on the surface of GO [24,25]. Although a lot of attempts have been made to enable the large-scale practical use of graphene-based adsorbents, more facile and feasible routes are urgent to be developed.

Herein, based on the colloidal nature of GO suspensions and screening property of dialysis membrane, we have developed a novel and general approach for adsorptive removal of trace metal ions from aqueous solutions by combining colloidal GO suspension with dialysis membrane, which promises huge potential in practical application of water pollution remediation due to no re-pollution of the treated solutions, convenient adsorbent separation, feasibility in a flowing system and greatly reduced application cost. The goals of this study are to (a) test and verify the adsorptive removal feasibility of trace Gd(III) from aqueous solutions using colloidal aqueous suspensions of GO loaded in dialysis bags; (b) study the effects of pH, ionic strength and temperature on Gd(III) adsorption; (c) preliminarily investigate the desorption of Gd(III) and regeneration of Gd(III)-saturated GO; (d) deal with the mechanism of Gd(III) adsorption on colloidal GO.

2. Experimental

2.1. Materials

Natural flake graphite was obtained from Xianfeng nano Co., Ltd. with a particle size of 325 mesh. All other chemicals used in experiment were of analytical grade and used without further purification. BIOSHARP dialysis bags with 8000–14,000 in molecular weight cut-off and 21 mm in diameter were used after pretreatment in boiling deionized water for 3–5 min.

Colloidal GO suspension was synthesized by using modified Hummer method. In a typical procedure, potassium permanganate (KMnO$_4$) and concentrated sulfuric acid (H$_2$SO$_4$) were added to a mixture of graphite flakes and NaNO$_3$ to oxidize the graphite layers. When the suspension became bright yellow, 30 wt% H$_2$O$_2$ were added to remove the excess KMnO$_4$. Subsequently, such purification processes as rinse with deionized water, centrifugal separation, ultrasonication and membrane dialysis were repeated until the deionized water for dialysis was neutral, thus the stock suspension of GO was obtained, whose concentration was determined by gravimetric method. The GO suspensions for ion adsorption were prepared by diluting according to the experimental requirements. The Gd(III) aqueous standard solution at 12 mg L^{-1} was prepared by dissolving Gd$_2$O$_3$ (purity 99.999 wt%) in nitric acid and heating until the excessive nitric acid had evaporated.

2.2. Characterization of graphene oxide

Graphene oxide were characterized by transmission electron microscopy (TEM), atomic force microscopy (AFM), powder X-ray diffraction (XRD), Raman spectroscopy and Fourier transformed infrared spectra (FT-IR). The TEM micrograph was obtained by a JEOL transmission electron microscope (JEM-2100, Japan). The AFM image was obtained in air using a Digital Instrumental Nanoscope III in tapping mode. The XRD patterns were measured using an Advance D8 diffractometer with Cu-$K\alpha$ radiation. The Raman spectrum was recorded with a JobinYvon Lab Ram HR800 spectroscopy at room temperature. The FT-IR spectroscopy measurement was conducted by using a Nicolet 5700 spectrometer in KBr pellet. The zeta potentials of 100 mg L^{-1} colloidal aqueous GO suspensions as a function of pH were measured by a Zetatrac dynamic light scattering detector (Microtrac Limited Corp., USA) at 30 °C.

2.3. Experiments of Gd(III) adsorption and desorption on GO nanosheets in colloidal suspensions

In the adsorption experiment, 10 mL 100 mg L^{-1} pH = 5.9 ± 0.1 colloidal GO suspension was sealed into a dialysis bag to constitute an adsorption unit. The batch adsorption experiments of Gd(III) on GO nanosheets in colloidal suspensions were carried out by immersing an adsorption unit in 25 mL 12 mg L^{-1} Gd(III) aqueous solutions in a large-mouth conical flask placed in a water-bathing thermostatic shaker. Two aliquot parts of the treated solutions were sampled at regular intervals to determine Gd(III) concentrations by visible adsorption spectrophotometric method using arsenazo-III as the chromogenic agent at the wavelength of 656 nm. The average of duplicate determinations with the relative errors below 5% was the Gd(III) concentration of the treated solution. The amounts of Gd(III) adsorbed by the colloidal GO suspensions were calculated