Novel high-gluten flour physically cross-linked graphene oxide composites: Hydrothermal fabrication and adsorption properties for rare earth ions

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A B S T R A C T

Graphene oxide (GO) nanosheets were immobilized and cross-linked by high-gluten flour (HGF), and a series of biomass-GO composites with various HGF-to-GO mass ratios were fabricated through a one-step hydrothermal method. The HGF-GO composites were used as novel adsorbents to adsorb rare earth ions (REE^{3+}: La^{3+}, Yb^{3+}, Y^{3+}, Er^{3+} and Nd^{3+}) from aqueous solutions, and their adsorption properties were also investigated detailly. To evaluate the physicochemical properties of HGF-GO composites and further understand the mechanisms of adsorption of REE^{3+} onto HGF-GO composites, the HGF-GO composites were characterized by scanning electron microscopy (SEM), thermal gravimetric analyzer (TGA), Raman spectroscopy and Fourier transform infrared (FT-IR) spectroscopy. Several important condition parameters including contact time, initial REE^{3+} concentrations, solution pH values and temperature that might affect the adsorption process were studied in detail. The maximum adsorption capacities of $HGF-GO_{1:1}$ composite toward La^{3+}, Yb^{3+}, Y^{3+}, Er^{3+} and Nd^{3+} were 30.32, 36.64, 32.84, 42.36 and 48.68 mg g^{-1}, respectively. The experimental data indicated that the adsorption of REE^{3+} onto $HGF-GO_{1:1}$ was well fitted by the pseudo-second order kinetic model and the Langmuir isotherm model, and the adsorption process was a spontaneous and endothermic reaction. The $HGF-GO_{1:1}$ composite could be well regenerated and reused after five adsorption-desorption cycles, and its removal efficiency for Yb^{3+} remained as a constant of 100%.

1. Introduction

Rare earth elements (REEs) including the lanthanide series from the atomic number 57–71 and the elements scandium (Sc) and yttrium (Y) are well-known as industrial vitamins. REEs have been widely used in various fields such as petrochemical refining, chemical engineering, information storage, metallurgical technology and nuclear energy (Lekha et al., 2014). To cope with the urgent demands of REEs, numerous REE minerals have been progressively mined. Consequently, industrial wastewater containing REE ions has been largely discharged into the aquatic environment (Protano and Riccobono, 2002), which has damaged the crop planting, the rearing livestock and even the drinking water around the mining area. The indiscriminate discharges would cause the loss of valuable REE resources. The removal and the recovery of REEs from the underutilized resources or wastewater have been becoming an issue of great importance (Li et al., 2013).

To provide highly-purified REEs for the development and

preparation of advanced functional materials, and to promote the sustainable development of rare earth industry, the efficient separation and enrichment of REEs have attracted more and more attention in recent years. Many technologies such as chemical precipitation (Borai et al., 2016), dialysis method (Chen et al., 2014b) solvent extraction (Khan et al., 2016; Vahidi and Zhao, 2017), membrane filtration (Blöcher et al., 2003), ion-exchange (Gu et al., 2017) have been applied to the separation, the enrichment and the purification of REEs. It is worth noting that these technologies also have some shortcomings including high operational complexity, reagent consumption, time-consuming, high investment costs, and the formation of secondary pollutants. Compared with these conventional treatments, the adsorption-desorption method has been considered to be more suitable for the separation and enrichment of metal ions owing to its advantages such as relatively low cost, reutilization, non-toxicity, low reagent consumption, simplicity, rapidity and less pollution (Chai et al., 2010; Li et al., 2010; Wang et al., 2015, 2014).

Due to its large specific surface area and numerous oxygen-containing functional groups as well as self-assembly characteristics, graphene oxide (GO) could be used as an efficient substrate material for constructing novel adsorbents (Yang et al., 2017; Yue et al., 2018; Zou et al., 2017). The adsorption capacity of GO nanosheets for Eu^{3+} was approximately $175.44\,mg\,g^{-1}$, indicating GO-based composites might be better adsorbents for REEs (Soylak et al., 2017; Sun et al., 2012a). However, the practical application of as-prepared GO suspension was greatly restricted due to its hard-to-recycle properties, and various functionalized GO composites were developed as more efficient adsorbents. For example, graphene aerogel modified by N,N,N,N-tetra-octyldiglycolamide (TODGA) was used as solvent impregnated adsorbents for removal of thorium (Th), and its adsorption capacity was much higher than other solvent impregnated adsorbents (Chen et al., 2018). La^{3+} and Ce^{3+} recycling from aqueous solutions could be realized by magnetic $MnFe_2O_4$-GO nanoparticles which showed better experimental values than any previously mentioned composites (Ghobadi et al., 2018). Recently, biomass-polymers such as chitin, cornzein (Xu et al., 2018), chitosan (Roosen and Binnemans, 2014), β-cyclodextrin (β-CD) (Zhao et al., 2016), cellulose (Zhu et al., 2015) and starch (Ma et al., 2015; Teng et al., 2018) modified nano-carbon materials have attracted significant attentions. These biomass-polymers could be used as efficient decoration materials due to its plentiful nitrogen- (N-) or oxygen- (O-) containing functional groups which can chelate metal ions (Michels et al., 2002; Zhao et al., 2016, 2015a). As one of polysaccharides with vast repeating glucose units, high gluten flour (HGF) contains abundant oxygen-containing groups, and a few amide (O=C-NH) and sulfhydryl (-SH) groups. Specially, -SH groups could be converted into disulfide (-S-S-) bonds under oxidization or high-temperature hydrothermal conditions, providing additional intermolecular cross-linking effects for the gluten. The emerging macromolecular network was beneficial to the formation of three-dimensional (3D) HGF-based structure, indicating HGF could be used as the scaffolds of GO nanosheets for the fabrication of loosely and porous 3D HGF-GO macrostructures.

