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Performance of magnetic graphene oxide/diethylenetriaminepentaacetic acid nanocomposite for the tetracycline and ciprofloxacin adsorption in single and binary systems



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ABSTRACT

Adsorption of tetracycline (TC) and ciprofloxacin (CIP) in single and binary systems by diethylenetriaminepentaacetic acid-functionalized magnetic graphene oxide (DDMGO) was explored. DDMGO were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and zeta potential measurements. The adsorption kinetics and equilibrium data of single antibiotic were well fitted by pseudo-second-order and Freundlich isotherm models, respectively. Negative ΔG° values hinted the spontaneous nature of TC and CIP sorption. Moreover, the ΔH° was positive for TC removal and negative for CIP removal, indicating that TC adsorption was endothermic and CIP adsorption was exothermic. Various experimental conditions (pH, ionic strength and foreign ions) presented an important influence on TC and CIP removal. In binary systems, TC sorption onto DDMGO exhibited stronger inhibition effect by the coexisting competitive antibiotics than that for CIP. The reusability experiment revealed that the DDMGO had an excellent regeneration performance in single and binary systems. TC and CIP removal mechanism on DDMGO was mainly dependent on π - π interaction, hydrogen bonds and amidation reaction. Besides, TC and CIP uptake could also be explained by cation- π and electrostatic interaction, respectively. These findings showed that DDMGO was an efficient and reusable adsorbent for antibiotics elimination. © 2018 Elsevier Inc. All rights reserved.

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1. Introduction

Graphene is a two-dimensional monolayer sheet of carbon atoms covalently connected via sp² sigma bonds to form a honeycomb crystal lattice [1]. Over recent decades, graphene industry has witnessed the important scientific development of graphene as a promising material, owing to its unique morphological structure, outstanding electron conductivity, scalability and optical properties [2]. Notably, graphene possesses a double-sided polvaromatic scaffold with large surface area (2630 m^2/g) and high surface hydrophobicity, making it a promising candidate for the adsorption of many hydrophobic organic contaminants, particularly these with molecules containing π -electrons that can interact with polarized graphene surface via π - π interaction. Unfortunately, in scale environmental application, graphene is hard to separate and retrieve from a suspension after adsorption. Many researchers have worked to overcome these deficiencies and successfully found that grafting magnetic nanoparticles onto graphene surface could promote the solid-liquid separation after adsorption by a magnet. While the extra load magnetic particles will occupy the adsorption sites, which is not conducive to adsorption. Further loading the substances contained abundant of amino and carboxyl groups can effectively combine with functional groups of organic pollutant [3]. Thus, aminated magnetic graphene-based composite offers the potential to develop for organic pollutant removal.

Antibiotics, as one of the most frequently detected organic contaminants in sewage, often exist in the environment as mixtures instead of single compound. Residual antibiotics in the environment have low biodegradability under natural conditions, which can cause potential risk to the ecological environment and human health. Therefore, it is desirable to find an efficient and feasible method to remove antibiotics from aqueous solution. Tetracycline (TC) and ciprofloxacin (CIP) are two kinds of typical antibiotics extensively used for human and veterinary animals and frequently detected in the aquatic environment [4,5]. In the past decades, multiple chemical and physical methodologies had been conducted to deal with these antibiotics wastewater, such as photocatalysis [6– 8], chemical oxidation [9], biodegradation [10], liquid extraction [11], adsorption [5,12], and membrane separation techniques [13]. Among these methods, adsorption has been considered as a promising method for the elimination of antibiotics from water and wastewater since its high efficiency, simple operation, low cost and less production of toxic intermediates [14]. In fact, various carbonaceous adsorbents, including various functionalized carbon nanotubes (CNTs) [15], graphene oxide (GO) [16], activated carbons [17], biochar [18], carbon xerogel [19], have been successfully used for eliminating TC and CIP from aqueous systems. However, considering the high sorption capacities, low production cost, and the aromatic rings in their molecular structures of the two antibiotics, the adsorption of these antibiotics might be particularly suited for graphene-based materials by strong π - π interactions [13]. Many studies have confirmed that graphene-based materials were highefficiency adsorbents for the removal of antibiotic pollutants. For examples, Gao et al. [16] reported that the maximum adsorption capacities of TC reached 313 mg/g on GO; Chen et al. [5] found GO effectively adsorbed both CIP and sulfamethoxazole (SMX) with maximum sorption capacity of 379 and 240 mg/g. Wang et al. [20] demonstrated various graphene-based materials had high adsorption affinity for SMX. In ours previous study, a nitrilotriacetic acid-functionalized magnetic graphene oxide was prepared, which could be an efficient adsorbent for TC and CIP removal from real wastewater [3,21]. Hence, aminated magnetic graphene-based materials might be an ideal choice for antibiotic removal because of its high efficiency and ease separation.

