Study on removal of volatile organic compounds by metal-organic framework composite material

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Research

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Abstract

For decades, people have made many efforts to improve air quality. Volatile Organic Compounds (VOCs) in the chemical and textile industries are indeed listed as serious problems that need to be controlled to avoid the emission of toxic substances and reduce the concentration of ozone in the atmosphere. In this study, a novel β -cyclodextrin-metal-organic framework (β -CD-MOF) was produced by a green and simple method to achieve the goal of making environmentally friendly adsorption materials through a green process. Compared with pure β -CD (the specific surface area is only 22 m²/g), β -CD-MOF has higher crystallinity and larger specific surface area (up to 869 m²/g). Through the dynamic acetone adsorption device, the adsorption capacity of β -CD-MOF for acetone can reach 211 mg/g at room temperature, which is higher than that of activated carbon (the adsorption capacity is only about 192 mg/g). In addition, the adsorption of acetone by β -CD-MOF is a single-layer physical adsorption behavior through isothermal adsorption simulation, and it is known from the kinetic simulation that the adsorption mainly occurs on the surface, and the limiting condition of the adsorption is mainly external mass transfer. According to the results of thermodynamic analysis, the adsorption reaction is a spontaneous and exothermic reaction. Because the adsorption is a physical adsorption behavior, β -CD-MOF adsorbent has good reusability. After four cycling experiments, the adsorption capacity of acetone is only reduced by about 10%. This research has provided an environmentally friendly, low-cost, and high-efficiency solution for the removal of VOCs.

1. Introduction

According to the definition of the World Health Organization (WHO), volatile organic compounds (VOCs) are organic compounds with a boiling point of 50 to 260°C. They are precursors of photochemical oxidants. Some pollutants are easily harmful to the human nervous system and may even cause cancer [1]. Among them, acetone is a common typical compound in pharmaceutical, pesticide, chemical, and other industries [2]. Therefore, it is very important to control the concentration of acetone in the air [3]. A variety of acetone treatment technologies have been developed, including gas adsorption [4], catalytic oxidation [5], plasma catalytic oxidation [6], and so on. Generally, the adsorption method is widely used to capture the acetone on the surface of the adsorbent [7], and the most commonly used adsorbent is activated carbon (AC) because activated carbon has the characteristics of developed pore structure and high specific surface area, and low cost, surface reaction, high activity and an excellent adsorbent [8]. However, the structure and surface chemistry of activated carbon is very complex, which easily affects the adsorption capacity of acetone [9].

There have been many studies discussing the influence of the adsorbent pore structure and the chemical properties of the carbon surface on the adsorption of VOCs. For example, Gil et al. [10] used alkaline agents to modify the adsorption material to develop a microporous carbon material. The research results showed that the developed carbon material has a developed microporous structure, which can increase the adsorption capacity of toluene from 27 mg/g to 288 mg/g. Shu et al. [11] used ultrasonic oscillation to prepare iron-loaded activated carbon with different texture characteristics but similar surface

functional groups. The results of the study showed that micropores in the range of 0.7-2.0 nm can enhance adsorption [11]. Qi et al. have synthesized spherical porous carbon with a controllable pore structure and proposed that carbon spheres with similar microporosity on the surface chemically play a key role in the VOCs adsorption reaction. A study by Almazan et al. [12] found that the existence of micropores of appropriate size plays a very important role in pollutant treatment, and oxygen-containing groups can inhibit the adsorption of alkanes and benzene. Ghimbeu et al. [13] studied the interaction between oxygen-containing groups and ethanol, and learned that oxygen-containing groups can enhance the adsorption capacity. Liang et al. [4] performed molecular adsorption simulations, and their results confirmed that the addition of oxygen-containing functional groups can increase the adsorption capacity of acetone [4]. It can be seen that the physical and chemical interaction between oxygen-containing groups and pollutants on carbon materials is quite complicated [14]. Some pollutants are physically adsorbed in the pores and easily desorbed due to the airflow, but some can be chemically adsorbed by combining functional groups on the material with the pollutants [15]. Many researchers have studied the physical and chemical adsorption of VOCs, such as toluene, xylene, and alkyl halides, and explored the adsorption characteristics of strongly polar VOCs (such as acetone) and non-polar or weakly polar VOCs, and the characteristics of different pollutants relationship [16].

