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Multi-walled carbon nanotube/amino-functionalized MIL-53(Fe) composites: Remarkable adsorptive removal of antibiotics from aqueous solutions

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HIGHLIGHTS

- It was used firstly to adsorb antibiotics.
- H-bond and π-π interaction played a major role.
- It was a good adsorbent.

GRAPHICAL ABSTRACT



A R T I C L E I N F O

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ABSTRACT

A novel adsorbent composite was synthesized by combining amino-functionalized MIL-53(Fe) with multi-walled carbon nanotubes (MWCNT), and used to adsorb tetracycline hydrochloride (TCN) and chlortetracycline hydrochloride (CTC). The maximum adsorption capacities of TCN and CTC over MWCNT/NH₂-MIL-53(Fe) at 25 °C were 368.49 and 254.04 mg g⁻¹, which are, respectively, 1.79 and 8.37 times higher than that of chaff biochar. Interestingly, the mesoporosity of MWCNT/NH₂-MIL-53(Fe) significantly increased through introduction of MWCNT into NH₂-MIL-53(Fe), which proved to be favorable for the production of active adsorption sites. Besides, the remarkably increased adsorption capacity can be ascribed to the hydrogen bonding between amino functional groups on MWCNT/NH₂-MIL-53(Fe) and hydroxyl functional groups on TCN or CTC. Moreover, the π - π interaction between adsorbate and adsorbent was considered the main reason for the adsorption of TCN and CTC. The great adsorption capacity, as well as excellent reusability, demonstrated the potential application of MWCNT/NH₂-MIL-53(Fe) in the removal of TCN and CTC from aqueous solutions.

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1. Introduction

Antibiotics, especially tetracycline antibiotics, have wide range of applications in medicine and aquaculture (Martins et al., 2015; Defuria et al., 2016; Qin et al., 2017), due to their anti-bacterial, antifungal, anti-virus and anti-parasite qualities. Antibiotics are rarely degraded and metabolized by organisms, and about 30–90 percent of them are discharged into the natural aquatic environment through urine or feces (Abejon et al., 2015; Wu et al., 2015; Hirsch et al., 1999). Moreover, a considerable number of antibiotics in the artificial feed are directly dissolved into the water due to their high solubility. The majority of antibiotics can be protonated/deprotonated at various pH values, existing in different places (Parolo et al., 2012). Contamination of water caused by antibiotics has become a serious international problem, due to their low biodegradability in the water. According to a previous report, the concentration of antibiotics in domestic wastewater ranges from 100 ng/L to 6 mg L^{-1} (Cetecioglu et al., 2013). Hence, it is imperative to efficiently remove antibiotics from aqueous solutions.

Nowadays, a variety of technologies have been used to remove antibiotics from aquatic environment, such as advanced oxidation processes (AOPs), electrochemistry, membranes separation, and biodegradation (Zhou et al., 2018; Belkheiri et al., 2015; Lu et al., 2017; Cheng et al., 2016, 2018; Wan et al., 2018; Ren et al., 2018; Zhang et al., 2015; Song et al., 2017; Chen et al., 2015; Hu et al., 2017). However, there are some deficiencies in the aforementioned strategies, and thus they cannot be widely used to remove antibiotics. For example, AOPs and electrochemistry are not only costly, but may also produce some byproducts, leading to secondary pollution. A part of membranes used for adsorption and separation are easily contaminated, resulting in a decline of permeability. Besides, due to antibacterial effects on some microbes, biodegradation methods are not effective in removing antibiotics (Reyes et al., 2006). Adsorption is considered as the most appropriate method due to its simplicity of operation, low-cost and high-efficiency (Xiong et al., 2017; Zhang et al., 2016; Long et al., 2011; Xu et al., 2012a). So far, a variety of materials, especially carbonaceous or porous materials have been used to adsorb antibiotics due to their high surface areas, many kinds of functional groups, low price and good environmental benignity (Carabineiro et al., 2011; Carabineiro et al., 2012; Tan et al., 2015; Wu et al., 2017; Gong et al., 2009; Deng et al., 2013; Tang et al., 2014; Xu et al., 2012b; Liang et al., 2017; Qin et al., 2018; Jiang et al., 2017; Yu et al., 2016). For example, sulfamethazine (SMZ) has been removed using carbonaceous nanocomposites (Zhang et al., 2016). Tetracycline (TCN) and sulfamethazine (SMZ) have been adsorbed by highly porous carbon (He et al., 2016). Exploring more efficient adsorption materials for antibiotics removal still remains challenging.

Recently, metal-organic frameworks (MOFs), a kind of porous crystalline materials, have obtained wide attention due to their simple synthesis, large specific surface area, well-defined pore diameter, easy modification and other features (Howarth et al., 2016; Yamada et al., 2016; Song et al., 2017). The properties of MOFs are suitable for various applications, including energy storage, catalysis, sensing and gas capture (Zheng et al., 2017; Gao et al., 2017; Miller et al., 2016; Gelfand et al., 2016). Especially, the application of MOFs has broad prospects in adsorption. For example, Jhung et al. have applied MIL-100(Fe), MIL-101(Cr), UiO-66 and ZIF-8(Zn) on adsorption (Ahmed et al., 2014; Seo et al., 2017; Hasan et al., 2016; Bhadra et al., 2017). Concerning MOFs, the MIL-53(M) family is an important class that has drawn much attention due to its chemical versatility, flexible structure, breathing feature and stability (Naeimi and Faghihian, 2017). Moreover, the Fe³⁺ metal center with normal carboxylate-type ligands can be easily synthesized with the characteristic of water stability (Wang et al., 2016a; Liu et al., 2017).

In this study, as the surface of MOFs can be easily operated by introducing functional groups on organic ligands (Bhadra et al., 2016), amino-functionalized MIL-53 (Fe) was fabricated using organic ligands with amino. Moreover, after introducing the very small amount of multi-walled carbon nanotube (MWCNT), the adsorption capacity of MWCNT/NH₂-MIL-53(Fe) for tetracycline hydrochloride (TCN) and chlortetracycline hydrochloride (CTC) showed an obvious enhancement. Hence, we studied the adsorption behavior of TCN and CTC on MWCNT/NH₂-MIL-53(Fe), and potential adsorption mechanisms were proposed. Furthermore, the main factors affecting the maximum adsorption on MWCNT/NH₂-MIL-53(Fe), including pH and ionic strength, were analyzed. Excellent adsorption capacity and reusability of MWCNT/NH₂-MIL-53(Fe) sheds a new light on antibiotics removal.

