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In-situ growing of metal-organic frameworks on three-dimensional iron network as an efficient adsorbent for antibiotics removal



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HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- A solvothermal method was used to in-situ growing a series MILs onto the iron network.
- The 3D Fe/MILs showed high adsorption capacity and excellent recovery ability towards TC.
- The growth process of MILs on iron network was discussed.
- The adsorption mechanism of Fe/MIL-100(Fe) was investigated.
- The Fe/MIL-100(Fe) system exhibited high removal efficiency in actual water.

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ABSTRACT

Considering the low recyclability of powder adsorbents, an efficient method is needed to fabricate a novel threedimensional (3D) adsorbents. Take advantage of the 3D iron network and admirable adsorption performance of the Fe-based metal-organic framework (Fe-MOF), a solvothermal method was used to in-situ growing a series of Fe-based MOFs (MIL-53(Fe) MIL-100(Fe) and MIL-101(Fe)) onto the iron network (MIL stands for Materials of Institute Lavoisier). The successful growing of MILs(Fe) on the iron network was verified by optical microscopy, SEM, XRD, FT-IR and XPS characterizations. As expected, the 3D MILs(Fe) (Fe/MILs) inherited the high adsorption capacity of powdery MILs(Fe), while excellent recycling performance was obtained. Among them, Fe/ MIL-100(Fe) exhibited the highest performance towards tetracycline (TC), more than 95% of TC could be removed at fifth adsorption cycle. Mechanism indicated that the π - π and hydrogen bonding (H-bonding) interactions between Fe/MIL-100(Fe) and TC molecules played an essential role in the adsorption process. Besides, the Fe/MIL-100(Fe) kept a high adsorption performance towards TC in a wide pH range of 2–10 and suffered minor influence from the anion and humic acid in solution. Even in actual aqueous solution (tap water, river water and pharmaceutical wastewater), high performance was presented by the Fe/MIL-100(Fe) adsorbent. This work provided a new method to synthesis 3D MILs(Fe) adsorbents for wastewater remediation.

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1. Introduction

Over that last decades, antibiotics were extensively used in clinical medicine and animal husbandry [1,2]. According to report, China's total antibiotics production in 2013 was expected to reach 248,000 tons and using antibiotics was estimated at 162,000 tons [3]. The related research estimates indicated that the using amount of antibiotics will rise to 200,235 tons in 2030 [4]. A mass use of antibiotics may result in the relatively high environmental concentrations and increase the risk of antibiotic resistance in environment [5–7]. According to the recent research, the antibiotic resistance was increasing significantly in aqueous water by 2019 [8]. An estimated 700,000 deaths were caused by antibiotic resistance in 2016, if unchecked, to 10 million by 2050 [9]. However, a challenging problem which arises in this domain is removing the antibiotics from the aqueous solutions due to the inferior biodegradability and complicated molecular structures [10].

In the last decades, abundant studies have been carried out to seek methods to remove antibiotics from water. There are plenty of methods to solve this problem. For example: advanced oxidation processes (AOPs) [11–13], membrane separation process [14], photocatalytic degradation [15] and biofiltration [16]. Adsorption, as an efficient method, has received extensive concern for its easy operation, low economic cost and high removal rate [17]. Recently, plentiful adsorbents were applied in water treatment, such as multiwall carbon [18], graphene oxide [19] and activated carbons [20]. More and more methods were constantly sought to control recalcitrant organic compounds at the forefront of the pollution control field [21].

