

## Easy Route to Modified Activated Carbon Honeycombs for Removal of Methyl Mercaptan

HEE-SEUNG YOON<sup>1,2</sup>, SEUNGKON RYU<sup>1</sup>, WON-CHUN OH<sup>2,\*</sup> and FENG-JUN ZHANG<sup>2,3</sup>

<sup>1</sup>Department of Chemical Engineering, Chungnam National University, Yuseung, Daejeon, South Korea

<sup>2</sup>Department of Advanced Materials & Engineering, Hanseo University, Seosan-si, Chungnam 356-706, South Korea

<sup>3</sup>School of Materials and Chemical Engineering, Anhui University of Architecture, Hefei 230022, Anhui Province, P.R. China

\*Corresponding author: Fax: +82 041 6883352; E-mail: wc\_oh@hanseo.ac.kr

(Received: 27 January 2011;

Accepted: 12 October 2011)

AJC-10493

In this paper, removal efficiencies of methyl mercaptan on virgin activated carbon honeycomb and surface modified activated carbons honeycombs using NaOH, CuSO<sub>4</sub> and MnSO<sub>4</sub> solutions were studied. The activated carbons were characterized by nitrogen adsorption, XRD, SEM, TEM and adsorption tests. The treatment of NaOH, CuSO<sub>4</sub> and MnSO<sub>4</sub> solutions on the activated carbon significantly enhanced the adsorption capacity of methyl mercaptan, despite a notable decrease in microporosity for the case of MnSO<sub>4</sub> modified samples. Among the three treatments, copper sulfate modified activated samples have the best results. It is likely that copper sulfate may act as adsorption site for methyl mercaptan.

**Key Words:** Methyl mercaptan, Activated carbon, Honeycomb, Removal efficiency.

### INTRODUCTION

Methyl mercaptan (CH<sub>3</sub>SH) is a volatile organic compound containing sulphur. It is a colourless gas with a smell like that of rotten or cooked cabbage. Methyl mercaptan is known to be produced in aerobic or anaerobic environments, mainly from natural sources, petroleum refining processes, the wood-pulping industry, sewage treatment and energy-related activities. The presence of a very little amount of CH<sub>3</sub>SH in air (minimum odor threshold: about 5 ppm) makes uncomfortable<sup>1</sup>. The removal of CH<sub>3</sub>SH in air is important for our comfortable life. To remove methyl mercaptan from air, activated carbons are widely applied as one of the effective adsorbents<sup>2,3</sup>. In these applications of activated carbons, methyl mercaptan is physically or chemically adsorbed on activated carbons.

In general, the adsorption of organic compounds by activated carbons is largely influenced by surface characteristics such as pore size and pore volume<sup>4,7</sup>, surface oxygen groups<sup>5</sup>, surface pH 6 and the affinity of carbon to adsorb water<sup>4,6</sup>. Because methyl mercaptan molecule is small in size, surface property in pore characteristics is supposed to play an important role in the adsorption of methyl mercaptan. It was reported that the oxidation of methyl mercaptan to dimethyl disulfide takes place at the surface of activated carbons having functional groups such as carboxyl group in dry/wet air<sup>8</sup>. In reference to the surface modification of activated carbons, the introduction of carboxyl groups and amino groups and the preparation of

functional group-free activated carbons have been reported<sup>9-11</sup>. It has been pointed out in the literature that different functional groups on the surface and/or metal ions such as iron ion can catalyze the oxidation of mercaptans to disulfides<sup>12-14</sup>. Moreover, the impregnation of activated carbons with various chemicals such as potassium iodide, potassium iodate, potassium carbonate and ammonia enhances their sorption capacity several times<sup>13</sup>. The modification of the carbon surface has received considerable attention as a method to enhance the adsorption capacity of volatile organic compounds on activated carbon. The functional groups of the carbon surface can be modified either by the chemical and thermal treatments or by the impregnation method.

