

Alkoxy-Group-Functionalized UiO-66 as Highly Efficient Adsorbents for Hydrogen Chloride Removal from Aqueous Solution

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S Supporting Information

ABSTRACT: A series of alkoxy group-functionalized UiO-66 were designed for hydrogen chloride adsorption from aqueous solution, which were characterized by various methods to verify the structures and study the adsorption mechanism. A volcano-shaped change of adsorption capacity was discovered. UiO-66-C₂ exhibited the highest adsorption capacity and excellent structure stability. The adsorption kinetics, isotherms, and thermodynamics were studied. It was found that the pseudo-second-order kinetic model fit the experimental



data well in kinetic studies. Meanwhile, both Henry and Freundlich models fitted the isotherm experiment data well. The thermodynamics parameters further confirmed that hydrogen chloride adsorption on UiO-66-C2 was a spontaneous and exothermic physisorption process. Regeneration experiment demonstrated that UiO-66-C2 has high regeneration efficiency and no significant change in adsorption capacity was confirmed after recycles. All the results substantiated that UiO-66- C_2 could be an efficient solution to treatment of acidic wastewater.

1. INTRODUCTION

Annually, a huge amount of acidic wastewater is produced in pharmaceutical, chemical, and iron and steel industries.¹⁻³ Acidic wastewater could cause serious corrosion of steel pipes and misbalance of acid and base in soil, and also represent a significant hazard to the health and safety of people and environment. Therefore, acidic wastewater needs to be treated, disposed, or recycled effectively to satisfy environment requirements.

Among these acidic wastewaters, wastewater containing hydrochloric acid is one of the major and urgent concerns. Vast amounts of hydrochloric acid wastewater are produced from the stainless steel pickling process and electroplating industry every year.⁴⁻⁶ Chloride ion is the main acidified ion present in coal plant emissions. HCl is a greater driver of pollution and environmental damage than previously thought, influencing water and terrestrial ecosystems alike. Due to the high mobility of Cl, HCl can effectively acidify both the soil and surface water. The increase in acidity in the soil prevents some organisms from growing, which could have a knock-on effect on the entire ecosystem. Moreover, the effects of HCl deposition may extend beyond acidification to include a broader range of ecosystem processes by affecting the carbon cycle.⁷ Therefore, there is great demand to develop highly efficient separation techniques to remove hydrogen chloride from wastewater. However, this kind of wastewater often contains only 5-10 wt % free hydrogen chloride, which is extremely difficult to remove.8 Several techniques including neutralization,⁹ roasting,¹⁰ extraction,¹¹⁻¹³ evaporation,

distillation,¹⁵ and membrane separation¹⁶ have been reported to remove hydrogen chloride. Although these methods show good separation selectivity, some disadvantages, including secondary pollution, high cost, and energy consumption, make them commercially unfeasible. For example, neutralization is commonly used in industrial applications, while it could produce a large volume of sludge that requires further disposal.¹⁷ Adsorption is considered as a potential way to deal with dilute hydrochloric acid (≤ 5 wt %), and adsorption technique possesses higher efficiency and flexibility in design and operation compared with the above-mentioned methods.^{18,19} After adsorption, ideally, the adsorbent can be regenerated, so it renders significant cost savings and no secondary pollution. Although widely used adsorbents, such as activated carbon²⁰ and zeolite,^{21,22} have been tested to adsorb hydrogen chloride, disadvantages of poor adsorption performance and low recyclability rate greatly hinder their further industrial applications.

Metal-organic frameworks (MOFs) are porous coordination polymers composed of organic linkers and metal ions or clusters to form three-dimensional structures.^{23,24} Since they can be potentially used for gas storage and separation,² sensing,²⁶ catalysis²⁷ and energy storage,²⁸ MOFs have stimulated significant interest. Particularly, MOFs can be used to adsorb contaminants from wastewater.²⁹⁻³¹ However,

Received: September 6, 2018 Accepted: December 6, 2018 Published: December 13, 2018

Scheme 1. Synthetic Method of Organic Linkers



because of the water-unstable coordination bond, most of metal-organic frameworks have limited applications in industry. Fortunately, an increasing number of water-stable and even acid-stable MOFs have been reported as promising agents for removing pollutants, such as ZIFs,^{32,33} UiOs,³⁴ and MILs.³⁵

