Article

Facile Synthesis of MOFs-Templated Carbon Aerogels with Enhanced Tetracycline Adsorption Performance

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Abstract: Three-dimensional aerogels have great potential for antibiotic removal from aqueous solution due to their excellent solution mass transfer channels and special morphology. Herein, the metal ions were bound with alginate to form alginate-Fe, alginate-Cu, and alginate-Fe-Cu hydrogels, then they were used as nucleation sites for metal organic framework (MOF) growth to obtain MAIgs gels, respectively. Considering the aqueous environmental stability of MOFs particles, the alginate and MOF particles in MAIgs aerogels were pyrolyzed as templates to obtain the derived carbon aerogel CMAIgs. The results showed that the adsorption capacity of MAIgs-Fe-Cu aerogel was higher than that of MAIgs-Cu and MAIgs-Fe aerogels, up to $\sim 130 \text{ mg} \cdot \text{g}^{-1}$. The adsorption performance of carbon aerogel CMAIgs-Cu decreased obviously because of the decrease of pore size and oxygen-containing functional groups. The adsorption process is a combination of physical adsorption and chemical adsorption. In addition, CMAIgs aerogels exhibit better recyclability than MAIgs aerogels. This work provides a new strategy for fabricating MOFs-templated in-situ grown carbon aerogels for water purification.

Keywords: alginate; aerogel; adsorption; tetracycline

Citation: Kong, Y.; Han, K.; Zhuang, Y.; Shi, B. Facile Synthesis of MOFs-Templated Carbon Aerogels with Enhanced Tetracycline Adsorption Performance. *Water* **2022**, *14*, 504. <https://doi.org/10.3390/w14030504>

Academic Editors:

Jesus Gonzalez-Lopez and Alexandre T. Paulino

Received: 21 December 2021

Accepted: 28 January 2022

Published: 8 February 2022

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1. Introduction

As a broad-spectrum antibiotic, tetracycline is widely used in human health care and animal feed additives because of its low cost and good inhibition and killing effect on many pathogens [1,2]. Antibiotics enter wastewater treatment plants in various forms as persistent substances due to their low metabolic rate and low biodegradation [3,4]. The presence and concentration enrichment of tetracycline in the aquatic environment can cause the enhancement and spread of tetracycline-resistant bacteria and resistance genes, even posing a potential risk to the ecosystem and human health [5–7]. The advanced treatment techniques include adsorption, flocculation, advanced oxidation technology, chemical degradation, and biological treatment [8–11]. Among them, the adsorption separation method is widely used to remove antibiotic contaminants because of its low cost and easy operation [12,13]. Therefore, developing efficient and inexpensive adsorption materials is the key to practical applications. The antibiotics adsorption materials mainly include carbon materials, clay minerals, resins, metal oxides, and metal-organic frameworks [14–16]. However, there are some problems such as low adsorption capacity, difficulty recycling and reusing powder materials, and possible secondary pollution. Research and development of new efficient and inexpensive adsorbent materials is the key to practical applications.

Three-dimensional polymer aerogels have attracted extensive attention in the field of water treatment because of their excellent biodegradability, non-toxicity, easy functionalization and solid-liquid separation properties [17,18]. Sodium alginate is an anionic polysaccharide extracted from seaweed, and it has abundant oxygen-containing functional groups [19–23]. Alginic acid has good gel properties and chelates metal ions (Fe^{3+} ,

Al^{3+} , Cu^{2+} , Zn^{2+} , Co^{2+} , etc.) to form a hydrogel with an open lattice network. The three-dimensional spatial network structure of the hydrogel provides an effective binding site for the introduction of some functional nanomaterials and can also inhibit the agglomeration of nanomaterials, which is a good encapsulation carrier material [24–30].

