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Sorptive removal of ionizable antibiotic sulfamethazine from aqueous solution by graphene oxide-coated biochar nanocomposites: Influencing factors and mechanism

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HIGHLIGHTS

- Graphene oxide-coated biochar nanocomposites (GO-BC) were synthesized.
- Sorption capacity of SMT onto GO-BC increased by 1.14 times compared to biochar (BC).
- Chemical aging can significantly improve sorption performance of BC and GO-BC.
- The main sorption mechanism for SMT was π-π electron-donor-acceptor interaction.

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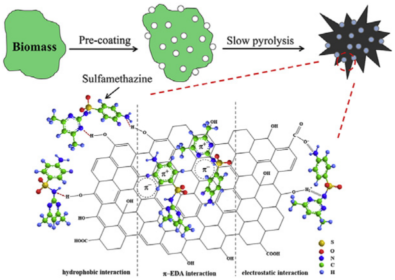
GRAPHICAL ABSTRACT



ABSTRACT

Significant concerns have been raised over antibiotics pollution in aquatic environments in recent years. In this study, sorption of sulfamethazine (SMT) by novel graphene oxide-coated biochar nanocomposites (GO-BC) based on graphene oxide (GO) with bamboo sawdust biochar (BC) was investigated. In comparison with the original BC, the sorption capacity of GO-BC for SMT increased by 1.14 times. Sorption of SMT onto GO-BC was proved to be dominantly by chemisorption, and Freundlich isotherm described the sorption adequately. It was found that variation of pH and ionic strength obviously affected the sorption of SMT, and GO-BC had a good sorption effect on SMT at pH 3.0–6.0 and lower ionic strength. Obvious enhancement (by 30%) in sorption of SMT on GO-BC was observed, which might be attributed to the increase of functional groups on the surface of GO-BC. Moreover, the main sorption mechanism for SMT was π-π electron-donor-acceptor interaction, while auxiliary sorption mechanisms were inferred as pore-filling, cation exchange, hydrogen bonding interaction and electrostatic interaction. The results indicated that GO-BC sorption was an efficient way for the removal of SMT.

1. Introduction

With the advent of penicillin, pharmaceutical antibiotics are becoming more and more extensively used in farming industry and human therapy all around the world.

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To improve the growth rate of animal, animal feed was usually incorporate with veterinary antibiotics in some countries (Sarmah et al., 2006; Zhou et al., 2013). Most antibiotics given to livestock cannot be metabolized and excreted via urine and faeces, and these residues eventually end up in soil, in which they may play a positive role in the proliferation of antimicrobial-resistant pathogens, thus affect humans potentially (Zhou et al., 2013). The effluent and sludge from domestic wastewater, hospitals or livestock farms with antibiotics lead to their release to the environments (surface and groundwater, soil and sediment) (Zhang et al., 2015). It cannot be denied that antibiotics are gradually becoming prevalent contaminants in our environment, and the augment in its concentrations are being observed whether in soil or in water. There has been found that the content of antibiotics in manure reached up to 900 mg kg^{-1}, even in surface water and sediment, the concentration ranged from ng L^{-1} to μg L^{-1} (Teixidó et al., 2013). In 1982, antibiotics were first detected in a river located in England, the concentration of sulphonamides, tetracyclines and macrolides were 1 μg/L. Thirty years later, the occurrence of antibiotic residues in aquatic ecosystems have been reported, and concentration of them 100 ng/L to 6 mg/L (Wang et al., 2016a,b). In the long run, antibiotic contamination is becoming more and more serious, and its pollution remediation is also imminent.

The object we studied is sulfamethazine (SMT; 4-amino-*N*-[4, 6-dimethyl-2-pyrimidinyl] benzenesulfonamide), which is commonly used among many veterinary medicine and has been continually reported in high concentration (García-Galán et al., 2010; Li et al., 2012). As a major sulfonamide drug, SMT is extensively used to control infectious diseases as well as treatment. Neutral form of SMT predominates between pH 3.0 and 7.0 and its high hydrophilicity (octanol water partition coefficient log $K_{ow} = 0.27$) still remained. SMT exist in water via several forms including uncharged molecule (SMT^0), zwitterion ($SMT^{\pm}$), cation (SMT^+) and anion (SMT^-), owing to proton exchange of aromatic amine and sulfonamide groups on molecule (pK_{a1}, 2.28; pK_{a2}, 7.42). In the aqueous system, the complexity of the SMT speciation indicates the complexity of the sorption behavior during its removal. Moreover, researchers have conducted lots of experiments and verified that sulfonamides are not easy to be adsorbed and not readily biodegradable, but leachable (Kim et al., 2010). Sorption behaviors of SMT have been investigated on materials such as multi-wall carbon (Ji et al., 2009; Yang et al., 2015) and graphene oxide (Gao et al., 2012; Nam et al., 2015), biochar (Zheng et al., 2013; Jing et al., 2014; Lian et al., 2014; Huang et al., 2016b), activated biochar (Rajapaksha et al., 2015), clay minerals (Gao and Pedersen, 2005), organophilic zeolite (Braschi et al., 2010), soils (Thiele-Bruhn et al., 2004; Rajapaksha et al., 2014), and even molecularly imprinted polymers (Xu et al., 2012; Huang et al., 2015, 2017; Wang et al., 2016a,b). A decrease in SMT sorption was observed with the pH increasing in both loamy sand and loam sediments, for the change of pH values affected the speciation of SMT (Vithanage et al., 2014). Such changes in environmental conditions are likely to have a great influence on the removal efficiency. Among numerous different parameters which may exist, ionic strength, pH, and ionic speciation were regarded as the most significant factors affecting the sorption of SMT to the majority of adsorbing materials (Lertpaitoonpan et al., 2009; Braschi et al., 2010). Varieties of mechanisms of SMT sorption including hydrophobic partitioning, cation exchange, and complex surface reactions (hydrogen bonding and other polar interactions) between the functional groups (carboxyl, phenol, and amino) of the adsorbate molecules have been proposed (Chen et al., 2014a,b).

