Applied Surface Science 459 (2018) 544–553

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

One-step fabrication of β-cyclodextrin modified magnetic graphene oxide nanohybrids for adsorption of Pb(II), Cu(II) and methylene blue in aqueous solutions

Ying-Xia Ma[a,*], Wen-Jie Shao[a], Wen Sun[a], Ya-Lan Kou[a], Xin Li[a], Hai-Peng Yang[b]

[a] State Key Laboratory of Advanced Processing and Recycling of Nonferrous Metals, School of Materials Science & Engineering, Lanzhou University of Technology, Lanzhou 730050, China

[b] Guangdong Research Center for Interfacial Engineering of Functional Materials, College of Materials Science and Engineering, Shenzhen University, Shenzhen 518060, China

ARTICLE INFO

Keywords:
β-cyclodextrin
Magnetic graphene oxide
Adsorption
Heavy metal ion
Methylene blue

ABSTRACT

In this study, using graphene oxide (GO) as carrier, ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) and ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) as iron sources, sodium hydroxide (NaOH) as precipitant, β-cyclodextrin (β-CD) as a modifier, β-cyclodextrin modified magnetic graphene oxide (β-CD/MGO) nanohybrids were fabricated by a simple one-step reverse phase co-precipitation method. The as-prepared β-CD/MGO nanohybrids were characterized by transmission electron microscope (TEM), scanning electron microscope (SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), vibrating sample magnetometer (VSM), N_2 adsorption/desorption isotherm, X-ray photoelectron spectroscopy (XPS) and Zeta potential analysis. Simultaneously, the adsorption properties of the β-CD/MGO nanohybrids for Pb(II), Cu(II) heavy metal ions and methylene blue (MB) in single aqueous solution were explored by batch experiments. The results revealed that the β-CD/MGO nanohybrids with high superparamagnetism were successfully fabricated, the maximum adsorption capacities of β-CD/MGO nanohybrids for Pb(II), Cu(II) and MB were 279.21, 51.29 and 93.97 $mg \cdot g^{-1}$ at 298 K, respectively. The adsorption process could be better fitted by pseudo-second-order model and Langmuir model.

1. Introduction

With the rapid development of industries, wastewater containing heavy metal ions and dyes are generated in the processes of mining and manufacture of storage batteries, colorants, textiles and paint, etc. [1–3], and discharged into the river, which have been drawing public increasing attentions. Among all the heavy metal ions, Pb(II) is one of the most dangerous because it is difficult to exclude once entering into the human body, and will directly harm human brain cells, especially the fetal nervous system. Meanwhile, excessive Pb(II) can affect the growth and development of adults brought about mental retardation and interfered with immune system function [4,5]. Copper is the trace element which is needed for the human body, but excessive ingestion of copper will appear abdominal pain, nausea, vomiting or diarrhea [6], in serious cases, it can lead to liver necrosis and even death. Methylene blue (MB) is an organic aromatic compound with relatively complex structure, high molecular weight and low biodegradability [7], moreover, it can adsorb light and consume the oxygen of water resulting in the fatal damage to organisms and microbes. Hence, it is very urgent and crucial to remove heavy metal ions and dyes contaminants from water prior to their discharge into the environment. Various treatment techniques, such as chemical precipitation, membrane filtration, ion exchange and adsorption [8–10] for heavy metal ions, electrochemical degradation, biological processes, chlorination, photocatalytic degradation and adsorption for dyes [11–14]. Among the above methods, adsorption is considered as a high-profile method because of the considerable choice of adsorbent materials, operational ease and high efficiency [15].

Graphene is a two dimensional material for its unique flat structure, largest specific surface area, highest thermal conductivity and good electrical conductivity that has been attractive applications. Graphene oxide (GO), as a derivative of graphene, has not only large specific surface area but also abundant oxygen-containing functional groups on the edges and basal planes, such as hydroxyl, carboxyl and epoxy groups, which makes GO be well dispersed in water and easily to be modified. Therefore, the GO-based materials have been widely used as

* Corresponding authors.
E-mail address: mayx2011818@163.com (Y.-X. Ma).

