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Tannic acid functionalized graphene hydrogel for organic dye adsorption

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ABSTRACT

Water purification provides a feasible way to relieve the pressure of water shortage and water pollution which we are facing and adsorption is one of the most effective ways to turn polluted water into clean water. Here, we prepared graphene-tannic acid hydrogel using graphene oxide and tannic acid, a natural green reducer and adsorbent, through one-step hydrothermal method. The composition, structure, and morphology of the compounds were systematically examined. The adsorption of dyes was mainly influenced by the morphology and chemical properties of gel. The addition of tannic acid, a molecule rich in oxygen containing functional groups, changed the surface chemistry of graphene sheets and microstructures of gels, which was beneficial for contaminate adsorption. Compared with reduced graphene oxide hydrogel, the graphene-tannic acid hydrogel showed an outstanding adsorption capacity for organic dye methylene blue, more than 500 mg/g at pH 10 and the maximum adsorption capacity was up to 714 mg/g. After adsorption, ethanol and inorganic acid solution can be used as desorption agent and there was no significant adsorption capacity loss after 5 cycles.

1. Introduction

Water resource has become one of the most important concerns for the whole world since last century. At present, human beings can only utilize water from rivers, shallow ground and freshwater lakes, accounting for only 7/100,000 of total water, about 9000 cubic kilometers of fresh water resources that can be effectively used in the world every year (Niemczynowicz, 2000).

With the economic development and population boom, the water consumption of the world is dramatically increasing, resulting in great water scarcity. Recent reports have showed that 4–5 billion people are facing severe water scarcity at least 1 month of a year, and 1/10 of world's population severely lack water in the whole year (Mekonnen and Hoekstra, 2016; Rodell et al., 2018).

With the urbanization, development of agriculture, and fast growth of industries, more and more wastewater are produced and sent out. For example, one ton of textiles consume 100–200 tons of water, of which 80–90% become waste water (Chen, 2015). Wastewater, such as printing and dyeing wastewater, containing a huge amount of organic dyes, which have large biological toxicity, has been shown to reduce the transparency of the water, consume a lot of oxygen in the water, affect the growth of aquatic organisms and microorganisms, and destroy the self-purification ability of water bodies (S. Hosseinzadeh et al., 2018; Riswan Ahamed et al., 2017; Tiwari et al., 2013).

Unfortunately, according to UNESCO, 80% of wastewater flows back into the ecosystem without being treated or reused globally until 2017 (Rodell et al., 2018). Deterioration of the ecological environment declines its ability to purify water, and most of wastewater discharged into the ecosystem cannot be naturally purified. Consequently, water purification is imperative as it strongly influences the human health, agricultural production, industrial output and environmental quality (Elimelech and Phillip, 2011).

Water treatment aims to remove or reduce pollutants in sewage by ways of physical, chemical and biological processes including precipitation (O'Melia, 1985), filtration (Muppalla et al., 2013), adsorption (Abukhadra et al., 2018; Gouthaman et al., 2018; H. Hosseinzadeh et al., 2018; Shaban et al., 2018; Tiwari et al., 2013), photocatalytic degradation (Banerjee et al., 2018), activated sludge (Bougrier et al., 2008) and so on (Fu and Wang, 2011; Fu et al., 2018; Si et al., 2012). At present, water treatments are mainly performed in factories, wastewater treatment plants and homes. Sewage in factory is full of toxic and harmful substances, such as dyes in printing and dyeing industry sewage, which can be reused. General treatment is hard to deal with it and may cause toxic sludge and waste of resources. In this regard, adsorption can effectively remove these substances from water, and realize the recycling and reuse, which is environmental friendly and resource-saving.

The low cost, easy operation, flexibility, design simplicity and

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limited secondary pollution make adsorption promising for water treatment. More importantly, accompanied by adsorption/desorption process, adsorption strategy can fulfill the goal of zero waste (Rafatullah et al., 2010). Conventional adsorbents, take the most commonly used activated carbon for example, suffer from difficulty in regeneration, high cost, low adsorption capacity etc, making it necessary to develop new adsorbents.

Graphene, a fascinating 2D carbon material, attracts a lot of attention because of its fantastic properties. As a rapidly rising star (Materials, 2007), graphene is a hopeful candidate for water purification owing to its high specific surface area, with a theoretical value of 2630 m^2/g (Stoller et al., 2008). Reduced graphene oxide (rGO) has a high adsorption capacity of contaminants due to hydrophobic effect, π-π conjugation and π electron donor-acceptors effect, hydrogen bonding and electrostatic attraction.

The adsorption behavior of graphene and graphene oxide (GO) has been reported in many works (Ersan et al., 2017; Zhou et al., 2015). but their dispersion and transportation in water brings security threat (Suárez-Iglesias et al., 2016). Hydrophobic graphene gel with three-dimensional interconnected porous network structure improves its safety and reliability. Graphene based composite hydrogels as adsorbents have been widely studied in recent years (see Table S1) (Chen et al., 2013; Cong et al., 2015; Gan et al., 2015; Gao et al., 2013; Liu et al., 2012; Sui et al., 2012; Tiwari et al., 2013; Varaprasad et al., 2017; Wei et al., 2013; Zhang et al., 2013) and great achievements have been achieved, but graphene-based hydrogels with even higher adsorption capacity and low cost is still highly desired.