Biochar (BC) is a kind of porous carbon material, and favored in environmental remediation with the characteristic of alternative and low-cost (Tan et al., 2015). It has been applied to remove varieties of organic and inorganic pollutants including PAHs, PCBs, phenolic compounds, aldehydes, organic pesticides, and heavy metals (Zhang et al., 2014; Tran et al., 2015; Huang et al., 2016a,c; Liang et al., 2017), especially the removal of SMT, which has aroused wide public concern gradually (Zheng et al., 2013; Lian et al., 2014). Nevertheless, the sorption capacity of BC cannot meet the needs of the contaminants removing, no matter in water or in soil. Therefore, researchers have made efforts to prepare BC-based composite, considering that combine BC with organic or inorganic materials via physicochemical methods can improve its properties, create or incorporate new structure, and enhance the sorption capacity of BC (Inyang et al., 2014). There has been reported that synthesized BC-based nanomaterials exhibited strong capability of sorbing phosphate and nitrate (Zhang et al., 2012; Tang et al., 2014), methylene blue (Inyang et al., 2014), phenanthrene (Tang et al., 2015), lead, cadmium (Liu et al., 2016) and mercury (Tang et al., 2015), respectively. Graphene oxide (GO), exfoliated from graphite, has been considered as an emerging sorbent for various functional groups including hydroxyl, carboxylic, and epoxy groups on the surface (Wang et al., 2013a,b,c). Though this emerging nanomaterial possess excellent sorption ability, it is not appropriate for applying on a large scale because of the huge cost and potential risk to the environment (Wang et al., 2013a,b,c). If only incorporate this emerging nanotechnology with the available biochar technology to create novel nanocomposites, the performance of biochar can be improved. Besides, the carbonaceous nanocomposites still maintain low-cost (Zhang et al., 2016b; Wang et al., 2013a,b,c).

Consequently, the overall objectives of this study were to prepare hybrid GO-BC nanocomposites, and further test the SMT sorption behavior on the novel carbonaceous nanocomposites. Sorption kinetics, sorption isotherms, influence factors and the related mechanisms were investigated to obtain a deep understanding of the sorption behavior. Finally, the aging of GO-BC (primarily chemical oxidation) was also explored to simulate the effects of actual conditions in environment.

2. Materials and methods

2.1. Materials

Deionized water (resistivity of 18.2 MΩ cm) was used to prepare various solutions in this experiment. Sulfamethazine (99%, w/w) was purchased from Sigma-Aldrich, and some primary properties of which were shown in Table S1. Graphite powder was obtained from Sinopharm Chemical Reagent Co. Ltd. (China). Standard solution (365.23 mmol L^{-1}) was prepared via sulfamethazine dissolved in methanol and was used for preparing the starting concentrations of SMT in the following experiment. Biochar samples were produced from bamboo sawdust and ground in a knife mill to a size of 0.5–1.0 mm before production. Synthetic graphite powder (<20 mm particle size) and 1, 3, 6, 8-pyrenetetrasulfonic acid tetrasodium salt hydrate (PySA) were purchased from Energy Chemical (Shanghai, China). All the other chemicals used were analytical grade or better.

2.2. Preparation of biochar and graphene oxide/biochar nanocomposites

A modified Hummers method (Hummers and Offeman, 1958) was used to prepare graphene oxide. Briefly, 2 g of graphite and 1 g of $NaNO_3$ were mixed and placed in a 500 mL beaker. Under an ice bath condition, 46 mL of sulfuric acid (98%) was added. When the temperature was below 10 °C, slowly added 6 g of $KMnO_4$ and 1 g of $NaNO_3$ to the suspension and stirred vigorously. After keeping stirring for 2 h in ice bath, the mixture was stirred at 30 °C for 30 min. Next, the mixture was diluted with 92 mL deionized water, heated to 95 °C and then kept for 30 min. While the suspension cooled to 60 °C, 10 mL H_2O_2 (30%) solution was added to the suspension and continued stirring for 2 h at room temperature. Finally, the precipitate was purified and washed with 5% HCl and deionized water several times until the solution was neutral. The prepared GO was bath sonicated and dried under vacuum at 65 °C.