In a previous study, Li et al. [22] reported a method to synthesize a magnetic graphene oxide supported by diethylenetriaminepentaacetic acid composite (DDMGO). This composite was proved to be an outstanding adsorbent for metal ions removal because it contained a lot of oxygen and nitrogen containing functional groups and could be rapidly and effectively separated by a magnet from the medium. It was well known that oxygen and nitrogen containing functional groups also had a high reactivity and easily reacted with various organic compounds [23]. Therefore, the DDMGO might be an ideal adsorbent for TC and CIP removal through multiple mechanisms, such as the hydrogen bonds and π - π interaction.

In general, TC and CIP coexisted in aqueous solution is common, which may result in overlap and complementary occupation of sorption sites, thus altering mobility and leaching of these chemicals [24]. However, the behaviors of the antibiotic as affected by other antibiotic were rarely reported. Herein, in this study, we employed the DDMGO as the adsorbent to evaluate the removal of aqueous phase TC and CIP in single and binary systems by batch experiments. The obtained DDMGO were characterized by SEM, TEM, XRD, FTIR, XPS and zeta potential measurements. The main objective of this work was to (1) assess the sorption ability and regeneration performance of DDMGO to the two antibiotics; (2) probe the influences of contact time, temperature, solution pH, ionic strength, and background electrolytes on uptake of the two antibiotics in single component solution; (3) investigate the mutual effects of TC and CIP in binary systems; and (4) discuss the main adsorption mechanism through the relevant models and characterization analysis.

2. Materials and methods

2.1. Materials

Diethylenetriaminepentaacetic acid (DTPA) was provided by Xiya Reagent Research Center (Shandong, China). 1-ethyl-3-(3dimethylaminopropyl) carbodiimide hydrochloride (EDC) and Nhydroxyl succinimide (NHS) were obtained from Shanghai Civi Chemical Technology Co., Ltd. TC and CIP (\geq 99% purity) were supplied by Hefei Bomei Biotechnology Co., Ltd., China. Graphite powder, diethylenetriamine, KMnO₄, FeCl₃·6H₂O, and FeSO₄·7H₂O and some other chemical reagents were all purchased from Sinopharm Chemical Reagent Co., Ltd., China (Shanghai, China). All chemicals used in the experiments were analytical purity, and all solutions were prepared with the deionized water (18.25 Ω /cm).

2.2. Preparation of DDMGO composite

The preparation process of GO and magnetic graphene oxide (MGO) had been described in detail in former study [21,25]. The aminated magnetic graphene oxide (DDMGO) was prepared by grafting DTPA onto the MGO surface through diethylenetriamine [22]. Concisely, 0.4 g EDC and 0.4 g NHS were added into the 0.8 g DTPA dissolved in low-concentration ammonia solution with continuous stirring for 2 h at room temperature in order to activate the carboxyl groups of DTPA. Next, the 40 mL diethylenetriamine and 2 g MGO dispersion were added to the mixed solution under continuous stirring at 80 °C for 6 h. After being cooled to room temperature, the obtained product was rinsed repeatedly with Milli-Q water until the solution pH was about neutral, and then stored at room temperature. The schematic depiction of the synthesis of DDMGO is shown in Graphical abstract.

2.3. Adsorbent characterization

The microstructure and surface morphologies of DDMGO before and after TC and CIP sorption were studied by scanning electron microscopy (SEM) (Hitachi S-4800, Japan) and transmission electron microscopy (TEM) (Tecnai G2 F20, USA). The identification of crystalline phase was obtained on a Bruker D8-Advance X-ray diffractometer (XRD) (Bruker, German). The BET surface area and pore structure of the adsorbent were obtained by using nitrogen adsorption-desorption measurements (Quantachrome, USA). FTIR measurements were conducted using a Nicolet 5700 spectrometer at room temperature. Surface elemental composition of the samples was quantified using an X-ray photoelectron spectroscopy (XPS) analysis based on an ESCALAB 250Xi spectrometer (Thermo Fisher, USA). The zeta potentials of DDMGO were examined in deionized water at pH 2.0–10.0 using a zeta potential meter (Zetasizer Nano-ZS90, Malvern).

