EVALUATION OF ACTIVATED CARBON FIBERS (ACF) FOR REMOVAL OF VOLATILE ORGANIC COMPOUNDS (VOCS) IN INDOOR ENVIRONMENTS

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To my parents Zongxiang Lu and Nayu Zhu. Thank you for your unwavering encouragement. Without your love and support none of my accomplishments in life would have been possible

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ABSTRACT

Lu, Huajun Ph.D., Purdue University, December 2005. Evaluation of Activated Carbon Fibers (ACF) for Removal of Volatile Organic Compounds (VOCs) in Indoor Environments. Major Professor: Neil J. Zimmerman.

The purpose of this research was to address the applicability of activated carbon fiber (ACF) for removal of VOCs in indoor environments. Adsorption isotherms were characterized in both the passive mode (without air drawn through the ACF specimen) and the active mode (with air penetrating through the ACF specimen) at various concentrations for acetone, toluene and limonene and three species of ACF. The Langmuir, Freundlich and Dubinin-Redushkevich models were used to predict adsorption capacities at untested concentrations for the three adsorbates and three ACF adsorbers in the both passive and active modes. Empirical statistical models based on the Freundlich equation were then established and evaluated by comparisons made between experimental results and predicted results for trichloroethylene and methyl ethyl ketone. Sorption experiments were performed in order to determine the sorptive kinetics of ACF, cotton, polyester, gypsum board, carpet and empty chamber surfaces for acetone, toluene and limonene. Tested VOC adsorption rates and adsorption capacities on ACF are greater than tested indoor sink materials by a factor of 1 to 3 orders of magnitude in the 10 to 1000 mg/m^3 concentration range and by a factor of 3 to 6 orders of magnitude in the 0.01 to 10 mg/m^3 concentration range, respectively. The linear Langmuir sink model was examined for indoor sink materials and found to be applicable, while the non-linear sink model was successfully applied for ACF, with the assumption that the adsorption process follows the non-linear isotherm and the desorption process follows the linear isotherm. The breakthrough time of ACF filters was examined in the concentration range of 60 ppb to 13 ppm. The relationship of breakthrough times at different concentration levels was established and the breakthrough time of ACF filters at lower concentrations can be extrapolated from the results obtained at higher concentrations. Competitive adsorption of indoor VOCs shortens the breakthrough time of ACF filters and reduces their adsorption capacities on each individual VOC. The Ideal Adsorbed Solution Theory effectiveness was examined for predicting adsorption capacity of each chemical in a binary mixture, and the prediction was found to agree quite well with experimental results.

CHAPTER I

INTRODUCTION

Background

Indoor volatile organic compounds (VOCs) are one of the major contributors to indoor air quality problems. Activated carbon has demonstrated its efficiency in industrial applications for removing water or gaseous contaminants for decades. However, little literature has been found to evaluate the use of activated carbon to remove low concentrations of volatile organic compounds from various indoor environments. In this study, activated carbon fiber (ACF) was evaluated for its applicability to removal of VOCs in both the passive mode (no air drawn through the ACF) and the active mode (air drawn through the ACF). If the results show that ACF can remove VOC at indoor concentration levels, ACF then could be placed directly on a floor or hung as a curtain in newly furnished or waxed rooms to remove indoor VOCs, or filters made from ACF could be placed in new or existing air circulation ventilation systems to control the buildup of indoor VOCs.

Indoor Air Quality (IAQ)

IAQ is an issue of concern in industrialized countries, including the United States. Indoor pollutant levels are often higher than outdoor levels, and at times may exceed ambient and even occupational standards (Yocom, 1982). Energy conservation measures which include tightening building structures and decreasing fresh air intake have intensified IAQ problems. Concern about IAQ is driven mainly by health problems that are thought to be attributable to indoor air pollutant exposure. Indoor air pollutants may be categorized into four groups (Liu, 1995): bioaerosols (microorganisms); respirable particles; gaseous contaminants (e.g. SO_2) and organic vapors (e.g. acetone, toluene). Bioaerosols include fungi, bacteria and viruses. Bioaerosols are commonly present in outdoor air, and they can be transported indoors by ventilation, infiltration and human activities. Moreover, if conditions permit (nutrients and moisture), microorganisms can also grow in indoor environments. Respirable particles refer to particles with a diameter less than 10 μm, which may penetrate into the lower respiratory tract . Submicron particles are mainly from combustion sources and tobacco smoke. Gaseous contaminants are primarily from outdoor ventilation air and human activities such as cooking. The most common gaseous contaminants are ozone, nitrogen oxides, carbon monoxide and sulfur dioxide. Vaporous contaminants are primarily produced from indoor materials and human activities such as cleaning, waxing, painting etc., and VOCs are one of most common indoor pollutants. Due to the toxicity of formaldehyde, it is singled out from VOCs and is often addressed specifically.

Health Effects

The main route of entry of indoor air pollutants into the human body is inhalation. In addition, some pollutants affect mucous membranes, and a few can cause skin rashes and itching. Health effects associated with IAQ can be classified into two categories: sick building syndrome and building–related diseases. Typical sick building syndrome symptoms are (Gammage and Berven, 1996):

- Headache
- Irritation of the eyes and of mucous membranes
- Irritation of the respiratory system
- Drowsiness
- Fatigue
- General malaise

Usually, the cause of the symptoms is unknown and symptoms are reduced after leaving the building. However, the term building-related disease is used for cases of specific infections, allergies, or toxin-induced disease with objective clinical findings related to building occupancy (e.g., Legionnaires' disease, hypersensitivity pneumonitis).

Indoor air pollution consistently ranks among the top five environmental risks to public health in the United States (US EPA, 1990). One-half of US 110,000 schools in America have problems linked to indoor air quality (EPA, 2005). Lost productivity associated with indoor air pollution costs businesses an estimated $40 billion per year for the United States alone (Haymore and Odom, 1993). A particular issue of IAQ for developing countries is the use of biomass fuels for unvented cooking and heating, which results in two million deaths annually. IAQ in developing countries is also associated with adverse pregnancies and increasing the risk of serious childhood respiratory infection (WHO, 2005). Studies have shown that these emissions may produce the highest air pollution exposures to many pollutants including respirable particulate matter, CO, VOCs, and polycyclic aromatic hydrocarbons. The health effects include acute respiratory infections, chronic pulmonary disease, and lung cancer (DiNardi, 2003).

Indoor VOC Sources and Concentrations

VOCs are ubiquitous in the indoor environment. Over 900 VOCs had been identified by USEPA by 1989 (Maroni et. al., 1995). Indoor VOCs are generated from almost all materials, consumer products, furnishings, pesticides and fuels. Outdoor VOCs can penetrate indoors through ventilation systems and diffuse from polluted soil or drinking water (typically contaminated well-water) into the indoor environment. In office or industrial scenarios, there are many means of releasing VOCs into indoor environments such as photo copying machines, spills of chemicals, and so on. Commonly encountered VOCs and their potential sources are presented in the Table 1.1 (DiNardi, 2003).

Indoor VOC sources vary tremendously, depending the nature and activities of the facility, and are too diverse for any simple classification. However, some broad categories may be listed as follows:

- Long term steady state sources such as moth crystals,
- On/off sources such as heaters,
- Decaying or freshly applied coating sources (“wet” materials”) such as paints, waxes, varnishes and stains, and

- Burst sources such as aerosol products

According to Zhang et al. (1999), based on the mechanism of VOC generation, the emission process from wet materials may be categorized into three phases:

- Evaporation dominated emission phase,
- Transitional phase, and
- Diffusion controlled emission phase.

The period following coating application provides high emission rates but fast decay, with emission rates related to the area of the materials applied. As the coating materials dry, the emission changes from an evaporation-dominant phase to an internal-diffusion controlled phase. In this phase, the emission rate is much lower and continues to decrease but at a much slower rate. Figure 1.1 is as an illustration of the three emission phases for indoor VOCs. The transitional time between the emission and diffusion phases can be variable. Chemical emission rates as shown in profile 1 represents the emission curve of total VOCs. Profile 2 describes the emission curve of a single VOC, in this case, texanol-1. For occupied spaces with evaporation dominated emissions, higher concentration levels would be expected in indoor environments due to fast emission rates of VOCs. On the contrary, for facilities with diffusion controlled emissions, much lower concentration levels would be anticipated. Different strategies for controlling indoor VOCs proposed in this study will be discussed in the following sections.

Table 1.1 Common Indoor VOCs and Potential Sources

Chemical	Potential Sources
Formaldehyde	Particle board, furnishings, fabrics
Other aldehydes (acetaldehyde, acrolein benzaldehyde, ketene)	Plastics, resins, sealants, wood preservatives, biocides
Acetone, isopropanol	Paint, coatings, finishes, paint remover, thinner, caulking
Amines (butylamine, dimethylamine, ethylamine, hexylamine)	Fungicidal treatments
Aliphatic hydrocarbons (octane, decane undecane, hexane, isodecane etc.)	Paint, adhesives, gasoline, combustion sources, carpet, flooring Caulking
Aromatic hydrocarbons (toluene, xylenes, ethylbenzene, benzene, stylene)	Combustion sources, paint, adhesives, gasoline, flooring Wall coating
Chlorinated solvents (dichloromethane methylene chloride, trichloroethane etc.)	Upholstery and carpet cleaner or protector, paint, paint remover Lacquers, solvents, dry-cleaning clothing
Carboxylic acides (acetic acid, acrylic acid)	Used in production of acrylic esters for coating and adhesives
Isocyanates (methylene bisphenyl isocyanate (MDI), toluene diisocyanate)	Concrete sealer, formaldehyde-free fiberboard, foam and paint
Pesticides (organochlorine, organophosphrous, carbamates, paraquat)	Biocidal treatments in paints, textiles
n-Butyl acetate	Acoustic ceiling tile, flooring, caulking
Dichlorobenzene	Carpet, moth crystals, air fresheners
Phenol	Paint, rubber, wood preservatives, synthetic resins, textiles, leather
4-Phenylcyclohexene (4-PC)	Carpet, paint
Terpenes (limonene, a-pinene)	Deodorizers, cleaning agents, polishes, fabrics, cigarettes
2-Butoxyethanol, ethanol, isopropanol	Cleaners, disinfectants

(DiNardi, 2003)

VOC concentrations depend on the type and quantity of building materials used, human activities, the operation of combustion appliances, office machine and environmental conditions such as relative humidity, air velocity, ventilation rates, temperature, and material-air interface thickness. Usually, higher temperature and air velocity may cause higher emission rates and thus lead to higher indoor concentrations if the ventilation rate is low.

Formaldehyde can be major pollutant in some indoor environments. The primary sources of formaldehyde are from building materials and furnishings such as particleboard, medium-density fiberboard, plywood, carpet, furniture, tobacco smoke, and to a lesser extent from combustion appliances. Based on Gammage and Berven's summary (1996), indoor formaldehyde's concentrations are usually lower than 0.1 ppm, with elevated levels as high as 4 ppm in some complaint buildings.

For VOCs other than formaldehyde, their indoor concentrations are usually very low, much below their threshold limit values (TLVs). Shah and Singh (1988) reported that for only 25% of cases of indoor air the mean single VOC concentration exceeds 1 ppb, based on their established national indoor VOC database summarizing 52,810 records on 66 VOCs from 30 cities in 16 states. Maroni et al. (1995) consolidated a data set based on various sources from both Europe and the United States. They found that the 50% percentiles of most compounds amount to only a few micrograms per cubic meter and are several orders of magnitude below existing occupational threshold limit values, but much higher concentrations up to tens of milligrams per cubic meter may occur indoors when special products are used or when permanent sources exist in or near a particular building. A review of Hines et al. (1993) shows that indoor VOC concentrations vary with the types of materials used indoors, personal habits, the activities taking place in the particular indoor environment, the number of habits, and the frequency, time and volume of use of various products. The majority of VOC concentrations are below 10 mg/m^3, regardless of the types of buildings and materials used. However, for newly furnished environments with volatile new materials such as paints, wall and floor glue, and sealing agents, the total VOC concentration can be as high as 1400mg/m^3 (Yu and Crump, 1998; Hines, et 1993). Combining the results of the aforementioned reviews, it would be

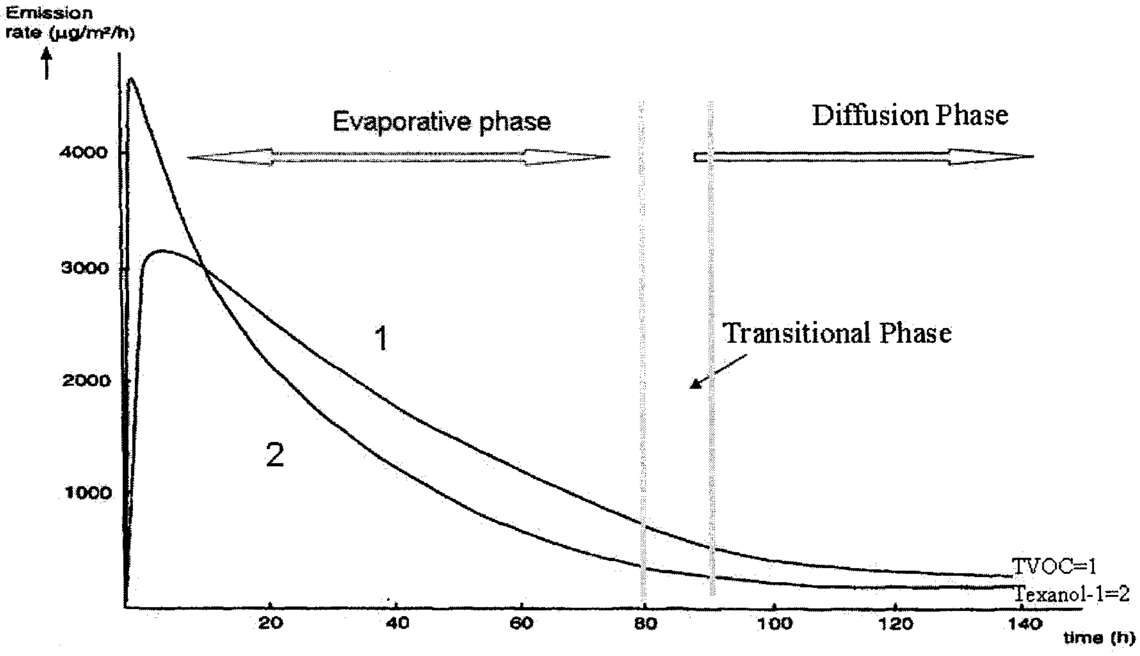


Figure 1.1 Representative Emission Profiles of VOCs from Painting (Yu and Crump, 1998).

reasonable to state that typical indoor VOC concentrations are less than 3 mg/m^3, either for individual VOCs or mixtures of VOCs. Although the number is arbitrary, it is used in this study to distinguish the two different periods. In addition, as presented in the next section of this chapter, a VOC concentration of 3 mg/m^3 can be considered a division in differentiating possible adverse health effects from probable adverse health effects. Thus, in this study, typical VOC concentrations refer to less than 3 mg/m^3, while concentrations above 3 mg/m^3 are considered to be an increase from “normal” indoor situations.