To prepare GO suspensions, 0.2 g of GO was added into beaker with 200 mL of deionized water. After adding 0.4 g of PySA powder, the suspension was then stirred and sonicated for 1 h in an ultrasonicator with an output frequency of 20 kHz at pulse intervals of 12 min. About 10 g of bamboo sawdust was thoroughly immersed in the mixture for 2 h and dried. The dried pretreated biomass and untreated biomass were then pyrolysis in a tubular furnace (OTL1200) at 600 °C for 1 h in a N_2 environment. The original biochar and graphene oxide-biochar nanocomposites were referred to as BC and GO-BC, respectively. The two sorbents were rinsed with deionized water repeatedly, and dried for later use.

2.3. *Chemical aging of sorbents*

Chemical aging of BC and GO-BC were carried out with a mixture of concentrated H_2SO_4 and HNO_3. Each sorbent sample (4 g) was immersed in 320 mL of a 3:1 (v/v) H_2SO_4/HNO_3 mixture (Qian and Chen, 2014). The chemical aging process was highly exothermic, therefore the solution was allowed to cool to 70 °C, and then slightly heated on the muffle furnace, keeping the temperature at 70 °C for 6 h by adjusting the muffle furnace continually. In order to remove residual acid, aged samples were first drained through a 325 mesh sieve and then rinsed several times with deionized water until the pH stabilized around 6.0. The aged BC and GO-BC were denoted as ABC and AGO-BC.

2.4. *Characterization methods*

Elemental carbon, hydrogen, nitrogen and oxygen content (C, H, N, and O) of the carbonaceous nanocomposites were determined using the methods that had been reported in previous studies, as well as pH and zeta potentials (Yao et al., 2011). For all the sorbents were prepared at 600 °C, the volatile matter content was not determined. Surface area and pore volume of the two materials were determined by the BET adsorption method (TRI-STAR3020, Micromeritics Instrument Corporation, USA). Binding energies were measured based on the X-ray photoelectron spectroscopy (XPS) (Thermo Fisher Scientific-KAlpha 1063, UK), and setting C1s at 284.4 eV to calibrate the high resolution spectra.

2.5. *The sorption of SMT*

All batch experiments of SMT sorption were carried out in a constant temperature (25 ± 1 °C) controlled by water bath shaker at an agitation speed of 170 rpm. Methanol used in the experiment functions as carrier solvent, and always kept the final methanol concentration in SMT solutions below 0.5% (v/v). The desired pH value of solutions was controlled with 0.1 M HCl or 0.1 M NaOH and ionic strength with NaCl. To investigate the sorption kinetics, 50 mg of BC or GO-BC was added to 50 mL of 36.52 mmol L^{-1} SMT solution in 50 mL flasks. All the experimental groups including their corresponding controls were withdrawn from the agitator after reacted for different time up to 48 h, and filtered through 0.45 μm PVDF disposable filters for measurements. Sorption isotherms were performed in varies concentrations. 50 mg of BC, GO-BC, ABC and AGO-BC samples were added to flasks, then mixed with 50 mL SMT solutions of concentrations 7.30–73.05 mmol L^{-1} for shaking. In order to investigate the effects of pH and ionic strength on the sorption of SMT, the pH of solutions was adjusted to 3.0–9.0 and ionic strength was adjusted to 1–8 g L^{-1}. Except the pH experiment groups, pH of all the other experiment groups were controlled around 5.0–6.0. All the experiments were performed in duplicate.

2.6. *Measurement of SMT concentration*

SMT in experimental solutions were determined by Agilent HPLC Series 1100 (Agilent, Waldbronn, Germany) with an autosampler and a UV-VIS detector. Determination of SMT was conducted with a Zorbax SB-C18 column (4.6 × 250 mm, 5 μm) at 268 nm. The column was maintained at 25 °C with a flow rate of 1 mL min^{-1}. Mobile phase A was composed of 80% HPLC grade 10 mM acetic acid/ammonium acetate while mobile phase B was 20% HPLC grade acetonitrile. The injection volume was 50 μL (Zhang et al., 2016).

3. Result and discussion

3.1. *Characterization of original biochar and graphene oxide/biochar*

Incorporation of GO improved the properties of BC obviously (Table 1). The molar (O + N)/C ratios can be used to measure polarity of carbonaceous nanocomposites (Chen et al., 2008). Relatively lower (O + N)/C values of BC (0.12) than GO-BC (0.18) suggested the increase of surface polar functional groups. The O/C atomic ratio of BC was lower than that of GO-BC, which indicated that the prepared carbonaceous nanocomposites showed higher hydrophobicity compared with BC. Particularly, the surface areas of GO-BC were more than double that of the BC. However, the pore volume value was much lower than that of BC. These changes may suggest that the GO possibly dispersed on the surfaces of BC or stabilized within the pore structure, thus increasing the surface area, and reducing the pore volume. In addition, the pores or pore openings of BC might be blocked. Results of zeta potential measurements revealed that surfaces of the BC became more negatively charged with GO added. It probably attribute to the highly negative of GO used in this work (Yan et al., 2014).