With the development of the new materials, metal-organic frameworks (MOFs) which are consisted of metal centers combining with organic ligands structure have attracted numerous concern [10,22]. Due to its nanoscale pore sizes and superior surface areas, MOFs have shown great capacity in adsorption of pollutants from aqueous environment, such as dyes and organics [23]. For the past few years, many researches were conducted on MOFs-derivatives, including carbonbased materials and metal-based materials (like phosphides, chalcogenides, carbides, and oxides), which vastly optimize the structure and component of MOFs [24,25]. For example, in Ding et al. study, the -NH2 functional group was added into UiO-66 and enhanced the original material adsorption capacity [26]. Compared to MIL-53(Fe), the adsorption capacity of Ni-doped MIL-53(Fe) to doxycycline from aqueous solution was improved in Xiong et al. experiment [27]. Though these MOFs have excellent water stability and high removal rate towards pollutants from aqueous solution, a key issue is the recycling performance of these adsorbents, which is vital in the practical application. Most of these adsorbents are in powder form which are difficult to recycle. Moreover, the residual particulate adsorbents in water body may result in secondary contamination. Therefore, MOFs on the recovery matrix has become a hot topic nowadays. For example: in Guo et al. study, MOFs grew on the wood successfully [28]. Meanwhile, MOFs and iron network as a system to remove the pollutants by Wang et al. [29]. These systems inherit the properties of powdery MOFs, and the recycling capacity of MOFs was greatly improved which has attracted our attention. In a multitude of matrix, the iron network is an ideal material for MOF growth matrix because of its low cost and easy preparation. At the same time, solvothermal method with simple synthesis conditions and low price has attracted extensive application in the field of MOFs. Thus, combining solvothermal method and iron network as matrix together may be an ideal strategy to fabricate efficient absorbents for removing pollutants from the aqueous solution.

The MILs series with the advantages of stable chemical characteristics, flexible structure and breathing function stability were considered a typical type of MOFs [30]. Moreover, the Fe³⁺ served as a high-valence metal center which could easily combined with carboxylate-type ligands to formation water stable MOFs [31]. In this study, the Fe-MILs (MIL-53, MIL-100, MIL-101) were growing onto the iron network by the solvothermal method. The iron network served as iron sources which avoided introducing additional sources of iron. Scanning electron microscope (SEM), Brunauer-Emmett-Teller (BET), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectrum (FT-IR) and X-ray powder diffractometer (XRD) were used to characterized physicochemical property of the synthetic the three-dimensional (3D) MILs(Fe) and confirmed the successful growing of MOFs. The optimal material was determined by adsorption and circulation experiments of tetracycline (TC) under the same conditions. The TC adsorption experiments were used to evaluate the capacity of system under different conditions at various temperatures, initial pH values, ionic strength and water bodies. This study provided a convenient and economical way for growing MOFs materials on 3D iron network.

2. Experimental

2.1. Materials and reagents

N,N-dimethylformamide (DMF; (CH₃)₂NCHO), 1,4-benzenedicarboxylic (1, 4-H₂BDC), 1, 3, 5-Benzenetricarboxylic acid (1, 3, 5-H₃BTC), ethanol (C₂H₅OH), hydrochloric acid (HCl), sodium chloride (NaCl), sodium sulfate (Na₂SO₄), sodium phosphate (Na₃PO₄), humic acid (HA), methyl alcohol (CH₃OH) and tetracycline (TC) were of analytical reagent and purchased from Shanghai Rhawn Technology Development Co. Ltd. All of the chemicals were used as received without further purification, iron network (30 mm × 30 mm network, diameter of single iron wire = 0.14 mm), ultrapure water (resistivity of 18.2 MΩcm⁻¹) was used throughout the experiments.

2.2. Synthesis of Fe/MILs

Synthesis of Fe/MIL-53(Fe) and Fe/MIL-101(Fe): 0.8100 g (0.4050 g) 1, 4-benzenedicarboxylic acid and 55 mL DMF were mixed in a beaker. Then, the mixture kept magnetic stirring at room temperature for 2 h. Subsequently, three pieces of iron network (the iron network was cleaned for three times with methanol in an ultrasonic cleaner to remove impurities) were placed into a 100 mL Teflon liner. After adding 3 mL hydrochloric acid, the mixture was put in stainless steel reactor. The reaction system was transferred into the oven and heated at 170 °C for 24 h. After nature cooling, the networks were washed with DMF and ethanol for three times. Finally, the obtained products were vacuum dried overnight at 60 °C. The final products were labeled as Fe/MIL-53(Fe) and Fe/MIL-101(Fe).

Synthesis of Fe/MIL-100(Fe): 0.3000 g 1, 3, 5-benzenetricarboxylic acid and 55 mL H_2O were mixed. The solution was stirred at room temperature for 2 h, then three pieces of iron network were put into a 100 mL Teflon liner. With 3 mL hydrochloric acid mixed into the solution, the reaction system was transferred into in stainless steel reactor and heated at 140 °C for 24 h. After cooled into room temperature, the obtained products were purified with ultrapure water for 2 h and dried under oven at 60 °C overnight.

