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15 Abstract

A novel adsorbent composite was synthesized by combining amino-functionalized 16 17 MIL-53(Fe) with multi-walled carbon nanotubes (MWCNT), and used to adsorb tetracycline hydrochloride (TCN) and chlortetracycline hydrochloride (CTC). The 18 maximum adsorption capacities of TCN and CTC over MWCNT/NH2-MIL-53(Fe) at 19 25 °C were 368.49 and 254.04 mg g⁻¹, which are, respectively, 1.79 and 8.37 times 20 higher than that of chaff biochar. Interestingly, 21 the mesoporosity of MWCNT/NH₂-MIL-53(Fe) significantly increased through introdu ion of MWCNT 22 into NH₂-MIL-53(Fe), which proved to be favorable for production of active 23 adsorption sites. Besides, the remarkably increased adsorption capacity can be 24 ascribed to the hydrogen bonding bet real amino functional groups on 25 MWCNT/NH₂-MIL-53(Fe) and hydroxyl functional groups on TCN or CTC. 26 Moreover, the π - π interaction b asorbate and adsorbent was considered the 27 TCN and CTC. The great adsorption capacity, as main reason for the adsorption 28 use bility, demonstrated the potential application of 29 well excel as MWCNT/NH₂-MIL **5**3(Fe) in the removal of TCN and CTC from aqueous solutions. 30 **Keywords:** Adsorption; tetracycline hydrochloride; chlortetracycline hydrochloride; 31 MWCNT/NH₂-MIL-53(Fe); removal. 32

33 **1. Introduction**

Antibiotics, especially tetracycline antibiotics, have wide range of applications in 34 35 medicine and aquaculture (Martins et al., 2015; Defuria et al., 2016; Qin et al., 2017), due to their anti-bacterial, anti-fungal, anti-virus and anti-parasite qualities. 36 Antibiotics are rarely degraded and metabolized by organisms, and about 30 to 90 37 percent of them are discharged into the natural aquatic environment through urine or 38 feces (Abejon et al., 2015; Wu et al., 2015; Hirsch et al., 1999). Moreover, a 39 considerable number of antibiotics in the artificial feed are directly issolved into the 40 water due to their high solubility. The majority antibiotics can be 41 protonated/deprotonated at various pH values, exist g in different places (Parolo et 42 al., 2012). Contamination of water caused by anuoiotics has become a serious 43 international problem, due to their low biod gradability in the water. According to a 44 biotics in domestic wastewater ranges from previous report, the concentration 45 100 ng/L to 6 mg/L (Cete oglu et al., 2013). Hence, it is imperative to efficiently 46 ous solutions. remove antibiotic 47 from

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; Cheng et al., 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 55 pollution. A part of membranes used for adsorption and separation are easily 56 57 contaminated, resulting in a decline of permeability. Besides, due to antibacterial effects on some microbes, biodegradation methods are not effective in removing 58 antibiotics (Reyes et al., 2006). Adsorption is considered as the most appropriate 59 method due to its simplicity of operation, low-cost and high-efficiency (Xiong et al., 60 2017; Zhang et al., 2016; Long et al., 2011; Xu et al., 2012). So far, a variety of 61 materials, especially carbonaceous or porous materials have be used to adsorb 62 antibiotics due to their high surface areas, many kinds of the 63 groups, low price and good environmental benignity (Carabineiro et a 2011; Carabineiro et al., 2012; 64 Deng et al., 2013; Tang et al., Tan et al., 2015; Wu et al., 2017; Gong et al., 65 2014; Xu et al., 2012; Liang et al., 2017; Qh et al., 2018; Jiang et al., 2017; Yu et al., 66 2016). For example, sulfameth Z) has been removed using carbonaceous 67 nanocomposites (Zhang et ., 2(16). Tetracycline (TCN) and sulfamethazine (SMZ) 68 nly porous carbon (He et al., 2016). Exploring more 69 have been adsord efficient adsorption naterials for antibiotics removal still remains challenging. 70

