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Adsorption behaviors of tetracycline on magnetic graphene oxide sponge

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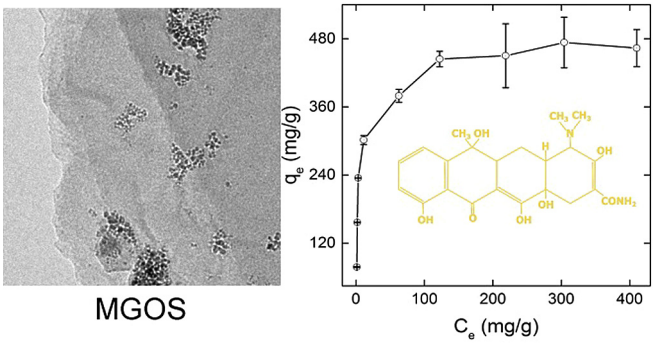
HIGHLIGHTS

- Magnetic graphene sponge (MGOS) was prepared for antibiotics tetracycline adsorption.
- MGOS had huge capacity for tetracycline (473 mg/g), 50% higher than that of graphene oxide.
- The adsorption process was moderately fast and could be described by pseudo-second-order model.
- The small size and negative charge of Fe_3O_4 contributed to the improved performance of MGOS.

GRAPHICAL ABSTRACT



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ABSTRACT

Magnetic nanoparticles were adopted for the synthesis of magnetic graphene adsorbents, but the incorporation of magnetic nanoparticles significantly reduced the adsorption capacity of graphene for antibiotics. In this study, we prepared magnetic graphene oxide sponge (MGOS) by lyophilizing the dispersion of Fe_3O_4 nanoparticles and graphene oxide (GO) for tetracycline adsorption. GO self-assembled to form large sheets that built the large pores in MGOS. Fe_3O_4 nanoparticles were attached on GO sheets, enabling the magnetic property of MGOS. The adsorption capacity of MGOS for tetracycline was 473 mg/g, showing 50% increase comparing to GO. The adsorption was moderately fast and could be described by pseudo-second-order model. The thermodynamics investigation indicated that the adsorption was endothermic and the driving force was entropy increase. The pH had mild influence on the adsorption, while ionic strength nearly had no impact. The implication to the applications of MGOS in antibiotics remediation is discussed.

1. Introduction

Since the discovery of penicillin, the great developments in antibiotics have been achieved, where pharmaceutical antibiotics has been worldwide used in the treatment of human and animal diseases [1,2]. However, a huge amount of antibiotics is discharged into the environment during the production, delivery and application [3]. In particular, most antibiotics could not be absorbed and metabolized, thus, antibiotics would be excreted into excreta and released to the environment. The antibiotics pollution leads to

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several serious hazards [4,5]. First, antibiotics are toxic to bacteria in water and soil, which would disturb the balance of microflora and ecosystem. Second, the continuous exposure to antibiotics increases the drug resistance of germs. Third, the uptake of unnecessary antibiotics by human would arouse toxicity in body [6,7]. To these regards, it is very important to remediate the antibiotics pollution.

Among the efficient treatments of antibiotics, adsorption is widely researched, because adsorption is convenient, fast and economic [7,8]. Many adsorbents have been applied in the remediation of antibiotics, including active carbon [9], kaolinite [10], palygorskite [11], alumina [9] and chitosan [12]. More recently, nanomaterials show great promising in adsorbing antibiotics due to the large surface area and controllable surface functionalities [3,4,13–15]. Among these high-performance nanomaterial adsorbents, graphene has been regarded as the most effective adsorbent for antibiotics. All atoms of graphene are surficial atoms and the oxidation degree of graphene could be well designed [16]. Several adsorption demonstrations have been reported. In 2012, Gao et al. firstly reported that graphene oxide (GO) could be applied in adsorbing tetracycline (313 mg/g) and oxytetracycline (212 mg/g) [6]. Rostamian and Behnejad compared the adsorption performances of graphene and GO for sulfamethoxazole, where graphene showed lower capacity (103 mg/g) than GO (122 mg/g) [17]. The value was dramatically increased in another independent investigation, where Nam et al. measured the capacity of GO for diclofenac and sulfamethoxazole as 500 and 3709 mg/g [18]. Upon sonication, the adsorption capacity for sulfamethoxazole further increased. Peng et al. attributed the adsorption of antibiotics on graphene to π-π interaction between aromatic rings on adsorbed substance and carbon based materials [19]. Zhang et al. used experimental and theoretical approaches to confirm the coexists of π-π interaction and H-bonds during the adsorption of norfloxacin and tetracycline on GO and reduced GO (RGO) [20]. To optimize the properties of graphene adsorbents, several graphene composites were also prepared for the adsorption of antibiotics, such as GO/chitosan [14], GO-TiO_2 [3], GO/calcium alginate fibres [21], graphene-soy protein aerogel [22] and sodium alginate/GO beads [2].