In recent years, many researchers have developed adsorption materials with higher adsorption capacity, such as metal-organic framework (MOF). MOF is a highly ordered crystalline material composed of metal ions and organic multifunctional ligands [17]. This material has a high specific surface area, multiple functional groups, and adjustable porosity, and can have a wide range of potential applications in gas separation, gas storage, catalysis, chemical sensing, and drug delivery [18]. In order to improve the adsorption capacity of MOF, many researchers have recrystallized cyclodextrin (CD) in the presence of alkali metal cations, and successfully prepared a series of non-toxic α -, β - and γ -cyclodextrin-based MOF (Cyclodextrin metal-organic framework, CD-MOF) [19]. CD-MOFs have good application prospects in the field of gas adsorption and separation. For example, by forming a carbonic acid group, CO_2 binds firmly and reversibly with the free primary alcohol group in γ -CD-MOF [20]. Formaldehyde can be adsorbed through the hydrogen bonding of the hydroxyl group in γ -CD-MOFs [21]. γ -CD-MOF can also be used to adsorb sulfur hexafluoride, and the packaging capacity can reach $2.7 \pm 0.5\%$ (w/w) after 12 hours of treatment at 1.2 MPa [22]. Al-Ghamdi et al. (2016) used γ -CD-MOF for acetaldehyde adsorption, and its adsorption capacity can be as high as $53 \mu\text{g/g}$ [23]. Li et al. (2018) used γ -CD-MOF to separate the mixture of CO_2 and acetylene (C_2H_2) and learned that high-purity C_2H_2 can be obtained by γ -CD-MOF to adsorb CO_2 through selective adsorption [24].

Therefore, this study is based on the carbohydrate metal-organic framework of the biocompatible cyclic oligosaccharide cyclodextrin, and the developed CD-MOFs can be biodegraded and reused, and are less harmful to the environment than other metal-organic frameworks. Therefore, the purpose of this study is to explore the CD-MOF treatment of volatile organic compounds and the treatment mechanism.

2. Experimental Section

2.1. Materials and Methods

β -Cyclodextrin (β -CD, 98%) was purchased from PanReac AppliChem (Europe), sodium hydroxide (NaOH) was purchased from Nihon Shiyaku (Japan), and methanol (MeOH) was purchased from Honeywell (Germany). All other chemicals are reagent grade drugs provided by local suppliers.

2.2. Synthesis of β -CD-MOFs

First, dissolve β -CD (1.46 g) and NaOH (0.48 g) in deionized water (20 mL), and then add MeOH (50 mL) to diffuse vapor into the solution at 30°C for 7 days. The crystals obtained were filtered and washed 3 times with MeOH. In order to remove the interstitial solvent, β -CD-MOF crystals were immersed in CH_2Cl_2 for 3 days, and the samples were dried in a vacuum oven at 40°C for 12 hours.

2.3. Characterization

Advance D8 X-ray diffractometer (Bruker, MA, USA) was used for crystal characteristics analysis, and CuK α radiation ($\lambda = 0.15405 \text{ nm}$) was used for X-ray diffraction (X-ray Diffraction, XRD) analysis at 40 kV and 40 mA. The model is Rigaku TTRAX 3, and the measurement was performed at a scan rate of 0.5°/min, a step interval of 0.02°, and a 2θ angle range of 3–40°. The thermal gravity analyzer (TGA) model STA (Perkin Elmer Inc.) was used, and the sample (3–6 mg) was heated from 40°C to 600°C at a heating rate of 10°C min⁻¹.

X-ray photoelectron spectrometer (X-ray photoelectron spectrometer, XPS) can be used to determine the element composition, chemical formula, chemical state, and electronic state of the elements contained in the material. The model is Theta Probe (Thermo Scientific Inc.). A scanning electron microscope (Scanning Electron Microscopy, SEM) was used to observe the structure of the adsorption material, the model is JSM-IT100 (In Touch Scope™). Fourier Transform Infrared spectroscopy (FTIR) with model of Nicolet iS10 (Thermo Scientific™) was used to confirm the functional group.

