Journal of Colloid and Interface Science 530 (2018) 154–162

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

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

Regular Article

Investigation of the adsorption mechanisms of Pb(II) and 1-naphthol by β-cyclodextrin modified graphene oxide nanosheets from aqueous solution

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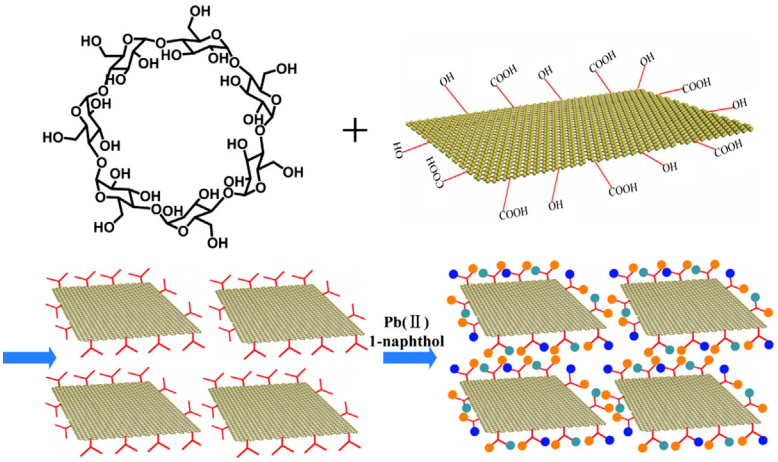
GRAPHICAL ABSTRACT

Preparation of β-CD-GOhybridmaterialvia in-situ oxidative polymerization procedure and its efficient use for Pb(II) and 1-naphtholremoval are discussed.



ARTICLE INFO

Article history:
Received 18 April 2018
Revised 22 June 2018
Accepted 26 June 2018
Available online 27 June 2018

Keywords:
Adsorption
Graphene oxide

ABSTRACT

β-cyclodextrin decorated graphene oxides (β-CD-GO) was prepared by using an *in-situ* aggregation treatment, and used to remove inorganic (Pb(II)) and organic pollutants (1-naphthol) from water environment. The batch adsorption experiments of as-prepared β-CD-GO were carried out as a function of pH values, initial Pb(II) and 1-naphthol concentration, ionic strength, contact time and temperature. β-CD-GO kinetic results indicated that the adsorption was dominated by chemisorptions and followed a pseudo-second order model. The maximum adsorption capacities of β-CD-GO toward Pb(II) and 1-naphtholon the base of the Langmuir model were 149.56 and 207.6 $mg \cdot g^{-1}$ at 293 K, respectively. The thermodynamic experiments revealed that the adsorption of Pb(II) and 1-naphthol was spontaneous

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https://doi.org/10.1016/j.jcis.2018.06.083
0021-9797/

β-cyclodextrin
Pb(II)
1-naphthol

and endothermic. The surface compexation, hydrogen bonds and π-π interactions contributed to Pb(II) and 1-naphthol adsorption by means of the hydroxy and carboxyl functional groups on the surface of the β-CD-GO. The experimental results indicate that the β-CD-GO is an excellent composite for the elimination of Pb(II) and 1-naphthol from wastewater.

1. Introduction

The elimination of heavy metal ions and organic compounds from wastewater has been an attractive subject of research, because they caused serious environmental issues and harm to human health [1]. Pb(II), a longstanding toxic element due to its non-degradable property and bioaccumulation, has been recognized as a prior toxicant and carcinogenic heavy metal ions in natural water bodies [2]. The primary sources of man-made Pb(II) pollution in ground water come from mining operations, battery manufactures, ammunition, and many other industries [3].1-naphthol, a developing menace to the ecosystem because of its acute toxicity, has been widely applied in various manufacture productions, such as plastics, pesticides and resultant rubbers, etc. [4]. However, it was well known that 1-naphthol is easily discharged into aquatic environment resulting in industrial or anthropogenic wastewater, which is more stable and difficult to biodegrade because of complex aromatic structure in the ecosystem [5]. Therefore, it is important to prevent wastewater-containing Pb(II) and 1-naphthol discharging into the environment [6,7].

Various methods including photo catalysis, precipitation and adsorption have been employed to remove pollutants from water solution [8–10]. Usually, the adsorption has been considered one of the most economic and common methods in environmental pollution purification because of its low cost, friendly approach, simple operation and perfect remediation effect [11]. Up to now, adsorbents including carbon nanotubes, clay minerals, metal oxides and bio-adsorbents have been widely employed to remove contaminants [12–17]. However, these materials don't have a wide application and high adsorption performance resulting from limited numbers and types of oxygen-containing functional groups. Therefore, the preparation of new materials with high adsorption capacity and high chemical stability attracts more attention.