In our previous study, the adsorption capacity of hydrogen chloride on several kinds of well-studied MOFs with waterstability, such as MIL-53(Cr), MIL-100(Cr, Fe), and UiO-66, were carefully assessed. As a highly porous MOF with great chemical and thermodynamic stability, UiO-66 exhibited excellent adsorption capacity toward hydrogen chloride (up to 289.81 mg·g⁻¹).¹⁸ On that basis, inspired by alkyl ether extractant of acid, a sequence of UiO-66 MOFs with various alkoxy functionalized groups (C1-C4) have been designed and synthesized, abbreviated as UiO-66-C₁, UiO-66-C₂, UiO- $66-C_3$, and UiO- $66-C_4$, respectively. All of them showed their potential for the adsorption capacity of hydrogen chloride from dilute aqueous solution. Particularly, UiO-66-C₂ possessed the up-to-date highest adsorption capacity. The adsorption kinetics, isotherms, thermodynamics, adsorptive mechanism, and regeneration of this material toward hydrogen chloride were further studied. The results substantiated the potential of UiO-66-C₂ as an effectual hydrogen chloride adsorbent from aqueous solution.

2. EXPERIMENTS

2.1. Chemicals. Hydrochloric acid (36 wt %, Yuanli, Tianjin, China), 2-hydroxyterephthalic acid (TCI, Shanghai, China), 2-bromoethane (Yuanli, Tianjin, China), 2-bromopropane (TCI, Shanghai, China), 2,5-dimethylanisole (Adamas, Shanghai, China), potassium permanganate (Tianjin University Kewei, Tianjin, China), methanol (Kermel, Tianjin, China), sulfuric acid (Jiangtian, Tianjin, China), potassium carbonate (Yuanli, Tianjin, China), *N,N*-dimethylformamide (DMF, Concord, Tianjin), ZrCl₄ (Strem Chemicals, USA), ethanol (Jiangtian, Tianjin, China), dichloromethane (Yuanli, Tianjin, China), sodium hydroxide standard solutions (0.01 mol·L⁻¹, Yuanli, Tianjin, China), and deionized water (Yuanli, Tianjin, China). All reagents and solvents were obtained from commercial sources and were used as received.

2.2. Synthesis of the Organic Linkers. The organic linkers were prepared according to the reported methods.^{36,37} For the synthesis of H₂BDC-C₁ (H₂BDC = terephthalic acid), H₂BDC-C₁ was obtained through potassium permanganate oxidation of 2,5-dimethylanisole. As for the synthesis of H₂BDC-C₂, H₂BDC-C₃, and H₂BDC-C₄, these linkers were obtained via nucleophilic substitution of 2-hydroxyterephthalic acid and bromoalkane (Scheme 1). Detailed synthetic methods are depicted in the Supporting Information. Structures of the organic linkers were confirmed by ¹H NMR. ¹H NMR spectra (Figure S1) of the compounds in dimethyl sulfoxide-*d*₆ (DMSO-*d*₆) were measured with a BRUKER spectrometer.

2.3. Synthesis of the UiO-66-C_x. According to the synthetic method of UiO-66 reported in the literature, UiO-66- C_x were synthesized by substituting the H₂BDC linker with alkoxy functionalized linkers.³⁸ In the Supporting Information, the detailed synthetic procedure is depicted.

2.4. Characterization of the UiO-66-C_x. X-ray diffraction (XRD) analysis (D8-Advance, Bruker AXS, Germany, Cu K α radiation, 15 mA and 40 kV) over $2\theta = 5-50^{\circ}$ was employed to ascertain the crystal structures of the UiO-66-C_v. The morphologies of microcrystalline were characterized by field emission scanning electron microscopy (FE-SEM, Hitachi SU-4080, Japan, S-4800, 3 kV). Transmission electron microscopy (TEM, JEOL, Japan, JEM-2100F) operated at an accelerating voltage 100 kV was utilized to observe the morphology of the nanoparticles. The thermal behaviors of the structures were confirmed by thermogravimetric analysis (TGA, Q5000IR, TA Instruments, USA), which was performed from room temperature to 800 °C with an increasing rate of 5 °C \cdot min⁻¹ at an air flow rate of 60 mL·min⁻¹. A porosity and surface area analyzer (Quantatech Co., USA, Autosorb-iQA 3200-) was used to examine the N₂ adsorption isotherms of the materials at 77 K after evacuating the samples at 100 °C. Fourier transform infrared spectroscopy (FT-IR, Nicolet 6700, Thermo Fisher, USA) was utilized to investigate the functional groups of the UiO-66-C_X. X-ray photoelectron spectroscopy (XPS, PHI-5000C ESCA, Japan) was measured to study the mechanism of hydrogen chloride adsorption.