2.3. Characterization techniques

The powder X-ray diffraction (XRD, D8 ADVANCE) was tested by Bruker AXS D8 Advance diffractometer. Scanning electron microscopy (SEM, Quanta 250 FEG) was used to characterize the morphology of samples. X-ray photoelectron spectroscopy (XPS, Thermo Fisher, USA) spectrum and Fourier transform infrared spectroscopy (FT-IR, Bruker Vertex 70) were applied to investigate the valence state and chemical composition of samples. The zeta potential of sample was detected by a Zeta-sizer Nano-ZS (Malvern, UK). The N₂ adsorption-desorption isotherm and Brunauer-Emmett-Teller (BET, ASAP 2460) method were used to characterize the porous nature and surface area.

2.4. Adsorption experiments

The dark adsorption experiments were conducted in 100 mL beakers containing 50 mL of 20 mg L^{-1} TC solution to investigate the adsorption capacity of Fe/MIL-53(Fe), Fe/MIL-100(Fe) and Fe/MIL-101(Fe) to TC. Notably, a piece of material was added into TC solution for 120 min. Samples were collected after a regular time interval (5 min, 10 min, 15 min, 20 min, 30 min, 45 min, 60 min and 120 min) and the TC concentration was measured by UV–Vis spectrophotometer (Shimadzu, Japan) at 357 nm.

The TC solutions in different pH (2, 4, 6, 8, 10) which were changed by dilute HCl and NaOH solution. It was used to measure the Fe/MILs adsorption performance in different pH value. The TC solutions with various concentrations of NaCl, Na₂SO₄ and Na₂CO₃ were chosen to study the effect of solution ionic strength on the adsorption performance of Fe/MILs. Besides, the thermodynamic studies were performed at three temperatures of 25 °C, 35 °C and 45 °C. Moreover, the zeta potentials of Fe/MIL-100(Fe) at the pH values of 2, 4, 6, 8, 10, 12 in water and TC solution were estimated.

3. Result and discussion

3.1. Structure characterization

The original iron network was washed with methanol. As showed in Fig. 1a, the pristine iron network was smooth and metallic. Then, the cleaned iron networks were immersed in terephthalic acid and 1, 3, 5-Benzenetricarboxylic acid solution, respectively. After adding hydrochloric acid (HCl) into the solutions, the above mixtures were transferred to Telfon reactor. With the addition of HCl, the iron network was corroded and released the iron ions. Subsequently, organic linkers reacted with the dissolved metal ions, leading to the generation of nucleation and followed by growing crystals [32]. Finally, three kinds of materials were washed and dried. Apparent changes were presented after in-situ growing of MOFs. It can be observed that the surface of Fe/MILs were rough and colorful (Fig. 1b–d). Besides, the iron network was uniformly covered by crystals.

Scanning electron microscopy (SEM) further confirmed the optical microscope results [33–35]. According to the SEM images, Fe/MIL-53(Fe) displayed an algae morphology with loose structure (Fig. 1e and h), which was similar to the previous research [36]. Fe/MIL-100(Fe) presented a rod-like structure with an average size of $1.1 \times 11.3 \,\mu$ m (Fig. 1f and i) [37]. It was worth noting that Fe/MIL-101(Fe) had a

smooth sheet morphology (Fig. 1g and j). In addition, elemental mapping under SEM mode was a powerful method to investigate the compositional distribution of the Fe/MILs. Elemental mapping showed that C, O and Fe elements of Fe/MILs were evenly distributed, in which Fe element was more than other elements (Fig. S3- 5). At the same time, the MILs which grow successfully on the iron network was confirmed by extensive presence of C elements.