2. Experimental section

2.1. Chemicals and syntheses of adsorbents

All the chemicals were analytical grade and used as received without further purification. *N*, *N*-dimethylformamide (DMF, 99.5%), ferric chloride hexahydrate (FeCl₃·6H₂O, 99%) and ethanol (99.5%) were purchased from Sinopharm Chemical Reagent Co., Ltd. 2-Aminoterephthalic acid (98%) was purchased from Shanghai Macklin Biochemical Co., Ltd. The chaff biochar was purchased from Beijing hele biotechnology Co., Ltd. Multi-walled carbon nanotubes (MWCNT) with diameters ranging from 10 to 20 nm were purchased from the Chengdu Organic Chemicals Co. Ltd. (PR China). Tetracycline hydrochloride (TCN) and chlortetracycline hydrochloride (TCC) were obtained from bomei biotechnology Co., Ltd (Hefei, China). The ultra-pure water (resistivity of $18.25 \text{ M}\Omega \text{ cm}^{-1}$) was used throughout the experiment.

NH₂-MIL-53(Fe) was prepared by a solvothermal method (Shi et al., 2015), which was obtained by organic linker substitution. The typical synthesis procedure was as follows: 0.674 g of ferric chloride hexahydrate, 0.452 g of 2-aminoterephthalic acid and 56 mL of DMF solution were mixed by stirring at room temperature, and then transferred into a 100 mL Teflon-lined stainless steel autoclave. After that, the autoclave was heated at 170 °C for 24 h. The product was washed with DMF and ethanol, filtered, and dried.

To synthesize the MWCNT/NH₂-MIL-53(Fe) composites, purified MWCNT (PR China) were dispersed in precursor mixtures of the NH₂-MIL-53(Fe). The remaining synthetic steps were the same as those in the synthesis of NH₂-MIL-53(Fe). The proper amount of purified MWCNT was introduced in DMF and then mixed with ferric chloride hexahydrate, 2-aminoterephthalic acid and DMF. The resulting mixture was stirred at room temperature, then transferred into a 100 mL Teflon liner in stainless steel autoclave and heated at 170 °C for 24 h. The powder was collected by centrifugation, washing and drying.

2.2. Characterization

The structural characteristics of adsorbents were obtained by a D8 X-ray diffractometer (XRD; Bruker, utilizing Cu K α radiation, Germany). Binding energies were characterized by X-ray photoelectron spectrum (XPS) (Thermo Fisher Scientific-ESCALAB 250Xi, USA). The Fourier transform infrared spectrum (FT-IR) measurements were used to confirm the introduced functional groups of MOFs from a Nicolet 5700 Spectrometer in KBr pellet at room temperature (Nicolet, USA). The morphology of MWCNT, NH₂-MIL-53(Fe) and MWCNT/NH₂-MIL-53(Fe) was analyzed via environmental scanning electron microscope (SEM) (Carl Zeiss, EVO-MA10, Germany). The specific surface areas of adsorbents were measured using the Brunauer-Emmett-Teller (BET), and the total pore volume and pore size were measured by automatic surface analyzer (Quantachrome, USA). The zeta potential of MWCNT/NH₂-MIL-53(Fe) was measured by a Zeta potential analyzer (Zetasizer Nano zs90) at varying pH values. Thermogravimetric analysis (TGA) was measured by a Mettler TGA/SDT Q600 analyzer under nitrogen flow with a temperature growth rate of 10 °C min⁻¹.

2.3. Adsorption experiments

Stock solutions (200 mg L⁻¹) of TCN and CTC were obtained by using deionized water and diluted to solutions of their desired concentrations (1–200 mg L⁻¹). The adsorbents of chaff biochar, MWCNT, NH₂-MIL-53(Fe) and MWCNT/NH₂-MIL-53(Fe) were dried for 8 h in a vacuum oven and used for adsorption of TCN and CTC in aqueous solutions. Adsorbents (10 mg) were added into the TCN and CTC solutions (50 mL, 20 mg L⁻¹), and the mixture was shaken at room temperature using an incubator shaker in the stipulated time.

After adsorption of the TCN and CTC in aqueous solutions, the solutions were centrifuged at 5000 rpm and then filtered using 0.45 µm PVDF disposable filters. The remaining TCN and CTC concentrations were evaluated by UV spectrophotometer (UV-2700, SHIMADZU, Japan). In order to determine the effect of pH on the amounts of adsorbed TCN and CTC, the pH value of the TCN and CTC solutions (20 mg L^{-1}) was altered with aqueous NaOH (0.1 M) or HCl (0.1 M) and adjusted by using a pH meter (FE20, China). The effect of ionic strength on adsorption was determined by using TCN and CTC solutions (20 mg L^{-1}) containing different concentrations of NaCl. Various methods of our calculations including the pseudofirst-order, pseudo-second-order, intra-particle diffusion models and Langmuir, Freundlich, Temkin isotherm equations were applied to analyze the adsorption experiment results. Besides, kinetics models, isotherm models and calculation equations were shown in Table S1 (Tang et al., 2018).

The recyclability of MWCNT/NH₂-MIL-53(Fe) was evaluated after the adsorption of TCN and CTC. The used MWCNT/NH₂-MIL-53(Fe) was washed with deionized water, and then placed into acetone and soaked for 12 h, following a method in the previous literature (Seo et al., 2017). The regeneration process was repeated three times to completely remove the adsorbed TCN and CTC. The recovered MWCNT/NH₂-MIL-53(Fe) was applied similarly for the fourth runs.

3. Results and discussion

3.1. Characterization of the adsorbents

The morphology of NH₂-MIL-53(Fe) and MWCNT/NH₂-MIL-53(Fe) was observed using environmental scanning electron microscope (SEM). Fig. 1a showed that the surface of NH₂-MIL-53(Fe) crystal was relatively smooth. After combining NH₂-MIL-53(Fe) with MWCNT (Fig. 1b), there was an obvious change on the surface morphology of MWCNT/NH₂-MIL-53(Fe), as shown in Fig. 1c. In comparison, the surface area of MWCNT/NH₂-MIL-53(Fe) was larger than NH₂-MIL-53(Fe) since the MWCNT was attached on its surface.

