Adsorption (2008) 14: 533–538
DOI 10.1007/s10450-008-9118-9

Adsorption dynamics of hydrogen sulfide in impregnated activated carbon bed

Do-Young Choi · Jae-Wook Lee · Seong-Cheol Jang · Byoung-Sung Ahn · Dae-Ki Choi

Received: 1 May 2007 / Revised: 4 March 2008 / Accepted: 20 March 2008 / Published online: 15 May 2008

Abstract Potassium iodide (KI) impregnated activated carbons were prepared and applied for the removal of hydrogen sulfide. The adsorption dynamics of the prepared adsorbents were investigated in fixed-bed column as functions of the concentration of hydrogen sulfide and oxygen, and relative humidity. It was found that the adsorption capacity was highly dependent on the oxygen concentration because of the chemical adsorption of hydrogen sulfide on KI impregnated activated carbon. The adsorbents before and after adsorption of hydrogen sulfide were characterized by BET, SEM and EDS analysis.

Keywords Adsorption · Hydrogen sulfide · Impregnation · Humidity · Activated carbon

1 Introduction

Hydrogen sulfide originating from various sources such as chemical processing gases from coal, natural gas and synthetic gas can be regarded as a major air pollutant (Ikeda et al. 1988). For the removal of hydrogen sulfide, many techniques such as amine absorption, liquid redox processes, adsorption process, and catalytic oxidation. Among them, activated carbon adsorption has been widely used for the pollution control of odor gases like hydrogen sulfide (Smisek and Cerny 1970; Bansal et al. 1988; Turk et al. 1989, 1993; Bandosz 1999). In especial, activated carbons treated with caustic materials such as KOH, NaOH and KI have been widely used for hydrogen sulfide adsorption (Ikeda et al. 1988; Takeuchi et al. 1999; Lee and Reucroft 1999). Potassium iodide (KI) used as impregnant in this study has positioned itself as one of the promising chemical substances to increase removal efficiency of hydrogen sulfide by enhancing selective adsorptivity of hydrogen sulfide. It has been known that the increase in removal efficiency of hydrogen sulfide is caused by the changes in the surface functional groups of activated carbon due to the impregnation of KI and its catalytic action. Unfortunately, systematic studies on the surface chemistry and column dynamics of KI impregnated activated carbon for the removal of hydrogen sulfide has not yet been addressed.

This study focused on the adsorption column dynamics of KI impregnated activated carbon for the removal of hydrogen sulfide under key operating conditions such as concentrations of hydrogen sulfide and oxygen, and relative humidity. The adsorbents properties before and after adsorption of hydrogen sulfide were investigated by BET, SEM and EDS analysis.

2 Experimental

2.1 Materials

The KI impregnated activated carbon (KAEL-GAC, Korea) was used as the adsorbent material in this study. The surface area of the KI impregnated activated carbon used was 944 m^2/g and the pore size (0.36 nm) and pore volume (0.33 cm^3/g) were determined by nitrogen adsorption data. Prior to use, the samples were kept in a drying vacuum oven at 423 K for more than 24 hours to remove impurities.

D.-Y. Choi · S.-C. Jang · B.-S. Ahn · D.-K. Choi (✉)
Environment & Process Technology Division, Korea Institute of Science Technology, 39-1 Hawolgok-dong, Sungbuk-gu, Seoul 136-791, Korea
e-mail: dkchoi@kist.re.kr

J.-W. Lee
Department of Chemical and Biochemical Engineering, Chosun University, Gwangju 501-759, Korea

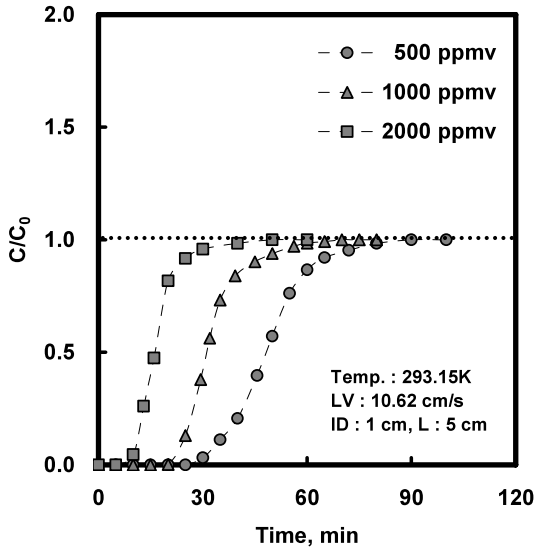

Fig. 1 Effect of hydrogen sulfide concentrations on KI impregnated activated carbon