Graphene oxide (GO), a newly-developing carbon nanomaterial and the important graphene derivatives, has individual sheet structure with a variety of oxygen-containing functional groups on its edges and surfaces [18]. These functional groups can bind heavy metal ions and organic pollutants by complexation or redox reaction to formmetal complexes because of shared electron pairs [19–21]. However, due to powerful interplanar reciprocities, GO tends to form a polymerized layer structure, resulting in loss of surface area of the layers [22,23]. To address the flaw, therefore, the surface of GO needs to be modified [24]. Therein, β-cyclodextrin (β-CD), an excellent ringlike oligosaccharides, can be implanted into different materials to remove contaminants because of its hydrophilic surface and hydrophobic chamber. Meanwhile, β-CD grafted on various materials has a powerful combination of metal ions and organic compounds, and can promote the adsorption capacity of support materials [25–28]. The β-CD-GO simultaneously has two unique properties, large surface property of GO and hydrophobic cavity capability of β-CD. The grafting β-CD onto GO surface can help to improve GO adsorption ability [26].

In present work, β-CD-GO was prepared through an *in-situ* aggregation method and adopted to remove Pb(II) and 1-naphthol. The various solution factors such as pH, ionic strength, contact time and temperature on the adsorption were investigated. X-ray photoelectron spectroscopy (XPS) wasused to further study the possible interaction mechanism between β-CD-GO and pollutants.

2. Experimental section

2.1. Chemicals

The chemicals used were analytical pure grade. $Pb(NO_3)_2$ was dissolved in deionized water (resistivity of 18.2 $M\Omega \cdot cm^{-1}$) for preparing Pb(II) stocking solution (concentration of 2000 $mg \cdot L^{-1}$). 1-naphthol, bought from Sinopharm Chemical Reagent Co. Ltd, its stock solution was prepared by dissolving 1-naphthol in deionized water (concentration of 120 $mg \cdot L^{-1}$).

2.2. Synthesis of GO

Using graphite as a raw material, the improved Hummers' methodwas used to synthesize the GO [29,30]. First, 1.5 g graphite and 1.5 g sodium nitrate were added into a conical flask containing 60 mL vitriol at 10 °C for 1.5 h in water bath. Second 9.0 g potassium permanganate was slowly added at 20 °C for 40 min. Third, 120 mL deionized waterwas added, stirred at 90 °C for 30 min and then cooled to 60 °C. To remove the possible residual potassium permanganate, 6 mL hydrogen peroxide was slowly added into the mixed solution. Finally, the mixed solution was filtered, washed and dried for 24 h.

2.3. Synthesis of β-CD-GO

The β-CD-GO was prepared by using an *in-situ* aggregation treatment. 0.01 g GO and 3.6 g β-CD were dissolved in 200 mL deionized water until a homogeneous solution was obtained. Ammonia solution was slowly added into the mixed solution to adjust solution pH to 11 [29]. And then, modification reaction started by adding 2.0 mL of hydrazine solution at 60 °C for 5 h in water bath. In the end, the product (β-CD-GO) was filtered, washed for several times and dried in freeze for 24 h.

2.4. Characterization

The Scanning electron microscopic (SEM, FEI-JSM 6320F produced Japan) was used to observe the morphology of the prepared GO and β-CD-GO. The Rigaku/Max-3A X-ray diffractometer examined the powder X-ray diffraction (XRD) patterns at 40 kV operation voltage and 200 mA current. Fourier transform infrared spectroscopy (FT-IR)spectroscopy was measured by using the Perkins Elmer 100 spectrometer in a KBr pellet. Thermal gravimetric analysis (TGA) was used to measure the grafting content. XPSspectra (ESCALAB 250 system) were carried by using Al *Kα* radiation at 150 W. Nitrogen adsorption-desorption on a Novawin 3000e Surface Area and Pore size Analyzer determined BET specific surface areas of β-CD-GO. The zeta potentials were determined by using a Malvern Zeta Nano-ZS90.

2.5. Adsorption experiment

The batch experiment of Pb(II) and 1-naphthol was carried out in 10 mL plastic centrifuge tube. The stock solutions of Pb(II) or 1-naphthol and $NaClO_4$ solution were added to the predetermined concentration of individual component. The initial pH of mixed solution was adjusted to desired values by adding very little