Purification of Indoor Air Pollutants Utilizing Hydrophobic Adsorbents

Master *of* Applied Science in Chemical and Biological Engineering Thesis

By

Ji Sub Yun

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Supervisor:

Dr. F. Handan Tezel

Department of Chemical and Biological Engineering

Faculty of Engineering

University of Ottawa

Ottawa, Canada

Abstract

Sick building syndrome (SBS) is a particular concern in places with inadequate ventilation and frequently attributed to chemical contaminants such as volatile organic compounds (VOCs) released from indoor sources that are frequently encountered in everyday life such as adhesives, carpeting, upholstery, manufactured wood products, copy machines, pesticides, cleaning agents inside buildings, plumbing vents, and painting. Furthermore, it is a major issue for modern human beings who spend most of their time indoors or must stay indoors for self-isolation due to special circumstances such as the coronavirus disease-19 (COVID-19) pandemic that occurred in 2019 and 2020. Main indoor VOCs are trichloroethylene (TCE), benzene, toluene, and para-xylene (p-xylene). In general, these compounds are not present in indoor spaces at acute concentrations, but prolonged exposure to these compounds can have chronic health effects such as allergic sensitization, increased cancer risks, and respiratory diseases.

In this study, the adsorption process with various advantages has been applied to remove VOC's using commercially available hydrophobic adsorbents. The hydrophobic adsorbents can contribute to reducing the possibility of chemical adsorption (chemisorption) of moisture from the air, which can decrease the capacity of adsorbent by clogging the pores. The adsorption of these major VOCs was investigated in this work for three major types of industrial hydrophobic adsorbents: activated carbons, zeolites, and polymer.

This study will show the investigation into finding the most promising hydrophobic adsorbent for removal of TCE, benzene, toluene, and p-xylene, which are the main VOCs found indoors. The promising hydrophobic adsorbent has been determined by comparing Henry's law constants and heat of adsorption values for the different adsorbents, which were estimated by using a concentration pulse chromatographic technique by utilizing a gas chromatograph equipped with a flame ionization detector.

For all adsorbents, Henry's law constants at room temperature of p-xylene were always the highest followed by toluene, benzene, and TCE. For all adsorbates, Henry's law constants at room temperature of AC BPL and HiSiv 3000 were higher than the other hydrophobic adsorbents.

For a developing modern society dealing with a pandemic, this study can contribute to producing the optimized gas masks and indoor filters for the removal of indoor air pollutants, which can help people who suffer from SBS. It can also help society for taking preventative actions towards dealing with SBS.

Sommaire

Le syndrome des bâtiments malsains (SBS) est particulièrement préoccupant dans les endroits où la ventilation est inadéquate. Il est souvent attribué à des contaminants chimiques tels que les composés organiques volatils (COV) rejetés par des sources intérieures que l'on rencontre fréquemment dans la vie quotidienne, comme les adhésifs, les tapis, les tissus d'ameublement, les produits en bois manufacturés, les photocopieuses, les pesticides, les produits de nettoyage à l'intérieur des bâtiments, les conduits de plomberie et la peinture. En outre, il s'agit d'un problème majeur pour les êtres humains qui, de nos jours, passent la plupart de leur temps à l'intérieur ou doivent rester à l'intérieur pour s'isoler en raison de circonstances particulières telles que la pandémie de maladie à coronavirus 19 (COVID-19) survenue en 2019 et 2020. Les principaux COV intérieurs sont le trichloroéthylène (TCE), le benzène, le toluène et le para-xylène (p-xylène). En général, ces composés ne sont pas présents en concentrations élevées dans les espaces intérieurs. Cependant, une exposition prolongée à ces composés peut avoir des effets chroniques sur la santé, tels qu'une sensibilisation allergique, une augmentation des risques de cancer et des maladies respiratoires.

Dans cette étude, le processus d'adsorption, qui présente divers avantages, a été appliqué pour éliminer les COV en utilisant des adsorbants hydrophobes disponibles dans le commerce. Les adsorbants hydrophobes peuvent contribuer à réduire la possibilité d'adsorption chimique (chimisorption) de l'humidité de l'air, ce qui peut diminuer la capacité de l'adsorbant en bouchant les pores. L'adsorption de ces principaux COV a été étudiée dans ce travail pour trois grands types d'adsorbants hydrophobes industriels : les charbons actifs, les zéolites et les polymères.

Cette étude cherche à identifier l'adsorbant hydrophobe le plus prometteur pour l'élimination du TCE, du benzène, du toluène et du p-xylène, qui sont les principaux COV présents à l'intérieur. L'adsorbant hydrophobe le plus prometteur a été déterminé en comparant les constantes de la loi de Henry et les valeurs de chaleur d'adsorption pour les différents adsorbants, qui ont été estimées par la technique de chromatographie par impulsions de concentration en utilisant un chromatographe en phase gazeuse équipé d'un détecteur à ionisation de flamme.

Pour tous les adsorbants, les constantes de la loi d'Henry à température ambiante du p-xylène étaient toujours les plus élevées, suivies par le toluène, le benzène et le TCE. Pour tous les adsorbants, les constantes de la loi d'Henry à température ambiante de AC BPL et HiSiv 3000 étaient relativement plus élevées que celles des autres adsorbants hydrophobes.

Dans notre société moderne en développement présentement confrontée à une pandémie, cette étude pourrait contribuer au développement et à la production de masques à gaz et de filtres intérieurs optimisés pour l'élimination des polluants de l'air intérieur, ce qui pourrait aider les personnes souffrant du SBS. Elle peut également aider la société à prendre des mesures préventives pour lutter contre le SBS.

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III. Thesis Structure and Organization

The current thesis based on articles consists of four chapters.

Chapter 1 is a general introduction to inform the principles and concepts corresponding to the overall thesis. This chapter includes the importance of indoor air quality, causes of sick building syndrome, symptoms caused by major indoor air pollutants, adsorption process for removing indoor air pollutants, a review of three different types of commercially available adsorbents, and overall objectives of this work.

Chapter 2 pertains to the conference presented in the *CCEC 2020* and *AIChE 2019 Annual Meeting* titled “Improving Indoor Air Quality: Determining Adsorption Properties of VOCs Using Concentration Pulse Chromatography”. This chapter contains a brief literature review about major indoor air pollutants and activated carbon adsorbents and the results of experiments using the concentration pulse method. Based on Henry’s law constants at room temperature, commercially available four different activated carbon adsorbents were compared for removing major indoor air pollutants which are para-xylene, toluene, benzene, and trichloroethylene.

Chapter 3 relates to the conference presented in the *CCEC 2020* and *AIChE 2019 Annual Meeting* titled “Improving Indoor Air Quality: Determining Adsorption Properties of VOCs Using Concentration Pulse Chromatography”. This chapter includes a brief literature review about major indoor air pollutants and zeolites and polymer adsorbents, and the results of experiments carried out based on the concentration pulse method. Based on Henry’s law constants at room temperature, commercially available two different zeolite adsorbents and one polymer adsorbent were studied and discussed for removing major indoor air pollutants which are para-xylene, toluene, benzene, and trichloroethylene.

Chapter 4 summarizes the conclusions proving the overall discussion of this thesis and the recommendations for future work. Also, the most promising adsorbent for removing major indoor air pollutants was determined by a decision matrix.

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IV. Contribution of Collaborators

I declare that I am the sole author and primary contributor to this thesis. I performed all experimental works, calculations, and writing this thesis under the supervision of Dr. F. Handan Tezel.

The experimental set-up was previously built, designed by myself, and with the help of the technical staff, Sean Wilson, and Franco Ziroldo. I performed all the experiments for Henry's law constants.

Dr. Sean Wilson, Dr. Dean Kennedy and Dr. F. Handan Tezel greatly contributed to building the topic of this thesis and fundamental knowledge of adsorption. Dr. F. Handan Tezel's supervision, discussion, and advice significantly contributed to improving this thesis.

V. List of Abbreviations

ACs	activated carbons
ACN	acrylonitrile
ACF	activated carbon fiber
Al	aluminum
BET	Brunauer-Emmett-Teller
Co.	company
CMS	carbon molecular sieves
CPM	concertation pulse method
CSA	concentration swing adsorption
COVID-19	coronavirus disease-19
D/A	data acquisition
DVB	divinylbenzene
EGDM	ethyleneglycoldimethacrylate
EPA	environmental protection detector
FAU	faujasite
F-600	filtrasorb-600
FID	flame ionization detector
GAC	granular activated carbon
GC	Gas chromatography

GC-FID	gas chromatography equipped with flame ionization detector
GM	geometric mean
HiSiv	high-silica molecular sieve
H_2	hydrogen
Ltd.	limited
LLC	limited liability company
Max	maximum
Min	minimum
N_2	nitrogen
NV2P	N-vinyl-2-pyrollidinone
p-xylene	para-xylene
PAC	powdered activated carbon
PSA	pressure swing adsorption
PEI	polyethyleneimine
PIB	polyisobutylene
SBS	sick building syndrome
SHS	sick house syndrome
Si	silicon
Si/Al	ratio of silicon over aluminum
SSS	sick school syndrome
TCE	Trichloroethylene
UOP	universal oil product
US EPA	united states environmental protection agency

vs	versus
VSA	vacuum swing adsorption
VOCs	volatile organic compounds
WHO	world health organization
4VP	4-vinyl-ptridine
ZSM-5	zeolite socony mobil-5

CHAPTER 1: Introduction

Ji Sub Yun

Department of Chemical and Biological Engineering, University of Ottawa

161 Louis Pasteur, Ottawa, ON, KIN 6N5 CANADA

1.1. Indoor Air Quality

So far, air pollution has been globally issued as having adverse human health and environmental effects. In terms of air pollution, numerous studies and the public mainly have continued to concern the outdoor air pollution issue such as smog, exhaust gas released from vehicles, greenhouse gas problem, global warming, and so on. However, they overlook another jeopardy which is indoor air pollution.

The people normally spend most of their time indoors for living, working, studying, eating, driving, and shopping in a recently developed society. United States environmental protection agency (US EPA) found that on average, people were outside only 5 % of the day. The rest of the time was spent inside buildings: 88 % and inside vehicles: 7 %[1]. In the case of the coronavirus disease-19 (COVID-19) pandemic that occurred in 2019, people inevitably had to stay the whole time at home to prevent the spread of the virus to others.

The indoor air pollutants are not present in acute exposure concentrations, but over prolonged exposure to poor indoor air quality can cause severe chronic health effects such as allergic sensitization and increased cancer risks. Furthermore, the health effect of VOC's as indoor air pollution can be more severe than outdoors due to their higher concentrations in indoor air than outdoor air (detailed information is shown in Section [1.3])[1]-[4].

Therefore, improving indoor air quality is a significant subject for the better life and health effects of all human beings who spend most of their time indoors in modern society.

1.2. Sick Building Syndrome

Sick building syndrome (SBS) is described as the publicized medical condition in which building occupants have the experience of acute health and comfort effects related to over prolonged exposure to poor indoor air quality in a building. The symptoms of SBS are normally unspecific illnesses (Table 1.1) and the cause can not be identified. This medical condition can appear in a particular room or throughout the entire building as a temporary or long-term problem. The contributing factors to SBS are entirely associated with the inadequate ventilation system and chemical contaminants emitted from indoor sources[1][3][5].

Table 1.1- The symptoms of Sick Building Syndrome[1].

- chest congestion (wheezing, shortness of breath, chest tightness)
- chills and fever
- dizziness
- dry skin
- eye problems (dry, itching, tearing, or sore eyes, blurry vision, burning eyes, problems with contact lenses)
- fatigue (unusual tiredness, sleepiness, or drowsiness)
- headache and nausea
- muscle pain (aching muscles or joints, pain or stiffness in the upper back, pain or stiffness in the lower back, pain or numbness in shoulder/neck, pain or numbness in hands or wrists)
- nasal congestion (runny/stuffy nose, sinus congestion, sneezing)
- neurological symptoms (difficulty remembering or concentrating, feeling depressed, tension or nervousness)
- throat problems (sore throat, hoarseness, dry throat)

1.2.1. Inadequate Ventilation System

The purpose of ventilation is to remove or dilute the indoor air pollutants by providing fresh air. There have two different ventilation systems which are the natural method and mechanical method. In natural ventilation (also called passive ventilation), outdoor air is naturally entering or penetrating into cracks in the building, open windows, and entry and exit points, but the natural ventilation relies on the surrounding outdoor air condition. On the other hand, mechanical ventilation is mechanically controlled to exchange indoor and outdoor air, but the wrong design and improper inspection of ventilation can result in poor air quality and unbalanced air ventilation between rooms in the building. The indoor air pollutants can also be formed by the inflow of outdoor air pollutants such as motor vehicle exhausts, plumbing vents, and building exhausts entering through air intake vents, windows, and other openings [3][6][7].

1.2.2. Chemical Contaminants from Indoor Sources

According to the world health organization (WHO) committee, 30 % of new or remodelled commercial buildings in the world had serious problems with indoor air quality because various construction chemical materials such as paint, adhesive, and mold are involved to construct new or remodelling buildings and readily release a lot of pollutants, constantly[8][9]. Not only for construction materials, but indoor air pollutants are also released from various indoor items such as furnishing, clothing, combustion appliances, housekeeping products, and maintenance products that can easily encounter in everyday life. On average, indoor sources constantly release more than 900 types of chemical and biological contaminants in total. Among these indoor pollutants, volatile organic compounds (VOCs) account for more than 40 % of total chemical and biological contaminants, which exceed 1 ppb (one part per billion) concentration[10][11].

1.3. Volatile Organic Compounds (VOCs)

Volatile organic compounds (VOCs) are the main indoor chemical pollutants that cause SBS. Due to the properties of VOCs having high vapour pressure and volatility at ordinary room temperature and atmosphere, VOCs composed of a large number of molecules can be readily evaporated or sublimated from the liquid or solid states such as paint, adhesives, and polymer resin[1][7]. As mentioned in Section [1.1], people spend most of their time indoors. The prolonged exposure to even low concentrations of VOCs can cause the medical condition, SBS.

Up to 100 to 5000 VOCs have been detected in indoor air. Among theses indoor VOCs, the main VOCs frequently encountered indoors are benzene, toluene, trichloroethylene (TCE), and para-xylene (p-xylene), which were investigated in this study. Depending upon the location and indoor condition, the concentrations of main VOCs can be varied, but these chemical compounds are commonly detected on more than 75 % of indoor air samples [10][12]. Numerous studies have reported that the concentrations of main VOCs measured in air samples indoors were often higher than their outdoor concentrations (Table 1.2)[1][10][13][14]. As shown in Table 1.2, minimum concentrations of indoor VOCs were similar, but indoor concentrations of VOCs were higher than their corresponding maximum and mean concentrations. The highest frequency and concentration for indoors were commonly seen for toluene followed by p-xylene, benzene, and TCE. According to WHO and numerous environmental institutions, there has no recommended safe level of these pollutants. Therefore, the air should be purified or these pollutants should be removed to as low a concentration as possible[15].

Table 1.2 – The comparison of public indoor and outdoor concentrations of main VOCs (μg/m^3) based on 759 indoor air samples and 30 outdoor air samples[14].

Compounds	Indoor Concentration (μg/m^3)			Outdoor Concentration (μg/m^3)		
	Min	Max	GM	Min	Max	GM
Toluene	< 0.64	737.51	8.47	< 0.64	33.50	5.13
p-Xylene	< 0.91	73.44	3.85	< 0.91	18.36	1.62
Benzene	< 1.43	78.79	1.89	< 1.43	13.43	1.71
TCE	< 1.38	11.15	0.87	< 1.38	3.75	0.82

Min: minimum
Max: maximum
GM: geometric mean

1.3.1. Benzene

Benzene is an aromatic compound composed of six-member unsaturated carbon ring and six hydrogen atoms joined with each carbon atom. Benzene is a colourless, highly flammable volatile liquid with a sweet odour and a boiling point of 80.1 ℃. At room condition (temperature: 25 ℃ and pressure: 1 atm), the vapour pressure of benzene is 12.7 kPa.

Various household items and other products used indoors release benzene constantly. Among these products, cigarette smoke is a major source of benzene. On average, the benzene concentrations of smoker indoors are approximately 3 μg/m^3 higher than non-smoker indoors[16]. The inhaled benzene is distributed to the body through mostly the lungs and the skin. Chronic exposure to benzene can mainly cause acute myeloid leukemia, a decrease in red blood cells, leading to anemia, and chronic diseases. The unit risk of benzene concentration is 6 x 10^{-6} μg/m^3[15]-[17].

1.3.2 Toluene

Toluene is an aromatic hydrocarbon composed of a monosubstituted CH_3 group on a phenyl group. Toluene is a colourless and highly flammable volatile liquid with a pungent odour and a boiling point of 110.6 ℃. At room conditions, the vapour pressure of toluene is 3.8 kPa[15].

The toluene normally has the highest concentration and frequency among indoor VOCs. It is released from the indoor household, automotive products, construction materials, and petroleum refining process. Prolonged exposure to toluene can cause chronic diseases such as headaches, dizziness, lack of coordination, disturbed sleep, eye irritation and feelings of intoxication. According to the report of residential maximum exposure limit for toluene in Health Canada, exposure to toluene concentration of 4 ppm for short-term (about 8 hours) showed neurologically related symptoms such as headaches, dizziness, and feelings of intoxication[18][19].

1.3.3. Trichloroethylene (TCE)

Trichloroethylene (TCE) is a halocarbon widely used as an industrial solvent. It is a colourless volatile liquid with low flammability and a sweet ethereal (chloroform-like) smell. It has a boiling point of 86.7 ℃. At room conditions, the vapour pressure of TCE is 7.8 kPa.

In industry, TCE is mainly used to produce the hydrofluorocarbon chemicals, refrigerants, and grease removal on metal parts, spot removal in the dry-cleaning operation, and some aerosol cleaning products. The prolonged exposure to TCE can cause chronic disease and cancer (liver, kidney, bile duct, and non-Hodgkin’s lymphoma) with the assumption of genotoxicity. The unit risk of TCE concentration is 4.3×10^{-7} ug/m^3[15][20].

1.3.4. para-Xylene (p-Xylene)

Para-xylene is an aromatic hydrocarbon composed of two methyl groups located on opposite substituents of 1 and 4 positions of a central benzene ring. p-xylene is a highly flammable, and volatile colourless liquid with an aromatic odour and has a boiling point of 138 ℃. At room conditions, the vapour pressure of p-xylene is 0.9 kPa.

p-xylene is mostly released from industrial processes, solvent sources, and transportation sources. The medium to high concentrations of p-xylene exposure in the short and long-term can cause cardiovascular problems, irritation of the skin, eyes, nose, and throat, hepatic, neurological effects and nervous system problems such as headaches, lack of muscle coordination, dizziness, and confusion[21][22].

1.4. Adsorption

There are various technologies to remove or control VOC emissions. These technologies are largely classified into (i) destruction and (ii) recovery. In the first group, VOCs can be removed by destruction methods such as catalytical and thermal oxidation processes and biological treatment by bio-filtration. On the other hand, VOCs can also be removed by recovery methods such as condensation, adsorption, absorption, and membrane separation. Among these various methods, the adsorption process has been widely applied to remove VOCs compared to other methods due to various advantages such as high VOC removal efficiency up to 80 to 96 %, high capacity by the high surface area of adsorbent, low-temperature discharge at room temperature, easy operation, low operation cost, re-usable adsorbent by regeneration, various types of adsorbents optimized to operation, and availability as household products (gas mask and air purificator)[6][23].

Adsorption is a surface phenomenon that leads to interaction between molecules of adsorbate (in this study, VOC is adsorbate) and a solid surface. The VOC pollutants come to deposit on the solid object composed of highly porous surface structure material which is called adsorbent. There are two kinds of adsorption: (i) physical adsorption (physisorption) is a kind of adsorption that happens when inter-molecular attractive forces between adsorbate and adsorbent such as the weak electrostatic force and Van Der Waals force (weak force) are higher than those between molecules of the adsorbate itself. On the other hand, (ii) chemical adsorption (chemisorption) involves a chemical reaction sharing of electrons between adsorbate and surface of adsorbent to make a covalent or ionic bond. The chemisorption with heats of adsorption up to 100 to 400 kJ/mol released between adsorbent and adsorbate has a much stronger interaction than physisorption[24]-[26].

1.5. Hydrophobic Adsorbents

As mentioned in section [1.4.], the adsorption process has various advantages to remove VOCs. However, the problem of adsorption is that pores of adsorbent clogged by VOCs can reduce the capacity of the adsorbent. There are several regeneration methods to desorb VOCs attached to an adsorbent such as pressure swing adsorption (PSA), vacuum swing adsorption (VSA), concentration swing adsorption (CSA), temperature swing adsorption (TSA), or any other processes. However, the adsorbate chemically adsorbed is difficult to be separated from the adsorbent due to the bond strength between adsorbate and adsorbent[27]-[29].

Atmospheric air contains a large amount of water in vapour. Moreover, humid air places such as washrooms, kitchens, sewage disposal waste plants, waterfront indoor buildings have higher indoor water vapor concentrations. The water vapour can significantly reduce the VOC adsorption capacity of an adsorbent due to the decrease of sites by chemical interaction with the adsorbent[26].

In this study, hydrophobic adsorbents were investigated to remove the VOCs and to reduce the possibility of chemisorption with moisture in the atmosphere. Three representative types of hydrophobic adsorbents were investigated in this study: activated carbons (ACs), zeolites, and divinylbenzene (DVB) polymer.

1.5.1. Activated Carbons (ACs)

The activated carbons (ACs) are the adsorbents composed of a carbonaceous microcrystalline structure of graphite stacked in random orientation. Due to this orientation, the spaces between crystals make the micropores. The ACs are produced from the source materials such as coal, lignite, wood, nutshell, and petroleum containing carbon components. These carbonaceous materials are firstly pyrolyzed and carbonized to decompose them into the volatile fraction and low molecular products at several hundred degrees. Then, the thermally decomposed carbonaceous materials undergo the activation process using steam at above 800 ℃ or carbon dioxide at 700 to 1100 ℃. During this process, the volatile fraction, and low molecular products (carbonization products) formed in the pyrolysis are removed, which means that the pores of ACs are opened. The conditions of the initial pyrolysis and activation process affect the total pore volume and actual pore distribution associated with each pore size range. After pyrolysis and activation processes, the ACs are made of non-polar carbon chains with oxygen and some ashes. Surface oxidation and ashes can make ACs slightly hydrophilic, but ACs tend to be hydrophobic in general because of the dominance of non-polar carbon chains.

