Thesis for the Degree of Master of Engineering

Characteristics and application of competitive adsorption of BTEX by various adsorbents

by

Tae-Wan Ock

Division of Earth Environmental System Science
(Major of Environmental Engineering)
The Graduate School
Pukyong National University

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(흡착제에 따른 기체상 BTEX의 경쟁 흡착 특성 및 적용)

Advisor: Prof. Youn-Suk Son

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Tae-Wan Ock

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Approved by:

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(Chairman) Lee, Taeyoun

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(Member) Noh, Youngmin

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(Member) Son, Youn-Suk

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흡착제에 따른 기체상 BTEX의 경쟁 흡착 특성 및 적용

옥 태 완

부경대학교대학원 지구환경시스템과학부 환경공학전공

요 약

본 연구에서는 흡착제에 따른 BTEX의 경쟁흡착 특성을 파악하고 흡착제를 공기청정기형 필터에 적용하여 실내에 존재하는 VOCs를 효과적으로 제거하고자 하였다. 이를 위해서 제올라이트, 실리카겔, 활성탄의 흡착제들을 이용하였고 흡착제별, 온도에 따른 파과시간을 확인하였다. 그 결과 활성탄의 파과시간이 가장 길게 나타난 반면 제올라이트의 가장 짧았다. 이는 흡착제의 비표면적이 클수록, 평균기공크기가 작을수록 흡착이 잘 일어나는 것을 확인하였다. 또한 끓는점이 낮은 벤젠, 톨루엔 순으로 유입농도보다 높은 농도로 배출되는 것을 할 수 있었다. 두 번째 실험에서 가장 좋은 흡착제를 공기청정기형 필터에 적용하여 실내에 존재하는 BTEX를 제거하고자 하였다. 고농도의 BTEX 상황을 모사하기 위하여 밀폐된 챔버에서 두 사람이 담배를 폈으며 이때 PM과 VOCs가 측정되었다. PM의 제거효율은 흡착제의 유무와 종류에 따라 달라지지 않았지만 VOCs는 달라지는 것을 확인할 수 있었다.

Ⅰ. Introduction

1.1. Background

Concerns about indoor air pollution are increasing. This is because indoor air pollutant concentrations ae known to be often higher than those of outdoors (Guo et al., 2004; Toor et al., 2014). Additionally, people typically spend more than 80% of their time indoors (Klepeis et al., 2001) and intake toxic substances primarily through inhalation of polluted air and dust intake (Harrad et al., 2006).

Benzene, toluene, ethylbenzene and xylene known as BTEX are environmentally important VOCs (Volatile Organic Compounds). They are released into the atmosphere from both artificial and natural sources (Caselli et al., 2010; Davil et al., 2013; Fazlzadeh et al., 2012; Liu et al., 2009; Sturaro et al., 2010).

BTEX compounds are known to have important impacts on human health including cancer and may induce neurological disorders and symptoms such as weakness, loss of appetite, fatigue, confusion and nausea (Hoskins, 2011). Benzene is the most toxic chemical among BTEX, and long−term exposure to benzene may increase incidence of leukemia and aplastic anemia in human (Baker et al., 1985; Mehlman, 1990; Niri et al., 2009; Wong, 1995). International Agency for Research on Cancer (IARC) has classified benzene as an intense carcinogenic agent and ethylbenzene as a suspected carcinogenic compound (IARC, 1999). In indoor environments, causes of BTEX include penetration of outdoor air pollution, smoking, paints, adhesives and other VOC emitting substances that are used inside buildings (Singh et al., 1992; WHO, 2000; Jia et al., 2008; Kim and Bernstein, 2009; Symanski et al., 2009).

Previous field studies of indoor BTEX concentration levels at homes (Liu et al., 2013; Fan et al., 2018), schools (Demirel et al., 2014; Raysoni et al., 2017), libraries (Cincinelli et al., 2016), hospitals (Lü et al., 2006) and restricted areas such as garages (de Castro et al. 2015) have been reported. The impact of BTEX on human health has become a global concern. In China, for example, Liu et al. measured BTEX at homes in Beijing and found a higher cancer risk when people were exposed to benzene (Liu et al., 2013). Also, in Turkey, Demirel et al measured BTEX concentrations in primary schools and investigated their effects on individual concentrations. Excessive cancer risk levels have been shown to be higher among elementary school students in urban areas (Demirel et al., 2014). In Iran, Baghani et al measured BTEX at hairdressing salons, and as a result, it was found that the concentration of ethylbenzene was the highest at the hairdressing salon among BTEX. Although xylene was the only non-cancer risk, benzene and ethylbenzene had a significantly higher cancer risk (Baghani et al., 2018).

Accordingly, treatment methods have been developed to remove VOCs from indoor including adsorption, catalytic decomposition (Qin et al., 2019; Luo et al., 2018; Li et al., 2019; Héquet et al., 2018; Yi et al., 2019), biological purification and non-thermal plasma (NTP) (Bahri et al., 2017; Wu et al., 2017).

Among these technologies, adsorption technology has several advantages: simplicity, convenient operation, high safety (no toxic by-product formation), low energy (no additional equipment or energy required), high efficiency and recyclability (Xiao et al., 2014; Shafiei et al., 2018; Herm et al., 2014; Xu et al., 2013). Due to its advantages in removing harmful substances from indoors, adsorption technology is a promising technology, and is applied to air purifiers and used in real life (Khan et al., 2013; d Niknaddaf et al., 2016; Vellingiri et al., 2016).

1.2 Purpose

Materials such as activated carbon, zeolite clay, silica gel, activated alumina, mineral clay and some polymers showed surface adsorption ability. Among them, activated carbon and hydrophobic zeolites are the most commonly-used adsorbents in commercial air purifiers due to their large surface areas and high adsorption capacities (Kim and Ahn, 2012; Huang et al., 2003; Shen et al., 2014; Zaitan et al., 2016; Mobasser et al., 2022).

However, studies on the adsorption of aromatic hydrocarbons mainly focused on single-component adsorption, and studies on complex components are rare. In the actual adsorption application, the adsorption of a single gas is rarely performed, and most of the adsorption of complex gases are performed. In addition, research on the effect of temperature on multi-component adsorption is insufficient.

Hence, in this study, multi-component adsorption experiments were conducted by selecting zeolite, silica gel and activated carbon as adsorbents so as to understand the properties of adsorption of multiple components of the aromatic hydrocarbon BTEX (benzene, toluene, ethylbenzene, p-xylene). In addition, since adsorption is affected by temperature, it is necessary to understand the effect at room temperature. Among adsorbents, the purpose is to select an adsorbent with excellent adsorption performance and apply it to an air purification filter to effectively remove VOCs emitted from the indoor.

Ⅱ. Theoretical background

2.1 VOCs characteristics

Volatile organic compounds are liquid or gaseous organic compounds that are easily volatilized into the atmosphere due to their low boiling points, ranging from solvents used in industrial facilities to organic gases emitted from chemical and pharmaceutical factories and plastic drying process (Brown et al., 1994). Volatile organic compounds emitted by industrial facilities and transportation vehicles react with NOx and ultraviolet rays in the atmosphere (Li et al., 2014; Stockwell and Goliff, 2004; Barletta et al., 2008). Additionally, volatile organic compounds cause photochemical smog as ozone precursors and deteriorate air quality as secondary particulate matter along with SOx and NOx (Deng et al., 2019; Field et al., 2014; Han et al., 2019; Wu et al., 2017). Volatile organic compounds discharged indoors by building materials, furniture and paint cause serious damage when they are exposed to the human body (Kim and Bernstein, 2009; Symanski et al., 2009). Acute exposure causes dysfunction of the central nervous system and damage to the respiratory tract, and chronic exposure causes hearing and memory impairment and birth defects (Bernstein et al., 2008; Malherbe and Mandin, 2007).

2.2 VOCs removal technique

VOCs are emitted in different types and characteristics in various environments, so various technologies are used to control them. VOCs control technology is basically divided into (1) process and facility improvement and (2) additional facility installation. (1) In the case of the method, VOCs control is a method to reduce the amount generated by changing process facilities and raw materials, and (2) is a way of installing additional control facilities to reduce the amount of emission. (2) The method is again divided into two methods: complete removal of VOCs or recovery of VOCs. Figure 2.1 is a schematic diagram of a technology that classifies a method of controlling VOCs. In many cases, a method of reducing the generation of VOCs is the most efficient, but there is no raw material to replace, or it is difficult to modify the existing facilities of the process, so methods of additional installation of control facilities have been researched.