The XRD patterns of pure MWCNT, NH₂-MIL-53(Fe) and MWCNT/NH₂-MIL-53(Fe) were shown in Fig. 2a. The characteristic peaks of MWCNT were observed in the diffractogram of MWCNT/NH₂-MIL-53(Fe), which indicated that MWCNT and NH₂-MIL-53(Fe) coexisted in the MWCNT/NH₂-MIL-53(Fe) material. After combining with MWCNT, the XRD peaks of MWCNT/NH₂-MIL-53(Fe) were very similar to the diffraction patterns of NH₂-MIL-53(Fe).

53(Fe) (Shi et al., 2015). Thus, the introduction of MWCNT had not a significant impact on the crystalline structure.

As shown in Fig. 2b, the FT-IR spectra of MWCNT/NH₂-MIL-53(Fe) contained the characteristic peaks of MWCNT and NH₂-MIL-53(Fe). The band at 537 cm⁻¹ was attributed to Fe–O vibration. Bands at 1375, 1560, and 1650 cm⁻¹ could be assigned to C–O and C=O vibration of carboxylic groups. The band at 770 cm⁻¹ was attributed to C–H vibration of benzene rings. Bands at 1253 and 3372 cm⁻¹ were attributed to C–N and N–H vibrations of amino group, respectively (Gao et al., 2017; Jia et al., 2017). Bands at 2360 and 3450 cm⁻¹ were due to O–H vibration from MWCNT, which confirmed the successful synthesis of the MWCNT/NH₂-MIL-53(Fe).

The XPS spectra of MWCNT/NH₂-MIL-53(Fe) are shown in Fig. 3. The survey spectrum of MWCNT/NH₂-MIL-53(Fe) consisted of Fe, O, C, and N elements, as seen in Fig. 3a. For the XPS spectrum of Fe 2p (Fig. 3b), two strong peaks at 725.83 eV and 712.87 eV were attributed to Fe 2p1/2 and Fe 2p3/2, respectively, which indicated that Fe³⁺ species were present in MWCNT/NH₂-MIL-53(Fe). As shown in Fig. 3c, the C 1s peak of MWCNT/NH₂-MIL-53(Fe) could be deconvoluted into four peaks at 284.65 eV, 284.83 eV, 286.22 eV and 289.36 eV, which could be attributed to benzoic rings (C=C), carbon atoms bond in MWCNT (C-C and C-O) and organic linkers in MWCNT/NH₂-MIL-53(Fe) and carboxylate groups in MWCNT (C=O), respectively. The O 1s peak also can be divided into two peaks at 531.86 and 532.38 eV, corresponding to the oxygen atoms on the H₂BDC linkers (C=O) and the Fe-O bonds of NH₂-MIL-53(Fe), respectively (Fig. 3d). The N 1s spectrum was displayed in Fig. 3e, showing that three kinds of pyridine N, pyrrole N and graphite N existed in MWCNT/NH₂-MIL-53(Fe), which was in good accordance with the results reported in other works (Han et al., 2016). The overall XPS results matched well with the SEM, XRD and FT-IR analysis.

The N₂ adsorption isotherms of adsorbents were shown in Fig. S1. Besides, BET specific surface area, pore size distribution and pore volumes of composites were summarized in Table S2 and Fig. S1b. As shown in Fig. S1a, all curves were type IV isotherms with a typical H₃ hysteresis, due to the presence of mesopores and macropores (Song et al., 2015), which was consistent with the results shown in Table S2. However, after the modification with MWCNT, the BET specific surface area, pore volumes and pore size of MWCNT/NH₂-MIL-53(Fe) showed an increase. The TGA profiles of MWCNT/NH₂-MIL-53(Fe) exhibited a slightly higher thermal stability due to the introduction of MWCNT, as seen in Fig. S1c. This is because crystals were formed with heterogeneous nucleation and carboxylate groups on MWCNT were treated as nucleation sites (Yang et al., 2009).

3.2. Comparison of adsorption capacity of adsorbents

For comparison, the chaff biochar was used as a traditional adsorbent to absorb antibiotics. Figs. S2 and S3 showed the results of adsorption for TCN and CTC with different concentrations and times. The adsorption capacity decreased in the order of MWCNT/ NH₂-MIL-53(Fe) > NH₂-MIL-53(Fe) > MWCNT > chaff biochar for both TCN and CTC. The excellent adsorption capacity of MWCNT/ NH₂-MIL-53(Fe) was possibly attributed to the changes in the porous structure. As shown in Table S2, BET specific surface area, pore size and pore volumes of MWCNT/NH₂-MIL-53(Fe) increased after MWCNT modification, as expected.

3.3. Adsorption kinetics

The adsorption of TCN and CTC from aqueous solutions on three adsorbents (MWCNT, NH_2 -MIL-53(Fe) and MWCNT/ NH_2 -MIL-53(Fe)) was carried out at room temperature. In order to



Fig. 1. SEM images of NH₂-MIL-53(Fe) (a), MWCNT (b) and MWCNT/NH₂-MIL-53(Fe) (c).



Fig. 2. XRD diffractograms (a) and FT-IR absorption spectra (b) of NH₂-MIL-53(Fe), MWCNT and MWCNT/NH₂-MIL-53(Fe).

understand the adsorption performance in more detail, the experimental results analyzed by three kinetics models were shown in Fig. 4. The kinetic parameters of TCN and CTC for the adsorbents were summarized in Table 1 and Table S3. Compared to the pseudo-first-order model, the pseudo-second-order model fitted better to the experimental results, indicating that chemisorption occurred between adsorbates and adsorbents (Tang et al., 2018).

The intra-particle diffusion model was applied to further analyze the adsorption mechanism. As shown in Fig. 4e and f and Table S3, all plots of q_t were distributed in three linear portions. The first line section was attributed to TCN and CTC transfer diffusion to the external surface of adsorbents, which was managed by the molecule and film diffusion. The second section was the slow adsorption, where the TCN and CTC diffused from the external surface to the internal pore and capillary structure of adsorbents. The third section indicated that adsorption was almost balanced, where the low concentration of TCN and CTC and insufficient active sites of adsorbents limited the adsorption rate. Moreover, it was obvious to observe that three linear portions did not go through the origin coordinate, indicating that intra-particle diffusion was not the only rate-limiting step (Wang et al., 2016b).