2.4. Batch adsorption experiments

Adsorption of TC and CIP on DDMGO in single and binary systems were carried out by batch adsorption experiments in 25 mL conical flasks with a shaking speed of 150 rpm. The stock solutions of TC and CIP were prepared by dissolving a certain amount of TC and CIP powder into the hydrochloric acid solution. The desired TC and CIP working solutions were achieved by diluting the TC and CIP stock solution with Milli-Q water. All batch adsorption experiments were repeated three times, and about 2.28 mg DDMGO were added into the each reaction solution. Effect of initial solution pH on antibiotic sorption was examined at initial antibiotic concentration of 50 mg/L and 30 °C. The pH of the system was adjusted by adding small volumes of HCl or NaOH solutions. Kinetic studies were performed in 50 mg/L antibiotic solutions at 30 °C with a contact time ranging from 0 to 1560 min. For the sorption isotherms and thermodynamic experiments, 0-500 mg/L TC or CIP was analyzed at pH 3.0 and the experimental temperatures were controlled at 293, 303, and 313 K, respectively. To investigate the effect of ionic strength and background electrolytes, 0-0.5 mol/L of NaCl and 0–0.1 mol/L four foreign ions (K^+, Mg^{2+}, Cl^-) and SO_4^{2-}) were added into the single 50 mg/L TC or CIP solution.

For binary adsorption, the equilibrium adsorption capacities of 50 mg/L TC in the simultaneous presence of 0–20 mg/L CIP and 50 mg/L CIP in the simultaneous presence of 0–20 mg/L TC were studied. And the experiments were performed under the same experimental conditions as the single sorption system.

To take account for reuse potential of DDMGO, four successive adsorption-desorption cycles of DDMGO were carried out in TC and CIP single and mixed systems using 0.01 M NaOH as the analytic solution. In each cycle of adsorption, suspension liquid contained 250 mL TC and CIP single (50 mg/L) and mixed (50 mg/L TC and 10 mg/L CIP, 50 mg/L CIP and 10 mg/L TC, respectively) solution shaking for 24 h at 30 °C and pH 3.0. The adsorbent dosage of DDMGO was about 22.8 mg.

Then, after adsorption, the solid and liquid phases were separated by a permanent magnet. The concentrations of TC and CIP in supernatant solution were analyzed directly by using an UV–Vis spectrophotometer (UV-2550, SHIMADZU, Japan) at 357 nm [16] and 276 nm [24], respectively. The sorption capacities q_e (mg/g) of the two antibiotics were calculated according to the following equation:

$$q_e = \frac{(C_o - C_e)V}{m} \tag{1}$$

where C_o and C_e are the initial and equilibrium concentrations of the two antibiotics, respectively (mg/L); *V* is the initial solutions volume (L); and *m* is the weight of the adsorbent (g).

3. Results and discussion

3.1. Characterization of sorbents

The morphology studies of DDMGO are carried out by SEM and TEM displayed in Fig. 1. From Fig. 1a, it is clear found that DDMGO surfaces exhibit many wrinkles after modification, which could be ascribed to the introduction of magnetic nanoparticles and DTPA [3]. It was further confirmed by TEM image and its inset (Fig. 1e), which indicated that a large amount of nanoparticles were effectively dispersed on the GO surface due to the successful combination of magnetic Fe₃O₄ particles with GO [26]. After TC and CIP loaded alone, the DDMGO surface became flat (Fig. 1b and c), notably after the competitive sorption of TC and CIP (Fig. 1d). The SEM images show that TC and CIP have been adsorbed on the surface of DDMGO, and the conformation and aggregation of DDMGO after antibiotics sorption might be due to the striking alternation of the potential sorption sites of DDMGO and its strong surface interactions [4].

The crystal structure of the synthesized magnetic adsorbent was characterized using the XRD techniques. Fig. 1f presents the XRD patterns of DDMGO. As shown in Fig. 1f, several characteristic peaks are detected at 30.19, 35.61, 37.25, 43.20, 53.89, 57.28 and 62.99° (2 θ), matched well with the Fe₃O₄ indices (JCPDS 19-0629) [27], suggesting that the synthetization process do not cause the change of Fe₃O₄ crystalline phase, and thus DDMGO possesses good magnetic performance for magnetic separation [28].