The crystal structure and composition of Fe/MILs was analyzed by X-ray diffraction (XRD) method. As presented in Fig. 2a-c, the characteristic peaks of three synthetic materials could be matched, respectively, which confirmed the successful growing of MILs(Fe) on the iron network [30,38,39]. Meanwhile, the XRD result was also confirmed by FT-IR spectroscopy. The FT-IR data of various samples (included Fe/ MIL-53(Fe), Fe/MIL-100(Fe) and Fe/MIL-101(Fe)) were detailed in Fig. 2d. The results indicate that the three kinds of materials have analogous FT-IR spectra. The peak of the Fe/MIL-53(Fe) and Fe/MIL-101(Fe) at 635 cm^{-1} was consistent with the peak of MIL-53(Fe) and MIL-101(Fe), which correspond to the Fe-O stretching vibration [40,41]. Also, there were peaks that can be seen in both materials about $1380 \text{ cm}^{-1} 730 \text{ cm}^{-1}$ and 1656 cm^{-1} , which could be ascribed to C–H, C-O and C=O, respectively [42,43]. Besides, in the Fe/MIL-100(Fe) infrared spectrum, the characteristic peaks appeared on 710 cm⁻¹ 792 cm^{-1} 1376 cm⁻¹ and 1696 cm⁻¹, which does tally with the Fe-O stretching vibration, C-H, C-O and C=O, respectively [44]. The FT-IR spectra of all systems were consistent with previously synthesized powder monomers, which demonstrates the successful growth of the MILs on the iron network [27].

XPS analysis provided the information of chemical information and valence state of samples. The results of the survey spectrum and highresolution spectra were detailed in Fig. 3a, which indicated the presence of Fe, C and O, elements on the iron network. Fig. 3b revealed the high-resolution XPS spectra of C 1s. All of materials have characteristic peaks of C-H bond, phenyl group and carboxyl group. The peaks at 284.80 eV, 286.03 eV (Fe/MIL-53(Fe)), 284.77 eV, 285.54 eV (Fe/MIL-100(Fe)) and 284.78 eV, 284.91 eV (Fe/MIL-101(Fe)) could be contributed to the sp²⁻ bonded and sp³⁻ bonded in benzene ring [45–47]. As displayed in Fig. 3c, all three materials contain Fe-O bonds. The Fe²⁺ and Fe³⁺ characteristic peaks and corresponding satellite peaks in Fig. 3d indicated that Fe²⁺ and Fe³⁺ co-existing in the material [45,48]. The analysis results of the XPS spectra were consistent with the results of FT-IR, which further proved the successful growing of MOFs on the iron network. Based on the XPS characterization, the information of peak position and atomic percentage of Fe/MILs were listed in



Fig. 1. The original network (a); optical microscopy images of after growing of MILs iron network. (b–d); SEM images of Fe/MIL-53(Fe) (e and h); SEM images of Fe/MIL-100(Fe) (f and i); SEM images of Fe/MIL-101(Fe) (g and j).



Fig. 2. XRD patterns of the Fe/MIL-53(Fe) (a); Fe/MIL-100(Fe) (b); Fe/MIL-101(Fe) (c). FT-IR spectra (d) of Fe/MIL-53(Fe), Fe/MIL-100(Fe), Fe/MIL-101(Fe).



Fig. 3. Fe/MILs high-resolution XPS spectra survey (a); C 1s (b); O 1s (c); Fe 2p (d).

Table 1

XPS analysis of Fe/MIL-53(Fe), Fe/MIL-100(Fe) and Fe/MIL-101(Fe).

	Peak BE (eV)			At.%		
	Fe/MIL-	Fe/MIL-	Fe/MIL-	Fe/MIL-	Fe/MIL-	Fe/MIL-
	53(Fe)	100(Fe)	101(Fe)	53(Fe)	100(Fe)	101(Fe)
C 1s	284.80	284.80	284.80	51.95	52.10	54.12
O 1s	531.76	531.82	531.77	36.64	41.07	35.47
Fe 2p	710.58	711.54	710.60	11.41	6.83	10.41

Table 1. According to Table 1, high C element content of 51.95%, 52.1% and 54.12% in Fe/MIL-53(Fe), Fe/MIL-100(Fe) and Fe/MIL-101(Fe) can be obtained respectively, indicating that a large number of MILs were successfully growing on the surface of the iron network.

The BET surface area, pore size of Fe/MILs were exhibited in Fig. S2 and Table S4. It was vital to notice that the BET surface area of Fe/MILs was much larger than the pristine iron network. The result proved that the MOFs were successfully growing on network. In addition, Fe/MIL-100(Fe) had the largest BET surface area. Therefore, highest BET surface area of Fe/MIL-100(Fe) should be the reason of the excellent adsorption performance towards TC.