3.4. Adsorption isotherms

The adsorption isotherm experiment was carried out at room temperature using various TCN and CTC concentrations, and the experimental results were analyzed by three isothermal adsorption models, presented in Fig. 5. The isotherm parameters of Langmuir, Freundlich and Temkin models for TCN and CTC adsorption were listed in Table 2. It was obvious that the correlation coefficients (R^2) of Langmuir model were much higher than those of Freundlich and Temkin isotherm models, which demonstrated monolayer molecular adsorption on the surface of adsorbents. This phenomenon indicated that chemical adsorption might play the main role in the process of absorbing TCN and CTC. The maximum adsorption capacity ($q_{m,cal}$) of the MWCNT/NH₂-MIL-53(Fe) calculated by the Langmuir model was larger than that of MIL-53(Fe). In addition, a separation factor (R_L) was used to analyze the Langmuir isotherm. As seen in Table 2, all of the calculated parameters (R_L) below 1 indicated that the adsorption process was favorable. Furthermore, the lower R_L values indicated that the interaction between adsorbates and NH₂-MWCNT/MIL-53(Fe) was considerably strong (Saliby et al., 2013).

As for Temkin model, the correlation coefficients (R^2) were much lower, indicating that there were other interactions except from chemical adsorption. Based on Freundlich model, all the values of the heterogeneity factor 1/n were between 0 and 1, demonstrating that the adsorption was favorable (Bhatt et al., 2012). The relatively high linear relationships and low heterogenous factors showed evidence of physical interaction. Thus, chemical adsorption played an important role in the TCN and CTC adsorption.

3.5. Effect of solution pH and ion strength

As the pH had a great influence on the surface charge, adsorption efficiency of MWCNT/NH₂-MIL-53(Fe), and physicochemical characteristics of TCN and CTC, it was an important factor to consider for TCN and CTC adsorption. There were four forms of



Fig. 3. XPS spectra of MWCNT/NH₂-MIL-53(Fe): (a) survey, (b) Fe 2p, (c) C 1s, (d) O 1s and (e) N 1s.

existence in aqueous solutions, owing to three dissociation constants for TCN (pKa = 3.32, 7.78 and 9.58) and CTC (pKa = 3.33, 7.55 and 9.33), respectively (Qiang and Adams, 2004). Moreover, the zero potential point (pH_{ZPC}) of MWCNT/NH₂-MIL-53(Fe) was approximately 3.42, as seen in Fig. S5. As shown in Fig. S4, both TCN and CTC adsorption were strongly related to the pH of the solution. Along with the progressively increasing pH value from 3.42 to 9.0, the zeta potentials were more electronegative and adsorption capacity was slowly reduced, since the electrostatic repulsion might become the main force of interaction.

There are different concentrations of salts in the wastewater, which may affect the TCN and CTC removal. Therefore, different concentrations of NaCl were added to the aqueous solutions and the experimental results were shown in Fig. S6. Obviously, the TCN and CTC adsorption decreased significantly with the increasing NaCl concentration. This phenomenon indicated that the electrostatic interaction was not the major interaction between adsorbates and MWCNT/NH₂-MIL-53(Fe). However, competition at the adsorptive sites of MWCNT/NH₂-MIL-53(Fe) between TCN, CTC molecules and Na⁺ was the predominant interaction (Yu et al., 2014).

3.6. Mechanisms for TCN and CTC adsorption

The qt of TCN and CTC over MWCNT/NH₂-MIL-53(Fe) was larger than those of MWCNT and MIL-53(Fe). Additionally, as the pH values increased in solution, the adsorption capacity of MWCNT/NH₂-MIL-53(Fe) was smaller. Consequently, both physisorption and chemisorption were present in the adsorption of TCN and CTC on MWCNT/NH₂-MIL-53(Fe). The physisorption primarily depended on the pore size distribution of MWCNT/NH₂-MIL-53(Fe). After the addition of MWCNT, the significantly increased mesopores of MWCNT/NH₂-MIL-53(Fe) could hold more TCN and CTC and provide more active adsorption sites.

As for the chemisorption, various mechanisms, such as electrostatic interaction, hydrogen bonding, coordination and π - π interactions can be used to demonstrate the adsorption from aqueous solutions. Firstly, electrostatic interaction was tried to explain the adsorption between adsorbates and MWCNT/NH₂-MIL-53(Fe) with the increasing pH from 3.0 to 9.0. Considering the pKa of TCN (3.32, 7.78 and 9.58) and CTC (3.33, 7.55 and 9.33), TCN (CTC) had a positive charge at pH < 3.32 (3.33), neutral charge at 3.32 (3.33) < pH < 7.78 (7.55), negative charge at pH > 7.78 (7.55). On the



Fig. 4. Pseudo-first order plots for TCN (a) and CTC (b) adsorption; pseudo-second order plots for TCN (c) and CTC (d) adsorption; intra-particle diffusion model for TCN (e) and CTC (f) adsorption. Reaction conditions: TCN and CTC concentration = 20 mg L⁻¹; adsorbent loading = 0.2 g L⁻¹; temperature = 25 °C; initial pH = 7.

Table 1	
Adsorption kinetic	parameters of TCN and CTC on adsorbents.

Pollutants	Kinetics	Parameters	Adsorbents			Adsorbents		
			MWCNT	NH ₂ -MIL-53(Fe)	MWCNT/NH ₂ -MIL-53(Fe)			
TCN	pseudo-first-order kinetic	$q_{e,exp}(mg/g)$ $k_1(1/h)$ $q_{e,cal}(mg/g)$ R^2 $k_2(g/(mg/b))$	$64.62 \\ 8.5 \times 10^{-3} \\ 63.18 \pm 3.89 \\ 0.921 \\ 1.4 \times 10^{-4}$	$70.469.5 \times 10^{-3}69.86 \pm 2.980.9661.9 \times 10^{-4}$	$85.40 \\ 9.7 \times 10^{-3} \\ 85.62 \pm 3.04 \\ 0.976 \\ 1.8 \times 10^{-4}$			
	pseudo-second-order kinetic	$q_{e,cal}(mg/g)$ R^2	66.73 ± 1.72 0.992	76.92 ± 1.91 0.997	90.09 ± 2.13 0.997			
стс	pseudo-first-order kinetic	$\begin{array}{c} q_{e,exp}(mg/g) \\ k_1(1/h) \\ q_{e,cal}(mg/g) \\ R^2 \end{array}$	$\begin{array}{c} 11.02 \\ 8.9 \times 10^{-2} \\ 9.15 \pm 0.67 \\ 0.819 \end{array}$	$\begin{array}{c} 33.68 \\ 6.4 \times 10^{-3} \\ 34.43 \pm 2.75 \\ 0.907 \end{array}$	$\begin{array}{c} 40.89 \\ 6.2 \times 10^{-3} \\ 41.99 \pm 3.41 \\ 0.918 \end{array}$			
	pseudo-second-order kinetic	$\begin{array}{c} k_2(g/(mg.h)) \\ q_{e,cal}(mg/g) \\ R^2 \end{array}$	$\begin{array}{c} 2.9\times 10^{-3} \\ 10.91\pm 0.16 \\ 0.981 \end{array}$	$\begin{array}{c} 3.3 \times 10^{-4} \\ 35.97 \pm 0.42 \\ 0.984 \end{array}$	$\begin{array}{c} 2.3\times 10^{-4} \\ 44.31\pm 0.36 \\ 0.990 \end{array}$			