Through the nitrogen adsorption/desorption analyzer (N₂ adsorption/desorption analyzer), the specific surface area and pore distribution analysis of β -CD-MOF was analyzed with model of ASAP 2000. A gas chromatography flame ionization detector (GC-FID, Clarus 680) was used to connect the adsorption tube for understanding the adsorption capacity of the developed material.

3. Results And Discussion

This study is to explore the surface appearance characteristics of adsorbent materials, the total types of oxidized compounds, element valence, functional groups, specific surface area, and pore size, reduction ability, and thermal stability with using XRD, XPS, TGA, FTIR, SEM, BET, etc. The instrument analyzes various characteristics of the material, and the analysis results are as follows.

3.1. Characteristic analysis results

3.1.1. XRD

The cyclodextrin-based MOF, namely β -CD-MOF, was prepared by methanol vapor diffusion. Compared with β -CD, the X-ray diffraction pattern of β -CD-MOF has obvious changes, as shown in Fig. 1. Many peaks in the XRD pattern of β -CD disappeared and were replaced by two sharp peaks at 5.6° and 11.2° at 2θ . From the change of XRD pattern, it can be understood that β -CD in β -CD-MOF reacts with metal ions to form a highly ordered crystal structure during the crystallization process. The XRD pattern of β -CD-MOF after adsorption is not much different from that of β -CD-MOF. It can be seen that the crystal structure of β -CD-MOF before and after adsorption is stable.

3.1.2. XPS

Single crystal X-ray diffraction was used to determine the β -CD-MOF crystal structure. The XPS result of β -CD-MOF showed the corresponding peak of Na 1s, which indicated that β -CD-MOF was successfully synthesized. It can be seen from the XPS diagram of Fig. 2 that β -CD-MOF has the corresponding peaks of Na 1s, O KLL, O 1s, and C 1s, and O KLL, O 1s, and C 1s. Corresponding peaks still exist after adsorption of β -CD-MOF. In addition, the corresponding peak of Na 1s disappears because the metal ion will undergo an adsorption reaction with the adsorbed acetone during the adsorption process. It can promote the adsorption of acetone on the metal-organic framework with causing the corresponding peak of Na 1s to disappear.

3.1.3. TGA

The thermodynamic properties of β -CD-MOF can be understood from the TGA diagram in Fig. 3. At about 100°C , all of β -CD, β -CD-MOF, and adsorbed β -CD-MOF have partial weight loss, which is caused by the evaporation of water. β -CD loses its weight rapidly at $300\text{--}350^\circ\text{C}$. β -CD becomes smaller molecules since it cracks due to high temperature, and finally becomes inorganic CO_2 and H_2O . Due to high-temperature evaporation, the final weight of β -CD is almost zero. Compared with β -CD, β -CD-MOF cracks at $200\text{--}300^\circ\text{C}$ both before and after adsorption. The cracking temperature is lower than that of the original β -CD since β -CD-MOF has more functional groups. The cracked β -CD-MOF only leaves about 30% of its weight, while the adsorbed β -CD-MOF reacts with pollutants, and part of it can become CO_2 and H_2O . Therefore, the weight loss is more obvious, only remaining under 20% of the weight.

3.1.4. FTIR

In this study, the structure, functional groups, and structural stability of β -CD-MOF were investigated through FTIR spectroscopy. Figure 4 shows the FTIR diagrams of β -CD and β -CD-MOF. The results show that β -CD has OH functional group at 3400 cm^{-1} ; CH_2 functional group near 2900 cm^{-1} ; H-O-H functional group at 1600 cm^{-1} ; CH functional group near 1100 cm^{-1} , while the functional group at 1000 cm^{-1} is C-O-C. Compared with β -CD-MOF, it is found that all functional groups of β -CD can be found on β -CD-MOF.

In addition, the CH₂ functional group at about 2900 cm⁻¹ changed from a single peak to a bimodal, and C-N functional groups can be found at about 1250 cm⁻¹. Herewith, the functional groups of β-CD are all present in β-CD-MOF with showing a stable structure.