To investigate the changes of the oxygen functional groups on the outer surface of BC and GO-BC, the XPS C1s peaks of them were presented in Fig. S1. The peak at approximately 284.4 eV was attributed to aliphatic/aromatic carbon like C—C, and C═C. The peaks at 285.7–285.9 eV were assigned to carbon species in the form of C—O bonds including phenolic, alcohol and ether groups. Then the peaks at 287.1–287.2 eV and 289.7 eV were corresponded to carbon double-bonded to O, that is, C═O and O—C═O. The relative percentages of the functional groups were listed in Table 2. It was also showed in Fig. S1b that GO introduced plenty of carboxyl groups lactonic groups to the original BC. For the original BC, the only form of double bond of carbon to oxygen can be the C═O while for the prepared GO-BC, the relative percentages of O—C═O were apparently rised.

3.2. *Sorption kinetics*

As is shown in Fig. 1, the sorption trends of SMT to BC and GO-BC appeared to be similar versus time. It is obvious that the sorption of SMT to the two sorbents both achieved sorption equilibrium in 12 h. The initial high sorption rate was due to the abundant of active sites on BC and GO-BC surface, the strong interaction force between sorbents and sorbates also accelerated the reaction. With the reaction going on, the approximately saturated combination sites and the weakening of interaction force may lead to ultimate

Table 1
Structural and basic physiochemical properties of BC and GO-BC.

Sample	Proximate analysis[a]									
	pH				Zeta potential (mV)			Production yield (%)		
BC	6.83 ± 0.02				−28.69 ± 0.57			52.62 ± 0.18		
GO-BC	6.62 ± 0.01				−33.41 ± 0.39			39.06 ± 0.44		
	Ultimate analysis									
	C[b] (%)	H[b] (%)	N[b] (%)	O[b] (%)	Molar H/C	Molar O/C	Molar (O + N)/C	Surface area (m^2 g^{-1})	Pore volume (cm^3 g-1)	Pore diameter (nm)
BC	83.34	3.20	2.14	11.32	0.46	0.10	0.12	184.9	0.027	4.102
GO-BC	80.12	1.18	2.33	16.37	0.18	0.15	0.18	348.2	0.008	3.075

[a] Mean ± standard deviation (SD) in triplicate determinations.
[b] Ash free and moisture free.

Table 2
C1s bonding state and its relative atomic percentage on BC and GO-BC as determined by XPS.

Sample	C–C/C=C (%)	C–O (%)	C=O (%)	O–C=O (%)
BC	81.77	12.92	N/D[a]	5.31
BC-GO	76.79	11.82	2.43	8.96

[a] No presence or extremely low content.

equilibrium. More importantly, for SMT sorption, the sorption capacity of GO-BC was more than twice of BC (23.42 μmol g^{-1} for GO-BC and 10.95 μmol g^{-1} for BC), indicating better application in purification of SMT contaminated water. From the above kinetic sorption data, 24 h were selected in the following studies to ensure the sorption equilibrium of SMT on BC and GO-BC.

To analyze the kinetics of SMT sorption onto BC and GO-BC, the commonly used pseudo first-order and pseudo second-order models were applied to simulate the kinetic data of BC and GO-BC (Inyang et al., 2014). By calculation, the kinetic parameters of pseudo first-order and pseudo second-order models were tabulated in Table S2. As can be seen from the table, for pseudo-second-order model, the sorption rate constant *k* of GO-BC was higher than that of original BC, which showed that GO-BC exhibited greater SMT sorption ability than BC. For both BC and GO-BC, experimental data correlated with pseudo second-order model more closely (R^2 > 0.99) than pseudo first-order model, indicating that the