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 77 adsorption. For example, Jhung et al. have applied MIL-100(Fe), MIL-101(Cr), 78 79 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 80 important class that has drawn much attention due to its chemical versatility, flexible 81 structure, breathing feature and stability (Naeimi et al., 2017). Moreover, the Fe³⁺ 82 metal center with normal carboxylate-type ligands can be easily synthesized with the 83 characteristic of water stability (Wang et al., 2016; Liu et al. 84 In this study, as the surface of MOFs can be easily ted by introducing 85 functional groups on organic ligands (Bhadra et 2016), amino-functionalized 86 MIL-53 (Fe) was fabricated using organic listed with amino. Moreover, after 87 introducing the very small amount of multivalled carbon nanotube (MWCNT), the 88 adsorption capacity of MWC IL-53(Fe) for tetracycline hydrochloride 89 (TCN) and chlortetracycline hydrochloride (CTC) showed an obvious enhancement. 90 adsorption behavior 91 Hence. of TCN and CTC on we MWCNT/NH₂-MIL 3(Fe), and potential adsorption mechanisms were proposed. 92 Furthermore, the main factors affecting the maximum adsorption 93 on MWCNT/NH₂-MIL-53(Fe), including pH and ionic strength, were analyzed. 94 Excellent adsorption capacity and reusability of MWCNT/NH₂-MIL-53(Fe) sheds a 95 new light on antibiotics removal. 96

97 **2. Experimental section**

98 **2.1** Chemicals and syntheses of adsorbents

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All the chemicals were analytical grade and used as received without further 99 purification. N,N-dimethylformamide (DMF, 99.5%), ferric chloride hexahydrate 100 (FeCl₃ 6H₂O, 99%) and ethanol (99.5%) were purchased from Sinopharm Chemical 101 Reagent Co., Ltd. 2-Aminoterephthalic acid (98%) was purchased from Shanghai 102 Macklin Biochemical Co., Ltd. The chaff biochar was purchased from Beijing hele 103 biotechnology Co., Ltd. Multi-walled carbon nanotubes (MWCNT) with diameters 104 ranging from 10 to 20 nm were purchased from the Chengdu Organic Chemicals Co. 105 Ltd. (PR China). Tetracycline hydrochloride (TCN) and shlortetracycline 106 hvdrochloride (CTC) were obtained from bomei bioted 107 Co., Ltd (Hefei, China). The ultra-pure water (resistivity of 18.25 M cm⁻¹) was used throughout the 108 experiment. 109

olyothermal method (Shi et al., 2015), 110 NH₂-MIL-53(Fe) was prepared by a bstitution. The typical synthesis procedure which was obtained by organic 111 was as follows: 0.674 g of prric hloride hexahydrate, 0.452 g of 2-aminoterephthalic 112 acid and 56 mL CDNE solution were mixed by stirring at room temperature, and 113 then transferred into a 100 mL Teflon-lined stainless steel autoclave. After that, the 114 autoclave was heated at 170 °C for 24 h. The product was washed with DMF and 115 ethanol, filtered, and dried. 116

117 To synthesize the MWCNT/NH₂-MIL-53(Fe) composites, purified MWCNT (PR 118 China) were dispersed in precursor mixtures of the NH₂-MIL-53(Fe). The remaining 119 synthetic steps were the same as those in the synthesis of NH₂-MIL-53(Fe). The 120 proper amount of purified MWCNT was introduced in DMF and then mixed with 121 ferric chloride hexahydrate, 2-aminoterephthalic acid and DMF. The resulting mixture 122 was stirred at room temperature, then transferred into a 100 mL Teflon liner in 123 stainless steel autoclave and heated at 170 °C for 24 h. The powder was collected by 124 centrifugation, washing and drying.

125 **2.2 Characterization**

The structural characteristics of adsorbents were obtained by a D8 X-ray 126 diffractometer (XRD; Bruker, utilizing Cu Ka radiation, Germany). Binding energies 127 were characterized by X-ray photoelectron spectrum Thermo Fisher 128 Scientific-ESCALAB 250Xi, USA). The Fourier transform d spectrum (FT-IR) 129 measurements were used to confirm the introduced excitonal groups of MOFs from a 130 Nicolet 5700 Spectrometer in KBr pellet at for emperature (Nicolet, USA). The 131 morphology of MWCNT, NH₂-MIL-53(F) and MWCNT/NH₂-MIL-53(Fe) was 132 electron microscope (SEM) (Carl Zeiss, analyzed via environmental 133 EVO-MA10, Germany). The specific surface areas of adsorbents were measured 134 Empett Teller (BET), and the total pore volume and pore size using the Brunat 135 were measured by automatic surface analyzer (Quantachrome, USA). The zeta 136 potential of MWCNT/NH₂-MIL-53(Fe) was measured by a Zeta potential analyzer 137 (Zetasizer Nano zs90) at varying pH values. Thermogravimetric analysis (TGA) was 138 measured by a Mettler TGA/ SDT Q600 analyzer under nitrogen flow with a 139 temperature growth rate of 10 $\,^{\circ}$ C min⁻¹. 140