Among the VOCs decomposition technologies, oxidation mainly uses thermal oxidation applying high−temperature heat and catalyst oxidation that oxidizes pollutants at a relatively low temperature using a catalyst. Thermal oxidation may remove all VOCs at 700℃ or more and may treat a high flow rate (Marks and Phoads, 1991). Catalyst oxidation has a treatment capacity and efficiency similar to thermal oxidation at 350 to 500℃, and energy consumption is less than thermal oxidation (Ruddy and Carroll, 1993). Biological treatment of VOCs is a technology that decomposes low−concentration pollutants into water, carbon dioxide and biomass using aerobic microorganisms, and has the advantage of low operating costs and high removal efficiency (Ottenger and Van Den Oever, 1983).

Among VOCs recovery technologies, condensation is a technology that recovers gaseous VOCs with high vapor pressure and high concentration in liquid phase by cooling or applying pressure, and has a relatively low removal efficiency (Ozturk and Yilmaz, 2006). Absorption is a method of removing the exhaust gas containing water soluble VOCs by contacting it with a liquid solvent. Various absorption towers that increase the contact between the absorption liquid and the exhaust gas have been developed and installed in the field (William and Lead, 1997). Adsorption is a technology to control VOCs using an adsorbent with a large surface area and many micropores, and the removal efficiency is high at a relatively low concentration. When an adsorbent with a physical adsorption mechanism is used, it is easily recovered and installed as a final control facility in many discharge facilities (Ruthven, 1984).

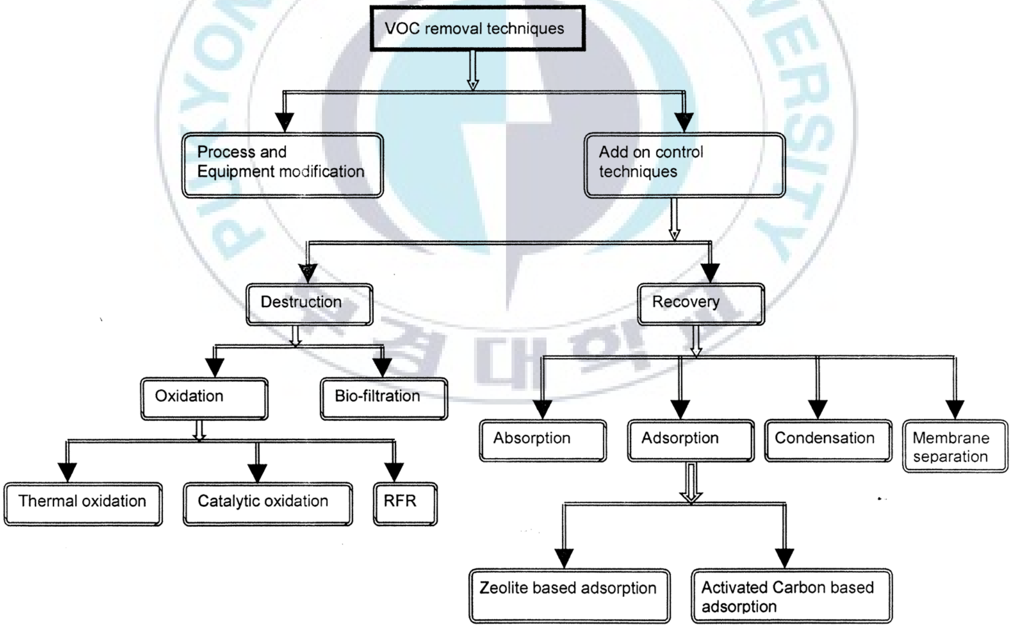


Fig. 2.1. Classification of VOC control techniques (Khan and Ghoshal, 2000).

2.3 Adsorption

2.3.1. Adsorption summary

Adsorption is a process in which ions or molecules located in one phase are condensed or concentrated on the surface of another phase (Crawford and Quinn, 2017). Fig 2.2 shows the concept of adsorption and desorption (Tuckermann, 2006). The concentrated material is called an adsorbate, and the solid that adsorbs is called adsorbent. In general, there are three types of adsorption: physical adsorption, chemical adsorption and exchange adsorption (Inglezakis and Poulopoulos, 2006). Physical adsorption is relatively common and occurs because of the action of weak intermolecular or van der waals forces. In this case, the adsorbed material condenses on the surface, but freely moves around the entire surface. Moreover, the adsorbent is to form several overlapping layers, and in general, physical adsorption is reversible. That is, when the concentration is reduced, the same amount of the original absorbed amount is desorbed again. On the other hand, chemisorption is much stronger and is comparable to forming chemicals bonds. Usually, adsorbed materials form a layer of only one molecular thickness on the surface, and molecules are thought to be not free to move from one part of the surface to another. Chemical adsorption is almost irreversible, and in order to remove adsorbed material, the adsorbent must generally be heated up to a high temperature.

Exchange adsorption is a phenomenon where an electrical attraction is applied between the adsorbed material and the surface to be adsorbed. Ion exchange belongs to this kind, and the ions of the material are attracted by electrostatic attraction to the opposite charge site on the surface and concentrated on the surface.

Adsorption is a surface phenomenon. Hence, the adsorption rate and the adsorption amount are expressed as a function of the solid surface area used. In addition, the adsorption is exothermic.

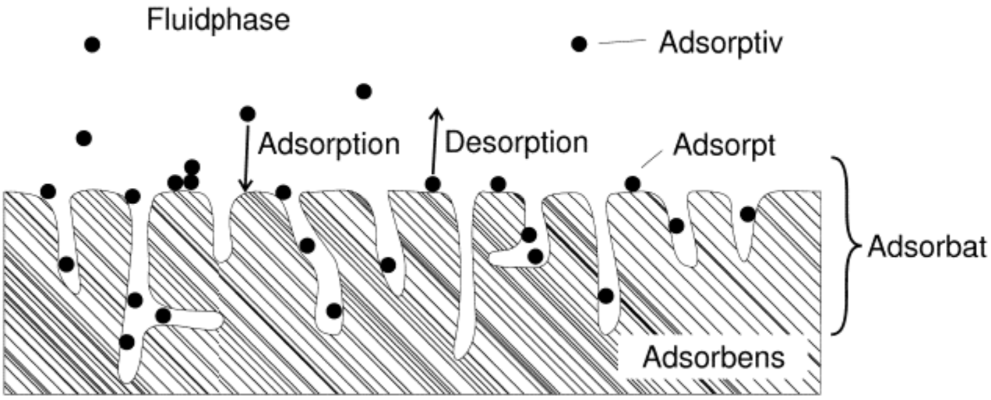


Fig. 2.2. Concept of adsorption and desorption (Tuckermann, 2006).

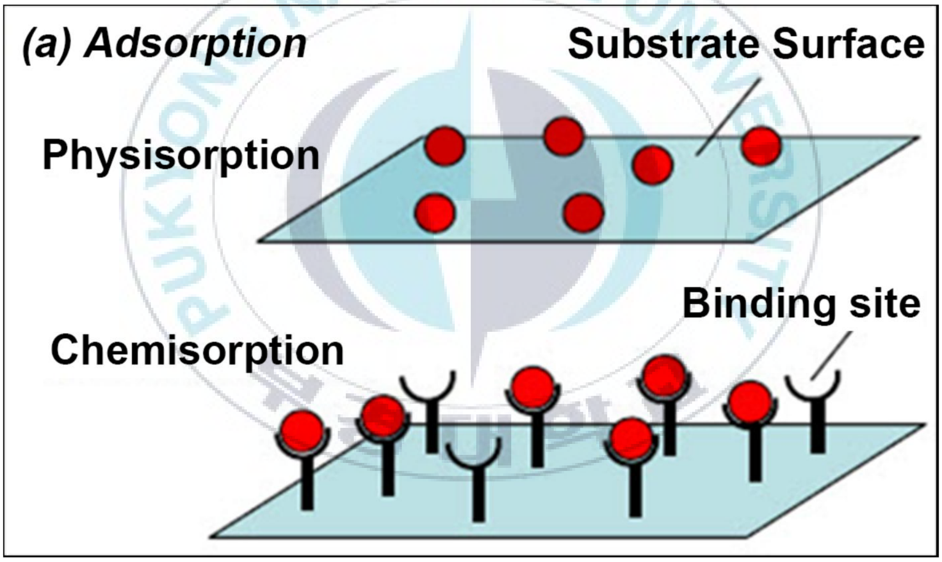


Fig. 2.3. Depiction of physisorption and chemisorption interaction between the substrate surface (adsorbent) and the adsorbate molecules (Kennedy et al., 2018).