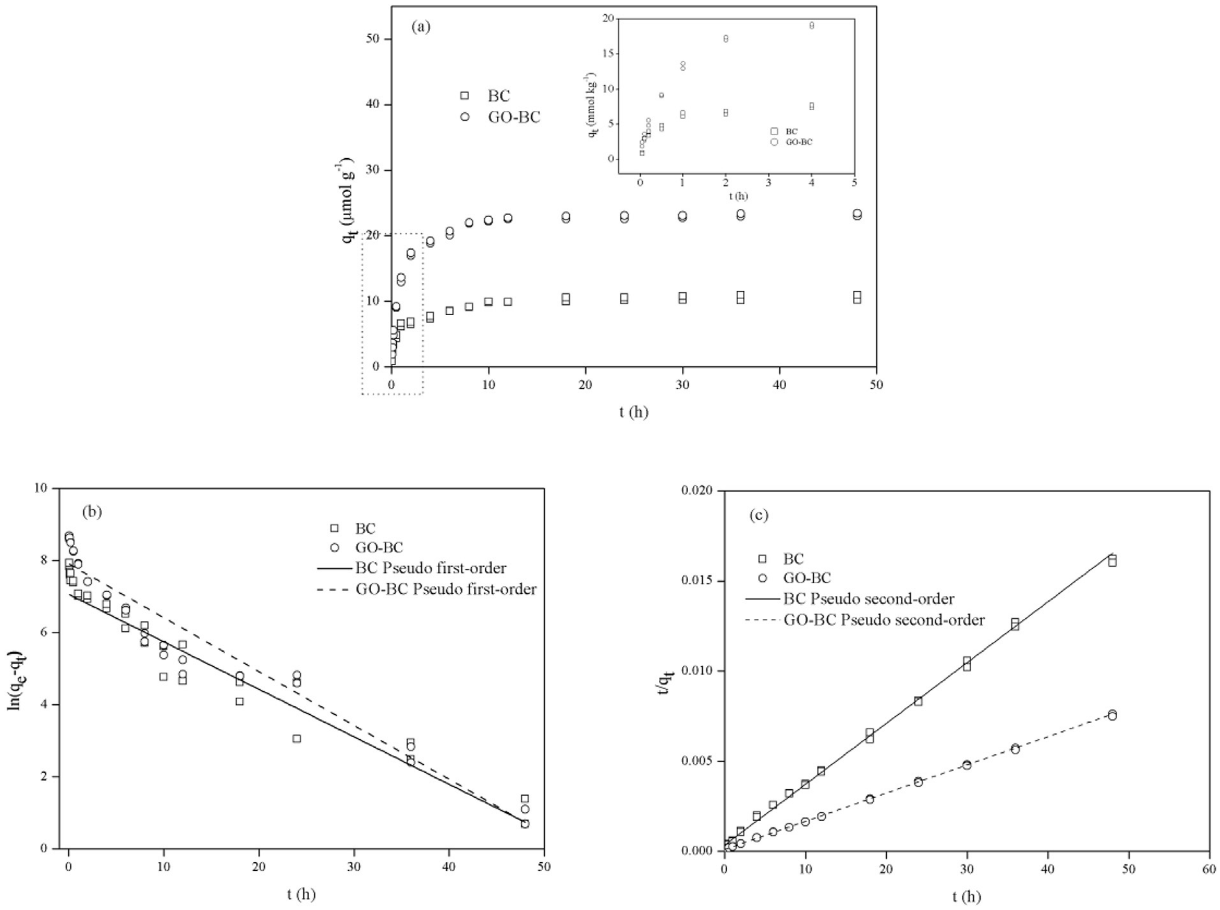

Fig. 1. Kinetics and linear regressions of SMT on BC and GO-BC (the mass of BC and GO-BC: 50 mg; the initial concentration of SMT: 36.52 mmol L^{-1}; temperature: 25 ± 1 °C; pH~6.0): (a) 0–48 h; (b) pseudo-first-order model; (c) pseudo-second-order model.

sorption of SMT onto both BC and GO-BC agreed fairly well with the pseudo second-order model. In addition, the sorption of SMT in aqueous solution was predominated by chemisorption process (Yang et al., 2015).

3.3. Sorption isotherms

In order to investigate the sorption capacity of BC and GO-BC, and the microscopic mechanism between SMT and GO-BC carbonaceous nanocomposites, the sorption isotherms had been studied on the base of the general Langmuir and Freundlich isotherm models (Inyang et al., 2014; Rajapaksha et al., 2015).

SMT sorption isotherms and sorption isotherms data by the BC and GO-BC fitted with Langmuir and Freundlich models were showed in Fig. S2 and Table S2, respectively. SMT can be sorbed more favorable on the GO-BC than BC (Fig. S2). In consideration of the goodness-of-fit (R^2), the Freundlich model ($R^2 = 0.979$ for BC and 0.969 for GO-BC) was more appropriate for the sorption for both BC and GO-BC compared with Langmuir model, indicating that the predominant sorption type on BC and GO-BC were surface multilayer and the sorption sites on the two were heterogeneous and nonspecific for SMT. The sorption affinity of GO-BC was higher than BC, indicating the incorporation of GO developed additional sorption sites on the biochar surfaces. Due to the large specific surface area and the bringing of abundant of functional groups (hydroxyl, carboxyl and epoxy groups) of GO, the sorption capacity was improved surly. In general, allowing for the diverse surface functional groups of GO-BC, it can be inferred that the mechanism of SMT sorption on GO-BC was multiple and complicated for the existence of different types of sorption sites on the surfaces of sorbents.

