Adsorption equilibrium and dynamics of toluene vapors onto three kinds of silica gels

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Abstract. The benzene is the representative of VOCs and widely exists in the industrial waste gas. In this study, adsorption equilibrium and dynamics of toluene vapors at five initial concentrations (1.39 g·m⁻³, 5.12 g·m⁻³, 8.38 g·m⁻³, 15.6 g·m⁻³, 21.3 g·m⁻³) onto three kinds of silica gels (GA, GB and GC) were investigated and compared. The experimental results showed that GA has the rich microporous and mesoporous distributions, and the larger surface area and microporous volume than GB and GC. It can be clearly seen that the order of the adsorption rate of adsorbents on the silica gels samples is GA, GB and GC. Due to the suitable pore distribution in the region of micropore and mesopore (1–4 nm), GA exhibits the comparable breakthrough adsorption capacities with GB and GC for a given initial concentration. Moreover, the experimental data were fitted to the Langmuir and Freundlich models, respectively. The Freundlich isotherms correlated with the experimental data presented a better fitting than Langmuir model. Take together, it is expected that GA silica gel would be a promising adsorbent for the removal of toluene vapors from gas streams.

1. Introduction

Nowadays, the emission of volatile organic compounds (VOCs) has gained more and more attention not only for their damage to human health and environment but for economic interests as well. Adsorption technology has been recognized as a preferred method for the removal of VOCs because it provides additional benefits from the recovery of the valuable VOCs for reuse [1]. The heart of an adsorption process is usually a porous solid adsorbent. The activated carbon considered as the major commercial adsorbent provides excellent adsorption capacity, but it has been recognized that it owns some disadvantages such as fire risk, pore blocking and hygroscopicity [2–5]. In addition, the activated carbons are predominantly consisted of micropores (< 2 nm in size) with the specific surface area and pore volume, so it is very difficult to regenerate adsorbed VOCs due to the strong dispersive force resulting from the overlap of attractive forces from opposite pore walls of micropore [6, 7].

As a result, alternative adsorbents such as hydrophobic zeolite and silica gels have attracted considerable attention to control VOCs. Hydrophobic zeolites have been found to be effective in VOCs removal [8]. However, serious diffusion restrictions imposed by the micropores (<2 nm) tend to inhibit its ability to adsorb large VOC molecules [9]. Silica gels with high surface areas have attracted a great deal of attention due to their wide range of application as adsorbents for environmentally hazardous chemicals, reaction catalysts, catalyst supports, chemical sensors, and electrical and optical
devices [10-13]. Recently, Sui et al. [14] demonstrated that the silica gel would be a good candidate for the removal and recovery of high concentrations of toluene vapor from gas stream through atmospheric pressure adsorption and vacuum desorption. However, studies on the dynamic adsorption performance of silica gels in regards to VOCs have been very limited in comparison to those on their adsorption equilibria [15].

In this study, three kinds of silica gels, were chosen and considered as representatives of silica gels. The textural properties of the above three silica gels were systematically characterized. In addition, the adsorption behavior of the toluene vapors onto the silica gels at five initial concentrations were investigated. Meanwhile, the experimental data were correlated with Langmuir and Freundlich adsorption models.

2. Experimental

2.1. Materials

Three kinds of silica gels with different pore structures were used as the adsorbents, and named GA, GB and GC, respectively. The silica gel samples were supplied from Qingdao Meigao Co. Ltd.. All samples were desiccated in vacuum at 423.15 K for 12 h and preserved in a vacuum sealed bag as the samples were cooled to room temperature in vacuum. Toluene was supplied from Tianjin Guoyao Co. Ltd. with a purity of 99.5% by mass.

2.2. Characterization

Dried silica gels were characterized for its structure properties, such as surface area, pore volume and mean pore diameter. The nitrogen adsorption/desorption isotherms of three silica gels were determined using an adsorption analyzer ASAP 2020 (Micromeritics Instrument Co., USA) operated at 77 K. The experimental procedure was described briefly as follows: The silica gel particles were weighed (0.1 g) and poured into a sample bottle. The sample bottle was circulated in a heating jacket, heated to 523 K and vacuumed below 3 μm Hg to remove the moisture within the silica gel particles. After the silica gel sample was completely dried, it was weighed again and placed into liquid nitrogen to keep the sample temperature at 77 K. The freezing silica gel sample bottle was filled with nitrogen gas to determine the surface area and pore volume. The specific surface area was determined using the Brunauer-Emmett-Teller (BET) method. The total pore volume ($V_{\text{total}}$) was estimated to be the liquid volume of nitrogen at a relative pressure of about 0.98. The micropore volume ($V_{\text{micro}}$) was calculated from the N$_2$ isotherms data by means of the Barrett-Joyner-Halenda (BJH) method. The pore size distributions were calculated by applying the density functional theory (DFT) to N$_2$ isotherm data.