Workers engaged in activities involving the increase of VOCs may become over-exposed to VOCs during the higher emission stage in the short term, due to limited control measures and the presence of mixtures of a wide variety of VOCs. Occupants can also be exposed over a much longer period to moderate or low levels of VOCs.

Standards Regarding Indoor VOCs

When setting criteria for indoor VOCs, a number of factors, in addition to traditional occupational health effects, must be considered such as odor, sensory irritation caused, and the hypersensitive human groups. Because of the complex nature of the presence of VOCs in indoor environments, the combined effects of various VOCs on human health are not yet well understood. Synergistic effects of various VOCs may cause adverse health effects to workers and indoor occupants, even at ppb levels of individual VOCs. Exposure standards proposed for healthy workers, such as the U.S Occupational Safety and Health Administration (OSHA) Permissible Exposure Limits (PELs) and the American Conference of Governmental Industrial Hygienists (ACGIH) Threshold limit values (TLVs), are not applicable to indoor occupants. Currently, no accepted allowable concentration limits for VOCs have been established for non-industrial environments such as office, school, residential or other similar buildings. The American Society of Heating, Refrigerating and Air-Conditioning Engineers, Inc. (ASHRAE) Standard 62-1999 suggested use of 1/10 TLV values as guidance for indoor occupants, not including hypersensitive groups (Zhang et al., 2001). Molhave (1990) suggested a total VOC concentration of less than 0.2 mg/m^3 as not having long-term health effects. For VOC mixtures, exposure range of from 0.2 to 3 mg/m^3 may cause irritation, headaches and other symptoms. From 3 to 25 mg/m^3, irritation, headaches and other symptoms are expected. Above 25 mg/m^3, toxic effects may appear. Under most circumstances, exposures to indoor VOCs are well below corresponding occupational exposure limits (OELs). Yu and Crump (1998) reviewed several studies and indicated that recommended OELs for white spirits and aromatic hydrocarbons are often exceeded even with ventilation in the rooms using different paints and ventilation conditions. The exposure to VOCs from indoor sources is a continuous process and can last for months or even years if no abatement action has been taken.

Indoor VOC Control Strategies

There are three methods of controlling indoor airborne contaminants: source control, ventilation control, and removal control. Source control should always be the first strategy evaluated, following by ventilation control, and ending with removal control. The sources of airborne contaminants cannot always be readily identified, and source removal is not always practical; for example, photocopy machines, a source of VOCs, are necessary in modern offices. Diluting the indoor air is another type of solution to control indoor VOCs problem, but increasing the outdoor air rates can increase energy consumption, which may not be an economically feasible choice. Moreover, according to Muller and England (1995), in some urban areas today, the outdoor air does not meet the National Primary Ambient Air Quality Standards. Thus, it could make ventilation control technically unfeasible. If neither source nor ventilation control will effectively reduce the level of indoor VOCs, removal control should be employed. Possible removal control technologies for indoor VOCs include: thermal decomposition, bio-filtration, botanical air cleaning, photo-catalytic oxidization (PCO), building " bake-out" (the process for removing indoor VOCs by which new or renovated buildings are heated and ventilated prior to occupancy), ultraviolet treatment, and adsorption, etc. (Hunter and Oyama, 2000). Adsorption on activated carbon, however, appears to be a popular technique currently in use for removing indoor VOCs (Ramanathan and Debler, 1994), although its effectiveness, usage and lifetime remain not well documented. In this current research, in order to better control VOC exposures, two strategies have been proposed based on the two general concentration levels indicated in Figure 1.1, the higher but shorter concentrations of the evaporation-controlled phase and the lower but more sustained concentrations of the diffusion-controlled phase. The actual concentration that will be reached depends on the activities going on indoors, for example, the size of the waxed floor. When ventilation is not available or not designed for these activities, occupants or workers in this environment may tend to develop sick building syndrome symptoms or even develop some acute responses because of synergistic effects of VOC mixtures. As such, if some control strategy can be applied to reduce the concentration peaks due to higher emission rates, it would have practical significance in reducing the exposures in two aspects: 1) it can reduce the immediate exposures to high concentrations of VOCs, and 2) it can also reduce the exposures to VOCs from indoor secondary emitters such as carpet in the following diffusion phase. Thus, the proposed control strategy to be studied for achieving this objective is to use an adsorbent to remove indoor VOCs in the passive mode (without air pulling through the adsorbent). The adsorbent must have large surface areas, excellent adsorption properties at low concentration levels and convenience of use. Based on all of the above requirements, activated carbon fiber appears to an ideal adsorbent for this purpose. A detailed description will be presented in the following section of the chapter.

For lower emission rates, VOCs may not be a concern for well ventilated buildings. However, because of the drive to save energy, most buildings re-circulate indoor air and reduce fresh outside makeup air. As a result, the VOCs inside the building would build up and finally reach levels that may cause sick building syndromes. Thus, an in-duct ventilation filter that can adsorb recirculated VOCs is needed to control the indoor VOC levels. The proposed strategy for lower VOC levels is to use an in-duct ventilation filter to control indoor VOCs levels. This test mode is described as "active mode" since the air is drawn through the test filters.

Activated carbon fibers (ACF)

Granular activated carbon (GAC) and powdered activated carbon (PAC) have demonstrated their efficiencies for removal of VOCs and have been widely used in the treatment of drinking water, waste water and industrial gas streams for decades. While numerous literature references provide data on activated carbon for its application in industrial scenarios, very little literature has been found on describing the use of activated carbon to remove indoor VOCs from evaporative sources in the passive mode (without air pulling through ACF) and to remove indoor VOCs from diffusional sources in the active mode (with air drawn through ACF). ACF, a relatively recent form of activated carbon, offers a number of advantages over GAC, which include greatly improved contact efficiency with adsorbates leading to greater rates of adsorption, superior breakthrough capacity and excellent adsorption properties to low concentration of contaminants (Yue, et al., 2001). Moreover, the availability of felt or fabric forms and electrical reactivation add new dimensions for designing indoor adsorption units in an effective and economical manner by occupying smaller space than that occupied by other forms of activated carbon (Suzuki, 1994) and saving reactivation cost (Economy and Lin, 1976). Thus, it seems that it may offer encouraging solutions for the removal of indoor VOCs, but its performance in indoor applications is not very clear. Thus, ACF was used for this project to test its adsorption properties in the passive mode and in the active mode at indoor concentrations. The test samples used in this study were purchased from American Kynol, Inc. (New York, NY). The raw material of ACF is cross-linked phenol-aldehyde fibers (novoloid fibers). Novoloid fibers are carbonized and activated in an atmosphere of steam and/ or carbon dioxide with one step or a continuous process to produce ACF. As the fibers are activated for longer times, the surface areas of the ACF and the pore size all increase (Hayes, 1985). If the experimental results prove viable, ACF can be placed in rooms with high VOC emission rates and in air circulation systems as in-duct ventilation filters to remove trace VOCs indoors.

Purpose and Objectives

Vapor adsorption on solid materials is a complicated phenomenon. The adsorption capacities and sorptive kinetics depend on such characteristics as surface chemistry of the solid material, pore size distribution, surface area, and VOC physico-chemical properties. The purpose of the research presented in this dissertation is to examine ACF in detail for use in the removal of indoor VOCs in both the passive mode and the active mode. Knowledge gained in this study will be useful for designing in-duct ventilation filters in air circulation systems for removal of indoor VOCs and for examining the applicability of ACF for reducing VOCs' exposures in the passive mode in indoor environments. The objectives of this study are to:

1). To characterize the ACF adsorption capacities in the passive mode for selected chemicals and to use Freundlich and Dubinin-Dushkevich isotherms to predict adsorption capacities for untested concentrations;

2). To establish and validate empirical equations for ACFs to predict adsorption capacities for untested chemicals in the passive mode;

3). To characterize and compare sorptive kinetics of ACF and selected indoor sorptive materials based on selected volatile organic compounds (VOCs);

4). To establish and examine an IAQ model based on linear sink effects for fabrics and non-linear adsorption for ACF;

5). To investigate competitive adsorption in VOC mixture in the sub-ppm concentration range; and

6). To measure ACF adsorption capacities and breakthrough times based on ACF-20 in the active mode with challenge of VOCs at typical indoor concentrations (sub-ppm), which are often encountered in indoor air.

This dissertation details all the work of this study. It is organized as follows. In Chapter 2, introduction to adsorption on activated carbon is presented, including a description of factors influencing its adsorption properties. Adsorption isotherms for single compound adsorption and the Ideal Adsorbed Solution Theory for predicting binary VOC mixture adsorption capacities are introduced. Previous studies, including experimental methods for testing adsorption capacity and breakthrough time, indoor air quality models, existing data on adsorption capacities and breakthrough times, are reviewed. In Chapter 3, characterization of adsorption capacities of ACF for selected VOCs in the passive mode is performed and experimental data are used to best fit the selected three adsorption isotherms for predicting VOC adsorption capacity in untested concentrations. Empirical statistical models based on the Freundlich isotherm are developed and validated to predict adsorption capacity of ACF for untested VOCs. In Chapter 4, the effectiveness of ACF for removal of indoor VOC in the passive mode is demonstrated experimentally. The kinetics of sorption for each test material are obtained and the linear Langmuir model for indoor sink materials and the non-linear Freundlich model are evaluated. Comparison of sorption strength of various test materials is made. In Chapter 5, the adsorption capacities and breakthrough times for the selected VOCs are tested at typical indoor concentration levels in the active mode. The relationship of breakthrough time among different concentration levels is established. The Ideal Adsorbed Solution Theory is used to predict each compound's adsorption capacity in the binary mixtures. In Chapter 6, the main findings in this study are summarized and recommendations for future research are made.

Hypotheses

1). ACF adsorption capacity for untested chemicals in both the passive mode (without air drawn through) and the active mode (with air penetrating through) can be predicted based on VOC physico-chemical properties.

2). Linear adsorption isotherm can be used to characterize adsorption capacities for indoor sink materials at indoor concentration levels while a non-linear adsorption isotherm is suitable for characterizing ACF adsorption profiles.

3). Breakthrough times at lower concentrations for ACF filters can be extrapolated from results based on higher concentration levels.

4). Competitive adsorption exists for volatile organic compounds in a mixture in ppb levels, which shortens breakthrough times of individual VOCs and reduces adsorption capacities of individual VOCs.

References

DiNardi, S. R. The Occupational Environment: Its Evaluation, Control and Management, AIHA press, Second edition, 2003

Economy, J. and Lin, R. Y.; Adsorption characteristics of activated carbon fibers, Applied Polymer Symposium 29:199-211, 1976.

Gammage, R. B. and Berven B. A., Indoor Air and Human Health, CRC Lewis Publishers, page 391, 1996.

Hayes J. S., Novoloid nonwovens, Nonwoven Symposium, TAPPI press, 257-263, April, 1985.

Haymore, C. and Odom, R., Economic effects of poor IAQ, EPA Journal, 19(4):28-29, 1993

Hines, A. L, Loyalka, S.K., Ghosh, T.K. and Warder, R. C., Indoor Air Quality and Control, 29-43, Englewood Cliffs, N.J. : PTR Prentice Hall, 1993

Hunter, P., and Oyama, S. T., Control of Volatile Organic Compound Emissions: Conventional and Emerging Technologies, 18-27, John Wiley & Sons, Inc. 2000

Liu, R.T.; Filtration and indoor air quality: a practical approach, ASHRAE Journal, February, 18-23, 1995

Maroni M., Seifert B., and Lindvall T., Indoor Air Quality: A Comprehensive Reference Book, page 35, New York, Elsevier Science, 1995.

Molhave, L., Volatile organic compounds, indoor air quality and health, Indoor Air '90: The Fifth International Conference on Indoor Air Quality and Climate, 5:15-33, 1990.

Muller, C. O., and England, W. G., Achieving your indoor air quality goals: which filtration system works best? ASHRAE Journal, February, 24-32, 1995.

Ramanathan, K., and Debler, V., Evaluation of control strategies for volatile organic compounds I indoor air, Environmental Progress, 7(4): 230-235, 1988.

Shah, J. J. and Singh, H. B., Distribution of volatile organic chemicals in outdoor and indoor air, Environmental Science Technology, 22 (12):1381-1388, 1988.

Suzuki, M., Activated carbon fiber: fundamentals and applications, Carbon 32(4): 577-586, 1994.

U.S. EPA, Reducing risk: setting priorities and strategies for environmental protection, Science Advisory Board, U.S. Environmental Protection Agency, Washington, D.C., 1990.

U.S. EPA, http://www.epa.gov/iaq/, 2005

World Health Organization (WHO): Indoor air pollution and health, Retrieved from http://www.who.int/mediacentre/factsheets/fs292/en/index.html, Geneva, Switzerland: WHO, 2005

Yocom, J., Indoor-outdoor air quality relationships, Journal of Air Pollution Control Association. 32(5):500-520, 1982.

Yu, C. and Crump, D., A review of the emission of VOCs from polymeric materials used in buildings, Building Environment, 33(6):357-374, 1998

Yue, Z.; and Economy, J., Removal of chemical contaminants from water to below USEPA MCL using fiber glass supported activated carbon filters, Environment Science Technology, 35(13): 2844-2848, 2001

Zhang, J.S., Nong, G., Shaw, C., and Wang, J., Measurements of volatile organic compound (VOC) emissions from wood stains using an electronic balance, ASHRAE Transactions: Research, 279-288, 1999

Zhang, J.S., Zhang, Z. and Chen, W., An overview of indoor VOC concentration strategies: source control , ventilation and air purification, the 4th International Conference on Indoor Air Quality, Ventilation and Energy Conservation in Buildings, Changsha, China, 2001

CHAPTER II

LITERATURE REVIEW

The Adsorption Process

Adsorption refers to the trapping of pollutants (adsorbates) on the surfaces of solid materials (adsorbents). The pollutants are adsorbed onto the surface or its pores of a solid material such as activated carbon or molecular sieve by physical or chemical attraction. There are two mechanisms of adsorption: physical attraction (van der Waals) and chemical bonding. These types of adsorption are termed physical adsorption and chemisorption, respectively. The nature of the bond formed between the adsorbed molecules and the adsorbent surface is the primary difference between physical adsorption and chemisoprtion. There is no clear line between the two adsorption mechanisms although chemical and physical adsorption are characterized by different thermal effects. In practice, if the activation energy is less than two or three times the latent heat of evaporation, the adsorption is physical, if it is greater, chemisorption is taking place (Ruthven, 1984).