other hand, MWCNT/NH₂-MIL-53(Fe) had positive surface charge at pH < 3.42 and negative surface charge at pH > 3.42, based on its zeta potential. Therefore, along with the pH value from 3.32 (3.33) to 7.78 (7.55), there would be little electrostatic interaction, indicating that there was a little change in the q_e of TCN and CTC on MWCNT/NH₂-MIL-53(Fe). With the gradually increasing pH values from 7.78 (7.55) to 9.0 (9.0), repulsive interactions would be observed. However, the tendency showed in Fig. S4 was very different from that expectation, indicating that electrostatic interaction was not the main adsorption mechanism.

Due to the existence of amino functional groups on MWCNT/ NH₂-MIL-53(Fe) and hydroxy functional groups on TCN and CTC, the H atoms from the -OH could act as H-bond donors and the N atoms from the $-NH_2$ could act as an H-bond acceptors, indicating that hydrogen bonding interactions could be a probable mechanism (Song et al., 2017). Meanwhile, in spite of the electrostatic exclusion, with the pH value increasing to 9.0, there was still a certain amount of adsorption for TCN and CTC. Therefore, the π - π interaction (Sarker et al., 2017) was considered as a dominant mechanism for the TCN and CTC adsorption.

3.7. Reusability of MWCNT/NH₂-MIL-53(Fe)

For any kind of adsorbents, reusability is an important parameter that should be taken into account, since it is crucial for commercial applications. MWCNT/NH₂-MIL-53(Fe) can be readily regenerated by using acetone, owing to the solubility of TCN and CTC. In this study, after MWCNT/NH₂-MIL-53(Fe) was dried at 100 °C in a vacuum oven, there was no significant decrease in adsorption up to four recycling cycles, as seen in Fig. S7. The easy desorption of TCN and CTC could likely explain the weak hydrogen bonding between MWCNT/NH₂-MIL-53(Fe) and adsorbates.

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Fig. 5. Langmuir isotherm model for TCN (a) and CTC (b) adsorption; Frendich isotherm model for TCN (c) and CTC (d) adsorption; Temkin isotherm model for TCN (e) and CTC (f) adsorption. Reaction conditions: adsorbent loading = 0.2 g L^{-1} ; temperature = $25 \degree$ C; initial pH = 7.

Table 2

Isotherm parameters for the adsorption of TCN and CTC on adsorbents.

Pollutants	Isotherms	Parameters	Adsorbents		
			MWCNT	NH ₂ -MIL-53(Fe)	MWCNT/NH2-MIL-53(Fe)
TCN	Langmuir	$\begin{array}{c} q_{m,cal}(mg/g) \\ K_L(L/mg) \\ R_L \\ R^2 \\ 1/n \end{array}$	$\begin{array}{c} 287.91 \pm 13.98 \\ 2.7 \times 10^{-2} \\ 0.63 \\ 0.991 \\ 0.45 \pm 0.03 \end{array}$	$\begin{array}{c} 302.63 \pm 10.99 \\ 4.2 \times 10^{-2} \\ 0.55 \\ 0.992 \\ 0.42 \pm 0.04 \end{array}$	$\begin{array}{c} 368.49 \pm 14.05 \\ 6.4 \times 10^{-2} \\ 0.44 \\ 0.989 \\ 0.37 \pm 0.04 \end{array}$
	Freundich Temkin	K _F (L/mg) R ² K _T f	$24.63 \pm 4.07 \\ 0.952 \\ 47.72 \pm 3.13 \\ 0.68$	36.03 ± 5.85 0.967 49.12 ± 2.77 1.13	60.73 ± 8.92 0.964 49.01 ± 5.21 3.95
СТС	Langmuir	$\begin{array}{c} R^2 \\ q_{m,cal}(mg/g) \\ K_L(L/mg) \\ R_L \\ R^2 \end{array}$	$\begin{array}{c} 0.963 \\ 54.01 \pm 1.98 \\ 1.3 \times 10^{-2} \\ 0.73 \\ 0.995 \end{array}$	$\begin{array}{c} 0.972 \\ 152.29 \pm 6.08 \\ 2.4 \times 10^{-2} \\ 0.680 \\ 0.993 \end{array}$	$\begin{array}{c} 0.907\\ 254.04 \pm 9.52\\ 4.4 \times 10^{-2}\\ 0.531\\ 0.990\end{array}$
	Freundich	1/n $K_{f}(L/mg)$ R^{2} K_{-}	0.51 ± 0.02 2.79 ± 0.61 0.962 7.49 ± 0.96	0.47 ± 0.06 11.74 ± 2.96 0.946 25.03 ± 2.28	$0.39 \pm 0.04 \\ 33.58 \pm 5.91 \\ 0.958 \\ 39.97 \pm 2.74$
	Temkin	f R ²	0.54 0.868	0.56 0.910	1.34 0.919

4. Conclusions

In conclusion, MWCNT/NH₂-MIL-53(Fe), a novel efficient adsorbent, was successfully prepared by a facile solvothermal method. The properties of MWCNT/NH₂-MIL-53(Fe), including porosity and specific surface area, improved after the introduction of MWCNT. MWCNT/NH₂-MIL-53(Fe) was used for the first time to remove TCN and CTC, and the adsorption efficiency of this composite was higher than MWCNT, NH₂-MIL-53(Fe) and a traditional chaff biochar. Among of the tested kinetic and isotherm models, the adsorption process was better fitted with a pseudo-second-order

and Langmuir isotherm models. The hydrogen bonding between -OH of the TCN (CTC) and $-NH_2$ of the modified MWCNT/NH₂-MIL-53(Fe), the π - π interaction, and pore-filling effect were three main reasons for the adsorption process. In addition, MWCNT/NH₂-MIL-53(Fe) could be readily regenerated and maintained good adsorption performance. Therefore, MWCNT/NH₂-MIL-53(Fe) could be used as a promising adsorbent for the removal of TCN and CTC from aqueous solutions. Moreover, the MOFs can work easily by changing the organic ligands, and more MOFs-based composite adsorbents with single or multiple functional groups will be expected for environmental applications dealing with water treatment.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.chemosphere.2018.07.084.