3.1.5. SEM

Figure 5 is an optical microscope image of β-CD and β-CD-MOF. Figures 5(a) and (b) are SEM images of β-CD, and Fig. 5(c) and Fig. (d) are SEM images of β-CD-MOF. It can be seen from the figures that both pure β-CD and MOF show an amorphous structure. The size of the β-CD clusters is relatively large, and it can be observed that the particles are uniformly agglomerated together after adding the linking agent to make the MOF.

3.1.6. N₂ isothermal adsorption and desorption analyzer

The N₂ isothermal adsorption and desorption experiment was carried out at 25°C and atmospheric pressure, as shown in Fig. 6. This isotherm drawing belongs to type II isotherm (S-type isotherm), and there is an inflection point at low P/P₀, which is the first steep part of the isotherm. It can indicate the saturation of the monolayer adsorption capacity. As the relative pressure increases, a second layer begins to form. The number of adsorption layers can increase indefinitely when the saturated vapor pressure is reached. Compared with pure β-CD (the specific surface area is only 22 m²/g), β-CD-MOF has higher crystallinity and larger specific surface area (up to 869 m²/g). Figures 7 (a) and (b) show the distribution of BJH adsorption and desorption pores. It can be seen from the figure that most of the pore distribution is a mesoporous structure, which corresponds to Fig. 6.

3.2. Performance evaluation results

In this study, a self-made device was designed using flow meters, adsorption tubes (quartz tubes), and other connecting tubes, and connected with GC-FID to understand the adsorption capacity of the developed materials. A flow meter was used to control the flow and maintain a certain inflow concentration, and GC-FID was used to monitor the adsorption behavior to understand the penetration time and saturation time, and calculate the adsorption capacity.

The research results show that at different concentrations (200, 400, 600, and 800ppm), the adsorption capacity increases with increasing the inflow concentration, whereas the breakthrough time and saturation time decreases with increasing with increasing the inflow concentration. Using β-CD-MOF at four inflow concentrations, the penetration time is 130, 100, 70, and 68 minutes, and the adsorption capacity for acetone at room temperature is 145, 196, 197, and 211 mg/g. The highest adsorption capacity (211 mg/g) is higher than the adsorption capacity of activated carbon (only about 192 mg/g), as shown in Fig. 8.

In order to understand the recyclability of β -CD-MOF. The adsorption material is adsorbed and recycled four times, as shown in Fig. 9. The adsorption capacity for acetone was reduced from the original 211 mg/g to 189 mg/g, and the adsorption capacity was only reduced by 10%. Therefore, this material can be recycled and reused, which can reduce costs and promote environmental friendliness.

4. Conclusion

This study used a green and simple method to produce a novel β -CD-MOF. Through characteristic analysis, it can be known that its specific surface area is 869 m²/g and much higher than pure β -CD (22 m²/g). In addition, it can adsorb 211 mg/g of acetone at room temperature, which is higher than that of activated carbon (only about 192 mg/g). The adsorbent can be reused because β -CD-MOF's adsorption of acetone is a single-layer physical adsorption behavior. After four repeated recovery experiments, the adsorption capacity of acetone is only reduced by about 10%. This research has provided an environmentally friendly, low-cost, and high-efficiency solution for the removal of VOCs.

Declarations

Availability of data and materials

All data generated or analyzed during this study are examined by our group and certified for several times.

Competing interests

The authors declare they have no competing interests.

Funding

Not applicable

Authors' contributions

Yong-I Xiao provided real test data, Joy Thomas supported the test data, Nhat-Thien Nguyen wrote the paper, Thuy-Trang Le analyzed the test data, and Chang-Tang Chang organized the researched full structure. All authors read and approved the final manuscript.

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Figures

Figure 1

X-ray diffraction patterns of β -CD and β -CD-MOF

Figure 2

Single crystal X-ray diffraction patterns of β -CD and β -CD-MOF

Figure 3

Thermogravimetric analysis diagram of β -CD and β -CD-MOF.

Figure 4

Fourier transform infrared spectra of β -CD and β -CD-MOF.

Figure 5

(a)-(b) Optical microscope images of β -CD and (c)-(d) optical microscope images of β -CD-MOF.

Figure 6

N₂ adsorption and desorption experiment.

Figure 7

Pore distribution (a) BJH adsorption and (b) BJH desorption.

Figure 8

Adsorption saturation at different concentrations.

Figure 9

Recycling experiment.