2.5. Adsorption Experiment. The adsorbents were stored in a desiccators and dried overnight at 100 °C in vacuum



Figure 1. (a) Simulated XRD pattern of UiO-66 and patterns of synthesized UiO-66- C_{X} . (b) FT-IR spectrum of UiO-66- C_{X} . (c) TGA curves of the synthesized UiO-66- C_{X} . (d) Left: N₂ adsorption–desorption isotherms; right: pore diameter distributions.

before adsorption experiments. During the adsorption experiments, 100 mg (\pm 0.1 mg) of MOFs was added into 20 mL 0.5 mol·L⁻¹ HCl solutions in a dosage of 5 g·L⁻¹, and continuously stirred for 24 h at 25 °C. Syringe filters (aqua system, 0.22 μ m) were utilized to filter solid MOFs from hydrochloride solution. The concentration of hydrochloride solution can be obtained through titrating with sodium hydroxide standard solution (0.01 mol·L⁻¹) and the indicator was phenolphthalein. Each data was obtained by titration at least three times and the average number, as a final result, was applied to further analysis. The adsorption capacities of hydrogen chloride on adsorbents Q_t (mg·g⁻¹), was determined by eq 1:

$$Q_t = (C_0 - C_t) VM \times 1000/m$$
(1)

where V(L) is the volume of hydrochloric acid solution; C_0 is the initial concentration of HCl; C_t is the concentration of HCl on sampling time $t \pmod{L^{-1}}$; m (g) is the weight of spent adsorbents; and $M(g \cdot mol^{-1})$ is the relative molecular mass of hydrogen chloride.

2.6. Adsorption Kinetics. The impact of adsorption time on the adsorption of hydrogen chloride on UiO-66-C₂ was carefully studied in the investigation of adsorption kinetics. An amount of 100 mg (± 0.1 mg) of UiO-66-C₂ was put in 20 mL hydrochloride solutions at a dose ratio of 5 g·L⁻¹ with initial HCl concentration range of 0.6–1.4 mol·L⁻¹ at 25 °C. Approximately 0.3 mL of samples was extracted at different times to calculate the amount of unadsorbed HCl for kinetic analysis.

2.7. Adsorption Isotherms and Adsorption Thermodynamics. Batch adsorption isotherms experiments were carried out at 25, 35, 45, and 55 °C with the initial HCl concentration ranging from 0.4 to 1.8 mol·L⁻¹. With a dosage of 5 g·L⁻¹, the vacuum-dried UiO-66-C₂ was added to those hydrochloride solutions.

2.8. Regeneration of UiO-66-C₂. The spent UiO-66-C₂ was recycled through a washing process by using deionized water and anhydrous ethanol three times and then dried in vacuum at 150 °C overnight. Under the same conditions as former experiment (dosage: 5 g·L⁻¹; C_0 : 0.5 mol·L⁻¹; *T*: 25 °C), an adsorption experiment of recycled UiO-66-C₂ was conducted.

3. RESULTS AND DISCUSSION

3.1. Characterization of UiO-66-C_x. The XRD patterns (Figure 1a) of the synthesized UiO-66-C_x showed two main peaks at 7.4 and 8.5° , which was consistent with the simulated UiO-66, indicating that the structures of synthesized UiO-66-C_x were basically the same as that of UiO-66.³⁷ However, there was also some amorphous phase present, and its influence on adsorption performance was ignored in this study.

FT-IR patterns (Figure 1b) displayed bands ranging from 3000 to 2840 cm⁻¹ and 1275 to 1200 cm⁻¹, which could be credited to C-Hst (st: stretching vibration) and arC-O-alC (ar: aromatic; al: alkane), clearly proving the presence of alkoxy groups in the structures. TGA was performed to examine the three-dimensional framework stability and structural integrity of the synthesized UiO-66-C_X. As is shown in the TGA curve (Figure 1c), the removal of H₂O molecules resulted in slight weight loss of all UiO-66-C_X powders from 30 to 150 °C. Then, the removal of DMF molecules leads to a weight loss from 150 to 350 °C. Decomposition occurred when the temperature was higher than 350 °C, and the organic linker

molecules lost gradually. The decomposition temperature was quite lower than the typical value of 500 $^{\circ}$ C of pristine UiO-66 mentioned in literature.^{39,40}