2.3. Adsorption Experiment

The experimental setup is shown in figure 1. It basically consisted of a toluene vapor generator, an adsorption column (10 mm in inner diameter and 150 mm in height) where silica gel samples were held, and a gas analysis system. Firstly, the nitrogen steam passed through a dryer bed in order to remove water, and was divided into two streams using two mass flows. One nitrogen flow was conducted to the bubble saturator containing pure toluene, which was held at a constant temperature by means of a thermostatic water bath. Secondly, the third nitrogen stream was used to diluted and attain a given toluene concentration. Then, the given concentration toluene vapor was passed through the adsorption column, and the flow rate of toluene vapor was fixed at 50 ml/min at room temperature. At the outlet of the adsorption column, a gas chromatograph (HP 6890, Agilent, Japan) with a flame ionization detector (FID) was used to measure the concentrations of toluene. The exhaust was discharged into the atmosphere after several rounds of purification.
2.4. Isotherm Models

Adsorption experimental data were correlated with two different isotherms, namely, Langmuir and Freundlich models.

**Langmuir model.** The well-known Langmuir isotherm can be expressed by equation (1):

\[
\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{1}{q_m C_e} \tag{1}
\]

where \( q_e \) is the amount adsorbed (mg·g\(^{-1}\)), \( q_m \) is the saturated amount adsorbed (mg·g\(^{-1}\)), \( C_e \) is the equilibrium concentration (g·m\(^{-3}\)), and \( b \) is the adsorption affinity (m\(^3\)·g).

**Freundlich model.** The Freundlich isotherm is expressed by equation (2):

\[
q_e = K_f C_e^{n_f} \tag{2}
\]

where \( q_e \) is the amount adsorbed (mg·g\(^{-1}\)), \( K_f \) and \( n_f \) are empirical constants that are generally temperature-dependent, and \( C_e \) is the equilibrium concentration (g·m\(^{-3}\)). The Freundlich equation is very popularly used in the description of adsorption VOCs from gas stream.

3. Results and Discussion

3.1. Characteristics of Silica gels

In order to understand more clearly the pore structure of adsorbents, the N\(_2\) adsorption-desorption isotherms and pore size distributions of three kinds of silica gels were shown in figure 2; the textural properties of all the adsorbents studied were included in table 1. It can be seen from figure 2 that at lower relative pressure (\( p/p_0 \)) below 0.05, the nitrogen uptake increases sharply with the increment of relative pressure, proving the existence of micropore structure in the GA and GB. Meanwhile, visible hysteresis loop means that GB and GC contain mesopore distribution. According to IUPAC classification, the adsorption–desorption isotherms of GA are close to type I, reflecting the domination of micropores in the pore structure. And GB is typical of adsorbents with mixed micro- and mesoporous structure. Also, it is significantly learned from the pore size distributions of three silica gels that GA is also typical of adsorbents with mixed micro- and mesoporous structure, the pore size is mainly distributed in the regions of 1-4 nm. GB is a typical mesopore adsorbent with a small amount of micropore (< 2 nm). In contrast, the pore sizes of GC are distributed in the regions of 10-40 nm near the macropore. It can be clearly seen from table 1 that three adsorbents have obvious different textural properties. GA has the largest surface area (700.5961 m\(^2\)·g\(^{-1}\)) and micropore volume \( V_{\text{micro}} \) (0.088194 cm\(^3\)·g\(^{-1}\)).
Figure 2. The N\textsubscript{2} adsorption-desorption isotherms at 77 K and pore size distributions of three kinds of silica gels.