Depending upon the required conditions, ACs can be produced in various types such as powdered activated carbon (PAC), granular activated carbon (GAC), carbon molecular sieves (CMS), and activated carbon fiber (ACF)[27][30][31].

1.5.2. Zeolites

Zeolites are porous crystalline aluminosilicate materials composed of tetrahedra framework structure of $(SiO_4)^0$ and $(AlO_4)^{-1}$ balanced out by cations, which can form the regular arrangement of crystal lattice pores. Due to the crystal lattice structure, zeolites have uniform pore size distribution.

Zeolites can be naturally occurring, or they can be synthesized. Natural zeolites can be excavated by mining in some specific countries, but production is limited to certain structures such as clinoptilolite, chabazite and mordenite as examples. On the other hand, synthetic zeolites can be produced by the hydrothermal process (or microwave process) in an autoclave which is a synthesis reaction between sodium silicate, sodium hydroxide, and sodium aluminate. After the hydrothermal process, metal salts such as Ca, Na, K, and Li, are added to balance out the zeolite framework by ion-exchange. Depending upon the addition of metal cation, zeolites can have different properties such as different pore size, polarity, and framework structure. Therefore, the optimized zeolites can be produced by controlling the operating conditions of the synthesis process.

The hydrophobic property of zeolite is determined by the Si/Al ratio. The increase in silicon atoms makes the surface of zeolite homogeneous since the cationic variability decreases. Therefore, a higher Si/Al ratio has a higher hydrophobic property of zeolite, conversely, a lower Si/Al ratio has higher hydrophilic property. The Si/Al ratio exceeding about 10 is regarded as hydrophobic zeolite[27][30]-[33].

1.5.3. Divinylbenzene (DVB) Polymers

Polymers are chemical compounds composed of monomers, which are the basic units repeated in their structure. They are also referred to as plastics. The unique properties of polymers are attributed to the structures of the monomers that make up their structure.

The polymers can occur in nature or can be synthesized. The synthetic polymers are processed by a polymerization method in which small monomer molecules are combined repeatedly to make long chains. Synthetic polymers can be classified into two types depending on their response to heating: thermoplastics and thermosets. Thermoplastics have linear monomer molecule chains with secondary bonds. They soften when they are heated, and they become firm again when they are cooled. On the other hand, thermosets have cross-links with covalent bonds in their structure and they can be molded to a certain shape permanently. The polymers can be fine-tuned by various processes and operating conditions. The conventional process sequences are: i) heating and melting the polymer, ii) pumping the polymer to the shaping unit, iii) forming or tailoring the melt into the required shape and size, iv) cooling and solidification, and v) other processes such as calendaring, blow moulding, thermoforming, compression moulding, or rotational moulding [34].

The conventional commercial polymer adsorbent for removal of VOCs is the divinylbenzene (DVB) polymer adsorbent due to its low affinity for water vapour (hydrophobic property by hydrocarbon compounds), low catalytic reactions with VOCs, and regeneration at low temperatures[35].

DVB consists of two vinyl groups on a benzene ring. DVB polymer adsorbents can be produced by crosslinked copolymerization of DVB and monomers. Therefore, depending upon the type of monomer, various types of DVB polymer adsorbents can be produced. Commercially, well-known DVB polymers are DVB-ethyleneglycoldimethacrylate (DVB-EGDM), DVB-polyethyleneimine (DVB-PEI), DVB-acrylonitrile (DVB-CAN), DVB, DVB-styrene (DVB-St), DVB-N-vinyl-2-pyrollidinone (DVB-NV2P), and DVB-4-vinyl-pyridine(DVB-4VP)[27][35].

1.6. Objectives

Benzene, toluene, trichloroethylene (TCE), and para-xylene (p-xylene) are major VOCs in indoor air as pollutants and were studied because their concentrations and frequencies in indoor air are often relatively higher than outdoors[10][13][36]. In this study, the investigation into finding a promising hydrophobic adsorbent among four types of ACs, two types of zeolites, and one type of DVB polymer was conducted by comparing their Henry's law constants for these VOC's at room temperature. Corresponding heat of adsorption values were also determined for the VOCs with these seven different hydrophobic adsorbents, by carrying out experiments at many different temperatures.

Until recently, most studies on indoor main VOCs and adsorbents in the literature have analyzed breakthrough curves, adsorption isotherms at room conditions and theoretical Henry's law constants based on adsorption isotherm data[37]-[44]. However, VOCs are not present at high concentrations indoors. Their concentrations (or partial pressures) are very small. Henry's law constant is an effective indicator to see the potential of adsorption interaction between adsorbate and adsorbent when VOC concentrations are low in Henry's Law region [27]. Furthermore, Henry's law constant can be effectively measured experimentally using the concentration pulse method (CPM). A gas chromatograph equipped with a flame ionization detector (GC-FID) can be used for flammable liquid samples[27]. The main indoor VOCs are all liquids at room condition due to high boiling points and have all flammability, as mentioned in section [1.3.]. More details on GC-FID used in this study can be found in Chapters 2 and 3. Henry's law constants have been determined experimentally at many different high temperatures and corresponding van’t Hoff plots were created for the above mentioned VOC’s with the 7 adsorbents studied. Henry’s law constants at room temperature (25 °C) were estimated by the extrapolation of these plots to room temperature. The heat of adsorption values were determined from the slopes of the van’t Hoff plots.

The most promising adsorbent for removal of these VOCs has been determined by the decision matrix based on Henry’s law constant at room temperature.

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CHAPTER 2:

Improving Indoor Air Quality Utilizing Activated Carbon Adsorbents

Ji Sub Yun, F. Handan Tezel

Department of Chemical and Biological Engineering, University of Ottawa

161 Louis Pasteur, Ottawa, ON, KIN 6N5 CANADA

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Corresponding Author’s Contact Information

e-mail: Handan.Tezel@uottawa.ca

phone: +1 (613) 562 – 5800 (ext 6107)

2.1. Abstract

Sick Building Syndrome (SBS) is caused by indoor air pollution. Modern humans normally spend most of their time indoors. Therefore, indoor air pollutants should be removed to as low a concentration as possible. In this study, several commercially available activated carbon adsorbents (ACs) for the removal of major indoor air pollutants were investigated to find a promising activated carbon. This was done by determining the experimental adsorption Henry's law constants of pure trichloroethylene (TCE), benzene, toluene, and para-xylene (p-xylene) at different temperatures (90 to 400 ℃) in the presence of nitrogen gas (representing air) by using concentration pulse chromatography technique on a set-up which included a gas chromatograph equipped with a flame ionization detector (FID). Since the concentrations of all of these pollutants are very small in the air, their behaviours will be controlled by Henry's Law. The experimental Henry's law constants have been extrapolated to room temperature, (which is considered to be 25 ℃) by using the van't Hoff plot, for comparison of the studied activated carbons. For the removal of these indoor air pollutants, AC F-600 (Calgon Carbon), AC BPL (Calgon Carbon), AC NZ (Activated Carbon NZ Ltd.), and spectra carb 2225 AC (Engineering Fibers Technology, LLC) were studied as adsorbents. The heat of adsorption values were obtained from the plots of the logarithm of Henry's law constants as a function of the inverse absolute temperature, according to the van't Hoff plot behaviour. The results of this study showed that among the major indoor VOCs, for all ACs, p-xylene had the highest Henry's law constant followed by toluene, benzene, and TCE. Among the ACs, AC F-600 had the highest Henry's law constants for all the VOCs, followed by AC BPL, AC cloth, and AC NZ. The trends for the heats of adsorption were also similar to the ones for Henry's law constants. The heat of adsorption values were in the range of 60 to 80 kJ/mol.

Based on Henry’s law constants at room temperature, AC F-600 was determined as a promising adsorbent among studied ACs for purification of all of these major indoor air pollutants. This study is important for the future design of gas masks and indoor filters for the purification of indoor pollutants.

Key Words

Sick Building Syndrome, Adsorption, Henry’s law constant, Heat of adsorption Activated Carbon, TCE, Benzene, Toluene, p-Xylene

2.2. Introduction

Indoor air pollution in the present day has been considered harmful to human health. Human health is affected by the poor indoor air quality in residences, workplaces, and public buildings. The publicized medical conditions such as Sick Building Syndrome (SBS), Sick School Syndrome (SSS), and Sick House Syndrome (SHS) are primarily caused by prolonged exposure to poor indoor air quality produced by inadequate ventilation and chemical contaminants from indoor sources. The medical syndromes are frequently attributed to chemical contaminants such as volatile organic compounds (VOCs). VOCs are emitted from adhesives, carpeting, upholstery, manufactured wood products, copy machines, pesticides, cleaning agents inside buildings, plumbing vents, and exhausts entering from outside buildings. Normally, there are up to 100 to 5000 VOCs in indoor air. Among these indoor VOCs, trichloroethylene (TCE), benzene, toluene, and para-xylene (p-xylene) account for around 70 percentage. These major VOCs are often in higher concentrations indoors than outdoors. In general, the compounds are not present in acute exposure concentrations, but prolonged exposure to the indoor pollutants can have chronic health effects such as allergic sensitization, increased cancer risks, and respiratory diseases[1]-[10].

There are various techniques to remove the VOCs such as incineration, biological degradation, thermal oxidation, photo or catalytic oxidation, reverse flow reactor, adsorption, absorption, condensation, and membrane separation. Among these techniques, adsorption has been widely applied to reduce the amount of VOCs compared to other methods due to several advantages such as high VOC removal efficiency, high capacity of adsorbents, simple operation, low-cost, and re-usable adsorbents by regeneration[11]-[13]

Atmospheric air contains a large amount of water vapor, which can significantly contribute to reducing the VOC adsorption capacity of an adsorbent due to its competitive adsorption with

VOCs and causing a decrease of sites for VOC adsorption[14]-[16]. Therefore, the use of hydrophobic adsorbents with non-polar properties can reduce the possibility of water vapor adsorption and increase the VOC adsorption. The activated carbon (AC) adsorbents composed of non-polar carbonaceous microcrystalline chains are typical hydrophobic adsorbents. The ACs are produced from the source materials such as coal, lignite, wood, nutshell, and petroleum containing carbon components. These raw materials go through several processes such as pyrolysis and activation, which affect the total pore volume and actual pore distribution associated with each pore size range. At the end of these processes, the ACs are made of non-polar carbon chains with oxygen and some ash material. Surface oxygen and ashes can make ACs slightly hydrophilic, but ACs tend to be mostly hydrophobic due to the dominance of non-polar carbon chains. Furthermore, ACs can be of various types such as powdered activated carbons (PAC), granular activated carbons (GAC), carbon molecular sieves (CMS), and activated carbon fiber (ACF). Numerous studies have found excellence in AC adsorbents for VOC removal[17]-[22].

The past studies mainly have reported the breakthrough curves and adsorption isotherms [17][23]-[30]. However, indoor VOCs are not present in high concentrations. Their concentrations are very small in the air. Therefore, Henry's law constant, the initial slope of the adsorption isotherm would be an effective indicator to screen adsorbents to analyze their potential for indoor VOC removal. Adsorption Henry's law constant can experimentally be determined by using the concentration pulse method (CPM)[31]-[41].

2.3. Objective

Benzene, toluene, TCE, and p-xylene are major VOCs of indoor air pollutants and they were studied in the literature because their concentrations and frequencies are often relatively higher than their outdoor concentrations[42]-[44]. In this study, the investigation into finding a promising hydrophobic adsorbent among four AC adsorbent candidates was conducted by the comparison of their Henry's law constants at room temperature conditions. Henry's law constants of the above-mentioned main indoor VOCs were measured experimentally at ranges of high temperatures (90 ℃ to 400 ℃) for four different AC adsorbents. At lower temperatures, it was not possible to get accurate measurements of Henry's law constants, due to VOCs' high boiling points and their strong interactions with the AC adsorbents. For the comparison of the adsorption potential of different ACs, Henry's law constants observed at these higher temperatures were extrapolated to 25 ℃, which is considered to be the average room temperature.

The concentration pulse method (CPM) was used in this study, which included an experimental set-up that used a gas chromatograph (GC) equipped with a flame ionization detector (FID). Nitrogen was used as the carrier gas representing air since it accounts for 79 % of air and since the adsorption of oxygen gas, which is the other component in the air, behaves very similarly to nitrogen. To compare the interaction intensity between major indoor VOCs and the AC adsorbents, the heat of adsorption values were also determined from the slopes of the van't Hoff plots.

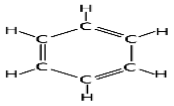
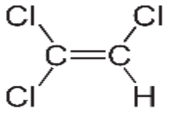
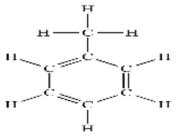
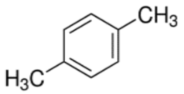
2.4. Materials

In this study, N_2 carrier gas was obtained from Messer Canada Inc. (Ottawa, Ontario, Canada) at a purity of 99.999%. High purity liquid benzene, TCE, toluene, and p-xylene were used as adsorbates. These adsorbates are all combustible. The adsorbents tested were four different types of activated carbons. The details of adsorbents and adsorbates are listed in Table 2.1 and Table 2.2, respectively.

Table 2.1 - Details of the adsorbents used in this study.

Properties	AC BPL	AC F-600	AC NZ	AC Cloth
Supplier	Calgon Carbon	Calgon Carbon	Activated Carbon NZ Ltd.	Engineering Fibers Technology, LLC
Location (city, province, country)	Pittsburgh, Pennsylvania, USA	Pittsburgh, Pennsylvania, USA	Taupo, New Zealand	Shelton, Connecticut, USA
Adsorbent Form	Pellet (4 x 10)	Pellet (12 x 40)	Flake	Cloth
BET surface area (m^2/g)	1,159	678	1,934	1,590
Mean pore size (Å)	26.19	21.90	19.33	18.68
Pore volume (cm^3/g)	0.76	0.37	0.93	0.74

Table 2.2 - Details of the major indoor VOCs studied in this work

Properties	Benzene	TCE	Toluene	p-Xylene
Suppliers	Sigma-Aldrich Canada Co.	Sigma-Aldrich Canada Co.	Sigma-Aldrich Canada Co.	Fisher Scientific Company
Location (city, province, country)	St. Louis, Missouri, USA	St. Louis, Missouri, USA	St. Louis, Missouri, USA	Ottawa, Ontario, Canada
Purity (%)	99.89	≥ 99	99.8	99
Boiling point (°C)	80.10	87.20	110.60	138.4
Structure				
Kinetic Diameter (Å)	5.85[45]	5.60[46]	5.85[45]	5.85[45]
Polarizability (Å^3)	10 ~10.74[47]	9.61~9.75[48]	11.80 ~12.30[47]	13.70 ~14.90[47]
Dipole Moment (x 10^{18} Deby)	---[47]	0.9[49]	0.375[47]	0.1[47]
Quadrupole Moment (x 10^{-26} Deby)	---[47]	---[49]	---[47]	---[47]

2.5. Experimental Details and Methodology

Henry's law constants and heat of adsorption values were measured by 8610C model GC purchased from SRI Instruments (Torrance, California, USA). The concentration pulse chromatographic technique was used in this study which uses a GC equipped with an FID (GC-FID). This method was observed to be simple, and accurate for the determination of experimental Henry's law constants[38]-[41]. A schematic diagram of the experimental set-up is depicted in Figure 2.1. N_2 gas was selected as the carrier gas since it accounts for 79 % of ambient air. The volumetric flow rate of N_2 carrier gas must be optimized to obtain accurate and clear peaks that can be integrated easily for the calculation of Henry's law constants. The low volumetric flow rate causes the baseline shift and high oscillation on the baseline of the peak sample due to longer experiments. The high volumetric flow rate could reduce the experimental time but, the peak would not be well detected and the flame for combusting the adsorbate would not be produced in time.

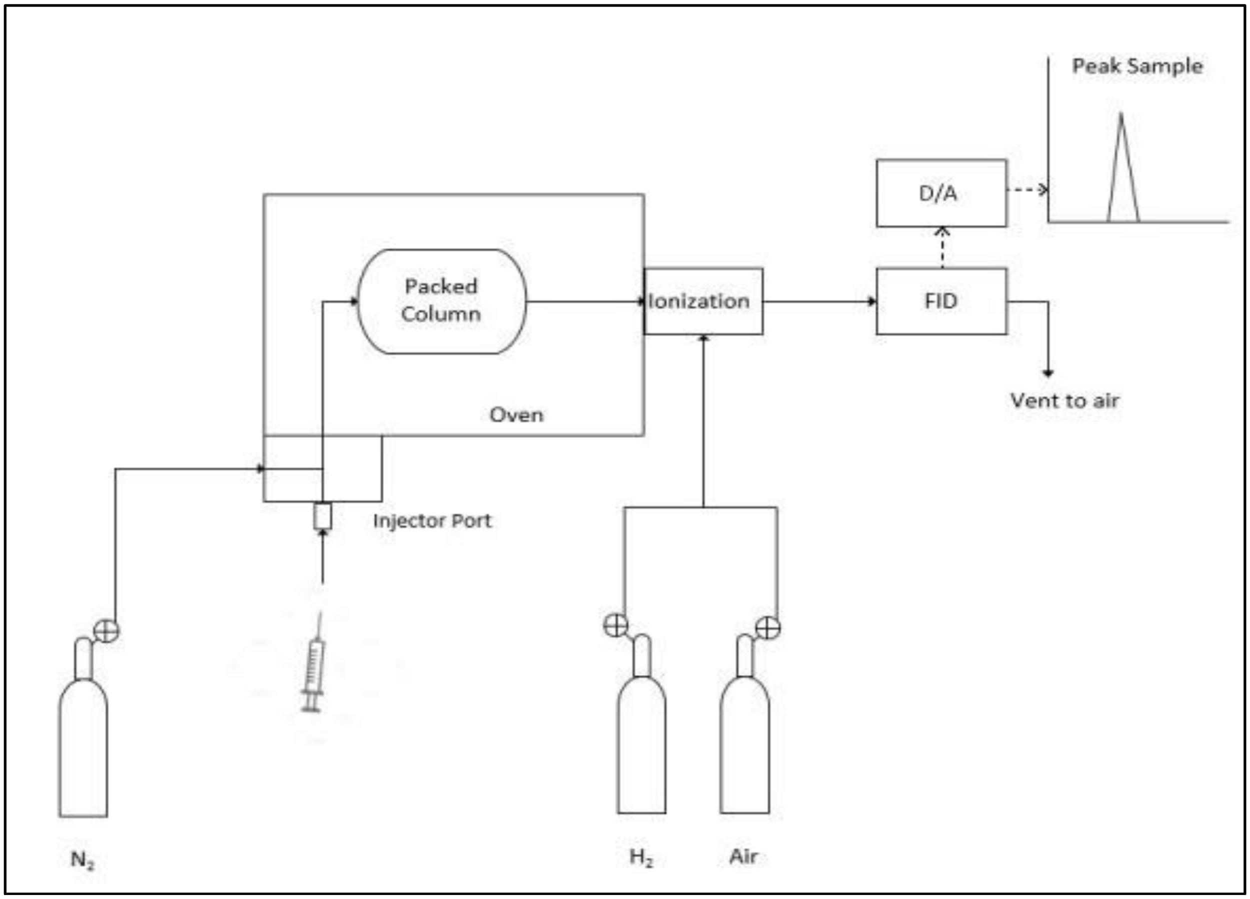


Figure 2.1 - Schematic diagram of the experimental set-up for GC with FID used in this study.

All adsorbents were crushed to 20 x 60 mesh size by mortar and pestle, except the AC cloth, which was cut up to ≤ 3 mm pieces and then packed into the column. In the case of AC BPL, AC F-600, and AC NZ, a 10.33 cm long column was used for experiments at temperatures over 300ºC and a 3.14 cm long column was used for experiments carried out at temperatures less than 300ºC. The short column was able to show clear peaks at lower temperatures in shorter experimental time, increasing the accuracy of the results. For experiments with AC cloth, only 3.14 cm column was used for all temperatures. Both columns had an inside diameter of 0.44 cm. Each adsorbent was regenerated at 400°C at atmospheric pressure with N_2 purge with a flow rate of 250 mL/min for at least 12 hours before experiments.

To calculate Henry's law constant, the density of the adsorbent, as well as the bed void fraction of the column should be determined. They were determined with a Micrometrics volumetric adsorption analyzer using helium as the probe gas. The bed void fractions were determined by using non-porous glass beads identical to the particle size range of adsorbent in the same columns and determining the void volumes of the columns. However, Spectra Carb 2225 AC cloth composed of fiber could not be measured by using glass beads due to their shape difference. Therefore, the porosity of the AC cloth in the column used was measured by using the AC cloth in the column. The details of the columns used, together with the N_2 carrier gas flow rate ranges are shown in Table 2.3.

Table 2.3 - Specifications of columns, bed void fractions, and N_2 flow rates used in this study.

Column length (cm)	Column inner diameter (cm)	Bed void fraction	N_2 flow rates (mL/min)
10.33	0.44	0.39 (AC BPL, AC F-600, AC NZ)	40 – 180
3.14	0.44	0.61 (AC cloth) 0.39 (other adsorbents)	20 – 220

To determine the retention time of the sample peak, one microliter of pure VOC liquid sample was injected into the carrier gas using the microliter syringe. The injected liquid sample was evaporated at higher temperatures at the injection point and then it was carried by preheated N_2 carrier gas into the packed column inside the GC oven. The adsorbate sample at the outlet of the column was ionized by flame using an FID ignitor, gas mixture of H_2 and air (ratio 1:10) and then detected on the FID collector electrode. Therefore, the adsorbates should be combustible to be ionized. The measurable current flow of the adsorbate ionized on the detector was measured and recorded on PeakSimple Chromatography software in SRI Instruments as the signal (millivolt) versus time (sec) [50].

The experiments were conducted at high temperatures as well as at the lowest temperatures for which the peak samples of the VOCs can accurately be detected with the FID for each AC adsorbent.