References

- Abejon, R., De Cazes, M., Belleville, M.P., Sanchez-Marcano, J., 2015. Large-scale enzymatic membrane reactors for tetracycline degradation in WWTP effluents. Water Res. 73, 118–131.
- Ahmed, I., Jun, J.W., Jung, B.K., Jhung, S.H., 2014. Adsorptive denitrogenation of model fossil fuels with Lewis acid-loaded metal-organic frameworks (MOFs). Chem. Eng. J. 255, 623–629.
- Belkheiri, D., Fourcade, F., Geneste, F., Floner, D., Aït-Amar, H., Amrane, A., 2015. Combined process for removal of tetracycline antibiotic - coupling pretreatment with a nickel-modified graphite felt electrode and a biological treatment. Int. Biodeterior. Biodegrad. 103, 147–153.
- Bhadra, B.N., Ahmed, I., Jhung, S.H., 2016. Remarkable adsorbent for phenol removal from fuel: functionalized metal-organic framework. Fuel 174, 43–48.
- Bhadra, B.N., Ahmed, I., Kim, S., Jhung, S.H., 2017. Adsorptive removal of ibuprofen and diclofenac from water using metal-organic framework-derived porous carbon. Chem. Eng. J. 314, 50–58.
- Bhatt, A.S., Sakaria, P.L., Vasudevan, M., Pawar, R.R., Sudheesh, N., Bajaj, H.C., Mody, H.M., 2012. Adsorption of an anionic dye from aqueous medium by organoclays: equilibrium modeling, kinetic and thermodynamic exploration. RSC Adv. 2, 8663–8671.
- Cetecioglu, Z., Ince, B., Gros, M., Rodriguez-Mozaz, S., Barcelo, D., Orhon, D., Ince, O., 2013. Chronic impact of tetracycline on the biodegradation of an organic substrate mixture under anaerobic conditions. Water Res. 47, 2959–2969.
- Cheng, M., Zeng, G.M., Huang, D.L., Lai, C., Xu, P., Zhang, C., Liu, Y., Wan, J., Gong, X.M., Zhu, Y., 2016. Degradation of atrazine by a novel Fenton-like process and assessment the influence on the treated soil. J. Hazard Mater. 312, 184–191.
- Cheng, M., Zeng, G.M., Huang, D.L., Lai, C., Xu, P., Zhang, C., Liu, Y., Wan, J., Gong, X.M., Zhu, Y., 2018. High adsorption of methylene blue by salicylic acidmethanol modified steel converter slag and evaluation of its mechanism. J. Colloid Interface Sci. 515, 232–239.
- Chen, M., Xu, P., Zeng, G.M., Yang, C.P., Huang, D.L., Zhang, J., 2015. Bioremediation of soils contaminated with polycyclic aromatic hydrocarbons, petroleum, pesticides, chlorophenols and heavy metals by composting: applications, microbes and future research needs. Biotechnol. Adv. 33, 745–755.
- Carabineiro, S.A.C., Thavorn-Amornsri, T., Pereira, M.F.R., Figueiredo, J.L., 2011. Adsorption of ciprofloxacin on surface-modified carbon materials. Water Res. 45, 4583–4591.
- Carabineiro, S.A.C., Thavorn-Amornsri, T., Pereira, M.F.R., Figueiredo, J.L., 2012. Comparison between activated carbon, carbon xerogel and carbon nanotubes for the adsorption of the antibiotic ciprofloxacin. Catal. Today 186, 29–34.
- Defuria, M.D., Zeller, M., Genna, D.T., 2016. Removal of pharmaceuticals from water via π-π stacking interactions in perfluorinated metal-organic frameworks. Cryst. Growth Des. 16, 3530–3534.
 Deng, J.H., Zhang, X.R., Zeng, G.M., Gong, J.L., Niu, Q.Y., Liang, J., 2013. Simultaneous
- Deng, J.H., Zhang, X.R., Zeng, G.M., Gong, J.L., Niu, Q.Y., Liang, J., 2013. Simultaneous removal of Cd(II) and ionic dyes from aqueous solution using magnetic graphene oxide nanocomposite as an adsorbent. Chem. Eng. J. 226, 189–200.
- Gao, Y., Li, S., Li, Y., Yao, L., Zhang, H., 2017. Accelerated photocatalytic degradation of organic pollutant over metal-organic framework MIL-53(Fe) under visible LED light mediated by persulfate. Appl. Catal. B Environ. 202, 165–174.
 Gelfand, B.S., Huynh, R.P., Mah, R.K., Shimizu, G.K., 2016. Mediating order and
- Gelfand, B.S., Huynh, R.P., Mah, R.K., Shimizu, G.K., 2016. Mediating order and modulating porosity by controlled hydrolysis in a phosphonate monoester metal-organic framework. Angew. Chem. Int. Ed. 55, 14614–14617.
- Gong, J.L., Wang, B., Zeng, G.M., Yang, C.P., Niu, C.G., Niu, Q.Y., Zhou, W.J., Liang, Y., 2009. Removal of cationic dyes from aqueous solution using magnetic multiwall carbon nanotube nanocomposite as adsorbent. J. Hazard Mater. 164, 1517–1522.
- Hasan, Z., Khan, N.A., Jhung, S.H., 2016. Adsorptive removal of diclofenac sodium from water with Zr-based metal-organic frameworks. Chem. Eng. J. 284, 1406–1413.
- Han, Y., Zhai, J., Zhang, L., Dong, S., 2016. Direct carbonization of cobalt-doped NH₂-MIL-53(Fe) for electrocatalysis of oxygen evolution reaction. Nanoscale 8, 1033–1039.
- He, J., Dai, J., Zhang, T., Sun, J., Xie, A., Tian, S., Yan, Y., Huo, P., 2016. Preparation of highly porous carbon from sustainable α-cellulose for superior removal

performance of tetracycline and sulfamethazine from water. RSC Adv. 6, 28023–28033.