Table 1. Textural properties of three kinds of silica gels.

| Adsorbent | BET \(m^2\cdot g^{-1}\) | Average pore diameter (nm) | \(V_{total}\) \(cm^3\cdot g^{-1}\) | \(V_{micro}\) \(cm^3\cdot g^{-1}\) |
|-----------|----------------|---------------------------|----------------|----------------|
| GA        | 701            | 2.2                       | 0.3855         | 0.088194       |
| GB        | 523            | 6.0                       | 0.7861         | 0.001273       |
| GC        | 322            | 11.4                      | 0.9223         | 0.00012        |

3.2. Dynamic adsorption properties

In this study, five initial toluene concentrations including 1.39 g·m\textsuperscript{-3}, 5.12 g·m\textsuperscript{-3}, 8.38 g·m\textsuperscript{-3}, 15.6 g·m\textsuperscript{-3}, 21.3 g·m\textsuperscript{-3}, were chosen to investigate the adsorption dynamic adsorption behavior on the different kinds of silica gels. Figure 3 just shows the breakthrough curves of toluene vapors adsorbed on three silica gels at 21.3 g·m\textsuperscript{-3}, where \(C_0\) is the inlet toluene concentration (g·m\textsuperscript{-3}), \(C_t\) is the outlet concentration (g·m\textsuperscript{-3}) and \(t\) is the adsorption time (min).

Figure 3. Breakthrough curves of toluene on three kinds of silica gels.

Evidently, under a given concentration, the breakthrough curves of toluene vapors onto three silica gels are similar, however, GA shows longer adsorption breakthrough time (the outlet concentration is equal to 95 percent of the inlet concentration of toluene) for toluene vapors than GB and GC. For
example, the adsorption breakthrough times of GA, GB and GC at the initial concentration of 8.38 g·m⁻³ are 280 min, 240 min and 200 min, respectively. Meanwhile, it can be clearly seen that the order of the adsorption rate of adsorbents on the three silica gels samples is GA, GB and GC. The pore structure parameters of the three silica gel samples suggest that there is a close relationship between the mass transfer rate internally in the silica gels and the pore structure (surface area and micropore pore volume). The bigger surface area and micropore pore volume, the slower the mass transfer rate.

3.3. Adsorption equilibrium
The equilibrium adsorption capacities of toluene on three kinds of silica gels were shown in Table 2. It can be seen that the equilibrium adsorption capacities of toluene increased with the increase of the initial concentration for a given silica gel type. For example, the equilibrium adsorption capacity is just 21.0 mg·g⁻¹ when the concentration is 1.39 g·m⁻³, however, the equilibrium adsorption capacity increases to 220.5 mg/g at the initial concentration of 21.3 g·m⁻³. Moreover, the order of the equilibrium adsorption capacity of toluene is GA, GB and GC for a given initial concentration. For example, the equilibrium adsorption capacities of toluene for GA, GB and GC are 113.5 mg·g⁻¹, 51 mg·g⁻¹ and 26 mg·g⁻¹ at the initial concentration of 5.12 g·m⁻³.

Table 2. Equilibrium adsorption capacities of toluene on three kinds of silica gels.

| Concentration (g·m⁻³) | Adsorption capacities (mg·g⁻¹) |
|-----------------------|-------------------------------|
|                       | GA   | GB   | GC   |
| 1.39                  | 21   | 14.5 | 12   |
| 5.12                  | 113.5| 51   | 26   |
| 8.38                  | 155.4| 71.1 | 37.5 |
| 15.6                  | 201  | 98   | 54   |
| 21.3                  | 220.5| 113.5| 60   |

It is clearly that the adsorption capacities of the GA and GB increased sharply with the increase of toluene vapors concentrations at lower concentrations, manifesting the existence of microporous structure inside the two adsorbents while those on GC slowly increased with the increment of concentration, which is typical of adsorption in a mesoporous adsorbent. It is well-known that the adsorption energy in the micropore is much larger than in the mesopores due to the overlapping of adsorption forces from the opposite walls of the micropores. Therefore, the adsorption capacities of GA and GB for the low concentration of toluene vapors were much higher than GC. By comparison of the adsorption capacities of toluene vapors on three adsorbents in the experimental concentration range, it is found that, GA has the best adsorption capacities. The results were mainly due to the fact that GA has the largest BET surface area and micropore volume. Among the three adsorbents, GC has the lowest adsorption capacities for toluene vapors, which is consistent with its lowest values of micropore volume and surface area.