MOFs are a class of coordination polymers consisting of two- and three-dimensional network topologies composed of metal ions and organic linkers [31,32]. They are regarded as promising candidate materials for water treatment and purification due to their large specific surface, high porosity, abundant active sites, and size controllability [33–35]. Wang et al. [36] reported that the Mn-doped UiO-66 adsorbent has a maximum adsorption capacity of $184.49 \text{ mg}\cdot\text{g}^{-1}$ for tetracycline, which is mainly controlled by π - π and hydrogen bond interactions. Tian et al. [37] reported that the tetracycline adsorption capacity of NH2-MIL-101(Cr) with mesoporous structure for tetracycline reached 36.15 and 48.80% in 10 min and 240 min, respectively. Xia et al. reported that the adsorption of antibiotics on the UiO-66 adsorbent can quickly reach the adsorption equilibrium within 40 min. The adsorption process is mainly dominated by π - π interaction and the pore structure is larger than the tetracycline molecule [38]. However, MOF adsorbents in water treatment still suffer from the critical problems like poor water stability, difficult recovery, and easy aggregation. Considering the aqueous environmental stability of MOFs particles, there is still a need to explore MOFs-templated adsorbent materials with high adsorption and stability.

This paper reports an easy-to-synthesize MOFs-functionalized aerogel (MAIgs) and MOFs-derived carbon aerogel (CMAIgs) for tetracycline adsorption removal. The adsorption properties of MAIgs and CMAIgs aerogels were investigated by varying the central metal ions within the MOFs particles. Adsorption kinetics and adsorption isotherms were studied to investigate the adsorption process. The physicochemical properties of MAIgs and CMAIgs aerogels were analyzed by the Fourier transform infrared (FT-IR), X-ray diffraction (XRD), BET, Zeta potential, etc. Possible adsorption mechanisms of MAIgs and CMAIgs aerogels were proposed. In addition, the effects of solution pH and solid-liquid ratio of MAIgs and CMAIgs aerogels on the removal of tetracycline were evaluated, and the cycling stability.

2. Materials and Methods

2.1. Materials

All chemicals, eg. sodium alginate (molecular weight: 216.2), $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$, $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$, 1,3,5-Benzenetricarboxylic acid (BTC) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Tetracycline was purchased from the Chinese Pharmacopoeia (Beijing, China).

2.2. Preparation of MAIgs and CMAIgs Aerogels

Synthetic routine of aerogels is shown in Scheme 1. Two g of sodium alginate was dissolved in 100 mL of deionized water and mechanically stirred to obtain a homogeneous solution. The uniform solution was dropped into $0.10 \text{ mol}\cdot\text{L}^{-1}$ $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ and $0.10 \text{ mol}\cdot\text{L}^{-1}$ $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ solution and cross-linked for 10 h to obtain Alg-Cu and Alg-Fe hydrogels, respectively [39,40]. Similarly, the Alg-Fe-Cu hydrogel can be obtained by replacing the crosslinking solution with a mixture of $0.05 \text{ mol}\cdot\text{L}^{-1}$ $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ and $0.05 \text{ mol}\cdot\text{L}^{-1}$ $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$. The hydrogels were washed three times with deionized water to remove uncrosslinked metal ions. Then, the hydrogels were transferred to ethanol solution of 30 mg mL^{-1} 1,3,5-benzenetricarboxylic acid for 18 h to obtain MAIlg-Fe, MAIlg-Cu and MAIlg-Fe-Cu hydrogels, respectively. All the prepared hydrogels were washed three times with ethanol and deionized water, and then freeze-dried for 24 h to obtain MAIlg-Fe, MAIlg-Cu and MAIlg-Fe-Cu aerogels [41]. The MAIlg-Fe, MAIlg-Cu and MAIlg-Fe-Cu aerogels were pyrolyzed at 500°C in N_2 atmosphere for 1 h with a heating rate of 5° min^{-1} , respectively, to obtain CMAIlg-Fe, CMAIlg-Cu, and CMAIlg-Fe-Cu aerogels.

Scheme 1. Synthetic routine of aerogels.