https://doi.org/10.1016/j.apsusc.2018.08.025
Received 27 January 2018; Received in revised form 31 July 2018; Accepted 3 August 2018
Available online 04 August 2018
0169-4332/

adsorbents to remove the heavy metal ions and dyes from wastewater. However, it is inconvenient to separate from the aqueous solution. Fe_3O_4 nanoparticles with relatively low cost, large specific surface area and convenient separation by an external magnetic field [16,17] have been anchored on the GO-based materials surface and applied in various wastewater treatment. Wang [18] developed and selected magnetic graphene nanosheets (Fe_3O_4@GNs) and magnetic graphene oxide (Fe_3O_4@GO) as adsorbents to investigate the adsorption performances for MB. The results showed that Fe_3O_4@GNs had a maximum adsorption capacity for MB of 211.34 $mg \cdot g^{-1}$ at 318 K. Moreover, the Fe_3O_4 nanoparticles could prevent the aggregation of GNs and the adsorption ability was improved. Vu et al. [19] prepared the magnetite graphene oxide (mGO/bead) for removal Cr(VI) and As(V) in wastewater. Compared with other carbon materials, the mGO/bead presented greater adsorption efficiency for Cr(VI) and As(V), and could be reused for at least 5 cycles without the leaching of core mineral contents. However, Fe_3O_4 nanoparticles anchored on the GO-based materials surface are highly susceptible to oxidation when they are exposed to the atmosphere. To overcome the drawback, β-CD functionalized magnetic graphene oxide composites used as adsorbents have attracted more and more attention in recent years.

β-cyclodextrin (β-CD) is a cyclic oligosaccharide with a truncated cone-shaped structure composed of seven D-glucopyranose unit connected by α-1,4 glycosidic bond [20]. Its special structure of hydrophilic exterior and hydrophobic interior contributes to selectively connect various size-matched compounds via Van der Waals forces and hydrogen bonds to form host-guest inclusion complexes [21]. Meanwhile, β-CD has abundant primary hydroxyl groups on its surface and secondary hydroxyl groups in the cavity which is easily modified by various functional groups. Besides, β-CD has the nontoxicity, simplicity of obtainment and stable chemical structure which makes it become as an environment-friendly and biocompatible candidate to fabricate adsorbents for removing contaminants from water. Ragavan et al. [20] synthesized the Beta-cyclodextrin capped graphene-magnetite (G-Fe_3O_4-BCD) nanocomposites by ethylenediamine conjugation and used as an adsorbent for selective removal of Bisphenol-A (BPA) in water with an adsorption capacity of 59.6 $mg \cdot g^{-1}$. Wang et al. [22] prepared β-cyclodextrin/ethylenediamine/magnetic graphene oxide (CD-E-MGO) for decontamination of Cr(VI) from aqueous solution, the q_{max} was found to be 89.15 $mg \cdot g^{-1}$ at 50 °C. Kumar et al. [23] prepared the Fe_3O_4 nanoparticles decorated with β-cyclodextrins (CDs)-functionalized graphene oxide (GO) (β-CDs-GO@Fe_3O_4NPs) by chemical reaction and applied in adsorption of As(III)/As(V). It turned out that the prepared adsorbent showed extensive prospects for arsenic removal.

In this work, β-cyclodextrin modified magnetic graphene oxide (β-CD/MGO) nanohybrids were first fabricated by a simple one-step reverse phase co-precipitation method, meanwhile, the adsorption properties for Pb(II), Cu(II) heavy metal ions and cationic dye MB were explored in single aqueous solution in details. Compared with other preparation processes of β-CD functionalized magnetic graphene oxide composites, the one-step reverse phase co-precipitation method for the fabrication of β-CD/MGO nanohybrids is an economic, effective and environment-friendly approach. In this system, GO has large specific surface area and abundant hydrophilic functional groups on the edges and basal planes, meanwhile, β-CD has abundant hydrophilic primary hydroxyl groups on its surface. Therefore, iron(III) and iron(II) cations in the solution could be anchored on the hydrophilic functional groups of GO and β-CD, and then in situ formed Fe_3O_4 nanoparticles at these particular sites in the presence of NaOH, which prevented the agglomeration of pulverized Fe_3O_4 and avoided the stack of GO. Simultaneously, GO provided a large contact surface for these nanoparticles Fe_3O_4, which could prevent the detachment of Fe_3O_4 nanoparticles. In addition, β-CD played a protection function to prevent the oxidation of Fe_3O_4 nanoparticles exposed in the air. Moreover, the β-CD/MGO nanohybrids could be easily separated from the liquid phase system by an external magnetic field during the process of preparation and application due to the introduction of Fe_3O_4 nanoparticles. The β-CD/MGO nanohybrids showed the excellent adsorption property for Pb (II) and the maximum adsorption capacity of 279.21 $mg \cdot g^{-1}$ at 298 K. Meanwhile, the β-CD/MGO nanohybrids had the adsorption property for Cu(II) and MB. Hence, the β-CD/MGO nanohybrids could be used as adsorbents and have potential applications in wastewater treatment.