The N_2 adsorption isotherms of pristine UiO-66 (Figure S2) and the prepared UiO-66- C_{y} (Figure 1d) at 77 K were in accord with type I isotherm. BET surface area, pore diameter, and total pore volume of pristine UiO-66 and UiO-66-C_x are listed in Table S1. BET surface areas of UiO-66-C1 and UiO-66-C₂ were 922 and 930 $m^2 \cdot g^{-1}$, respectively, which were consistent with the data of UiO-66 in literature.^{41,42} However, the addition of propoxy and butoxy group on the ligand, which were linked to UiO-66-C3 and UiO-66-C4, had an obvious negative influence on the BET surface areas, which were 791 and 549 $m^2 \cdot g^{-1}$, respectively. Since the propoxy or butoxy group on the ligand had larger volume, porous channel was blocked by these bulky substituents. Consequently, surface area was significantly reduced. It may explain the decreased adsorptive capacity of UiO-66-C3 and UiO-66-C4. The pore volume, estimated at $P/P_0 = 0.99$ was $0.51 \text{ cm}^3 \cdot \text{g}^{-1}$ for UiO-66-C₁, 0.55 cm³ \cdot \text{g}^{-1} for UiO-66-C₂, 0.53 cm³ \cdot \text{g}^{-1} for UiO-66-C₃, and 0.61 cm³ \cdot \text{g}^{-1} for UiO-66-C₄. Two pore diameters of 16.1 and 19.1 Å were found in pore size distribution calculated by DFT method, which were accordance with the pore diameters of tetrahedron and octahedron in UiO-66 respectively.⁴

SEM (Figure 2) showed that the sizes of UiO-66- C_X nanocrystals were approximately located in the range of



Figure 2. SEM images of the synthesized UiO-66- C_x .

100–150 nm. TEM images of UiO-66-C₂ are shown in Figure S3a, the results observed by TEM were in accordance with SEM, and no obvious impurities could be observed in the surface of UiO-66-C₂.^{44,45}

3.2. Adsorption Capacity. The adsorption capacities of the MOFs are shown in Figure 3. Apparently, except for UiO- $66-C_4$, alkoxy group-functionalized UiO-66 displayed a higher adsorption capacity of hydrogen chloride than that of original UiO-66. The weaker adsorption capacity of HCl on UiO- $66-C_4$ can be attributed to its smaller surface area and larger pore diameter than the pristine UiO-66. The reduced adsorption site concentration on the surface can be observed with an increase of pore size and BET surface area reduction.^{46,47} Consequently, the adsorption capacity of UiO- $66-C_4$ decreased. The BET surface area decrease of alkoxy group-



Figure 3. Adsorption capacities of hydrogen chloride on alkoxy group-functionalized UiO-66 (C_0 : 0.5 mol·L⁻¹; T: 25 °C, dosage: 5 g·L⁻¹).

functionalized UiO-66 is possiblely related to the introduction of alkoxy group. By introducing the alkoxy group, the structure of alkoxy group-functionalized UiO-66 was modified in terms of BET surface area and pore size. The hydrogen chloride adsorption capacity represented a volcano-shaped variation with increasing carbon number of alkoxy groups. UiO-66-C₂ presented the greatest adsorption capacity of 398.0 mg \cdot g⁻¹. To the best of found knowledge, its capacity was 1.4 times that of pristine UiO-66. Additionally, compared to other adsorbents reported in the literature (Table S2), UiO-66- C_2 not only exhibited excellent adsorption capacity, but it can be recycled after adsorption, which is an important property for adsorbents. The surface area, pore diameter, total pore volume, and HCl adsorption capacity of the synthesized UiO-66- C_X are listed in Table S1. The substituted groups played an important role in the HCl adsorption. Therefore, UiO-66-C₂ showed the highest adsorption capacity because it had more adsorbed sites provided by ethoxy groups and still kept a high surface area.

3.3. Adsorption Kinetics. Adsorption kinetics were measured to study the impact of adsorption time of hydrogen chloride on UiO-66-C₂ (Figure 4a). The adsorption capacity of hydrogen chloride grew quickly in the first and second hours, then increased slowly and eventually achieved equilibrium in 4 h, which suggested that UiO-66-C₂ can remove hydrogen chloride faster than other adsorbents reported in literature (Table S2). Three adsorption kinetics models, namely, pseudo-second-order, intraparticle diffusion, and Elovich models, were harnessed in the analysis of adsorption kinetics results, and the results are summarized in Table 1 and Figure 4.