2.3. Batch Adsorption Experiments

Batch experiments were conducted to evaluate the performance of MAIgs and CMAIgs aerogels for the adsorption of TC. The isotherm experiments were conducted in a thermostatic shaker at 298 K and 150 rpm for 480 min with a solid to liquid ratio of $0.8 \text{ g} \cdot \text{L}^{-1}$ and under varying the initial tetracycline concentrations ($20\text{--}150 \text{ mg} \cdot \text{L}^{-1}$). The kinetics experiments were studied in $150 \text{ mg} \cdot \text{L}^{-1}$ TC solution with a solid to liquid ratio of $0.8 \text{ mg} \cdot \text{mL}^{-1}$ under varying reaction time (5, 15, 30, 60, 90, 120, 180, 240, 360, and 480 min). The effects of pH were studied in $30 \text{ mg} \cdot \text{L}^{-1}$ TC solution with a solid to liquid ratio of $0.8 \text{ mg} \cdot \text{mL}^{-1}$ in a pH range varying from 3 to 11. The effects of solid to liquid ratio were carried out varying the MAIgs and CMAIgs aerogels dosage from 0.1 to $2 \text{ mg} \cdot \text{mL}^{-1}$. The regeneration performance of the aerogel for the adsorption of TC was studied in $30 \text{ mg} \cdot \text{L}^{-1}$ TC solution with a solid to liquid ratio of $0.8 \text{ mg} \cdot \text{mL}^{-1}$ and using DMF and methanol solution as the resolving solution. The MAIgs and CMAIgs aerogels were separated from the solution after adsorption and the concentrations of TC were measured at 360 nm using a UV-vis spectrophotometer (UV-6100, Mapada, Shanghai, China). All the experiments were performed in triplicate and the result selected the numerical average of three results.

Langmuir and Freundlich isotherms were used to evaluate the adsorption equilibrium. The Langmuir and Freundlich isotherm equation is as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (1)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (2)$$

where C_e ($\text{mg} \cdot \text{L}^{-1}$) is the equilibrium TC concentration in the solution, q_m ($\text{mg} \cdot \text{g}^{-1}$) is the monolayer adsorption capacity and K_L ($\text{L} \cdot \text{mg}^{-1}$) is the Langmuir constant. K_F and n are Freundlich constants.

Pseudo-first-order and pseudo-second-order to evaluate the adsorption process, which is based on solid phase adsorption. These two models can be expressed by Equations (3) and (4), respectively.

$$\lg(q_e - q_t) = \lg q_e - k_1 t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

where q_t ($\text{mg} \cdot \text{g}^{-1}$) and q_e ($\text{mg} \cdot \text{g}^{-1}$) are the amounts of TC adsorbed at any time and equilibrium, respectively. k_1 (min^{-1}) and k_2 (min^{-1}) are the rate constants of pseudo first-order and pseudo second-order, respectively.

3. Results

3.1. Syntheses and Material Characterization of the Adsorbent

3.1.1. Morphological Characterization

Sodium alginate is a natural linear polysaccharide obtained from brown algae, which has unique gel properties. The Fe^{3+} , Cu^{2+} metal ions can independently ion-exchange Na^+ in sodium alginate and chelate with alginate chain to produce Alg-Fe and Alg-Cu hydrogel with a “egg-box” structure. Alginate chains can also simultaneously chelate Fe^{3+} and Cu^{2+} alginate chains to produce Alg-Fe-Cu hydrogel. Subsequently, the hydrogel spheres as mentioned above are dispersed in an ethanol solution of organic ligand trimellitic acid to obtain MAlgs (MAlg-Fe, MAlg-Cu, and MAlg-Fe-Cu) hydrogel spheres with uniformly dispersed internal MOFs crystal particles. This is mainly because the metal ions are anchored in the three-dimensional network through the coordination of COO^- related to guluronic acid on the alginate chain, which facilitates the further coordination of the anchored metal ions with the organic ligands to form crystal in situ. CMAlgs (CMAlg-Fe, CMAlg-Cu, and CMAlg-Fe-Cu) aerogel with multilayer pore structure was obtained by thermal decomposition based on MAlgs aerogel of in-situ grown MOFs materials as templates.

