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Fabrication of three-dimensional porous β-cyclodextrin/chitosan functionalized graphene oxide hydrogel for methylene blue removal from aqueous solution

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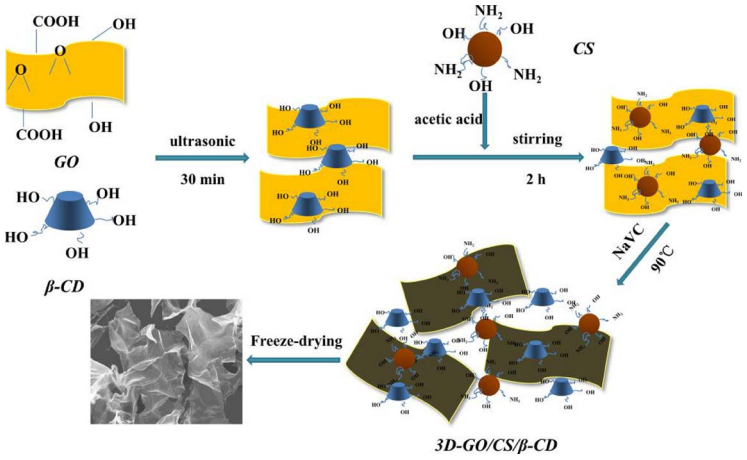
GRAPHICAL ABSTRACT



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ABSTRACT

A three-dimensional porous β-cyclodextrin/chitosan functionalized graphene oxide hydrogel (3D-GO/CS/β-CD) was synthesized by a simple and facile chemical reduction method in the presence of sodium ascorbate which acted as a reducing agent, and its application as an adsorbent for MB removal was investigated. The unique 3D structure enabled the rapid reuse and recyclability of 3D-GO/CS/β-CD without a complicated filtration system. The adsorbent was characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy, X-ray diffraction (XRD), thermogravimetric analysis (TGA) and Brunauer–Emmett–Teller (BET) analysis, and the results of the characterization indicated the successful synthesis of 3D-GO/CS/β-CD. The 3D-GO/CS/β-CD showed an ultrahigh adsorption capacity (1134 mg/g) for MB. The investigation of the adsorption behavior demonstrated that the adsorption was well fitted with the pseudo-second-order model and Freundlich model. The simulation of the intra-particle diffusion model illustrated that both film diffusion and intraparticle diffusion were involved in the adsorption process. The thermodynamics analysis suggested that the adsorption process of MB onto 3D-GO/CS/β-CD was spontaneous and endothermic. Furthermore, the regeneration study showed that the 3D-GO/CS/β-CD can be

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reused in the wastewater treatment application. All these findings demonstrated that the 3D-GO/CS/β-CD could be a cost-effective and promising adsorbent for MB removal from the aqueous solution.

1. Introduction

Owing to the extensive use of organic dyes in various industrial fields, such as textile, paper printing, food, leather and paint industries, large volumes of dyeing effluents are produced in these industrial production processes [1–3]. The dyeing wastewater with high color degree, toxicity and low biodegradability has provoked increasing environmental concern for public health [4,5]. Up to now, a wide range of biological and physicochemical approaches, including chemical oxidation [6], biodegradation [7], electrolysis [8], photo-catalytic degradation [9], membrane separation [10] and adsorption [11], have been developed to treat dyeing wastewater. Among these methods, adsorption is the most broadly used method owing to its easy and safe operation, high efficiency and comparatively low cost. In the previous studies, several adsorbents, such as activated carbon [12], metal–organic frameworks [13], nature zeolites [14], and carbon nanotube based material composites [15], have been reported to eliminate the dyes from wastewater. However, the low adsorption capacity and poor separation ability of those adsorbents limit the application in practice, and it may even lead to secondary pollution without a full separation from the wastewater.

Graphene, a two-dimensional (2D) nanostructured carbon material, possesses numerous superior physical and chemical properties, such as great mechanical strength, high theoretical surface area, and excellent chemical and thermal stability [16], which has aroused widespread concerns of researchers in various fields. However, 2D graphene tends to aggregate through strong π-π bond interaction between the 2D graphene sheets, which leads to the substantial decrease of these outstanding characteristics. Recently, many researchers [17,18] have assembled 2D graphene sheets into three-dimensional (3D) architectures to overcome the aggregation of the 2D graphene sheets. Graphene oxide (GO), with abundant oxygen-containing functional groups on the surfaces, is the oxidation product of graphene [19]. It has been used in environmental applications as a substrate material modified with other materials to assemble three-dimensional (3D) graphene composites [20–22]. The three-dimensional (3D) graphene composites not only possess the intrinsic excellent properties of 2D graphene, but also have a special 3D porous structure with various functional groups on the surfaces, which result in a better adsorption capacity for many kinds of contaminants compared with traditional 2D graphene materials. It is worth noting that the tremendous ascendency of 3D assembled macrostructures enables them to be easily separated from aqueous solution for further reuse by simple filtration after adsorption.