Although studies of activated carbons to remove methyl mercaptan are widely described in literature. But to our best of knowledge, no similar approach has been described in the bibliography devoted to the technology of activated carbon honeycombs to remove methyl mercaptan. In this study, an easy route to modify the activated carbon honeycombs for removal of methyl mercaptan was explored. Activated carbon honeycombs were prepared by molding of honeycombs from a mixture of activated carbon, polyethylene and some metal compounds, followed by thermal treatments at low temperature. The main objective of this research is to study the removal efficiency of activated carbon honeycombs for methyl mercaptan and to determine the role of NaOH, CuSO<sub>4</sub> and MnSO<sub>4</sub> on the surface of activated carbon in the adsorption of methyl mercaptan and to discover the effect of metal compound

loading on the adsorption capacity of methyl mercaptan. Removal characteristics of methyl mercaptan on activated carbon honeycombs were studied by using gas chromatography.

## EXPERIMENTAL

Raw activated carbon obtained from Samcheonri (Korea) was used in the present investigations. Before mixing, the raw activated carbon was dried for overnight at 110 °C. After mixing, the samples were dried at 135 °C for overnight. Copper sulfate modified activated carbons (having a  $\text{CuSO}_4$  content of 2, 5 and 10 wt %, respectively) were prepared by mixture of the raw activated carbon with an aqueous solution of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (Aldrich) following the incipient wetness method. Manganese sulfate modified activated carbons (having a  $\text{MnSO}_4$  content of 2, 5 and 10 wt %, respectively) were prepared by mixture of the raw activated carbon with an aqueous solution of  $\text{MnSO}_4$  (Aldrich) with the similar method. With comparison, NaOH with different content of (having a NaOH content of 2, 5 and 10 wt %, respectively) modified the raw activated carbon were also studied at the same time, respectively.

**Preparation of activated carbon honeycombs:** Briefly, the surface modified activated carbon are milled and sieved to particles size below 0.14 mm and then mixed with certain amounts of polyethylene in a blender to form homogeneous dough. This dough is extruded through a die into a honeycomb structure with a wall thickness of 2 mm and a cell density of 9 cells per square inch (cpsi). Subsequently, the green monoliths are dried in air at 145 °C for 4 h and cooled at room temperature for 1 h. A photograph of the prepared activated carbon honeycombs structure is shown in Fig. 1.

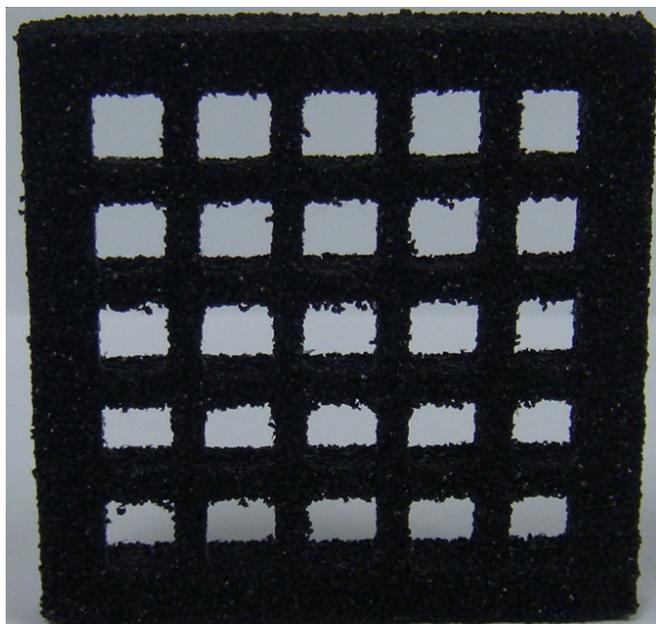


Fig. 1. Photograph of activated carbon honeycomb monolith; Sample cell density, 9 cpsi; wall thickness, 2 mm

**Characterization of samples:** Pore characteristics of the samples were measured by  $\text{N}_2$  adsorption at 77 K using an automatic adsorption system (Micromeritics ASAP 2010). Prior to the measurement, the monolithic samples were pulverized to sizes smaller than 1 mm and degassed overnight at

300 °C in a vacuum oven. XRD technique was used for crystal phase identification. XRD patterns were obtained at room temperature with a diffractometer Shimata XD-D1 (Japan) using  $\text{Cu K}\alpha$  radiation. SEM was used to observe the surface state and porous structure of the surface modified activated carbon honeycomb composites using a scanning electron microscope (JOEL, JSM-5200, Japan). TEM (JEOL, JEM-2010, Japan) at an acceleration voltage of 200 kV was used to investigate the size and distribution of the metal particles deposit on the activated carbon surface of various samples. TEM specimens were prepared by placing a few drops of the sample solution on a carbon grid.