141 **2.3 Adsorption experiments**

142 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 143 adsorbents of biochar, MWCNT, NH₂-MIL-53(Fe) chaff 144 and MWCNT/NH₂-MIL-53(Fe) were dried for 8 h in a vacuum oven and used for 145 adsorption of TCN and CTC in aqueous solutions. Adsorbents (10 mg) were added 146 into the TCN and CTC solutions (50 mL, 20 mg L^{-1}), and the mixture was shaken at 147 room temperature using an incubator shaker in the stipulated time. 148

After adsorption of the TCN and CTC in aqueous solutions, the solutions were 149 centrifuged at 5000 rpm and then filtered using 0.45 µm PVDF dis sable filters. The 150 remaining TCN and CTC concentrations were evaluated 151 spectrophotometer (UV-2700, SHIMADZU, Japan). In order to determine the effect of pH on the 152 amounts of adsorbed TCN and CTC, the pH value of the TCN and CTC solutions (20 153 mg L^{-1}) was altered with aqueous NaOH (1 M) or HCl (0.1 M) and adjusted by 154 ffect of ionic strength on adsorption was using a pH meter (FE20, Chin 155 determined by using TCI and CTC solutions (20 mg L^{-1}) containing different 156 Na Various methods of our calculations including the 157 concentrations pseudo-first-order, pseudo-second-order, intra-particle diffusion models and Langmuir, 158 Freundlich, Temkin isotherm equations were applied to analyze the adsorption 159 experiment results. Besides, kinetics models, isotherm models and calculation 160 equations were shown in Table S1 (Tang et al., 2018). 161

162 The recyclability of MWCNT/NH₂-MIL-53(Fe) was evaluated after the 163 adsorption of TCN and CTC. The used MWCNT/NH₂-MIL-53(Fe) was washed with 164 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 165 repeated three times to completely remove the adsorbed TCN and CTC. The 166 recovered MWCNT/NH₂-MIL-53(Fe) was applied similarly for the fourth runs. 167

3. Results and discussion 168

3.1 Characterization of the adsorbents 169

The morphology of NH₂-MIL-53(Fe) and MWCNT/NH₂-MIL-53(Fe) was 170 observed using environmental scanning electron microscope (SEM). Fig. 1a showed 171 that the surface of NH₂-MIL-53(Fe) crystal was relatively smoot After combining 172 NH₂-MIL-53(Fe) with MWCNT (Fig. 1b), there was a 173 us change on the surface morphology of MWCNT/NH₂-MIL-53(P as shown in Fig. 1c. In 174 comparison, the surface area of MWCN f/ MIL-53(Fe) was larger than 175 NH₂-MIL-53(Fe) since the MWCNT was attached on its surface. 176

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XRD patter pure NH₂-MIL-53(Fe) The MWCNT, 178 and were shown in Fig. 2a. The characteristic peaks of MWCNT/NH₂-MN 179 MWCNT were observed in the diffractogram of MWCNT/NH₂-MIL-53(Fe), which 180 indicated that **MWCNT** and NH₂-MIL-53(Fe) coexisted in the 181 MWCNT/NH₂-MIL-53(Fe) material. After combining with MWCNT, the XRD peaks 182 of MWCNT/NH₂-MIL-53(Fe) were very similar to the diffraction patterns of 183 NH₂-MIL-53(Fe) (Shi et al., 2015). Thus, the introduction of MWCNT had not a 184 significant impact on the crystalline structure. 185