The N₂ adsorption-desorption isotherms and corresponding pore size distribution of DDMGO are displayed in Fig. S1. The BET analysis showed that the specific surface areas and average pore diameter of DDMGO were 176 m²/g and 3.8 nm, respectively, which were much higher than that of MGO (115 m²/g and 1.4 nm, respectively) [21]. The pore size distribution indicated DDMGO was a mesoporous material. The pore volume of DDMGO was 0.24 cm³/g.

According to the FTIR analysis, we could find out the functional groups contained in the materials. The FTIR spectra of GO, MGO, and DDMGO are illustrated in Fig. 2. It could be seen that the three nanomaterials had similar functional groups, including O—H, C=O, C=C, O=C–O and C–O bonds at the absorption band about 3402–3436, 1723–1736, 1600–1635, 1384–1391, and 1052–1066 cm⁻¹, respectively [29,30]. In addition, two extra strong peaks at 566 and 1458 cm⁻¹ were observed on DDMGO, which corresponded to the vibration of Fe–O and –NHCO–, respectively [25]. Above results indicated that –COOH groups of GO had combined with the –NH₂ groups of DTPA and thus had been converted to –NHCO– chemical bond in DDMGO.

3.2. Adsorption kinetics

To gain insights into the variation of adsorption amount with contact time, sorption kinetics of TC and CIP on DDMGO at different time intervals were studied in this paper. As shown in Fig. 3, the CIP sorption rate is faster than that of TC. The adsorption capacity of both TC and CIP increased quickly during the first 1 h, and then the sorption of CIP reached adsorption equilibrium after 1 h, nevertheless, TC adsorption continued to increase slowly as time goes on, subsequently reached a plateau at approximately 24 h. In the following experiment, 24 h was chosen as the incubation time to ensure that the adsorption equilibrium of all samples was established.

The pseudo-first and second-order kinetic models are often widely adopted to test the fitness of the experimental data and to assess the adsorption kinetics [16]. Therefore, the linear fits of pseudo-first and second-order models are used for the fitting of



Fig. 1. Characterization of DDMGO: SEM images of DDMGO (a), DDMGO after TC adsorption (b), DDMGO after CIP adsorption (c), and DDMGO after TC and CIP adsorption (d); (e) TEM image of DDMGO (the inset shows the DDMGO dispersed in ultrapure water); (f) XRD pattern of DDMGO.



Fig. 2. FTIR spectra of GO, MGO, DDMGO, DDMGO after TC adsorption, and DDMGO after CIP adsorption.

TC and CIP adsorption data and the fitting results are illustrated in Fig. S2a and b, respectively. Details of the kinetic models information were provided in Supporting Information and the related kinetic parameters of these models are tabulated in Table S1. Clearly, both of TC and CIP adsorption followed pseudo-second-



Fig. 3. TC and CIP adsorption as a function of reaction time. $C_{0(TC/CIP)} = 50 \text{ mg/L}, m/V = 0.09 \text{ g/L}, T = 30 °C, pH = 3.0.$

order kinetics better than pseudo-first-order kinetics. Since the correlation coefficient of kinetics data of TC and CIP in the pseudo-second-order kinetics model (both R^2 values above 0.99) were higher than the pseudo-first-order model. Moreover, the cal-

culated q_e values of TC and CIP obtained from the pseudo-secondorder equation were 294.12 and 111.73 mg/g, respectively, which were closer to the experiment values. These results suggested the adsorption rate TC and CIP on DDMGO were both controlled by chemisorption [31].

3.3. Adsorption isotherms and thermodynamics

Adsorption isotherms of TC and CIP under different temperatures are depicted in Fig. 4. In order to evaluate the adsorption capacities of TC and CIP on DDMGO, the equilibrium data in single system were simulated by the nonlinear models of Langmuir and Freundlich, and their correlate equations were provided in Supporting Information. The isothermal parameters and correlation coefficients (R^2) obtained from the two classical models are listed on Table S2. From Table S2, compared to the Langmuir model, Freundlich model exhibits higher correlation coefficients, smaller root mean square error (RMSE) and chi-square test (χ^2), indicating the Freundlich model describes the sorption isotherms of TC and CIP better than the Langmuir model under different temperatures.