2.3.2. Breakthrough curve

When sorbent is adsorbed and removed, a breakthrough curve is drawn depending on the capacity of the gas to be processed, and after adsorption begins, it is divided into three zones as shown in Fig. 2.4 (Kim, 2021). It is divided into a zone that maintains the equilibrium concentration consistent with the concentration at inlet (C_o) inside of the inlet, a zone where the concentration of adsorbate called MTZ (mass transfer zone) decreases, and a zone where adsorbate is not adsorbed on the outlet side.

As the adsorption time in the adsorption tower increases, the adsorption zone moves. If the upper part of the MTZ reaches the end of the adsorption tower, the breaking point is reached, and if a predetermined solvent concentration is measured at the outlet (adsorption time), adsorption must be stopped.

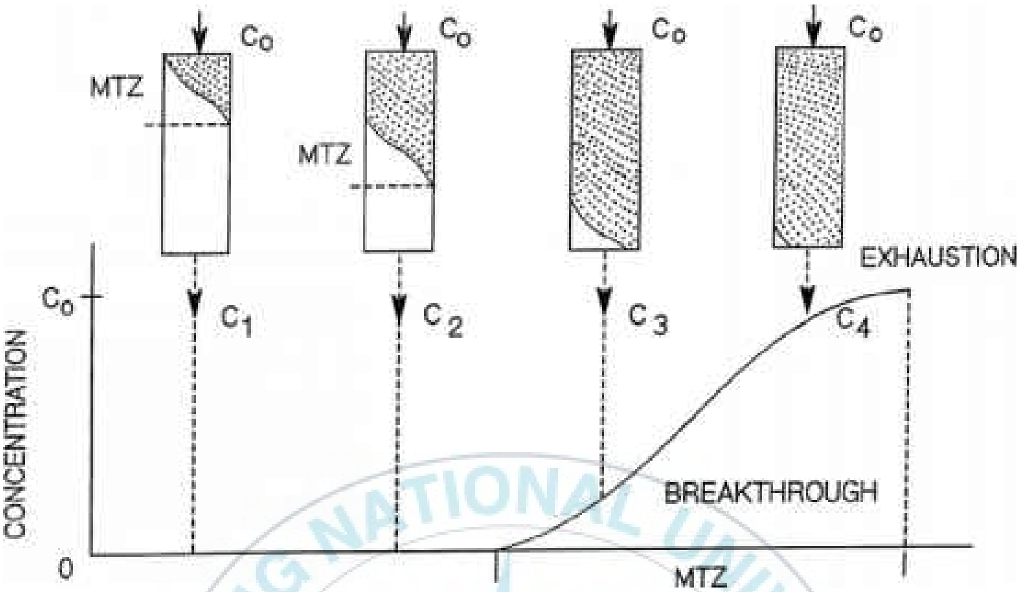


Fig. 2.4. Idealized breakthrough curve of a fixed bed adsorber (Kim, 2021)

2.3.3. Competitive adsorption

Competitive adsorption is one of the important phenomena in adsorption, and it refers to an adsorption phenomenon where several components of adsorbate have competitive effects on each other, and different chemical species are adsorbed competitively on the same surface (interface) (Lillo–Ródenas et al., 2006; Maitlo et al., 2019). Even on the same surface, this is not the case when each chemical species separately selects, adsorbs a specific adsorption site and does not invade the adsorption site with each other. Fig. 2.5. is a schematic diagram which shows the adsorption state depending on the characteristics of the adsorbate (molecular weight, boiling point, shape, etc.) during competitive adsorption.

In general, adsorption of high boiling point substances is preferentially adsorbed over low boiling point substances (Yanxu et al., 2008; Li et al., 2012; Wang et al., 2012; Yao et al., 2020; Megías-Sayago et al,. 2020). However, it is known that in the case of substances with similar boiling points, the size and function of the adsorbate are preferentially affected (Hsieh and Chen, 2002; Lu and Sorial, 2004 (a); Wang et al., 2012). It is also reported to be determined by the thermodynamic properties of the solvent, boiling point, heat of evaporation, saturated vapor pressure, vapor pressure, and etc. (Hsieh and Chen, 2002; Lu and Sorial, 2004 (b); Wang et al., 2012; Stähelin et al., 2018).

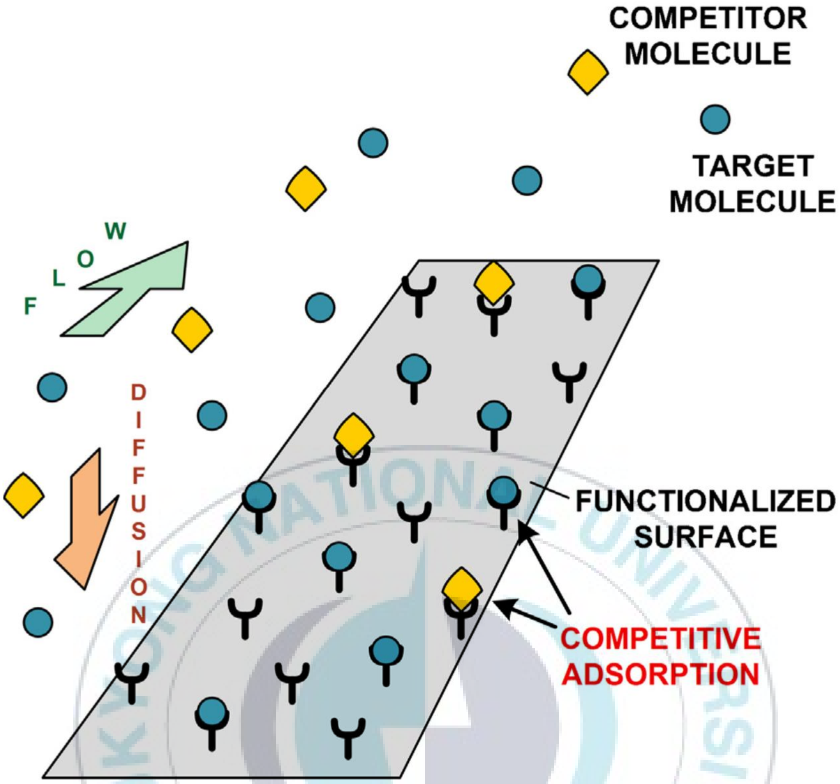


Fig. 2.5. Illustration of adsorption–desorption and mass transfer processes of both the target and the competitor molecules (Frantlović et al., 2013).

Ⅲ. Method and Materials

3.1 Competitive adsorption

3.1.1. Materials

3.1.1.1. Adsorbents

The adsorbents used in this experiment are commercially available activated carbon, silica gel and zeolite, and they were dried 100℃ for 24 hours to remove moisture and impurities. The specific surface area and pore structure characteristics were determined by the standard N_2 adsorption isotherm at 77 K (Belsorp mini 2, Bel Japan, Inc.), and then the porous parameters were evaluated by analyzing them. The 'monolayer equivalent surface area' (S_{BET}) from the BET (Brunauer Emmett Teller) plot, the pore volume estimated from the amount of adsorbed nitrogen at $p/p° = 0.95$ (V_p), and the average pore radius from

$r=2V_p/S_{BET}$ were obtained, assuming cylindrical pore dimensions with circular cross-section (Daifullah and Girgis, 1998).

3.1.1.2 Chemicals

The reagents used in this study are benzene, toluene, ethylbenzene and p-xylene. Benzene, toluene and ethylbenzene were purchased from Sigma Aldrich, and p-xylene was purchased from Daejeong. Benzene, toluene, ethylbenzene and p-xylene all used a GR grade (≥ 99%).