Henry's law constant is obtained from the retention time of the peak response produced by the injected adsorbate sample. This adsorption parameter is the initial slope of the adsorption isotherm for the corresponding VOC adsorbate and the AC adsorbent pair. The first moment of the peak is the mean retention time of the sample, μ. Dimensionless Henry's law constant K can be calculated from the mean retention time of peak using Equation [1][31]-[42].

$$\mu = \frac{\int_0^\infty c(t-\mu_D)dt}{\int_0^\infty c dt} = \frac{L}{v}[1+\frac{(1-\varepsilon_B)K}{\varepsilon_B}] \qquad [1]$$

where t is the time (sec), c is the adsorbate concentration detected on the FID, L is the column length (cm), ε_B is the bed void fraction (dimensionless), v is the interstitial fluid velocity of carrier gas (cm/sec), K is the dimensionless Henry's law adsorption equilibrium constant, and μ_D is the dead time (sec).

The dimensional Henry's law constant is the initial slope of the adsorption isotherm of the pure component VOC. Dimensional Henry's law constant, K_p can be obtained from dimensionless Henry's law constant as shown in Equation [2][31]-[42].

$$K_p = \frac{K}{RT\rho_s} \qquad [2]$$

where R is the ideal gas law constant, T is the absolute temperature (K), ρ_s is the adsorbent density (g/cm^3), and K_p is the dimensional Henry's law adsorption equilibrium constant (mol/g/atm).

The heat of adsorption, ΔH can be calculated from the van't Hoff equation in Equation [3], after determining Henry's law constant for multiple temperatures[41][42].

$$K_p = K_0 \, e^{-(\frac{\Delta H}{RT})} \qquad [3]$$

Where K_0 is the pre-exponential factor and ΔH is the heat of adsorption (kJ/mol).

2.6. Results and Discussion

2.6.1. Henry's Law Constants

The potential of adsorption between adsorbate and adsorbent at low concentrations of the adsorbate can be effectively measured by Henry's law constant which is the initial slope of the adsorption isotherm as adsorbate concentration (or its partial pressure) approaches zero[51]. Henry's law constant is the most significant factor for air purification since VOC concentrations in indoor air are very law. Therefore, the screening of AC adsorbents can be effectively carried out by comparing measured Henry's law constants to see their potential for adsorption separation of VOCs from indoor air.

In this study, the sample peaks produced from adsorption of VOCs by ACs were experimentally obtained using the CPM technique. The retention time, μ of the sample peak recorded by CPM was used to determine Henry's law constants at different temperatures using Equations [1] and [2]. Henry's law constants were plotted against inverse temperature as van't Hoff plots and were extrapolated to room temperature (25 °C) since accurate results for Henry's law constants could not be obtained at temperatures close to the room temperature. Therefore, Henry’s law constants were measured at the lowest temperatures that can be accurately calculated and the van’t Hoff plot was extrapolated to the room temperature.

Figure 2.2 shows Henry’s law constant values plotted against inverse temperature (van’t Hoff plots) to compare the adsorption of different VOC adsorbates with each adsorbent studied.

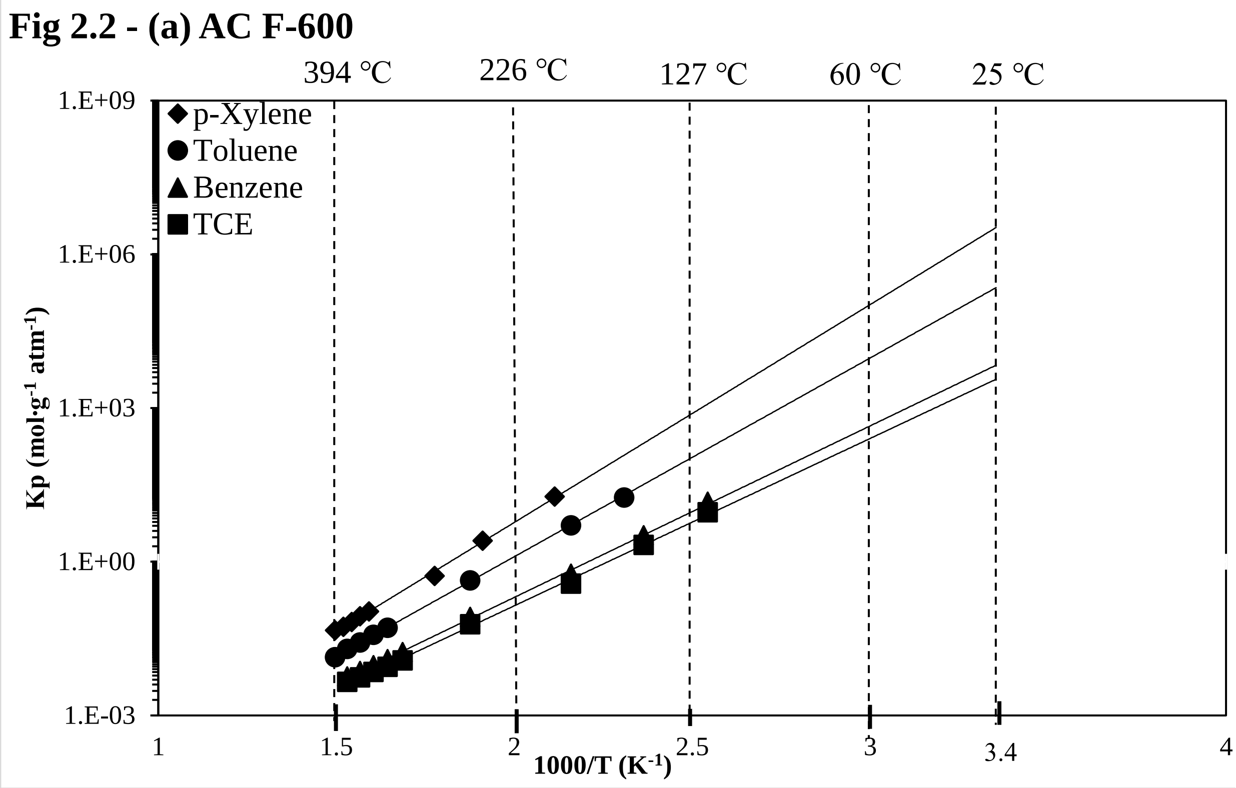


Fig 2.2 - (a) AC F-600

Fig 2.2 - (b) AC BPL

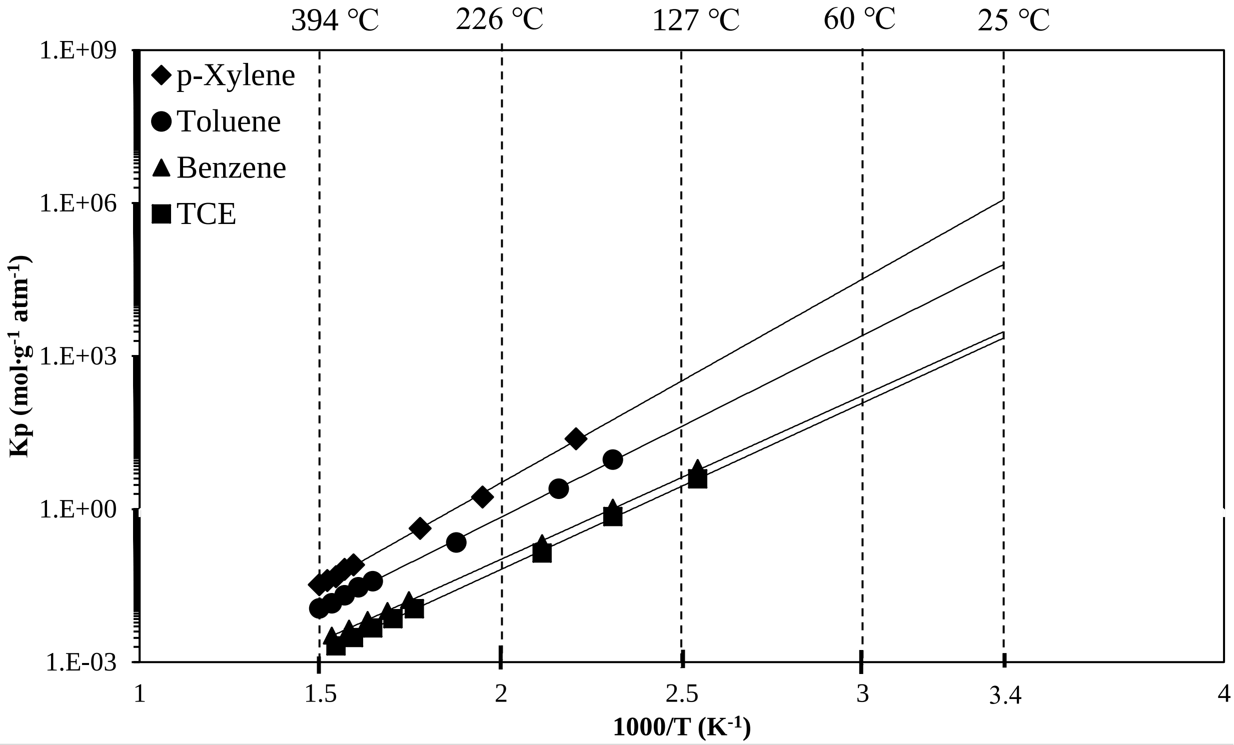
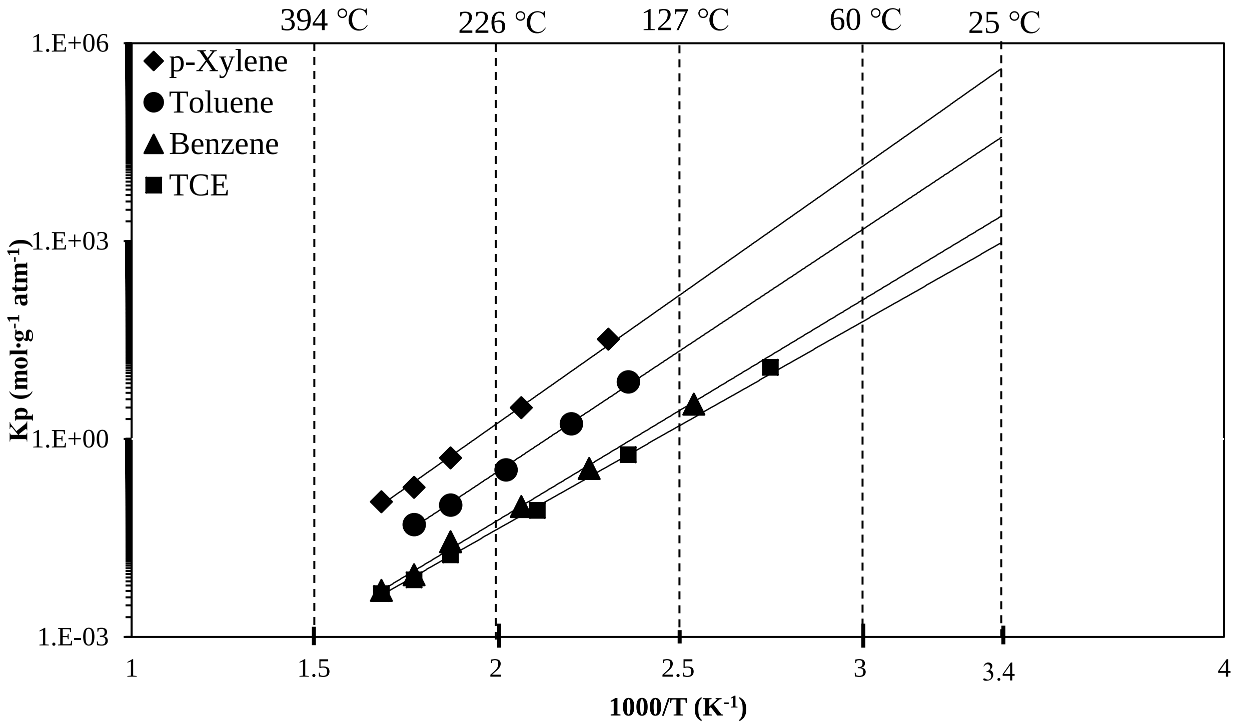


Fig 2.2 - (c) AC Cloth



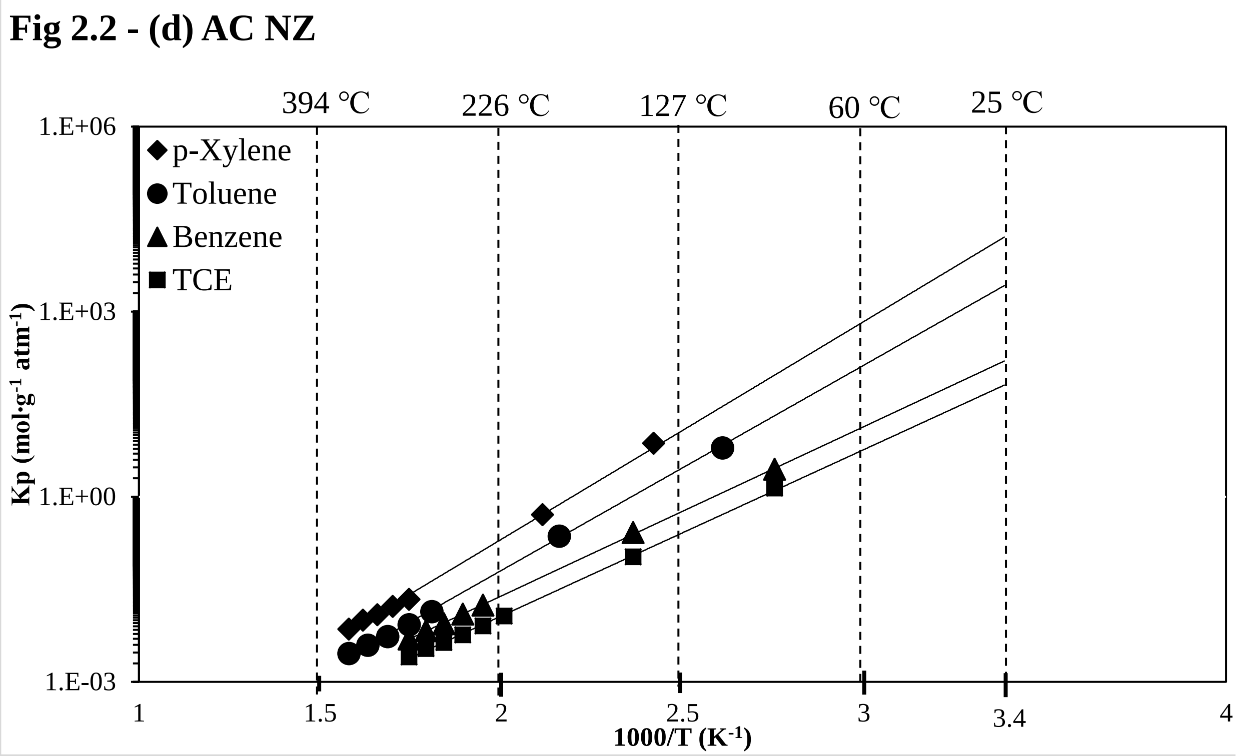


Figure 2.2 - The comparison of Henry's law constant values for p-xylene, toluene, benzene, and TCE for each adsorbent with N_2 as the carrier gas. Black dots represent experimental data points and the lines represent extrapolation to 25 °C room temperature.

As shown in this figure, Henry's law constants for each adsorbate increased as temperature decreases, as expected. This indicates exothermic physical adsorption occurring between VOCs and AC adsorbents. Henry's law constant values for the VOCs on each adsorbent show the same order: p-xylene > toluene > benzene > TCE. In order to explain this trend in Henry's law constants, one has to look at the properties of adsorbates such as kinetic diameter, structure, polarizability, dipole moment, and quadrupole moment. As shown in Table 2.2, the kinetic diameters of the adsorbates are relatively similar. Their dipole and quadrupole moments are zero or close to zero since they all show non-polar properties. Therefore, the kinetic diameters, dipole moment, and quadrupole moment of adsorbates are not expected to explain this order in Henry's law constants observed. However, the polarizabilities of these adsorbates showed differences. The intensity of polarizabilities of the VOCs followed the trend: p-xylene > toluene > benzene > TCE. This was the same trend as the results of Henry's law constants on each adsorbent. The higher the polarizability of the adsorbate, the lower the force of the nucleus charge that controls the electrons, which causes the greater distance between electrons and the nucleus charge. The electrons away from the nucleus charge of adsorbate increase the interaction with the adsorbent. Therefore, the adsorbate with higher polarizability can have a stronger interaction with the adsorbent, which resulted in a trend of p-xylene > toluene > benzene > TCE on all adsorbents for Henry's law constants[31][51].

Figure 2.3 represents Henry's law constants plotted at different temperatures to compare the adsorbents for each adsorbate. All of Henry's law constants are extrapolated to room temperature in this study.

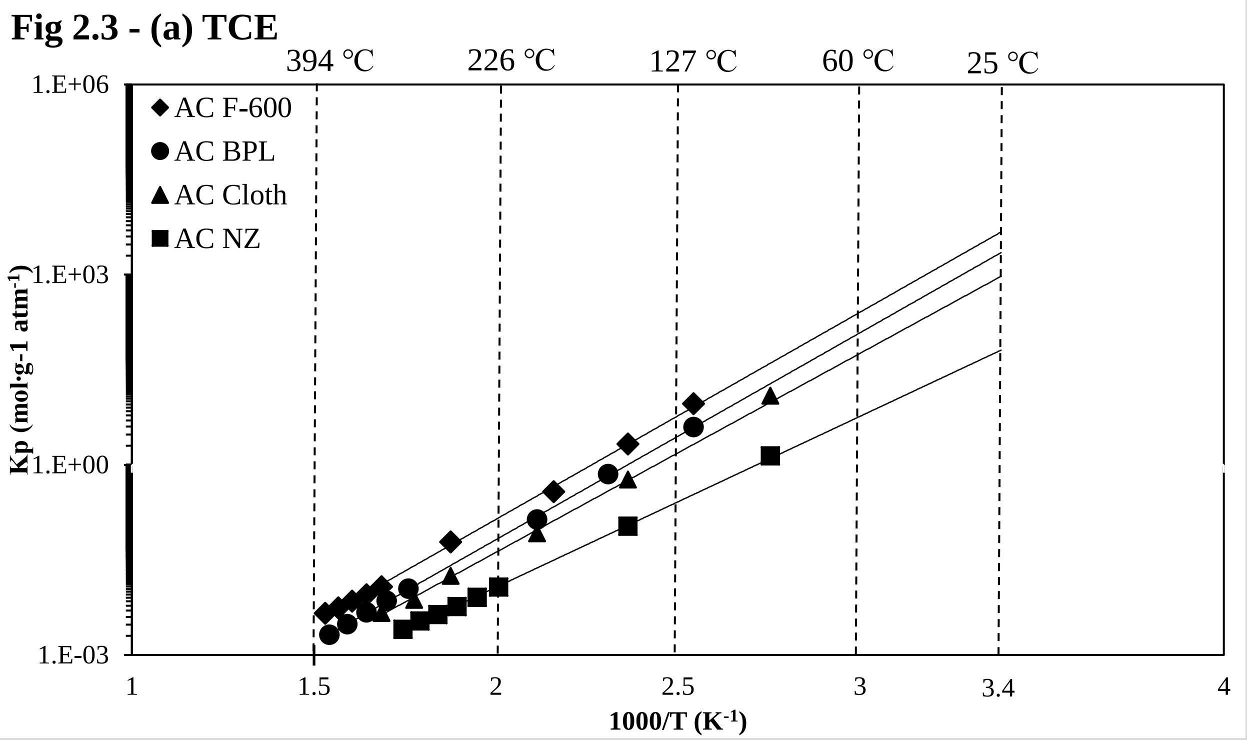


Fig 2.3 - (b) Benzene

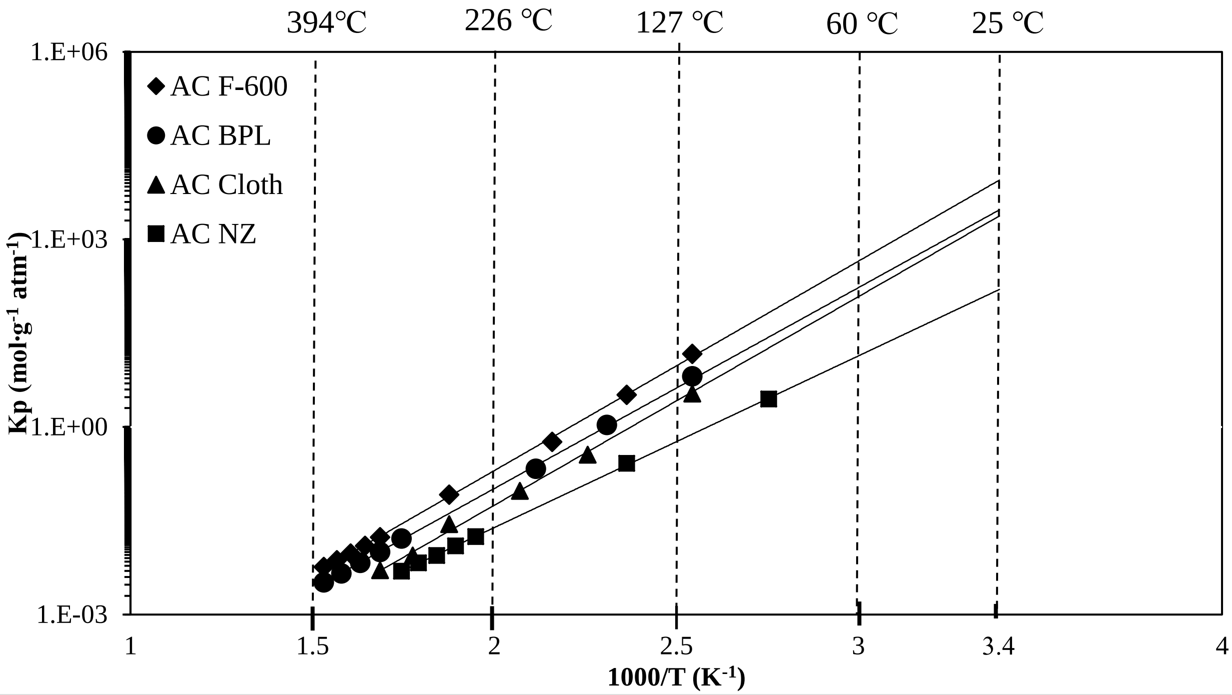
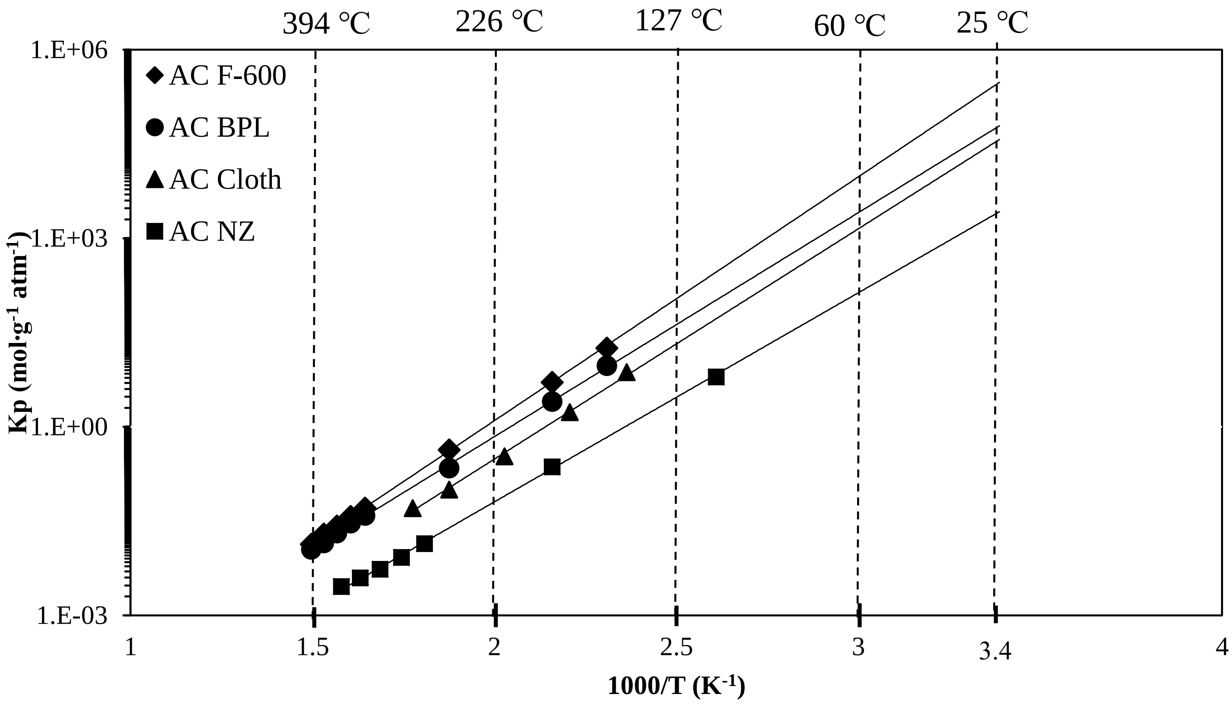