Besides, thermodynamic considerations of TC and CIP adsorption are necessary to determine whether the reaction is spontaneous or not [32]. The thermodynamic parameters (including ΔG° , ΔH° and ΔS°) calculated by relative equations (presented in the Supporting Information) were expected to assess the feasibility and nature of the adsorption process. As shown in Table S3, for TC adsorption, the negative ΔG° values are found to decrease with temperature increase from 293 to 313 K, suggesting that TC adsorption on DDMGO is spontaneous process and higher temperatures is more conducive to this adsorption [33]. The conclusion is consistent with the result shows in Fig. 4 that the adsorption capacity of TC increases with increasing temperature. Base on this support, we could infer that the TC adsorption was endothermic from the positive ΔH° values. Furthermore, the positive values of ΔS^{o} implied an increase in randomness at the interface of solidliquid, which might reflect the possible micro-structural changes of the adsorbate and adsorbent [34]. Before adsorption, TC was closely surrounded by a bound hydration layer where water molecules were more highly ordered than in the bulk water. Once the TC molecules came into close interaction with the hydration surface of DDMGO, the ordered water molecules were compelled and disturbed in these two hydration layers, which would help to increase the entropy. Although the degree of freedom of TC molecules decreased by adsorption, positive entropy might be due to the entropy increase of water molecules overweighing the entropy decrease of TC molecules [35]. But for CIP removal, these values were different. In Table S3, the negative ΔG° values confirm

that the adsorption process is spontaneous and thermodynamically favorable. Nonetheless, the values of ΔH° and ΔS° were negative, which revealed the typical exothermic nature of CIP adsorption and the decreased randomness at solid-liquid interface during the adsorption process. It seems likely negative entropy associated with the adsorption of CIP on DDMGO was the result of the entropy decrease of CIP molecules overweighing the entropy increase of water molecules.

3.4. pH effect

All the time, solution pH is considered to be one of the most important effects on adsorption process owing to it can effectively change existing speciation of TC and CIP as well as surface bindingsites of DDMGO [36]. Therefore, it is essential to explore the pH effect on the sorption. Batch sorption experiment had investigated the influences of solution pH from 2.0 to 10.0 for TC and CIP uptake (Fig. 5). The results showed that the maximum adsorption capacity of TC and CIP could be achieved at pH around 3.0 and 8.0, respectively, corresponding to initial concentration of 50 mg/L. In order to reasonably explain the influence of pH on adsorption, the chemical formula (Fig. S3a and b) and speciation plots (Fig. S4a and b) of TC and CIP, and the surface zeta potentials of DDMGO (Fig. 5) are given.

As seen from Fig. 5, for TC, the adsorption is rapid with the increase of pH from 2.0 to 3.0, while the adsorption capacity decreases gradually as the pH value continues to rise from 3.0 to 10.0. The trend presented in this research was similar to our earlier study [21], which was difficult to explain by electrostatic attraction. According to Fig. S4a, the cationic TC (TCH₃⁺) would repelled with positive DDMGO surface at pH < 3.3, and the electrostatic repulsion might also exist between the anionic TC (TCH⁻ or TC²⁻) and negative DDMGO surface at pH > 7.8. However, the maximum adsorption capacity of TC was achieved at pH around 3.0. Consequently, electrostatic attraction was not the main driving force in the TC adsorption by DDMGO, and also, other mechanisms might be involved in adsorption of TC by graphene-based materials [16,21,37].

For CIP, at pH below 8.0, the adsorption capacity was enhanced with the increase of pH, when solution pH was above 8.0, CIP sorption started to decrease. Investigate Fig. S4b shows the dominant speciation of CIP and the results indicate the relative distribution of CIP species existed in cation (CIP⁺), zwitterion (CIP[±]), and anion (CIP⁻) forms at pH < 5.9, pH 5.9–8.9 and pH > 8.9, respectively. As shown in Fig. 5, the surface charge of DDMGO is positive at pH < 4.0. Thus, the weak sorption of CIP on DDMGO at pH < 4.0 could be attributed to the electrostatic repulsion between CIP⁺ and pos-



Fig. 4. Single sorption isotherms of TC and CIP on DDMGO at different temperatures: (a) TC sorption; (b) CIP sorption. (the solid lines and dotted lines are the Freundlich and Langmuir model simulation, respectively). m/V = 0.09 g/L, pH = 3.0, t = 24 h.



Fig. 5. The solid lines are the pH effect on TC and CIP uptake onto DDMGO and dotted line is the pH effect on surface zeta potentials of DDMGO. $C_{0(TC/CIP)} = 50 \text{ mg/L}$, m/V = 0.09 g/L, T = 30 °C, t = 24 h.

itively charged DDMGO. When the pH value exceeded 4, the zeta potential of DDMGO surfaces shifted from positive to negative, which was easily bonded with neutral CIP[±], but not for binding with negatively charged CIP species. Therefore, the highest adsorption capacity of CIP appeared at pH around 8.0 might be due to electrostatic attraction.