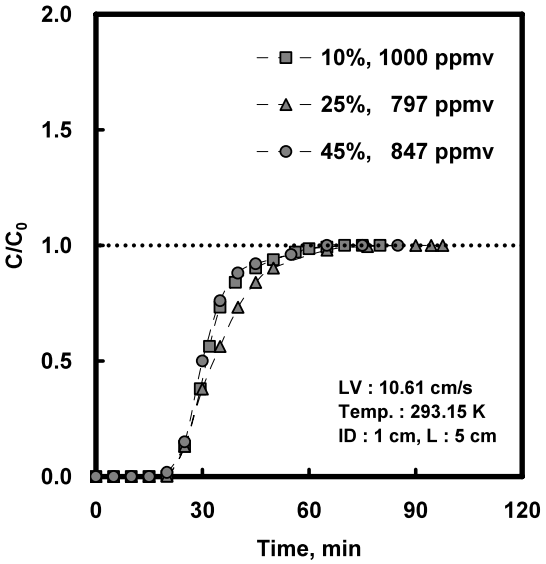

Fig. 2 Effect of relative humidity on KI impregnated activated carbon

2.2 Methods

2.2.1 H_2S breakthrough capacity

An H_2S simulated blend of cylinder gases was passed through a glass column 20 cm in length and 10 mm in diameter. The bottom of the adsorption column was packed with a layer of 15 cm glass beads. 5 to 10 grams of activated carbon (8–12 mesh) was packed in the column for each run. Cylinder gases of H_2S 20000 ppm) were certified by suppliers (Rigas Company, Korea). High purity nitrogen (99.95%) gas was used for the H_2S dilution. The flow-rate, which ranged from 500 ml/min, was controlled by a mass flow meter (Bronkhorst, HI-TEC). Oxygen was added to keep oxygen inlet concentration in anaerobic digester gas either 0.2 or 0.3 vol% (small concentrations were chosen arbitrary to have ratio oxygen to hydrogen sulfide bigger then 2 and they are non-interfering with the fuel cell operation). The breakthrough curves were measured at outlet hydrogen sulfide concentration and RH. The adsorption capacities of adsorbent in terms of milligrams of sulfur containing gases per gram of adsorbent are calculated by integration of the area above the breakthrough curves and from the H_2S concentration in the inlet gas, breakthrough time and mass of adsorbent. The concentration of H_2S was determined using a gas chromatography (HP5890, Japan) equipped with a SCD. The concentration of water vapor was determined using gas chromatography with a TCD and hygrometer (TCEPCL-332, Taiwan).

2.2.2 Characterization of carbon surface

Nitrogen isotherms were measured using an ASAP 2010 analysis (Micromeritics) at 77 K. Before the experiment, the samples were heated at 393 K and then outgassed at this temperature under a vacuum of 10^{-5} Torr to constant pressure. The isotherms were used to calculate the specific surface area (S_t), micropores volume (V_{mic}), and total pore volume (V_t). The content of sulfur in the original activated carbon and before and after adsorptive KI impregnated activated carbons was measured by SEM-EDS, XPS and AES/SAM. The morphologies of sample before and after adsorption were examined using SEM-EDS (HITACHI S-4100 WITH ACC'S) operated at 15 kV. It was used at magnifications of wide range (typically 50–50,000× for samples) to reveal fine detail in structure. The X-ray Photoelectron Spectroscopy (XPS) was used to characterize the chemical state of the KI impregnated activated carbon. The Auger Electron Spectroscopy/Scanning Auger Microscopy (AES/SAM, Perkin-Elmer, PHI model 670) survey scan and sputter depth profile were recorded using the following experimental conditions: primary beam energy $E_p = 10$ keV, primary beam current $I_p = 0.0099$ μA, and beam diameter 0.4 μm. The resolution of the cylindrical mirror analyzer was set to 0.6%. In this analysis, AES was used quantitatively to help determine the chemical state of potassium (K), oxygen (O), carbon (C), sulfur (S) on the KI impregnated activated carbon. SAM was applied for the morphology analysis of the KI impregnated activated carbon.