**Evaluation of adsorption performance:** The analysis was performed on a Hewlett-Packard (Agilent Technologies, Palo Alto, CA, USA) HP 7890 series GC, equipped with PFPD and split/splitless injector. The chromatographic data were recorded using HP Chemstation software, which was controlled by Microsoft Windows NT. The analytes were separated on a 30 m  $\times$  0.32 mm i.d.  $\times$  0.25  $\mu\text{m}$  film thickness DB-5 gas chromatographic column (J & W Scientific, Folsom, CA, USA) coated with polyethylene glycol with the following oven temperature program: the initial temperature was 50 °C, was increased from 50 to 140 °C at a rate of 10 °C  $\text{min}^{-1}$  in 2 min and then raised to 250 °C at a rate of 40 °C  $\text{min}^{-1}$  and finally held for 15 min. The injector and detector temperatures were 250 and 280 °C, respectively. The injection port was operated at a split ratio of 1:2. The gas flow rates were as follows: carrier (helium, 99.999 %) 2.0  $\text{mL min}^{-1}$ , make-up (nitrogen, 99.999 %) 30  $\text{mL min}^{-1}$  and hydrogen and air (for PFPD) 30 and 300  $\text{mL min}^{-1}$ , respectively. Schematic diagram of activated carbon honeycomb adsorption system was shown in Fig. 2.

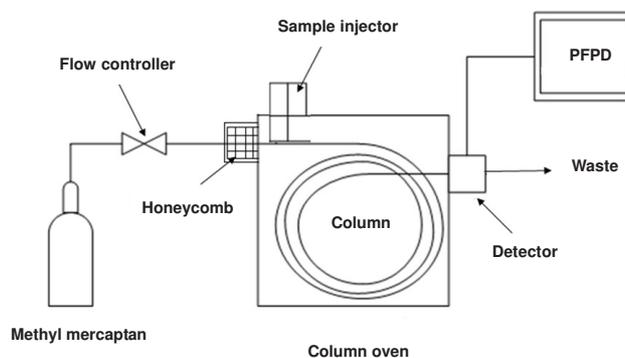


Fig. 2. Schematic diagram of activated carbon honeycomb adsorption system

## RESULTS AND DISCUSSION

The values of BET surface areas of the powdery activated carbons are shown in Table-1. Table-1 shows that the BET surface areas of copper sulfate-modified activated carbon almost not changed in the range of 1120-1130  $\text{m}^2/\text{g}$  with an increase of copper sulfate concentration, while the BET surface areas of manganese sulfate-modified activated carbon decreased gradually from 730 to 810  $\text{m}^2/\text{g}$  with an increase of manganese sulfate concentration. It was considered that Mn modified activated carbon particles were heavily agglomerated to form larger clusters, which these results can be seen clearly from SEM and TEM images obtained from powdered manganese

sulfate-modified composites. It was suggested that some porosity was developed during the surface treatment. It was considered that the composites are micropore materials majorly including a lot of micropores. Adsorption isotherms of non modified activated carbon and surface modified activated carbon composites are shown in Fig. 3. Fig. 3 shows an idealized form of the adsorption isotherm for physisorption on the composites. The formation of type II (classified with an IUPAC) adsorption isotherms confirmed a mixed micro-and mesoporous texture. There are almost not seen the different of the raw activated carbon and surface modified activated carbon composites.