Fig 2.3 - (c) Toluene



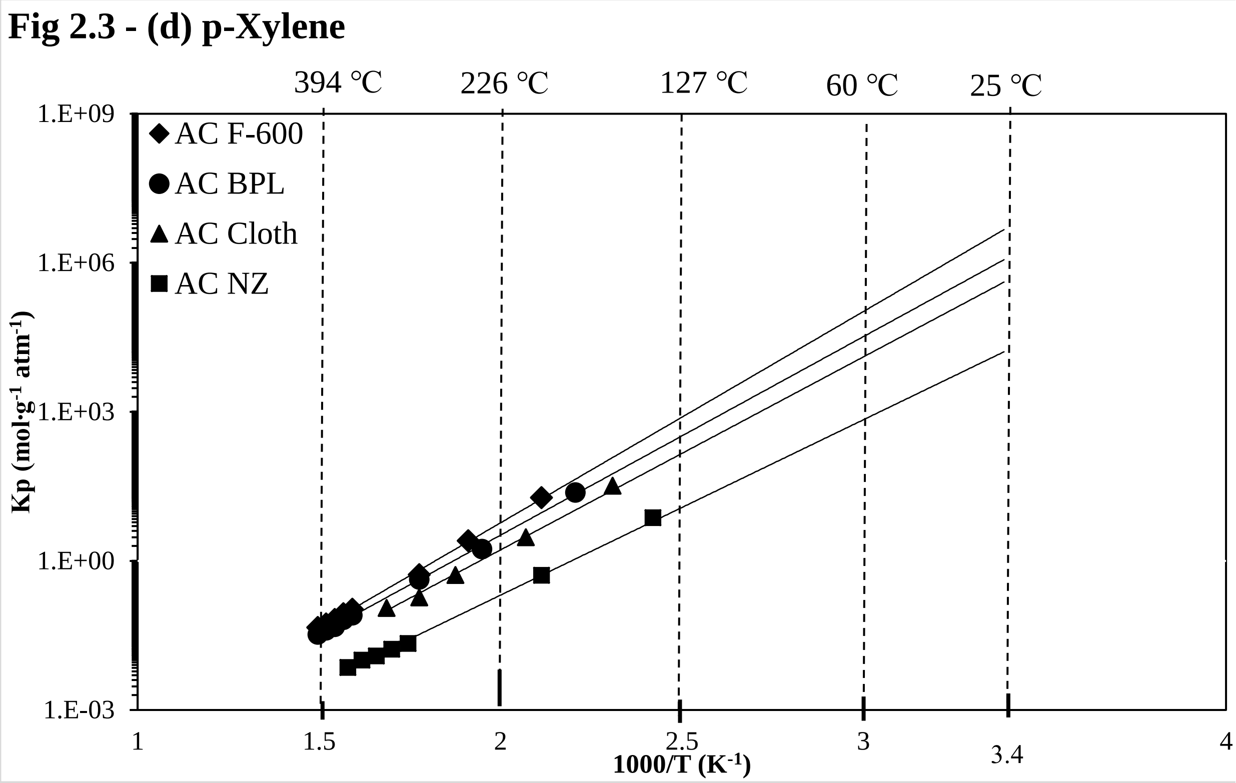


Figure 2.3 - The comparison of Henry's law constant values for four adsorbents with each adsorbate (with N_2 carrier gas). Black spherical dots represent experimental data points. The lines represent extrapolation to room temperature 25 °C.

As shown in Figure 2.3, Henry's law constant values of AC adsorbents had the same trends for all adsorbates: AC F-600 > AC BPL > AC Cloth > AC NZ. As can be seen in Table 2.1, the BET surface area and pore volume of AC F-600 and AC BPL were relatively similar or lower than AC cloth and AC NZ, but their Henry's law constants were always higher than AC cloth and AC NZ. This observation indicates that pore size would be an important factor for these results. The adsorption mostly occurs in micropores[31] and it has been reported that VOC adsorption in micropores is proportional to pore size[52]-[54]. This is because adsorbates would more easily enter the pores of the adsorbents if they have larger mean pore sizes for the micropores. Furthermore, the adsorbate adsorbed in the pores with small pore sizes could hinder the transport of other adsorbates passing through the pores. Therefore, it is expected that the larger mean pore sizes of AC F-600 (21.9 Å) and AC BPL (26.19 Å) would cause to have them higher Henry's law constant values compared to AC cloth (18.68 Å) and AC NZ (19.33 Å). On the other hand, Henry's law constants of AC BPL were always lower than AC F-600, although the mean pore size of AC BPL is larger than AC F-600. The adsorbate can easily enter adsorbent with larger mean pore size, but adsorbate can also easily come out from larger pores due to the weak force for physical adsorption. It has been observed in the literature that VOC adsorption tends to decrease when the pore size is greater than the micropore size (20 Å)[52]-[54]. One of these studies has reported that AC with 19.97 Å pore size had stronger VOC adsorption than ACs with 30 Å and 40 Å pore sizes[52]. It is also assumed that the pore volume of AC F-600 is around half of AC BPL. This smaller pore volume of AC F-600 could tightly have held the adsorbate molecules inside the pores more than AC BPL. Therefore, the pore structure of optimized AC is an important factor to improve the VOC adsorption.

As can be seen in Table 2.1, AC NZ has a higher mean pore size, BET surface area, and pore volume than AC cloth. Therefore, it was expected to have higher Henry's law constant than AC cloth, but all Henry's law constants of AC cloth were higher than those of AC NZ. Higher heat of adsorption values for AC cloth would have resulted in higher Henry's law constant values compared to AC NZ. The experimentally determined heat of adsorption values are discussed in Section [2.6.2].

Figure 2.4 is the bar chart showing Henry's law constants in logarithmic scale at room temperature. This bar chart shows all the trends of the adsorbates and adsorbents observed in this study.

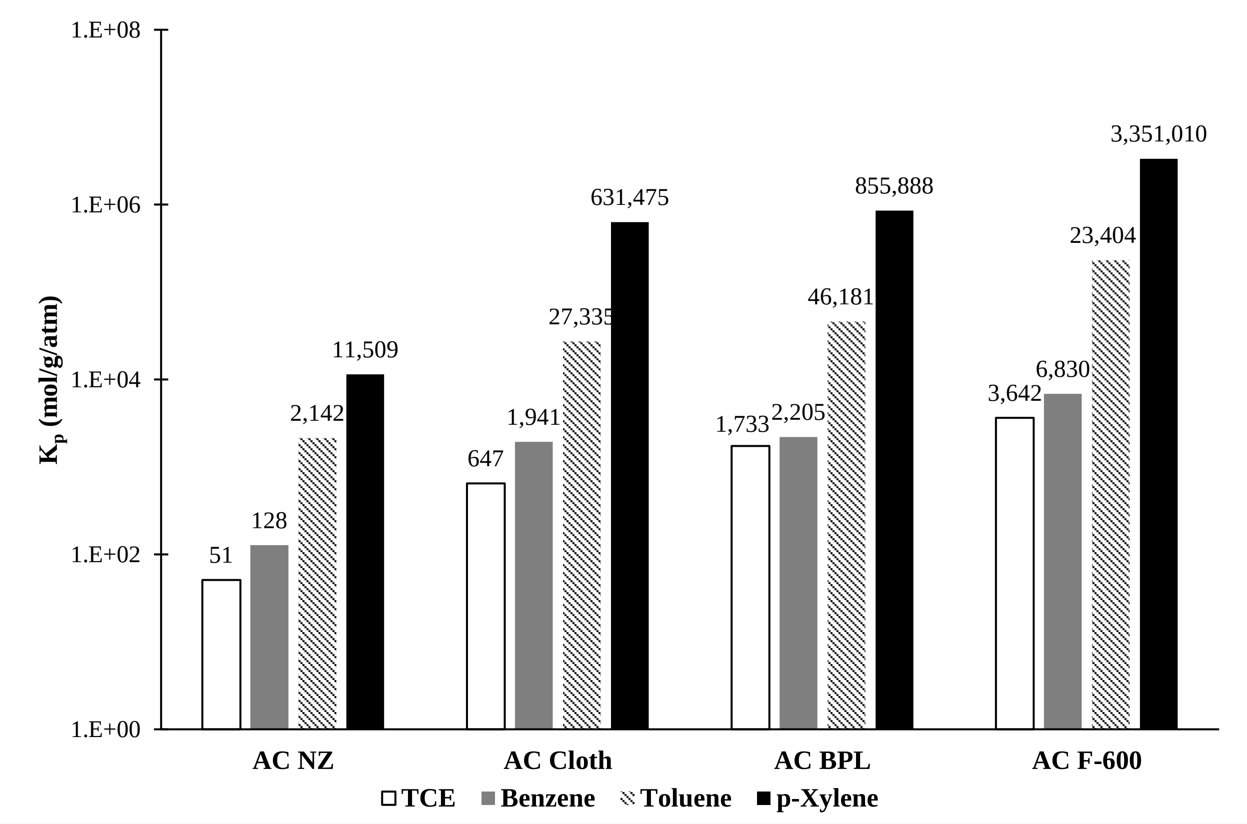


Figure 2.4 – Henry's law constants, K_p (mol/g/atm) at room temperature determined in this study.

When Henry's law constants are compared to the literature values in Table 2.4, we can see that AC F-600 was either the best (for toluene and TCE) or the second-best for the removal of these VOC's. Also, the differences in Henry's law constants were quite substantial.

Table 2.4 – Henry's law constants, K_p (mol/g/atm) at room temperature determined in this study and their comparisons to the literature values for four adsorbates studied.

Adsorbates	Adsorbents	Temperature (°C)	Henry's law constants, K_p (mol/g/atm)	Reference
p-Xylene	AC F-600	25	3,351,010	This study
	AC BPL	25	855,888	This study
	AC Cloth	25	631,475	This study

	AC NZ	25	11,509	This study
	AC Calgon	25	43,671,087	[55][1]
	AC	25	53,742	[56][2]
Toluene	AC F-600	25	231,404	This study
	AC BPL	25	46,181	This study
	AC Cloth	25	27,335	This study
	AC NZ	25	2,142	This study
	AC KC58C	25	10,234	[57][1]
	AC WVA 1100	12	7,802	[57][1]
	AC NORIT RB3	25	5,877	[57][1]
	AC KC	25	5,573	[57][1]
	AC Duksan	25	1,783	[58][1]
Benzene	AC F-600	25	6,830	This study
	AC BPL	25	2,205	This study
	AC Cloth	25	1,941	This study
	AC NZ	25	128	This study
	AC F-16	25	377	[57][2]
	AC Sorbonorit B4	25	34,237	[59][2]
	AC Sorbent A	25	14	[60][1]
	AC Sorbent B	25	5,502	[60][1]

TCE	AC F-600	25	3,642	This study
	AC BPL	25	1,733	This study
	AC Cloth	25	647	This study
	AC NZ	25	51	This study
	AC A10	25	1013	[61][1]
	AC Xtrusorb-600	25	227	[62][2]

[1]: Henry’s law constants in the literature
[2]: Henry’s law constants determined by parameters in the literature

2.6.2. Heat of Adsorption

The energy is released by the exothermic adsorption process when adsorbate is adsorbed on the adsorbent[27]. The heat of adsorption indicates the amount of energy released by adsorption. The intense interaction between adsorbent and adsorbate can release more energy. Therefore, the heat of adsorption is also a significant factor in potential interactions between the adsorbent and the adsorbate. For adsorbate recovery during column regeneration, a smaller heat of adsorption value is preferred since a higher heat of adsorption could cause a lower working capacity of the adsorbent[63]. The heat of adsorption values were obtained from the slope of the van’t Hoff plots according to Equation [3]. Figure 2.5 shows these van’t Hoff plots and the corresponding heat of adsorption values are presented in Table 2.5.

Due to the strong interaction between ACs and the indoor VOCs, the heat of adsorption values observed in this study were around 60 to 80 kJ/mol which are in the range of physisorption [51]. As expected, the heat of adsorption values for p-xylene were the highest for all adsorbents studied which shows the strong interaction between this adsorbate and all the ACs. The heat of adsorption values showed the same trends as Henry’s law constant trends: p-xylene > toluene > benzene > TCE. Furthermore, the heat of adsorption values of AC F-600 were also the highest following the same trend as Henry's law constants. It is shown that a higher heat of adsorption value would indicate a higher Henry's law constant due to the strong interaction between the adsorbate and the adsorbent.

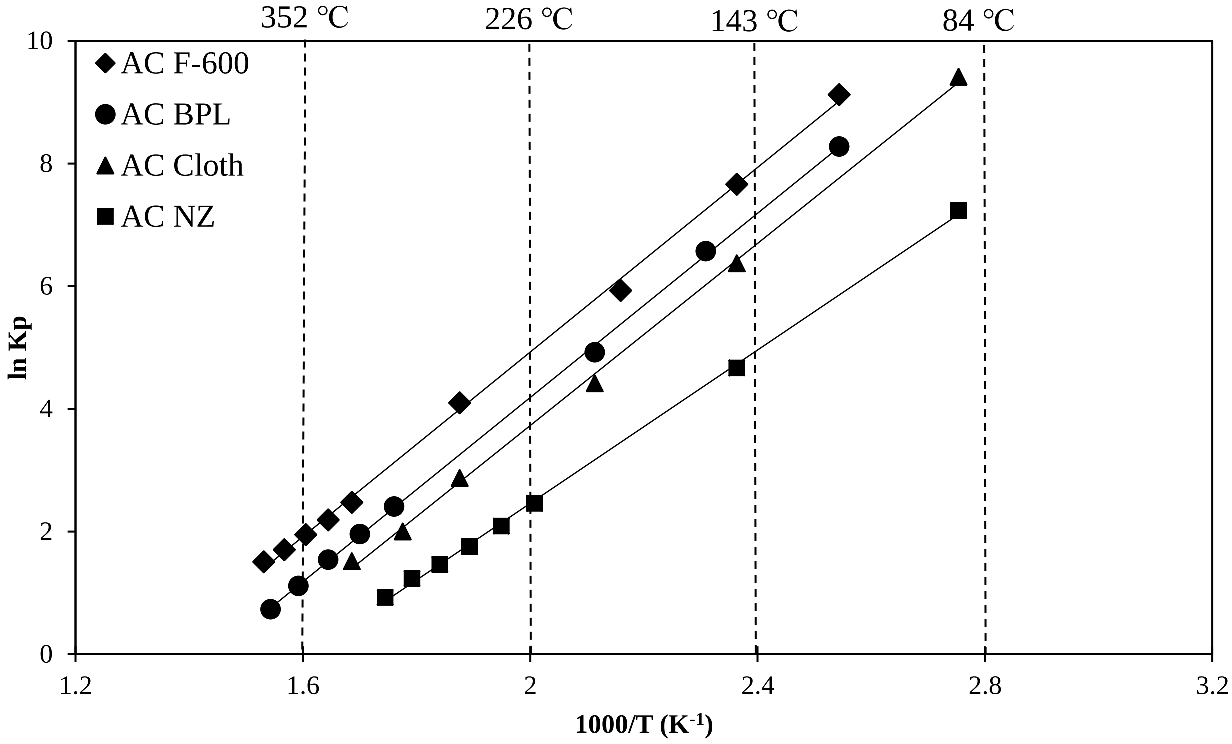


Fig 2.5 - (a) TCE

Fig 2.5 - (b) Benzene

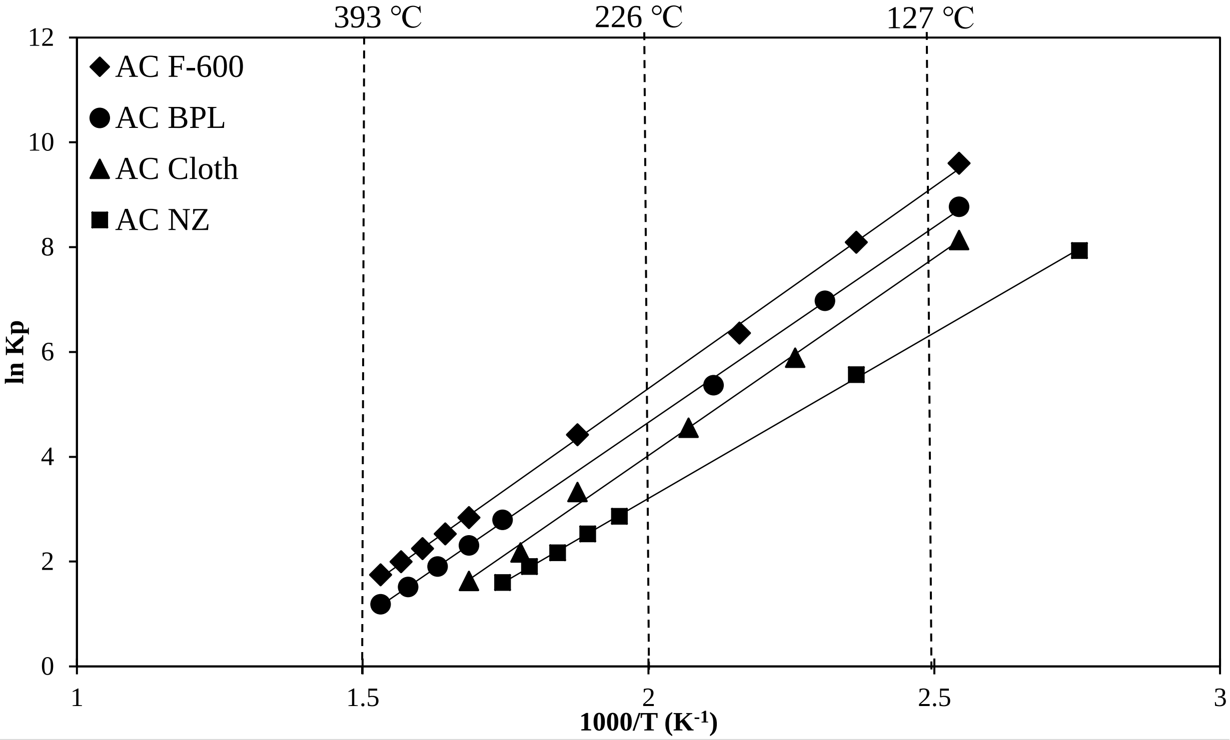
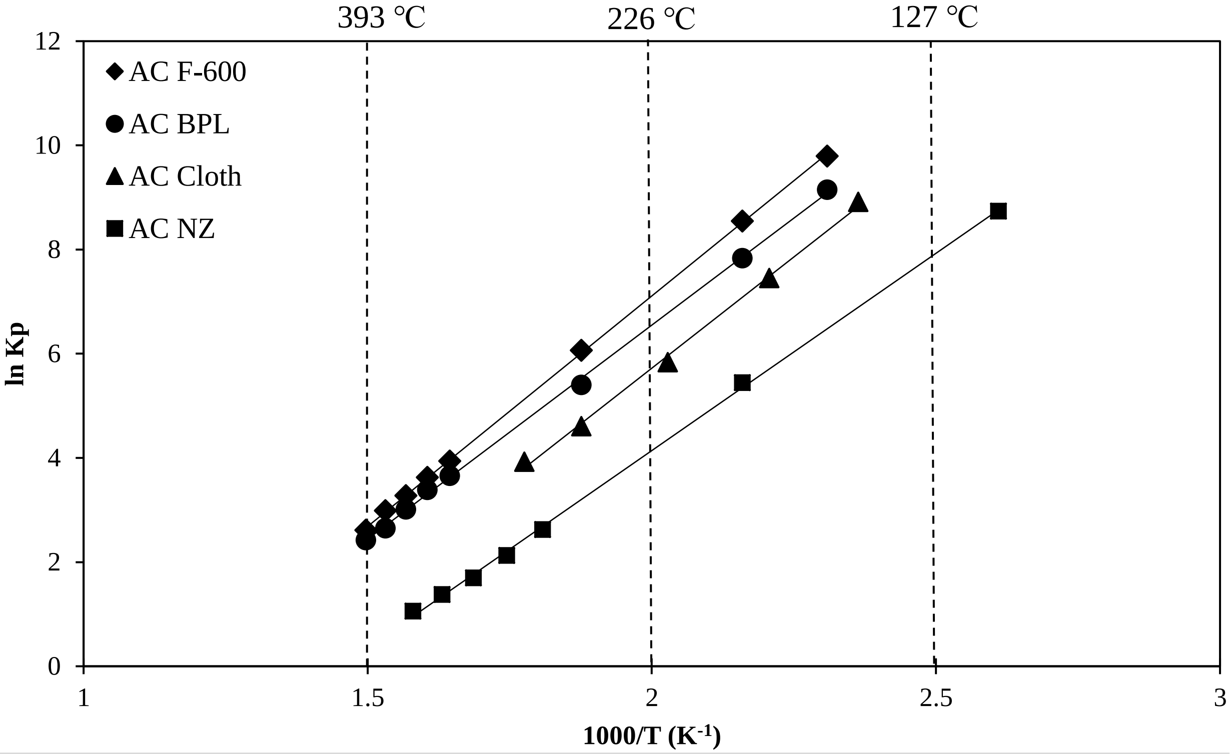