3.2. Adsorption kinetics

The kinetics of different MOFs systems were essential. The adsorption kinetic experiment was carried out at optimal conditions (initial concentration = 20 mg/L; V = 50 mL, reaction time = 2 h). According to the previous research, the adsorption behavior of adsorbents can be described by pseudo-first-order adsorption kinetics equation [49]. The equation was shown in as followed:

$$C_t = C_e + (C_0 - C_e)e^{-kt}$$
(1)

where C_t is the TC total concentration (mg/L), C_e is symbol of the concentration of TC at adsorption equilibrium (mg/L), C_0 describe the initial concentration of TC (20 mg/L), t (min) is the reaction time and k is the pseudo-first-order rate constant (min⁻¹) representing for the adsorption capacity. The data based on pseudo-first-order kinetic model were listed in the Table 2. As showed in Table 2, the adsorption behavior of three materials can be described by the pseudo-first-order kinetic model because the R-square parameters (R²) of Fe/MILs were closed to '1'.

In addition, the pseudo-second-order kinetic model was also applied to fit the experimental data. The equation was as follows:

$$C_t = \frac{t}{\left(\frac{m}{k_2 C_e^2 + \frac{t}{C_e}}\right)}$$
(2)

where C_t is the TC total concentration of adsorption (mg/L), the reaction time is represented by t (min), the equilibrium concentration of TC is measured in terms of Ce (mg/L), k represents the second-order rate constant (min⁻¹), m (g) is symbol of the mass of the adsorbents. However, the standard errors based on pseudo-second-order were too large, thus reduced the credibility of model.

In a word, the pseudo-first-order was considered as the ideal model. The reaction constant k could measure the reaction rate. Compared to Fe/MIL-53(Fe), the k values of Fe/MIL-100(Fe) and Fe/MIL-101(Fe) were much higher. The kinetics results suggested a rapid adsorption reaction in Fe/MIL-100(Fe) and Fe/MIL-101(Fe), which was in superior accordance with the experimental data.

3.3. Adsorption performance

Adsorption performance experiments were designed to explore the removal capacity of TC through different MOFs systems in aqueous

Table 2

The fitting parameters of the first-order dynamic and second-order dynamic equation of Fe/MIL-53(Fe) Fe/MIL-100(Fe) Fe/MIL-101(Fe).

Equation	$C_t = C_e (C_0 - C_e) e^{-kt}$		
		Value	Standard Error
Fe/MIL-53(Fe)	Ce	9.160	1.060
	Co	19.245	0.289
	k	0.0153	0.00332
	R-Square	0.980	
Fe/MIL-100(Fe)	Ce	0.621	0.365
	Co	19.418	0.438
	k	0.0453	0.00306
	R-Square	0.994	
Fe/MIL-101(Fe)	Ce	0.560	0.360
	Co	19.351	0.511
	k	0.0562	0.00403
	R-Square	0.992	
Equation	$C_t = \frac{t}{\left(\frac{m}{k_2 C_e^2 + \frac{t}{C_e}}\right)}$		
		Value	Standard Error
Fe/MIL-53(Fe)	m	0.0932	12.396
	Ce	13.293	4.634
	k ₂	1.26×10^{-4}	0.0167
	R-Square	0.971	
Fe/MIL-100(Fe)	m	0.231	10.958
	Ce	23.212	1.354
	k ₂	5.18×10^{-4}	0.0245
	R-Square	0.993	
Fe/MIL-101(Fe)	m	0.306	18.441
	Ce	22.624	1.341
	k ₂	9.51×10^{-4}	0.0572
	R-Square	0.988	

solution. Different MOFs system were transferred into the TC solution, and the adsorption curve was shown in Fig. 4a. According to the Fig. 4a, the adsorption capacity of Fe/MIL-53(Fe) was poor, which the removal rate only 46.61%. The removal rate of Fe/MIL-100(Fe) and Fe/MIL-101(Fe) at adsorption equilibrium was approximately 96.14% and 96.60%, respectively. However, it was not accurate to judge the properties of a material from the removal rate. Therefore, we designed a cyclic experiment to distinguish what was the most suitable system to apply in TC removal.