TABLE-1  
TEXTURAL STUDY OF NON MODIFIED ACTIVATED CARBON  
AND SURFACE MODIFIED ACTIVATED CARBON

	BET [m <sup>2</sup> /g]	Micro pore volume [cm <sup>3</sup> /g]	Average pore diameter [Å]
As received	1230	0.5	18.9
B (2 wt %) AC	1220	0.5	18.6
B (5 wt %) AC	1230	0.51	18.6
B (10 wt %) AC	1226	0.51	18.2
Cu (2 wt %) AC	1220	0.51	18.9
Cu (5 wt %) AC	1160	0.48	18.9
Cu (10 wt %) AC	1060	0.44	19
Mn (2 wt %) AC	730	0.27	23
Mn (5 wt %) AC	730	0.22	24
Mn (10 wt %) AC	810	0.23	25.6

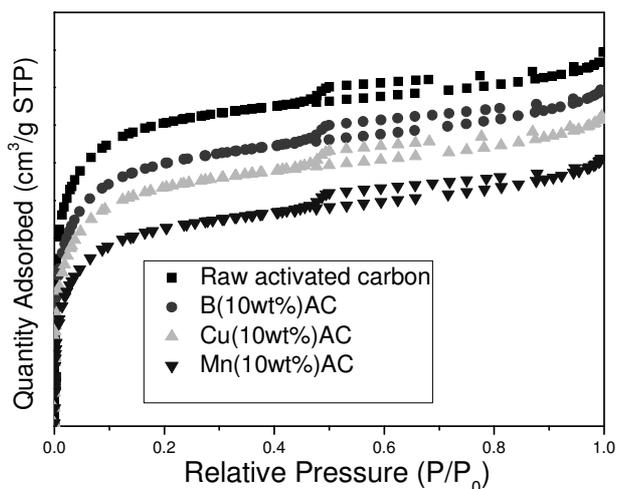


Fig. 3. Adsorption isotherms of non-modified activated carbon and surface modified activated carbon

XRD patterns of powdery activated carbon honeycombs are shown in Fig. 4. All the samples show two peaks at 23 and 43.5° (broad) corresponding to 002 and 100 bands, respectively. There are the peaks (002) and (100) in the XRD pattern of the raw-activated carbon. A similar effect has observed by Zhao *et al.*<sup>15</sup> graphitization process of activated carbon. For both peaks, intensity and width are almost not changed with an increase in metal content, any XRD patterns corresponding to copper compounds or manganese compounds are not detectable even at 10 wt% in CuSO<sub>4</sub> or MnSO<sub>4</sub> loading. Only activated carbon peaks are detected at all samples. This suggests that the copper compounds or manganese compounds on the activated carbon exist as amorphous materials<sup>3</sup>.

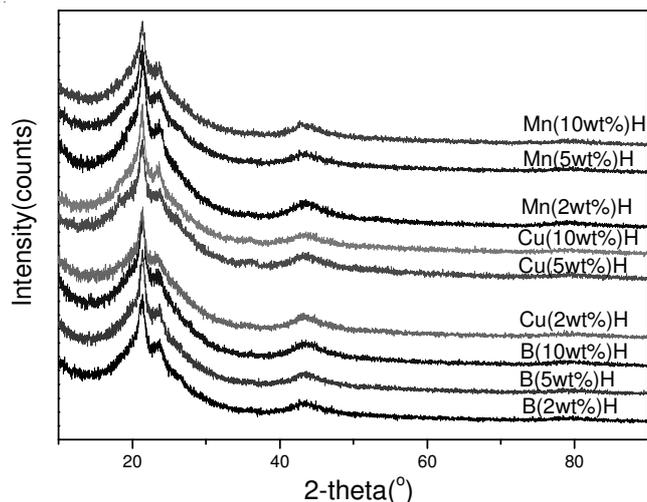
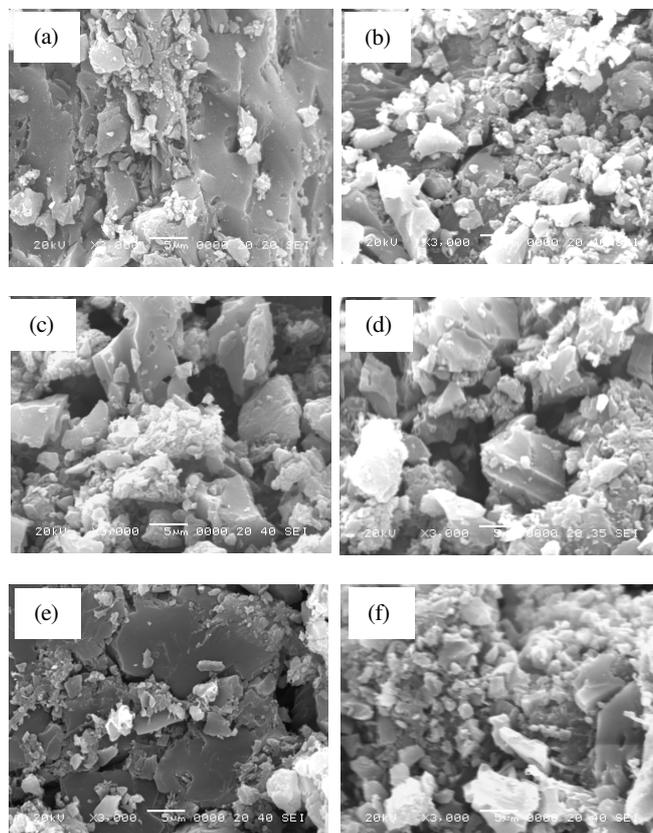


