

# Adsorption characteristics of the silica gels as adsorbent for gasoline vapors removal

K L Yan<sup>1,2,3</sup>, and Q Wang<sup>1,2</sup>

<sup>1</sup>SINOPEC Research Institute of Safety Engineering, Qingdao 266071, P. R. China

<sup>2</sup>State Key Laboratory of Safety and Control for Chemicals, Qingdao 266071, P. R. China

<sup>3</sup>yankele214@163.com

**Abstract.** Adsorption characteristics of three kinds of silica gels named GA, GB and GC as adsorbents for cyclohexane removal at five initial concentrations ( $2.1 \text{ g}\cdot\text{m}^{-3}$ ,  $5.4 \text{ g}\cdot\text{m}^{-3}$ ,  $9.2 \text{ g}\cdot\text{m}^{-3}$ ,  $16.3 \text{ g}\cdot\text{m}^{-3}$ , and  $21.2 \text{ g}\cdot\text{m}^{-3}$ ) were systematically investigated. 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 Langmuir isotherms correlated with the experimental data presented a better fitting than Freundlich model. Taken together, it is expected that GA silica gel would be a promising adsorbent for the removal of gasoline vapors from gas streams.

## 1. Introduction

Gasoline is a mixture of hydrocarbons with chains containing 4–12 carbons, and its vapor mostly consists of light hydrocarbons ( $\text{C}_4\text{--C}_7$ ) <sup>[1–4]</sup>. It is well-known that adsorption is one of the most practical methods for separating and recovering volatile organic compounds (VOCs) from industrial waste gas. 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 <sup>[5]</sup>. 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 <sup>[6–9]</sup>. 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 <sup>[10,11]</sup>.

## 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. 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. Cyclohexane was supplied from Tianjin Guoyao Co. Ltd. with a purity of 99.5% by mass.



## 2.2. Characterization

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 specific surface area was determined using the N<sub>2</sub> isotherms data by means of 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<sub>2</sub> isotherms data by Barrett-Joyner-Halenda (BJH) method. The pore size distributions were calculated by applying the density functional theory (DFT) to N<sub>2</sub> isotherm data.

## 2.3. Adsorption Experiment.

The experimental setup is shown in Figure 1. It basically consisted of a cyclohexane 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 cyclohexane, 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 cyclohexane concentration. Then, the given concentration cyclohexane vapor was passed through the adsorption column. 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 cyclohexane.

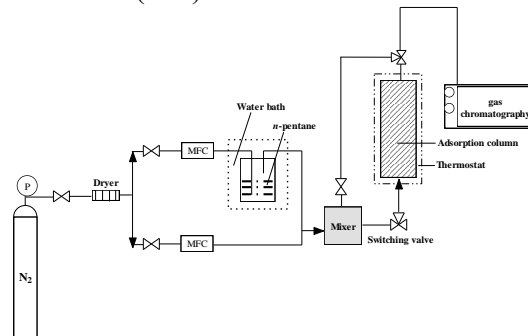


Figure 1. Schematic diagram of the experimental apparatus

## 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):

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

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

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

$$q_e = K_f C_e^{n_f} \quad (2)$$

where  $q_e$  is the amount adsorbed ( $\text{mg} \cdot \text{g}^{-1}$ ),  $K_f$  and  $n_f$  are empirical constants that are generally temperature-dependent, and  $C_e$  is the equilibrium concentration ( $\text{g} \cdot \text{m}^{-3}$ ). 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

The N<sub>2</sub> 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 BET ( $700.5961 \text{ m}^2\cdot\text{g}^{-1}$ ) and micropore volume  $V_{\text{micro}}$  ( $0.088194 \text{ cm}^3\cdot\text{g}^{-1}$ ).