- Hirsch, R., Ternes, T., Haberer, K., Kratz, K.L., 1999. Occurrence of antibiotics in the aquatic environment. Sci. Total Environ. 225, 109–118.
- Howarth, A.J., Peters, A.W., Vermeulen, N.A., Wang, T.C., Hupp, J.T., Farha, O.K., 2016. Best practices for the synthesis, activation, and characterization of metalorganic frameworks. Chem. Mater. 29, 26–39.
- Hu, L., Wan, J., Zeng, G.M., Chen, A.W., Chen, G., Huang, Z.Z., He, K., Cheng, M., Zhou, C., Xiong, W.P., Lai, C., Xu, P., 2017. Comprehensive evaluation of the cytotoxicity of CdSe/ZnS quantum dots in Phanerochaete chrysosporium by cellular uptake and oxidative stress. Environ. Sci. Nano 4, 2018–2029.
- Jia, Z., Jiang, M., Wu, G., 2017. Amino-MIL-53 (Al) sandwich-structure membranes for adsorption of p-nitrophenol from aqueous solutions. Chem. Eng. J. 307, 283–290.
- Jiang, L.H., Liu, Y.G., Liu, S.B., Zeng, G.M., Hu, X.J., Hu, X., Guo, Z., Tan, X.F., Wang, L.L., Wu, Z.B., 2017. Adsorption of estrogen contaminants by graphene nanomaterials under natural organic matter preloading: comparison to carbon nanotube. biochar. and activated carbon. Environ. Sci. Technol. 51, 6352–6359.
- Liang, J., Yang, Z., Tang, L., Zeng, G.M., Yu, M., Li, X., Wu, H.P., Qian, Y., Li, X., Luo, Y., 2017. Changes in heavy metal mobility and availability from contaminated wetland soil remediated with combined biochar-compost. Chemosphere 181, 281–288.
- Liu, X., Zhou, Y., Zhang, J., Tang, L., Luo, L., Zeng, G., 2017. Iron containing metalorganic frameworks: structure, synthesis, and applications in environmental remediation. ACS Appl. Mater. Interfaces 9, 20255–20275.
- Lu, T., Xu, X., Liu, X., Sun, T., 2017. Super hydrophilic PVDF based composite membrane for efficient separation of tetracycline. Chem. Eng. J. 308, 151–159.
- Long, F., Gong, J.L., Zeng, G.M., Chen, L., Wang, X.Y., Deng, J.H., Niu, Q.Y., Zhang, H.Y., Zhang, X.R., 2011. Removal of phosphate from aqueous solution by magnetic Fe-Zr binary oxide. Chem. Eng. J. 171, 448–455.
- Martins, A.C., Pezoti, O., Cazetta, A.L., Bedin, K.C., Yamazaki, D.A.S., Bandoch, G.F.G., Asefa, T., Visentainer, J.V., Almeida, V.C., 2015. Removal of tetracycline by NaOHactivated carbon produced from macadamia nut shells: kinetic and equilibrium studies. Chem. Eng. J. 260, 291–299.
- Miller, S.E., Teplensky, M.H., Moghadam, P.Z., Fairen-Jimenez, D., 2016. Metalorganic frameworks as biosensors for luminescence-based detection and imaging. Interface Focus 6, 20160027.
- Naeimi, S., Faghihian, H., 2017. Application of novel metal organic framework, MIL-53(Fe) and its magnetic hybrid: for removal of pharmaceutical pollutant, doxycycline from aqueous solutions. Environ. Toxicol. Pharmacol. 53, 121–132.
- Parolo, M.E., Avena, M.J., Pettinari, G.R., Baschini, M.T., 2012. Influence of Ca²⁺ on tetracycline adsorption on montmorillonite. J. Colloid Interface Sci. 368, 420–426.
- Qiang, Z., Adams, C., 2004. Potentiometric determination of acid dissociation constants (pKa) for human and veterinary antibiotics. Water Res. 38, 2874–2890.
- Qin, L., Zeng, G.M., Lai, C., Huang, D.L., Zhang, C., Xu, P., Hu, T., Liu, X., Cheng, M., Liu, Y., 2017. A visual application of gold nanoparticles: simple, reliable and sensitive detection of kanamycin based on hydrogen-bonding recognition. Sensor. Actuator. B Chem. 243, 946–954.
- Qin, Y.X., Li, G.Y., Gao, Y.P., Zhang, L.Z., Ok, Y.S., An, T.C., 2018. Persistent free radicals in carbon-based materials on transformation of refractory organic contaminants (ROCs) in water: a critical review. Water Res. 137, 130–143.
- Ren, X.Y., Zeng, G.M., Tang, L., Wang, J.J., Wan, J., Liu, Y., Yu, J.F., Yi, H., Ye, S.J., Deng, R.C., 2018. Sorption, transport and biodegradation - an insight into bioavailability of persistent organic pollutants in soil. Sci. Total Environ. 610–611, 1154–1163.
- Reyes, C., Fernández, J., Freer, J., Mondaca, M.A., Zaror, C., Malato, S., Mansilla, H.D., 2006. Degradation and inactivation of tetracycline by TiO₂ photocatalysis. J. Photochem. Photobiol., A 184, 141–146.
- Saliby, I. El, Erdei, L., Kim, J.H., Shon, H.K., 2013. Adsorption and photocatalytic degradation of methylene blue over hydrogen-titanate nanofibres produced by a peroxide method. Water Res. 47, 4115–4125.
- Sarker, M., Bhadra, B.N., Seo, P.W., Jhung, S.H., 2017. Adsorption of benzotriazole and benzimidazole from water over a Co-based metal azolate framework MAF-5(Co). J. Hazard Mater. 324, 131–138.
- Seo, P.W., Khan, N.A., Jhung, S.H., 2017. Removal of nitroimidazole antibiotics from water by adsorption over metal-organic frameworks modified with urea or melamine. Chem. Eng. J. 315, 92–100.
- Shi, L., Wang, T., Zhang, H., Chang, K., Meng, X., Liu, H., Ye, J., 2015. An aminefunctionalized iron(III) metal-organic framework as efficient visible-light photocatalyst for Cr(VI) reduction. Adv. Sci. 2, 1500006.
- Song, H.Q., Zhu, Q., Zheng, X.J., Chen, X.G., 2015. One-step synthesis of threedimensional graphene/multiwalled carbon nanotubes/Pd composite hydrogels: an efficient recyclable catalyst for suzuki coupling reactions. J. Mater. Chem. A 3, 10368–10377.
- Song, P.P., Yang, Z.H., Zeng, G.M., Yang, X., Xu, H.Y., Wang, L.K., Xu, R., Xiong, W.P., Ahmad, K., 2017. Electrocoagulation treatment of arsenic in wastewaters: a comprehensive review. Chem. Eng. J. 317, 707–725.
- Tang, L., Yu, J., Pang, Y., Zeng, G.M., Deng, Y.C., Wang, J.J., Ren, X.Y., Ye, S.J., Peng, B., Feng, H.P., 2018. Sustainable efficient adsorbent: alkali-acid modified magnetic biochar derived from sewage sludge for aqueous organic contaminant removal. Chem. Eng. J. 336, 160–169.
- Tan, X.F., Liu, Y.G., Zeng, G.M., Wang, X., Hu, X., Gu, Y.L., Yang, Z., 2015. Application of biochar for the removal of pollutants from aqueous solutions. Chemosphere 125, 70–85.

