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Synthesis of citric acid functionalized magnetic graphene oxide coated corn straw for methylene blue adsorption

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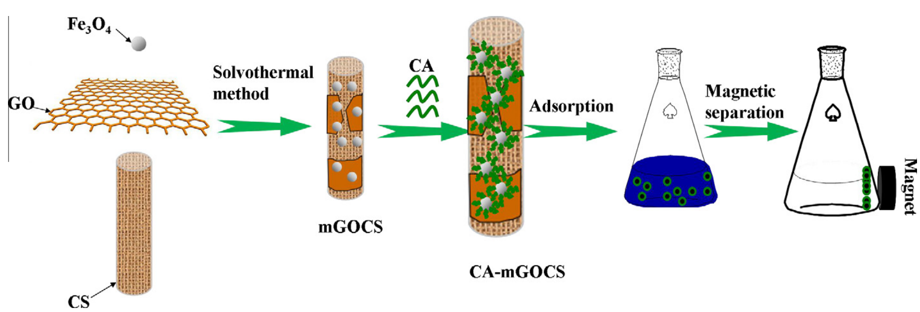
HIGHLIGHTS

- The CA-mGOCS was synthesized for the removal of MB from aqueous solution.
- The adsorption performance obeyed the pseudo-second-order and Freundlich models.
- The adsorption mechanism was a spontaneous, exothermic and randomness decrease process.
- CA-mGO5CS had an excellent reproducibility.

GRAPHICAL ABSTRACT

The schematic illustration of preparing CA-mGOCS and adsorption MB process.



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ABSTRACT

The citric acid functionalized magnetic graphene oxide coated corn straw (CA-mGOCS) as a new adsorbent was synthesized in this work for the elimination of methylene blue (MB) from waste water. The as-prepared CA-mGOCS was tested by SEM, FTIR, XRD, Roman spectrum, TGA, particle size analyzer, BET and magnetic properties analyzer. Some factors affecting adsorption removal efficiency were explored. As a result, the addition of 5 g CS (CA-mGO5CS) had the better adsorption performance than other adsorbents. The pseudo-second-order model and the Freundlich described the adsorption behavior well. The equilibrium adsorption capacity was 315.5 mg g^{-1} for MB at pH = 12 and 298 k. The electrostatic incorporation as well as hydrophobic interactions between CA-mGO5CS and MB determined the favourable adsorption property. Besides, the thermodynamic studies results $\Delta G < 0$, $\Delta H < 0$, $\Delta S < 0$ suggested that the adsorption was a spontaneous, exothermic and randomness decrease process. Finally, reusability studies imply that CA-mGO5CS has an excellent reproducibility.

1. Introduction

The synthetic dyes have been widely used in plastic, leather, communication, food, paper printing and textile industries. Dyes wastewater is affecting the ecological environment and human health seriously because of its complex composition, depth color, high content organic pollutants, poor biodegradability and most of them as well as their intermediate holding mutagenicity, carcinogenicity and other toxicity (Hoa et al., 2016; González et al., 2015; Gan et al., 2015). Therefore, the treatment of dyes effluents has increasingly become the focus attention. Methylene blue (MB) is a representative compound of water-soluble azo dyes. MB forms a monovalent organic cationic quaternary ammonium ionic group, which has serious pollution for environment

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(Pirbazari et al., 2014; Feng et al., 2012; Li et al., 2016). At present, various ways have been commonly explored for the treatment of dyes effluents, including of biological treatment, chemical oxidation, flocculation, precipitation, adsorption and photocatalytic degradation methods. Among them, adsorption method with the low cost, strong operability, easy design and environmental protection has been recognized as the most suitable approach to separate various dyes from wastewater (Çelekli et al., 2013; Oei et al., 2009; Baldikova et al., 2015). Therefore, an adsorbent owning various excellent characteristics is urgently expected.

The straw is a rich source of agricultural by-product. Its main component is hemicellulose and lignin (Pirbazari et al., 2014; El-Bindary et al., 2014). So far, the most common way to deal with about 300 million tons of straw in China every year is incineration or deserting, which destroys the soil and atmosphere as well as is the waste of resources (Pirbazari et al., 2014; Zhang et al., 2012a, b). The straw holds the porous structure and rich available reactive groups, which can promote MB solution to penetrate easily into its interior. Therefore, preparation of straw-based adsorbents is one of the most promising ways to make full use of this abundant bioresource (Zhao et al., 2014; Xu et al., 2010; Zhang et al., 2011; El-Bindary et al., 2015). In recent years, in order to easily separate and collect adsorbent from water after adsorption, magnetic adsorbent shows a predominance future due to accomplishment the separation rapidly under an portable magnet, omitting the complex filtration or centrifugation (Tian et al., 2011; Yao et al., 2015). There are many reports about magnetic straw as adsorbents, such as magnetic rye straw for acridine orange and methyl green (Baldikova et al., 2015), magnetic wheat straw for MB (Pirbazari et al., 2014), magnetic wheat straw for arsenic (Tian et al., 2011), magnetic rice straw for heavy metals (Khandanlou et al., 2016), magnetic wheat straw biochar for MB (Li et al., 2016), and so on. However, the adsorption capacity of raw straw is inefficiency. Normally, chemical treatment particularly acid modification is one of the most universal methods to prepare straw owning the typical functional groups with the high adsorption capacity (Feng et al., 2012). So far, citric acid (CA) is frequently utilized to deal with various pollutions in waste water due to environment friendly, efficient and low-cost compound (Gong et al., 2008; Franklin and Guhanathan, 2015). Sun et al. reported that the maximum adsorption capacity of CA coated biochar derived from eucalyptus saw dust for MB was 178.57 mg g^{-1} (Sun et al., 2015). Leyva-Ramos et al. found that the biochar originated in corncob treatment with CA was more efficient than that of treatment with nitric acid, 55.2 and 19.3 mg g^{-1} adsorption capacities for Cd(II), respectively (Leyva-Ramos et al., 2005).