3.1.2. Equipment

The device used in this experiment is shown in Fig.3.1. It consists of VOC generating part, adsorption part and GC part. The VOC generating part includes zero air generator (GT 30000 plus 30 L/min Ultra Zero Air Generator, YOUNGIN Chromass, Korea), temperature control device, gas washing bottle containing liquid adsorbate, MFC (Mass flow controller, LTI-1000, Line Tech, Korea) and mixing chamber. The adsorption part consists of a constant temperature water bath (WB-6, DAIHAN scientific, Korea) and adsorption tube containing the adsorbent and glass wool. An adsorption tube is made of stainless steel with an inner diameter of 11 mm, an outer diameter of 13 mm and a length of 70 mm. And 0.5 g of dried adsorbent was added and fixed with glass wool. Adsorption tube was placed in a constant temperature water bath to allow adsorption to proceed at a constant temperature.

3.1.3. Method

The adsorption experiment for BTEX removal was performed using a dynamic method. After making the temperature of gas washing bottle constant with a temperature control device, gaseous BTEX was generated by injecting air into gas washing bottle which contained liquid BTEX. The concentration of generated gas was 250 ppm for each gas, and a total of 1000 ppm by mixing 4 types of gas. The flow rate was 300 mL/min. The generated BTEX was sufficiently mixed in the mixing chamber and then adsorbed to the adsorption tube. Adsorption tube was placed in a constant temperature water bath to allow adsorption to proceed at a constant temperature. The temperature of the constant temperature water bath was set to 15, 25 and 35℃ so as to evaluate the adsorption capacity depending on temperature.

3.1.4 Analysis

The gas concentration was analyzed by using Gas Chromatography Flame Ionization Detector (GC−FID, Model: 6890, Agilent, USA) every 30 minutes during adsorption, and when the outflow gas concentration (C_o) at the outlet of the adsorption tube reached the same level as the inflow gas concentration (C_i), the adsorption experiment was terminated. The conditions of the GC used are shown in Table 3.1.

Table 3.1 Analysis conditions by gas chromatography

Variable	Description or Value
GC	6890 Agilent
Carrier gas	N_2 and 25.2 mL/min
Detector	FID
Oven temperature program	50℃, 2min 50 to 150 ℃ (heating rate: 25 ℃/min), 2min
Injector temperature	200 ℃
Detector temperature	250 ℃
split ratio	20:1
Column	SUPELCO-WAX

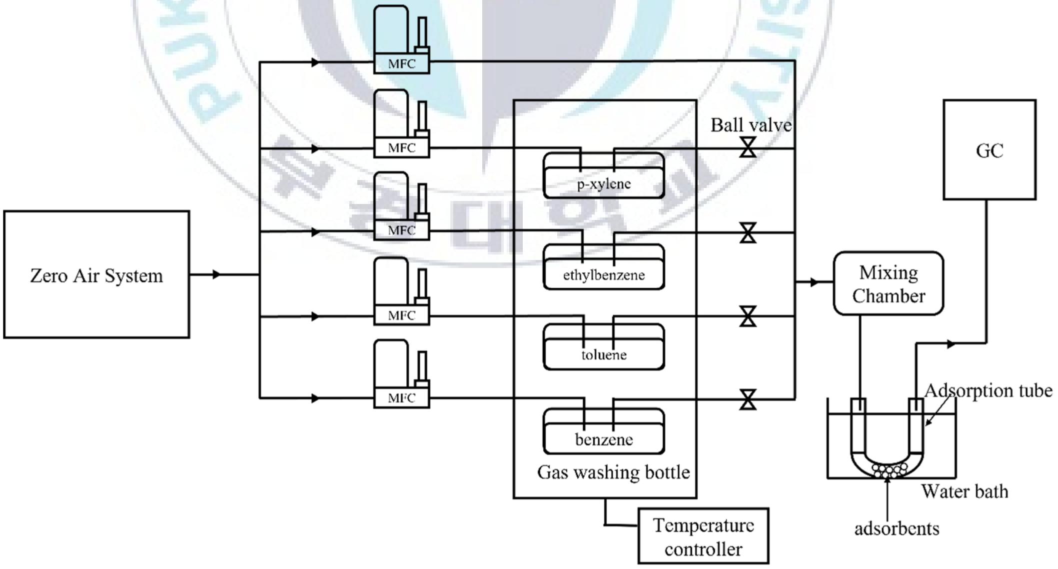


Fig 3.1. Schematic diagram of adsorption experiment.

3.2 Adsorption filter application

3.2.1. Equipment

Tenax TA (60/80 mesh, Markes, UK) was used for sampling of VOCs and pump (MP−Σ30KN Ⅱ Mini Pump, Sibata, Japan) was also used. Thermal Desorber (TD, Model: Unity2, Marks, UK) and Gas Chromatography (GC, Model: 6890 N, Agilent, USA)/Mass Spectrometer Detector (MS, Model:5975, Agilent, USA) were used for quantitative and qualitative analyses. Nanoparticles generated during smoking were measured with a Scanning Mobility Particle Sizer (SMPS, Model: 3938, TSI, USA), and the range of nanoparticles measured was 17.5 ~ 532.8 nm. In addition, nanoparticles were recorded every minute. $PM_{2.5}$ and PM_{10} were analyzed by using two personal aerosol monitor (AM520 Aerosol Monitor, TSI, USA) using different impactor, and recorded every 10 seconds. A commercially available air purifier (Model: AX40M3030WMD, Samsung, Korea) was used, and the usable area was 40m^2, which was suitable for use with an exposure chamber of 29.92 m^2.

3.2.2. Method

In order to simulate an environment with high concentrations of BTEX indoors, cigarettes were smoked, and for cigarette smoke, KT&G's THIS PLUS containing 5.5 mg of tar and 0.55 mg of nicotine was used. Also, to measure harmful substances generated by indoor secondhand smoke and the performance of the air purifier type filter, the experiment was conducted using an exposure chamber (4.4 m * 6.8 m * 2.7 m (81 m^3)) which was equipped with constant temperature, ventilation and air purifier. Two people entered the exposure chamber and smoked once every 10 seconds for a total of 12 times. VOCs, nanoparticles, PM_{10} and $PM_{2.5}$ were measured when two people smoked cigarettes in the exposure chamber. At this time, the air purifier was operated according to the conditions and maintained in a closed state for 1 hour. After 1 hour of measurement, the VOCs and particles which were present in the chamber were made equal to the background concentration through 1 hour of ventilation. The experiment was repeated twice for each condition, and the experiment was conducted under four conditions. The background concentration was determined by measuring the blank before and after the experiment.

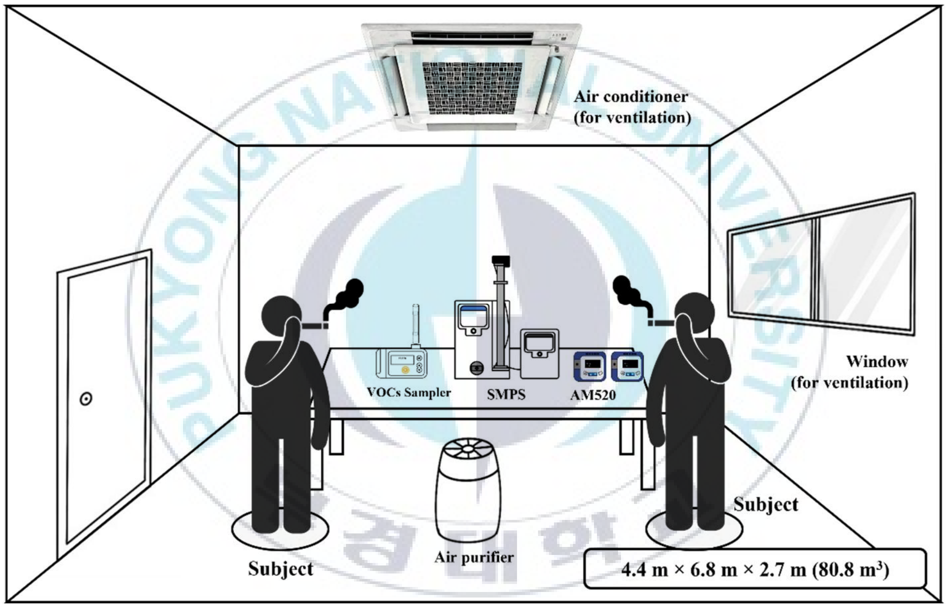


Fig. 3.2. Schematic diagram of exposure chamber

3.2.3. Analysis

After smoking, VOCs, nanoparticle and particulate matter were all collected and measured for 60 minutes. The filter of the air purifier consists of activated carbon and a HEPA filter, and three conditions were set to check the removal efficiency of harmful substances by the air purifier, filter and activated carbon. The experimental conditions were in three different states: when the air purifier was not operated, when the air purifier was operated using an existing filter, and when the activated carbon inside the filter was removed. That is, the experiment tried to analyze whether the air purifier was operated or not and the presence or absence of activated carbon.

