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# Adsorption–desorption characteristics of VOCs over impregnated activated carbons

Ki-Joong Kim [a], Chan-Soon Kang [a], Young-Jae You [a], Min-Chul Chung [a],
Myung-Wu Woo [a], Woon-Jo Jeong [b], Nam-Cook Park [c], Ho-Geun Ahn [a,*]

[a] *Department of Chemical Engineering, Sunchon National University, 315 Maegok-dong,*
*Suncheon-si, Jeonnam 540-742, Republic of Korea*
[b] *Department of Information and Communications, Chosun College Science and Technology,*
*290 Seosuk-dong Dong-gu Gwangju, Republic of Korea*
[c] *Department of Chemical Engineering, Chonnam National University, 300 Yongbong-dong, Buk-gu,*
*Gwangju 500-757, Republic of Korea*

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## Abstract

An activated carbon was modified by impregnating with various acids or bases. The effects of adsorption capacity and impregnated contents on the textural properties of the impregnated activated carbons (IACs) were investigated. Furthermore, VOC adsorption and desorption experiments were carried out to determine the relationship between the adsorption capacity and chemical properties of the adsorbents. The effects of various parameters such VOC concentration, aspect ratio, flow rate, and impregnated contents were investigated. High adsorption capacity for the selected VOCs was obtained over 1 wt.% $H_3PO_4$/AC (1 wt.% PA/AC). As a result, IAC was found to be effective for VOC removal by adsorption with the potential for repeated use through desorption by simple heat treatment.

*Keywords:* VOCs; Impregnated activated carbon; Adsorption isotherm; TPD

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## 1. Introduction

Volatile organic compounds are one of the most common pollutants emitted by the chemical process industries, which include most solvents such as thinner, degreasers, cleaners, lubricants, and liquid fuels. VOCs are pollutants because they almost always contribute to ozone formation, and in addition are odorous and sometimes toxic. In other words, they react in sunlight with other pollutants such as nitrogen oxides to form ozone and the other compounds (known as photochemical oxidants), which make up photochemical smog.

Several techniques for VOCs have been investigated such as thermal incineration, catalytic oxidation, condensation, absorption, bio-filtration, adsorption, and membrane separation [1]. VOCs are present in many types of waste gases and are often removed by adsorption [2,3]. Activated carbon (AC) is commonly used as adsorbents of gases and vapors because of their developed surface area and large pore volumes [4]. Molecules, when adsorbed on the carbon surface, are strongly held by adsorption forces that are enhanced in small pores [5]. Modification and impregnation techniques for AC were used to increase the surface adsorption and hence removal capacity, as well as to improve the selectivity to organic compounds [6,7].

Also, a novel hybrid system processes were suggested as an effective control method for the VOCs removal of very low concentration [8,9]. A new hybrid system was intended to develop by combining adsorption–desorption and catalytic oxidation in a single bed. However, this system usually consists of adsorption periods being periodically followed by regeneration periods where the packed adsorbent is in situ desorbed by heating. If a continuous purification process of waste gases is required, a two beds arrangement has to be considered [10].

In this study, IAC were prepared with various acids and bases for application to adsorption part of the hybrid system. The surface properties of IAC and its adsorption capacity for VOCs were investigated. The effects of concentration, aspect ratio, flow

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* Corresponding author. Tel.: +82 61 750 3583; fax: +82 61 750 3580.
*E-mail address:* hgahn@sunchon.ac.kr (H.-G. Ahn).

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rate, and impregnated contents on adsorption performance were studied. Furthermore, adsorption and desorption of VOCs were carried out to evaluate the adsorption capacity and desorption characteristics after saturated adsorption.

## 2. Experimental

### 2.1. Preparation of IAC

The AC used in this study was a granular type (30–35 mesh) prepared from coconut shell. The purified AC (PAC) was prepared by boiling the AC for 5 h in a water bath. The acidic and alkaline solutions for preparation of IACs were made with $HNO_3$ (NA), $H_2SO_4$ (SA), HCl (HA), $H_3PO_4$ (PA), $CH_3COOH$ (AA), KOH (PH), and NaOH (SH). The AC was impregnated into each solution according to the conventional wet process. The obtained AC after evaporating was dried in oven at 100 °C, and stored in a desiccator. Before adsorption experiment, the IAC was pretreated for 1 h in an adsorbent column of 250 g, and 0.2 g of the adsorbent was used for each experiment.