It is hypothesized that the availability of unoccupied sites on the surface of the adsorbent plays a determinant role on adsorption rate in pseudo-second-order model.⁴⁸ The pseudosecond-order model can be described as eq 2:

$$\mathrm{d}Q_t/\mathrm{d}t = k_2(Q_e - Q_t)^2 \tag{2}$$

In which Q_t and Q_e (mg·g⁻¹) are hydrogen chloride adsorption capacities per unit weight of the used MOFs at time t (h) and at equilibrium. k_2 (g·mg⁻¹·h⁻¹) is the rate constant. The equation for the boundary range from t = 0 to t and $Q_t = 0$ to Q_t are integrated and rearranged as eq 3:

$$t/Q_t = 1/(k_2 Q_e^2) + 1/Q_e t$$
(3)

With the presence of high adj. R^2 , the kinetic results were fitted with pseudo-second-order model quite well, and measured Q_e values were almost equal to the calculated



Figure 4. (a) Relationship between time and adsorption capacity of HCl adsorption on UiO-66-C₂. (b) Pseudo-second-order kinetics. (C) Intraparticle diffusion kinetics. (d) Elovich model of hydrogen chloride adsorption with UiO-66-C₂ (C_0 : 0.6, 1.0, and 1.4 mol·L⁻¹; T: 25 °C; dosage: 5 g·L⁻¹).

Table 1. Kinetics Parameters of HCl Adsorption on UiO-66-C2

		pseudo-se	econd-order mode	intraparticle	e diffusion 1	nodel	Elovich model			
$C_0 \pmod{\mathrm{L}^{-1}}$	$\begin{array}{c} Q_{e} \; (expt) \\ (mg \cdot g^{-1}) \end{array}$	$\begin{array}{c} Q_e \ (ext{calcd}) \ (ext{mg} \cdot extbf{g}^{-1}) \end{array}$	$\overset{k_2}{(g \cdot m L^{-1} \cdot h^{-1})}$	adj. R ²	$k_{ m ip} \begin{array}{c} ({ m mg} \cdot { m g}^{-1} \cdot { m h}^{-0.5}) \end{array}$	с	adj. R ²	$10^{6} \times \alpha$ $(\text{mg} \cdot \text{g}^{-1} \cdot \text{h}^{-1})$	$\beta \; (g \cdot m \cdot g^{-1})$	adj. R ²
0.6	284.15	282.49	0.0515	0.9998	151.87	121.29	1.0000	2.5313	0.0489	0.8246
1.0	398.00	400.00	0.0230	0.9999	110.32	220.71	0.9386	1.8030	0.0330	0.8406
1.4	429.53	432.90	0.0223	0.9998	122.88	224.23	0.9985	1.3376	0.0296	0.8200

ones, which meant the adsorption of hydrogen chloride on UiO-66- C_2 was controlled by two elements. Since the pseudo-second-order model was an empirical formula, it cannot determine whether hydrogen chloride adsorption was mono-layer or multilayer.^{49,50}

The equation of intraparticle diffusion model can be expressed as follows eq 4:

$$Q_t = k_{\rm ip} t^{0.5} + c \tag{4}$$

where *c* is the constant of diffusivity; k_{ip} is the constant referring to thickness and boundary layer. It means that intraparticle diffusion is controlled by a single rate, when the plots Q_t against $t^{0.5}$ are straight line and pass origin. As shown in Figure 4*c*, they were three-phase nonlinear diagrams, which meant that adsorption of hydrogen chloride on UiO-66-C₂ was a continuous but sectionalized process, in which the first phase was linear adsorption related to surface diffusion, the second phase was intraparticle diffusion process, and the third phase was the dynamic equilibrium process of adsorption and desorption.⁵¹

The liner equation of Elovich model can be given as eq 5:

$$Q_{t} = 1/\beta \times \ln(\alpha\beta) + 1/\beta \times \ln t$$
(5)

where α is the adsorption rate and β is the coefficient of desorption. The values of α and β can be acquired from the slope and intercept of the straight line of Q_t versus ln *t*. The adj. R^2 values of the Elovich model were less than those of pseudo-second-order model.