Ⅳ. Result and discussion

4.1 Adsorbent characteristics

The specific surface area, pore structure and chemical functionality are the three important factors of adsorbent materials and directly determine the VOC adsorption performance (Carter et al., 2011; Dou et al., 2011). In order to compare the adsorption performance of the adsorbents, BET analysis was performed to determine the specific surface area and pore structure. Table 4.1 shows the specific surface area (S_{bet}), mesh pore volume (V_m), total pore volume (V_t) and average pore diameter (R) of the adsorbent used in this experiment. It was expressed as zeolite, silica gel, activated carbon A and activated carbon B in the order of adsorbents with low specific surface area. The specific surface areas of the used adsorbents were in the range of 439.74 to 1405.5 m^2/g. Activated carbon D had the largest specific surface area, and zeolite A had the smallest one.

Table. 4.1 Characteristics of adsorbents.

Adsorbents	S_{bet} (m^2/g)	V_m (cm^3/g)	V_t (cm^3/g)	R (nm)
Zeolite	439.74	101.03	0.562	5.1118
Silica gel	764	173.53	0.4211	2.2045
Activated carbon – A	791.57	181.87	0.3272	1.6534
Activated carbon – B	1405.5	322.92	0.6202	1.7651

4.2 Adsorption properties

4.2.1. Comparison of adsorption characteristics by adsorbent

Table 4.2 shows the time when the concentration (C_o) of the outflow gas becomes equal to the concentration (C_i) of the inflow gas. It was confirmed that the time to the saturation point took the longest in the order of activated carbon A, activated carbon B, silica gel and zeolite. The longer time it takes to reach the saturation point means that more adsorbates can be adsorbed, and the adsorption capacity is high. It is considered that more gas molecules are adsorbed because the specific surface area of the adsorbent is high (Das et al., 2004; Shih and Li, 2008). A high specific surface area for all adsorbents means good adsorption performance because the surface area provides sites for the adsorption process, which increases the interaction potential between the adsorbent and VOCs (Kim and Ahn, 2012), and this tendency is well shown in this experiment.

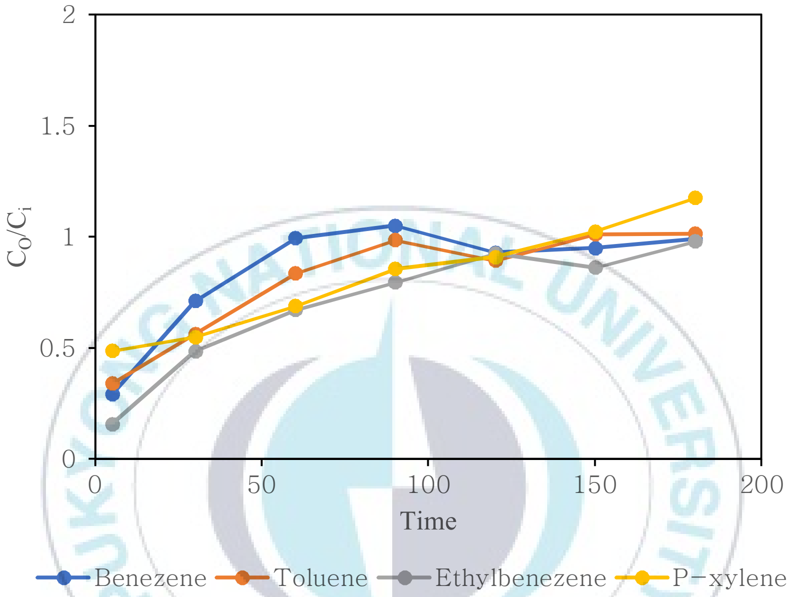
For porous adsorbents, the morphological structure, especially the pore size distribution, affects the ability to adsorb VOCs (Li et al., 2011). Their pores can be divided into micropores (pore diameter < 2 nm), mesopores (2 nm < pore diameter < 50 nm) and macropores (pore diameter > 50 nm). In general, micropores provide the main adsorption sites (Mao et al., 2015; Mao et al., 2016), while mesopores enhance intraparticle diffusion and shorten adsorption time (Tsai et al., 2008; Wang et al., 2014). Among adsorbents, zeolite has the largest average pore radius, and is regarded as the cause of the short saturation time because it is larger than the micropore size. On the other hand, silica gel and activated carbon A show a slight difference in specific surface area, but it is judged that the difference in average pore radius creates a difference in saturation time.

Table 4.2 Saturation time of adsorbents

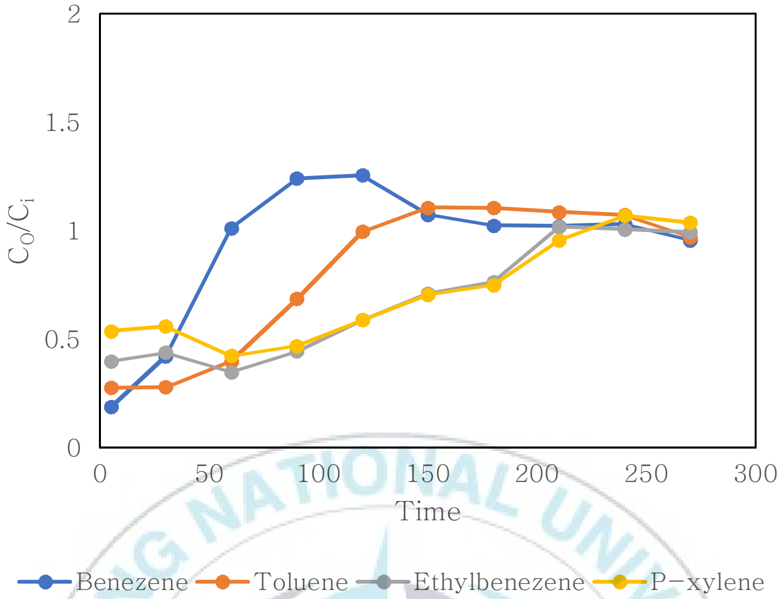
Adsorbents		Temperature (℃)		
		15	25	35
Zeolite	Time (min)	180	120	90
Silica gel		240	210	180
Activated carbon – A		360	240	240
Activated carbon – B		300	270	330