Until now, extensive attempts [17,23,24] have been made for developing the specific surface area of three-dimensional (3D) graphene to enhance the removal of dyes; however, a limited number of studies have focused on the modification of the porous structure. Chitosan (CS), the deacetylation derivative of chitin, and its derivatives have been widely used as biosorbents in the removal of several types of contaminants owing to the abundant amine and hydroxyl groups on CS chains [25]. Furthermore, β-cyclodextrin (β-CD) is a cyclic oligosaccharide that consists of seven α-D-glucose units connected through α-(1, 4) linkages, which has an interesting structure with a hydrophobic inner cavity and a hydrophilic exterior [26]. This characteristic enables β-CD to form inclusion complexes with contaminants such as dye pollutants. However, the poor mechanical and easy dispersibility of CS and β-CD limit the wide range of their applications in adsorption.

Based on the hypothesis that the composites formed by combination of GO, CS and β-CD would exhibit the specific surface area of 3D graphene coupled with the excellent adsorption ability of CS and β-CD, in this paper, we report a one-step green-assembly strategy to fabricate an environmentally-friendly three-dimensional porous β-cyclodextrin/chitosan functionalized graphene oxide hydrogel (3D-GO/CS/β-CD), which is based on the chemical reduction method in the presence of sodium ascorbate which acted as a reducing agent. Compared with other synthesis methods, the preparation process does not involve any toxic chemicals to prevent secondary pollution. Furthermore, the adsorption behavior of methylene blue (MB) to 3D-GO/CS/β-CD, including the adsorption kinetics, isotherms, thermodynamics, and other factors (i.e. pH and ionic strength) potentially affecting the adsorption were investigated. The 3D-GO/CS/β-CD showed an ultrahigh adsorption capacity (1134 mg/g) for MB, which suggests that the 3D-GO/CS/β-CD has great potential and a promising future to remove methylene blue from industrial dye wastewater.

2. Experimental section

2.1. Materials

Natural graphite powders (99.95% metals basis, ≥325 meshes), Methylene blue (MB), β-cyclodextrin (β–CD), chitosan (CS, with deacetylation degree of 95%, a viscosity of 100–200 mPa s) and sodium ascorbate (NaVC, 99%) were purchased from Aladdin (Shanghai, China). Genipin (GNP, purity > 98%) was purchased from LinChuan ZhiXin biological technology company (Fuzhou, China). Potassium permanganate ($KMnO_4$), concentrated sulfuric acid, hydrochloric acid, hydrogen peroxide, acetic acid, ethyl alcohol and phosphoric acid were purchased from Guangzhou Chemical Reagents Company (Guangzhou, China). All reagents and chemicals were analytical grade and used without further purification. The deionized water used in the experiments was purified by Millipore Milli-Q system.

2.2. Preparation of graphene oxide (GO)

Graphene Oxide (GO) was synthesized from natural graphite powders by a modified Hummers method [27]. Briefly, a 9:1 mixture of concentrated H_2SO_4/H_3PO_4 (360: 40 mL) was slowly added to a mixture of graphite flakes (3.0 g) and $KMnO_4$ (18.0 g), and the solution temperature will up to 35–40 °C owing to a slight exothermic of the reaction. Then the mixture was placed in a water bath at 50 °C and kept stirring for 12 h. After cooled to room temperature (25 ± 2 °C), the mixture was poured onto ice (~400 mL), 30% H_2O_2 (6–7 mL) was added into the mixture dropwise, and then stirred the mixture constantly until bright yellow products appeared. The obtained GO washed with hydrochloric acid (~5 wt%) and deionized water, and finally freeze-dried for further use.

2.3. Preparation of three-dimensional GO/CS/β-CD hydrogel

Graphite oxide was dispersed in deionized water and sonicated 2 h to obtain GO aqueous dispersion (2.0 mg/mL). 0.24 g β-CD was added to 20 mL GO solution (2.0 mg/mL) under magnetic stirring until β-CD uniformly dispersed in the suspension and the mixed solution was further sonicated for 30 min. Then, 0.4 mL glacial acetic acid and 0.12 g CS were added to the mixed solution, and a 2 h magnetic stirring follows. Afterward, 1 wt% GNP alcohol solution and 0.2 g NaVC were added, and the whole system was kept stirring for 10 min. The resulting solution was transferred into a 100 mL Teflon-lined autoclave and heated at 90 °C for 12 h to get the 3D-GO/CS/β-CD composites. The obtained 3D-GO/CS/β-CD was placed in deionized water for 24 h to