The microstructure images of MAlgs aerogel and CMAlgs aerogel were obtained by SEM. As shown in Figure 1, MAlg aerogel presents an interconnected three-dimensional network structure and the MOFs particles contained therein exhibit good dispersibility, which further proves that the three-dimensional network structure can effectively limit the growth and aggregation of MOF particles. Different central metal ions in MAlgs gel lead to different morphologies and structures of MAlg-Fe and MAlg-Cu, MAlg-Fe-Cu aerogels. The MAlg-Fe aerogel shows a honeycomb-like 3D network structure with MOFs particles grown in its grid. The MAlg-Cu aerogel is covered with MOFs particles on its flat gel matrix. The MAlg-Fe-Cu aerogel has an uneven surface due to the growth of MOFs particles. The three-dimensional network structure is still maintained after pyrolysis. The polycondensation of the metal-organic framework leads to the formation of micropores between metal particles and the alginate framework. However, it was obviously observed that the porosity of CMAlg-Cu aerogel was lower than that of CMAlg-Fe and CMAlg-Fe-Cu aerogels. The decomposition and collapse of the alginate gel framework and the etching of the metal particles are favorable for the formation of mesoporous structures. The multilayer pore structure is beneficial to the adsorption of pollutants.

Figure 1. SEM microphotographs of (a) MAlg-Fe, (b) MAlg-Cu, (c) MAlg-Fe-Cu, (d) CMAlg-Fe, (e) CMAlg-Cu, and (f) CMAlg-Fe-Cu aerogels.

3.1.2. FTIR and XRD Analysis

The crystal phase and structure of the sample were analyzed by XRD pattern, as shown in Figure 2a. The XRD peaks of the synthesized MAlg-Fe aerogel have diffraction peaks of certain intensity at $2\theta = 10.3^\circ$ and 20.1° , which are similar to the characteristic peaks in the XRD spectrum of MIL-100 (Fe) reported in the literature [42,43]. The broadening of the main diffraction peaks is mainly due to the three-dimensional pores of the gel network restricting crystal growth, resulting in high dispersion and small particle size of MIL-100 (Fe) crystals. The diffraction peaks of MAlg-Cu aerogel are in good agreement with the standard spectrum of HKUST-1, which confirms that HKUST-1 crystals are successfully deposited in situ in MAlg-Cu aerogel [44–46]. For the MAlg-Fe-Cu aerogel, the diffraction peaks are broadened, and the degree of crystallinity is poor. CMAlg-Fe aerogel has a diffraction peak of nano-zero-valent iron at 43.1° , which confirms that metal particles can be reduced to Fe^0 after carbonization with alginate and MOF as template materials. In addition, Fe_3O_4 characteristic diffraction peaks appear at $2\theta = 30.1^\circ, 35.4^\circ, 57.6^\circ$ and 62.5° , which is speculated to be caused by the presence of organic ligands and oxygen-containing groups in alginate. The XRD diffraction peaks at $2\theta = 43.3^\circ, 50.6^\circ$ and 74.2° of CMAlg-Cu are distributed to the (111), (200) and (220) planes of Cu^0 , indicating that the copper ions in the MAlg-Cu aerogel structure are reduced to copper particles during the carbonization process. For CMAlg-Fe-Cu aerogel, the XRD diffraction peaks at $2\theta = 18.3^\circ, 30.1^\circ, 35.4^\circ, 43.0^\circ, 56.9^\circ$, and 62.5° are distributed to the (111), (220), (311), (400), (511), and (440) planes of cuprospinel ($\text{Cu}_{0.86}\text{Fe}_{2.14}\text{O}_4$).

Figure 2. (a) XRD spectra of MAlgs and CMAlgs aerogels, (b) FTIR spectra of MAlgs and CMAlgs aerogels.