3.4. Adsorption Isotherms. Batch adsorption isotherms experiments were conducted at 25, 35, 45, and 55 °C with the initial HCl concentration ranging from 0.4 to 1.8 mol·L⁻¹. Just as is demonstrated in the Figure 5a, the HCl adsorption capacity increased as the initial HCl concentration increased. But the increasing rate was slow at the beginning, and then became faster, which can be explained by the hydrophobicity of the MOFs. Finally, the rate became low again, indicating that the adsorption process reached equilibrium. The equilibrium adsorption capacity Q_e decreased as temperature increased, which meant the adsorption process was exothermal. Three different models were utilized to analyze the results of adsorption isotherms.

Langmuir isotherm model is an ideal model, hypothesizing that adsorption is a monomolecular layer and it happens in the surface of the adsorbent whose adsorption sites are uniformly distributed.⁵² The Langmuir isotherm equation (eq 6) is described as follows:

$$Q_{\rm e} = K_{\rm L} Q_{\rm m} C_{\rm e} / (1 + K_{\rm L} C_{\rm e})$$
⁽⁶⁾



Figure 5. (a) Adsorption isotherms of hydrogen chloride on UiO-66-C₂. (b) Langmuir isotherms, (c) Freundlich isotherms, and (d) Henry isotherms of hydrogen chloride adsorption on UiO-66-C₂ (C_0 : 0.4–1.8 mol·L⁻¹; T: 25, 35, 45, and 55 °C; dosage: 5g·L⁻¹).

Table 2. Isotherms and Thermodynamic Parameters of Hydrogen Chloride Adsorption with UiO-66-C2

	Lar	Freundlich model			Henry model						
T (°C)	$1/Q_{m}$ (mol·g ⁻¹)	$\begin{array}{c} K_L \\ (L \cdot mol^{-1}) \end{array}$	adj. R ²	1/n	$K_{\rm F}$	adj. R ²	$K_{\rm H} \ (m L \cdot g^{-1})$	adj. R ²	$\Delta G \ (\mathrm{KJ}\cdot\mathrm{mol}^{-1})$	$\Delta H \ (\mathrm{KJ}\cdot\mathrm{mol}^{-1})$	$\Delta S \ (J \cdot mol^{-1} \cdot K^{-1})$
25	43.96	0.58	0.9533	0.68	0.0081	0.9667	7.17	0.9706	-4.90		
35	34.75	0.32	0.8453	0.79	0.0068	0.9807	6.22	0.9841	-4.66	12.12	-24.21
45	14.80	0.09	0.0512	0.96	0.0055	0.9665	5.32	0.9884	-4.42	-12.12	
55	13.55	0.07	0.1273	0.97	0.1060	0.9688	4.59	0.9885	-4.17		

where $K_{\rm L}$ (L·mol⁻¹) is the constant of adsorption equilibrium; $Q_{\rm e}$ (mol·g⁻¹) is adsorption capacity of HCl at equilibrium; $Q_{\rm m}$ (mol·g⁻¹) is the maximum adsorption capacity of the adsorbent; and $C_{\rm e}$ (mol·L⁻¹) is the liquid-phase concentrations of HCl at equilibrium. The equation can be linearized as eq 7:

$$C_{\rm e}/Q_{\rm e} = 1/K_{\rm L}Q_{\rm m} + 1/Q_{\rm m}C_{\rm e}$$
(7)

All the parameters are listed in Table 2. The Langmuir model cannot fit isotherm results with low adj. R^2 .

The Freundlich isotherm model is an experiential model which can explain heterogeneous adsorption system. The equation of Freundlich isotherm is presented as eq 8:

$$Q_{\rm e} = K_{\rm F} C_{\rm e}^{1/n} \tag{8}$$

where $K_{\rm F} \,({\rm mol} \cdot {\rm g}^{-1} ({\rm L} \cdot {\rm mol}^{-1})^{1/n})$ is the Freundlich constant. 1/ *n* is a measure of adsorption intensity. The linear equation of Freundlich isotherm model can be displayed as

$$\log Q_{\rm e} = \log K_{\rm F} + 1/n \log C_{\rm e} \tag{9}$$

The Freundlich model could elucidate the results of adsorption isotherms with high value of adj. R^2 , which describes multilayer adsorption and nonideal adsorption on heterogeneous surfaces. The Freundlich parameter 1/n is a

degree of adsorption intensity related to the surface heterogeneity. If 1/n = 0 to 1, it is a favorable physisorption process (n > 1); if 1/n = 1, it is a homogeneous adsorption without interaction among the adsorbates (n = 1); and if 1/n > 1, it is an unfavorable chemisorption process (n < 1). Therefore, the values of 1/n (1/n < 1) demonstrated that the HCl adsorption was favored, and physical force, rather than chemical interactions, contributed more to adsorption.^{53,54}