The specific surface area of the adsorbents was measured by BET method (ASAP 2010, Micrometrics, USA). The surface of IAC was observed through scanning electron microscope (SEM, Hitachi, Japan) after being impregnated with acids or alkalis.

### 2.2. Adsorption and desorption of VOCs

Experimental apparatus for measuring the amount of VOCs adsorbed is shown in Fig. 1. The variation of concentration in the course of adsorption was continuously obtained as thermal conductivity detector (TCD) signal. The amount of VOCs adsorbed were calculated by cutting and weighing method on basis of TCD signal that was obtained after starting the adsorption of VOC on the adsorbent in a fixed bed. Model gases were BTX (benzene, toluene and *o*-, *m*-, *p*-xylene), alcohols (methanol, ethanol, *i*-propanol), and methylethylketone (MEK). All reagents for model gas were GR grade (Junsei Chem., 99.0–99.5%). The concentration of VOCs for adsorption were controlled by vaporizing VOCs in the saturator with helium, and maintained in the range of 10,000–15,000 ppm. The temperature in the saturator was maintained with a constant temperature vessel. Total VOC flow rate was mainly 40 ml/min as it passed through a U-type adsorbent column (i.d. 1/4″, ss). The temperature of the stream line was maintained to 80 °C by using heating band and insulating material, and adjusted by an on/off temperature controller. The VOC concentrations were monitored with (TCD) of gas chromatograph (GC). In addition, the IAC desorption characteristics were investigated by temperature programmed desorption (TPD) technique.

## 3. Results and discussion

### 3.1. Impregnated effect of activated carbon

The specific surface areas of 5 wt.% IACs prepared in this study are shown in Table 1, and SEM photographs of acid- or alkali-impregnated AC are shown in Fig. 2. Purified AC showed a pure surface, which was due to the removal of particulate powder from the pore and surface. The pore was not observed on the surface of IAC with alkali, which was attributed to the pore being blocked by surface deposition of alkali, thereby greatly decreasing the BET surface area.

Both surface and pore structure of 5 wt.% IAC with acids were partially destroyed or enlarged. In addition, impregnating

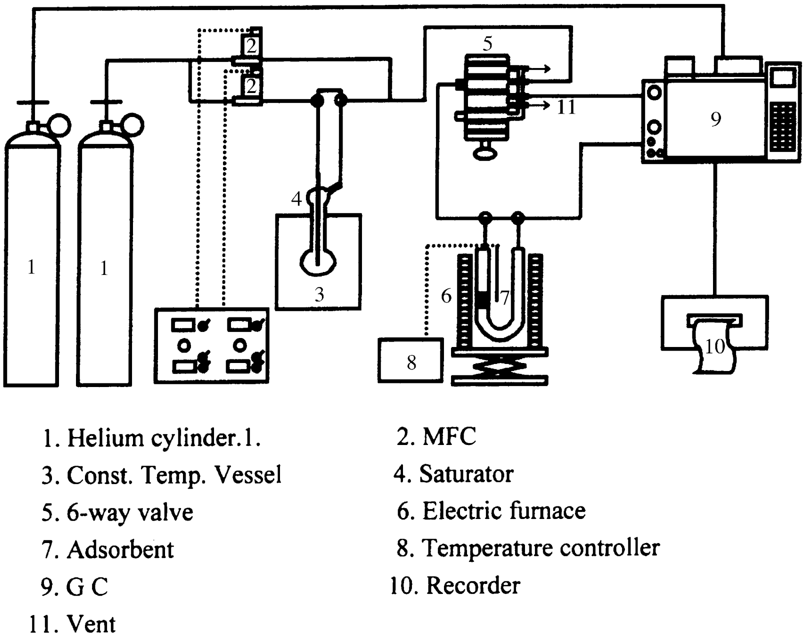

Fig. 1. Schematic diagram of experimental apparatus for measuring the amounts of VOCs adsorbed.