3.4. Effect of pH on SMT sorption

It has been proved that the surface charge of sorbent and sorbate varies with changing in the pH of the solution (Zhang et al., 2011). In our study, the variation of pH influenced the surface charge of BC and GO-BC inevitably as is mentioned above, and the species distribution of SMT in aqueous phase differed at the same time. Previous study had explored the chemical speciation of SMT sorption on biochar particles (Teixidó et al., 2011), and Table. S1 showed the two pK_a values of SMT ($pK_{a1} = 2.28$, and $pK_{a2} = 7.24$). On the condition of alkaline pH, the deprotonated form of SMT is prevalent, while for neutral and lower pH, the dominant form of SMT would be non-ionized. Experiments in this work were conducted at pH 3.0–9.0, which was above the pK_{a1} of 2.28, so the cationic form of SMT was limited (Ter Laak et al., 2006). Fig. 2 exhibited the influence of pH on the sorption of SMT onto BC and GO-BC. When the pH of solution increased from 3 to 6, the sorption capacity fluctuated up and down slightly and can be thought nearly constant, while the pH increased to 9.0, it decreased apparently. This course of change implied that BC and GO-BC showed similar patterns of pH-dependent sorption, and further indicated the predominant role of the graphite structures for the sorption of SMT. Under the condition of neutral and lower pH, the protonated and the neutral species are both available π-electron-acceptors. These effective π-electron-acceptors can induce strong π-π electron-donor-acceptor (π-π EDA) interaction with the graphitic surfaces. On the contrary, deprotonation of sulfonamide group can dramatically weaken the π-withdrawing ability of the group and suppress the interaction force (Ji et al., 2009). Additionally, the deprotonated anionic form is manifestly more hydrophilic than the protonated and neutral form; this well explained the significantly stronger sorption of the protonated and neutral species than the anionic species, as well as the similar sorption between them. With pH increasing, the percentage of the anionic increased, and the electrostatic repulsion between the anions of SMT molecules and the deprotonated O-functionalities of sorbents also increased, which might ascribed to the decrease of sorption affinities of anionic species. (Xie et al., 2014). Besides, the speciation of functional group of GO on GO-BC varies with pH changed. The stability of GO sheets may alter when GO charge changes, and undoubtedly affect the sorption of antibiotics (Chowdhury et al., 2013). Typically, the pK_a value of alkyl carboxyl (COOH) is 4.5. Therefore, nearly all the carboxyl groups on GO are protonated and become natural charge ($COOH^0$) at pH = 2.0. And around 80% of the carboxyl groups get deprotonated (COO^-) at pH of 5.0, and exist in the form of negatively charged; when the pH~9.0, approximately all the carboxyl groups are deprotonation (COO−) and get negative charged. This may well demonstrate the reason why the sorption decrease of GO-BC was more than BC.

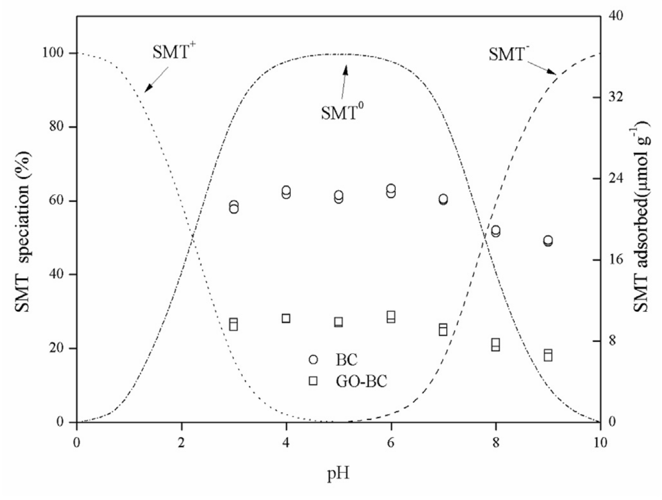

Fig. 2. Effect of solution pH on sorption of SMT on BC and GO-BC (the mass of BC and GO-BC: 50 mg; contact time: 24 h; temperature: 25 ± 1 °C).

3.5. Effect of ionic strength on SMT sorption

For the purpose of exploring the effect of ionic strength on the sorption of SMT in aqueous solution by carbonaceous nanocomposites, different amounts of NaCl were added to the mixture of SMT solutions and BC or GO-BC. As showed in Fig. 3, the sorption capacities of either BC or GO-BC decreased apparently with the addition of NaCl. And compared with BC, GO-BC obtained greater reduction in SMT sorption capacity (for BC from 7.84 $\mu mol\ g^{-1}$ to 2.24 $\mu mol\ g^{-1}$ and GO-BC from 19.10 $\mu mol\ g^{-1}$ to 7.26 $\mu mol\ g^{-1}$). It has been reported that the existence of NaCl can affect the sorption capacities of pharmaceutical on carbonaceous material via electrostatics screening effect (Gao et al., 2012). Hence, we can assume that the increasing ionic strength would weaken the electrostatic interactions between SMT and the deprotonated carboxyl groups of carbon nanomaterials. There already studies showed that relatively high ionic strength could facilitate the aggregation of carbonaceous nanomaterials (Wu et al., 2013). Moreover, for GO-BC, the increasingly ionic strength may compress the electric double layers, causing the aggregation of GO. As a result, this sorbent become more compact, namely not all the sorption sites are available for SMT (Yang et al., 2015). What should not be ignored is that the ever increasing ionic strength enhances the competition between Na^+ and the SMT on surface for sorption sites, thus the decrease of SMT sorption observed here was significant.