186

As shown in Fig. 2b, the FT-IR spectra of MWCNT/NH₂-MIL-53(Fe) contained

187	the characteristic peaks of MWCNT and NH ₂ -MIL-53(Fe). The band at 537 cm^{-1} was
188	attributed to Fe-O vibration. Bands at 1375, 1560, and 1650 cm^{-1} could be assigned to
189	C-O and C=O vibration of carboxylic groups. The band at 770 cm^{-1} was attributed to
190	C-H vibration of benzene rings. Bands at 1253 and 3372 cm^{-1} were attributed to C-N
191	and N-H vibrations of amino group, respectively (Gao et al., 2017; Jia et al., 2017).
192	Bands at 2360 and 3450 cm^{-1} were due to O-H vibration from MWCNT, which
193	confirmed the successful synthesis of the MWCNT/NH ₂ -MIL-53(Fe).
194	"Here Fig. 2"
195	The XPS spectra of MWCNT/NH ₂ -MIL-53(Fe) are shown in Fig. 3. The survey
196	spectrum of MWCNT/NH ₂ -MIL-53(Fe) consisted Fe, O, C, and N elements, as
197	seen in Fig. 3a. For the XPS spectrum of Fe 16 (1g. 56), two strong peaks at 725.83
198	eV and 712.87 eV were attributed to Fe 2p1/2 and Fe 2p3/2, respectively, which
199	indicated that Fe^{3+} species were preserved MWCNT/NH ₂ -MIL-53(Fe). As shown in
200	Fig. 3c, the C 1s peak of MWCNT/NH ₂ -MIL-53(Fe) could be deconvoluted into four
201	peaks at 284.65 eV 284.83 eV, 286.22 eV and 289.36 eV, which could be attributed to
202	benzoic rings (C=C, carbon atoms bond in MWCNT (C-C and C-O) and organic
203	linkers in MWCNT/NH ₂ -MIL-53(Fe) and carboxylate groups in MWCNT (C=O),
204	respectively. The O 1s peak also can be divided into two peaks at 531.86 and 532.38
205	eV, corresponding to the oxygen atoms on the H_2BDC linkers (C=O) and the Fe-O
206	bonds of NH ₂ -MIL-53(Fe), respectively (Fig. 3d). The N 1s spectrum was displayed
207	in Fig. 3e, showing that three kinds of pyridine N, pyrrole N and graphite N existed in
208	MWCNT/NH ₂ -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,

210 XRD and FT-IR analysis.

211

"Here Fig. 3"

The N₂ adsorption isotherms of adsorbents were shown in Fig. S1. Besides, BET 212 specific surface area, pore size distribution and pore volumes of composites were 213 summarized in Table S2 and Fig. S1b. As shown in Fig. S1a, all curves were type IV 214 isotherms with a typical H₃ hysteresis, due to the presence of mesopores and 215 macropores (Song et al., 2015), which was consistent with the res shown in Table 216 S2. However, after the modification with MWCNT, the 217 scific surface area. pore volumes and pore size of MWCNT/NH₂-MIL 3(Fe) showed an increase. The 218 TGA profiles of MWCNT/NH₂-MIL-53(Fe eniblied a slightly higher thermal 219 stability due to the introduction of MWCNT as seen in Fig. S1c. This is because 220 crystals were formed with he is nucleation and carboxylate groups on 221 MWCNT were treated as nucleation sites (Yang et al., 2009). 222

223 **3.2** Comparison of adsorption capacity of adsorbents

For comparison the chaff biochar was used as a traditional adsorbent to absorb 224 antibiotics. Fig. S2 and Fig. S3 showed the results of adsorption for TCN and CTC 225 with different concentrations and times. The adsorption capacity decreased in the 226 order of MWCNT/NH₂-MIL-53(Fe) > NH₂-MIL-53(Fe) > MWCNT > chaff biochar 227 for both TCN CTC. The excellent adsorption of 228 and capacity 229 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 230

volumes of MWCNT/NH₂-MIL-53(Fe) increased after MWCNT modification, as
expected.

233 **3.3 Adsorption kinetics**

The adsorption of TCN and CTC from aqueous solutions on three adsorbents 234 (MWCNT, NH₂-MIL-53(Fe) and MWCNT/NH₂-MIL-53(Fe)) was carried out at room 235 temperature. In order to understand the adsorption performance in more detail, the 236 experimental results analyzed by three kinetics models were shown in Fig. 4. The 237 kinetic parameters of TCN and CTC for the adsorbents were suprized in Table 1 238 and Table S3. Compared to the pseudo-first-order model eudo-second-order 239 model fitted better to the experimental results, indicing that chemisorption occurred 240 between adsorbates and adsorbents (Tang et a 241

"Here

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applied to further analyze the adsorption The intra-particle diffusion mo 243 mechanism. As shown in g. 4 f and Table S3, all plots of q_t were distributed in 244 e first line section was attributed to TCN and CTC transfer 245 three linear portion diffusion to the external surface of adsorbents, which was managed by the molecule 246 and film diffusion. The second section was the slow adsorption, where the TCN and 247 CTC diffused from the external surface to the internal pore and capillary structure of 248 adsorbents. The third section indicated that adsorption was almost balanced, where 249 the low concentration of TCN and CTC and insufficient active sites of adsorbents 250 251 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 252

diffusion was not the only rate-limiting step (Wang et al., 2016).