Table 1
The prepared impregnated activated carbons (5 wt.% IAC) and their specific surface area

| Adsorbents | Nomenclature | Specific surface area ($m^2/g$) |
|---|---|---|
| Purified AC | PAC | 892 |
| $CH_3COOH$/AC | AA/AC | 894 |
| $HNO_3$/AC | NA/AC | 867 |
| HCl/AC | HA/AC | 718 |
| $H_2SO_4$/AC | IAC SA/AC | 840 |
| $H_3PO_4$/AC | PA/AC | 719 |
| KOH/AC | PH/AC | 668 |
| NaOH/AC | SH/AC | 636 |

agents were not found on the surface as in the case of IAC with alkali. In the case of acid treatment, the impregnation might occur through alteration in the surface functional group chemically rather than physically. Interestingly, the BET surface area of 5 wt.% PA/AC was greatly decreased although the BET surfaces of another 5 wt.% IAC with acids were similar to that of purified AC. This was therefore considered to be the reason for the pore enlargement and surface destruction.

Adsorbent with high performance have to be selected to control VOCs of very low concentrations. The prepared IAC adsorbents were tested for benzene, toluene, *o*-, *m*-, *p*-xylene, methanol, ethanol, *i*-propanol, and MEK. The impregnated content of all IACs was 5 wt.% with respect to AC. The amounts of VOC adsorbed on adsorbents are shown in Table 2. The amounts of VOC adsorbed on 5 wt.% IAC with acids and alkali show a similar tendency. However, the amount of VOC adsorbed on 5 wt.% PA/AC was relatively large in spite of the decrease of specific surface area excepting in case of *o*-, *m*-xylene, and MEK. This suggests that the adsorption of relatively large molecules such as *o*-xylene, *m*-xylene, and MEK was suppressed, while that of small molecules was enhanced. It is therefore possible to speculate that the phosphoric acid narrowed the micropores but changed the chemical nature of surface to strongly adsorb the organic materials.

Furthermore, impregnated content of PA/AC was varied to see the optimum value giving the maximum amounts of VOCs adsorbed. The variation of amount of VOC adsorbed with impregnated contents is shown in Fig. 3. Also, the variation of BET surface area was contained in Fig. 3. The optimum impregnated content was 1 wt.% for benzene, toluene, *p*-xylene, methanol, ethanol and *i*-propanol, but the amount of *o*-xylene, *m*-xylene, and MEK adsorbed were decreased with increasing impregnated contents. Interestingly, the amount of

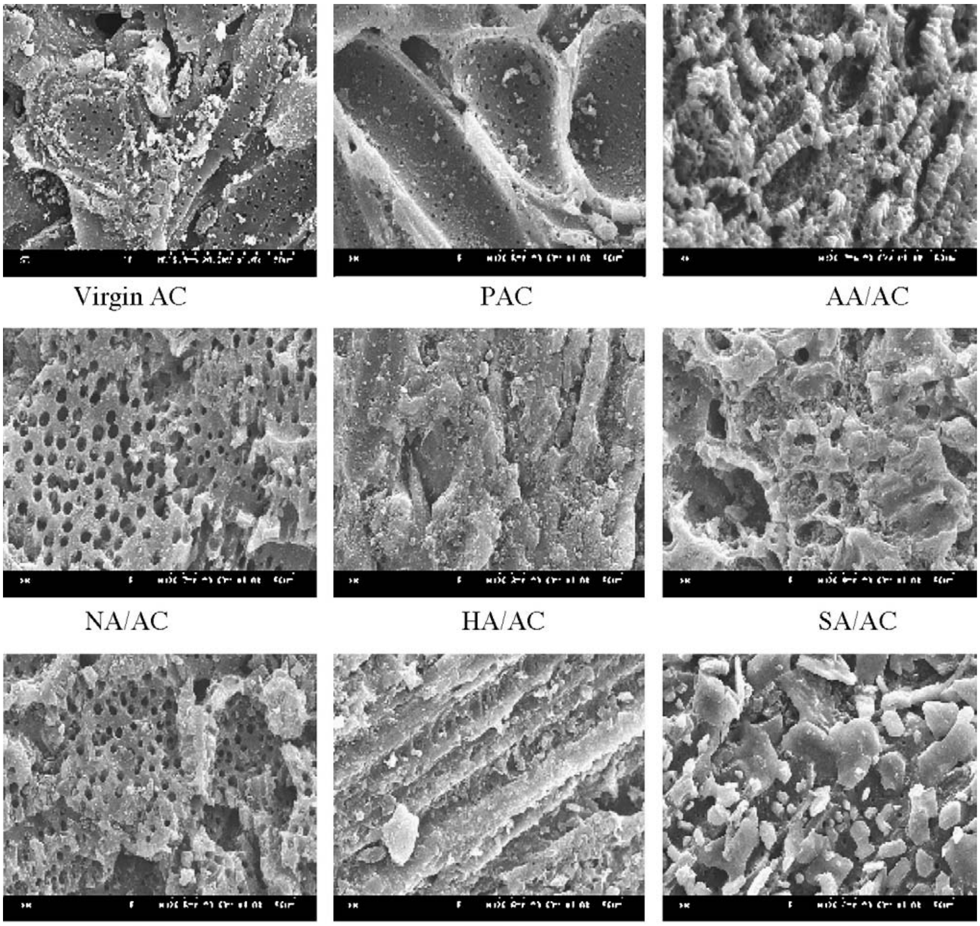
Virgin AC PAC AA/AC
NA/AC HA/AC SA/AC
PA/AC PH/AC SH/AC