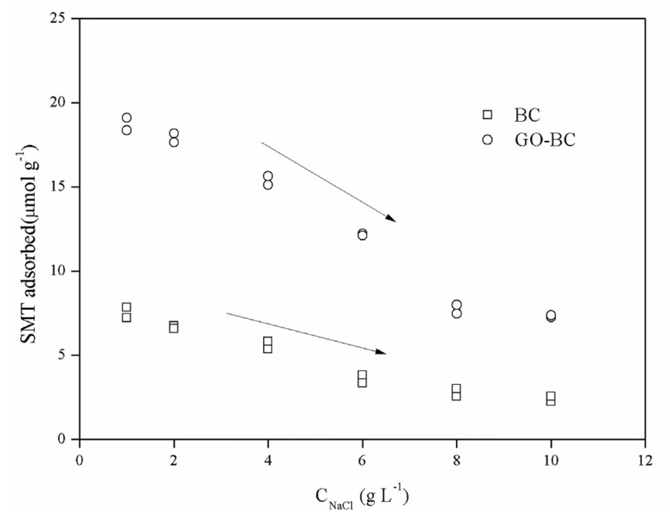

Fig. 3. Effect of solution ionic strength on sorption of SMT on BC and GO-BC (the mass of BC and GO-BC: 50 mg; contact time: 24 h; temperature: 25 ± 1 °C; pH~6.0).

3.6. *Effect of chemical aging*

Note that the proposed carbonaceous nanocomposites proved to have a high sorption capacity in contrast with the original biochar. Its aging performance bears more important research value. Chemical aging of BC and GO-BC in this experiment were performed in the mixture of H_2SO_4 and HNO_3 to simulate with the natural environment. The sorption capacity of SMT on BC, GO-BC, ABC and AGO-BC were showed in Fig. 4. It was clearly that aging in the manner used here had similar effects on either BC or GO-BC to a certain extent. For both of the two sorbents, the capacity of removing SMT gained some improvement, nearly increased 30% compared to their original ones. Chemical aging could not only alter the physical and chemical properties of the sorbents, but also develop functional groups on the surface (Hale et al., 2011). Having been surface oxidized, BC and GO-BC were more favorable to enhance the π−EDA interactions between sorbents' surface and SMT molecules, to which ascribed surface acidic groups of the two sorbents such as hydroxyl groups (−OH), carboxyl groups (−COOH), and lactonic groups (−COOR), which are strong electron-donating groups (Xie et al., 2014). It has also been proved that the concentration of surface acidic functional groups increased after oxidation, suggesting that chemical aging treatment enriched oxygen containing functional moieties on BC and GO-BC samples, therefore created a positive effect on the sorption. On the other hand, the force of hydrogen bonding between groups of SMT molecule such as the aniline, sulfonyl or pyrimidine and oxygen containing groups on the two sorbents could be enhanced at the same time.

3.7. *Sorption mechanisms*

Findings obtained in this study suggested that incorporating carbon nanomaterials like GO with biochar significantly enhanced SMT sorption in aqueous solutions. The sorption capacities of the GO-BC nanocomposites increased 1.5–2 times for SMT compared to BC. There has been reported that the sorption behavior between organic compounds and carbon based material generally follows mechanisms such as pore-filling, electrostatic interaction, hydrophobic interaction, hydrogen bonding interaction and π−EDA interactions, and sometimes the simultaneous occurrence of several sorption mechanisms (Ji et al., 2011). But for different type of organic contaminant, the predominant mechanism varies. While preparing carbonaceous nanocomposites, physicochemical properties of the original biochar changes, such as surface area, pore size, pore volume even the functional groups on surface, consequently improving the sorption capacity of SMT. As we all know, biochar is porous material consisting of number of micro-, meso- and macro pores, and the structure of biochar have not been destroyed for incorporation of GO into biochar. The molecular size of SMT was actually small enough to diffuse to micro-, meso- and macro pores. The antibiotic studied is amphoteric molecules with multiple charged or polar groups, these groups are capable of electronic coupling, thereby affect the sorption on BC and GO-BC. It has been verified that the π-EDA interaction is the primary mechanisms for SMT sorption on carbonaceous nanocomposites and can be well explained by pH dependencies (Zhang et al., 2016). The influence of pH on the sorption capacities of BC and GO-BC was closely related to the SMT species distribution regulated by pH, thus the significance of SMT species in its sorption was obvious. The sulfonamide antibiotic in this study possesses a benzene ring and an aromatic heterocyclic group, and the sulfonamide group between the two groups has a strong electron-withdrawing ability under the pH condition (5.0–6.0), hence causing the associated aromatic rings and unsaturated structures to act as π-electron-

