Synthesis and Adsorption Performance of MIL-101(Cr)/Active Carbon Composites on Toluene

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Abstract. This work was undertaken to analyze the synthesis and adsorption performance of MIL-101(Cr)/Active Carbon composites (MIL-101/AC) on toluene. MIL-101/AC composites were synthesized by in-situ incorporation of activated carbon powder in MIL-101 via solvothermal synthesis method. The synthesized materials were characterized by N₂ adsorption/desorption and thermo gravimetric analysis (TGA). Result shows that the BET surface area of MIL-101/AC-5 was larger than that of MIL-101/AC composites and pure MIL-101, the adsorption of toluene on MIL-101/AC-5 attained 1148.41mg/g, which was much higher than those of other adsorbents. Thus, the MIL-101/AC composites were potential adsorbents in toluene pollution control.

Introduction

As one of the main pollutants of atmospheric environment, volatile organic compounds (VOCs) have attracted wide attention recently in the control of the air pollution. Therefore, the abatement of VOCs emission becomes imperative. Among VOCs treatments, adsorption, owing to its stable operation and low energy consumption, is favored over other technologies[1]. The adsorbent performance is the key issue in the development of the adsorption technique. The adsorbents with high adsorption capacity are very important for the efficient removal of harmful VOCs[2].

Recently, metal-organic frameworks (MOFs) composites have attracted more attention for their potential application of the VOCs adsorption. MOFs have highly crystalline three-dimensional extended structures with metal-containing clusters and multidentate organic linkers. MOFs possess characteristic features of large surface area, permanent porosity, high purity, controllable structures, large-scale production capability and thermodynamic stability[3-5]. Incorporation of certain types and amounts of suitable substrates during the synthesis of MOFs result in the creation of additional porosity, which is beneficial to improve the adsorption capacity of VOCs[6] as well as providing extra adsorptive sites[7]. P. B. S. Rallapalli et al. [6] measured the hydrogen on the AC@MIL-101/A, shows that the highest hydrogen uptake of 10.1wt% at 77.4K and up to 6000kPa hydrogen pressure. R. H. Shi et al. [8] synthesized Cu-based MOF/activated carbon composites, results show that MAC-2 exhibits a maximum uptake 8.46% and 8.53% for H₂S and CH₃SCH₃, respectively, which increase by 51% and 41% compared to that of MOF-199. S. Kayal et al.[9] have presented MAX-MIL composite, results show that the composites MAX-MIL adsorbs more CH₄ and CO₂ as compared with original MIL-101(Cr)MOF.

Toluene is the typical and harmful component of VOCs and often emitted to the air from chemical process and oil operations. So, this paper is to prepare the composites of MIL-101 and activated carbon and investigate the adsorption capacity of toluene. MIL-101(Cr)/AC composites were synthesized by in-situ incorporation of activated carbon powder in MIL-101(Cr) via solvothermal synthesis method, and then characterized by N₂ adsorption/desorption and TGA. In addition, the adsorption capacity of toluene on MIL-101(Cr)/AC composites was measured.
Experimental

Materials
Chromium nitrate nonahydrate (Cr(NO$_3$)$_3$·9H$_2$O, 99.0%), terephthalic acid (H$_2$BDC, 99.0%) and hydrochloric acid (HCl) were purchased from Sinopharm Chemical Reagent Co. Ltd. N,N-Dimethyl formamide (DMF), ethanol and deionized water were obtained from Shanghai Lingfeng Reagent Factory. The AC was purchased from Fujian Xinsen.

Synthesis of MIL-101/AC Composites
The MIL-101/AC composites were prepared by hydrothermal method according to the following procedures$^{[10]}$. Firstly, 4.00g Cr(NO$_3$)$_3$·9H$_2$O, 1.66g H$_2$BDC and 1mL HCl dissolved in deionized 50mL water and the AC was added into the mixture solution. The resulting suspension was sonicated and stirred. The suspension was loaded into a Teflon-lined stainless steel reactor and sealed. Then the reactor was placed in autoclave, the temperature was set to 473K and held 12 h. After the reaction time, the reactor was gradually cooled down to the room temperature. The synthesized product was separated by centrifugation process. Fine green colored powders were obtained as the major product, while a significant amount of recrystallized H$_2$BDC could be found. The products were doubly filtered with glass filters. In order to acquire pure crystalline material with high porosity and surface area, a series of purifications were applied to remove the unreacted H$_2$BDC as well as other guest molecules in the sample. The procedure of purification was mainly comprised with two consecutive solvent treatments using N,N-Dimethyl formamide, hot ethanol solution. Finally, the products were dried 373K for 12 hours and thus the MIL-101/AC composites were obtained. The AC amounts added in the preparation of the composites were separately 2, 5, 10 wt% of added unmodified activated carbon, the composites are referred to as MIL-101/AC, MIL-101/AC-2, MIL-101/AC-5, MIL-101/AC-10.

Characterization
The BET surface area, pore volume and the pore diameter of the synthesized AC, MIL-101(Cr) and MIL-101(Cr)/AC composites were measured by N$_2$-based adsorption/desorption isotherms data at 77K(Automated gas sorption analyzer, Autosorb IQ$^2$). Prior to adsorption, the samples were degassed at 423K for 12 hours. The thermal stabilities of AC, MIL-101(Cr) and MIL-101(Cr)/AC composites were characterized by the thermo gravimetric analysis(TGA,DSC3+) heating from 303K up to 1073K at heating rate of 10K/min under air of 50 mL/min.