Fig 2.5 - (c) Toluene



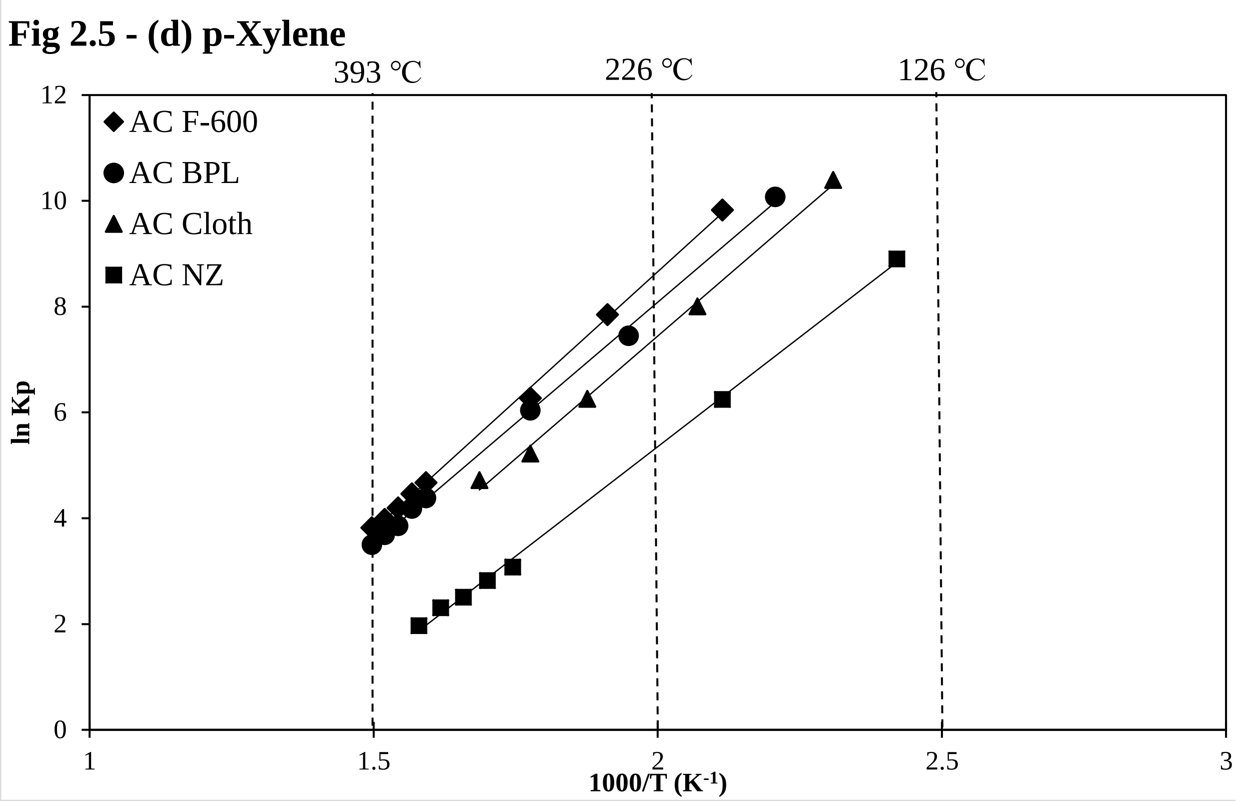


Figure 2.5 – Experimentally determined $\mathrm{LnK_p}$ vs. 1000/T plots for four adsorbents with each adsorbate (with N_2 carrier gas)

Figure 2.6 is the bar chart showing the heat of adsorption values obtained from slopes of van't Hoff plots in Figure 2.5. This bar chart represents all the trends of the interaction between adsorbates and adsorbents observed in this study.

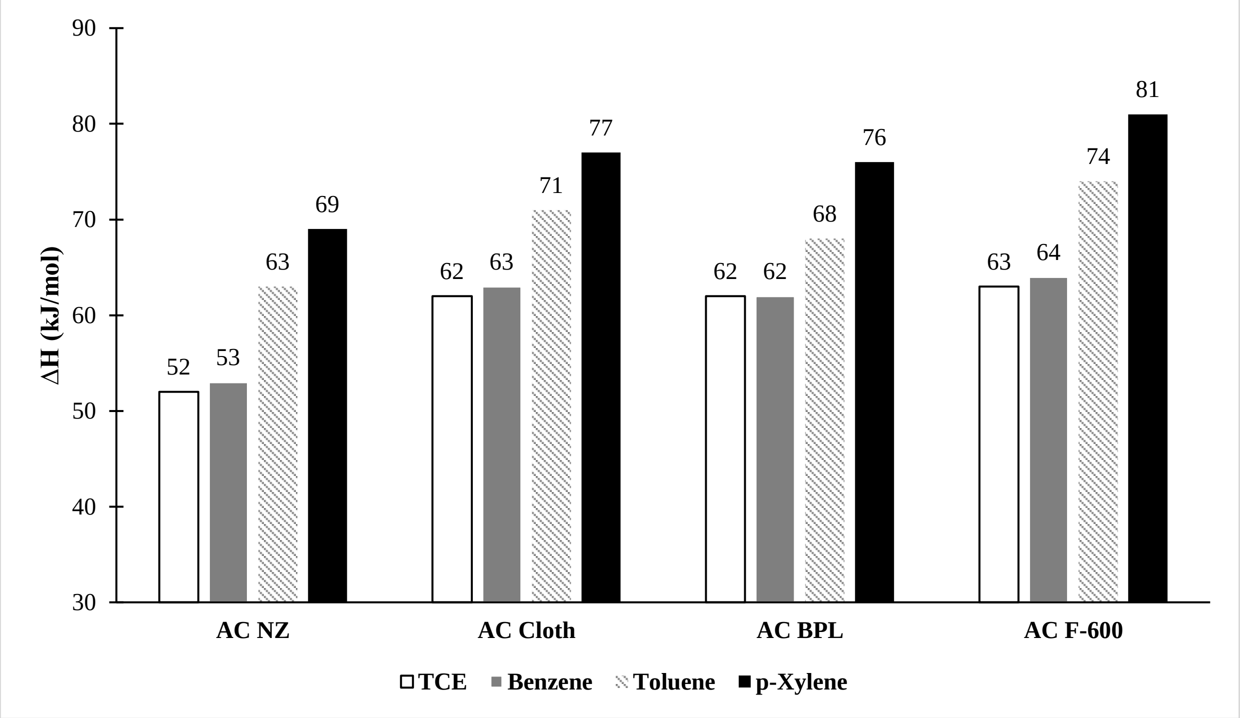


Figure 2.6 – Heat of adsorption values, ΔH (kJ/mol) determined in this study.

When the heat of adsorption values are compared to the literature values in Table 2.5, AC F-600 was the second highest. Also, the differences in the heat of adsorption values were quite substantial.

Table 2.5 - Heat of adsorption values (kJ/mol) experimentally determined from van't Hoff plots in this study and their comparisons with values obtained in the literature.

Adsorbates	Adsorbents	Heat of adsorption, ΔH (kJ/mol)	References
p-Xylene	AC F-600	81	This study
	AC BPL	76	This study
	AC Cloth	77	This study
	AC NZ	69	This study
	AC Calgon	96	[55][2]

Toluene	AC F-600	74	This study
	AC BPL	68	This study
	AC Cloth	71	This study
	AC NZ	63	This study
	ACM	46	[64][1]
	AC Maxsorb AW 20	79	[65][1]
	Pinewood chip-AC	44	[66][1]
Benzene	AC F-600	64	This study
	AC BPL	62	This study
	AC Cloth	63	This study
	AC NZ	53	This study
	AC GF 40	58	[67][1]
	AC Fiber Cloth (AC FC)	63	[68][1]
	Coal Derived AC (CDAC)	60	[68][1]
	AC Sorbonorit	38 - 50	[69][1]
	AC Norit	68 - 71	[69][1]
	AC F - 400	33 - 76	[69][1]
TCE	AC F-600	63	This study
	AC BPL	62	This study
	AC Cloth	62	This study
	AC NZ	52	This study

	AC GF 40	51	[67][1]
	AC Xtrusorb-600	53	[61][2]
	U-AC	30 - 70	[70][1]
	PT-AC1	10 - 30	[70][1]

[1]: Heat of adsorption values in the literature
[2]: Heat of adsorption values determined by the slope of van’t Hoff plots in the literature

2.7. Conclusions

In this present study, the VOCs, TCE, benzene, toluene and p-xylene were chosen since they have the highest concentrations and frequencies as indoor air pollutants. Four commercially available types of activated carbons (AC BPL, AC F-600, AC NZ, and AC Cloth) that have shown promise for the removal of major indoors VOCs were investigated. To find a promising activated carbon among them, Henry’s law constants at room temperature (25 °C) were estimated and compared. Henry’s law constants were obtained at a temperature range from 90 °C to 400 °C due to VOCs’ high boiling points and high interaction with ACs. These Henry’s law constants were extrapolated to room temperature by using the van’t Hoff plot. The results showed that Henry’s law constants increased as temperature decreased, as expected. For all adsorbents, p-xylene showed the highest Henry’s law constants followed by toluene, benzene, and TCE. For all VOCs, among adsorbents, AC-F600 showed the highest Henry’s law constants followed by AC BPL, AC cloth, and AC NZ. Based on the observed results, the pore structure of AC would be an important factor for improving VOC adsorption. The heat of adsorption values of the pure VOCs were obtained from the slope of the van’t Hoff plots and they were in the range of 60 to 80 kJ/mol. The heat of adsorption values showed a similar trend to the one for Henry’s law constants. p-xylene had the highest heat of adsorption values with all adsorbents. AC-F 600 showed the highest heat of adsorption values for all VOCs studied.

For the removal of indoor VOCs, the most promising activated carbon was the AC-F 600 based on the estimated Henry's law constant values at room temperature not only among the adsorbents considered in this study but also compared to the other adsorbents studied in the literature.

2.8. Nomenclature

C	concentration of adsorbate (indicated in mV from the GC)
ΔH	heat of adsorption (kJ/mol)
K	dimensionless Henry's law constant (-)
K_0	pre-exponential factor for dimensional Henry's law constant (mmol/g/atm)
K_p	dimensional Henry's law constant (mmol/g/atm)
L	column length (cm)
P	pressure (psi)
R	ideal gas law constant (82.06 cm^3·atm/K/mol or 8.314 J/K/mol)
t	time (sec)
T	temperature (K)

Greek Letters

μ_D	dead time (sec)
ε_B	bed void fraction (dimensionless)
μ	retention time (sec)
ν	interstitial fluid velocity (cm/sec)

2.9. Bibliography

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CHAPTER 3:

Improving Indoor Air Quality Utilizing Zeolite and Polymer Adsorbents

Ji Sub Yun, F. Handan Tezel

Department of Chemical and Biological Engineering, University of Ottawa

161 Louis Pasteur, Ottawa, ON, KIN 6N5 CANADA

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Corresponding Author’s Contact Information

e-mail: Handan.Tezel@uottawa.ca

phone: +1 (613) 562 – 5800 (ext 6107)

3.1. Abstract

Indoor air pollution and poor ventilation mainly incur sick building syndrome (SBS). It became one of the major issues for our modern daily lives, where we spend most of our time indoors. Therefore, it is important to minimize the concentration of indoor air pollutants by using proper methods for removing them. For this, commercially available zeolites and divinylbenzene (DVB) polymer were observed in this study. The experimental adsorption studies based on Henry's law constants of pure trichloroethylene (TCE), benzene, toluene, and para-xylene (p-xylene) were utilized to determine the promising adsorbent. Since the concentrations of major indoor air pollutants are very low in the air, Henry's law constant is an effective indicator to see the potential of adsorption interaction with the adsorbent. Henry's law constants in this study were obtained from the concentration pulse chromatography method (CPM) with a nitrogen carrier gas representing air. Henry's law constants plotted as van't Hoff plots at different temperatures (90 to 340 °C) were extrapolated to room temperature, which is considered to be 25 °C. For the removal of these indoor air pollutants, HiSiv 3000 (UOP Molecular Sieves), HiSiv 1000 (UOP Molecular Sieves), and DVB polymer (Supelco) were investigated as adsorbents in this study. The slope of the logarithmic Henry's law constants plotted as a function of the inverse absolute temperature could determine the heat of adsorption values. The results of this study showed that p-xylene, among the major indoor VOCs (volatile organic compounds) always had the highest Henry's law constant followed by toluene, benzene, and TCE for all zeolites and DVB polymer. Among the adsorbents studied, HiSiv 3000 always had the highest Henry's law constants for all the VOCs, followed by HiSiv 1000 and DVB polymer. The heat of adsorption values for zeolites were in the range of 40 to 90 kJ/mol, whereas the heat of adsorption values for DVB polymer were in the range of 30 to 60 kJ/mol. The heat of adsorption values also showed similar trends to Henry's law constant trends. Among the adsorbents studied, HiSiv 3000 was determined as the most promising adsorbent for purification of all of these major indoor air pollutants, based on Henry's law constants at room temperature. This study is important to minimize the potential of chronic diseases caused by sick building syndrome.

Key Words

Sick Building Syndrome, Adsorption, Henry's law constant, Heat of adsorption, Zeolite, DVB polymer, TCE, Benzene, Toluene, p-Xylene,

3.2. Introduction

It is one of the critical risks in our daily modern lives, as the continuous and repetitive exposure to poor indoor air quality and the inadequate ventilation system can lead to the publicized medical conditions such as sick building syndrome (SBS), sick school syndrome (SSS), and sick house syndrome (SHS). To make it worse, it is a major trend for the people who are required to spend most of their time indoors and had to stay indoors for self-isolation due to special circumstances such as the Coronavirus disease-19 (COVID-19) pandemic.

SBS is frequently attributed to volatile organic compounds (VOCs) readily released from indoor sources such as adhesives, paint, polish, carpeting, upholstery, manufactured wood products, copy machines, pesticides, cleaning agents inside buildings, and exhausts entering from outside of the buildings. These indoor sources are releasing around 100 to 5,000 different VOCs. The majority of indoor VOCs (more than 70 percent) are represented by trichloroethylene (TCE), benzene, toluene, and para-xylene (p-xylene). These major VOCs' concentrations and frequencies are often higher indoors than outdoors. Although these VOCs are not present in acute concentrations in indoor air, prolonged exposure to the VOCs can cause chronic health effects such as allergic sensitization, increased cancer risks, and respiratory disease[1]-[10].

The current prevalent methods to remove VOCs are destruction and recovery. The destruction methods include catalytic and thermal oxidation processes and biological treatment by bio-filtration. The recovery methods include condensation, adsorption, absorption, and membrane separation. Among these methods, adsorption has been widely applied to reduce the amount of VOCs due to various advantages such as high VOC removal efficiency, high capacity of adsorbent, simple operation, low-cost adsorbent, and re-usable adsorbents by regeneration[11]-[13].

In case of the humid indoor conditions, water can chemically interact with the adsorbent through chemical adsorption. This chemical adsorption can significantly lower the VOC adsorption capacity of an adsorbent due to the decrease of sites by the interaction of the water with the adsorbent. Therefore, the possibility of chemical adsorption of water in the air can be reduced if the hydrophobic adsorbent is used. Typical hydrophobic adsorbents can be divinylbenzene (DVB) polymer and zeolites[14]-[16].

DVB consists of two vinyl groups and one benzene ring. The DVB polymer adsorbents have various advantages such as low affinity for water vapour (hydrophobic property by hydrocarbon compounds), low catalytic reactions with VOCs, and regeneration at low temperatures[17][18].

The zeolites are composed of porous tetrahedra framework structure of SiO_4 and AlO_4 balanced out by cations. Since zeolites have crystal lattice structures, they are composed of uniform pore sizes. The ratio of Si/Al determines the hydrophobicity or hydrophilicity of a zeolite. The presence of aluminum would increase cationic variability leading to the increased heterogeneity of zeolite surface. This degree of energetic surface heterogeneity can strongly interact with polar molecules such as water, which makes the formation of an electrostatic field. Therefore, the hydrophobicity of zeolite increases as the Si/Al ratio increases, while the hydrophobicity decreases as the Si/Al ratio decreases[19]-[21]. Zeolites with a Si/Al ratio of 10 or higher are regarded as hydrophobic adsorbents [22].

Numerous studies have reported excellence of VOC removal in DVB polymer and zeolite adsorbents[23]-[36].

3.3. Objective

Benzene, toluene, TCE, and p-xylene were studied as adsorbates because their concentrations and frequencies are relatively higher compared to other indoor VOCs[37]-[39]. In this study, we wanted to find the most promising hydrophobic adsorbent among two zeolites (with Si/Al ratio over 10) and DVB polymer adsorbent for the removal of these adsorbates from the air. This was done by determining Henry's law constants for adsorption of the VOCs at 25 ℃ which is considered to be the average room temperature. For the two zeolites and the DVB polymer adsorbents, Henry's law constants of major VOCs indoors were experimentally obtained at different high temperatures in the range of 90 ℃ to 350 ℃. Due to their high boiling points and strong interactions with the studied adsorbents, accurate and dependable results were impossible to obtain at low temperatures. The results of high-temperature experiments were extrapolated to 25 ℃. A gas chromatograph (GC) equipped with a flame ionization detector (FID) was used by employing the concentration pulse method (CPM) to determine Henry's law constants. Nitrogen which accounts for around 79 percent of air was used as the carrier gas for these experiments. To compare the interaction intensity of major indoor VOCs with studied adsorbents, the heat of adsorption values were also determined. They were obtained from the slope of the van't Hoff plots of experimentally determined Henry's law constants.

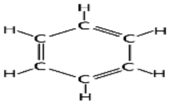
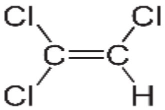
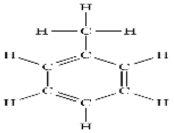
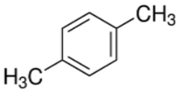
3.4. Materials

N_2 carrier gas was purchased from Messer Canada Inc. at a purity of 99.999%. High purity liquid benzene, TCE, toluene, and p-xylene were used as adsorbates. These adsorbates are all flammable. The adsorbents tested were two types of hydrophobic zeolites and a DVB polymer. The details of adsorbents and adsorbates are shown in Table 3.1 and Table 3.2, respectively.

Table 3.1 - Details of the adsorbents used in this study.

Properties	**HiSiv 3000**	**HiSiv 1000**	**DVB polymer**
Structure & Repeating Unit	ZSM-5	FAU	Divinylbenzene (DVB)
Supplier	UOP Molecular Sieves	UOP Molecular Sieves	Supelco
Location (city, province, country)	Des Plaines, Illinois, USA	Des Plaines, Illinois, USA	St, Louis, Missouri, USA
Pellet Form	Pellet (1/16”)	Pellet (1/16”)	Pellet (60 x 80)
BET surface area (m^2/g)	309.84	443.50	582
Mean pore size (Å)	6	8	75
SiO_2/Al_2O_3	≥ 1000	< 20	---
Metal Cations	Na^+	Na^+	---

Table 3.2 – Details of the major indoor VOCs used in this study.

Properties	Benzene	TCE	Toluene	p-Xylene
Suppliers	Sigma-Aldrich Canada Co.	Sigma-Aldrich Canada Co.	Sigma-Aldrich Canada Co.	Fisher Scientific Company
Location (city, province, country)	St. Louis, Missouri, USA	St. Louis, Missouri, USA	St. Louis, Missouri, USA	Ottawa, Ontario, Canada
Purity (%)	99.89	≥ 99	99.8	99
Boiling point (°C)	80.10	87.20	110.60	138.4
Structure				
Kinetic Diameter (Å)	5.85[40]	5.60[41]	5.85[40]	5.85[40]
Polarizability (Å^3)	10 ~10.74[42]	9.61~9.75[43]	11.80 ~12.30[42]	13.70 ~14.90[42]
Dipole Moment (x 10^{18} Deby)	---[42]	0.9[44]	0.375[42]	0.1[42]
Quadrupole Moment (x 10^{-26} Deby)	---[42]	---[44]	---[42]	---[42]

3.5. Experimental and Methodology

Henry's law constants and heat of adsorption values were experimentally determined by using a gas chromatograph (8610C GC purchased from SRI Instruments, (Torrance, California, USA) fitted with a flame ionization detector (FID). The concentration pulse method (CPM) was used to carry out the experiments, which is a simple and accurate technique for determining Henry's law constants[45]-[54]. Figure 3.1 shows the schematic diagram of the experimental set-up used. N_2 which accounts for around 79 % of ambient air was chosen as the carrier gas, representing air. To obtain accurate and clear peak samples from CPM, the volumetric flow rate of the N_2 carrier gas was adjusted depending on the properties of adsorbates and adsorbents. The low volumetric flowrate causes longer experimental time. It would cause a baseline shift and high oscillations on the peak sample and baseline. The experimental time could be reduced by using a higher volumetric flow rate, but the flame was not properly produced, and the accurate retention time could not be observed since the peak was produced too early in some cases. Therefore, for each pair of adsorbent and adsorbate, the flow rate needed to be optimized.