The Henry isotherm is suitable for adsorption from dilute solution. The equation of the Henry isotherm is expressed as eq 10:

$$Q_{\rm e} = K_{\rm P} C_{\rm e} \tag{10}$$

where K_P is a constant of the Henry model (mL·g⁻¹). The high adj. R^2 of the Henry model indicated that adsorption capacity of hydrochloric acid was linearly related to equilibrium concentration.

The thermodynamic parameters like enthalpy change (ΔH , kJ·mol⁻¹), entropy change (ΔS , J·mol⁻¹·K⁻¹) and Gibbs free energy change (ΔG , kJ·mol⁻¹) were calculated based on equations as follows:

$$\Delta G = -RT \ln K_{\rm p} \tag{11}$$

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$$\ln K_{\rm p} = \Delta S/R - \Delta H/RT \tag{12}$$

where *R* is the universal gas constant, and its value is 8.314 J·mol⁻¹·K⁻¹. *T* (K) is the Kelvin temperature. K_p is the constant of the Henry model. The van 't Hoff plot was obtained by plotting ln K_p against 1/T as illustrated in Figure S4. The values of ΔS , ΔH , and ΔG were obtained from the van 't Hoff plot (Table 2).

The values of thermodynamic parameters are given in Table 2. The negative values of $\triangle G$ suggested that the hydrogen chloride adsorption on UiO-66-C₂ was a spontaneous and thermodynamically favorable process, which was in accordance with the isotherm results. Also, the values of ΔG was in the range of -20 and 0 kJ·mol⁻¹, which suggested that the process was mainly physical adsorption.⁵⁵ The negative value of ΔH and ΔS illustrated that the HCl adsorption process was an exothermic and entropy decreasing process.

3.5. Adsorption Mechanism. The variations of chemical bonds between before and after adsorption of UiO-66- C_2 was analyzed by FT-IR (Figure 6). The appearance of adsorption



Figure 6. FT-IR spectra of prepared and adsorbed UiO-66-C₂.

bands 3417 and 3391 cm⁻¹ can be ascribed to the OH of -COOH or H_2O . The enhanced band after adsorption may indicated that water entered the adsorbent during adsorption. The adsorption bands 1699 and 1700 cm⁻¹, 1498 and 1498 cm⁻¹, and 1241 and 1306 cm⁻¹ represented C==O st, benzene ring, and arC-O-alC. According to Hooke's law, the enhancement of the stretching vibration of groups indicated carboxyl, benzene ring, and alkoxy group might be adsorption sites of

hydrogen chloride. Alkoxy group probably had an interaction with $H^{\scriptscriptstyle +}$ because of its alkalinity.

XPS was conducted to explore the hydrogen chloride adsorption mechanism of UiO-66-C₂. The peaks corresponding to O 1s, Cl 2p, and Zr 3d can be clearly identified in the XPS spectra (Figure 7a). As is demonstrated in Figure 7b, the variation of binding energy at Zr 3d and the expansion of peak intensity at Cl 2p indicated the interactions between Zr^{4+} and Cl⁻ during the adsorption process and Cl⁻ were adsorbed in the UiO-66-C₂. The increased binding energy of Zr 3d suggested that an electron transfer in the valence band between Cl⁻ and Zr⁴⁺. Moreover, The relative contents of elements C 1s:O 1s:N 1s:Zr 3d:Cl 2p before and after adsorption showed that before adsorption: 59.66:33.02:1:4.41:1.9; after adsorption: 56.7:33.95:0.68:4.65:4.03. The relative contents of Cl increased distinctly, further substantiating that hydrogen chloride was truly adsorbed on UiO-66-C₂.