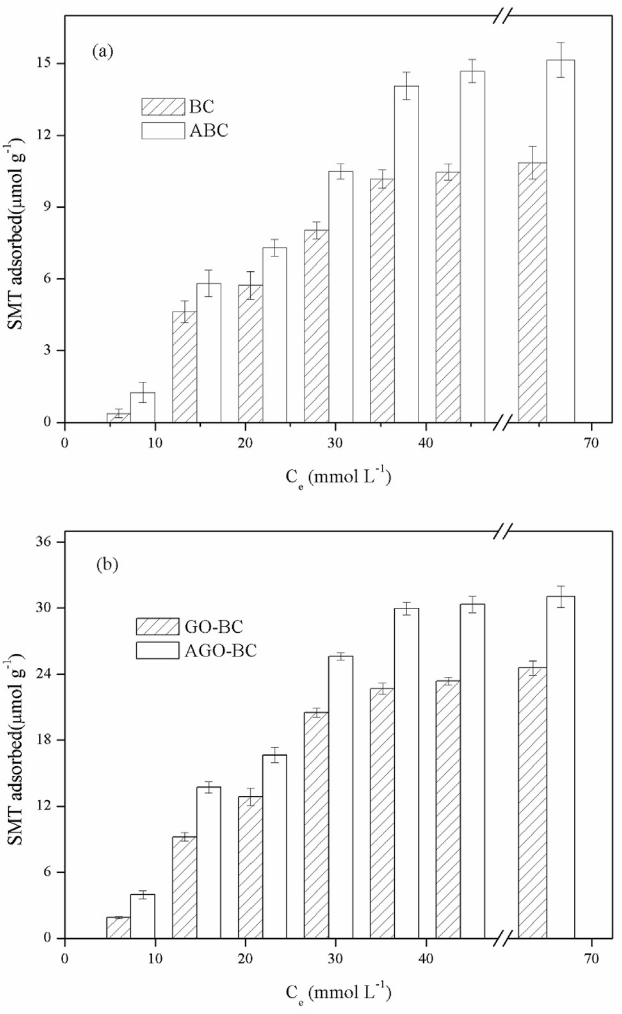

Fig. 4. Effect of chemical aging of BC (a) and GO-BC (b) on sorption of SMT (the mass of ABC and AGO-BC: 50 mg; contact time: 24 h; temperature: 25 ± 1 °C; pH~6.0). The error bars were calculated on the basis of standard deviation (n = 2).

acceptors. The highly polarized graphene surfaces of BC and GO-BC interact strongly with the predominant zwitterions of SMT via π-EDA interactions. What's more, the decrease of sorption capacity may indicate a partial cation exchange and zwitterions interactions as the other possible mechanisms for the sorption of SMT onto GO-BC. In the acidic region, SMT^{+} was predominant, π-EDA interactions between the protonated aniline ring and electron rich graphene surfaces of BC and GO-BC were much stronger compared to neutral condition. However, the cationic exchange reactions became weaker. While in the alkaline region, SMT^{-} species prevail in the mixture, which may enhance electrostatic repulsion between SMT and BC and GO-BC surfaces, possibly leading to reduction of sorption (Teixidó et al., 2011; Rajapaksha et al., 2015). Hydrogen bonding formed by groups of SMT including sulfonyl pyrimidine group or aniline and the oxygen containing function groups on BC and GO-BC was also perceived to be one of the significant forces in the process of sorption. Accordingly, the fact that sorption capacity of GO-BC was higher than that of original BC suggested that GO-BC is favorable in removing of SMT and remain efficiency over a broad pH range, and the results are also of great significance in antibiotic remediation processes.

4. Conclusion

In order to remove SMT from aqueous solution and improve the performance of biochar, GO-BC carbonaceous nanomaterials were synthesized by dip-coating the GO onto bamboo sawdust followed by slow pyrolysis, and applied to SMT contaminated water. Compared to the original BC counterpart, the properties of GO-BC showed drastic changes due to the incorporation of GO, such as pore volume, surface area. Sorption capacity of the GO-BC carbonaceous nanomaterials was much higher than BC. The sorption kinetics analyses showed that the sorption of SMT in aqueous solution onto BC and GO-BC was predominated by chemisorption process. Sorption of BC and GO-BC can be described by Freundlich adsorption isotherm model adequately, indicating that electrostatic interactions existed in the midst of heterogeneous sites in sorbents. Moreover, SMT sorption onto GO-BC was affected by chemical aging to a great extent. It was revealed that the main sorption mechanism of GO-BC was the π-EDA interaction, whereas it also should not be ignored that other sorption mechanisms such as pore-filling, cation exchange, hydrogen bonding interaction and electrostatic interaction may be auxiliary sorption mechanisms. The presented results have established the potential of GO-BC nanocomposites which can be applied to the remediation of SMT in environmental and perhaps other organic pollutants. Aspects of our following work should be forces on the effects of other heavy metals on SMT sorption and apply the GO-BC to treat actual medical wastewater in the future.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.chemosphere.2017.07.154.

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