Fig. 4. XRD patterns of powdery activated carbon honeycombs

Figs. 5(a-c) show the 3000 × magnified SEM photos of the powdery activated carbon honeycombs. As the SEM micrographs show, it is difficult to see the boundary between the carbon and the metal particles. Fig. 5a shows that NaOH modified activated carbon honeycombs had some large holes and walls within which there were many tiny holes. NaOH etching occurred on the surface. For CuSO<sub>4</sub> and MnSO<sub>4</sub> modified samples, in Figs. 5b and c, showed severe erosion on the mouths of both the huge and tiny holes within walls. These erosions increased with an increase of CuSO<sub>4</sub> or MnSO<sub>4</sub> contents. Thus, the BET specific surface area and the total pore volume decreased, resulting in a decreased micro pore volume. This is consistent with the data of Table-1.



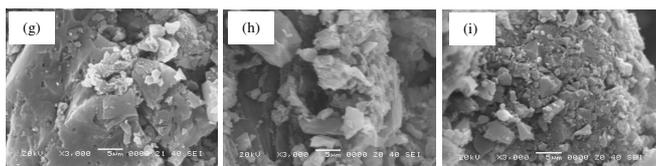


Fig. 5. SEM photographs of powdery activated carbon honeycombs; (a) B (2 wt%) H, (b) B (5 wt%) H, (c) B (10 wt%) H, (d) Cu (2 wt%) H, (e) Cu (5 wt%) H, (f) Cu (10 wt%) H, (g) Mn (2 wt%) H, (h) Mn (5 wt%) H and (i) Mn (10 wt%) H

Fig. 6 shows the TEM images of the powdery activated carbon honeycombs. Fig. 6(a) shows some grains of the NaOH-modified activated carbons honeycombs. There are well-dispersed particles for the NaOH-modified activated carbons and Figs. 6(b) and (c) correspond to the distribution of the  $\text{CuSO}_4$  and  $\text{MnSO}_4$  modified samples, respectively, with the same grains. However, partial clusters of packed particles can be seen in the samples of the  $\text{CuSO}_4$  and  $\text{MnSO}_4$  modified samples. All the samples are indeed homogeneously distributed in the form of particles. The size of the particles are typically 25 nm or lower, except the  $\text{CuSO}_4$  modified samples. This is consistent with the results of textural study. The particles aggregated more rapidly using copper and manganese sulfate-modified activated carbons and then confined mesopore development.