3.6. Recycle of UiO-66-C₂. Recyclability is an important factor for adsorbents. As is illustrated in Figure 8, after three



Figure 8. Changes of HCl adsorption capacities among original and regenerated UiO-66-C₂ (C_0 : 0.5 mol·L⁻¹; T: 25 °C; dosage: 5g·L⁻¹).

recycles, UiO-66- C_2 still exhibited excellent adsorptive performance and the adsorption capacity remained statistically stable, which meant UiO-66- C_2 could be recycled easily. However, there was some decrease in hydrogen chloride adsorption capacity during regeneration. The decrease of adsorption capacity might be caused by insufficient activation as the number of regenerations increases. In addition, the washing process requires centrifugation to separate the solute from the solvent. During the process of pouring the solvent,



Figure 7. (a) Original XPS patterns. (b) Partially magnified XPS patterns of prepared and adsorbed UiO-66-C₂.

some nanoparticles that are not separated from the solvent may be poured out, and the lost nanoparticles may have strong adsorption capacity, which may lead to the decrease of adsorption capacity. The XRD patterns of regenerated UiO-66- C_2 were compared with that of as-synthesized UiO-66- C_2 . As we can see in Figure S5, the locations and intensities of the peaks in the XRD patterns of regenerated UiO-66-C2 remained unchanged. On the other hand, SEM (Figure S6) was performed to measure the crystallite morphology of the regenerated UiO-66-C2. Distinctive changes cannot be found in the regenerated UiO-66-C2 in terms of particle size and crystal morphology. Meanwhile, the UiO-66-C₂ was treated by different concentrations of hydrochloric acid for 2 days, that is, 0.1, 0.5, 1.0, and 2.0 mol/L. TEM and BET were then performed to test its stability. The results of TEM (Figure S3) demonstrated that the surface morphology of UiO-66-C₂ before and after treatment retained unchanged. The adsorption isotherms (Figure S7) of treated UiO-66-C2 also did not deviate much from untreated UiO-66-C2 and the BET surface area of treated sample kept stable in Table S3. The above characterization results illustrated the excellent stability of UiO-66-C₂ in acidic solution.

4. CONCLUSION

In summary, we synthesized a sequence of UiO-66 analogues with various alkoxy groups, which exhibited high adsorption capacity of hydrogen chloride from aqueous solution. The adsorption capacity of hydrogen chloride represented a volcano-shaped variation with increasing carbon number of alkoxy groups. First, the introduction of alkoxy groups can enhance the performance of HCl adsorption for the addition of adsorption sites. Meanwhile, surface area had a significant influence on the HCl adsorption. UiO-66-C2 showed the highest adsorption capacity of 398.0 mg·g⁻¹ because it had more adsorption sites provided by ethoxy and large surface area. The kinetic, isotherm, thermodynamics, adsorptive mechanism, and regeneration performances of UiO-66-C₂ were studied. The results demonstrated that the adsorption process is a spontaneous and exthermic physisorption process. It was anticipated that the carboxyl group, benzene ring, alkoxy group, and Zr⁴⁺ were responsible for HCl sorption. According to XPS results, it was supposed that Zr⁴⁺ interacted with Cl⁻. The regeneration of UiO-66-C2 was feasible and easy, and there was no obvious change in the structure and adsorption capacity after recycles. All the results illustrated that UiO-66- C_2 could be an efficient solution toward disposal of acidic wastewater. The performance of HCl adsorption for UiO-66 can be improved via introducing alkoxy functional groups without significant decrease of surface area.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jced.8b00802.

¹H NMR spectrograms of UiO-66- C_{Xi} ; N₂ adsorption– desorption isotherm and pore diameter distribution of nonmodified/pristine UiO-66; TEM images of pristine UiO-66-C₂ and UiO-66-C₂ treated by 0.1, 0.5, 1.0, and 2.0 mol/L HCl solutions for 2 days; van 't Hoff plot; XRD patterns of synthesized and regenerated UiO-66-C₂; SEM images of regenerated UiO-66-C₂; Left: N₂ adsorption–desorption isotherms; right: pore diameter distributions of pristine UiO-66-C₂ and UiO-66-C₂ treated by 0.1, 0.5, 1.0, and 2.0 mol/L HCl solutions for 2 days; surface area, pore volume and pore diameter of UiO-66 and UiO-66-C_x; summary of hydrogen chloride adsorbents; surface area, pore volume, and pore diameter of pristine UiO-66-C₂ and UiO-66-C₂ treated by 0.1, 0.5, 1.0, and 2.0 mol/L HCl solutions for 2 days (PDF)

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Funding

This work was supported by the National Natural Science Foundation of China (No. 21202116), Independent Innovation Foundation of Tianjin University (2017XZY-0052) and Natural Science Foundation of Tianjin (16JCYBJC20300).

Notes

The authors declare no competing financial interest.

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