In the following study, for the convenience of study the difference of adsorption between single system and two component systems, pH 3.0 was selected for adsorption of TC and CIP.

3.5. Effect of ionic strength

High concentration of salt was often detected in industrial antibiotic sewage, and the influence of ionic strength on TC and CIP single uptake was carried out in NaCl solution with the concentration range from 0 to 0.5 M. The experimental results are illustrated in Fig. 6. It was found that lower ionic strength (0–0.01 M) appeared to restrain the TC and CIP adsorption. Afterwards, when ionic strength was high enough (>0.01 M), the TC and CIP removal capacity gradually increased with the increase of NaCl concentration. These phenomena could be explained by two possible impacts: (1) the ions might penetrate into diffuse double layer surrounding the DDMGO surfaces and reduce the repelling interaction



Fig. 6. Effects of ionic strength on the adsorption of TC and CIP by DDMGO. $C_{0(TC/CIP)} = 50 \text{ mg/L}, m/V = 0.09 \text{ g/L}, T = 30 °C, t = 24 \text{ h}.$

between the adsorbents, thereby increasing DDMGO particle aggregation (i.e. squeezing-out), which might lead to the decrease of adsorption amounts for TC or CIP sorption [31]. (2) increasing ionic strength improved the activity coefficient of hydrophobic organic compounds, and led to a decrease in their solubility (i.e. salting out effect), which was beneficial to TC and CIP uptake [38]. Accordingly, slight inhibition occurred at the NaCl concentration below 0.01 M, probably because of the competition of low salt solution with TC or CIP for the available binding sites of DDMGO by a squeezing-out effect [21]. However, when the NaCl concentration was >0.01 M, the adsorption capacity increased, which might be attributed to the fact that the salting-out effect played the key role in TC or CIP removal.

3.6. Effect of background electrolytes

The adsorption of TC and CIP as a function of two foreign cations $(K^+ \text{ and } Mg^{2+})$ and anions $(Cl^- \text{ and } SO_4^{2-})$ are studied at pH 3.0 and show in Fig. 7a and b, respectively. As depicted in Fig. 7, increase of the concentration of SO₄²⁻ have apparent promoting effects on TC and CIP adsorption by DDMGO, however, the adsorption capacities of TC and CIP first decrease and then increase obviously with the Cl⁻ concentration increasing from 0 to 0.1 mol/L, and also, the impacts of the SO_4^{2-} on TC or CIP uptake are stronger than that of Cl⁻. This phenomenon might be due to the negatively divalent SO₄²⁻ were easily adsorbed by positively charged DDMGO than negatively monovalent Cl⁻, which weaken the electrostatic repulsion between DDMGO and TC (or CIP), thereby resulting in the increase of the TC and CIP uptake [39]. While low concentration of Clexhibited a slight inhibitory effect on TC or CIP removal probably owing to the competition for the adsorption sites between Cland TC (or CIP).

When low concentration of K⁺ and Mg²⁺ were added to the CIP suspension, strong competition existed with CIP⁺ on positively charged DDMGO, which would lead to the CIP removal capacity significantly decreased. After the K⁺ and Mg²⁺ concentration increased from 0.01 to 0.1 M, the salting out effect might be stronger than the competition for the CIP adsorption. As a consequence, the adsorption capacity of CIP was gradually enhanced. Unlike CIP, the existence of K⁺ had no distinct effect on TC adsorption within the test concentration range. Nevertheless, the presence of Mg²⁺ reduced its sorption. This finding might be ascribed to the competition of the adsorption sites between Mg²⁺ and TC molecules. Theoretically, one K⁺ adsorbed on the DDMGO surface only took up one adsorption site, while Mg²⁺ could occupy two sites, which rendered a noticeable impact on the TC adsorption in the presence of Mg²⁺ [40].