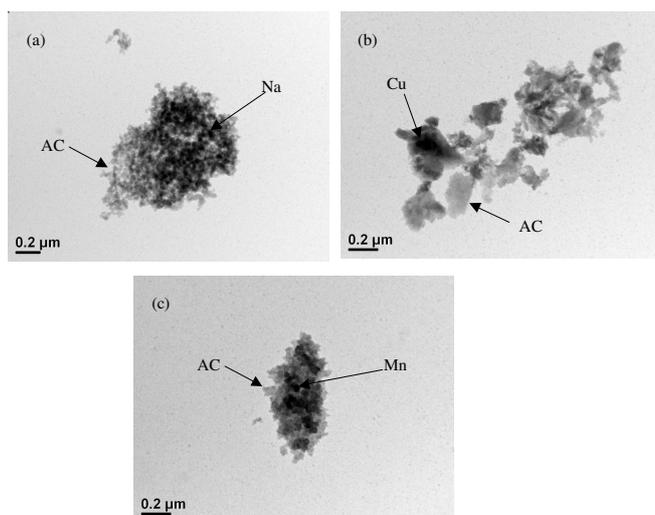


Fig. 6. TEM photographs of powdery activated carbon honeycombs; (a) B (10 wt%) H, (b) Cu (10 wt%) H and (c) Mn (10 wt%) H

Fig. 7 shows the removal efficiency of methyl mercaptan on the NaOH-modified activated carbons honeycombs as a function of time. The amounts of methyl mercaptan adsorbed on raw activated carbon honeycomb (RH) and NaOH-modified activated carbon honeycombs decreased with time, the adsorbed amounts of methyl mercaptan on RH is lower than that on NaOH-modified activated carbon honeycombs and after 170 min, the removal efficiency of the RH for methyl mercaptan is near zero. However, for NaOH-modified activated carbon honeycombs, except the sample B(2 wt%) H, the removal efficiency still maintain higher lever (over 90 %) even 200 min later. Moreover, the removal efficiency of NaOH-modified activated carbon honeycombs for methyl mercaptan increased with an increase of concentration of NaOH solution and the

removal efficiencies of B(5 wt%) H and B(10 wt%) H are much analogue. The almost methyl mercaptan adsorbs physically, *e.g.*, by a dispersive force, on the surface of surface-modified activated carbon honeycombs. On the other hand, the amounts of methyl mercaptan adsorbed on NaOH-modified activated carbons increased with time. In the case of NaOH-modified activated carbon honeycombs, the adsorption of methyl mercaptan increased with concentration of NaOH solutions used for treatment. Since the amounts of basic groups of activated carbons increase with concentration of NaOH solutions, the amounts of methyl mercaptan adsorbed are supposed to be influenced by basic groups. Therefore, other factors, *e.g.*, hydrogen bonding between carboxyl groups and thiol groups of methyl mercaptan rather than oxidation of methyl mercaptan are supposed to play a role in increase in adsorption of methyl mercaptan.

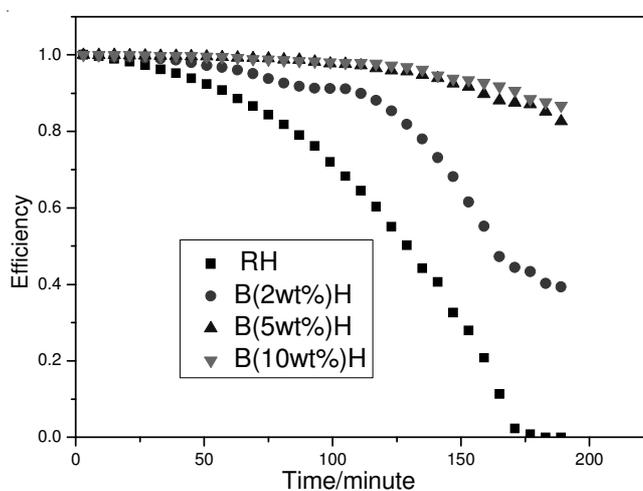


Fig. 7. Removal efficiency for methyl mercaptan on RH and activated carbons honeycombs modified with NaOH