3 Results and discussion

The performance of KI impregnated activated carbons for the adsorption of hydrogen sulfide was examined using the breakthrough capacity measurement method described

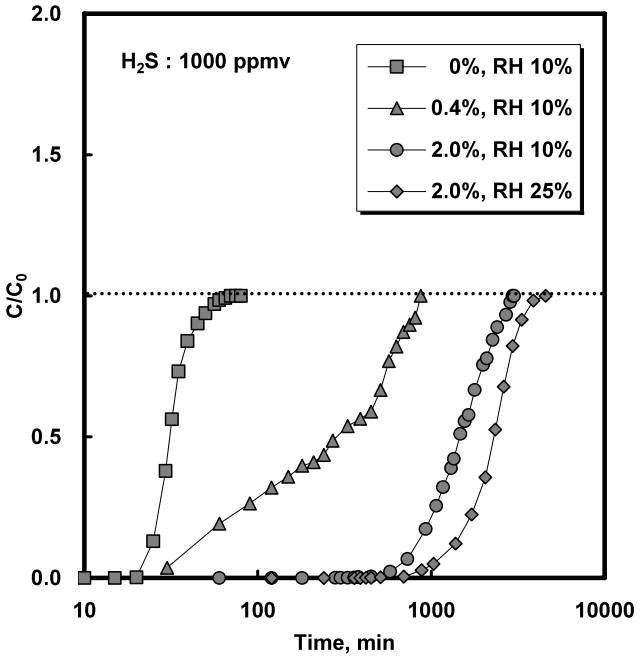

Fig. 3 Effect of oxygen content on KI impregnated activated carbon

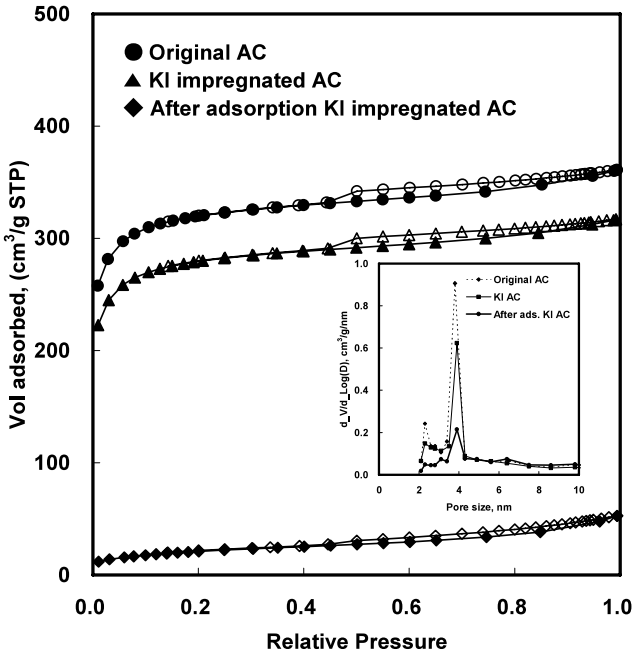

Fig. 5 Pore size distribution of original activated carbon and before and after adsorption adsorbents

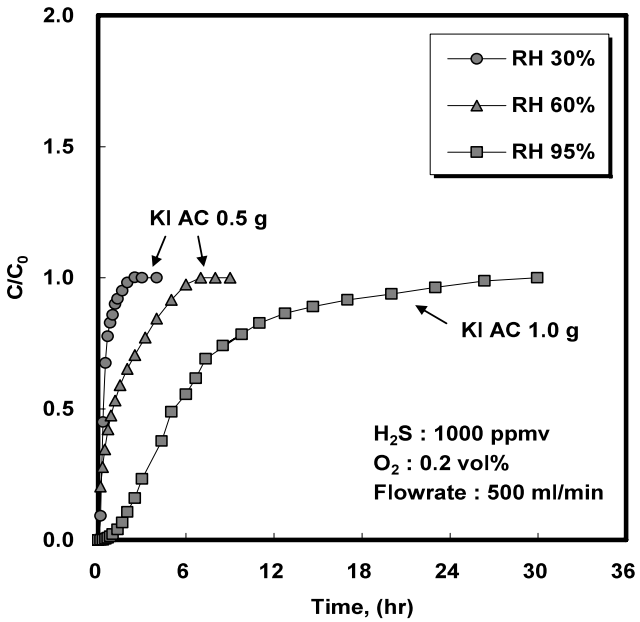

Fig. 4 Effect of relative humidity on KI impregnated activated carbon at 0.2 O_2 vol%