The retention time of each adsorbent-adsorbate pair can be obtained from the peak sample obtained at different temperatures. To get the peak, the microliter syringe was used to inject one microliter pure liquid VOC sample into the carrier gas. The injected liquid sample has evaporated at higher temperatures in the injection port of the GC. The evaporated sample was carried by the preheated N_2 carrier gas into the column packed with the adsorbent inside the GC oven and was adsorbed by the adsorbent. With the continuous flow of the carrier gas, the adsorbate was then desorbed from the column and was ionized by flame produced by an FID ignitor and a gas mixture of H_2 and air (with a ratio of 1:10 for H_2:air). At the end, the FID collector detected the ionized adsorbate. Therefore, the adsorbates should be flammable to be detected by the FID. The PeakSimple Chromatography software from SRI Instruments recorded the measurable current flow of the ionized adsorbate as the signal (in millivolt, which is proportional to the concentration of the adsorbate desorbing from the column) versus time (sec). The peak samples were observed until the baseline of the peak samples were steady [45].

To improve the accuracy of the estimation of Henry's law constants at room temperature, the experiments for zeolites and DVB polymer were observed at the lowest temperatures for which the peak samples of the adsorbates can accurately be obtained from the FID.

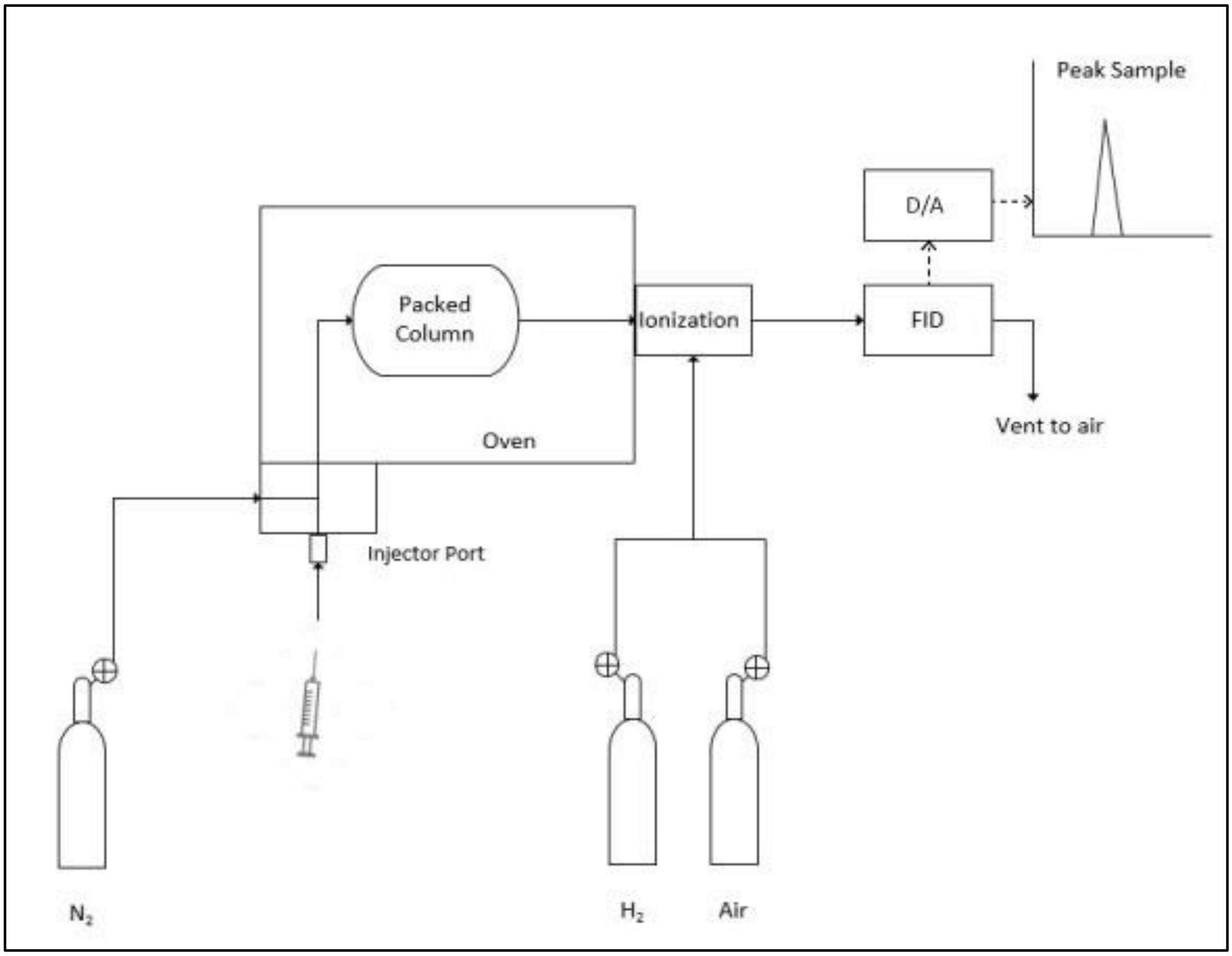


Figure 3.1 - Schematic diagram of the experimental set-up for GC with FID used in this study.

In this study, two zeolites were crushed to 20 x 60 mesh size by mortar and DVB polymer was used with the original size of 60 x 80 mesh. Each adsorbent was fully packed into columns. The specifications of these columns and N_2 carrier flow rates used are shown in Table 3.3.

Table 3.3 - Specifications of columns and N_2 carrier gas flow rates used in this study.

Column length (cm)	Column inner diameter (cm)	N_2 flow rates (mL/min)
9.82	0.44	10 – 240
2.45	0.44	30 – 260

In the case of HiSiv 1000 and HiSiv 3000, the 9.82 cm long column was used for experiments over 200 ℃ and the 2.45 cm column was used for experiments at temperatures lower than 200 ℃. In the case of DVB polymer, the 9.82 cm column was used for experiments over 150 ℃ and the 2.45 cm column was used for experiments at temperatures lower than 150 ℃. The short column was used to improve the accuracy of the results at lower temperatures. Before the experiments, each adsorbent was regenerated at atmospheric pressure with N_2 purge gas flow rate of 250 mL/min for at least 12 hours at high temperatures. Two zeolites and DVB polymer were regenerated at 400 ℃ and 260 ℃, respectively, since 400 ℃ was the maximum temperature attainable for the GC and the maximum temperature for DVB polymer was 275 ℃).

The density of the adsorbent and bed void fraction of the column should be determined to calculate Henry's law constants. A Micrometric volumetric adsorption analyzer was used to determine the adsorbent density and bed void fraction using pure helium gas as the probe gas. The adsorbent densities of HiSiv 1000, HiSiv 3000, and DVB polymer were 2.37 g/cm^3, 2.56 g/cm^3 and 1.2 g/cm^3, respectively. Their bed void fractions were all 0.39.

The injected adsorbate sample produces the peak response detected by the FID. The retention time of the peak response can be used to determine Henry's law constants. This adsorption parameter indicates the initial slope of the adsorption isotherm for the corresponding VOC adsorbate and the corresponding adsorbent.

The mean retention time of the adsorbate, μ, is the first moment of the peak. The mean retention time of the peak can be used to obtain the dimensionless Henry's law constant, K according to Equation [1][49]-[54].

$$\mu = \frac{\int_0^\infty c(t-\mu_D)dt}{\int_0^\infty c dt} = \frac{L}{v}[1 + \frac{(1-\varepsilon_B)K}{\varepsilon_B}] \qquad [1]$$

where t is the time (sec), c is the adsorbate concentration detected on the FID, L is the column length (cm), ε_B is the bed void fraction (dimensionless), v is the interstitial fluid velocity of the carrier gas (cm/sec), K is the dimensionless Henry's law adsorption equilibrium constant, and μ_D is the dead time (sec).

The initial slope of the adsorption isotherm of the pure component VOC is dimensional Henry's law constant. The dimensionless Henry's law constant can be used to determine the dimensional Henry's law constant, K_p, according to Equation [2][49]-[54].

$$K_p = \frac{K}{RT\rho_s} \qquad [2]$$

where R is the ideal gas law constant, T is the absolute temperature (K), ρ_s is the adsorbent density (g/cm^3), and K_p is the dimensional Henry's law adsorption equilibrium constant (mol/g/atm).

The slope of van't Hoff plots (ln K_p vs. $1/T$) can be used to determine the heat of adsorption, ΔH according to Equation [3][49]-[54].

$$K_p = K_0 \, e^{-\left(\frac{\Delta H}{RT}\right)} \qquad [3]$$

Where K_0 is the pre-exponential factor. ΔH is the heat of adsorption (kJ/mol).

3.6. Results and Discussion

3.6.1. Henry's Law Constant

VOCs are not present in acute exposure concentrations indoors. Since the VOCs' concentrations (partial pressure) indoors are low in the air, the potential of adsorption between adsorbate and adsorbent can effectively be measured by using the experimental Henry's law constant, which is the initial slope of the adsorption isotherm.

In this study, the peaks produced by adsorption of major indoor VOCs were experimentally measured by using CPM. The retention time obtained from the peak sample could determine Henry's law constants at different temperatures using Equations [1] and [2]. Henry's law constants determined at different temperatures were plotted as van't Hoff plots (K_p vs $1/T$). Due to VOCs' high boiling points and high interaction with adsorbents, Henry's law constants could not be accurately measured at temperatures close to the room temperature. Therefore, van't Hoff plots were extrapolated to room temperature. To improve the accuracy of estimating Henry's law constants at room temperature, Henry's law constants were determined at the lowest temperatures for which the peak samples of the adsorbates could accurately be calculated.

Figure 3.2 shows Henry's law constants plotted for different temperatures as semi-log van't Hoff plots (K_p vs 1000/T). This figure shows the comparison of Henry's law constants for different

VOC adsorbates for each adsorbent. The dashed lines in this figure show the corresponding temperature in ^{o}C at the top of the figures.

As shown in Figure 3.2, the physical adsorption occurred between major indoor VOCs and all adsorbents since Henry's law constant of all adsorbate increased as temperature decreases. For all adsorbents, Henry's law constants at the room temperature showed the same order: p-xylene > toluene > benzene > TCE. To explain this trend, the properties of adsorbates were observed such as kinetic diameter, polarizability, dipole moment, and quadrupole moment. In Table 3.2, the dipole moments, and quadrupole moments for major indoor VOCs are close to zero due to their non-polar nature. Their kinetic diameters are relatively similar. Therefore, it is expected that the dipole and quadrupole moments, and kinetic diameters did not affect the observed trend of Henry's law constants. However, the polarizabilities of the adsorbates are p-xylene > toluene > benzene > TCE, which is the same trend as Henry's law constants for respective adsorbents. This happens since higher polarizability reduces the interaction force between nucleus charge and electrons. The reduced interaction force makes electrons move further away from the nucleus charge. The electrons away from the nucleus charge can easily cause increasing interactions with the adsorbent[19][21]. Therefore, p-xylene with the highest polarizability could have the highest Henry's law constant followed by toluene, benzene, and TCE.

Fig 3.2 - (a) HiSiv 3000

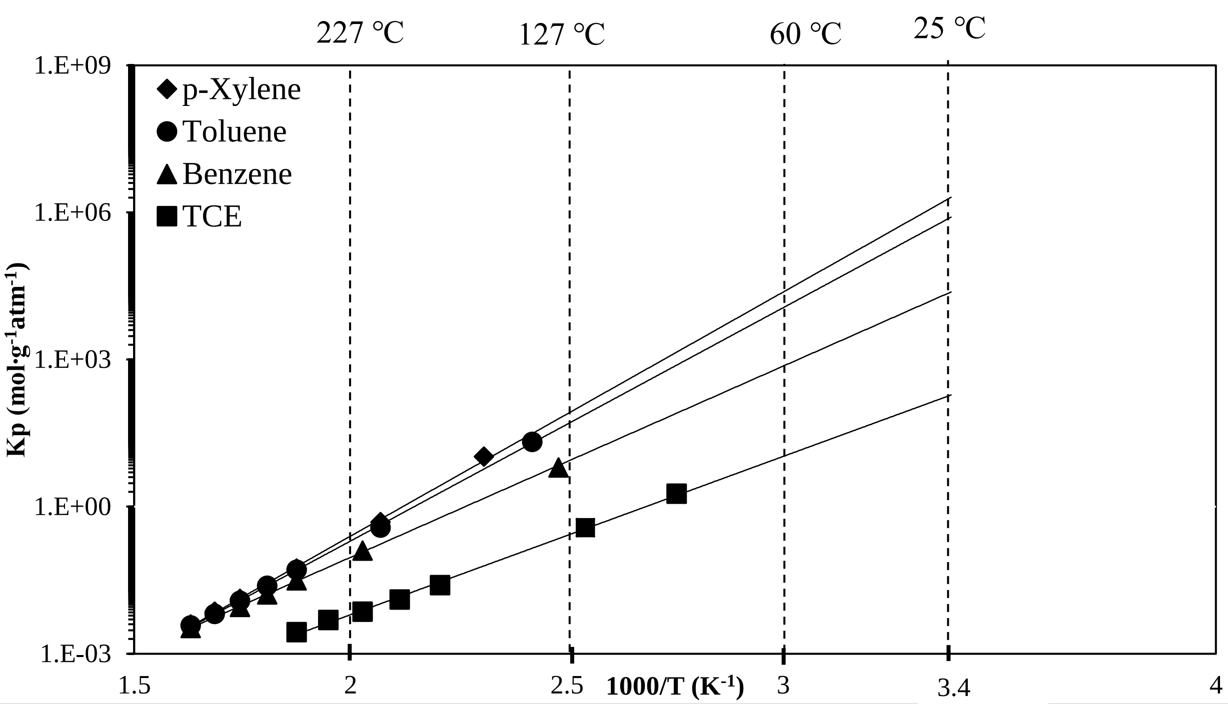
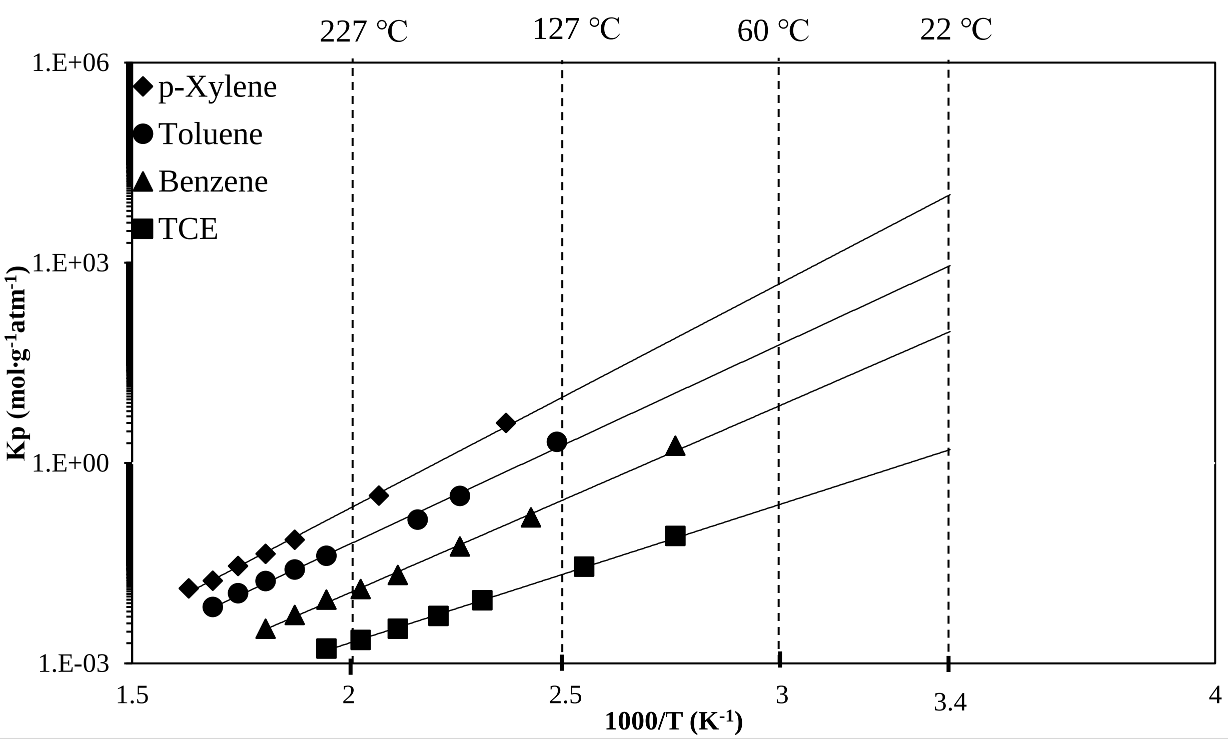


Fig 3.2 - (b) HiSiv 1000



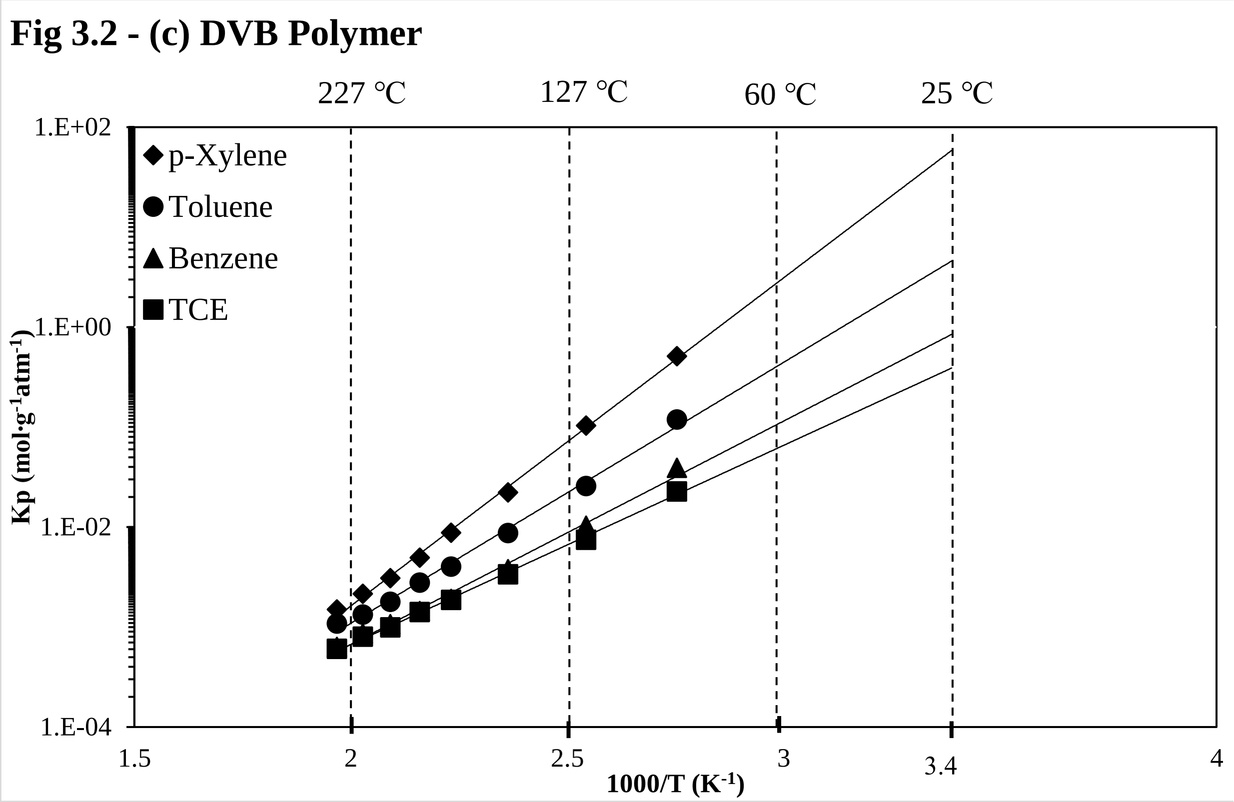


Fig 3.2 - (c) DVB Polymer

Figure 3.2 - The comparison of Henry's law constant values for p-xylene, toluene, benzene, and TCE for each adsorbent with N_2 as the carrier gas. Black dots represent experimental data points and the lines represent extrapolation to 25 °C room temperature.

Figure 3.3 shows Henry's law constants at different temperatures as a semi-log vant Hoff plot for each VOC to compare the adsorbents studied. All vant Hoff plots are extrapolated to room temperature in this study and Henry's law constants observed in the literature are tabulated in Table 3.4 and are compared to the values obtained in this study.

As shown in Figure 3.3, for all the VOC adsorbates, Henry's law constants for adsorbents studied had the same order: HiSiv 3000 > HiSiv 1000 > DVB polymer. As can be seen in Table 3.1, the BET surface area and mean pore size of DVB polymer are higher than those for both HiSiv 1000 and HiSiv 3000, but Henry's law constants of DVB polymer were always lower than those of zeolites (HiSiv 1000 and HiSiv 3000). To improve the adsorption, the adsorbate should be fitted-well into the pores of the adsorbents. Therefore, it is important to have the pore size optimized for the VOCs. The mean pore size of the DVB polymer (70 Å) is composed of macropores. It is much larger (around 12 times larger) than major indoor VOCs' kinetic diameters. Due to the large pore size of DVB polymer, adsorbate could not fit well into pores. The adsorbate could easily pass through the pores and come out of the pores. Furthermore, literature has reported that the VOC adsorption of adsorbent with macropores is lower than that for the adsorbent with micropores[56][57].