Tannin, a widely distributed complex secondary metabolite of higher plants, forms hundreds of millions of tons of renewable resources in the world. It has been found that the polyhydroxy structure and unique chemical properties of plant tannin endow it with inhibition of bacteria and enzymes, resistance to UV irradiation, capture of free radicals and a series of interesting chemical behaviors. Since 1950s, with the continuous exploration of chemical structures and properties of plant tannins, the applications of tannin have expanded into the fields of medicine, food, chemical industry, and so on (Ma et al., 2006). It can be used as bacteriostatic agent, anti-tumor drugs, antioxidants, preservatives, water purification agents and adsorption agents (Bacelo et al., 2016).

Tannic acid (TA) is a typical kind of hydrolysable tannin, which can be used as reductant of graphene (Lei et al., 2011). The tannin extraction process has been industrialized and it is low cost. In this work, we developed a simple one-step method to prepare graphene-tannic acid (GT) hydrogels using tannic acid and the hydrogels revealed outstanding adsorption capacity.

2. Experiment section

2.1. Materials

Natural graphite powders were purchased from Shenghua Research Institute (Changsha, China). Methylene blue (MB), phosphorus pentoxide (P_2O_5) and potassium persulfate ($K_2S_2O_8$) were bought from Aladdin. Potassium permanganate ($KMnO_4$) and sodium hydroxide (NaOH) were obtained from Kelong Chemical Reagent Factory (Chengdu, China). Hydrogen peroxide (H_2O_2), concentrated sulfuric acid (H_2SO_4), and hydrogen chloride solution (HCl) were from Xilong Chemical Co., Ltd (Shantou, China). All the chemicals were analytical-grade and used without further treatment.

2.2. Preparation of GO

GO was prepared from graphite with a two-step oxidation procedure (Yu et al., 2016). In a typical process, 1000 mL three-necked flask containing 20 g $K_2S_2O_8$, 20 g P_2O_5 and 150 mL H_2SO_4 were heated to 90 ℃ under continuous stirring. Next, 24 g natural graphite powders were added in and the mixture was left at 80 ℃ for 4.5 h. Then, the mixture was slowly poured into 2000 mL deionized water and kept for 12 h. After filtration, the mixture was washed using deionized water to remove soluble impurities and dried in oven at 60 ℃.

Second, 230 mL H_2SO_4, 6 g pretreated graphite and 30 g $KMnO_4$ were added to a 1000 mL flask in sequence and the mixture was held at 35 ℃ for 2 h. Then, 500 mL deionized water was dropped into the flask in ice-water bath. The mixture was poured into a beaker containing 1400 mL deionized water and stirred for 2 h. Next, enough H_2O_2 was added in (until no bubble) and the beaker was kept overnight without disturbance. The suspension was filtered and the filtration was thoroughly washed using HCl aqueous solution (5%) and deionized water. After centrifugation, the sediment was lyophilized to get solid GO.

2.3. Preparation of graphene-tannic acid hydrogels

Graphene-tannic acid (GT) hydrogels were prepared using a hydrothermal process. In a typical procedure, 120 mg GO powders were dissolved into 60 mL distilled water. Then various amounts of tannic acid powders were added in respectively. The weight ratios of GO to TA were 1:0, 1:0.25, 1:0.5, 1:1, 1:2, and 1:4. The mixtures were sonicated for 30 min to a homogeneous state. After sonication, the aqueous dispersions were added into Teflon–lined autoclaves and sealed, maintaining for 12 h at 180 ℃. Then, gels were taken out from the autoclaves. The obtained hydrogels were immersed in distilled water for 3 days to remove isolated TA and rGO. Then, after freezing in the refrigerator, the hydrogels were lyophilized at −40 ℃ and 30 Pa. Finally, the freeze-dried gels were well kept for characterizations and adsorption experiments. The obtained hydrogels were named as GT0, GT1/4, GT1/2, GT1, GT2, and GT4, respectively.

2.4. Characterization

To reveal the compositions of the hydrogels, Fourier transform infrared spectra (FTIR) of the samples (GO, TA, and GT hydrogels) were obtained with a Thermo Nicolet 6700 FTIR spectrometer from 4000 to 600 cm^{-1} at room temperature. X-ray photoelectron spectrum (XPS) was performed on an XSAM800 X-ray Photoelectron Spectrometer (Kratos Company, UK) with AlKα radiation (hv = 1486.6 eV). X-ray diffraction (XRD) analysis was carried out on a Japan Rigaku X-ray diffractometer (UItima IV) from 2° to 80° using CuKα radiation (λ = 0.154056 nm). Raman spectra were obtained on a Labram HR spectrometer (HORIBA Jobin Yvon). Thermogravimetic analysis (TGA) was carried out on a thermogravimetric analyzer (Q600, TA Instruments, USA) from 30 to 800 ℃ under nitrogen atmosphere. Specific surface area (SSA) of the hydrogel was obtained on a Brunner-Emmet-Teller (BET) measurement (Autosorb iQ/ASiQ, Quantachrome, USA). The microstructures and the morphology of the samples were characterized using a field-emission scanning electron microscope (SEM, JEOL JSM-5900LV) at an accelerating voltage of 20 kV and atomic force microscopy (AFM) (Anasys, AFM+ nano IR) in tapping mode.

2.5. Adsorption experiments

Adsorption experiments were performed at 20 ℃ to examine the adsorption behavior of MB on GT hydrogel. Generally, GT hydrogels with known weight were added into 100 mL MB solutions under magnetic stirring for 12 h to achieve adsorption equilibrium. Then, the mixtures were kept still without disturbance. The supernatants were taken out for further test. The influences of the initial concentration of MB and adsorption time were examined in the same way. The concentration of MB was calculated by UV − vis absorption spectra from an Ultraviolet- Visible Near-Infrared Spectrophotometer (UV3600, Shimadzu, Japan). The adsorption capacity of the adsorbent was calculated using Eq. (1):