Fig. 2. SEM photographs of activated carbons and acid-, alkali-impregnated activated carbons (1000×).

Table 2
Amount of VOCs adsorbed (mmol/g) on PAC and various 5 wt.% IACs

| Nomenclature | Aromatics | | | | | Alcohols | | | MEK |
|---|---|---|---|---|---|---|---|---|---|
| | Benzene | Toluene | *o*-Xylene | *m*-Xylene | *p*-Xylene | MeOH | EtOH | *i*-Propanol | |
| PAC | 5.05 | 3.60 | 4.65 | 6.33 | 4.21 | 5.31 | 1.87 | 1.59 | 4.41 |
| AA/AC | 5.69 | 3.63 | 4.52 | 6.21 | 4.18 | 5.35 | 1.56 | 1.86 | 3.50 |
| NA/AC | 4.72 | 3.08 | 5.16 | 3.91 | 3.93 | 4.43 | 1.91 | 1.56 | 3.11 |
| HA/AC | 4.00 | 2.25 | 3.85 | 3.06 | 3.49 | 3.68 | 1.50 | 1.31 | 3.00 |
| SA/AC | 5.13 | 3.17 | 4.40 | 3.86 | 4.35 | 5.11 | 1.92 | 1.65 | 3.52 |
| PA/AC | 6.41 | 4.05 | 4.92 | 4.11 | 5.19 | 5.65 | 2.18 | 1.92 | 4.02 |
| PH/AC | 4.52 | 2.87 | 4.11 | 3.64 | 4.31 | 4.32 | 1.80 | 1.36 | 3.15 |
| SH/AC | 3.81 | 2.73 | 4.04 | 4.50 | 3.92 | 4.67 | 2.02 | 1.51 | 3.12 |

benzene, *p*-xylene, and ethanol adsorbed on 1 wt.% PA/AC was 1.5–2 times that on purified AC. The BET surface area of 1 wt.% PA/AC (1109 $m^2$/g) took the maximum value. The reason for enhancement of adsorption performance of PA/AC was considered to be due to combination effect of increase of BET surface area and chemical modification by the treatment with PA. Consequently, 1 wt.% PA/AC was determined to be a best candidate as an adsorbent for removing benzene, toluene, *p*-xylene, methanol, ethanol, and *iso*-propanol. Therefore, 1 wt.% PA/AC was used as the adsorbent to investigate the adsorption isotherm, adsorption and desorption performance.

### 3.2. Adsorption isotherms

Langmuir and Freundlich adsorption isotherm models are shown in Table 3. In Langmuir, the adsorbed amount of monolayer ($X_m$) can be obtained from the slope of the plot of $C_e/Q_e$ with respect to $1/C_e$. The Langmuir constant $b$, the degree of surface adsorption shows a positive relationship with the extent of adsorbate; the adsorbed amount increases as constant $b$ increase. According to Freundlich isotherm, the constant $k$ shows a positive relationship with the adsorption capacity. However, the adsorption capacity is reduced when $1/n$ is larger than 2. Hence, $k$ and $1/n$ values can be determined by plotting the adsorbed amount with respect to the concentration of the adsorbate.