In this study, HGF was chosen as the binder and carrier for the immobilization of GO by a green and facile hydrothermal method. The novel 3D composites could provide more active sites for chelating with metal ions besides their relatively stable network structures. The composites possessed good reusability besides their relative excellent adsorption properties towards REEs. The HGF-based adsorbents are also more environmentally-friendly due to the assembled component, biodegradable HGF.

2. Experiments

2.1. Materials

Natural flake graphite (100 mesh, 99.5% purity) was obtained from Qingdao Braide Graphite Co., Ltd. (Qingdao, China). Concentrated sulfuric acid (H_2SO_4), potassium permanganate ($KMnO_4$), hydrochloric acid (HCl, 37%), hydrogen peroxide (H_2O_2, 30%) and phosphoric acid (H_3PO_4) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), and all reagents were of analytical grade. Lanthanum chloride heptahydrate ($LaCl_3 \cdot 7H_2O$; 99.99 wt%), Yttrium chloride heptahydrate ($YCl_3 \cdot 7H_2O$; 99.90 wt%), Ytterbium chloride hexahydrate ($YbCl_3 \cdot 6H_2O$; 99.99 wt%), Erbium chloride hexahydrate ($ErCl_3 \cdot 6H_2O$; 99.90 wt%) and Neodymium chloride hexahydrate ($NdCl_3 \cdot 6H_2O$; 99.90 wt%) were bought from Aladdin Chemical Co., Ltd. (Shanghai, China). HGF was purchased from a local supermarket (Better Life Commercial Chain Share Co.,Ltd.; Changsha, China). Ultrapure water with an electrical resistivity of $18.25\,M\Omega\,cm$ was obtained from a Millipore Milli-Q water purification system (Millipore Trading Co., Ltd.; Shanghai, China).

Colloidal GO stock solution was prepared by oxidizing natural flake graphite using a modified Hummer's method as-reported elsewhere. A
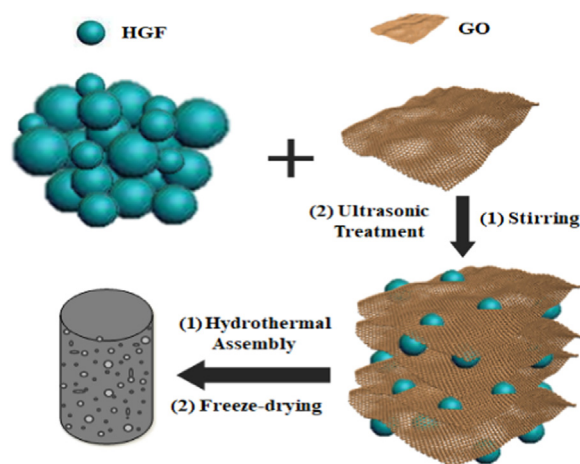

Fig. 1. Diagram for the synthesis of HGF-GO$_{x:y}$ composites.

mixed H_2SO_4-H_3PO_4 solution (72 mL + 8 mL) was slowly added into a homogeneous mixture of $KMnO_4$ and flake graphite (3.0 g + 0.6 g) under stirring. When the mixture turned to dark green, it was vigorously stirred and reacted at 50 °C for another 12 h, then the reaction was naturally cooled down to room temperature (~ 25 °C)·H_2O_2 was added to the reaction afterwards until the solution turned bright yellow, and the reaction was stirred for another 10 min. The bright yellow suspension was repeatedly rinsed using HCl (1 mol/L) and ultrapure water until the brown supernatant was neutral. Finally, a colloidal GO stock solution (5.0 mg mL^{-1}) could be obtained.

2.2. Hydrothermal self-assembly of HGF-GO$_{x:y}$ composites

The assembled 3D HGF-GO composites with various HGF-to-GO mass ratios, defined as HGF-GO$_{x:y}$, were prepared via a facile hydrothermal method (Fig. 1). Firstly, 500 mg of HGF and 0.2 mL of ultrapure water were mixed and vigorously stirred for 10 min; then 20 mL of colloidal GO solution (5 mg L^{-1}) was added and the mixture continued to stir for 30 min; and then the mixture was transferred into a reaction kettle and heated to 120 °C for 4 h. The reaction conditions including reaction temperature (80 °C, 100 °C and 120 °C) and time (2 h, 4 h and 6 h) on the physicochemical properties of the composites were investigated. As shown in Fig. S1a, 4 h was favorable for improving the adsorption capacities of the prepared composites when the temperature remained 80 °C, and the 120 °C was considered as the reaction temperature by observing the apparent mechanical property of HGF-GO$_{x:y}$ adsorbents (Fig. S1b). It should be mentioned that a series of HGF-GO$_{x:y}$ adsorbents with different mass proportions of HGF-to-GO (5: 1, 1: 1 and 1: 5) were prepared afterwards at 120 °C for 4 h.

2.3. Characterization methods

The surface morphologies of GO and HGF-GO$_{x:y}$ composites were characterized by scanning electron microscopy (SEM) (JEOL; JSM-6360LV; Japan). The surface functional groups of GO and HGF-GO$_{x:y}$ composites after and before adsorption were characterized by Fourier transform infrared (FT-IR) spectroscopy (Shimadzu IR-prestige 21; Tokyo, Japan). The crystallographic structures of the samples were characterized by a Renishaw system 2000 micro-Raman spectrometer (Gloucestershire, UK). Thermo-gravimetric analysis (TGA) was carried out between ambient temperature and 800 °C on a DTA analyzer (SDT Q600; Melbourne, Australia) with a heating rate of 10 °C/min under argon (Ar) atmosphere.