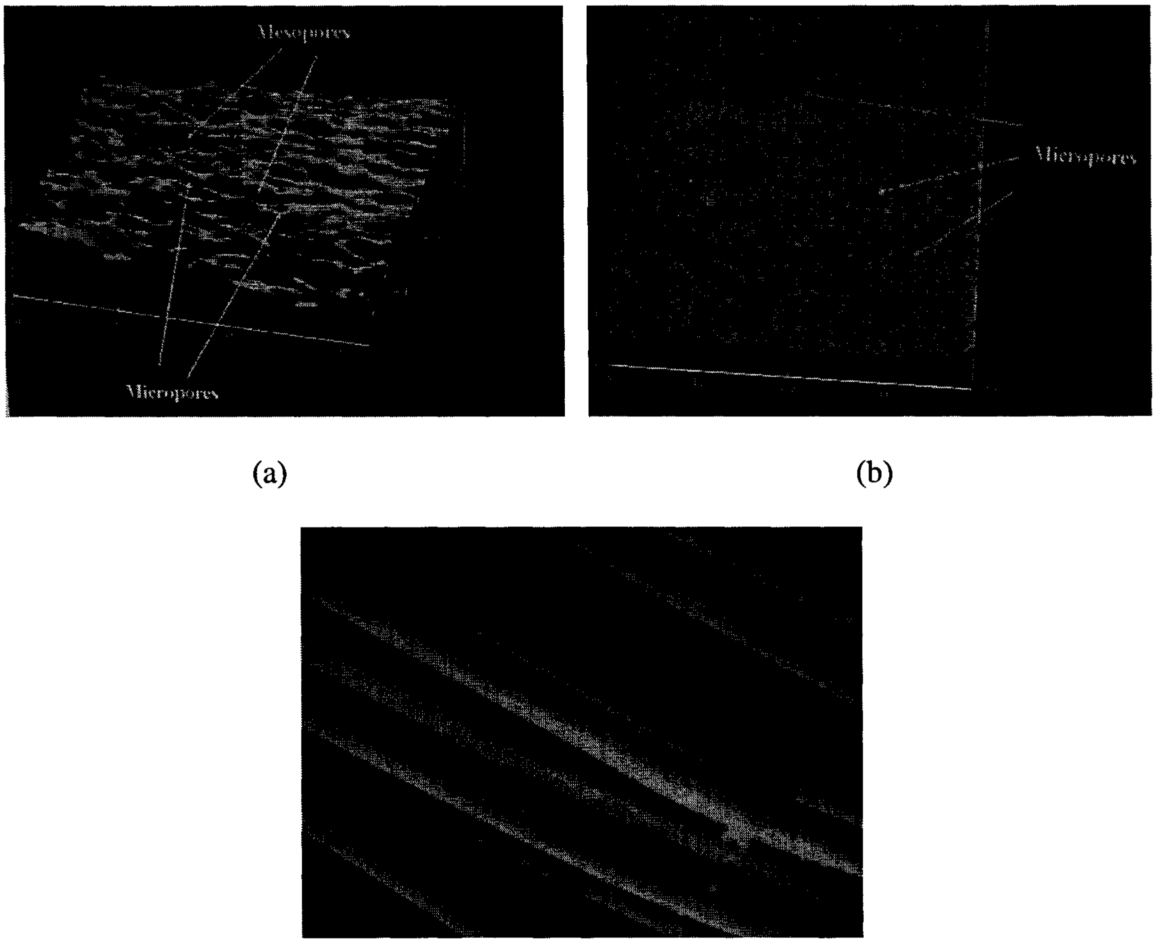
Activated carbon is one of most common adsorbents for removal of VOCs in gas streams. It has been reported that many factors, such as specific surface area and pore size distribution of activated carbon, physico-chemical properties and concentration of VOCs, adsorption temperature, and humidity can affect the adsorption process (Chuang et al., 2003).

Adsorption Forces, Adsorption Energy, and Pore Size

The forces involved in adsorption are of two main kinds: physical and chemical. Physical adsorption always includes dispersion forces (which are attractive in nature, also called London or van der Waals forces), short –range repulsive forces, and electrostatic (coulombic) forces if either the solid or the gas is polar. In chemisorption, electron transfer takes place between the solid and the adsorbed molecules and a chemical compound is formed. Valency forces are involved in the chemisorption process. When considering physical adsorption between a solid and a molecule of adsorbate gas or vapor, dispersion forces are always present and, unless the adsorbate molecule possesses a strong dipole moment, will represent the major contribution to the total energy of adsorption. The dispersion forces will be considerably stronger in micropores than above plane surfaces and will be the weakest on prominences (Gregg and Sing, 1967).

Pores in the adsorbent are usually characterized in terms of their width, defined by the diameter of a cylindrical pore or the distance between two sides of a slit-shaped pore. The pores may vary greatly both in size and in shape within a given solid. Pore size corresponds to adsorption energy: in a given solid, the smaller pores have higher adsorption energy than larger pores. Pore size distribution of an adsorbent can be estimated by the Horvath-Kawazoe (HK) and Dubinin-Stoeckli (DS) methods (Cal, 1995). In this research, pore size and specific surface area of ACF were not characterized for

ACF due to unavailability of the test instrument. The shape of an adsorption profile called an adsorption isotherm tells us indirectly about the volume of adsorption sites within the carbon at various adsorption energies. Adsorption first takes place in the higher-energy sites and progressively fills the lower-energy sites.



(a)

(b)

(c)

Figure 2.1. Micrograph Images of ACF; (a) ACF Surface, (b) ACF Cross-section, (c) ACF Fiber. (Foster, 1993)

As carbon is activated to create more surfaces, the adsorption capacity of the carbon to hold adsorbates increases. Longer activation times produce ACF with larger surface area; however, the number of high energy sites (smaller pores) decreases. These higher-energy sites are needed to adsorb molecules in low concentration, which may be suitable for removal of indoor VOCs. VOCs have a wide range of polarity, and, for most activated carbons, adsorption is more efficient with nonpolar molecules. Nonpolar VOCs are able to occupy larger micropores due to greater affinity with the adsorbent. Thus, compared to polar VOCs, nonpolar VOCs have greater adsorption capacities. Molecules with greater adsorption energy displace molecules of lower adsorption energy. Considering a wide variety of VOCs present in indoor environments, competitive adsorption among various VOCs may exist.

As shown in Figure 2.1, on the surface and in the cross-section of each ACF fiber, there are numerous micropores, mesopores, and macropores. As stated earlier, the micropores play the major role in removal of indoor VOCs. However, very large molecules may not be able to access some sizes of micropores because of molecular sieve effects. In order to be adsorbed in the activated carbon, those molecules may need to occupy pores with larger width if modest adsorption energy is sufficient to retain the compounds. According to the International Union of Pure and Applied Chemistry (IUPAC, 1972), pores with pore width less than 20 Å (2 nm) are categorized as mircopores, between 20 and 500 Å, mesopores, and more than 500 Å, macropores.

The Adsorption Isotherms

The graphical results in a plot of a chemical adsorbed on an adsorbent versus gas concentration or partial pressure at a constant temperature result in an adsorption isotherm. An adsorption isotherm is useful for characterizing adsorption capacity on different adsorbates for an adsorbent, and it therefore may be used for predicting adsorption capacity at untested conditions.

Thousands of adsorption isotherms, measured for many adsorbents, have been reported. The great majority of the isotherms observed to date can be categorized into five types, as classified by Brunauer, Deming, Deming and Teller (BDDT) (also called the BET classification) (Hines et al., 1993), and are listed in Figure 2.2. Type I is observed in physical adsorption of gases onto microporous solids. Type II comes from

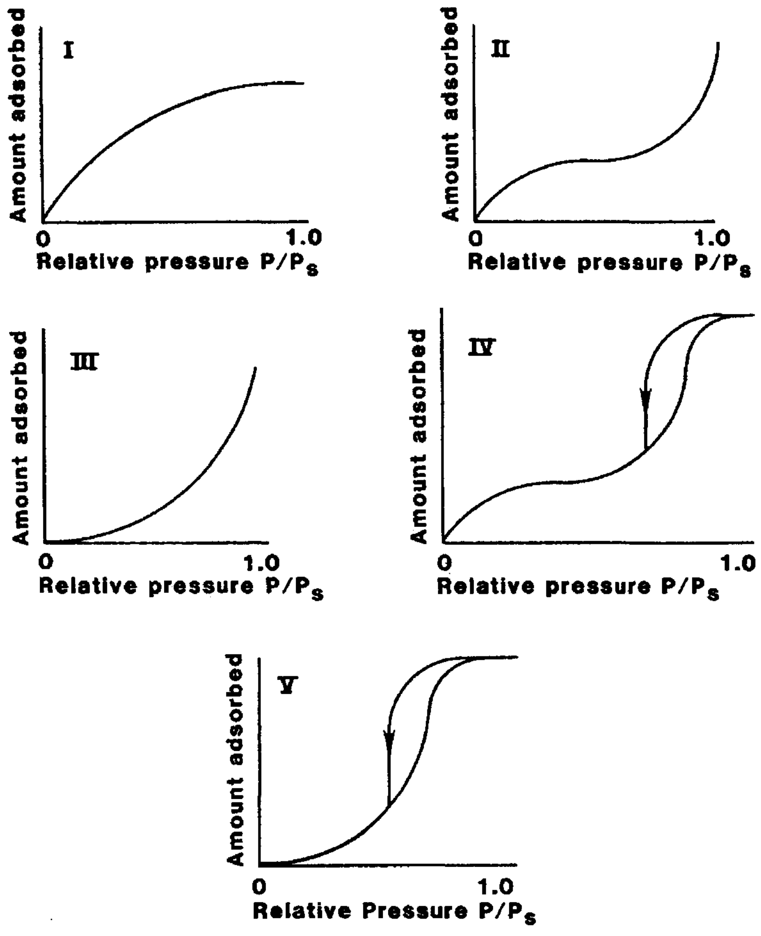


Figure 2.2 The five types of adsorption isotherm in the classification of Brunauer, Deming, Deming and Teller, showing amount adsorbed vs. final concentration in the fluid. P is gas pressure, P_s is the saturation pressure.

the physical adsorption of gases by nonporous solids. Type IV is from the physical adsorption of gases by mesoporous solids. Type III and V may originate from the adsorption of either polar or nonpolar molecules, provided that the adsorbate-adsorbent force is relatively weak. In this research, VOC adsorption onto ACF may be best described by Type I, while VOC adsorption onto indoor sink materials may be appropriately represented by Type II or Type III, depending on the test material. For example, adsorption of VOCs on surfaces of a stainless steel test chamber may follow a Type II adsorption isotherm; while VOC adsorption onto carpet may follow a Type III adsorption isotherm.

Adsorption Isotherm Equations for Single VOC Adsorption

The Langmuir Isotherm

The most widely used isotherm equation for modeling adsorption equilibrium data is the Langmuir equation (Tsai et al., 1999). The Langmuir isotherm assumes a monolayer of molecules on a homogeneous surface with all adsorption sites mutually independent and identical (i.e. all sites require the same energy to adsorb molecules). At equilibrium, the Langmuir isotherm can be represented by:

$$\frac{q}{q_m} = \frac{KC}{1+KC} \qquad \text{.................................... (2.1)}$$

where: q---the amount in moles adsorbed on 1 kg of adsorbent;

q_m---the maximum monolayer capacity (the adsorption of one molecular layer of the adsorbate on the adsorbent);

K--- an empirical constant; and

C--- the adsorbate equilibrium concentration (mol/m^3).

The Langmuir isotherm can also be written as:

$$C/q = C/q_m + 1/(q_m * K) \quad \text{...} \quad (2.2)$$

Using experimental data to fit the Langmuir isotherm (C/q vs C), the Langmuir constants K and q_m can be obtained. This method will be used in this study to estimate the constant K and the maximum monolayer adsorption capacities, q_m, of ACF for VOCs.

When the Langmuir isotherm is used for indoor air quality, at equilibrium, the Langmuir isotherm can be represented by:

$$K_a C_e(1-\theta) = K_d' \theta \quad \text{...} \quad (2.3)$$

where K_a is the adsorption rate constant, m/h; C_e is the equilibrium concentration of the VOC in the bulk air, mg/m^3, K_d' is a desorption rate constant; and θ is the proportion of the coverage on the available adsorption sites. At very low concentrations where the coverage is << 1, Equation (2.3) can be simplified to a linear form:

$$K_a C_e = K_d' \theta \quad \text{..} \quad (2.4)$$

At equilibrium, because mass per unit area of the sink material, M_e, mg/m^2, is proportional to θ. Equation (2.4) can then be written as:

$$K_a C_e = K_d M_e \quad \text{...} \quad (2.5)$$

where K_d is the desorption rate constant, h^{-1}. Equation (2.5) can be changed into the following form:

$$M_e = K_e \times C_e \quad \text{...................................} \quad (2.6)$$

Here, the equilibrium partitioning coefficient K_e, can be defined as: $K_e = K_a/K_d$. This new form of the Langmuir isotherm means that the adsorption capacity is proportional to the equilibrium concentration. This relationship will be applied for the IAQ model for indoor sink materials in this study.