The FTIR spectra of the MAlgs aerogel before and after carbonization are shown in Figure 2b. The peaks at $1629, 1451$, and 1364 cm^{-1} in MAlgs aerogel are attributed to the stretching vibration peak of $\text{C}=\text{O}$, the flexural vibration peak of the hydroxyl group, and the stretching vibration peak $\text{C}-\text{O}$, respectively. For MAlgs aerogels, the peak at 711 cm^{-1} is the fingerprint peak of MIL-100 (Fe), which is attributed to the Fe_3O structure, and 742 cm^{-1} is attributed to the stretching vibration peak of the $\text{Cu}-\text{O}$ bond coordinated by Cu and BTC. For the increased aromatic structure of CMAlgs aerogel after carbonization, the peak at 2951 cm^{-1} is attributed to the stretching vibration of $\text{C}-\text{H}$, and at 930 cm^{-1} is attributed to the $\text{C}-\text{O}-\text{C}$ stretching vibration. It is found that carbonization still retains a large number of oxygen-containing functional groups ($-\text{CO}$, $-\text{COO}$, $\text{C}=\text{O}$), which can improve the hydrophilicity between the adsorbent surface and the adsorption interface, making the adsorption process smoother.

3.1.3. The BET Surface Areas and Pore Volumes Analysis

The pore structure of MAlg aerogel before and after carbonization was analyzed by nitrogen adsorption-desorption test, as shown in the Figure 3a. Obvious hysteresis loops can be observed on the adsorption-desorption curves of MAlgs aerogel and CMAlgs aerogel, which belong to type IV curve, proving that the aerogel contains abundant mesoporous

pores. The specific surface areas of MAlg-Fe, MAlg-Cu, MAlg-Fe-Cu, CAlg-Fe-Cu are 375.37, 258.33, 685.56, and 329.51 $\text{m}^2 \text{g}^{-1}$, respectively. It is found that the specific surface area decreased after carbonization, which may be caused by the decomposition of three-dimensional network skeleton and the condensation of metal-organic ligands.

Figure 3. (a) N_2 adsorption–desorption isotherms (b) pore size distributions of aerogels.

As shown in Figure 3b, the sample single metal MAIlg shows mesoporous size distribution, and the center is in the range of 4–11 nm with an obvious peak. The pore structure of bimetal MAIlg-Fe-Cu is concentrated in the range of 10–100 nm. The pore structure of CMAIlg-Fe-Cu after carbonization becomes larger, which is consistent with the results of SEM. The prepared aerogel's mesoporous and three-dimensional macroporous structure is conducive to exposing more adsorption sites and the unobstructed pore structure is conducive to reducing the mass transfer resistance of pollutants.

3.1.4. The Raman and Pore VSM Analysis

The Raman test was performed on the aerogel CMAIlg aerogel obtained by pyrolysis, as shown in Figure 4a. Two resonance peaks were observed at 1350 cm^{-1} (peak D) and 1580 cm^{-1} (peak G), which were attributed to graphitized sp^2 carbon and disordered sp^3 carbon, respectively. The degree of defects of carbon materials is measured according to the intensity ratio of peak D to peak G (I_D/I_G). The results show that the I_D/I_G of CMAIlg-Fe, CMAIlg-Cu, and CMAIlg-Fe-Cu aerogels are 0.84, 0.82, and 0.83, respectively. This indicates that iron is more likely to make carbon materials highly disordered and can produce more defects, which is conducive to the exposure of adsorption sites, thereby improving the adsorption performance of aerogels.

Figure 4. (a) Raman spectra of CMAIlg aerogels, (b) VSM of CMAIlg aerogels.

CMAIlg aerogel has certain magnetic properties due to the inclusion of Fe^0 and Cu^0 . The saturation magnetic field intensity was tested. As shown in Figure 1, the saturation

magnetization of CMALG-Fe and CMALG-Fe-Cu aerogels were 0.02 and 0.04 emu g⁻¹ respectively, showing weak magnetic properties on the CMALgs aerogel surface.