above section. Figures 1–4 show the H_2S breakthrough curves obtained at different experimental conditions (i.e., different hydrogen sulfide concentrations of 500, 1000, 2000 ppmv, relative humidity of 10–45% and oxygen content of 0–2%). The breakthrough capacities of adsorbents per mass of the carbon bed were calculated. Figure 1 illustrates the influence of hydrogen sulfide concentrations on the adsorption breakthrough curves. As expected, the breakthrough times are reduced by increasing the concentration. The adsorption capacity for the concentration of 500, 1000, 2000 ppmv was 8.96, 11.25 and 12.30 mg/g, respectively. Figure 2 shows the influence of the relative humidity (10–45%) on the adsorption breakthrough curves of hydrogen sulfide in the absence of oxygen. The adsorption capacity was found to be 11.25, 10.02 and 9.40 mg/g for 10%, 25% and 45% relative humidity, respectively. It was found that the adsorption capacity was not highly dependent on the relative humidity in the absence of oxygen. Figure 3 illustrates the influence of oxygen concentration levels (0–2 vol%) to determine the optimal oxygen concentration for the effective removal of H_2S. The inlet H_2O and H_2S concentrations in the inlet gaseous stream were kept constant at RH 10% and 1000 ppmv. The adsorption capacity was 11.3, 119 and 494 mg/g for 0%, 0.4% and 2% of oxygen. The adsorption capacity was strongly dependent on the concentration of oxygen. For comparison, the adsorption breakthrough curve for 25% relative humidity was obtained. The adsorption capacity of hydrogen sulfide at constant oxygen concentration of 2 vol% was considerably increased (i.e., 645 mg/g) with relative humidity. The reason for the increase in the removal efficiency of hydrogen sulfide on KI impregnated activated carbon is caused by changes in the surface functional group due to the impregnation of KI and the effect of chemical reaction. This result suggests that hydrogen sulfide and oxygen adsorb on the active sites of the solid surface and then catalytically react with formation of elemental sulfur and water, which are then adsorbed in micropores (Bagreev et al. 2005). Figure 4

Table 1 Physical properties of original AC and before and after adsorption KI impregnated AC

	Surface area m^2/g	Micropore area m^2/g	Micropore volume cm^3/g	Pore diameter nm
Original AC	1077	836	0.3893	3.62
KI AC	944	720	0.3338	3.58
After ads. KI AC	77	7	0.0019	5.06