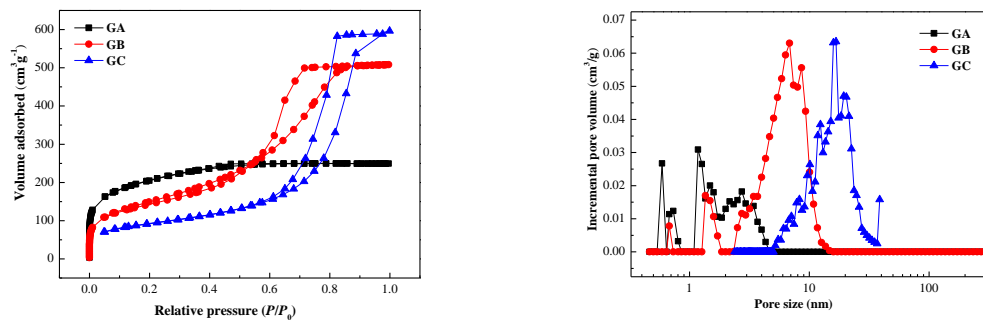


Figure 2. The  $\text{N}_2$  adsorption-desorption isotherms at 77 K and pore size distributions of three kinds of silica gels

Table 1. Textural properties of three kinds of silica gels

Adsorbent	BET ( $\text{m}^2\cdot\text{g}^{-1}$ )	Average pore diameter (nm)	$V_{\text{total}}$ ( $\text{cm}^3\cdot\text{g}^{-1}$ )	$V_{\text{micro}}$ ( $\text{cm}^3\cdot\text{g}^{-1}$ )
GA	700.5961	2.2012	0.3855	0.088194
GB	523.0259	6.0119	0.7861	0.001273
GC	322.2345	11.4482	0.9223	0.00012

### 3.2. Dynamic adsorption properties

In this study, five initial cyclohexane concentrations including  $2.1 \text{ g}\cdot\text{m}^{-3}$ ,  $5.4 \text{ g}\cdot\text{m}^{-3}$ ,  $9.2 \text{ g}\cdot\text{m}^{-3}$ ,  $16.3 \text{ g}\cdot\text{m}^{-3}$ , and  $21.2 \text{ g}\cdot\text{m}^{-3}$ , were chosen to investigate the adsorption dynamic adsorption behavior on the different kinds of silica gels. Figure 3 just shows the breakthrough curves of cyclohexane vapors adsorbed on three silica gels at  $5.4 \text{ g}\cdot\text{m}^{-3}$ , where  $C_0$  is the inlet cyclohexane concentration ( $\text{g}\cdot\text{m}^{-3}$ ),  $C_t$  is the outlet concentration ( $\text{g}\cdot\text{m}^{-3}$ ) and  $t$  is the adsorption time (min).

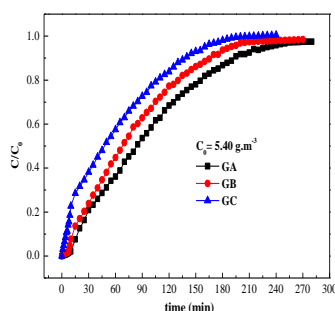


Figure 3. Breakthrough curves of cyclohexane on three kinds of silica gels

Evidently, under a given concentration, the breakthrough curves of cyclohexane vapors onto three silica gels are similar, however, GA shows longer adsorption breakthrough time (the outlet concentration is equal to 90 percent of the inlet concentration of cyclohexane) for cyclohexane vapors than GB and GC. For example, the adsorption breakthrough times of GA, GB and GC at the initial concentration of  $9.2 \text{ g} \cdot \text{m}^{-3}$  are 180 min, 135 min and 120 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 cyclohexane on three kinds of silica gels were shown in Table 2. It can be seen that the equilibrium adsorption capacities of cyclohexane increased with the increase of the initial concentration for a given silica gel type. For example, the equilibrium adsorption capacity is just  $41.9.0 \text{ mg} \cdot \text{g}^{-1}$  when the concentration is  $2.1 \text{ g} \cdot \text{m}^{-3}$  for GA, however, the equilibrium adsorption capacity increases to  $184.8 \text{ mg/g}$  at the initial concentration of  $21.2 \text{ g} \cdot \text{m}^{-3}$ . Moreover, the order of the equilibrium adsorption capacity of cyclohexane is GA, GB and GC for a given initial concentration. For example, the equilibrium adsorption capacities of cyclohexane for GA, GB and GC are  $168.5 \text{ mg} \cdot \text{g}^{-1}$ ,  $91.7 \text{ mg} \cdot \text{g}^{-1}$  and  $85.7 \text{ mg} \cdot \text{g}^{-1}$  at the initial concentration of  $16.3 \text{ g} \cdot \text{m}^{-3}$ .