3.2. Batch Adsorption Studies

3.2.1. Adsorption Isotherm Models

The adsorption processes of MAlgs and CMALgs aerogels were fitted with Langmuir and Freundlich models, respectively. Both the Langmuir and Freundlich models can fit the experimental data well, and the Freundlich model has a better fit ($R^2 > 0.99$).

The results showed that the uneven surface of aerogel could form adsorption active sites with different energy. The adsorption process of MAlgs and CMALgs aerogels consists mainly of multilayer physical interaction and monolayer chemical complexation. Figure 5 and Table 1 show that the maximum adsorption capacity of MAlg-Fe, MAlg-Cu, and MAlg-Fe-Cu aerogels are 128.37, 108.23 and 130.72 mg·g⁻¹, respectively, among which MAlg-Cu-Fe has the highest adsorption capacity. After carbonization of the prepared aerogels, the maximum adsorption amounts of CMALg-Fe, CMALg-Cu, and CMALg-Fe-Cu aerogels are 106.16, 56.66 and 131.06 mg·g⁻¹, respectively. The adsorption capacity of CMALg-Fe and CMALg-Cu decreased significantly, especially for CMALg-Cu aerogel. The hydroxyl and carboxyl functional groups of alginate in MAlgs aerogels can interact with water through hydrogen bonding and have hydrophilic properties, which facilitate the transport of tetracycline solution and adequate contact with gel adsorption sites in the pore channels of 3D network macropores and mesopores. In addition, the MOF-functionalized MAlgs have a large specific surface area as well as the protonated amino, carboxyl, and hydroxyl groups in the molecular structure of tetracycline can form hydrogen bonds with organic oxygen-containing functional groups on the MAlgs aerogels. CMALgs aerogel surface has strong aromaticity and few oxygen-containing functional groups. The large specific surface area is still maintained, especially for CMALg-Fe-Cu. The aromatic structure of CMALgs can form π - π stacking interactions with the benzene structure of tetracycline. It can also experience a cation- π mechanism with the protonated amino group of tetracycline, which is the main reason for the adsorption of CMALgs gel. The pores of CMALg-Cu show inhomogeneity due to carbonization as well as the formation of metal particles leading to the blockage of pore channels and occupying the corresponding active sites. The poor hydrophilicity is not conducive to the mass transfer of tetracycline solution. This means that some internal pores may be ineffective for the adsorption of large tetracyclines. Iron oxides and graphitized carbon mainly dominate CMALg-Fe-Cu and CMALg-Fe aerogel aerogels. The literature reports that iron oxides have a potent complexation tetracycline. Hence, their surface adsorption processes include chemical coordination and multilayer physical adsorption processes.

Figure 5. Adsorption isotherm models of (a) Langmuir, (b) Freundlich.

Table 1. Isotherm parameters of Langmuir, and Freundlich adsorption isotherm.

Isotherm	Langmuir				Freundlich		
	Characteristic	q_m (mg/g)	K_L (L/mg)	R^2	R_L	K_F (L/g)	n
MAlg-Fe		128.37	0.13	0.93	0.005	23.45	2.34
MAlg-Cu		108.23	0.14	0.94	0.0046	24.2	2.84
MAlg-Fe-Cu		130.72	0.2	0.95	0.0033	28.98	2.45
CMAlg-Fe		106.16	0.09	0.95	0.0077	7.37	2.48
CMAlg-Cu		56.66	0.04	0.96	0.0155	16.14	2.31
CMAlg-Fe-Cu		131.06	0.39	0.94	0.0017	42.85	3.29