4.2.2. Comparison of adsorption characteristics by adsorption temperature

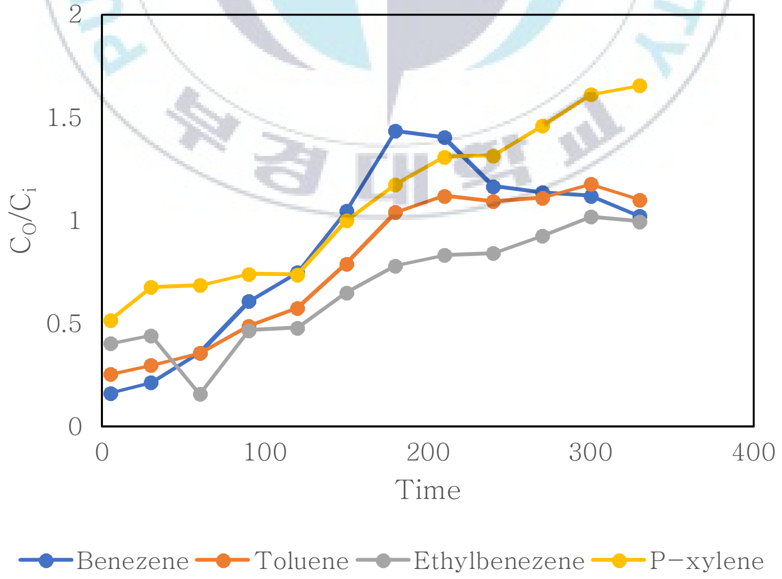
For most porous adsorbents, the adsorption of VOCs can be made mainly because of physical exothermic interactions where the adsorption temperature plays an important role (Tsai et al., 2008; Dou et al., 2011). In general, the adsorption of VOCs on carbonaceous adsorbents decreases with increasing adsorption temperature (Mao et al., 2016; Ramirez et al., 2004). Table 4.2 shows the saturation time of adsorbents depending on temperature. It can be seen that the saturation time decreases as the adsorption temperature increases. The physical adsorption process of the adsorbent on the porous adsorbent is similar to the vapor−liquid phase transition, and the adsorbate with a high boiling point is preferentially adsorbed over the adsorbate with a low boiling point due to stronger intermolecular forces (Guo et al., 2013). As a result, high−boiling VOCs could easily replace low−boiling VOCs in the competitive adsorption process, which was also shown in this experiment. In Fig 4.1., Fig 4.2. and Fig 4.3., it can be seen that benzene and toluene are discharged higher than the inflow concentration in adsorption. As the loading capacity of the adsorption bed increases, the adsorbed benzene is replaced by toluene, ethylbenzene and p−xylene, and then the toluene is replaced by ethylbenzene and p−xylene. The reason for such roll up may be competition where the relative dominance of a stronger adsorbate is observed over a weaker adsorbate (Do and Do, 2002; Liao et al., 2018; Xue et al., 2018). The physisorption−based interaction between the adsorbate and the adsorbent bed is controlled by a weak van der Waals force. A strong competition occurs between these compounds as it was evidenced by the adsorption of mixed VOCs in this study. A strong competition occurs between these compounds as it was evidenced by the adsorption of mixed VOCs in this study. Hence, a significant portion of the adsorbed VOC can be replaced on the adsorbent surface by adsorbents with stronger physical absorption binding energy (Gaálová et al., 2018).



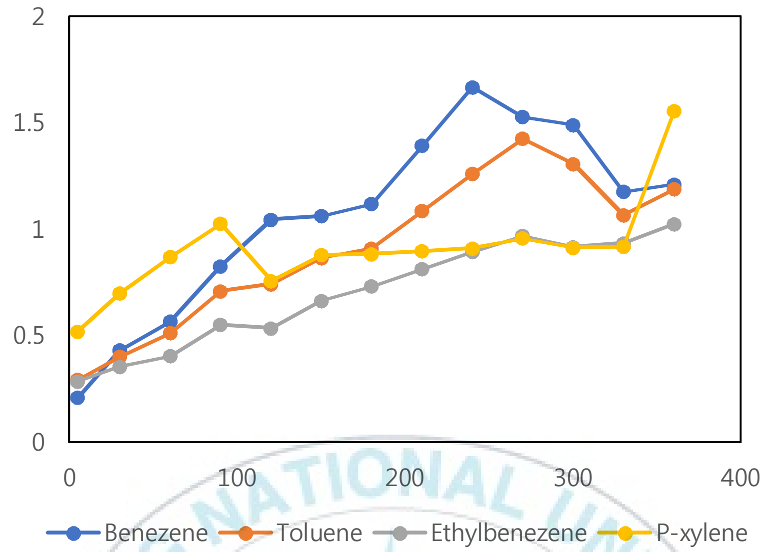
(a) Zeolite



(b) Silica gel

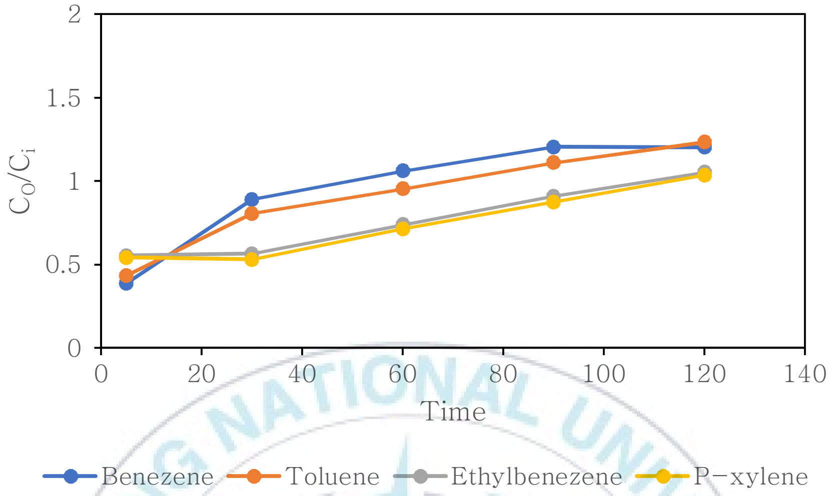


(c) Activated carbon A

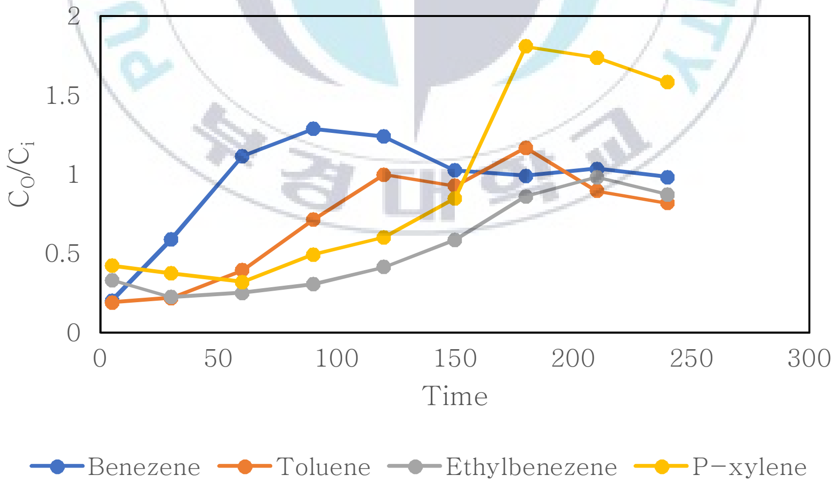


(d) Activated carbon B

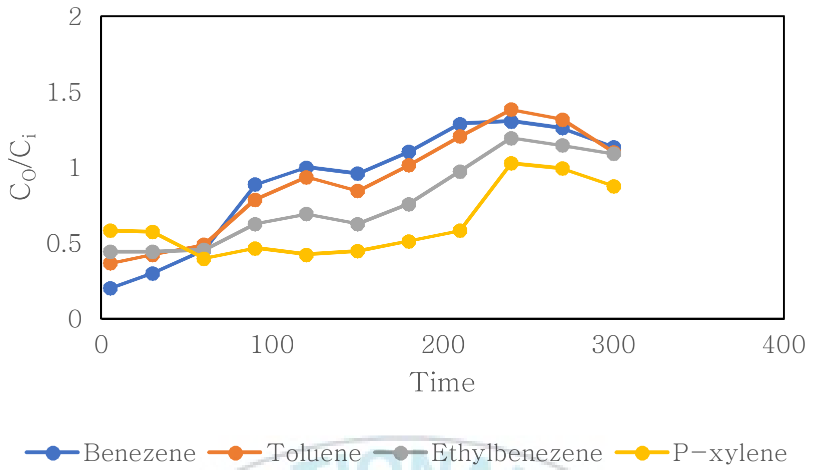
Figure 4.1. Breakthrough curve at adsorption temperature of 15°C.