Adsorption Experiments
The adsorption equilibrium experiment of toluene at 298K on MIL-101(Cr) and MIL-101(Cr)/AC composites were obtained on Quantachrome dual-station organic vapor adsorber. The experimental steps are as follows: the sample was weighed about 30 mg in cell, degassed at 423K for 12 hours, loaded in the adsorption station, then edited program and started analysis.

Results and Discussion
Physical Characteristics
The N$_2$ adsorption/desorption isotherms of AC, MIL-101 and MIL-101/AC composites at 77K are shown in Figure 1. The isotherm of AC presents type- I adsorption characteristic for microporous materials. The isotherms of MIL-101 and MIL-101/AC composites present secondary uptakes near 0.15 and 0.25 relative pressure, which are due to the presence of two types of microporous windows in its framework structure$^{[11]}$. The N$_2$ isotherms of MIL-101/AC composites are higher than that of MIL-101(Cr), which suggests that the incorporation of small amount of AC powder into the MIL-101(Cr) facilitates the formation of additional micropores in the framework. The textual properties of AC, MIL-101 and MIL-101/AC composites are listed in Table 1. These data include the BET surface area, total pore volume, micropore volume. The BET surface area, total pore volume and
The micropore volume are ordered as MIL-101/AC-5 > MIL-101/AC-10 > MIL-101/AC-2 > MIL-101 > AC. The pore size distribution (PSD) curves of AC, MIL-101 and MIL-101/AC composites are shown in Figure 2, which are calculated using nonlocal density functional theory method. It is observed from the PSD curve that the MIL-101/AC composites have pore width of 1.14-1.76 nm and 3.2 nm. So the MIL-101/AC composites have mixture of micropores and mesopores in its structure.

Figure 1. N$_2$ adsorption/desorption isotherms of AC, MIL-101 and MIL-101/AC composites at 77K.

Figure 2. Pore size distribution of MIL-101, and MIL-101/AC composites.

Table 1. The textual properties of AC, MIL-101 and MIL-101/AC composites.

| Sample         | Multipoint BET (m$^2$/g) | Micropore volume (cm$^3$/g) | Total volume (cm$^3$/g) |
|----------------|--------------------------|-----------------------------|-------------------------|
| AC             | 981                      | 0.33                        | 0.55                    |
| MIL-101        | 2509                     | 0.92                        | 1.48                    |
| MIL-101/AC-2   | 2627                     | 1.00                        | 1.74                    |
| MIL-101/AC-5   | 3345                     | 1.24                        | 2.29                    |
| MIL-101/AC-10  | 3182                     | 1.21                        | 1.98                    |
The thermo gravimetric analysis of MIL-101 and MIL-101/AC composites are shown in Figure 3. The total weight loss process of the samples were divided into three steps. The first weight loss occurred between 300K and 473K, related to the loss of guest water molecules from the large cage\(^{[12]}\). The second one happened between 473K and 623K, due to the release of water molecules from the middle sized cage\(^{[13]}\). The third weight loss occurred above 623K, attributed to the elimination of –OH and other coordinated groups\(^{[11]}\).

**Toluene Adsorption on Materials**

The isotherms of toluene on the MIL-101 and the MIL-101/AC composites are shown in Figure 4. It can be seen that at the relative pressures between 0.1 and 1, the order is MIL-101/AC-5>MIL-101/AC-10>MIL-101/AC-2>MIL-101. The toluene increases drastically with pressure at region of low pressure, which can be owed to the micropore adsorption. Meanwhile, multiple adsorption appeared mainly because MIL-101/AC composites have some adsorption sites. The adsorption isotherms of toluene on the MIL-101/AC composites are greatly higher than that on the pure MIL-101 sample. For comparison, the adsorption capacities of MIL-101 and MIL-101/AC composites and other adsorbents for toluene at 298K (P/P\(_0\)=0.2) are listed in Table 2. The result shows that the toluene adsorption capacity of the MIL-101/AC-5 is much higher than other adsorbents. The adsorption capacities of MIL-101/AC-5 for toluene reach up to 1148.41 mg/g at 298K and P/P\(_0\) of 0.2.

| Materials     | Q(mmol/g) | Q(mg/g) | Reference   |
|---------------|-----------|---------|-------------|
| MIL-101       | 10.04     | 925.14  | Present work|
| MIL-101/AC-2  | 10.20     | 940.25  | Present work|
| MIL-101/AC-5  | 12.46     | 1148.41 | Present work|
| MIL-101/AC-10 | 11.80     | 1087.36 | Present work|
Conclusion
In this study, the MIL-101/AC composites were synthesized via the hydrothermal method. In this work, the MIL-101/AC composites synthesized exhibited higher surface area compared to the pure MIL-101. The MIL-101/AC-5 showed optimal textural properties with large Multi-point BET surface area (3345 m$^2$/g) as well as large total pore volume of 2.29 cm$^3$/g. The adsorption capacity of toluene on the MIL-101/AC-5 was greatly higher than that on the MIL-101 and other samples. The MIL-101/AC-5 composite exhibited the maximum toluene uptake of 1250.04 mg/g at 298 K. Thus, the MIL-101/AC composites are potential adsorbents in toluene pollution control.

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