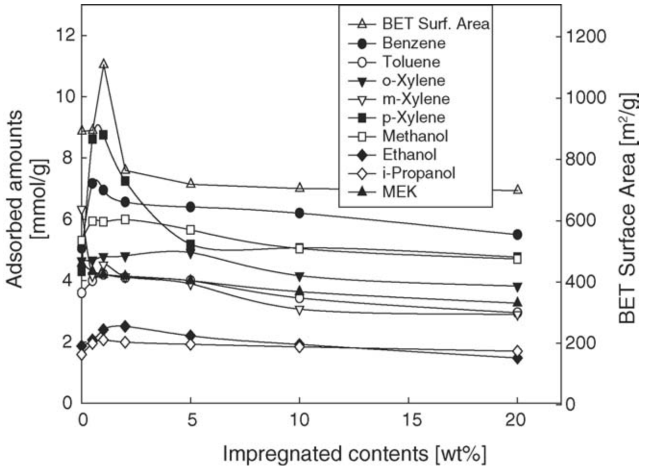

Fig. 3. BET surface area of PA/AC and effect of impregnated contents on amount of VOCs adsorbed on PA/AC.

Table 3
Langmuir and Freundlich isotherms and their parameters for toluene and MEK on 1 wt.% PA/AC

| Isotherms | Equations | Parameters | VOCs | |
|---|---|---|---|---|
| | | | Toluene | MEK |
| Langmuir | $Q_e = \frac{X_m b C_e}{1+bC_e}$ | $X_m$ | 5.68 | 5.39 |
| | $\frac{C_e}{Q_e} = \frac{1}{X_m b} + \frac{C_e}{X_m}$ | $b$ | 5.34 | 5.11 |
| Freundlich | $Q_e = kC_e^{1/n}$ | $k$ | 4.82 | 4.59 |
| | $\ln Q_e = \ln k + \frac{1}{n} C_e$ | $1/n$ | 0.26 | 0.27 |

Langmuir and Freundlich adsorption isotherms for toluene and MEK are shown in Figs. 4 and 5, respectively. Langmuir and Freundlich isotherms expressed relatively well the adsorption of toluene and MEK, indicating the dependence on both physical and chemical adsorption. From the plots of two adsorption isotherms, the parameters shown in Table 3 were calculated. This analysis indicated that the adsorption capacity of toluene on 1 wt.% PA/AC was larger than that of MEK.

### 3.3. Adsorption performance

The effect of concentration, flow rate, and aspect ratio on adsorption performance of 1 wt.% PA/AC was investigated for

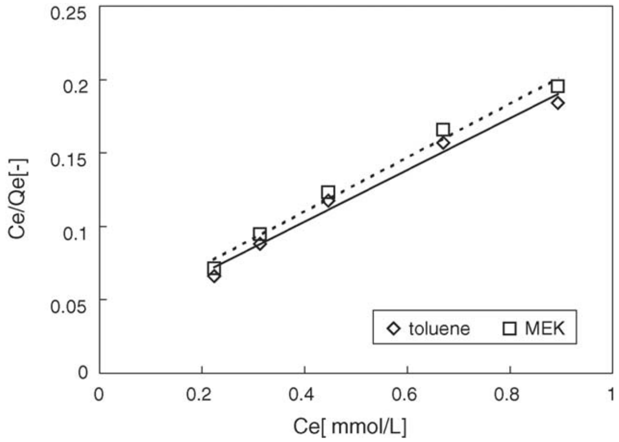

Fig. 4. Langmuir adsorption isotherm of toluene and MEK on 1 wt.% PA/AC.

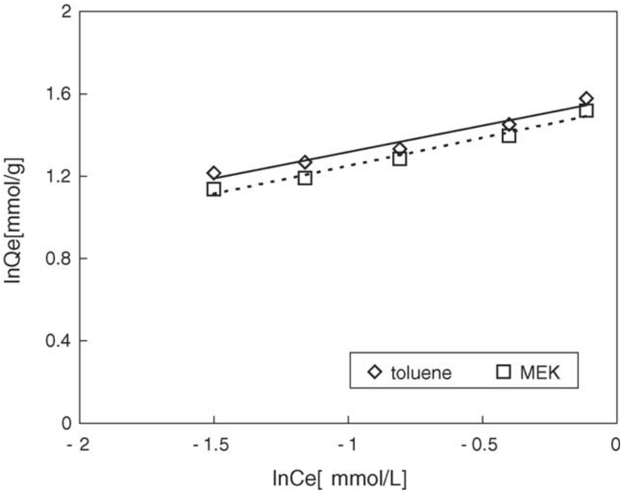

Fig. 5. Freundlich adsorption isotherm of toluene and MEK on 1 wt.% PA/AC.