Graphene oxide (GO) and graphene are considered good candidates for adsorbent due to unique two-dimension structure (Xing et al., 2015). GO is an oxidation of graphene. GO has a high surface area and abundant functional groups on surface introduced by the oxidation process of graphite. The groups are the key chemical skeletons which can be used as anchoring sites for dyes connection, making it become a potential material as a super and ideal adsorbent (Wang et al., 2015a; Zhao et al., 2015).

Our aim is to find a novel, cost-effective and high-efficiency CA modified magnetic GO coated corn straw (CA-mGOCS) adsorbent for removal of MB. There are many reports on absorption performance of mGO (Zhao et al., 2015; Cui et al., 2015; Ouyang et al., 2015; Ali et al., 2015; Hu et al., 2015), magnetic straw (Pirbazari et al., 2014; Li et al., 2016; Baldikova et al., 2015), CA coated straw (Gong et al., 2008). However, to the best of our knowledge, CA-mGOCS even GO coated CS as adsorbents has not been studied. In this work, mGOCS was synthesized using a simple one-step solvothermal method and then CA was decorated on mGOCS by adjusting the reaction pH, temperature and reaction time. The relevant factors that influenced the adsorption performance were discussed. The dynamics and thermodynamics were utilized to discuss the interactions between CA-mGOCS and MB. The recyclability and reproducibility of CA-mGOCS were measured to explore its potential environment and economic benefits.

2. Experimental section

2.1. Materials

Graphite powder (8000 meshes, 99.95%) and all chemical agents with analytical reagent grade were supplied by Aladdin Industrial Corporation (Shanghai, China). CS was gained from countryside of Jinan. The 100 mesh CS was obtained according to the method of (Chen et al., 2015a) mentioned.

2.2. Synthesis of CA-mGOCS

The GO aqueous suspension was prepared using the modified Hummers method (Wang et al., 2015b,c; Chen et al., 2014; Chen et al., 2015b).

The mGO was synthesized using a solvothermal system (Cui et al., 2015). Firstly, 16.2 g ferric trichloride hexahydrate ($FeCl_3{\cdot}6H_2O$) was added into ethylene glycol under magnetic stirring for dissolution completely. Then, 81.1 g GO aqueous suspension (10 mg g^{-1}) was dispersed into the above solution. With continuous magnetic stirring, 15 ml ammonium hydroxide was added to the solution by continuous dipping method. After forming the uniform mixture solution, 1 g polyvinylpyrrolidone was added slowly. Next, the above mixture was pour into six Teflon reactors for 20 h at 180 °C. After that, the reactors were cooled naturally and then the prepared mGO was obtained using magnetic separation and washing by ultrapure water and ethanol repeatedly. Finally, after the oven dry at 50 °C and grind process, the mGO power was collected for the following experiments. mGO5CS and mGO10CS were prepared by the same way with mGO except added 5 g and 10 g CS fiber during added GO. The CA-mGO and CA-mGOCS materials were synthesized according to the method of (Lin et al., 2014) mentioned.

2.3. Characterizations

The morphology properties of GO, CA-mGO and CA-mGOCA were characterized by SEM (FEI, QUANTA FEG 250, USA) system. FTIR measurement was carried out by a FTIR spectrometer (Nicolet 380, Thermo electron corporation, USA). The structure of the adsorbent was performed by XRD (D8 ADVANCE, Bruker, Germany). Raman spectra were measured using an inVia Reflex confocal Laser MicroRaman spectrometer (Renishaw, Britain). The TGA (TGA/DSC1/1600HTA) produced by Mettler-Toledo was utilized for recording thermal property of adsorbent with a heating rate of 10 °C/min under argon atmosphere. Particle size and distribution were recorded by dynamic laser particle analyzer (LS-13320, Beckman Coulter, United States). The pore size distribution and specific surface area were characterized by the Micromeritics ASAP 2020 and porosity analyzer (Quantachrome, United States). Before measurement, the sample was dried under vacuum at 200 °C for 12 h. The magnetic performances were detected by a vibrating sample magnetometer (VSM, Lakeshore, Model 7400 series). The UV–vis spectra of MB solution were operated using a Shimadzu UV2550 spectrometer. The zeta potentials of the adsorbents with the different pH values were tested by Zeta PALS (Phase Analysis Light Scattering) made by Brookhaven Instruments Corporation (USA).

2.4. MB adsorption

The concentration of the MB stock solution for adsorption experiment was 2000 mg L^{-1}. The magnetic adsorbent was added