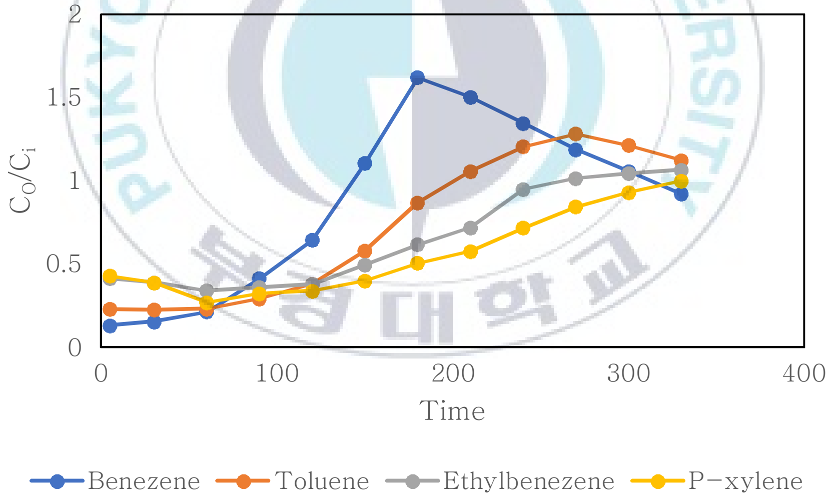
(a) Zeolite



(b) Silica gel

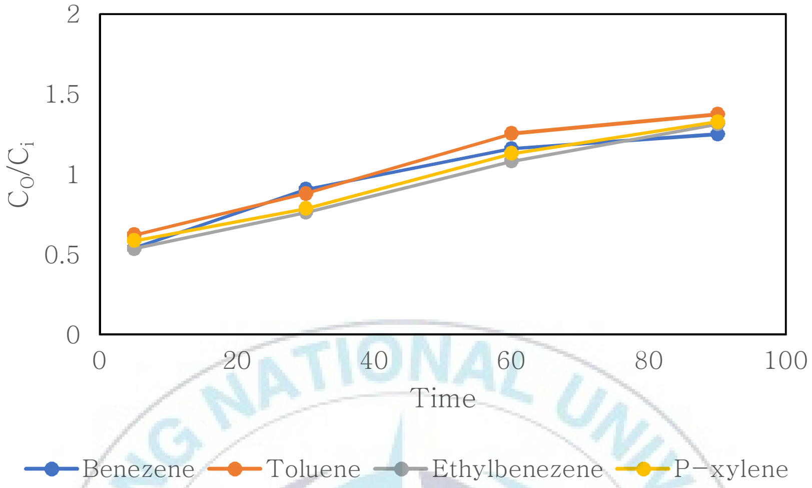


(c) Activated carbon A

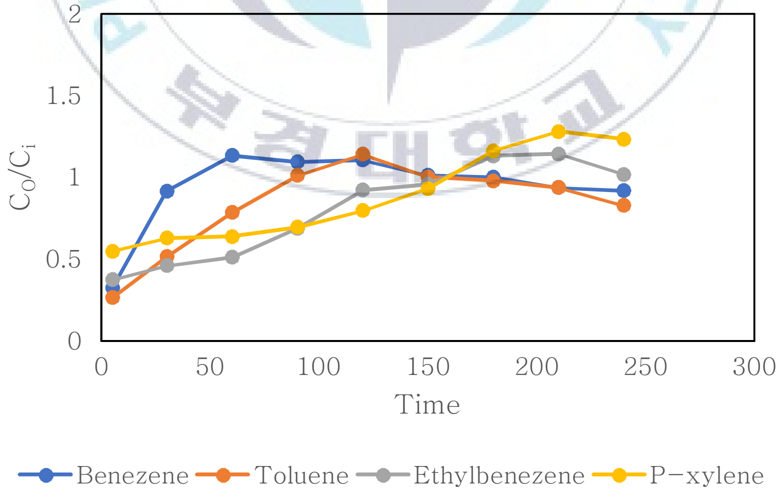


(d) Activated carbon B

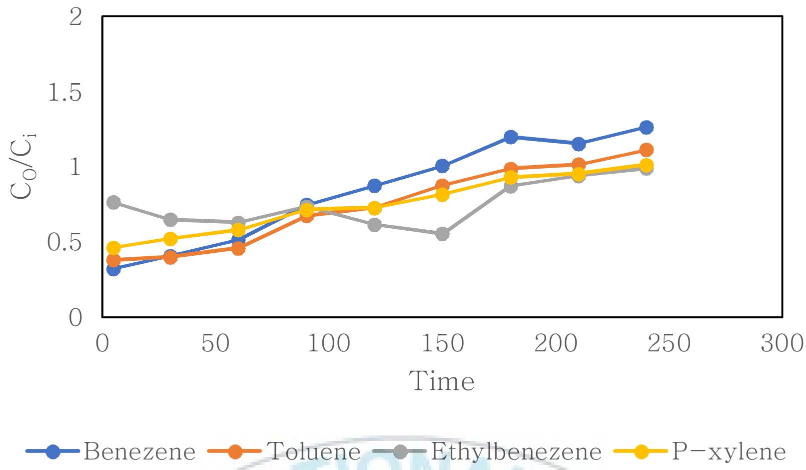
Figure 4.2. Breakthrough curve at adsorption temperature of 25°C.



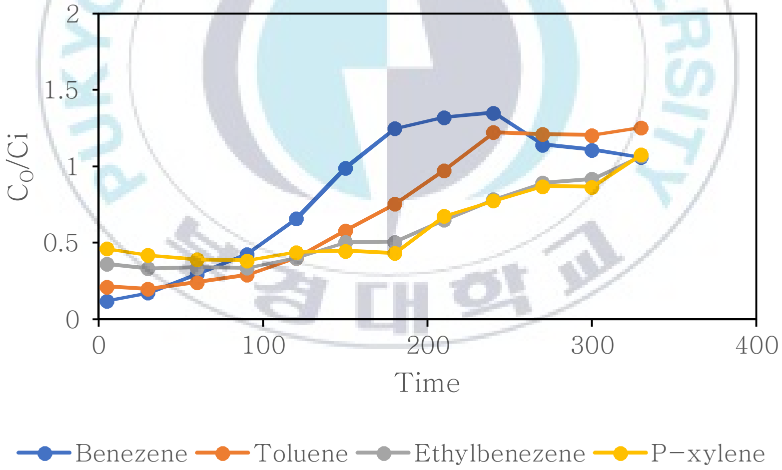
(a) Zeolite



(b) Silica gel



(c) activated carbon A



(d) activated carbon B

Figure 4.3. Breakthrough curve at adsorption temperature of 35°C.

4.3 application of air purifier type filter

4.3.1. Comparison of normal air filter and adsorbent applied filter

Figure 4.4. shows the change in concentration of PM_{10} and $PM_{2.5}$ over time. The background concentrations in the chamber are $PM_{2.5}$ (0.003 mg/m^3) and PM_{10} (0.015 mg/m^3), and $PM_{2.5}$ (0.2875 mg/m^3) and PM_{10} (1.534 mg/m^3) greatly increase while smoking. When comparing the conditions as the air purifier was operating, the time required for the concentration of PM to decrease to the background concentration after smoking did not differ significantly, and it could be confirmed that the air purifier decreased very slowly when the air purifier was not operated. Figure 4.5. shows the change of nanoparticles under each condition. It shows concentration decreased very slowly when the air purifier was not operated, but rapidly decreased over time when the air purifier was operated. At this time, there was no difference depending on the presence or absence of activated carbon, which suggests that activated carbon was not involved in the removal of nanoparticles. Figure 4.6. shows the concentration of VOCs

according to the operating conditions of the air purifier. Excluding toluene, the amounts of released VOCs followed the order of conditions: using HEPA filter only, using no air purifier and the using the existing filter. The best VOCs removal efficiency was obtained when the existing filter was used, and the filter using only the HEPA filter without any adsorbent showed the worst efficiency. Hence, it can be inferred that the amount of VOCs present in the chamber can vary depending on the condition whether there is an adsorbent inside the filter and whether the air purifier is running.