Fig. 8 shows the removal efficiency of methyl mercaptan on the copper sulfate-modified activated carbons honeycombs as a function of time. The amounts of methyl mercaptan adsorbed on raw activated carbon honeycomb (RH) decreased with time. However, the removal efficiency of methyl mercaptan on copper sulfate-modified activated carbon honeycombs maintain higher lever, even at 100 % for 200 min for the Cu (5 wt %) H and Cu (10 wt %) H. Moreover, the removal efficiency of copper sulfate-modified activated carbon honeycombs for methyl mercaptan increased with an increase of  $\text{CuSO}_4$  content and the removal efficiencies of Cu (5 wt %) H and Cu (10 wt %) H are much similar. Surface-treatment of copper sulfate leads to an enhancement of the adsorbed amount of methyl mercaptan, despite a notable decrease in microporosity. The reason is likely that  $\text{CuSO}_4$  may act as new adsorption site for methyl mercaptan. The adsorbed amount of methyl mercaptan on the copper sulfate-modified activated carbon increases, as  $\text{CuSO}_4$  concentration increases in 2-10 wt %  $\text{CuSO}_4$  loading. Starting at 2 wt % in  $\text{CuSO}_4$  loading, however, the adsorbed amount of methyl mercaptan on the activated carbon decreases gradually with time. It seems that a decrease in the degree of copper sulfate dispersion and an accessibility of small pores may lead to the decrease in the adsorbed amount of methyl mercaptan.

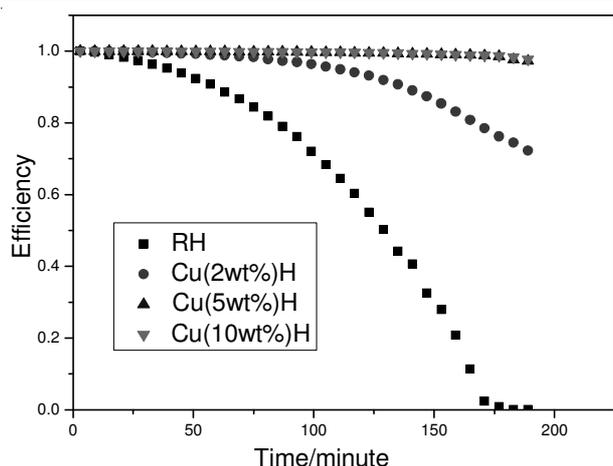
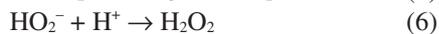
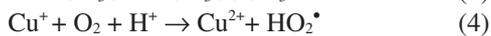
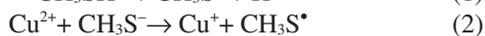


Fig. 8. Removal efficiency for methyl mercaptan on RH and activated carbons honeycombs modified with  $\text{CuSO}_4$

To explain the influence of copper, its catalytic redox abilities have to be explored. It is possible that besides the mechanism described above, the following reactions promoted by  $\text{Cu}^{2+}$  occur in the presence of moisture and oxygen form air:



As seen from the above listed reactions, the role of copper is to promote formation of thiolate radicals and reduction of oxygen resulting in the presence of very active superoxide species, which form radicals, either in wet or dry conditions of the methyl mercaptan removal process.

Fig. 9 shows the removal efficiency of methyl mercaptan on the manganese sulfate -modified activated carbons honeycombs as a function of time. The amounts of methyl mercaptan adsorbed on RH and manganese sulfate-modified activated

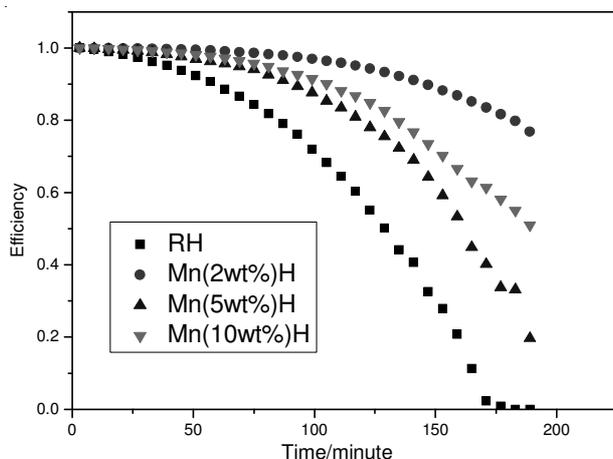


Fig. 9. Removal efficiency for methyl mercaptan on raw activated carbons honeycomb and activated carbons honeycomb modified with  $\text{MnSO}_4$