The Freundlich Isotherm

The Freundlich isotherm equation is an empirical expression and may be derived by assuming a heterogeneous surface with adsorption on each category of sites that obeys the Langmuir equation (Noll et al., 1991). Based on the Freundlich isotherm equation, the adsorption capacity increases infinitely with increasing concentration. In fact, this adsorption isotherm cannot be used to describe the entire range of concentration. The valid concentration range for the Freundlich equation varies according to the adsorbate-adsorbent combination. Most often, the equation is satisfactory for low concentrations (Tsai et al., 1999). The Freundlich equation is commonly represented as:

$$m = kC^n \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(2.7)}$$

where: m ----- The mass of adsorbate adsorbed per unit adsorbent, mg/g

C ----- Concentration in bulk gas phase

K, n --- Empirical constants

The constants k and n in Equation (2.7) can be obtained either by plotting log (C) vs log m (intercept and slope of the linear regression plot) or by fitting the non-linear regression model using the least squares method. Generally, n has a value less than unity (Satterfield, 1991). The Freundlich isotherm equation is useful in cases where the actual identity of the adsorbate is not known (Treybal, 1980). As indicated earlier, a disadvantage of using the Freundlich equation is that it is not useful for the entire range of concentrations. Cal (1995) indicated that the Freundlich isotherm equation has no predictive ability for similar adsorbates. However, with careful examination of the Freundlich constants, some relationships may exist for different adsorbates on the same adsorbent. In Chapter 3, the use of the Freundlich isotherm equation to predict untested VOCs was explored by establishing relationships for the Freundlich constants among different VOCs. A detailed description is presented in the next chapter.

Similarly to Equation (2.5), for ACF, we assume that the adsorption process follows the Freundlich isotherm (non-linear form) while the desorption rate constant is directly proportional to the adsorbed amount of VOCs on the ACF. Thus, one may define:

$$\mathrm{K_a}\, C_e^n = \mathrm{K_d}\, \mathrm{M_e} \quad \text{..............................(2.8)}$$

where $\mathrm{K_a}$ is an adsorption constant. Equations (2.7) and (2.8) could be employed for different adsorption strengths of indoor sink materials. For weak sink materials such as gypsum board, surfaces of furniture, and so on, Equation (2.6) may be suitable for describing the linear relationship. However, for strong sink materials, for example, activated carbon, Equation (2.8) may be better employed to describe the adsorption and desorption processes, that is, the nonlinear adsorption process, and the linear desorption process by assuming that the desorption rate of activated carbon is in the same order of magnitude as those of weak sink materials.

Equation (2.8) may be rewritten as:

$$\mathrm{M_e} = \mathrm{K_e}\, C_e^n \quad \text{..............................(2.9)}$$

Here, an equilibrium partitioning coefficient $\mathrm{K_e}$ is defined as: $\mathrm{K_e} = \mathrm{K_a}/\mathrm{K_d}$. Due to the nonlinear effect of concentration, $\mathrm{K_e}$ and $\mathrm{K_a}$ for ACF have different units from $\mathrm{K_e}$ and $\mathrm{K_a}$

for indoor sink materials. Applications of the two different forms of the equations [Equations (2.6) and (2.9)] will be discussed in Chapter 4.

The Dubinin-Radushkevich (D-R) Isotherm

Based on the theory of volume filling of micropores (TVFM) and the assumption of energetically homogeneous adsorption sites of adsorbents, Dubinin and his coworkers have developed several adsorption equilibrium equations for gaseous adsorbates onto microporous adsorbents (Dubinin, 1989), such as the Dubinin-Astakhov (D-A) Equation, and the Dubinin-Raduskevich (D-R) equation. The D-R equation has been demonstrated successfully in its application for describing adsorption of many individual chemicals onto activated carbon. The D-R equation can be represented as below:

$$\ln W = \ln W_0 - \left(\frac{1}{\beta E_0}\right)^2 A^2 \quad \text{.........................} \quad (2.10)$$

where: W----Volume of the adsorbate adsorbed at temperature T, cm^3/g

W_0---- Total volume of micropores of ACF, cm^3/g

$A = RT \times \ln(P_0/P)$, the maximum differential molar work, needed to transport one mole of the adsorbate from the liquid or gas phase to a surface of an infinitely large amount of the adsorbent, J/mol, P_0, saturation vapor pressure; P, partial pressure of adsorbate at equilibrium

β ---- Affinity coefficient and is the ratio of adsorption potentials of the adsorbate to a reference adsorbate, with respect to benzene

E_0----Characteristic adsorption energy

The value of β has been correlated by several physical properties such as liquid molar volume, molecular parachors, and electronic polarization (Noll, 1991). There are two methods commonly used to calculate β. One is to estimate β with the ratio of the parachor [P] of the adsorbate of interest to the parachor of the reference adsorbate $[P]_0$. Benzene is often used as the reference adsorbate. The parachor is an additive physical property of a substance related to its molar volume. The value of the parachor is determined by the kind and the number of atoms in a molecule as well as their manner of arrangement and binding. Parachor has been correlated with surface tension, density, and molecular weight of the adsorbate, and can be given as (Quayle, 1953):

$$[P] = \gamma^{1/4} \frac{M}{(D-d)} \quad \text{..} \quad (2.11)$$

where D and d are the densities of a liquid and its vapor, respectively. The term γ is the surface tension, and M is the molecular weight of the compound. Another often used method to estimate β is to use the ratio of the electronic polarizations, P_e (cm^3/mol) (Reucroft et al., 1971). The electronic polarization and affinity coefficient are represented as:

$$P_e = \frac{(n_r^2 - 1)M}{(n_r^2 + 2)\rho} \quad \text{..} \quad (2.12)$$

$$\beta = \frac{P_e}{(P_e)_{ref}} \quad \text{...} \quad (2.13)$$

where n_r is the refractive index of the liquid adsorbate, M is the molecular weight of the adsorbate (g/mol), and ρ is the density of the liquid adsorbate (g/cm^3). The two methods of calculating β do not generate significant differences for the tested VOCs in this study. Thus, Equation (2.12) and (2.13) were used to obtain β values for VOCs of interest.

Dubinin suggested a correlation among the slit-shaped micropore half-width, x_0, a structure factor, k, and adsorption energy, E_0, the relationship is given as below:

$$k = x_0 E_0 \quad \text{...} \quad (2.14)$$

Using Equation (2.14), Equation (2.10) can be rewritten as:

$$W = W_0 \exp\left[-\left(\frac{Ax_0}{\beta k}\right)^2\right] \quad \text{.............................} \quad (2.15)$$

or

$$W = W_0 \exp\left(-m x_0^2 A^2\right) \quad \text{.............................} \quad (2.16)$$

where

$$m = \left(\frac{1}{\beta k}\right)^2 \quad \text{.......................................} \quad (2.17)$$

By using benzene adsorption on microporous activated carbons, Dubinin (1985) suggested a value of 12.0 ±1.4 kJ-nm/mol for k. Once the micropore volume and slit pore half-width of the test activated carbon are obtained through characterizing a reference adsorbate such as benzene, the D-R equations (2.15) or (2.16) can be used to predict adsorption isotherms for other untested adsorbates by changing β, actual vapor pressure and saturation vapor pressure of the compound of interest. An attempt of using D-R equation predictive capacity was made by Cal et al. (1994). It showed varied accuracies for different pore sizes of activated carbon.

Adsorption Prediction for Binary Mixtures

Experimental data on the adsorption of vapor mixtures onto activated carbon are limited, since it is difficult to obtain data for complete breakthrough curves for different concentrations of VOCs in each vapor mixture/adsorbent system (Vahdat et al., 1994). Indoor air represents an extreme example of multi-component adsorption, because several hundred organic compounds may be present simultaneously. A method that can predict the adsorption performance of adsorbents in the presence of VOC mixtures based on performances of individual components will reduce the need to collect experimental data for the VOC mixtures. Several methods were proposed by Bering et al., Grant and Manes, Myers and Prausnitz, respectively (Bering et al., 1972; Grant and Manes, 1966; Myers and Prausnitz, 1965). In this study, only Ideal Adsorbed Solution Theory (IAST) proposed by Myers and Prausnitz was examined.

In IAST, the following basic equations are used to predict multi-component isotherms from single-component adsorption isotherms:

$$X_1 = \frac{py_1}{p_1^0(\Pi)} \qquad X_2 = \frac{py_2}{p_2^0(\Pi)} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.18)$$

where: X_1, X_2 : mole fractions of components in the adsorbed phase; y_1, y_2: mole fractions of components in the gaseous mixture; p: the total pressure of the test system [Pa]; $p_i^0(\Pi)$: partial vapor pressure of adsorbate in standard state [Pa]; π is the spreading pressure of the adsorbed phase [N/m], which corresponds to the difference in surface tension between a clean surface and an adsorbate covered surface. ψ_i^0 is surface potential of the adsorbent of ith component at standard state [mol/kg], which can be expressed as:

$$\psi_i = \frac{\Pi A}{RT} = \int_0^{p_i^0} \frac{W_i^0}{p} dp \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.19)$$

where: A: the specific surface area [m^2/kg]; R: the gas constant [8.3145 J/(mol-K)]; T: temperature [K]; and W_i^0 : adsorption capacity of single component i, mol/g.

Adsorption capacity of single component W_i^0 can be characterized by the Langmuir isotherm, the Langmuir equation is given by:

$$W_i^0 = \frac{m_i k_i P_i^0}{1 + k_i P_i^0} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \; (2.20)$$

where m_i and k_i are Langmuir constants for component i. In this study, they will be obtained through individual VOC adsorption tests and will be presented in Chapter 5.

At equilibrium, the spreading pressure should be the same for all compounds, for this study, we have:

$$\Pi_1 = \Pi_2 \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \; (2.21)$$

Combining Equation (2.19), (2.20), and (2.21) yields:

$$m_1 \ln(1 + k_i p_1^0) = m_2 \ln(1 + k_2 p_2^0) \quad \dots\dots\dots\dots\dots\dots\dots\dots \; (2.22)$$

Based on mole fraction of binary mixtures in this study, we have:

$$X_1 + X_2 = 1 \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \; (2.23)$$

Substituting Equation (2.18) into Equation (2.23) yields:

$$\frac{py_1}{p_1^0} + \frac{py_2}{p_2^0} = 1 \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \; (2.24)$$

Since *P*, y_1, y_2 and m_1, k_1, m_2, and k_2 are known parameters, combining with Equation (2.22), p_1^0 and p_2^0 will be solved. Thus, X_1 and X_2 will also be obtained. The total amount adsorbed can be calculated from the following equation (Myers and Prausnitz, 1965):

$$\frac{1}{W_t} = \frac{X_1}{W_1^0} + \frac{X_2}{W_2^0} \qquad \text{......................................} \quad (2.25)$$

The adsorption capacity for the individual components can be found from the following expression:

$$W_1 = W_t X_1 \qquad W_2 = W_t X_2 \quad \text{......................................} (2.26)$$

where: W_1^0, W_2^0 = adsorption capacity of single component 1 and 2, respectively (mol/g), W_t = total adsorption capacity (mol/g); W_1, W_2 = adsorption capacities of the components in a binary mixture (mol/g).

Adsorption Capacity and Breakthrough Time Test Methods

Two methods are available for characterizing activated carbon adsorption capacity and breakthrough time related to indoor applications. A single bed test in the form of test canister or adsorption column is a commonly used method for this purpose (VanOsdell et al., 1995; Muller and England, 1995; VanOsdell et al., 1996). This method includes the following steps. Challenge VOCs are pulled through adsorption column with various retention times. Samples are collected by charcoal traps and are then desorbed by a thermal desorber or preconcentrator. The inlet and outlet VOC concentrations are characterized by gas chromatography (GC) equipped with flame ionization detector (FID). Adsorption column is maintained in a temperature controlled water bath to test the adsorption efficiency of activated carbon at various temperatures. The contaminant sources can be generated by permeation tubing devices or by gas cylinders.

A Cahn gravimetric balance has also been frequently used for measuring the total mass adsorbed by activated carbon (Cal et al., 1996; Fuerman et al., 1991; Graham et al., 1990; Ramanathan et al., 1988). This device has a capability of weighing up to 100 g with an accuracy of 0.5 μg. The test specimen is placed in one side of the balance. After being challenged by VOCs, the test specimen gains and the balance continuously records the total weight until the adsorption equilibrium has been reached. In this way, the adsorbed amount of the test species is determined. Methods for generating contaminant sources and characterzing VOC concentration are the same as mentioned above.

Existing Data for Adsorption Capacity and Breakthrough Time

Although activated carbon in a granular form (GAC) has been proven to be an efficient adsorbent in industrial scenarios for decades (Hines et al., 1993), its application in indoor environments remains limited (VanOsdell, 1994, 1995, 1996; Muller, 1995; Liu, 1995; Graham, 1990; Ramanathan, 1988). This is due to limited research about its application in the passive mode (no contaminated air drawn through adsorbent) at higher concentrations (above subppm) or the active mode (air drawn through adsorbent) at low concentrations (at subppm). Low VOC concentrations are generated indoors from dry materials such as particle board, gypsum board, or any off-gassing materials with very low emission rates. For activated carbon application in this scenario, adsorption of indoor VOCs onto GAC has recently been addressed by some literature as shown in Table 2.1, Henschel (1998) reviewed usage of GAC and indicated that there still is insufficient data on activated carbon applications for removal of indoor VOCs.

Two important characteristics of activated carbon adsorption for its indoor applications are not clear. First, the life span of activated carbon for VOC adsorption in indoor environments remains controversial. Liu (1990) and Weschler (1992) suggested that the life spans of GAC adsorption devices range from a few months to several years based on anecdotal field experience and extrapolations from laboratory studies. Liu (1991) also predicted that GAC had a removal efficiency of 80% with a contact time of 0.06 second at the challenge concentration of 100 ppb after 4000 hours based on the prediction of a mathematical model. In contrast, Graham (1990) reported that the activated carbon breakthrough time for benzene at 287 ppb was 450 hours. Foster (1992) reported ACF breakthrough times for adsorption of benzene and acetone individually at concentrations of approximate10 ppm are around 100 hours. Ramanathan (1988) predicted much shorter life spans which suggests that GAC may not be suitable for indoor VOC removal.

Second, the adsorption capacity of activated carbon in indoor concentrations appears to also be inconclusive. Foster (1992) reported that adsorption capacities of different types of ACF vary from 0.5% to 20 wt% of GAC for benzene and acetone individually at concentrations of approximate 10 ppm which is not a typical concentration of indoor VOCs. Graham (1990) reported adsorption capacities for benzene several orders of magnitude higher (in the range of 4-15 wt% of GAC for the concentration range of 0.28-3.2 ppm) than those of Ramanathan's results (in the range of 0.001-0.006% wt% for the concentration range of 0.1-0.17 ppm). Thus, the adsorption capacity of GAC or ACF needs to be more accurately determined in indoor environments.