To facilitate the separation of graphene adsorbent, magnetic graphene composites have been developed for the treatment of antibiotics, where magnetic nanoparticles were incorporated on graphene sheets. Tang et al. prepared RGO/Fe_3O_4 composite for the adsorption of ciprofloxacin (19.0 mg/g) and norfloxacin (23.3 mg/g) [15]. Nodeh and Sereshti developed GO/Fe_3O_4-$SrTiO_3$ for the adsorption of tetracycline and cefotaxime with adsorption capacities of 65.78 mg/g and 18.21 mg/g, respectively [8]. Wang et al. used Fe_3O_4-chitosan grafted GO nanocomposite to treat ciprofloxacin with higher capacity of 282.9 mg/g, which could be regenerated easily [23]. Lin et al. compared the adsorption performance of Fe_3O_4-GO for tetracycline (39.1 mg/g), oxytetracycline (45.0 mg/g), chlortetracycline (42.6 mg/g), and doxycycline (35.5 mg/g) [24]. The major limit of current magnetic graphene adsorbents is the low capacity, which should be due to the occupation of adsorptive sites by overwhelming Fe_3O_4. It is urgent to develop magnetic graphene adsorbent with high adsorption capacity.

Herein, we coupled small amount of Fe_3O_4 with GO to prepare magnetic graphene oxide sponge (MGOS) for the adsorption of tetracycline with a high capacity of 473 mg/g. MGOS was characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), infrared spectrometer (IR) and magnetometer. The adsorption isotherm of tetracycline on MGOS was obtained and analyzed by Langmuir model, Freundlich model and Temkin model. The adsorption kinetics data were quantified and fitted to pseudo-first-order model, pseudo-second-order model and intraparticle model. The influence of temperature was investigated and the thermodynamics parameters were calculated. The influences of pH and ionic strength were also concerned. The implication to the applications of MGOS in antibiotics adsorption is discussed.

2. Materials and methods

2.1. Preparation of MGOS

Sodium citrate coated Fe_3O_4 nanoparticles were prepared by co-precipitation of Fe^{2+} and Fe^{3+} with OH^- in the presence of sodium citrate as reported in the literature with modifications [25]. GO was prepared by modified Hummers method following our previous reports [26–29]. To prepare MGOS, Fe_3O_4 and GO was well mixed at the mass ratio of 1:40 and lyophilized. The as prepared MGOS was characterized by IR (Magna-IR 750, Nicolet, USA), XRD (D/MAX 2000, Rigaku, Japan), SEM (Quanta 200FEG, FEI, Netherland), TEM (JEM-200CX, JEOL, Japan), XPS (Kratos, UK) and magnetometer (MPMS XL-7 tesla, Quantum Design, USA) before use.

2.2. Adsorption isotherm

Tetracycline hydrochloride was obtained from Alfa Aesar Chemical Reagent Co., Ltd., China. To quantify the adsorption isotherm, 8 mL of tetracycline (50–1000 mg/L, pH 3) was added to 5 mg MGOS. After shaking for 48 h at 308 K, the supernatant was collected upon 12000 rpm centrifugation for 5 min. As discussed in our previous report [30], centrifugation was adopted rather than magnetic separation, because centrifugation allowed the handling of multiple samples in the same time. The concentration of remnant tetracycline (C_e) was measured by UV–vis spectrometer at 364 nm, referring to a calibration curve. The equilibrium adsorption capacity at each C_e was calculated following equation (1), where C_0 was the initial concentration of tetracycline, V was the volume of solution (8 mL) and m_{MGOS} was the weight of adsorbent (5 mg). The isothermal data were analyzed by Langmuir model (equation (2)), Freundlich model (equation (3)) and Temkin model (equation (4)). In equation (2), q_m was the maximum adsorption capacity, and b was the adsorption constant. In equation (3), K_F was the Freundlich constant, and n was the linear indicator. In equation (4), A and B were the equilibrium binding constants, where Temkin constant b could be obtained from RT/B.

$$q_e = \frac{(C_0 - C_e) \times V}{m_{MGOS}} \tag{1}$$

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{bq_mC_e} \tag{2}$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{3}$$

$$q_e = B \ln A + B \ln C_e \tag{4}$$

2.3. Adsorption kinetics

The adsorption as a function of time was evaluated to obtain the kinetics information. For each time point, 5 mg of MGOS was mixed with 8 mL of tetracycline (400 mg/L, pH 3) and shaken at 308 K. Samples were collected at different time points (1–48 h) for tetracycline concentration (C_t) measurements. The adsorption capacity (q_t) and C_t were fitted to pseudo-first-order model (equation