3.2.2. Adsorption Kinetics

A kinetic model was used to fit the data to understand the reaction pathway and the adsorption rate of the aerogels. The adsorption of tetracycline by MAlgs and CMAlgs aerogels increased sharply during the first 30 min of the adsorption process, and then the adsorption process slowed down until it leveled off (Figure 6). At the beginning of the reaction, tetracycline molecules rapidly occupied the abundant active sites on the aerogel surface, and the adsorption amount decreased with time due to the saturation of the active sites as the reaction proceeded. The fitted parameters of the kinetics of tetracycline adsorption by MAlgs and CMAlgs aerogels are shown in Table 2. Both the fitted primary kinetic model and the fitted secondary kinetic model can fit the experimental data well, in which the fitted secondary kinetic model fits better ($R^2 > 0.99$). Meanwhile, the amount of tetracycline adsorption by aerogels obtained from the fitted secondary kinetic equation is closer to the actual adsorption amount. Among the adsorption processes that control the adsorption rate are chemisorption processes accompanied by physical adsorption. Studies have shown that the faster adsorption rate of CMAlg-Fe-Cu aerogel is due to its ability to provide more mesopore volumes and more adsorption sites.

Figure 6. (a) Kinetic curves, (b) pseudo-first-order model, (c) pseudo-second-order model of TC adsorption on aerogels.

3.2.3. Effect of Solid-Liquid Ratio

The effect of solid-liquid ratio on the removal of tetracycline by MAlgs and CMAlgs aerogels is shown in Figure 7. The solid-liquid ratio was set to increase from $0.1 \text{ g} \cdot \text{L}^{-1}$ to $2 \text{ g} \cdot \text{L}^{-1}$. The removal efficiency of MAlg-Fe-Cu and CMAlg-Fe-Cu aerogels had reached $\sim 90\%$ when the addition amount was $0.5 \text{ g} \cdot \text{L}^{-1}$, and then gradually increased and leveled off. However, the adsorption capacity of the MAlg-Fe-Cu and CMAlg-Fe-Cu aerogels showed a decreasing trend. It is attributed to the fact that tetracycline molecules quickly occupied the adsorption site at the MAlg-Fe-Cu and CMAlg-Fe-Cu aerogels surface. Then the adsorption site was gradually saturated, and the system tended to be in equilibrium. The higher removal efficiency is caused by the increase of total surface functional groups and effective contact area. Excessive addition of aerogel leads to the decrease of adsorption capacity because the overlap of active sites reduces the effective contact area of tetracycline.

and causes waste of adsorbent. $0.8 \text{ g} \cdot \text{L}^{-1}$ was selected as the most suitable solid-liquid ratio in consideration of removal efficiency and economy.

Table 2. Kinetic parameters of the pseudo-first-order and pseudo-second-order adsorption kinetic models.

Adsorbent	Pseudo-First-Order			Pseudo-Second-Order		
	q_e (mg g^{-1})	k_1	R^2	q_e (mg/g)	$k_2 \times 10^{-3}$	R^2
MAlg-Fe	89.50	0.03	0.989	121.80	0.24	0.998
MAlg-Cu	103.81	0.03	0.984	110.99	0.18	0.997
MAlg-Fe-Cu	55.78	0.02	0.929	124.69	0.41	0.999
CMAAlg-Fe	111.36	0.03	0.959	106.16	0.13	0.990
CMAAlg-Cu	40.19	0.02	0.982	50.58	0.26	0.990
CMAAlg-Fe-Cu	66.48	0.03	0.973	130.55	0.46	0.999

Figure 7. Effect of solid liquid ratio on the removal of tetracycline by MAlgs and CMAAlgs aerogels.

3.2.4. Effect of pH

It was found that the amount of tetracycline adsorbed by MAlg-Fe-Cu and CMAAlg-Fe-Cu aerogels was significantly pH-dependent. Both MAlg-Fe-Cu and CMAAlg-Fe-Cu aerogel adsorption were effective in the range of solution initial pH from 3 to 11, indicating that the aerogel could remove tetracycline by adsorption over a wide range of pH. When the initial solution pH = 3, the removal rate of tetracycline by MAlg-Fe-Cu and CMAAlg-Fe-Cu reaches 85.8% and 89.3%, and the removal effect decreases slightly when the pH is 11. The existing form of antibiotics in solution will change with the change of pH. There are three equilibrium constants of tetracycline in aqueous solution: $\text{pK}_{a1} = 3.30$, $\text{pK}_{a2} = 7.68$, $\text{pK}_{a3} = 9.68$. Therefore, it can be dissociated into four different forms at different pH: cationic form (TC^+), amphoteric form (TC^0), anionic form (TC^-), and the double anion form (TC^{2-}). The zeta potentials of MAlg-Fe-Cu and CMAAlg-Fe-Cu were further tested under different pH conditions (Figure 8b). TC completely loses electrons and assumes a cationic form (TC^+) at lower pH, at this time, the MAlg-Fe-Cu and CMAAlg-Fe-Cu aerogels showed electronegativity, which was favorable for electrostatic adsorption. The adsorption

