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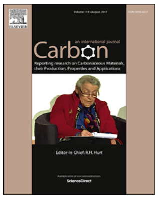

Preparation of porous graphene oxide by chemically intercalating a rigid molecule for enhanced removal of typical pharmaceuticals

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ABSTRACT

Porous graphene oxide (GO) adsorbents were successfully prepared by connecting GO sheets with tetrafluoroterephthalonitrile (TFT) or decafluorobiphenyl (DFB) through a nucleophilic aromatic substitution reaction. Textural characterization indicated that the enlarged surface area and pore size of the as-synthesized GO-based adsorbents were favorable for the diffusion and adsorption of the typical pharmaceuticals. The GO reacted with 20 mmol/L DFB (GO-DFB20) exhibited the highest removal for six pharmaceuticals among the prepared adsorbents, and can be separated easily. The adsorption capacities of GO-DFB20 for carbamazepine (CBZ), sulfamethoxazole (SMZ), sulfadiazine (SDZ), ibuprofen (IBP), paracetamol (PCT) and phenacetin (PNT) were 340.5, 428.3, 214.7, 224.3, 350.6 and 316.1 μmol/g, respectively. The adsorption kinetics of PCT on the GO-DFB20 was faster than SMZ. According to the Langmuir fitting, the maximum adsorption capacities of GO-DFB20 for SMZ and PCT were 749.6 and 663.9 μmol/g, respectively. The spent GO-DFB20 was successfully regenerated by methanol with little loss of adsorption capacity in five successive adsorption cycles. This study shows that the porous GO adsorbent has a promising application for the removal of typical pharmaceuticals from water or wastewater.

1. Introduction

Graphene exhibits many outstanding performances in electronic devices, photonics devices, biomedicine sensors and contamination purification owing to its unique physicochemical properties [1–6]. Especially, it possesses an open-layered structure that has a completely accessible adsorption surface, enabling the excellent performance in adsorption with numerous organic contaminants, such as polycyclic aromatic hydrocarbons (PAHs), dyes, antibiotics, and pesticides [7–9]. However, free-standing graphene and graphene nanosheets tend to agglomerate or restack through strong π-π interactions and van der Waals force between single layers, resulting in non-dispersibility and reduced surface area of graphene in aqueous solution [10,11]. It is afterwards difficult for pollutants to gain access into the inner layers of stacked graphene, leading to an unsatisfactory actual adsorption capacity.

Graphene oxide (GO) has been used as adsorbents, and GO sheets contain abundant hydroxyl and epoxy functional groups on their basal planes and carboxyl groups at the edges that make it dispersible in water and reactive with other materials [12–14]. All these advantages make GO a kind of promising material for design of adsorptive materials. Although GO has good adsorption for PAHs, pharmaceuticals, dyes and heavy metals, its hydrophilicity makes its collection from solution particularly difficult [4,15–18]. Since the feasibility of an industrial adsorption process partly depends on the separability of adsorbents, a strategy to design a novel structure of three-dimensional (3D) scaffolds (hydrogels, aerogels and films) from GO by thermal reduction method with or without reducing agents has been attempted recently [19–21]. These designed graphene architectures usually possess interconnected macropores that are favorable for organic solvents and oils [22–24]. However, the low density, large pore size and strong hydrophobicity characteristics were not suitable for adsorption of contaminants dissolved in water. Another approach is to intercalate GO with guest molecules or spacers through different types of covalent and non-covalent functionalization, such as polymers, metal containing

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materials (divalent ions, metal oxide and ferrocene) and nanomaterials (carbon nanotubes and fullerene) [25–30]. Most of these GO-based solids are obtained through weak forces such as van der Waals force, hydrophobic and π-π interactions, resulting in weak mechanical strength and undesirable structures. Few studies have reported chemical interconnection of GO. It is reported that glutaraldehyde containing two aldehyde groups can react with hydroxyl group on GO to form hemiacetal structures. In this way, it can bind two adjacent GO sheets, but the pore size is still uncontrollable, thus forming a material with macroscopic and low-density structures [31]. Therefore, further efforts are still needed to adjust the distance between the GO layers to form porous and easy-separation architectures for the enhanced adsorption of organic pollutants.

In this study, we came up with an idea to take advantage of a nucleophilic aromatic substitution reaction between GO and a rigid fluorine-containing molecule (TFT or DFB) to prepare a novel porous GO adsorbent. The optimal adsorbent was used to adsorb six typical pharmaceuticals (CBZ, SMZ, SDZ, IBP, PCT and PNT) in aqueous solution. Comparative adsorption studies were conducted with other carbonaceous nano-adsorbents including CNTs, 3D-rGO and GO. SMZ and PCT were selected to evaluate their adsorption behavior on the optimal adsorbent. Additionally, the regeneration and reuse of the spent adsorbent were also studied.