It is clearly shown in Figure 4 that the adsorption capacities of the GA and GB increased sharply with the increase of cyclohexane 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 cyclohexane vapors were much higher than GC. By comparison of the adsorption capacities of cyclohexane 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.

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

Concentration ( $\text{g} \cdot \text{m}^{-3}$ )	Adsorption capacities ( $\text{mg} \cdot \text{g}^{-1}$ )		
	GA	GB	GC
2.1	41.9	26.9	16.7
5.4	79.2	61.2	41.15
9.2	118.65	87.3	73.8
16.3	168.5	91.7	85.7

21.2

184.8

118.97

97.14

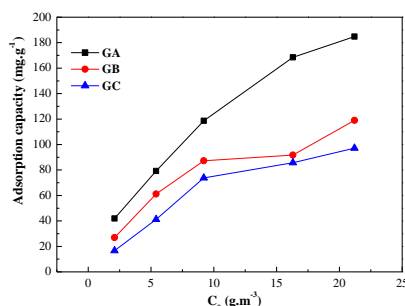


Figure 4. Adsorption isotherms of cyclohexane on three kinds of silica gels

### 3.4. Isotherm models

The adsorption equilibrium data of cyclohexane 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 cyclohexane 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 cyclohexane 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 Langmuir equation has a better correlation with experimental data than the Freundlich equation. The parameters  $K_F$  and  $n_f$  varied with different adsorbents; however, there was no apparent correlation between  $K_F$ ,  $n_f$ , 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 cyclohexane on three silica gels.

Adsorbent	Langmuir Model			Freundlich Model		
	$q_m$ (mg·g <sup>-1</sup> )	$B$ (m <sup>3</sup> ·g <sup>-1</sup> )	$R^2$	$K_f$ (m <sup>3nf</sup> ·mg·g <sup>nf+1</sup> )	$n_f$	$R^2$
GA	314.465	0.0676	0.9921	34.8225	0.5539	0.9884
GB	182.149	0.09021	0.9889	28.7496	0.4551	0.9268
GC	179.86	0.05594	0.9458	19.0962	0.5426	0.9407

### 4. Conclusions

Adsorption equilibrium and dynamics of cyclohexane 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 cyclohexane 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 cyclohexane 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 Langmuir model has a better correlation with experimental data than the Freundlich model for cyclohexane adsorption onto silica gels.

### Acknowledgments

This research was financially funded by Project of SINOPEC (Grant No 316049), National Natural Science Foundation of China (Grant No E080301).

### References

- [1] Melaina M W 2007 Energy Policy 35 4919.
- [2] Demirbas A 2004 J. Anal. Appl. Pyrol. 72 97.
- [3] Pakbin P, and Ning Z 2009 Environ. Sci. Technol. 43 4679.
- [4] Lin C W, and Chiang S B 2005 Environ. Monitor. Assess. 105 327.
- [5] Ghoshal A K, Manjare S D 2002 Loss Prevent. Proc. Ind. 15 413.
- [6] Zerbonia R A, Brockmann C M, and Peterson P R 2001 J. Air Waste Manage. Assoc. 51 1617.
- [7] Brennan J K, Bandosz T J, Thomson K T, and Gubbins K E 2001 Colloid Surf. A: Physicochem. Eng. Aspect 187 539.
- [8] Cosnier F, Celzard A, Furdin G, Bégin D, Maréché J F 2006 Adsorpt. Sci. Technol. 24 215.
- [9] Bradley R H 2011 Adsorpt. Sci. Technol. 29 1.
- [10] Inagaki M 2009 New Carbon Mater. 24 193.