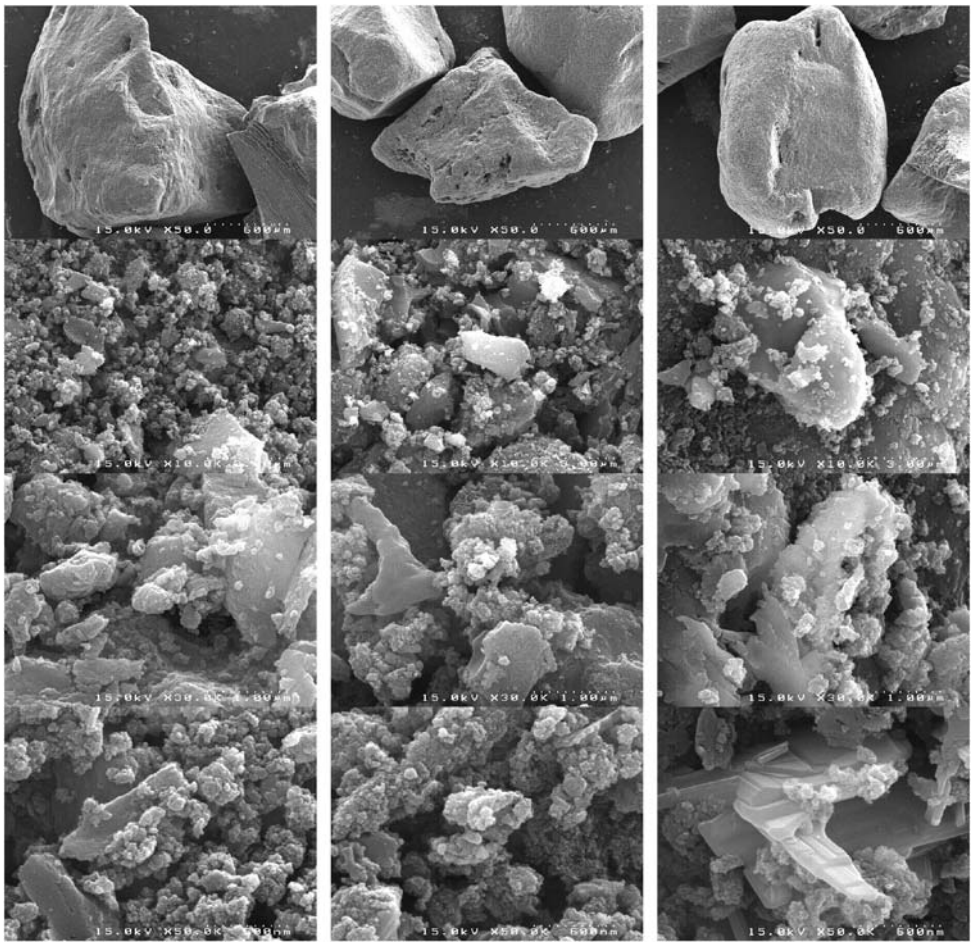

Fig. 6 SEM photograph of KI impregnated activated carbon (*left*: before adsorption, *center*: after adsorption (RH 30%, 0.2 O_2 vol%), *right*: after adsorption (RH 60%, 0.2 O_2 vol%))

illustrates the effect of relative humidity on the catalytic removal of H_2S when the H_2S and oxygen concentration levels in the inlet gas were kept constant at 1000 ppmv and 0.2 vol%. As expected, the adsorption amount was increased with relative humidity. The adsorption capacity was 45, 141 and 232 mg/g for RH 30%, 60% and 95%.

Before and after the adsorption of hydrogen sulfide, the KI impregnated activated carbons were characterized by BET and SEM-EDS analysis. Figure 5 shows the nitrogen adsorption isotherms with pore size distributions. The physical properties of adsorbents before and after adsorption are listed in Table 1. The reduction of the surface area after KI impregnation comes from the partial blocking of pores by potassium as reported by Illán-Goméz (Illán-Goméz et al. 1999) and co-workers. It is also observed that the surface area is remarkably reduced after the adsorption of hydrogen sulfide. Figure 6 shows the SEM images at the magnification of 50, 10,000, 30,000, and 50,000 for KI impregnated activated carbon before and after adsorption of hydrogen sulfide. On the other hand, the contents of elements before and after adsorption were analyzed by SEM-EDS. The results were listed in Table 2. As expected, the contents of sulfur increase with adsorption of hydrogen sulfide (Fig. 7). This result confirms that the adsorption of hydrogen sulfide on KI-impregnated activated carbon is caused by chemical adsorption.

Table 2 SEM-EDS analyzed results

Element	Before adsorption		After adsorption (RH 30%, O_2 0.2 vol%)		After adsorption (RH 60%, O_2 0.2 vol%)	
	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%
C	81.98	88.27	81.79	90.13	69.38	82.92
O	13.07	10.57	6.97	5.77	9.34	8.38
S	0.36	0.14	8.8	3.63	16.98	7.6
K	2.39	0.79	0.93	0.31	2.43	0.89
I	2.2	0.22	1.52	0.16	1.87	0.21
Totals	100		100		100	