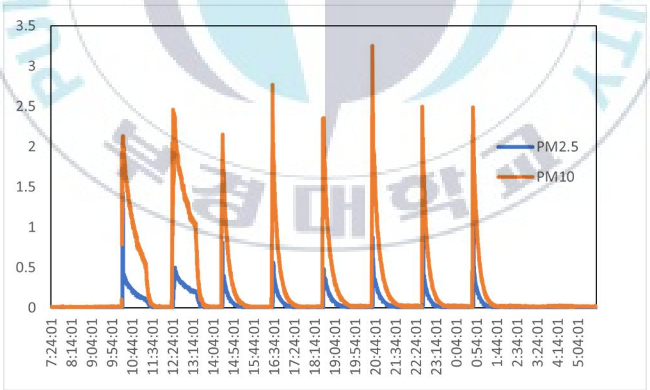
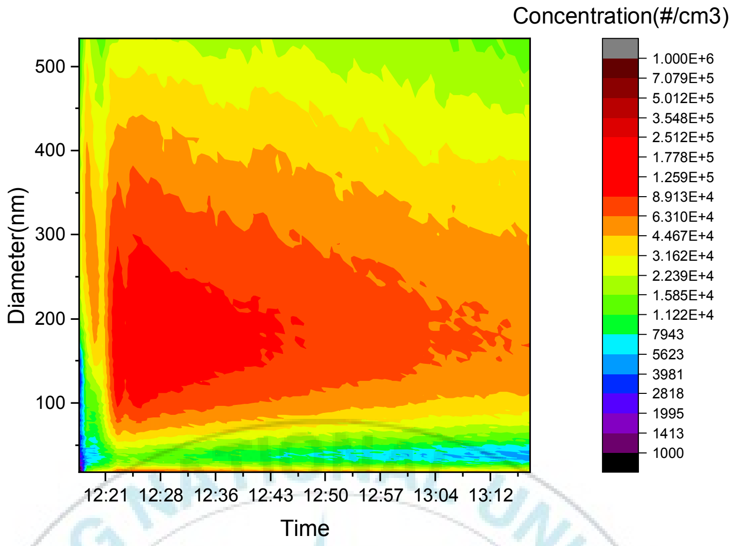
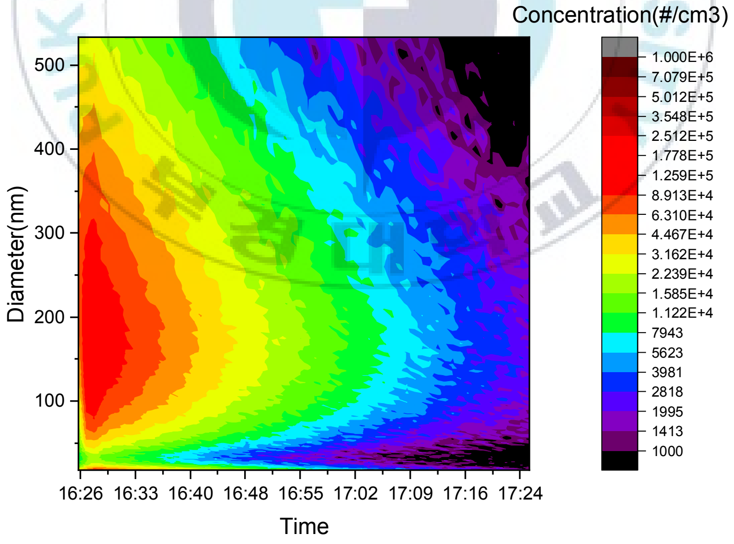


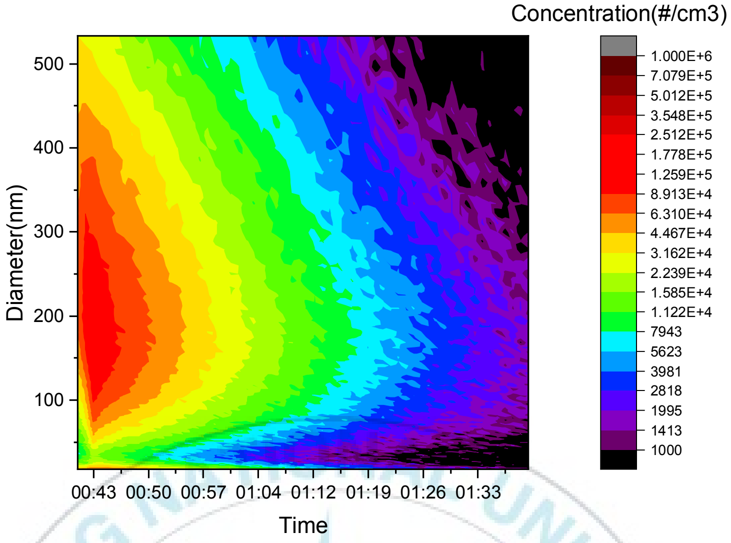
Figure 4.4. Concentration of particulate matter in cigarette smoking according to the application of air purifier filter


Concentration(#/cm3)
1.000E+6
7.079E+5
5.012E+5
3.548E+5
2.512E+5
1.778E+5
1.259E+5
8.913E+4
6.310E+4
4.467E+4
3.162E+4
2.239E+4
1.585E+4
1.122E+4
7943
5623
3981
2818
1995
1413
1000
Diameter(nm)
500
400
300
200
100
12:21
12:28
12:36
12:43
12:50
12:57
13:04
13:12
Time

(a)


Concentration(#/cm3)
1.000E+6
7.079E+5
5.012E+5
3.548E+5
2.512E+5
1.778E+5
1.259E+5
8.913E+4
6.310E+4
4.467E+4
3.162E+4
2.239E+4
1.585E+4
1.122E+4
7943
5623
3981
2818
1995
1413
1000
Diameter(nm)
500
400
300
200
100
16:26
16:33
16:40
16:48
16:55
17:02
17:09
17:16
17:24
Time

(b)



(c)

Figure 4.5. Concentration of particulate matter in cigarette smoking according to the application of air purifier filter; (a) air purifier operation X; (b) original filter and (c) filter without adsorbent

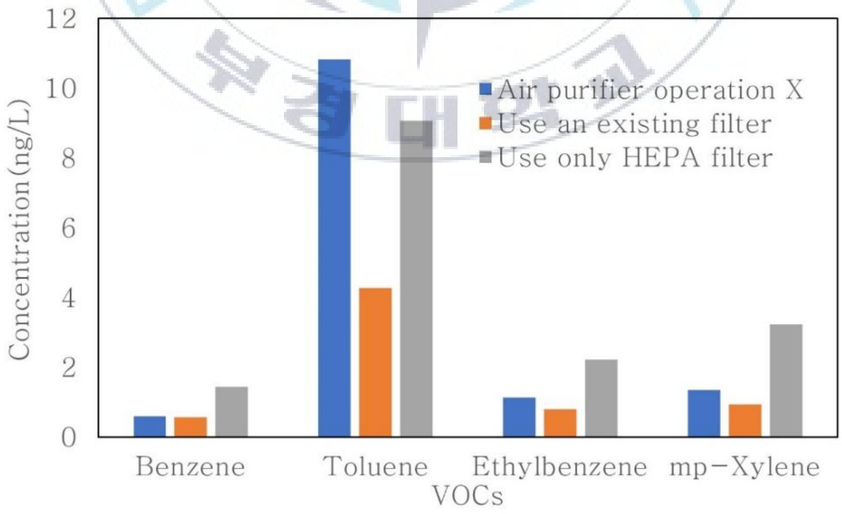


Figure 4.6 VOCs concentration in chamber air according to filter conditions

Conclusion

In this study, the adsorption characteristics of BTEX according to the adsorbent were identified, and an actual use experiment was conducted by applying the adsorbent to an air purifier−typed filter. The adsorption characteristics of BTEX were confirmed by using zeolite, silica gel and activated carbon as adsorbents. Breakthrough time and breakthrough curve were different as per adsorbent and the adsorption capacity was higher when the specific surface area and micropore ratio were higher. In addition, it was confirmed that competitive adsorption occurred and benzene and toluene having a small molecular weight were discharged at a higher concentration than the inlet concentration. The adsorbent with the best adsorption capacity was selected and applied to the air purifier−typed filter. And in order to create an environment with high VOCs concentration, cigarettes were smoked in the exposure room, and PM and VOCs were analyzed depending on filter conditions. The difference in PM removal efficiency according to the presence or absence of activated carbon was insignificant, but the existing filter showed the highest VOCs removal efficiency and the lowest removal efficiency when removing the adsorbent in the filter. For practical use, it is judged that more various adsorbents shall be used. In the air purifier filter application experiment, the removal efficiency was measured by the amount of VOCs adsorbed on the adsorption tube for 1 hour, but it was necessary to understand the real−time reduction in order to accurately measure the removal efficiency of the filter. In this study, BTEX was specified, and the concentration was also examined. But there are diverse types of VOCs in reality, so for the reason, more VOCs in a complex manner shall be analyzed. Hence, in future studies, it is necessary to simultaneously analyze ketones and aldehydes as well as aromatic hydrocarbons other than BTEX.

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