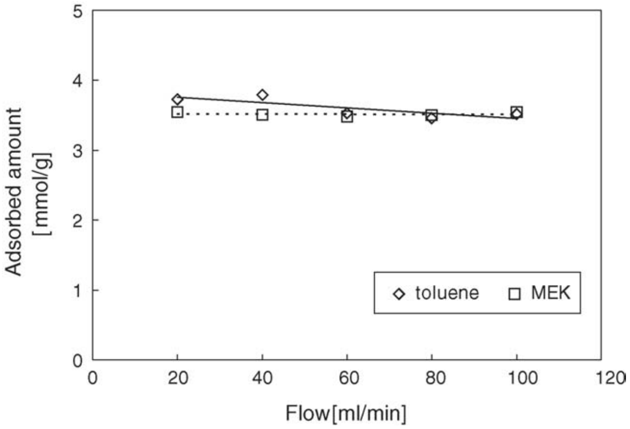

Fig. 7. Effect of flow rate on amount of toluene and MEK adsorbed on 1 wt.% $H_3PO_4$/AC.

toluene and MEK. Effect of concentration of toluene and MEK on the adsorbed amount was shown in Fig. 6. The amount of toluene and MEK adsorbed at equilibrium was increased with increasing the concentration of the adsorbate. That is because the adsorbate, toluene and MEK can be physically adsorbed on the adsorbent as multiplayer. As the adsorbate concentration was increased, mass transfer zone was shortened. Thus, a short time was required for reaching the bed saturation.

Fig. 7 shows the relationship between flow rate and amount of toluene and MEK adsorbed at equilibrium. With increasing the flow rate including the adsorbates, the amount of MEK adsorbed did not vary so much, but the amount of toluene adsorbed was slowly decreased. If the flow rate is increased, the removal efficiency of fixed bed is decreased, which subsequently inducing reduction of the amount adsorbed at equilibrium. Anyway, the adsorption performance might be kept to some extents even at larger flow rate.

Fig. 8 shows the effect of aspect ratio on amount adsorbed at equilibrium under constant flow rate and temperature. The aspect ratio means the ratio (*L*/*D*) of length (*L*) of adsorbent column to its diameter (*D*). Generally, the increase of aspect ratio induces the enhancement of adsorption capacity through increase of contacting probability. When aspect ratio in toluene adsorption was 6, adsorption capacity showed maximum point, and decreased slightly with increasing the ratio. This variation can be regarded to be constant for varying the aspect ratio if it is not too small or large. MEK was not showing significant variation of the adsorbed amount at equilibrium with varying the aspect ratio.

### 3.4. Desorption performance by TPD

Desorption characteristics of 1 wt.% PA/AC was investigated by TPD technique. Fig. 9 shows the TPD experimental results for 1 wt.% PA/AC with toluene and MEK. The desorption characteristics of 1 wt.% PA/AC with toluene and MEK were determined by raising the room temperature by 5 °C/min to 300 °C. Maximal desorption concentrations and temperatures of both toluene and MEK were 1.13, 1.25 (Co: 1) and 150 °C, 100 °C, respectively. The toluene and MEK adsorbed on 1 wt.% PA/AC was completely desorbed when the

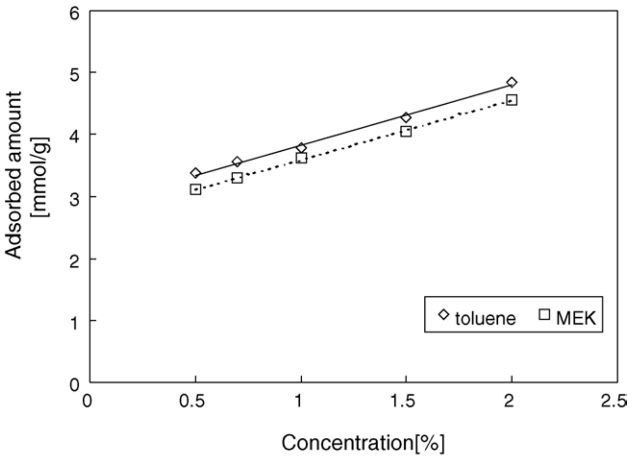

Fig. 6. Effect of concentrations on amount of toluene and MEK adsorbed on 1 wt.% $H_3PO_4$/AC.