In addition, mathematical modeling of ACF in indoor application is not well addressed although some modeling attempts for ACFs were reported (Lordgooei, 2001; Mangun, 1999). While modeling to predict granular activated carbon adsorption capacity and breakthrough time in industrial applications has been documented (Tien, 1994; Ruthven, 1984), most of those mathematical models may not be able to provide a practical direction on predicting activated carbon adsorption properties for engineers due to difficulty of obtaining parameters for the equations and complexity in their application. If extrapolation from activated carbon adsorption at high concentrations of industrial scenarios to low concentrations of indoor situations were possible, a great deal of effort would then be saved by predicting activated carbon adsorption properties for indoor applications. Information on breakthrough time is particularly important for indoor application of activated carbon. Only by knowing this, can a suitable replacement schedule be made. Nelson and Harder (1976) proposed the following equation to extrapolate breakthrough time between concentration levels:

$$\frac{t_{b,low\ conc.}}{t_{b,high\ conc.}} = \left(\frac{low\ concentration}{high\ concentration}\right)^{0.67} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(2.27)}$$

The Equation (2.27) was proposed for respirators for VOCs at industrial environments. Its applicability for VOCs at indoor levels needs to be examined in this study. As to predicting adsorption capacity for activated carbon, the Langmuir equation, the Freundlich equation, and the D-R equation will be examined in this research.

Table 2.1. Selected Data on Adsorption Capacity and Breakthrough Time for GAC from Literature

VOC	Test species	Challenge concentration	Adsorption temperature	Retention time	Adsorption capacity	Breakthrough time (10%)	Test method	Reference
		ppm	^{0}C	S	mg/g	hr		
Benzene	Coconut GAC	0.287	24	N/A	12.3	450*	TGA	Graham, 1990
Benzene	Coconut GAC	0.862	24	N/A	28.3	275*	TGA	Graham, 1990
Benzene	Coconut GAC	3.218	24	N/A	49.5	400*	TGA	Graham, 1990
Acetaldehyde	Coal GAC	0.119	N/A	N/A	0.0155	N/A	TGA	Ramanathan, 1988
Acetaldehyde	Coal GAC	0.153	N/A	N/A	0.044	N/A	TGA	Ramanathan, 1988
Benzene	Coal GAC	0.101	N/A	N/A	0.0097	N/A	TGA	Ramanathan, 1988
Benzene	Coal GAC	0.119	N/A	N/A	0.0498	N/A	TGA	Ramanathan, 1988
Benzene	Coal GAC	0.176	N/A	N/A	0.0569	N/A	TGA	Ramanathan, 1988
1,1,1-trichloroethane	Coal GAC	0.115	N/A	N/A	0.0153	N/A	TGA	Ramanathan, 1988
1,1,1-trichloroethane	Coal GAC	0.183	N/A	N/A	0.0374	N/A	TGA	Ramanathan, 1988
1,1-dichloroethane	Coconut GAC	0.1	25	0.11	0.4	28	Single bed	VanOsdell, 1996
1,1-dichloroethane	Coconut GAC	1.1	25	0.11	3.6	13.3	Single bed	VanOsdell, 1996
1,1-dichloroethane	Coconut GAC	10	25	0.11	13	6.3	Single bed	VanOsdell, 1996
1,1-dichloroethane	Coconut GAC	116	25	0.11	57	3.1	Single bed	VanOsdell, 1996
1,1-dichloroethane	Coconut GAC	1100	25	0.11	120	0.55	Single bed	VanOsdell, 1996
Decane	Coconut GAC	0.665	25	0.11	150	628	Single bed	VanOsdell, 1996

Note: * 100% breakthrough time

Table 2.1. Selected Data on Adsorption Capacity and Breakthrough Time for GAC from Literature (cont'd)

VOC	Test species	Challenge concentration	Adsorption temperature	Retention time	Adsorption capacity	Breakthrough time (10%)	Test method	Reference
		ppm	^{0}C	S	mg/g	hr		
Decane	Coconut GAC	7.6	25	0.11	160	77	Single bed	VanOsdell, 1996
Toluene	Coconut GAC	0.44	25	0.11	66	625	Single bed	VanOsdell, 1996
Toluene	Coconut GAC	1.07	25	0.11	92	344	Single bed	VanOsdell, 1996
Toluene	Coconut GAC	9.18	25	0.11	162	72	Single bed	VanOsdell, 1996
Toluene	Coconut GAC	9.67	25	0.11	165	66	Single bed	VanOsdell, 1996
Toluene	Coconut GAC	71.7	25	0.11	188	11.9	Single bed	VanOsdell, 1996
Toluene	Coconut GAC	72.7	25	0.11	180	11.8	Single bed	VanOsdell, 1996
Hexane	Coconut GAC	0.4	25	0.11	32	376	Single bed	VanOsdell, 1996
Hexane	Coconut GAC	2.3	25	0.11	60	123	Single bed	VanOsdell, 1996
Hexane	Coconut GAC	10.8	25	0.11	100	37.9	Single bed	VanOsdell, 1996
Hexane	Coconut GAC	107	25	0.11	110	4.3	Single bed	VanOsdell, 1996
Methylethylketone	Coconut GAC	0.39	25	0.11	18	261	Single bed	VanOsdell, 1996
Methylethylketone	Coconut GAC	2.3	25	0.11	35	86	Single bed	VanOsdell, 1996
Methylethylketone	Coconut GAC	5	25	0.11	47	45.2	Single bed	VanOsdell, 1996
Methylethylketone	Coconut GAC	34.3	25	0.11	82	9.7	Single bed	VanOsdell, 1996
Methylethylketone	Coconut GAC	37.4	25	0.11	73	9.2	Single bed	VanOsdell, 1996

Activated Carbon for Removal of Indoor VOCs in the Passive Mode

High VOC concentrations are often encountered indoors with newly applied paint, wet materials, spills of chemicals, leaks, and household cleaning. The dominant mechanism is evaporation. When ventilation or other means are not available to reduce local evaporative emissions such as from waxing, cooking, spills, etc., passive adsorption may provide a feasible and cost-effective way to reduce the exposure. However, the effectiveness of activated carbon in indoor passive adsorption is unclear since little literature has been found.

The phenomenon of adsorption of VOCs onto indoor surface materials is called a “sink effect” in the field of indoor air. Meininghaus (2000) suggested that while sink effects due to adsorption of indoor surface materials such as carpet, curtains, and wall coverings will lower peak concentrations, the subsequent emission or desorption will prolong the presence of compounds indoors. Thus, the secondary emission may worsen the indoor air quality and contribute to the uncertainty of VOC levels. The strength of the sink effect of an indoor material can be decribed by sorptive kinetics such as the adsorption constant K_a, desorption constant K_d, and equilibrium partitioning coefficient K_e, as introduced in a previous section of this chapter. Some selected adsorption and desorption constants are presented in Table 2.2. It is interesting to note that even apples can act as a sink reservior for indoor VOCs. Basically, a sink effect is ubiquitous, with the strength of the sink effect depending on the properties of the material and the VOC. In order to compare sink strength of sorptive materials, it is better to make the comparison based on the results from the same laboratory. Inter-laboratory comparison

Table 2.2 Selected Sorption Data on Indoor Materials from Literature

Materials	VOCs	Adsorption Constant Ka (m/h)	Desorption Constant Kd (h-1)	Equilibrium constant Ke (m)	Reference
Carpet	Tetracholoethylene	0.11	0.13	0.84	Tichenor et al. 1991
Wallboard	Tetracholoethylene	0.22	1.6	0.14	Tichenor et al. 1991
Ceiling tile	Tetracholoethylene	0.09	0.54	0.16	Tichenor et al. 1991
Pillow	Ethylbenzene	0.07	0.08	0.95	Tichenor et al. 1991
Carpet	Toluene	0.11	0.56	0.22	Won et al. 2000
Carpet	*o*- dichlorobenzene	0.52	0.25	2.1	Won et al. 2000
Painted dryall	Benzaldehyde	0.04	0.015	2.733	Zhang et al. 2003
Painted dryall	Dodecane	0.038	0.005	7.713	Zhang et al. 2003
Ceiling tile	Ethylbenzene	0.057	1.594	0.036	Zhang et al. 2003
Ceiling tile	Undecane	0.301	0.178	1.697	Zhang et al. 2003
Carpet	1,4-dichlorobenzene	0.577	10.05	0.057	Zhang et al. 2003
Carpet	Dodecane	0.573	55.63	0.01	Zhang et al. 2003
Nylon carpet	Toluene	0.251	0.408	0.615	Jorgensen et al. 2000
Nylon carpet	α-pinene	0.287	0.172	1.668	Jorgensen et al. 2000
Carpet	Toluene	0.00123	0.0415	N/A	Bouhamra and Elkilani, 1999
Curtain	Toluene	0.00097	0.0359	N/A	Bouhamra and Elkilani, 1999
Carpet	Toluene	0.00000162	0.336	0.000528	Elkilani et al. 2003
Carpet	1,2-Dichlorobenzene	0.00000118	0.104	0.000121	Elkilani et al. 2003
Carpet	1,1,1-trichloroethane	0.00000139	0.123	0.000116	Elkilani et al. 2003
Gypsum board	Toluene	0.21	1.7	0.12	Won et al. 2001
Gypsum board	Ethylbenzene	0.21	0.87	0.27	Won et al. 2001
Apple	Ethylbenzene	0.07	0.72	0.1	Won et al. 2001
Apple	1,2,4-trichlorobenzene	4.8	3.8	1.3	Won et al. 2001

of adsorption constants is difficult, and sometimes is impossible, because even for the same brand name of test material, the component and texture of the material may be different, and test method and/or parameter determination method may also be different. For example, as shown in Table 2.2, for the combination of carpet and toluene, results on K_a, K_d and K_e from Won et al. (2000) and Elkinali et al (2003) are significantly different. Therefore, in order to evaluate the effectiveness of ACF sink strength for removal of VOCs, comparison of the sink strength of ACF and indoor sink materials needs to be investigated in this study. Thus, characterization of sorptive kinetics of ACFs and indoor surface materials needs to be performed in this study.

Indoor Air Quality Models

Indoor air quality models were used for determining sorptive kinetics or parameters and predicting concentration profile in indoor environments. There are many models reported recently. The linear Langmuir IAQ model developed by Tichenor (1991) was one of the most commonly used models due to its simplicity and effectiveness of estimating parameters. The model may be represented as:

$$V\frac{dC}{dt} = R(t) - NVC - K_a CVL + K_d MVL \quad \text{.................................} (2.28)$$

$$\frac{dM}{dt} = K_a C - K_d M \quad \text{...} (2.29)$$

where: C: concentration, mg/m^3;

t: time, h;

R(t): emission rata of source, mg/h;

V: chamber volume, m^3;

N: air change rate, h^{-1};

K_a: adsorption rate, m/h;

L: the loading factor, defined as the ratio of sink area to chamber volume, m^{-1};

K_d: desorption rate, h^{-1};

M: mass per unit area in sink, mg/m^2.

Tichenor (1991) indicated that the Langmuir model may apply only to relatively flat, smooth surfaces (eg., ceiling tile, wall-board), but may be inappropriate for more complex surfaces (e.g., carpet and upholstery). As such, by assuming all sink surfaces behaved according to a Langmuir adsorption process and a non-Langmuir desorption process, Tichnor (1991) revised the previous IAQ model as:

$$V\frac{dC}{dt} = R(t) - NVC - K_a CVL + K_d M^n VL \quad \text{..(2.28')}$$

$$\frac{dM}{dt} = K_a C - K_d M^n \quad \text{..(2.29')}$$

where n is a constant that accounts for nonlinearitiy in the desorption process (dimensionless). Tichenor et al. (1991) obtained a good fit for the sink behavior of ethylbenzene on carpet when a n value of 1.5 was used. However, Tichenor et al. (1991) pointed out that the theoretical basis for Equations (2.28') and (2.29') is weak. Usually, n is assumed to equal unity.

There are some other models such as the two-sink model (Colombo et al., 1993), the diffusion model (Zhang, 2003), and the sink-diffusion hybrid model (Jørgensen, 2000), numerical model (Yang et al., 2001), boundary layer diffusion model (Axley, 1991), and so on.

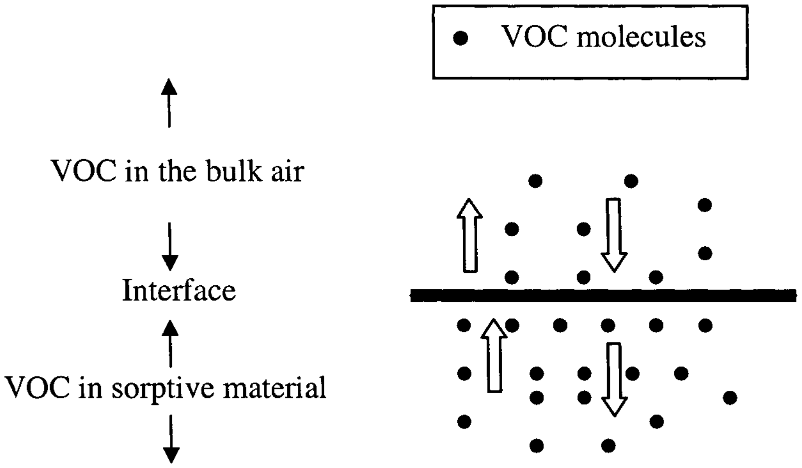


Figure 2.3 The Schematic of the Sorption Process

Figure 2.3 shows that VOCs in the air needs to transfer three regions in order to be adsorbed on the surface of a sorptive material (Yang et al., 2001). First, VOCs are transferred from the bulk air to the air-material interface due to a concentration gradient. VOCs are then adsorbed or desorbed dynamically at the interface. When VOCs are adsorbed on the surface of a material, VOCs are changed into liquid phase and adsorption energy is released, and when VOCs are desorbed into the bulk air, VOCs are changed back to gaseous phase and acquire energy. Finally, for a permeable material, the VOCs at the air-material interface can diffuse into the interior of the material. Different models were developed based on different assumptions, which only take into account the dominate mechanism since models are always simplified and idealized and not all factors can be considered in their development. Some researchers regard the sorption process as the dominant mechanism, with the adsorption and desorption processes occur on the surfaces of the material simultaneously. The linear Langmuir model considers only the fast surface sorption process. Other researchers view the sorption rate as mainly determined by the relatively slow diffusion process within the material on which the diffusion or numerical models are based. The two-sink model and the sink-diffusion hybrid model take into account the relatively slow in-materials diffusion process as well as the fast surface sorption process. A detailed comparison of different models was made by Zhang et al. (2002). In this study, for particle board or gypsum board, diffusion may be the major mechanism for determining the sorption rate, while for most of the materials, e.g. cotton, polyester, activated carbon fiber, or even carpet (due to its roughness and porous nature), the mechanism for the sorption rate may be dominated by surface sorption. Moreover, due to the strong sink effects of ACF, whether ACF follows the linear Langmuir isotherm during both adsorption process and desorption process was never examined before. Thus, the sorption only with the Langmuir model will be evaluated in this study.