2. Experimental

2.1. Materials

Natural flake graphite (NFG, 60 BS meshes, purity ≥99%) was purchased from Shandong Qingdao Tianhe Graphite Company (China) and used to prepare GO via the modified Hummers method [24,25]. Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) and β-cyclodextrin (β-CD) were supplied by Shanghai Macklin Biochemical Co., Ltd. (China). Ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) and sodium hydroxide (NaOH) were obtained from Tianjing Damao Chemical Co., Ltd. (China). Lead nitrate ($Pb(NO_3)_2$) and cupric nitrate ($Cu(NO_3)_2 \cdot 3H_2O$) were purchased from Guoyao chemical reagent Co., Ltd. (China). Methylene blue (MB) was derived from Tianjing Kaitong chemical reagent Co., Ltd. (China). Anhydrous ethanol was purchased from Tianjing Fuyu fine chemical Co., Ltd. (China). All reagents were analytical grade without further purification.

2.2. Characterization

Transmission electron microscope (TEM, JEM-2100F (JEOL, Japan)), scanning electron microscope (SEM, JSM-6701F (JEOL, Japan)), and energy-dispersive X-ray (EDX) were used to analyze the sizes, morphologies and elemental composition of β-CD/MGO nanohybrids, which supported by copper grid covered with 200 mesh carbon film. The crystal structures and chemical functional groups of the samples were characterized by X-ray diffraction (XRD, D/MAX-2400 (Rigaku, Japan)) with Cu Kα radiation for a 2θ range of 5–70° and Fourier transform infrared spectroscopy (FT-IR, Nexus 670 (Thermo Electron Corporation, United States)), respectively. The N_2 adsorption/desorption isotherm was performed by the Micromeritics ASAP 2020 (United States), and based on Brunauer-Emmett-Teller (BET) method and the Barret-Joner-Halenda (BJH) method to assess the surface area and pore width distribution, respectively. The surface elemental composition and all binding energies of adsorbents before and after adsorption were tested by X-ray photoelectron spectroscopy (XPS, Thermo Electron Corporation (United States)) with an Al Kα monochromatic X-ray sources. The thermal behavior and magnetic property were recorded using the thermogravimetric analysis (TGA, STA449C (Netzsch, Germany)) and vibrating sample magnetometer (VSM, LakeShore (America)). Zeta potential was measured in a Malvern Zetasizer by dispersing the adsorbent in distilled water at different pH values. The adsorption environment was provided by a constant temperature oscillator (HZQ-211C, Shanghai Yiheng Technical Co., Ltd. (China)). The absorbances of Pb(II), Cu(II) and MB were detected using the UV–vis spectrophotometer (UV-752 N, Shanghai Precision Scientific Instrument Co., Ltd. (China)). The pH values of the solution were adjusted by HCl and NaOH solution and monitored by pen type acidity meter pH-20 (Beijing Kewei yongxing instrument Co., Ltd. (China)).

2.3. Fabrication of β-CD/MGO nanohybrids

The β-CD/MGO nanohybrids were fabricated by a simple one-step reverse phase co-precipitation method. Firstly, a certain amount of β-CD was added into a 250 mL three-necked flask filled with 80 mL of 0.5 M NaOH solution, which gelatinized for 2 h at 80 °C under mechanical stirring in N_2 protection environment. Secondly, a certain amount of GO was dispersed in 80 mL of distilled water containing 0.004 mol $FeSO_4 \cdot 7H_2O$ and 0.008 mol $FeCl_3 \cdot 6H_2O$ by ultrasonication at