As shown in Fig. 4b, the removal rate of Fe/MIL-53(Fe) and Fe/MIL-100(Fe) after five adsorption cycles inherited the pulverous MOFs stability, which proved that the recycling performance of the MOFs system were reliable. Oppositely, Fe/MIL-101(Fe) decreased significantly in the fifth cycle, indicating that the system may be gradually destroyed with the increase of cycle times. From the figure of materials after treatment (Fig. S1d), we could also intuitively observe that the surface of Fe/MIL-53(Fe) and Fe/MIL-100(Fe) did not significantly alter after five cycles while Fe/MIL-101(Fe) showed mottled traces gradually. The XPS spectra of Fe/MIL-100(Fe) before and after reaction were researched because Fe/MIL-100(Fe) has excellent performance in each adsorption cycles. The Fig. 4c shown that, both of XPS spectra were nearly identical, which demonstrates the excellent stability of Fe/MIL-100(Fe). Furthermore, the post-reaction SEM characterization and FT-IR spectra were analyzed. As shown in the Fig. S1b, the Fe/MIL-100(Fe) still maintained the previous crystal morphology after the reaction. The Fig. S9 shown that the FT-IR spectra before and after the reaction were basically consistent. The result shown that the stability of Fe/MIL-100(Fe) was high. Therefore, stability and removal rates were considered. It was shown that Fe/MIL-100(Fe) has excellent cycling performance and high degradation rate with higher removal rate. It was proved that Fe/MIL-100(Fe) was an ideal choice to remove TC from the aqueous solution.



Fig. 4. Adsorption curve of Fe/MILs for TC (a); Fe/MILs five cycles of TC removal (b); Fe/MIL-100(Fe) Fe 2p XPS before and after the treatment (c); k value of the pseudo-first-order reaction model (d). Experimental conditions: absorbent dosage = a piece of Fe/MILs; initial TC concentration = 20 mg L^{-1} .



Fig. 5. Fe/MIL-100(Fe) XPS spectra after five cycles (a); Degradation rates of TC at different pH values (b); Fe/MIL-100(Fe) zeta potential curve (c); Schematic diagram of the possible removal mechanism of Fe/MIL-100(Fe) (d).



Fig. 6. Effects of NaCl (a); Na₂CO₃ (b); Na₂SO₄ (c) and humic acid (d) with various concentrations on adsorption of TC by Fe/MIL-100(Fe); adsorption in different temperature (e); effects of TC adsorption in various water bodies (f). Experimental conditions: absorbent dosage = a piece of Fe/MILs; initial TC concentration = 20 mg L⁻¹.

3.4. Adsorption mechanism

To determine the main mechanism in TC degradation, zeta potential and reaction sequence XPS spectra of Fe/MIL-100(Fe) were analyzed. Several theories have been proposed to explain MOFs adsorption, such as electrostatic interaction [50], π - π interaction [51], hydrogen bonding [52]. In this experiment, with pH was changed from two to ten and the removal rate increased gradually. Moreover, according to Fig. 5c, the MIL-100(Fe) zeta potential had a positive surface charge in pH < 4.45 TC solution. Oppositely, a negative surface charge appeared in pH > 4.45 TC solution. However, TC solution has positive charge, neutral charge and negative charge at pH < 3.32, 3.32 < pH < 7.78 and pH > 7.78, respectively [15]. Therefore, the experimental phenomena were not consistent with electrostatic adsorption mechanism, confirming that the primary adsorption mechanism of Fe/MIL-100(Fe) was not electrostatic interaction. At the same time, the XPS spectra before and after the reaction were analyzed. According to the Fig. 5a, the characteristic peak representing the benzene ring migrated from 285.54 eV to 286.14 eV, because the connection which exist between CONH₂ and Fe/MIL-100(Fe) will establish during the adsorption process [53,54]. Therefore, π - π interaction will result in adsorption.