Note that the Langmuir adsorption isotherm may be reduced to Henry's law at very low concentration of VOCs indoors. However, the linear relationship may only apply to flat materials as indicated by Tichenor (1991). For ACF, the adsorption isotherm may not be able to be reduced to the linear form; in other words, the amount adsorbed might not be proportional to the VOC concentration at equilibrium. Thus, the linear Tichenor IAQ model may not be applicable to ACF. Whether the linear Langmuir IAQ model is suitable or not for indoor sorptive materials also needs to be examined.

References

Axley, J. W., Adsorption modeling for building contaminant dispersal analysis, Indoor Air, 2, 147-171, 1991.

Being, B. P., Sperpinskii, V. V. and Surinova, S. I., Acad. Sci. USSR Bull.,Div.Chem. Sci., (2):381, 1972

Cal, M. P., Larson, S. M., Rood, M. J., Experimental and modeled resulted describing the adsorption of acetone and benzene onto activated carbon fibers, Environmental Progress, 13 (1), 26-30, 1994

Cal, M. P., Characterization of gas phase adsorption capacity of untreated and chemically treated activated carbon cloths, PhD Thesis, UIUC, IL, 1995.

Cal, M. P., Rood, M. J., and Larson, S. M., Removal of VOCs from humidified gas streams using activated carbon cloth, Gas. Sep. Purif., 10 (2):117-121, 1996.

Chuang, C. L., Chiang, P.C., and Chang, E. E., Modeling VOCs adsorption onto activated carbon, Chemosphere 53:17-27, 2003.

Colombo, A., Bortoli, M. D., Knoppel, H., Pecchio, E. and Vissers, H., Adsorption of selected volatile organic compounds on a carpet, a wall coating, and a gypsum board in a test chamber, Indoor Air, 3: 276-282, 1993.

Dubinin, M. M., Fundamentals of the theory of adsorption in micropores of carbon adsorbents: characteristics of their adsorption properties and microporous structures, Carbon, 27(3): 457-467, 1989.

Bouhamra, W. and Elkilani, A.S., Development of model for the estimation of indoor volatile organic compounds concentration based on experimental sorption parameters, Environmental Science & Technology, 33(12):2100-2105,1999

Elkilani, A.S., Baker, C. G. J., Al-Shammari, Q. H. and Bouhamra, W. S., Sorption of volatile organic compounds on typical fibers, Environmental International, 29: 575-585, 2003.

Foster, K.L., Fuerman, R. G., Economy, J., Larson, S. M., and Rood, M. J., Adsorption characteristics of trace volatile organic compounds in gas streams onto activated carbon fibers, Chem. Mater., 4: 1068-1073, 1992.

Foster, K.L., The role of micropore size and chemical and chemical nature of the pore surface on the adsorption properties of activated carbon fibers, Doctoral Dissertation, Department of Materials Sciences and Engineering, University of Illinois at Urbana-Champaign, IL, 1993.

Fuerman, R. G., Removal of gaseous organic contaminants from indoor air with activated carbon fibers, 84th Annual Air & Waste Management Association meeting & exhibition, Vancouver, British Columbia, June 16-21, 1991.

Graham, J. and Bayati, M., The use of activated carbon for the removal of trace organics in the control of indoor air quality, Proceedings of Indoor Air '90, Toronto, Canada, 133-138, 1990

Grant, R. J. and Manes, M., Correlation of some gas adsorption data extending to low pressures and supercritical temperatures, Ind. Eng. Chem. Fundam., 3(3):221-224, 1964

Gregg, S. J. and Sing, K. S. W., Adsorption, Surface Area and Porosity, pp 9-19 Academic press, London and New York, 1967

Henschel, D. B., Cost analysis of activated carbon versus photocatalytic oxidation for removing organic compounds from indoor air, Journal of the Air and Waste Management Association, 48: 985-994, October, 1998.

Hines, A. L, Loyalka, S.K., Ghosh, T.K. and Warder, R. C., Indoor Air Quality and Control, 235-236, PTR Prentice Hall, New Jersey, 1993

IUPAC Manual of Symbols and Terminology, Appendix 2, Pt.1, Colloid and Surface Chemistry, Pure Appl. Chem., 31: 578, 1972.

Jørgensen R.B., Dokka T. H. and Bjørseth O., Introduction of a sink-diffusion model to describe the interaction between volatile organic compounds(VOCs) and material surfaces, Indoor Air, 10: 27-38, 2000.

Liu, R., Removal of volatile organic compounds in IAQ concentrations with short carbon bed depths, Proceedings indoor air '90, pp. 177-182. Atlanta: American Society of Heating, Refrigerating and Air-Conditioning Engineers, Inc, 1990.

Liu, R.T., Modeling activated carbon adsobers for the control of volatile organic compounds in indoor air, Far East Conference on Environmental Quality, 1991, Hong Kong, Nov.,5-5, ASHRAE, 1991.

Liu, R.; Filtration and indoor air quality: a practical approach, ASHRAE Journal, February, 18-23, 1995

Lordgooei, M., Rood, M. J. and Rostam-Abadi, M., Modeling effective diffusity of volatile organic compounds in activated carbon fiber, Environmental Science and Technology, 35:613-619, 2001.

Mangun, C. L., Braatz, R. D., Economy, J., and Hall, A. J., Fixed bed adsorption of acetone and ammonia onto oxidized activated carbon fibers, Ind. Eng. Chem. Res., 38: 3499-3504, 1999.

Meininghaus, R., Diffusion and adsorption of volatile organic compounds in building materials-impact on indoor air quality, Environmental Science & Technology, 34: 3101-3108, 2000.

Muller, C. O. and England, W. G. Achieving your indoor air quality goals: which filtration system works best? ASHRAE Journal, February, 24-32, 1995

Myers, A. L. and Prausnitz, J. M., Thermodynamics of mixed-gas adsorption, AIChE Journal, 11(1):121-127, 1965.

Nelson, G. O. and Harder, C. A., Respirator cartridge efficiency studies: VI. Effect of concentration, American Industrial Hygiene Association Journal, 37: 205-216, 1976.

Noll, K. E., Gounaries, V., and Hou, W. S., Adsorption Technology for Air and Water Pollution Control, Lewis, Chelsea, MI, 1991

Quayle, O. R., The parachors of organic compounds: An interpretation and catalogue, Chem Rev., 53:439-589, 1953

Ramanathan K., Debler, V. L., Kosusko, M., and Sparks L.E., Evaluation of control strategies for volatile organic compounds I indoor air, Environmental Progress, 7(4): 230-235, 1988

Reucroft, P. J., Simpson, W. H., and Jonas, L.A., Sorption properties of activated carbon, Journal of Physical Chemistry, 75(23):3526-3531, 1971.

Ruthven M. D. Principles of Adsorption and Desorption Processes, New York: Wiley, 1984.

Satterfield, C. N., Heterogenous Catalysis in Industrial Practice, 2nd edition, Academic press, New York, 1991.

Tichenor, B. A., Guo, Z., Dunn, J.E., Sparks, L.E. and Mason, M. A., The interaction of vapour phase organic compounds with indoor sinks, Indoor Air, 1: 23-35, 1991.

Tien, C., Adsorption Calculations and Modeling, Butterworth Heinemann, Washington, 1994.

Treybal, R. E., Mass-Transfer Operations, 3rd ed., McGraw-Hill, New York, 581-582, 1980.

Tsai, W., Chang, C., Ho, C., and Chen, L., Adsorption properties and breakthrough model of 1,1-dichloro-1-fluoroethane on activated carbons, Journal of Hazardous Materials, B69: 53-66, 1999.

Vahdat, N., Swearengen, P. M., and Johnson, J. S., Adsorption prediction of binary mixtures on adsorbents used in respirators cartridges and air-sampling monitors, American Industrial Hygiene Association Journal, 55(10): 909-917, 1994

VanOsdell, D. W., Evaluation of test methods for determining the effectiveness and capability of gas-phase air filtration equipment for indoor air applications-phase I: literature review and test recommendations, ASHRAE transactions: Research, 100: 511-523, 1994.

VanOsdell, D. W. and Sparks, L. E., Carbon Adsorption for indoor air cleaning, ASHRAE Journal, February, 34-40, 1995

VanOsdell, D. W., Owen, M. K., and Jaffe, L. B., VOC removal at low contamination concentrations using granular activated carbon, Journal of the Air and Waste Management Association, 46: 883-890, September, 1996

Weschler, C.J., Shields, H. C., and Naik, D. V., An evaluation of activated carbon filters for the control of ozone, sulfur dioxide, and selected volatile organic compounds, environments for people: IAQ92: October 119-21, San Francisco USA, 1992.

Won, D., Corsi, R. L., and Rynes, M., New indoor carpet as an adsorptive reservoir for volatile organic compounds, Environmental Science & Technology, 34(19):4193-4198, 2000

Won, D., Corsi, R. L. and Rynes, M., Sorptive interactions between VOCs and indoor materials, Indoor Air, 11: 246-256, 2001.

Yang, X., and Chen, Q., A coupled airflow and source/sink model for simulated indoor VOC exposures, Indoor Air, 11: 257-269, 2001.

Zhang, J.S., Zhang, J.S., Chen, Q.Y., and Yang, X., A critical review on studies of volatile organic compound (VOC) sorption by building materials, ASHRAE Transactions: Research, 108(1):162-174, 2002.

Zhang, J.S., Zhang, J.S., and Chen, Q.Y., Effects of environmental conditions on the sorption of VOCS on building materials—part II: model evaluation, ASHRAE Transactions: Research, 2003

CHAPTER III

CHARACTERIZATION AND MODELING OF ACTIVATED CARBON FIBER ADSORPTION ON INDOOR VOLATILE ORGANIC COMPOUNDS IN THE PASSIVE MODE

Abstract

A series of adsorption experiments with acetone, toluene and limonene vapor and three species of activated carbon fibers (ACFs) were conducted in a stainless steel test chamber. The test species of ACFs were placed on the floor of the test chamber. The source of VOCs was from evaporation of chemicals in a Petri dish. When equilibrium had been reached, adsorption capacities were determined for each species of ACF and for each VOC by gas chromatography (GC) using a flame ionization detector (FID). It was found that the Langmuir, Freundlich, and Dubinin-Redushkevich adsorption equations were well fitted by the measured adsorption data. The values of the parameters for each VOC were determined for the three species of ACFs. Through examining the relationship of chemical properties and the Freundlich constants, empirical models were established and used to predict adsorption capacity for untested VOCs. Modeled results agreed reasonably well with experimental results for both methyl ethyl ketone and

trichloroethylene. These results indicate that ACF shows potential as an adsorbent for removing indoor VOCs in the passive mode.

Introduction

VOCs are present in indoor environments. The concentration and the number of VOCs detected in indoor air are usually higher than in outdoor air. The total VOC concentration in indoor air is typically ten times higher than outdoors (Yu and Crump, 1998). The concentration of VOCs emitted from new buildings or renovated older buildings using building materials can be as high as 1410 mg/m^3 (Molhave, 1982). More than 900 VOCs have been identified in indoor air, of which approximately two dozen are confirmed human carcinogens (e.g. benzene) or suspected human carcinogens (e.g. formaldehyde); a US EPA review suggests that there could be increased risk of cancer to residents from those VOC carcinogens (US EPA, 1989). Exposure to indoor VOCS may more often cause symptoms of sick building syndrome such as fatigue, headache, drowsiness, weakness, blurred vision, skin irritation, irritation of the eyes and respiratory tract, and cardiac arrhythmias (Maroni et al., 1995). The need to remove indoor VOCs is mainly driven by their adverse health effects and disagreeable odors.

While activated carbon has been used as an adsorbent to remove contaminants in gas streams and drinking water for decades, its application for removal of indoor VOCs is not well documented. Nearly all literature (Cal et al., 1994; Cal, 1995; Foster et al., 1992; Liu, 1993; Liu, 1995; Muller and England, 1995; Ramanathan et al., 1988; VanOsdell and Sparks, 1995; Wenger et al., 1996) examined its indoor applications based on the active test mode in which the challenge air is drawn through the activated carbon test specimen. However, when ventilation or active adsorption by activated carbon is not available or impossible, placing an activated carbon fiber cloth on the floor or hanging it as a curtain may provide a convenient method of removing indoor VOCs emitted from freshly applied coating materials, waxing, painting, and other human activities such as cleaning. The effectiveness of ACF for removal of indoor VOC in this manner remains unclear since no literature has been found for removing VOCs using activated carbon in the passive mode. The test conditions performed in this study and in the literature differ in two ways: 1) no air was drawn through the ACF test species in this study, while tests from the literature were all conducted with air drawn through; and 2) the VOC source of this study was from evaporation of VOC from a Petri dish, which more effectively simulates the indoor VOCs generated from waxing, cleaning, painting, etc.; in other words, the challenge VOC concentration was not constant, instead, increasing initially, then peaking, followed by a gradual decrease. For its application in the passive mode, ACF offers greater ease of use than granular activated carbon (GAC) because ACF is manufactured in the form of cloth. Moreover, ACF typically has greater adsorption rates and adsorption capacities over conventional GAC (Cal et al., 1994; Foster et al., 1992). Three species of ACF were used in this research.

The purpose of this study was to evaluate ACF as an adsorbent for removal of indoor VOCs in the passive mode. Specifically, the adsorption isotherms for three species of ACF were characterized with each test VOC (acetone, toluene and limonene) at concentrations ranging from 3 to 1200 mg/m^3 in the passive mode. The experimental results were then fitted to existing adsorption isotherm equations. Based on the adsorption isotherms generated by those adsorption isotherm equations, one is able to obtain VOC adsorption capacities for untested concentrations. More importantly, statistical models were established by analyzing the relationships between VOC physico-chemical properties and the constants of the Freundlich adsorption isotherms of VOCs. The models were validated by using trichloroethylene and methyl ethyl ketone, which were not involved in the establishment of the models. The knowledge gained through this study provides a better understanding in developing ACF as an alternative control strategy in removal of indoor VOCs and offers a novel way of predicting VOC adsorption capacity on ACF.