254

"Here Table 1"

255 **3.4 Adsorption isotherms**

The adsorption isotherm experiment was carried out at room temperature using 256 various TCN and CTC concentrations, and the experimental results were analyzed by 257 three isothermal adsorption models, presented in Fig. 5. The isotherm parameters of 258 Langmuir, Freundlich and Temkin models for TCN and CTC adsorption were listed in 259 Table 2. It was obvious that the correlation coefficients (R^2) nuir model were 260 much higher than those of Freundlich and Temkin 261 m models, which demonstrated monolayer molecular adsorption on be surface of adsorbents. This 262 phenomenon indicated that chemical adsorption might play the main role in the 263 process of absorbing TCN and CTC. The maximum adsorption capacity $(q_{m,cal})$ of the 264 the Langmuir model was larger than that of MWCNT/NH₂-MIL-53(Fe) calc 265 MIL-53(Fe). In addition, a separation factor (R_L) was used to analyze the Langmuir 266 le 2, all of the calculated parameters (R_L) below 1 indicated isotherm. As see 267 that the adsorption process was favorable. Furthermore, the lower R_L values indicated 268 that the interaction between adsorbates and NH2-MWCNT/MIL-53(Fe) was 269 considerably strong (Saliby et al., 2013). 270

271

"Here Fig. 5"

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.

279

"Here Table 2"

280 **3.5 Effect of solution pH and ion strength**

As the pH had a great influence on the surface charge, adsorption efficiency of 281 MWCNT/NH₂-MIL-53(Fe), and physicochemical characteristics **T**CN and CTC, it 282 was an important factor to consider for TCN and CTC a 283 **n**. There were four forms of existence in aqueous solutions, owing the hree dissociation constants for 284 TCN (pKa=3.32, 7.78 and 9.58) and CTC (7.55 and 9.33), respectively 285 the zero potential point (pH_{ZPC}) of 286 (Oiang et al., 2014). Moreover ately 3.42, as seen in Fig. S5. As shown in MWCNT/NH₂-MIL-53(Fe) was 287 Fig. S4, both TCN and CTC adsorption were strongly related to the pH of the solution. 288 veb increasing pH value from 3.42 to 9.0, the zeta potentials Along with the pre-289 tres were more electronizative and adsorption capacity was slowly reduced, since the 290 electrostatic repulsion might become the main force of interaction. 291

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 297 the major interaction between adsorbates and MWCNT/NH $_2$ -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).

300 3.6 Mechanisms for TCN and CTC adsorption

The qt of TCN and CTC over MWCNT/NH₂-MIL-53(Fe) was larger than those 301 of MWCNT and MIL-53(Fe). Additionally, as the pH values increased in solution, the 302 adsorption capacity of MWCNT/NH₂-MIL-53(Fe) was smaller. Consequently, both 303 physisorption and chemisorption were present in the adsorption **ECN** and CTC on 304 MWCNT/NH₂-MIL-53(Fe). The physisorption primarily 305 d on the pore size distribution of MWCNT/NH2-MIL-53(Fe). After he addition of MWCNT, the 306 significantly increased mesopores of MWC 2-MIL-53(Fe) could hold more 307 TCN and CTC and provide more active adsorption sites. 308

chanisms, such as electrostatic interaction, As for the chemisorption, 309 hydrogen bonding, coordination and π - π interactions can be used to demonstrate the 310 olutions. Firstly, electrostatic interaction was tried to 311 adsorption from ane explain the adsorption between adsorbates and MWCNT/NH₂-MIL-53(Fe) with the 312 increasing pH from 3.0 to 9.0. Considering the pKa of TCN (3.32, 7.78 and 9.58) and 313 CTC (3.33, 7.55 and 9.33), TCN (CTC) had a positive charge at pH < 3.32 (3.33), 314 315 neutral charge at 3.32 (3.33) < pH < 7.78 (7.55), negative charge at pH >7.78 (7.55). On the other hand, MWCNT/ NH₂-MIL-53(Fe) had positive surface charge at pH <316 317 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 318