3.4. Isotherm models
The adsorption equilibrium data of toluene vapors at five initial concentrations onto GA, GB and GC at 298 K were obtained. Langmuir and Freundlich equations are used to correlate the experimental equilibrium data of toluene vapors. A non-linear optimization routine is used to optimize the parameters of the models to fit the experimental data. The fitting parameters and correlation coefficients of Langmuir and Freundlich equations for the adsorption of toluene onto GA, GB and GC are presented in Table 3. It is found that all of the equilibrium data were correlated by Langmuir and Freundlich equations with large correlation coefficient. From Table 3, it is clear that the Freundlich equation has a better correlation with experimental data than the Langmuir equation. The curves of Freundlich fitting on three silica gels were shown in Figure 4. The parameters Kf and nf varied with different adsorbents; however, there was no apparent correlation between Kf, nf, and the adsorbent properties (surface area and porosity) within the examined concentration ranges. In the present work,
the adsorption isotherms are used mainly for comparing adsorption capacities between different adsorbents.

**Table 3.** Fitting parameters of Langmuir and Freundlich models for toluene on three silica gels.

| Adsorbent | Langmuir Model | Freundlich Model |
|-----------|----------------|------------------|
|           | $q_m$ (mg g$^{-1}$) | $b$ (m$^3$.g$^{-1}$) | $R^2$ | $K_f$ (m$^3$.mg$^{-nf}$) | $n_f$ | $R^2$ |
| GA        | 490.196         | 0.04359           | 0.9175 | 41.5025             | 0.5644 | 0.9478 |
| GB        | 201.082         | 0.06017           | 0.9743 | 18.2349             | 0.6069 | 0.9803 |
| GC        | 89.686          | 0.09247           | 0.9633 | 10.6588             | 0.5751 | 0.9891 |

![Graph showing Freundlich fitting on three silica gels.](image)

**Figure 4.** Curves of Freundlich fitting on three silica gels.

4. Conclusions

Adsorption equilibrium and dynamics of toluene vapors onto three kinds of silica gels with different textural properties were evaluated at five initial concentrations. It is concluded that GA will be an efficient and competitive adsorbent for toluene vapors adsorption. Due to the bigger surface area and micropore volume, the order of the adsorption rate of adsorbents on the three silica gels samples is GA, GB and GC. Compared with GB and GC, the results of adsorption equilibrium experiments confirmed that the equilibrium adsorption capacities of toluene increased with the increase of the initial concentration for a given silica gel type, and GA had the best breakthrough adsorption capacity for a given initial concentration. In addition, it also can be seen that the Freundlich model has a better correlation with experimental data than the Langmuir model for toluene adsorption onto silica gels.

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References

[1] Ghoshal A K, Manjare S D 2002 *J. Loss Prevent. Proc. Ind.* **15** 413
[2] Zerbonia R A, Brockmann C M, Peterson P R and Housley D 2001 *J. Air Waste Manage. Assoc.* **51** 1617
[3] Brennan J K, Bandosz T J, Thomson K T and Gubbins K E 2001 *Colloid Surf. A: Physicochem. Eng. Aspects* **187** 539
[4] Cosnier F, Celzard A, Furdin G, Bégin D and Marêché J F 2006 Adsorpt. Sci. Technol. 24 215
[5] Bradley R H 2011 Adsorpt. Sci. Technol. 29 1
[6] Inagaki M 2009 New Carbon Mater. 24 193
[7] Yun J H, Choi D K and Moon H 2000 Chem. Eng. Sci. 55 5857
[8] Brosillon S, Manero M H and Foussard J N 2001 Environ. Sci. Technol. 35 3571
[9] Christensen C H, Johannsen K and Schmidt I 2003 J. Am. Chem. Soc. 125 13370
[10] Kosuge K, Kubo S, Kikukawa N and Takemori M 2007 Langmuir 23 3095
[11] Qiao S Z, Bhattia S K and Nicholson D 2004 Langmuir 20 389–395
[12] Hartmann M, Bischof C 1999 J. Phys. Chem. B 103 6230
[13] Stein A 2003 Adv. Mater. 15 763
[14] Sui H, Liu H X, An P, He L, Li X G and Cong S 2017 J. Taiwan Inst. Chem. E. 74 218
[15] Lee J W, Shim W G and Moon H 2004 Microporous Mesoporous Mater. 73 109