As can be seen in Table 3.1, the BET surface area and mean pore size of HiSiv 3000 were lower than those of HiSiv 1000, but Henry's law constants of HiSiv 3000 were always higher than those of HiSiv 1000. In the literature, it has been reported that for the comparison of microporous adsorbents, the larger the pore size was, the higher was the adsorption. HiSiv 1000 (8 Å) and HiSiv 3000 (6 Å) used in this study are composed of micropores. Therefore, it was expected that Henry's law constants of HiSiv 1000 should be higher than those for HiSiv 3000. To explain this trend in Henry's law constants, one should observe the properties of zeolites such as the cations in the structure and the Si/Al ratio. The structure of zeolite is composed of porous crystalline aluminosilicate materials that are formed by tetrahedra framework of $(SiO_4)^0$ and $(AlO_4)^{-1}$ balanced out by cations. Therefore, the Si/Al ratio and the cations are important factors for determining the zeolite property. The cations of HiSiv 1000 and HiSiv 3000 were all balanced out by Na^+. However, the Si/Al ratio of HiSiv 3000 (over 1000) was much higher than HiSiv 1000 (less than 20) which means silicon atoms are dominant in the composition of the tetrahedra framework of SiO_4 and AlO_4 for HiSiv 3000. The dominance of silicon atoms makes the surface of zeolite more homogeneous. Therefore, higher Si/Al ratios result in higher hydrophobicity. The non-polar molecules prefer to interact with non-polar adsorbents (hydrophobic adsorbents). TCE, benzene, toluene, and p-xylene used in this study were all non-polar due to their none or low dipole moments, as shown in Table 3.2. Therefore, HiSiv 3000 with a higher Si/Al ratio would prefer to interact with the major VOCs indoors more than HiSiv 1000[30][58]. The comparison of Henry's law constants in logarithmic scale at room temperature is shown as a bar chart in Figure 3.4

Fig 3.3 - (a) TCE

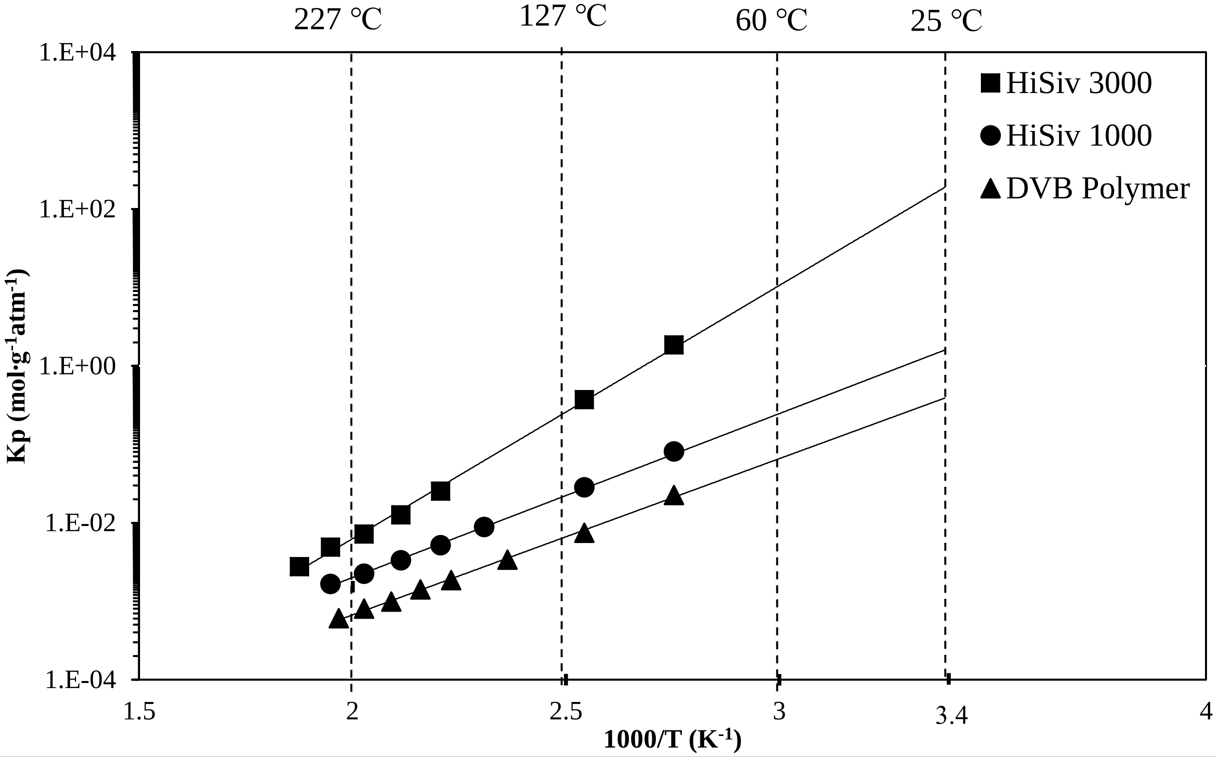


Fig 3.3 - (b) Benzene

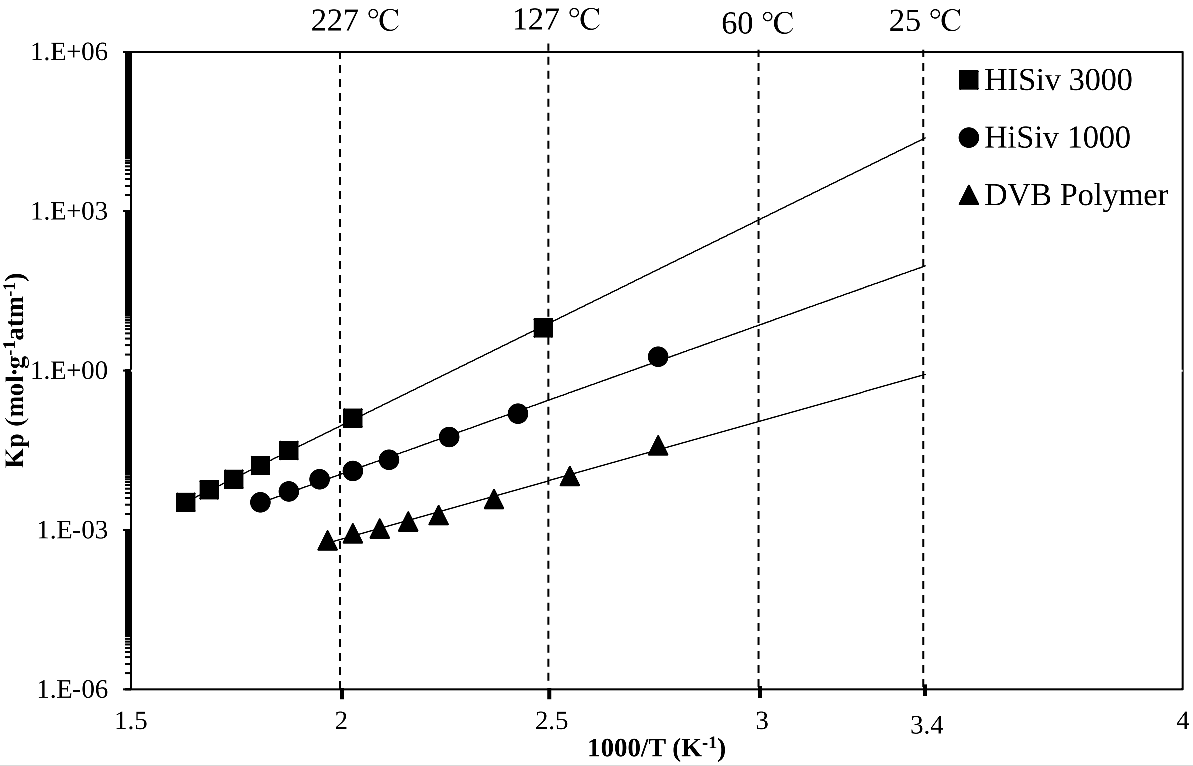
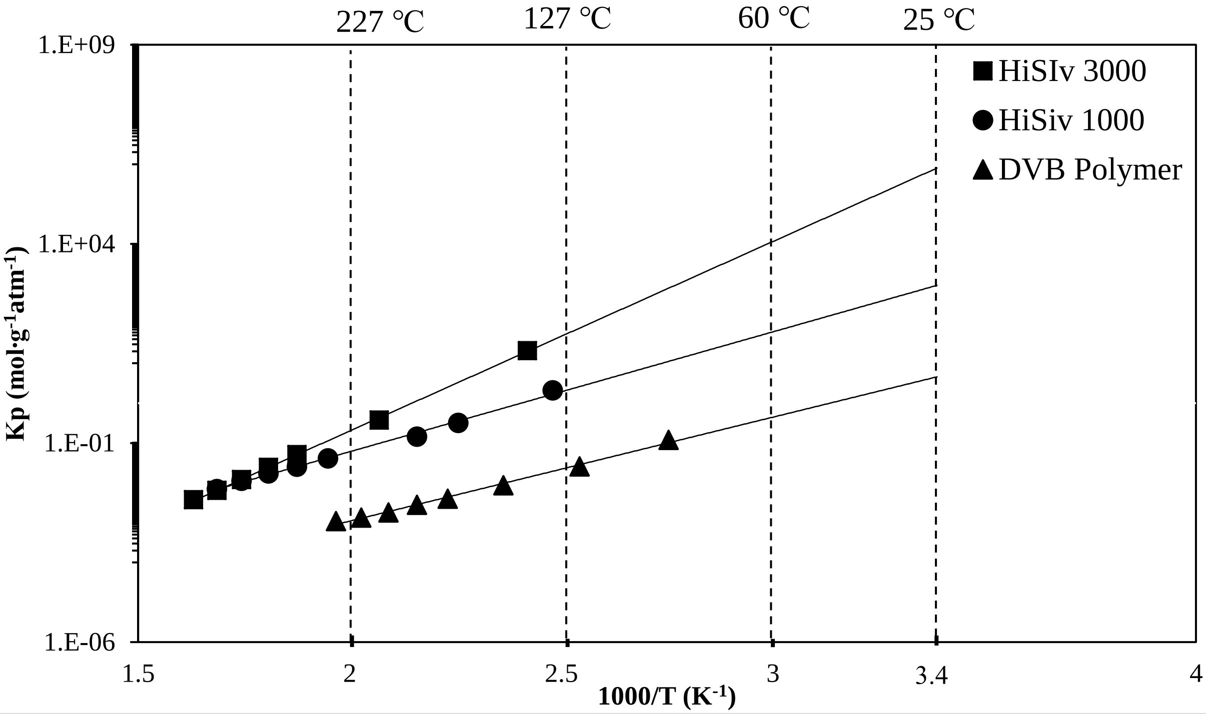


Fig 3.3 - (c) Toluene



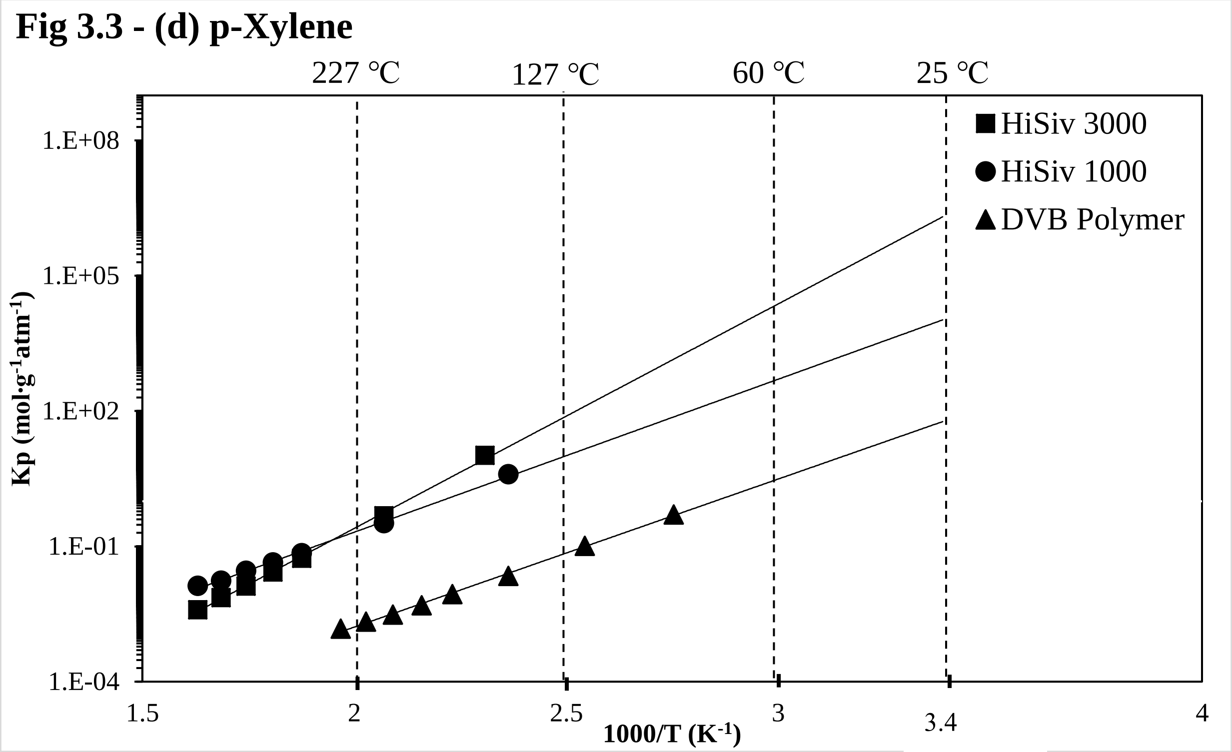


Fig 3.3 - (d) p-Xylene

Figure 3.3 - The comparison of Henry's law constant values for four adsorbents with each adsorbate (with N_2 carrier gas). Black spherical dots represent experimental data points. The lines represent extrapolation to room temperature 25 ℃.

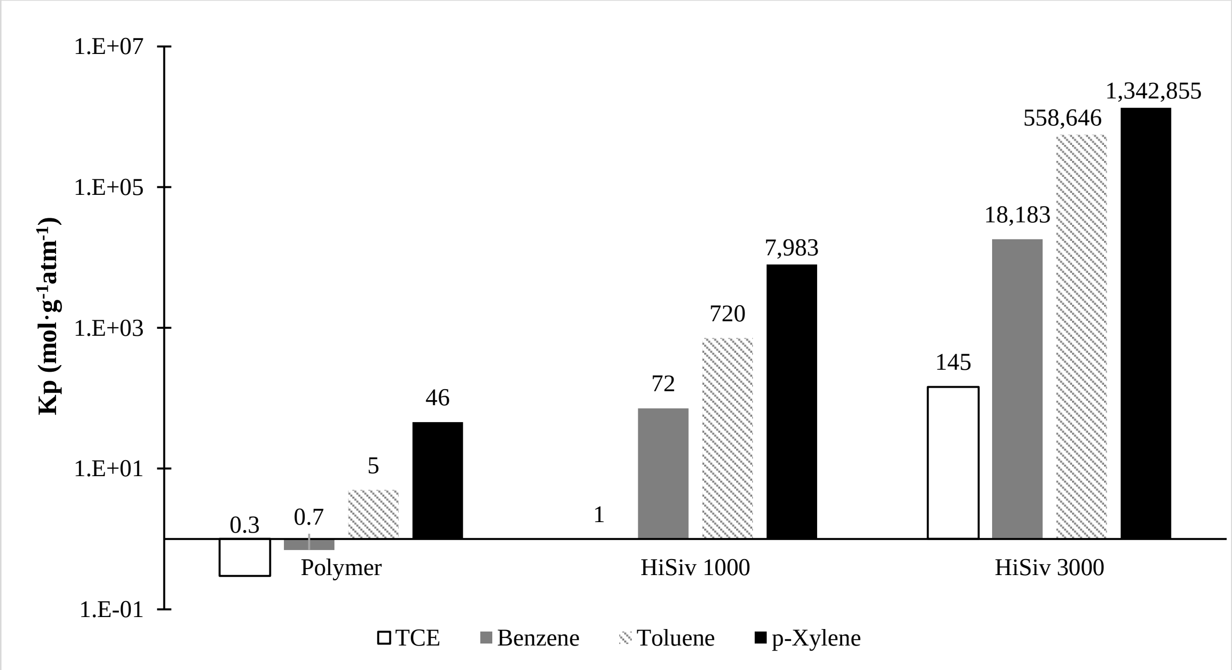


Figure 3.4 - Henry's law constants, K_p (mol/g/atm) at room temperature determined in this study.

Furthermore, when Henry's law constants are compared to the literature values in Table 3.4, we can see that HiSiv 3000 was the best adsorbent for the removal of these VOCs since it had the highest Henry's law constant. It can also be observed from this table that the differences in Henry's law constants were quite considerable.

Table 3.4 - Henry's law constants, K_p (mol/g/atm) determined in this study and their literature comparisons for four adsorbates.

Adsorbates	Types	Adsorbents	Temperature (°C)	Henry's law constants, K_p (mol/g/atm)	Reference
p-Xylene	Zeolite	HiSiv 3000	25	1,342,855	This study
	Zeolite	HiSiv 1000	25	7,983	This study
	Polymer	DVB Polymer	25	46	This study
	Zeolite	LaY	25	30,571	[33]^1
	Polymer	PIB	25	0.1	[35]^2
Toluene	Zeolite	HiSiv 3000	25	558,646	This study
	Zeolite	HiSiv 1000	25	720	This study
	Polymer	DVB Polymer	25	5	This study
	Zeolite	LaY	25	3,212	[33]^1
	Zeolite	DAY	25	1	[34]^2
	Polymer	PIB	25	0.05	[35]^2
Benzene	Zeolite	HiSiv 3000	25	18,183	This study
	Zeolite	HiSiv 1000	25	72	This study
	Polymer	DVB Polymer	25	0.7	This study

	Zeolite	LaY	25	336	[33][1]
	Polymer	PIB	25	0.02	[35][2]
	Polymer	NDA 201	25	226	[29][1]
TCE	Zeolite	HiSiv 3000	25	145	This study
	Zeolite	HiSiv 1000	25	1	This study
	Polymer	DVB Polymer	25	0.3	This study
	Polymer	NDA 201	25	10	[29][1]

[1]: Henry’s law constants from the literature

[2]: Henry’s law constants determined by parameters in the literature

3.6.2. Heat of Adsorption

Physical adsorption is the process of adhesion initiated by the interaction between the adsorbate and the adsorbent. When the adsorbate is adsorbed on the surface of the adsorbent, the energy is released. This released energy is defined as the heat of adsorption[27]. The stronger the adsorbate is adsorbed on the surface of the adsorbent, the higher energy it releases. Therefore, the heat of adsorption is an important factor indicating the strength of the interaction between the adsorbate and the adsorbent. However, the high heat of adsorption would make it difficult to remove the adsorbate from the adsorbent due to the high interaction between the adsorbate and the adsorbent. Therefore, the working capacity of the adsorbent would be lowered during repeated desorption and adsorption cycles. Therefore, smaller heat of adsorption values are preferred[58].

In this study, the heat of adsorption values were determined by the slope of the van’t Hoff plots (ln *Kp* vs *1/T*) according to Equation [3]. Figure 3.5 shows the comparison of van’t Hoff plots for different VOC’s studied for HiSiv 1000, HiSiv 3000, and DVB polymer adsorbents. Also, the heat of adsorption values estimated from the slopes of van't Hoff plots in Figure 3.5 are shown in Figure 3.6. The corresponding data of heat of adsorption are tabulated in Table 3.5, together with the corresponding values obtained from the literature.

The heat of adsorption values of zeolites were always higher than those for DVB polymer. These values for zeolites were in the range of 40 to 90 kJ/mol and for DVB polymer were in the range of 30 to 60 kJ/mol. As expected, the heat of adsorption values for p-xylene were always the highest with the respective adsorbents since Henry's law constants of p-xylene were also the highest with the respective adsorbents. The trends of the heat of adsorption values were p-xylene > toluene > benzene> TCE, which were the same as Henry's law constant trends. Furthermore, the heat of adsorption values of HiSiv 3000 were always the highest. These values for adsorbents for all of the VOCs studied also showed the same trends as Henry's law constant trends: HiSiv 3000 > HiSiv 1000 > DVB polymer.