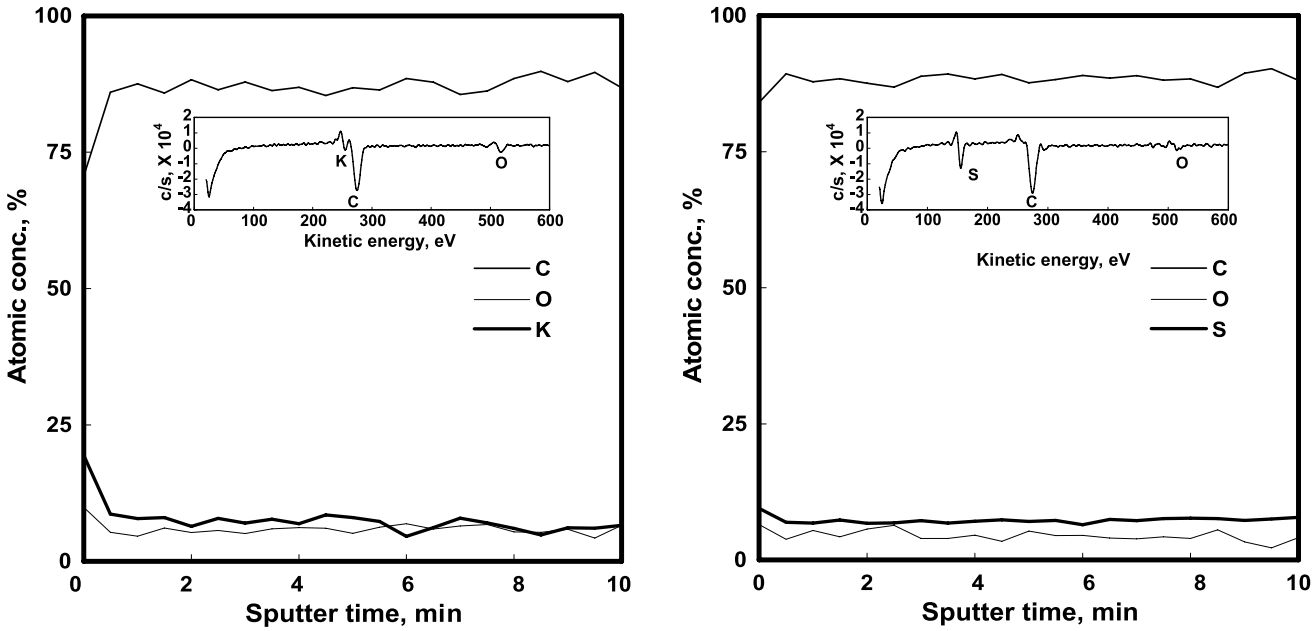

Fig. 7 AES depth profile after Matlab application for C, K, O and S (*left*: before adsorption, *right*: after adsorption)

4 Conclusions

The adsorption capacity of hydrogen sulfide adsorbed on KI impregnated activated carbon bed was 494 mg/g under the experimental conditions of the hydrogen sulfide concentration of 1000 ppmv, 0.2 O_2 vol%, and RH 10%. It was found that the adsorption capacity was strongly dependent on the oxygen concentration because of the chemical adsorption of hydrogen sulfide and the presence of water has a beneficial effect on KI impregnated activated carbon. Based on our experimental findings from fixed-bed dynamics, it can be concluded that KI impregnated activated carbon loaded with hydrogen sulfide could be successfully removed at relatively low temperature.

Acknowledgements This work was supported by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD, Basic Research Promotion Fund) (KRF-2006-351- D00007).

References

Bagreev, A., Katikaneni, S., Parab, S., Bandosz, T.J.: Desulfurization of digester gas: prediction of activated carbon bed performance at low concentrations of hydrogen sulfide. Catal. Today **99**, 329–337 (2005)

Bandosz, T.J.: Effect of pore structure and surface chemistry of virgin activated carbons on removal of hydrogen sulfide. Carbon **37**, 483–491 (1999)

Bansal, R.C., Donnet, J.B., Stoeckli, F.: Active Carbon. Marcel Dekker, New York (1988)

Ikeda, H., Asaba, H., Takeuchi, Y.: Removal of H_2S, CH_3SH and $(CH_3)_3N$ from air by use of chemically treated activated carbon. J. Chem. Eng. Jpn. **21**(1), 91–97 (1988)

Illán-Goméz, M.J., Raymundo-Piñero, E., García-García, A., Brnadán, S., Linares-Solano, A., Salinas-Martínez de Lecea, C.: Catalytic NOx reduction by carbon supporting metals. Appl. Catal. B **20**, 267–275 (1999)

Lee, W.H., Reucroft, P.J.: Vapor adsorption on coal- and wood-based chemically activated carbons (III) NH_3 and H_2S adsorption in the low relative pressure range. Carbon **37**, 21–26 (1999)

Smisek, M., Cerny, S.: Activated Carbon. Elsevier, Amsterdam (1970)

Takeuchi, Y., Hino, M., Yoshimura, Y., Otowa, T., Izuhara, H., Nojima, T.: Removal of single component cholrinated hydrocarbon vapor by activated carbon of very high surface area. Sep. Purif. Technol. **15**, 79–90 (1999)

Turk, A., Sakalis, E., Lessuck, J., Karamitsos, H., Rago, O.: Ammonia injection enhances capacity of activated carbon for hydrogen sulfide and methyl mercaptan. Environ. Sci. Technol. **23**, 1242–1245 (1989)

Turk, A., Mahmood, K., Mozaffari, J.: Activated carbon for air purification in New York City's sewage treatment plants. Water Sci. Technol. **27**(7/8), 121–126 (1993)