2. Materials and methods

2.1. Materials

Graphene oxide (GO, purity > 99%, layers < 3), multiwalled carbon nanotubes (CNTs, outer diameter: 20–30 nm, Length: 10–30 μm) were purchased from Chengdu Organic Chemicals Co. Ltd., and used as received without further purification. 3D reduced graphene oxide (3D-rGO) was synthesized in our lab according to a previously reported method [19]. TFT, DFB and K_2CO_3 were purchased from Aladdin Reagent. Six pharmaceuticals including CBZ (purity > 97%), SMZ (purity > 98%), SDZ (purity > 99%), IBP (purity >98%), PCT (purity >99%) and PNT (purity >98%) were purchased from J & K Scientific Co., Ltd (Beijing, China) and their physicochemical properties are listed in Table 1. Tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), methanol and dichloromethane (CH_2Cl_2) were obtained from Beijing chemical Works. Acetonitrile and phosphoric acid used in this study were HPLC grade (J.T. Baker Inc., USA). All chemical solutions were prepared in ultrapure water produced by a Milli-Q system (Millipore, USA).

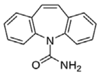
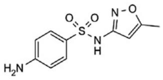
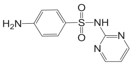
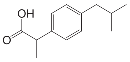
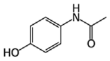
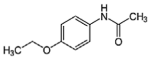
2.2. Preparation of porous GO-based adsorbents

Different GO-TFT and GO-DFB adsorbents were prepared under various conditions (Table S1). An amount of 0.1 g GO and 50 mL THF, DMF or DMSO were mixed in a 100 mL glass vials, and sonicated for 15 min, followed by addition of TFT/DFB (5, 20, 40, 80 mmol/L) and K_2CO_3 (0.6 g), and further sonicated for 10 min in an ice bath. The mixture was bubbled with N_2 gas for 10 min, then the mixture was heated at 65 °C and stirred at 500 rpm for 2 days. The final solution was cooled and then filtered. The impurity removal (residual K_2CO_3) was conducted by washing the resulted solid with 1 mol/L HCl for 1 h. The recovered solid was then soaked for 15 min in H_2O (200 mL), methanol (100 mL) and CH_2Cl_2 (50 mL), respectively. Finally, the as-prepared solid was vacuum dried in a liquid nitrogen bath for 10 min, and then dried at 50 °C for 3 days. The obtained materials were denoted as GO-TFT5, GO-TFT20, GO-TFT40, GO-TFT80, GO-DFB5, GO-DFB20, GO-DFB40 and GO-DFB80 based on different intercalating molecules and their concentrations.

2.3. Characterization

The thermal properties of the samples were recorded by a thermogravimeter (TGA) (Mettler Toledo, TGA/DSC 1 Stare, Switzerland) and all of the measurements were carried out under nitrogen gas over a temperature range of 25–500 °C with a ramp rate of 5 °C/min. The morphology of the prepared materials was examined by atomic force microscopy (AFM) (Shimadzu, SPM-9600 Series, Japan). The Brunauer–Emmett–Teller (BET) surface area and pore size distribution were measured by an automated gas sorption analyzer (Quantachrome, autosorb-iQ, USA). XRD patterns were obtained by an X-ray diffractometer (Rigaku S2, Japan). FTIR spectra were tested on a Thermo Nicolet NEXUS FTIR spectrometer at room temperature. Raman spectra were obtained with an

Table 1
Physicochemical properties of six selected pharmaceuticals.

Adsorbates	Molecular formula	Structure	MW	$\log K_{ow}$	pK_a
Carbamazepine (CBZ)	$C_{15}H_{12}N_2O$		236	2.47	2.3 13.9
Sulfamethoxazole (SMZ)	$C_{10}H_{11}N_3O_3S$		253	0.89	1.5 5.7
Sulfadiazine (SDZ)	$C_{10}H_{10}N_4O_2S$		250	−0.34	1.6 6.5
Ibuprofen (IBP)	$C_{13}H_{18}O_2$		106	3.5	4.5
Paracetamol (PCT)	$C_8H_9NO_2$		151	0.46	9.4
Phenacetin (PNT)	$C_{10}H_{13}NO_2$		179	1.58	14.9