Fig 3.5 - (a) TCE

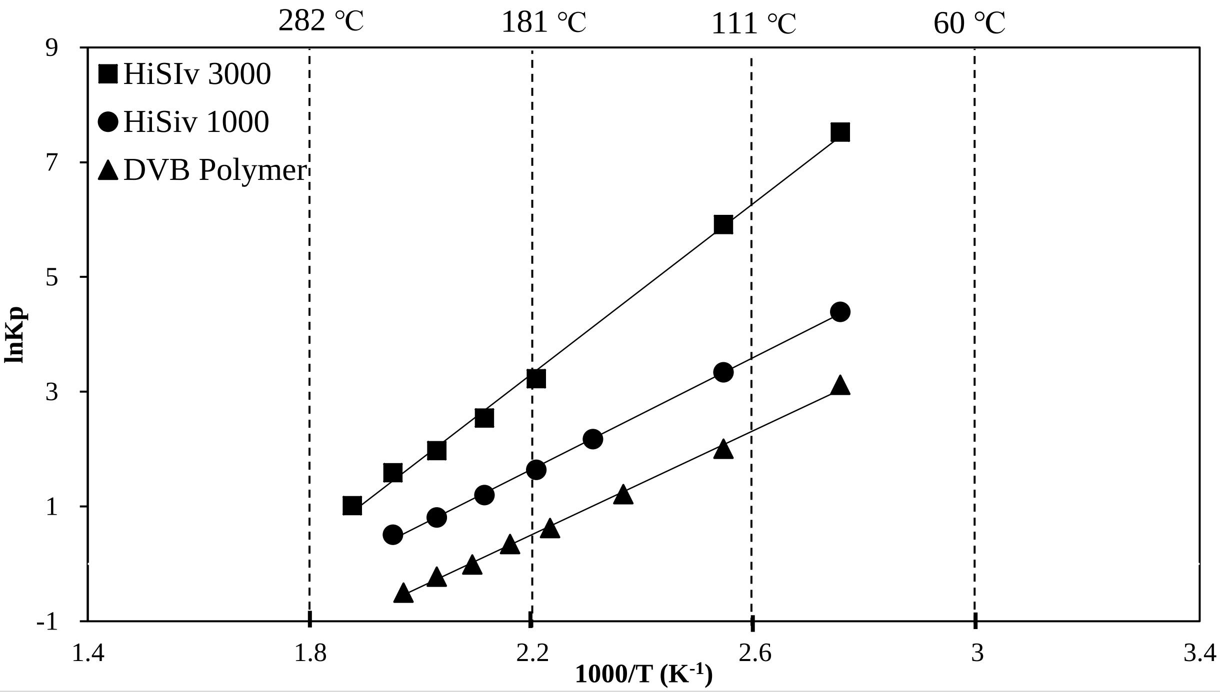


Fig 3.5 - (b) Benzene

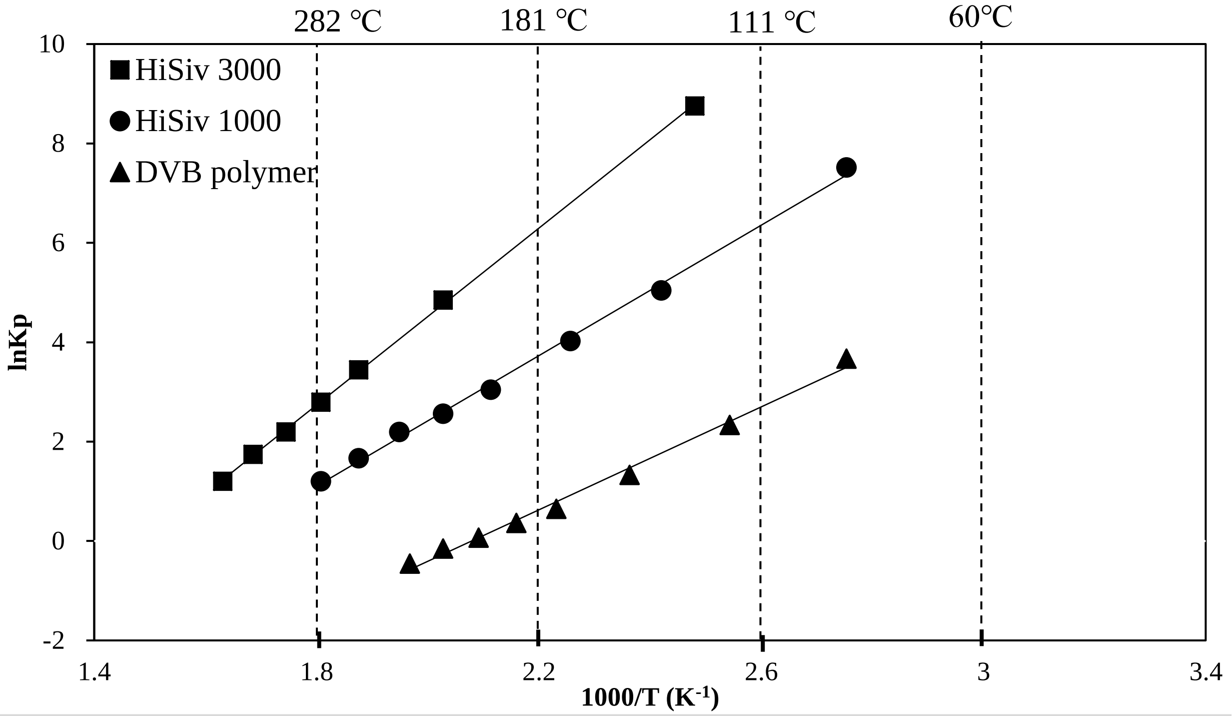
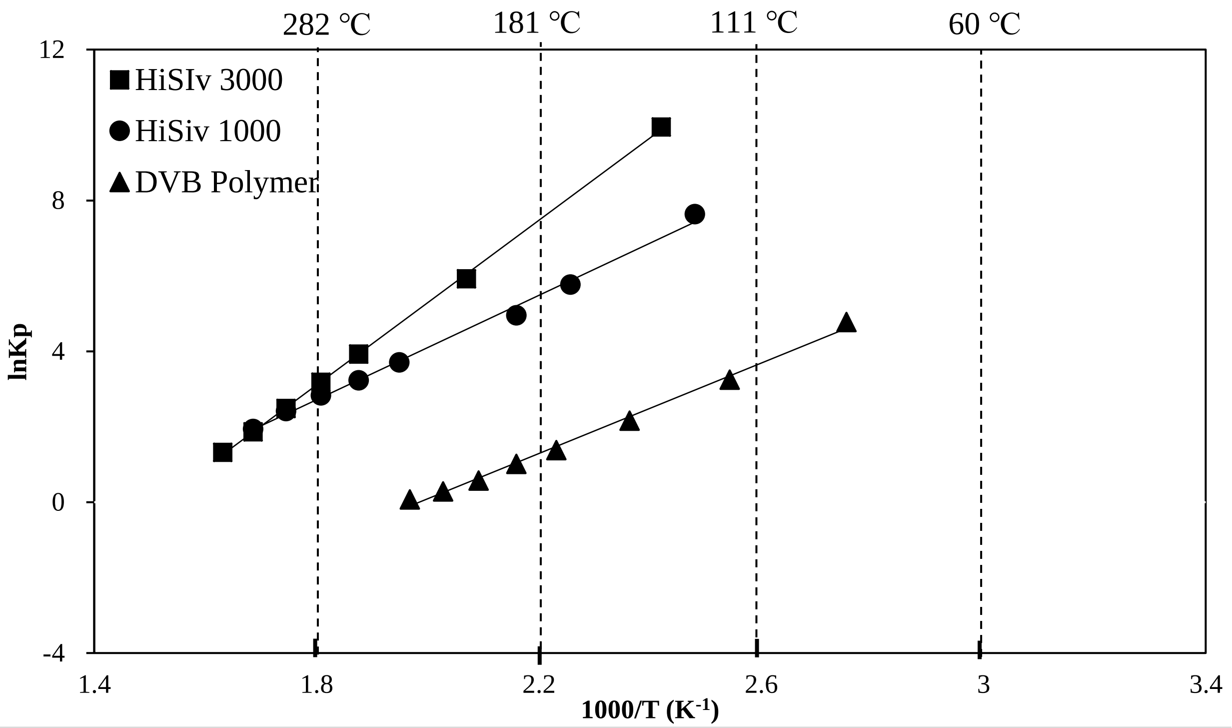


Fig 3.5 - (c) Toluene



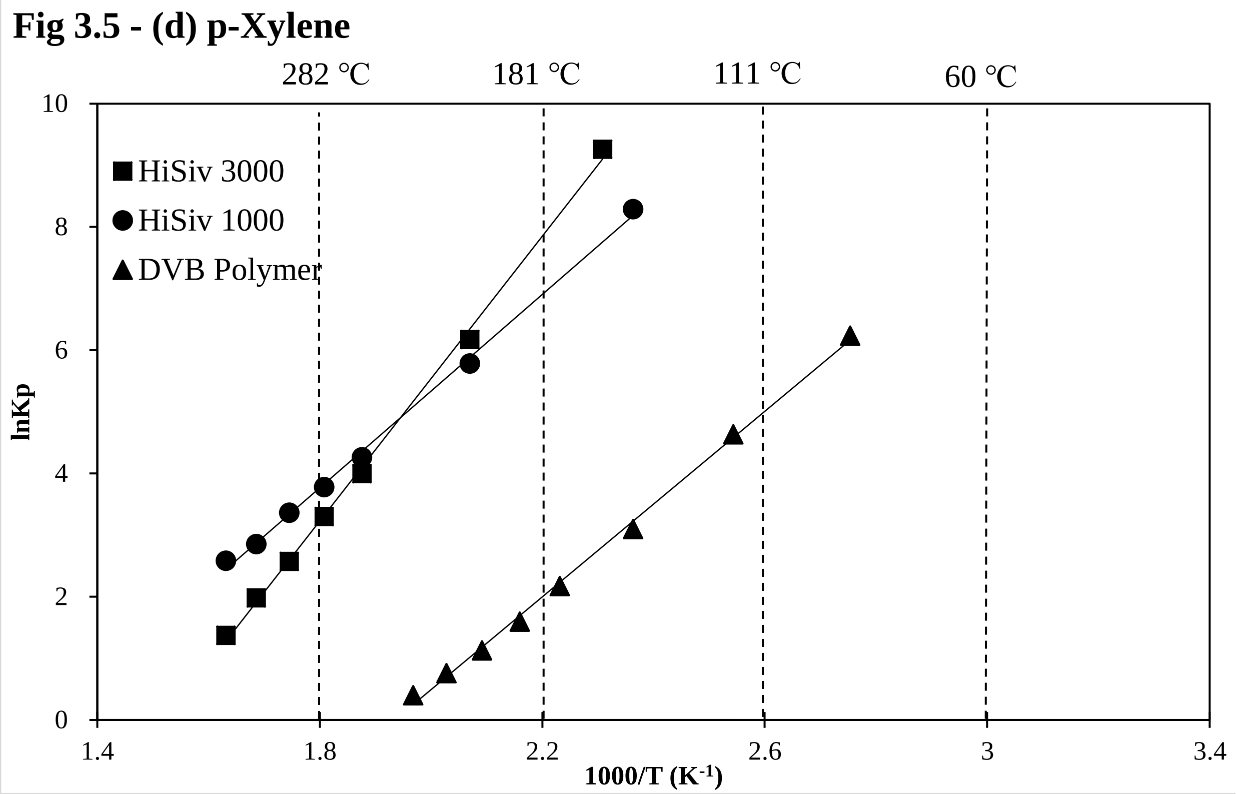


Figure 3.5 - Experimentally determined lnKp vs. 1000/T of three adsorbents with each adsorbate (with N_2 carrier gas).

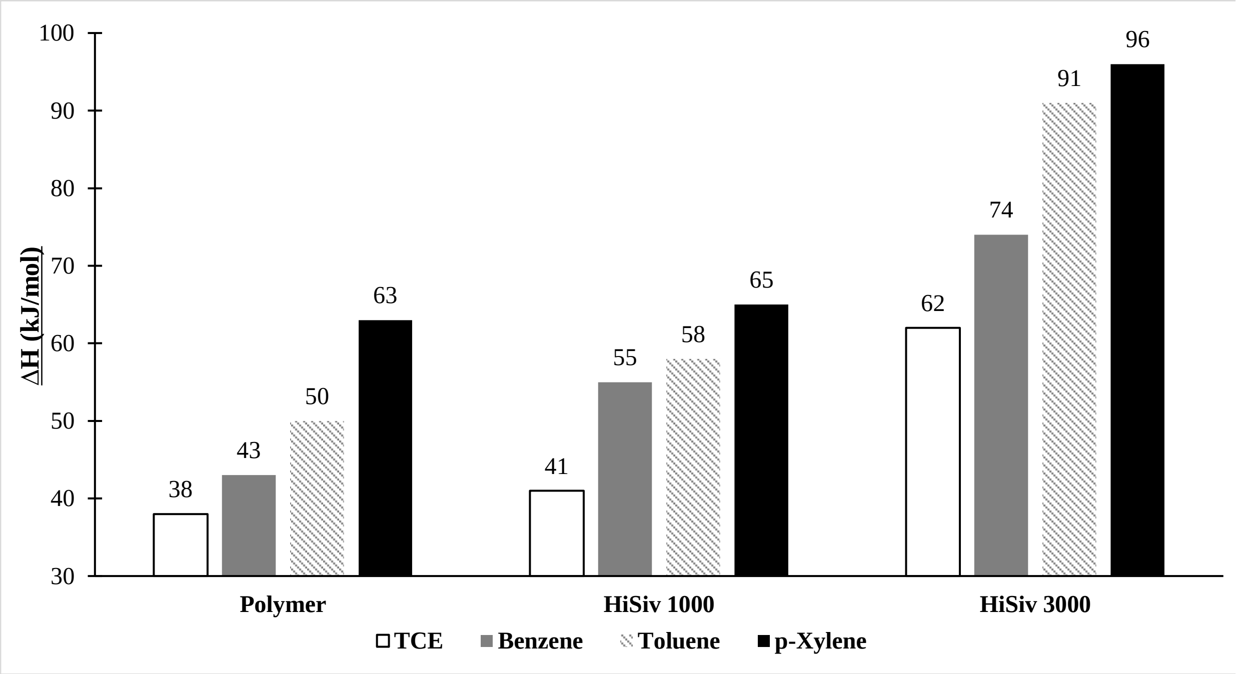


Figure 3.6 - Heat of adsorption values, ΔH (kJ/mol) determined in this study.

When the heat of adsorption values are compared to the literature values in Table 3.5, it can be seen that HiSiv 3000 had either the highest (p-xylene and toluene) or the second-highest interaction with these VOC's.

Table 3.5 - Heat of adsorption values (kJ/mol) experimentally determined from van't Hoff plots and heat of adsorption values in the literature.

Adsorbates	Types	Adsorbents	Heats of adsorption, ΔH (kJ/mol)	References
p-Xylene	Zeolite	HiSiv 3000	96	This study
	Zeolite	HiSiv 1000	65	This study
	Polymer	DVB Polymer	63	This study
	Zeolite	LaY	64	[33][1]
	Zeolite	DAY F20	46	[36][1]
	Polymer	PIB	38	[35][1]
Toluene	Zeolite	HiSiv 3000	91	This study
	Zeolite	HiSiv 1000	58	This study
	Polymer	DVB Polymer	50	This study
	Zeolite	LaY	60	[33][1]
	Zeolite	DAY F20	42	[36][1]
	Zeolite	Na Y	70 - 84	[32][1]
	Zeolite	DAY	17	[34][2]
	Polymer	PIB	32	[35][1]
Benzene	Zeolite	HiSiv 3000	74	This study

	Zeolite	HiSiv 1000	55	This study
	Polymer	DVB Polymer	43	This study
	Zeolite	LaY	57	[33][1]
	Zeolite	DAY F20	42	[36][1]
	Polymer	PIB	25	[35][1]
	Polymer	NDA 201	100	[29][2]
TCE	Zeolite	HiSiv 3000	62	This study
	Zeolite	HiSiv 1000	41	This study
	Polymer	DVB Polymer	38	This study
	Polymer	NDA 201	66	[29][2]

[1]: the heat of adsorption values in the literature
[2]: the heat of adsorption values determined by the slope of van’t Hoff plots in the literature

3.7. Conclusions

TCE, benzene, toluene and p-xylene were studied due to their highest concentrations and frequencies in indoor air. Two commercially available zeolite adsorbents (HiSiv 1000 and HiSiv 3000) and DVB polymer were investigated for the possibility of removing these VOCs from indoor air. They have shown promise for the removal of major indoor VOCs. Henry’s law constants at room temperature (25 °C) were observed and compared to find the most promising hydrophobic adsorbent among them. To estimate Henry’s law constants at room temperature, Henry’s law constants were experimentally determined at temperatures ranging from 90 °C to 340 °C. This is because VOCs had high boiling points and high interaction with selected adsorbents. Van’t Hoff plot was used to extrapolate these Henry’s law constants to room temperature. As expected, the results showed that physical adsorption occurred between major indoor VOCs for all of the adsorbents studied, as Henry's law constants increased as temperature decreases. For the respective adsorbents, p-xylene showed the highest Henry's law constants followed by toluene, benzene, and TCE. For all of the VOCs, HiSiv 3000 showed the highest Henry's law constants followed by HiSiv 1000 and DVB polymer. Based on the observed results, the Si/Al ratio and pore structure of the adsorbent would be a significant factor for improving the adsorption of VOC. The slopes of van't Hoff plots could be used to determine the heat of adsorption values of the pure VOCs. The heat of adsorption values for DVB polymer were in the range of 30 to 60 kJ/mol, whereas these values for zeolites were in the range of 40 to 90 kJ/mol. The heat of adsorption values showed similar trends to Henry's law constant trends. For all the adsorbents, p-xylene showed the highest heat of adsorption values followed by toluene, benzene, and TCE. For all of the VOCs, HiSiv 3000 showed the highest heat of adsorption values followed by HiSiv 1000 and DVB polymer.

Based on Henry's law constant values at room temperature compared in this study and literature, the most promising hydrophobic adsorbent for the removal of indoor VOCs was HiSiv 3000.

3.8. Nomenclature

C	concentration of adsorbate (mV)
ΔH	heat of adsorption (kJ/mol)
K	dimensionless Henry's law constant (-)
K_0	pre-exponential factor (mmol/g/atm)
K_p	dimensional Henry's law constant (mmol/g/atm)
L	column length (cm)

P	pressure (psi)
R	ideal gas law constant (82.06 cm^3·atm/K/mol or 8.314 J/K/mol)
t	time (sec)
T	absolute temperature (K)
m	dead time (sec)

Greek Letters

ε_B	bed void fraction (dimensionless)
ρ_s	adsorbent density (g/m^3)
μ	retention time (sec)
ν	interstitial fluid velocity (cm/sec)

3.9. Bibliography

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CHAPTER 4: Conclusions

Ji Sub Yun

Department of Chemical and Biological Engineering, University of Ottawa

161 Louis Pasteur, Ottawa, ON, KIN 6N5 CANADA

4.1. Decision Matrix

In this study, a total of seven commercially available adsorbents have been investigated as potential effective adsorbents to remove major indoors volatile organic compounds (VOCs). Among these adsorbents, four of them were of activated carbons (AC BPL, AC F-600, AC NZ, and AC Cloth), two of them were zeolites (HiSiv 1000 and HiSiv 3000) and one of them was divinylbenzene (DVB) polymer. The adsorption separation potentials of these adsorbents were compared by determining and comparing their Henry's law constants for the VOCs at room temperature. However, due to the different performance of these adsorbents for each major indoor VOC, it was difficult to determine the most effective adsorbent for the removal of all major VOCs. Therefore, in this study, the decision matrix based on Henry's law constants at room temperature was employed to determine the best promising adsorbent for all major VOCs. Table 4.1 shows the decision matrix.

Based on Henry's law constants at room temperature, each adsorbent had 1 to 7 scale points from low to high for each VOC, since seven-candidate adsorbents were investigated. As mentioned in Chapter 1, the major indoor VOCs considered in this study had different concentrations and frequencies indoors (toluene > para-xylene > benzene > trichloroethylene). Therefore, they had different weighting points (from 1 to 4, based on low to high) based on their indoors concentration and frequencies, as can be seen in Table 4.1.

The full point of scale points and weighting points was 70 in the decision matrix, as explained in the footnote of Table 4.1. The higher the points, the better is the adsorbent. As a result, the adsorbents with the highest total points (64) were AC F-600 and HiSiv 3000 followed by AC BPL, AC Cloth, AC NZ, HiSiv 1000, and DVB polymer.

Table 4.1 - Decision Matrix

Adsorbent / Adsorbate	Weighting Points	AC F-600[1]	AC BPL	AC Cloth	AC NZ	HiSiv 3000	HiSiv 1000	DVB Polymer
Toluene	**4**	6	5	4	3	7	2	1
p-Xylene	**3**	7	5	4	3	6	2	1
Benzene	**2**	6	5	4	3	7	2	1
TCE	**1**	7	6	5	3	4	2	1
Total Point[1]/Full Point[2]		**64/70**	51/70	41/70	30/70	**64/70**	20/70	10/70

[1]: AC F-600 total point for example = (6 · 4) + (7 · 3) + (6 · 2) + (7 · 1) = 64

[2]: full point = (7 · 4) + (7 · 3) + (7 · 2) + (7 · 1) = 70

4.2. Conclusions

The objective of this study was to determine the most effective adsorbent to remove major indoor VOCs. Therefore, hydrophobic adsorbents have been investigated to reduce the possibility of chemical adsorption with indoor water vapors. To determine the most effective hydrophobic adsorbent for removal of major indoor VOCs, Henry's law constants at 25 ℃ (considered to be the average room temperature) and heat of adsorption values were estimated and compared for different adsorbents. Henry's law constants and heat of adsorption values were experimentally determined by applying the concentration pulse method (CPM) by using a gas chromatograph (GC) equipped with a flame ionization detector (FID).

In order to remove the major indoors VOCs, four commercially available activated carbons, two zeolites, and one DVB polymer were screened in this study. With regards to these seven adsorbents studied, Henry's law constants for the VOCs showed the same trend: p-xylene > toluene > benzene > TCE. This is due to the polarizabilities of the VOCs studied. The higher the polarizability of adsorbate is, the larger the electron cloud orbits of the adsorbate are, which makes it easier to interact with the adsorbent surface.

For the comparison of AC adsorption for VOCs removal, the pore structure of AC could be an important factor. The results showed that VOC adsorption of AC is proportional to the increase in the pore size in the micropore range. However, as reported in the literature, it was observed that the adsorption decreases as the pores get larger than the micropore size limit (20 Å) in AC adsorbents. Furthermore, DVB polymer with pores close to the macropore size showed the lowest VOC adsorption among the seven adsorbents studied. Unlike ACs and DVB polymer, VOC adsorption of zeolites was not affected by the pore structure. The results for zeolites showed that the higher the Si/Al ratio of zeolite was, the higher was the VOC adsorption. This is due to the non-polar property of the indoor VOCs studied. The VOCs with non-polar properties would prefer to interact more with the non-polar or hydrophobic adsorbents.

As expected, van't Hoff plots of Henry's law constants at different temperatures confirmed that physical adsorption occurred in all adsorbents since Henry's law constants increased as temperature decreases. The heat of adsorption values were obtained from the slope of van't Hoff plots. The trend for the heat of adsorption was similar to the ones for Henry's law constants. Their heat of adsorption values were in the range of the physical adsorption.

The results of Henry's law constants at room temperature for different categories of adsorbents were in the order of AC > zeolite > polymer. However, as mentioned in section [4.1], each adsorbent had different adsorption potential for each VOC. Based on the decision matrix, the total points of the different adsorbents were: AC F-600 = HiSiv 3000 > AC BPL > AC Cloth > AC NZ > HiSiv 1000 > DVB polymer. Due to the lowest Henry's law constants for all of VOCs, DVB polymer had the lowest total points. AC F-600 had the highest Henry's law constant for p-xylene and TCE. HiSiv 3000 had the highest Henry's law constants for toluene and benzene. Therefore, AC F-600 and HiSiv 3000 had the same total points. Furthermore, the heat of adsorption values of AC F-600 were relatively lower than those for HiSiv 3000. The low heat of adsorption could help with the regeneration of the adsorbent for re-use easier. As a result, the most effective hydrophobic adsorbent for the major indoor VOCs has turned out to be AC F-600. The results of this study can also contribute to reducing VOCs outdoors since VOCs also exist outdoor.

4.3. Recommendations for Future Work

In order to achieve future works, there are four major recommendations for better understandings of the adsorbents and indoor air pollutants that cause sick building syndrome (SBS).

1. In this study, activated carbons (ACs) showed that VOC adsorption was proportional to the pore size up to certain pore size, but their adsorption decreased when pore sizes reach the mesopore size (20 Å). Therefore, it is recommended to experiment with other AC adsorbents with mesopores or macropores to observe the trends for VOC removal.
2. Results for zeolites showed that VOC adsorption is proportional to the Si/Al ratio. Since only two zeolites were observed in this study, it is recommended to observe trends of some other micropore zeolites with Si/Al ratios between 10 to 1000.
3. Due to the possibility of chemical adsorption between indoor water vapor and adsorbents, the adsorbents considered as hydrophobic were only investigated in this study. Therefore, it is recommended to observe the hydrophilic adsorbents for VOC removal.
4. The major indoor air pollutants that cause SBS are VOCs, ammonia, and formaldehyde. Therefore, it is recommended to observe the removal of ammonia and formaldehyde using different adsorbents.