effect of MAlg-Fe-Cu and CMAlg-Fe-Cu aerogels on tetracycline gradually increases with the increase of pH, which was attributed to the enhanced electronegativity of MAlg-Fe-Cu and CMAlg-Fe-Cu aerogels. When pH value increases to neutral, TC molecules gradually exist in amphoteric TC^0 and the adsorption process lacks electrostatic adsorption. As the pH continues to increase, the presence of negatively charged forms such as TC^- molecule TC^{2-} , however, the negative charge of MAlg-Fe-Cu and CMAlg-Fe-Cu aerogels reached a maximum electrostatic repulsion, leading to the lowest adsorption. At this time, the adsorption process of aerogels mainly relies on pore filling and π - π interaction between aromatic structures.

Figure 8. (a) The influence of the pH, (b) Zeta potential of MAlg-Fe-Cu and CMAlg-Fe-Cu aerogels.

3.2.5. Regenerability

Reusability is one of the essential criteria to evaluate the performance of adsorbent materials. The regeneration performance of the aerogel for the adsorption of tetracycline was studied using DMF and methanol solution as the resolving solution. The experimental results are shown in Figure 9. The equilibrium adsorption amounts of tetracycline adsorbed by MAlg-Fe-Cu and CMAlg-Fe-Cu aerogels are lost about 22% and 8% after six regeneration cycles by resolution, respectively. The main reason is that the adsorption capacity of the MAlg-Fe-Cu aerogel is reduced because the binding sites of the MOF backbone in the MAlg-Fe-Cu aerogel are destroyed during the desorption and recycling process. However, CMAlg-Fe-Cu aerogel has excellent stability and good regeneration performance, which is a selective adsorption material with good application prospects.

Figure 9. Adsorption cycles of TC by MAlg-Fe-Cu and CMAlg-Fe-Cu aerogels.

4. Conclusions

In summary, a series of functionalized MAlgs and CMAIgs aerogels were synthesized by simple in-situ growth and pyrolysis to solve environmental problems. The three-dimensional network of MAlgs aerogel can grow MOFs particles well and effectively prevent aggregation, presenting a mesoporous structure. CMAIgs aerogels have ineffective tetracycline adsorption due to the smaller shrinkage pore size after carbonization. In addition, CMAIgs aerogels exhibit weak magnetic properties. The maximum adsorption capacity of MAlgs and CMAIgs aerogels for tetracycline is $\sim 130 \text{ mg} \cdot \text{g}^{-1}$, respectively. The results of adsorption kinetics and adsorption isotherms indicate that adsorption process can be combined with physical adsorption and chemical adsorption and that the surface of the adsorbent is uneven. The adsorption mechanism shows that the adsorption process is dominated by π - π interaction and pore filling effect. The electrostatic adsorption enhances the adsorption process of aerogel because aerogel is negatively charged under acidic pH. In addition, CMAIgs aerogel exhibits better recyclability than MAlgs aerogel. This study is expected to provide a feasible strategy for removing tetracycline antibiotics and broaden the application range of carbon aerogels as adsorbents.

Author Contributions: Conceptualization, methodology, validation, formal analysis, investigation, data curation, writing—original draft preparation, Y.K. and Y.Z.; writing—review and editing, visualization, K.H.; supervision, project administration, funding acquisition, B.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China, grant number 51808538.

Institutional Review Board Statement: No applicable.

Informed Consent Statement: No applicable.

Data Availability Statement: No applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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