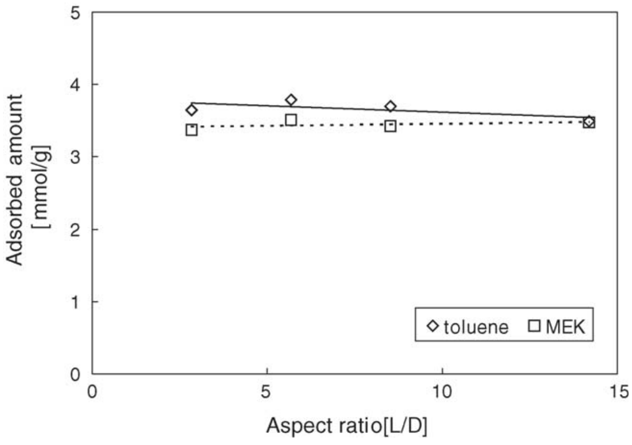

Fig. 8. Effect of aspect ratio on amount of toluene and MEK adsorbed on 1 wt.% $H_3PO_4$/AC.

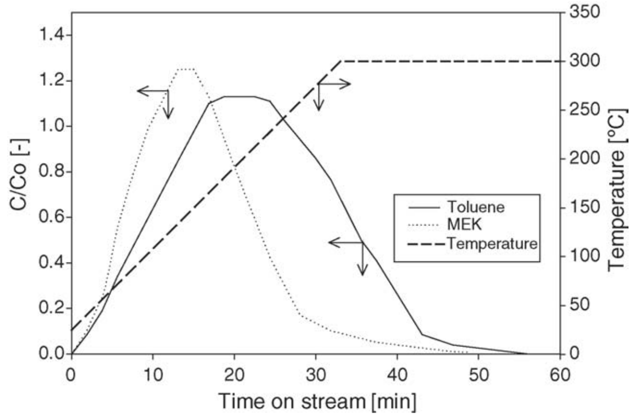

Fig. 9. TPD spectra obtained from toluene and MEK adsorbed on 1 wt.% PA/AC.

adsorbent was heated in an electric furnace. The temperature of the adsorbent was programmed, and concentration of VOCs desorbed could be controlled at some extents. Total desorbed amount were divided into the reversible and irreversible amounts; the former was desorbed by helium at room temperature and the latter was desorbed by TPD. The desorbed amount of 1 wt.% PA/AC with toluene and MEK at 300 °C was estimated, the desorbed efficiencies of toluene and MEK were 98.1% and 99.1%, respectively. Similar TPD patterns were obtained even though the adsorption–desorption operation was repeated. It is therefore considered that the adsorbents will be effective for repetition of adsorption–desorption processes.

## 4. Conclusions

Adsorption capacity and desorption characteristics of impregnated activated carbon (IAC) prepared with various acids and bases were investigated in order to apply to adsorption part of adsorption–desorption and catalytic oxidation hybrid system. Among the prepared IACs, PA/AC showed the greatest adsorption capacity for benzene, toluene, *p*-xylene, methanol, ethanol and *iso*-propanol due to chemical modification of its surface despite the decreased specific surface area. Also, the maximum BET surface area with impregnated content of PA/AC showed 1 wt.% PA/AC. The amount of VOC adsorbed on 1 wt.% PA/AC was larger than that on purified AC excepting that of *o*-xylene, *m*-xylene, and MEK. The adsorbed toluene and MEK were easily desorbed by heat treatment to 300 °C, suggested the possibility for repeated use. The findings confirmed the potential of 1 wt.% PA/AC as a promising adsorbent for the hybrid system in controlling VOC emissions with very low concentrations.

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