3.7. Multi-compound adsorption in binary solution systems

In binary mixtures, adsorption of TC and CIP was complicated due to the competitive adsorption at the binding site. Effects of compound adsorption of TC and CIP onto DDMGO at different concentrations are shown in Fig. 8 and the data is presented in Table S4. The adsorption quantity of TC in dual solutions evidently reduced compared with the single component solutions owing to the competitive adsorption of TC and CIP on DDMGO. Similar phenomenon was be observed by Song et al. [4]. With the increase of CIP concentration, the TC adsorption quantity was getting lower and lower. This may be resulted from the fact that both TC and CIP were positively charged at pH around 3.0, and competitive sorption for limited binding sites between TC and CIP was existed, which might be stronger with increasing the CIP concentration. The equilibrium values of q_b (binary solution system)/ q_s (single solution system) for TC (0.39-0.90 when 0-20 mg/L CIP was added) also indicated that simultaneous presence of CIP reduced



Fig. 7. Effects of background electrolytes on the adsorption of TC and CIP by DDMGO: (a) TC adsorption; (b) CIP adsorption. $C_{0(TC/CIP)} = 50 \text{ mg/L}, m/V = 0.09 \text{ g/L}, T = 30 \text{ °C}, t = 24 \text{ h}.$



Fig. 8. Effects of competitive adsorption on TC (a) and CIP (b) removal at different background concentrations. m/V = 0.09 g/L, T = 30 °C, t = 24 h.

the TC adsorption through competition for adsorption sites from DDMGO. However, the adsorption amounts of CIP in the binary systems showed a very slight decline compared to that in the single system with increasing the TC concentration to 20 mg/L (Fig. 8b). From the result of time effect, the CIP adsorption rate of CIP was much higher than that of TC, and CIP could occupy the adsorption sites as soon as possible due to the rapid adsorption. Moreover, the values of q_b/q_s for CIP was close to 1.00 with adding 0-20 mg/L TC, which was higher than those of TC, suggesting that the perturbing effect of TC adsorption onto DDMGO was stronger by the co-existing antibiotics than that for CIP. So when CIP and TC coexisted in the solution, the adsorption capacity of CIP was almost not affected by the existence of TC. The fall of adsorption amount was greater for TC than for CIP, which suggested that main competitive effects were related to the affinity of the individual compounds for the adsorbent [41].

3.8. Desorption and regeneration capacity

Desorption behavior is investigated using NaOH solution as eluents for TC and CIP in single and binary systems and the results are provided in Fig. 9. After four consecutive cycles, the uptake capacity of both TC and CIP competitive sorption and TC/CIP single sorption slightly reduced with increasing regeneration cycle numbers. The removal efficiencies of DDMGO remained steady at above 78% after at least 4 cycles in single and binary systems, indicating that the DDMGO adsorbent had the potential for regeneration in TC and CIP adsorption, which would effectively reduce the total cost of the adsorbent.

3.9. Mechanism of antibiotics adsorption onto DDMGO

The adsorption mechanism of TC and CIP on DDMGO were probed by FTIR and XPS analyses. The FTIR spectra of DDMGO before and after TC and CIP adsorption are shown in Fig. 2. As can be seen from Fig. 2, after TC or CIP loaded on DDMGO, the adsorption peak of C=C bond present a shift from 1635 to 1594 and 1614 cm⁻¹, respectively, which might be related with the π - π interaction. It was known that the structure of TC and CIP was composed of aromatic ring skeleton, which could be combined with the residual π -electrons on DDMGO [29]. Besides, for TC, the cation- π bonding probably participated in the adsorption owing to the easily protonated amino group were located on the ring C4 of the TC molecule and the DDMGO π -electrons. Similar interaction mechanism was also observed in graphene oxide and TC [42]. The peaks at 3436 cm⁻¹ belonged to the O–H bending vibration of DDMGO migrated to 3409 and 3422 cm⁻¹ for DDMGO-TC and DDMGO-CIP complexes, respectively. Likewise, the C=O peak of DDMGO at 1736 cm^{-1} were also shifted to 1763 (for DDMGO-TC) and 1723 cm⁻¹ (for DDMGO-CIP), respectively. The results implied that hydrogen bond reaction between hydroxyl and carboxyl groups might be responsible for this adsorption. In addition, the typical absorption peaks of DDMGO at 1458 cm⁻¹ was attributed to the secondary amide N-H bending, which had shifted to 1451 and 1465 cm⁻¹ after TC and CIP uptake, respectively. This result suggested that amino-groups were probably involved in the reaction with the TC and CIP since its strong chelating capability.

XPS studies of DDMGO before and after TC or CIP uptake were further used to elaborate the mechanism. Fig. 10 presents decom-



Fig. 9. Recycling of DDMGO in the removal of TC and CIP: (a) single and competitive sorption TC; (b) single and competitive sorption CIP. $C_0 = 50 \text{ mg/L}$, m/V = 0.09 g/L, $T = 30 \degree$ C, t = 24 h.