The previous research have shown that the hydrogen bonding (Hbonding) forces will appear between –COOH of Fe/MIL-100(Fe) and functional groups in TC such as –OH, –NH₂ [55]. The hydrogen bond has a very small bond energy, which means it's very easy to break. On the macro level, the Fe/MIL-100(Fe) desorption capacity also reflects the possibility of H-bonding which exist between TC and Fe/MIL-100(Fe) [56]. More importantly, by comparing the FT-IR spectra before and after the reaction, we found that N–H vibration peaks appeared near 3700 cm⁻¹ and 2400 cm⁻¹, and hydrogen bonds formed peaks near 2900 cm⁻¹ (Fig. S9). It was an evidence that H-bonding played a role in the adsorption to TC [57]. In terms of thermodynamic analysis, the enthalpy change of this reaction is 12 kJ/mol which means that the adsorption reaction may be dominated by physical adsorption (Table S1). H-bonding is a typical mechanism used to explain physical

Table 3

Pristine iron network and Fe/ MIL-100(Fe) were determined by ICP-MS.

Material	The concentration of Fe (mg/L)	The concentration of RSD
Pristine iron network	85.710	0.0031
Fe/MIL-100(Fe)	0.317	0.0025

adsorption. Therefore, we suggested that H-bonding played an important role in the adsorption of tetracycline.

3.5. Effects of experimental conditions on adsorption properties

To investigate the adsorption ability of the Fe/MIL-100(Fe) system, organic substance (humic acid), inorganic ions (Cl⁻, Na⁺, SO₄²⁻ and CO_3^{2-}) and pH on TC absorption were assessed comprehensively. As shown in Fig. 6a–c, we found that the inorganic ions with different concentrations had a neglected effect on the adsorption performance.

Abundant studies have reported that TC can be absorbed by iron ions and iron oxides solution [58]. It should be noted that, nearly 54% of TC were absorbed with pristine iron network as adsorbent after the 2 h adsorption, which may due to the eroded iron ions or iron oxides combining with TC. However, a large number of released iron ions will cause secondary pollution to the water. Hence, the effect of iron ions dissolution rate would be concerned. Content of iron ions was analyzed by ICP-MS in the solution after adsorption (Table 3). The results showed that the iron ions dissolution rate (0.316 mg/L) of Fe/MIL-100(Fe) was 0.369% of the original iron network. The result showed that Fe/MIL-100(Fe) had high stability in water.

As shown in Fig. 6d, the adsorption rate of TC can be improved by humic acid, which may be ascribed to intricate surface complexation in the Fe/MIL-100(Fe)-HA-TC ternary system [59]. TC⁺ or TC⁰, may combine with humic acid at the pH > 1.5 solution. All of them may form a complex compound that promotes the adsorption of TC. Besides, we performed adsorption experiments at different temperatures (25 °C, 35 °C, 45 °C). The experimental results shown that the adsorption rate was improved as the temperature went up (Fig. 6e). To verify Fe/MIL-100(Fe) could use in actual water. The Fe/MIL-100(Fe) adsorbed capital was tested in a 20 mg/L tetracycline solution, which river water, tap water and medical wastewater mixed with tetracycline powder. According to the Fig. 6f, TC can also be significantly removed in other aqueous solution, which proved that Fe/MIL-100(Fe) has a great application value.

4. Conclusion

In this study, three MOF materials (MIL-53(Fe), MIL-100(Fe) and MIL-101(Fe)) successfully grew on the 3D iron network by solvothermal method. Adsorption experiments exhibited that the Fe/MIL-100(Fe) adsorption performance towards TC was the highest. More importantly, excellent recycling property (95% of removal rate after five cycles) and structural stability (negligible iron leaching when immersed in water) made the Fe/MIL-100(Fe) had potential in wastewater treatment. The kinetic experiments shown that the adsorption behavior was described by pseudo-first-order kinetic. Besides, the adsorption performance of Fe/MIL-100(Fe) suffered less influence from initial solution pH, anion and humic acid. The Fe/MIL-100(Fe) was effective in different aqueous solution (tap water, river water and pharmaceutical wastewater). The π - π interaction and H-bonding between TC molecules and Fe/MIL-100(Fe) may become reason of the adsorption. Shortly, we have developed a low-cost and environmentally-friendly method for in-situ growing MOFs materials on the iron network for adsorptive removal of TC from aqueous solution. We hope our work could stimulate the researchers to 3D MOF-based materials for various applications.

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Appendix A. Supplementary data

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