Materials and Methods

Test Facility

As shown schematically in Figure 3.1., the experiments were carried out in a 3 mm thick, 316 stainless steel rectangular test chamber with a volume of 51.7 L (nominal dimension 50 cm × 40 cm × 25 cm). The chamber was maintained at a temperature of 23±1 ^{0}C. All components were made of 316 stainless steel, and included the inlet and outlet of the chamber, which were connected to a 20 cm long manifold tubing with 28 holes (hole diameter, 2 mm). A small computer case fan was installed at the center of chamber cover. Both the fan and the two manifolds were used for complete mixing. Figure 3.2 shows how the test chamber is configured and Figure 3.3 details the display of the small holes on the manifolds. A Teflon® gasket was used as the chamber flange. The difference between inlet flow rate and outlet flow rate was less than 3% measured

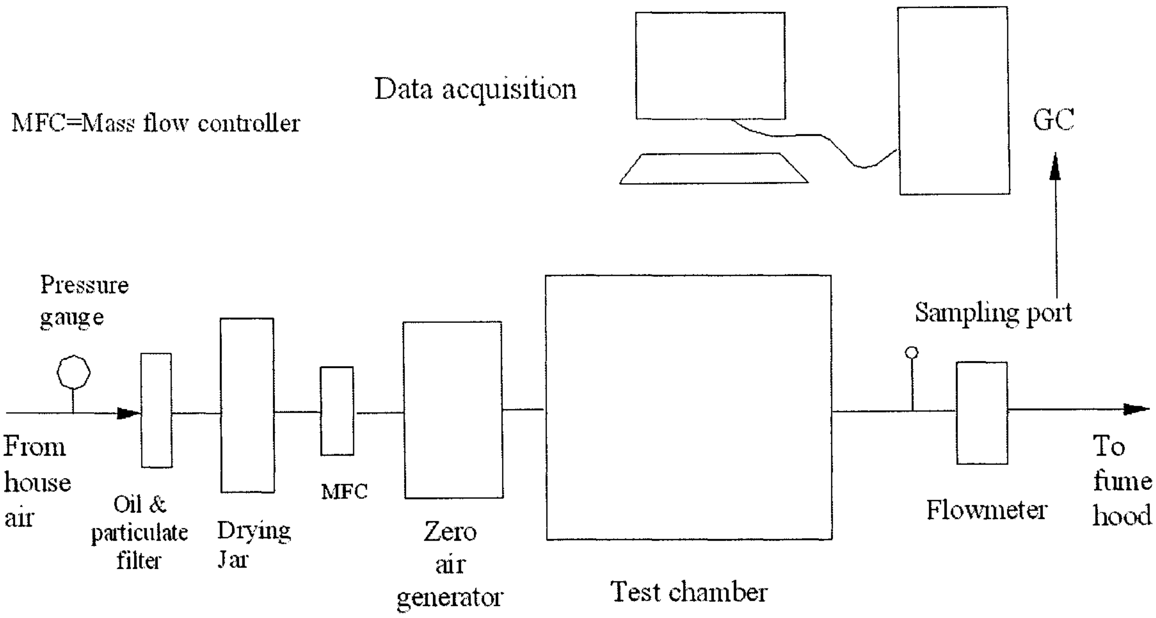


Figure 3.1 The Experimental Test System

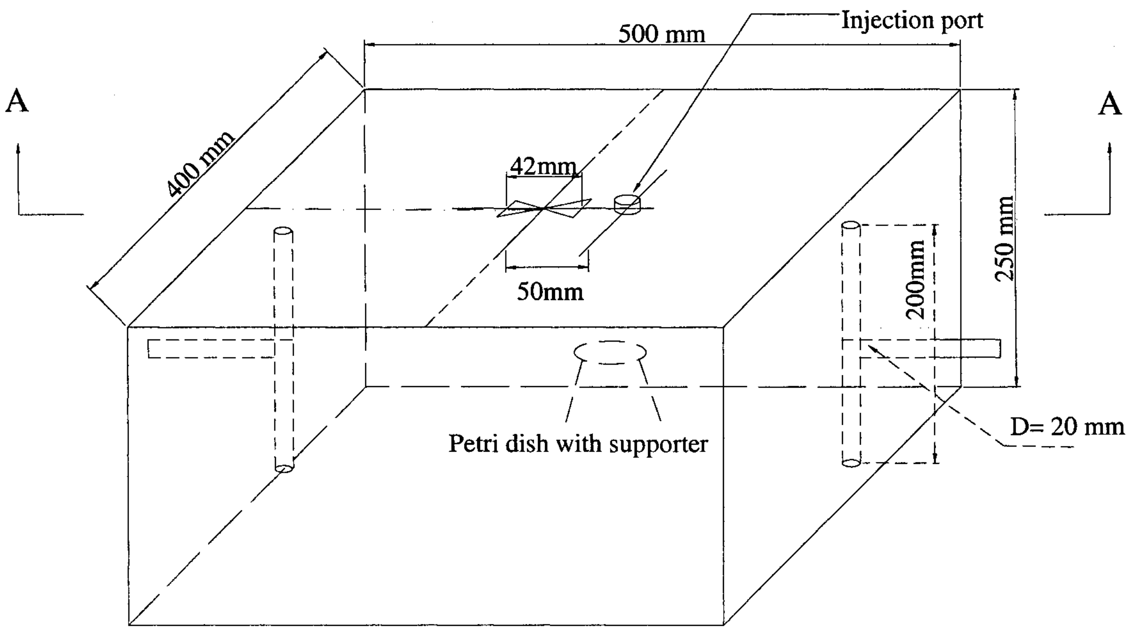
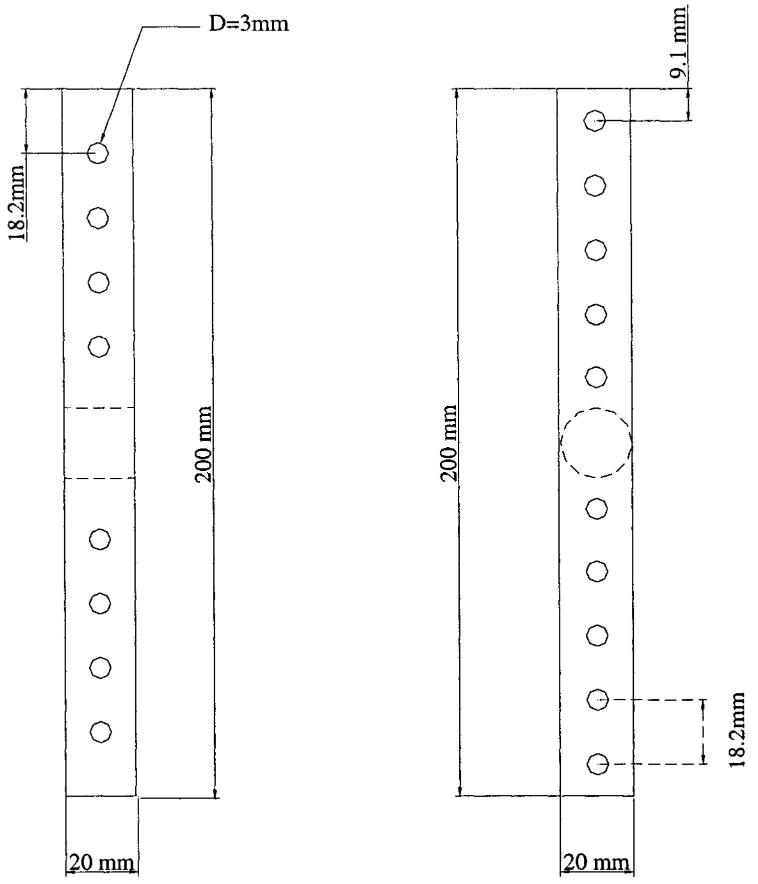


Figure 3.2 The Design of the Test Chamber



Manifold front and back view

Manifold sides' view

Figure 3.3 The Design of the Inlet and Outlet Manifolds

by two DryCal (BIOS, Model DC 1HC Rev. E) primary flow rate calibrators, indicating sufficient air tightness of the test chamber.

An oil filter and a particulate filter were used to pre-clean house air, followed by a Drierite gas drying jar to remove moisture and a zero air generator (Matheson Model MGEN-ZRC 3500, 3.5 L/min) to remove any excess organic compounds, resulting in purified air containing less than 0.1 ppm hydrocarbons measured as methane entering the test chamber. All the gas supplying and sampling lines were made of Tygon® tubing.

Before each experiment, the test chamber was purged for more than 12 hours with purified air to remove moisture and trace organics in the chamber. The air tightness of the chamber was examined through air flow checking.

Test Specimens

ACFs were from American Kynol Inc.. Three species of ACFs were tested: ACF-10, ACF-15, and ACF-20. The nominal specific surface areas for ACF-10, ACF-15, and ACF-20 are 1000 m^2/g, 1500 m^2/g and 2000 m^2/g, respectively. The actual surface area and pore size distribution of each ACF species were not characterized due to unavailability of instrumentation. The same species (but not necessarily in the same batch) were characterized in literature (Foster et al., 1992; Cal et al., 1994; Cal, 1995; Mangun et al., 1999; Mangun et al., 2001) for their surface area and pore size distribution. The reported surface areas are 730-760 m^2/g for ACF-10, 730-1670 m^2/g for ACF-15, 1330-1610 m^2/g for ACF-20. The literature indicates that the breadth of pore size distribution increases with increasingly activated (higher surface area) ACF. The reported average pore width for ACF is from 0.81 to 1.34 nm. ACFs were dried in a desiccator for more than one month before test.

Test Chemicals

Target chemicals were chosen base on their physico-chemical property differences in boiling point, polarity, vapor pressure and affinity coefficient (affinity between VOC and the surface of the adsorbent). Acetone, toluene and limonene, which represent ketones, aromatics and terpenes, respectively, are often found in many paints, adhesives, coatings and other indoor application products such as air-freshers, and cleaning agents. As such, these VOCs are often detected in indoor environments. Methyl ethyl ketone and trichloroethylene, two often observed indoor VOCS, were selected for validation of empirical equations established in this study. Together with acetaldehyde and benzene, whose adsorption properties on ACF were investigated in the literature (Cal, 1995), the physico-chemical properties of those VOCs are listed in Table 3.1. Affinity coefficient, β, was determined using Equations (2.12) and (2.13) with raw data from the literature (CRC Handbook of Chemistry and Physics, 1973).

Test Procedures

Before each experiment, the test chamber was soaked and cleaned with 2% Extran® (an alkaline agent) and then rinsed with distilled water several times. The test chamber was wiped by laboratory tissue and then dried with a hair-dryer. After a test specimen was placed on the floor of the test chamber, the test chamber was then purged for 12 hours with two air changes per hour to remove any moisture and trace organics left in the chamber. Before each test, the background concentration of the chamber was determined by a 30 minutes sampling and found to be negligible for this project. When each run began, no pre-cleaned air was supplied to the test chamber. Thus, the experiments were performed without air changes in the test chamber. Each chemical with a known volume was introduced as a liquid by syringe into a Teflon® Petri dish in the center of the test chamber. At that time, the fan was started for complete mixing. In this study, each piece of 2×2 cm^2 of each species of ACF was well distributed on four equally divided sections of the floor of the test chamber as shown in Figure 3.4. The purpose of this spacing was to eliminate error due to non-uniform concentration distribution in the test chamber, if any; in other words, if there is some difference in adsorption capacity among each species, this is most likely due to the difference in adsorption properties of each ACF species itself, and not likely due to concentration variation in the test chamber. After the chemical concentration in the chamber leveled off, which means that the sorption equilibrium had been reached, ACF specimens were then removed from the test chamber and desorbed with CS_2 in 4 ml vials for 30 minutes and then analyzed by GC. Desorption efficiency of this method was validated by injecting an equivalent known amount of test VOC into desorption vials with the same amount of ACF as in each run in the experiments. The calibration curves are presented in Appendix I. Judged on the slopes of the calibration curves, the desorption efficiency from ACF is chemical dependent in this study. Only one test specimen was tested each time. Surface adsorption of the empty chamber was also determined by subtracting the VOC in the chamber air and in the ACF from the amount injected in the test chamber.

Sampling and Analysis of Chemicals

Air samples were collected through a sampling port on tubing connected to a manifold of the test chamber by SKC activated coconut charcoal tubes with 400/200 mg charcoal in the front/rear sections. A sampling pump (SKC Pocket Pump® model 210-1002) was operated at a flow rate of 70 ml/min for 2 to 10 min. The charcoal tubes were desorbed with CS_2, and then analyzed by a Varian GC Analyzer Model 3900 using with flame ionization detector (FID) and with a CP-Wax 52CB (30 m*0.53 mm, ID, 1μm film) column.