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) 324 and hydroxy functional groups on TCN and CTC, the H atoms from the -OH could act 325 as H-bond donors and the N atoms from the -NH₂ could act a ap bond acceptors, 326 indicating that hydrogen bonding interactions could be a 327 mechanism (Song et al., 2017). Meanwhile, in spite of the electroster exclusion, with the pH value 328 increasing to 9.0, there was still a certain an our adsorption for TCN and CTC. 329 Therefore, the π - π interaction (Sarker et a 330 2017) was considered as a dominant mechanism for the TCN and CT 331

332 **3.7 Reusability of MWCNV/NH-MIL-53(Fe)**

orbants, reusability is an important parameter that should be For any kin 333 f ac since commercial taken into account. it is crucial for applications. 334 MWCNT/NH₂-MIL-53(Fe) can be readily regenerated by using acetone, owing to the 335 solubility of TCN and CTC. In this study, after MWCNT/NH₂-MIL-53(Fe) was dried 336 at 100 $\,^{\circ}$ C in a vacuum oven, there was no significant decrease in adsorption up to four 337 recycling cycles, as seen in Fig. S7. The easy desorption of TCN and CTC could 338 339 likely explain the weak hydrogen bonding between MWCNT/NH₂-MIL-53(Fe) and adsorbates. 340

341 **4.** Conclusions

In conclusion, MWCNT/NH2-MIL-53(Fe), a novel efficient adsorbent, was 342 successfully prepared by a facile solvothermal method. The properties of 343 MWCNT/NH₂-MIL-53(Fe), including porosity and specific surface area, improved 344 after the introduction of MWCNT. MWCNT/NH₂-MIL-53(Fe) was used for the first 345 time to remove TCN and CTC, and the adsorption efficiency of this composite was 346 higher than MWCNT, NH₂-MIL-53(Fe) and a traditional chaff biochar. Among of the 347 tested kinetic and isotherm models, the adsorption process ter fitted with a 348 pseudo-second-order and Langmuir isotherm models. The 349 n bonding between -OH of the TCN (CTC) and -NH₂ of the modified M-XCNT/NH₂-MIL-53(Fe), the π - π 350 interaction, and pore-filling effect were three fait asons for the adsorption process. 351 In addition, MWCNT/NH₂-MIL-53(Fe) could be readily regenerated and maintained 352 AWCNT/NH₂-MIL-53(Fe) could be used as good adsorption performance. T 353 a promising adsorbent for the moval of TCN and CTC from aqueous solutions. 354 n york easily by changing the organic ligands, and more 355 Moreover, the M MOFs-based composite adsorbents with single or multiple functional groups will be 356 expected for environmental applications dealing with water treatment. 357

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- 576 Figures:
- 577 figure captions:
- 578 Fig. 1. SEM images of NH_2 -MIL-53(Fe) (a), MWCNT (b) and
- 579 MWCNT/NH₂-MIL-53(Fe) (c).
- 580 Fig. 2. XRD diffractograms (a) and FT-IR absorption spectra (b) of NH₂-MIL-53(Fe),
- 581 MWCNT and MWCNT/NH₂-MIL-53(Fe).
- 582 **Fig. 3.** XPS spectra of MWCNT/NH₂-MIL-53(Fe): (a) survey, (b) Fe 2p, (c) C 1s, (d)
- 583 O 1s and (e) N 1s.
- **Fig. 4.** Pseudo-first order plots for TCN (a) and CTC (b) Acception; pseudo-second
- order plots for TCN (c) and CTC (d) adsorption: ara-particle diffusion model for
- 586 TCN (e) and CTC (f) adsorption. Reaction conditions. TCN and CTC concentration =
- 587 20 mg L⁻¹; adsorbent loading = 0.2 g L⁻¹; ten perature = 25 °C; initial pH = 7.
- 588 Fig. 5. Langmuir isotherm model for TCN (a) and CTC (b) adsorption; Frendich
- isotherm model for TCN (a) and CTC (d) adsorption; Temkin isotherm model for
- 590 TCN (e) and CT (f) absorption. Reaction conditions: adsorbent loading = 0.2 g L^{-1} ; 591 temperature = 25 °C initial pH = 7.
- 592

- 593 Tables:
- 594 Table captions:
- **Table 1.** Adsorption kinetics parameters of TCN and CTC on adsorbents.
- **Table 2.** Isotherm parameters for the adsorption of TCN and CTC on adsorbents.