carbon honeycombs decreased with time, the adsorbed amounts of methyl mercaptan on RH is lower than that on manganese sulfate -modified activated carbon honeycombs. However, the removal efficiency of manganese sulfate -modified activated carbon honeycombs for methyl mercaptan decreased from 2 to 5 wt % of  $\text{MnSO}_4$  content and then increased from 5 to 10 wt % of  $\text{MnSO}_4$  content. And the removal efficiency of Mn (2 wt %) H is arrived at 80 % even 200 min later. Similar to the case of copper sulfate-modified activated carbons honeycombs, surface-treatment of manganese sulfate leads to an enhancement of the adsorbed amount of methyl mercaptan, despite a notable decrease in microporosity.

## Conclusion

This work demonstrated the efficient application of activated carbons for removal of methyl mercaptan. The results suggest that chemistry of the carbon surface is very important for the efficient removal of methyl mercaptan. The surface modified samples with NaOH,  $\text{CuSO}_4$  and  $\text{MnSO}_4$  solutions on the activated carbon honeycombs significantly enhanced the adsorption capacity of methyl mercaptan than that virgin activated carbon honeycomb. The adsorption of methyl mercaptan increased with concentration of NaOH solutions and the adsorbed amount of methyl mercaptan on the copper sulfate -modified activated carbon increases with concentration increases in 2-10 wt %  $\text{CuSO}_4$  loading. However, the removal efficiency of manganese sulfate-modified activated carbon honeycombs for methyl mercaptan decreased from 2 to 5 wt % of  $\text{MnSO}_4$  content and then increased from 5 to 10 wt % of  $\text{MnSO}_4$  content. Among the three treatments, copper sulfate modified activated samples have the best results.

## REFERENCES

1. H. Tamai, H. Nagoya and T. Shiono, *J. Colloid. Interf. Sci.*, **300**, 814 (2006).
2. H. Katoh, I. Kuniyoshi, M. Hirai and M. Shoda, *Appl. Catal. B. Environ.*, **6**, 255 (1995).
3. D.J. Kim and J.E. Yie, *J. Colloid. Interf. Sci.*, **283**, 311 (2005).
4. S. Bashkova, A. Bagreev and T.J. Bandosz, *Environ. Sci. Technol.*, **36**, 2777 (2002).
5. S. Bashkova, A. Bagreev and T.J. Bandosz, *Ind. Eng. Chem. Res.*, **41**, 4346 (2002).
6. A. Bagreev, S. Bashkova and T.J. Bandosz, *Langmuir*, **18**, 1257 (2002).
7. S. Bashkova, A. Bagreev and T.J. Bandosz, *Langmuir*, **19**, 6115 (2003).
8. A. Bagreev, S. Bashkova and T.J. Bandosz, *Langmuir*, **18**, 8553 (2002).
9. L. Li, P.A. Quinlivan and D.R.U. Knappe, *Carbon*, **40**, 2085 (2002).
10. M.F.R. Pereira, S.F. Soares, J.J.M. Orfao and J.L. Figueiredo, *Carbon*, **41**, 811 (2003).
11. W. Yantasee, Y. Lin, G.E. Fryxell, K.L. Alford, B.J. Busche and C.D. Johnson, *Ind. Eng. Chem. Res.*, **43**, 2759 (2004).
12. S. Tanada, K. Boki and K. Matsumoto, *Chem. Pharm. Bull.*, **26**, 1527 (1978).
13. C.S. Shin, K.H. Kim, S.H. Yu and S.K. Ryu, Presented at Seventh International Conference on Fundamental of Adsorption, Nagasaki, Japan, May 20-25 (2001).
14. M. Ziolk and P. Decyk, *Langmuir*, **15**, 5781 (1999).
15. J.G. Zhao, L.X. Yang, F.Y. Li, R.C. Yu and C.Q. Jin, *Carbon*, **47**, 744 (2009).