Fig. 10. (a), (b) and (c) are the computer deconvolution C 1s spectra of DDMGO, DDMGO-TC and DDMGO-CIP, respectively; (d), (e) and (f) are the computer deconvolution N 1s spectra of DDMGO, DDMGO-TC and DDMGO-CIP, respectively; (g), (h) and (i) are the computer deconvolution O 1s spectra of DDMGO, DDMGO-TC and DDMGO-CIP, respectively.



Fig. 11. Adsorption schematic diagram of TC and CIP on DDMGO.

posed C 1s, N 1s and O 1s peaks of DDMGO, DDMGO-TC and DDMGO-CIP. The C 1s spectrum of DDMGO (Fig. 10a) was well fitted into five peaks at 284.70, 285.18, 286.48, 288.25 and 290.70 eV, corresponding to the C-C/C=C (31.64%), C-N (33.67%), C-O (17.57%), C=O (13.86%) and O-C=O (3.26%) groups, respectively [43]. After TC and CIP adsorption, the C–C/C=C both showed a shift to 284.75 eV, further confirming that π - π interaction might be responsible for TC and CIP removal. Moreover, the peak belonged to C-N group migrated to 286.12 (for DDMGO-TC) and 285.56 eV (for DDMGO-CIP), and the C=O group shifted to 288.33 (for DDMGO-TC) and 288.34 eV (for DDMGO-CIP). In addition, for the N 1s peaks of DDMGO after adsorption (Fig. 10d-f), the peak at 400.04 eV related to neutral and amine structure (-NH/C-N) after TC or CIP loaded on DDMGO also transferred to 399.10 and 400.14 eV, respectively [44]. These changes once again indicated that newly formed amide bonds (-CO-NH-) performed a significant effect on TC and CIP removal. While the percentage of N⁺ migrated obviously from 401.98 to 400.81 eV in TC removal, indicating that the cation- π bonding was likely to occur in the TC adsorption process. According to the O 1s XPS spectra of DDMGO before and after adsorption (Fig. 10g-i), all the decomposed O 1s peaks showed the shift of position and the change of the molar ratio after absorbed of the two kinds of antibiotics. It was possible because oxygencontaining functional groups (-COOH and -OH) of DDMGO reacted with the hydroxyl and carboxyl groups of TC or CIP through hydrogen bonding [45]. Hence, based on the above discussion, the molecule interactions simulation between DDMGO and TC and CIP could be illustrated by Fig. 11.

4. Conclusions

In the present work, DDMGO was prepared and exhibited excellent sorption performance for TC and CIP removal due to it contained rich oxygen or nitrogen-containing functional groups on the surface, and was easy to separate and reuse from aqueous solution. TC and CIP adsorption kinetic could be better described by pseudo-second-order model. The Freundlich model presented the better correlation for the TC and CIP isotherm adsorption data and the adsorption followed a spontaneous process. Furthermore, the ΔH° value suggested that TC and CIP adsorption were endothermic and exothermic, respectively. And ion strength and background electrolytes played important roles in the removal of TC and CIP by DDMGO. For the competitive adsorption on binary mixtures, the inhibitory effect of TC was more pronounced by the simultaneous presence of competitive antibiotics than that for CIP, which was attributed to the adsorption rate and the affinity of individual antibiotic for the adsorbent. Results also showed that π - π interaction, hydrogen bonds and amidation reaction might be the key driving forces both for TC and CIP uptake. In addition, TC uptake could be explained by cation- π interaction and CIP uptake could be affected by electrostatic interaction.

DDMGO possessed a higher efficiency for CIP and TC removal compared with the maximum adsorption capacities of other adsorbents [3,12,21,46]. Thus, DDMGO could be considered as a promising adsorbent applied in fast separation and adsorption of antibiotic wastewaters. Previous studies reported the behaviors of the antibiotic as affected by other antibiotic on GO-based composites [4,24], but the related research was rare. This research amplifies our understanding of the interaction mechanisms between the antibiotics and GO-based composites, and they are important for the application of adsorption technology in antibiotics wastewater treatment. Real wastewater contained both inorganic and organic pollutants that might affect the adsorption efficiency of the material, such as organic acid and inorganic nanoparticles. Further studies should be included to assess the potential impact of the media in the removal of antibiotics from wastewater.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jcis.2018.03.003.

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