- Tang, W.W., Zeng, G.M., Gong, J.L., Liang, J., Xu, P., Zhang, C., Huang, B.B., 2014. Impact of humic/fulvic acid on the removal of heavy metals from aqueous solutions using nanomaterials: a review. Sci. Total Environ. 468–469, 1014–1027.
- Wan, J., Zeng, G.M., Huang, D.L., Hu, L., Xu, P., Huang, C., Deng, R., Xue, W.J., Lai, C., Zhou, C.Y., Zheng, K., Ren, X., Gong, X.M., 2018. Rhamnolipid stabilized nanochlorapatite: synthesis and enhancement effect on Pb-and Cd-immobilization in polluted sediment. J. Hazard Mater. 343, 332–339.
- Wang, C., Liu, X., Keser Demir, N., Chen, J.P., Li, K., 2016a. Applications of water stable metal-organic frameworks. Chem. Soc. Rev. 45, 5107–5134.
- Wang, H., Yuan, X., Wu, Y., Zeng, G., Dong, H., Chen, X., Leng, L., Wu, Z., Peng, L., 2016b. In situ synthesis of In₂S₃@MIL-125(Ti) core-shell microparticle for the removal of tetracycline from wastewater by integrated adsorption and visiblelight-driven photocatalysis. Appl. Catal. B Environ. 186, 19–29.
- Wu, C.S., Xiong, Z.H., Li, C., Zhang, J.M., 2015. Zeolitic imidazolate metal organic framework ZIF-8 with ultra-high adsorption capacity bound tetracycline in aqueous solution. RSC Adv. 5, 82127–82137.
- Wu, H., Lai, C., Zeng, G.M., Liang, J., Chen, J., Xu, J., Dai, J., Li, X., Liu, J., Chen, M., Lu, L., Hu, L., Wan, J., 2017. The interactions of composting and biochar and their implications for soil amendment and pollution remediation: a review. Crit. Rev. Biotechnol. 37, 754–764.
- Xiong, W.P., Tong, J., Yang, Z.H., Zeng, G.M., Zhou, Y.Y., Wang, D.B., Song, P.P., Xu, R., Zhang, C., Cheng, M., 2017. Adsorption of phosphate from aqueous solution using iron-zirconium modified activated carbon nanofiber: performance and mechanism. J. Colloid Interface Sci. 493, 17–23.
- Xu, P., Zeng, G.M., Huang, D.L., Lai, C., Zhao, M.H., Wei, Z., Li, N.J., Huang, C., Xie, G.X., 2012a. Adsorption of Pb(II) by iron oxide nanoparticles immobilized Phanerochaete chrysosporium: equilibrium, kinetic, thermodynamic and mechanisms analysis. Chem. Eng. J. 203, 423–431.

- Xu, P., Zeng, G.M., Huang, D.L., Feng, C.L., Hu, S., Zhao, M.H., Lai, C., Wei, Z., Huang, C., Xie, G.X., Liu, Z.F., 2012b. Use of iron oxide nanomaterials in wastewater treatment: a review. Sci. Total Environ. 424, 1–10.
- Yang, S.J., Choi, J.Y., Chae, H.K., Cho, J.H., Nahm, K.S., Chong, R.P., 2009. Preparation and enhanced hydrostability and hydrogen storage capacity of CNT@MOF-5 hybrid composite. Chem. Mater. 21, 1893–1897.
- Yamada, T., Sadakiyo, M., Shigematsu, A., Kitagawa, H., 2016. Proton-conductive metal-organic frameworks, B. Chem. Soc. Jpn. 89, 1–10.
- Yu, F., Ma, J., Han, S., 2014. Adsorption of tetracycline from aqueous solutions onto multi-walled carbon nanotubes with different oxygen contents. Sci. Rep. 4, 5326.
- Yu, F., Li, Y., Han, S., Ma, J., 2016. Adsorptive removal of antibiotics from aqueous solution using carbon materials. Chemosphere 153, 365–385.
- Zhang, Y., Zeng, G.M., Tang, L., Chen, J., Zhu, Y., He, X.X., He, Y., 2015. Electrochemical sensor based on electrodeposited graphene-Au modified electrode and nanoAu Carrier amplified signal strategy for attomolar mercury detection. Anal. Chem. 87, 989–996.
- Zhang, C., Lai, C., Zeng, G.M., Huang, D.L., Yang, C.P., Wang, Y., Zhou, Y.Y., Cheng, M., 2016. Efficacy of carbonaceous nanocomposites for sorbing ionizable antibiotic sulfamethazine from aqueous solution. Water Res. 95, 103–112.
- Zheng, S., Li, X., Yan, B., Hu, Q., Xu, Y., Xiao, X., Xue, H., Pang, H., 2017. Transitionmetal (Fe, Co, Ni) based metal-organic frameworks for electrochemical energy storage. Adv. Energy Mater. 7, 1602733-n/a.
- Zhou, C.Y., Lai, C., Huang, D.L., Zeng, G.M., Zhang, C., Cheng, M., Hu, L., Wan, J., Xiong, W.P., Wen, M., Wen, X.F., Qin, L., 2018. Highly porous carbon nitride by supramolecular preassembly of monomers for photocatalytic removal of sulfamethazine under visible light driven. Appl. Catal. B Environ. 220, 202–210.