Table 3.1. Physico-chemical Properties of Surrogate Chemicals

Characteristics	Chemical Name						
	Acetaldehyde	Benzene	Limonene	Trichloroethylene	Toluene[a]	Methyl ethyl ketone	Acetone[a]
Formula	CH_3CHO	C_6H_6	$C_{10}H_{16}$	CCl_2CHCl	$C_6H_5CH_3$	$CH_3COCH_2CH_3$	CH_3COCH_3
[b]MW	44.1	78.1	136.24	131.4	92.1	72.1	58.08
[c]P^0	98.6	12.75	2.67	9.87	3.85	12.1	28.6
[d]T_b (°C)	21	80.1	175	87	110.8	79.6	56.2
[e]C_w	Highly miscible	1800.0	1.8	1100.0	526.0	270000.0	1000000.0
[f]*P'*	6.20	3.00	1.60	1.00	2.40	4.50	5.40
[g]Nr	1.33	1.50	1.47	1.48	1.50	1.38	1.36
[h]ρ	0.78	0.88	0.84	1.46	0.87	0.81	0.79
[i]β	0.43	1.00	1.73	0.97	1.18	0.79	0.62
Chem. class	Aldehydes	Aromatic HC	Terpene HC	Halogenated HC	Aromatic HC	Ketone	Ketone

[a] Excerpt from Schwerzenbach, et al, 1993 except polarity, refractive index, liquid density

[b] MW: molecular weight

[c] P^0: vapor pressure at 25°C,kPa

[d] T_b: boiling point (°C)

[e] C_w: water solubility (mg/L)

[f] *P'*: polarity index obtained and estimated from Snyder and Kirkland (1979)

[g] Nr: refractive index from CRC Handbook of chemistry and physics 1973/74 at 20°C

[h] ρ: density of liquid (g/cm^3) from CRC Handbook of Chemistry and Physics at 20^{0}C

[i] β: affinity coefficient

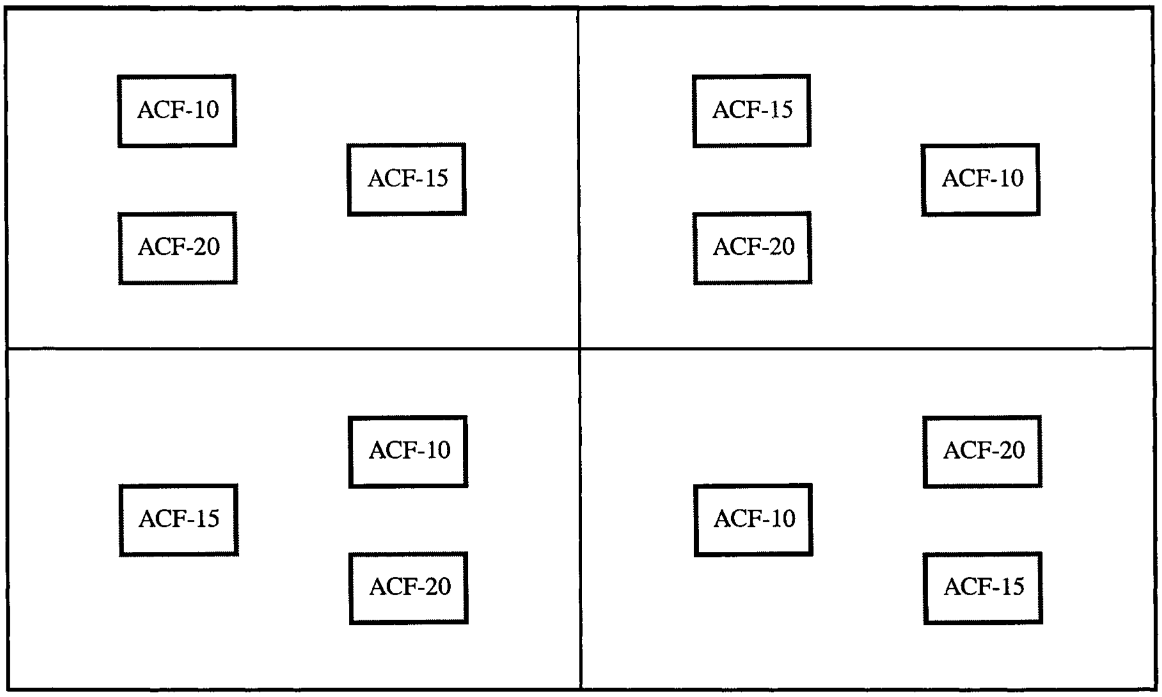


Figure 3.4. The Spacing Layout for Each Species of ACF

Results and Discussion

Characterization of the Adsorption of Volatile Organic Compounds onto ACF

The adsorption capacities for the three tested VOCs were measured in the concentration range of 3 to 1200 mg/m^3. The experimental results are presented in Table 3.2. The adsorption capacities of each species of ACF for all three selected VOCs increased with the increase of chemical vapor equilibrium concentration, exhibiting a type I isotherm by Brunauer's classification. The type I isotherm is observed by physical adsorption of gases onto microporus materials. It can be seen from the experimental results that limonene had a greater adsorption capacity than either toluene or acetone for the three ACF species in the same concentration levels.

This is mainly due to higher boiling point, lower vapor pressure, and more non-polar characteristics of limonene at 23 °C. It suggests that, similar to granular activated carbon, the ACF has a stronger affinity for non-polar adsorbates than polar adsorbates.

Table 3.2. Adsorption Capacities of VOC Adsorbates on ACFs in the Passive Mode

	Concentration mg/m3	ACF-10 mg VOC /g ACF	ACF-15 mg VOC /g ACF	ACF-20 mg VOC /g ACF
Acetone	20.2	25.53	35.61	31.89
	91.03±7.42	46.92±5.28	62.54±7.13	58.27±4.87
	160.85	71.16	86.59	69.85
	413.04±31.67	120.88±13.06	101.27±9.74	103.26±12.55
	868.33	134.25	154.27	137.27
	1190.27	144.21	182.75	152.02
Toluene	3.63	49.23	69.65	71.43
	46.85±5.36	60.35±10.27	103.17±12.58	96.51±10.71
	113.83	117.44	187.64	176.92
	272.67±26.16	170.72±19.88	247.13±21.34	283.23±30.64
	633.56	185.89	336.73	369.55
	959.76±98.83	237.44±31.29	382.67±42.94	427.21±38.52
	1093.52	235.71	390.43	451.74
Limonene	8.05	152.8	260.15	242.28
	138.97±11.28	242.13±22.74	400.76±43.92	446.56±41.37
	457.85	266.84	442.7	505.25
	559.04±47.67	284.13±26.53	461.53±51.82	530.37±60.47
	741.1	286.45	501.6	599.26

Note: Data reported as Mean ± SD are based on three replicates, others are single measurements

As shown in Figure 3.8, ACF-10 with a lower specific surface area had a higher adsorption capacity for acetone than ACF-20 with a higher specific area for concentrations between 100 and 800 mg/m^3. Similarly, ACF-15 had a greater adsorption capacity for toluene and limonene than ACF-20 in the range of 50 to 100 mg/m^3 and 8 to 40 mg/m^3, respectively. The location of crossover point for each species of ACF is dependent on the pore size distribution, the total available pore volume, and the adsorbate physico-chemical properties (Foster, 1992). As the concentration in the gas phase increases, for toluene and limonene, ACF-20 will eventually have a greater adsorption capacity than ACF-15, and ACF-15 will have a greater adsorption capacity than ACF-10, because ACF-20 has a greater micropore volume than ACF-15, and ACF-15 has a greater micropore volume than ACF-10. For acetone, however, due to a weaker affinity with ACF, acetone can not occupy larger micropores with which ACF-20 possesses a larger proportion than ACF-10 and ACF-15. Thus, ACF-20 has less adsorption capacity than ACF-10 and ACF-15. The adsorption capacities for limonene (Figure 3.10) were only measured up to 750mg/m^3, because limonene's evaporation rate is very slow and needs a long time to reach higher concentration levels. The adsorption capacities for limonene on ACFs were more than 150 mg limonene/g ACF even at 8 mg/m^3. However, in contrast to toluene and acetone, limonene adsorption capacities onto ACFs increase slowly with concentration in the range of 10 to 500 mg/m^3. This is probably because limonene has the greatest affinity among the three test chemicals, by which limonene is able to access a wide size range of micropores at very low concentrations, in this case; e.g., at 10 mg/m^3, additional potential from concentration increase plays a minor role in the increase of adsorption capacity since most of micropores were already occupied at low concentrations. As such, a slow increase with concentration was observed for the limonene adsorption isotherm.

Adsorption Modeling with Adsorption Isotherm Equations

The experimental adsorption data for acetone, toluene and limonene were fitted with the Langmuir, Freundlich and Dubinin-Radushkevich equations. The constants for the Langmuir, Freundlich and D-R equations are presented in this section along with their correlation coefficients. All plots of adsorption isotherms of ACFs for each chemical were in the concentration range of between 1 to 1200 mg/m^3, which is of interest in this study.

The Langmuir Isotherm Equation

The Langmuir isotherm assumes a monolayer of molecules on a homogeneous surface with all adsorption sites mutually independent and identical (i.e. all sites require the same energy to adsorb molecules). As shown in Figures 3.3, 3.4, and 3.5, the experimental data appear to fit the Langmuir isotherm equation very well as evidenced by excellent correlation coefficients. A least squares method was used to determine the Langmuir isotherm constants of q_m and K of each species of ACFs for each chemical. The physical meaning of q_m represents the adsorption capacity of

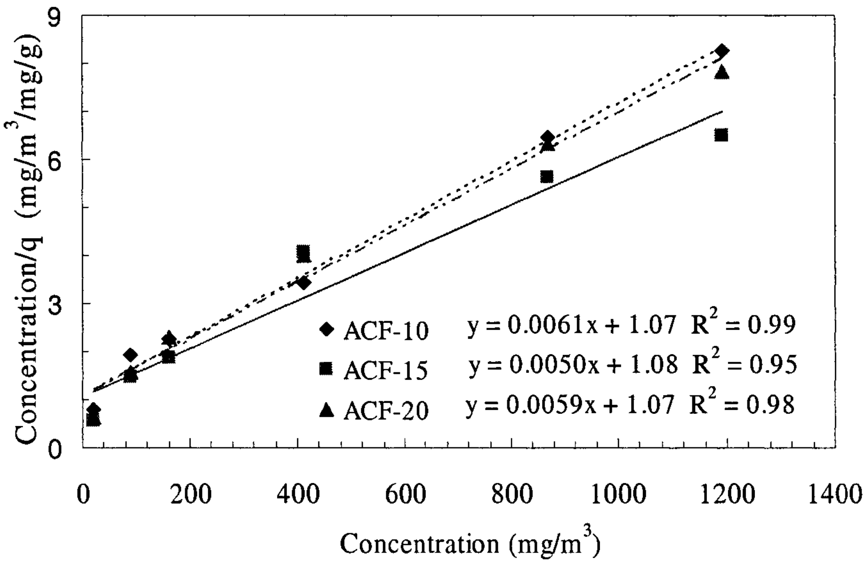


Figure 3.5 Langmuir Adsorption Isotherms for Acetone and ACFs

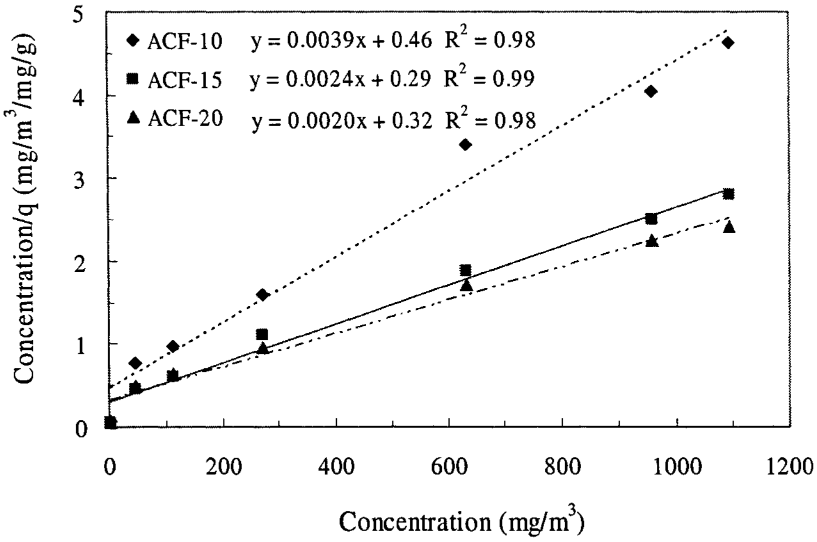


Figure 3.6 Langmuir Adsorption Isotherms for Toluene and ACFs

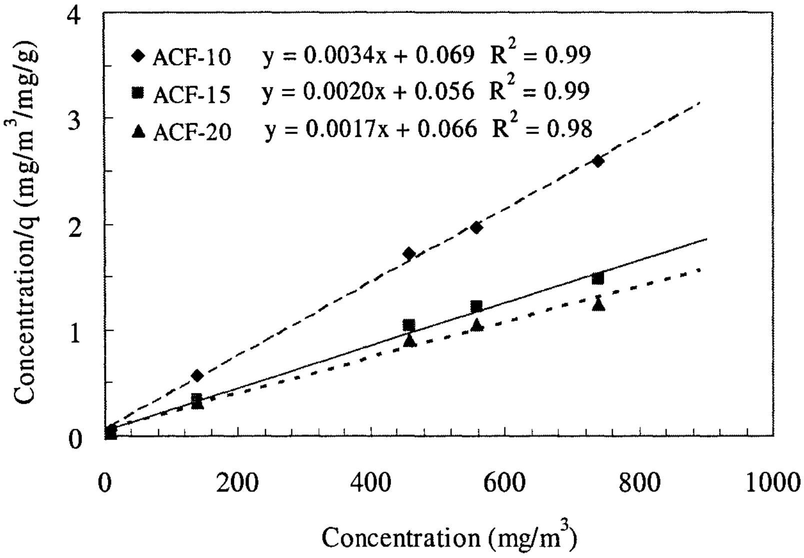


Figure 3.7. Langmuir Adsorption Isotherms for Limonene and ACFs

Table 3.3. Langmuir Parameters for VOC Adsorbates and ACFs

	ACF-10	ACF-15	ACF-20
Acetone			
q_m (mg/g)	163.93	200.00	169.49
k	0.0057	0.0046	0.0055
Correlation Coefficient (R)	1.00	0.98	0.99
Toluene			
q_m (mg/g)	256.41	416.67	500.00
k	0.0085	0.0083	0.0063
Correlation Coefficient (R)	0.99	1.00	0.99
Limonene			
q_m (mg/g)	294.12	500.00	588.24
k	0.049	0.036	0.026
Correlation Coefficient (R)	1.00	1.00	0.99

ACF, assuming that adsorption sites were fully occupied by a monolayer adsorbate. If the amount of the adsorbed chemical on the ACF at a given equilibrium concentration is less than q_m, it would suggest that the adsorption occurs on a monolayer mode. Conversely, if the amount of the adsorbed chemical at a given equilibrium concentration is greater than q_m, it would suggest the adsorption occurs on a multilayer mode or volume filling mode. This information is of importance to indoor VOC adsorption onto ACF and indoor sink materials. Since typical indoor VOCs are at less than 10 mg/m^3 levels, the amount of adsorbed VOC may usually be less than its q_m of an adsorbent, especially for weak adsorbents which have much lower adsorption capacities compared to microporous adsorbents. It can be seen from Table 3.3 that ACF had a greater monolayer adsorption capacity for limonene than toluene, and ACF had a greater capacity for toluene than acetone. This is probably due to the greatest molecular weight of limonene among the three tested VOCs.

Analyzing the data in Table 3.3, one can find that the mole number of limonene q_m is not always greater than those of toluene and acetone q_m. The mole number of molecules that can be adsorbed on the surfaces of an adsorbent is determined by a number of factors,

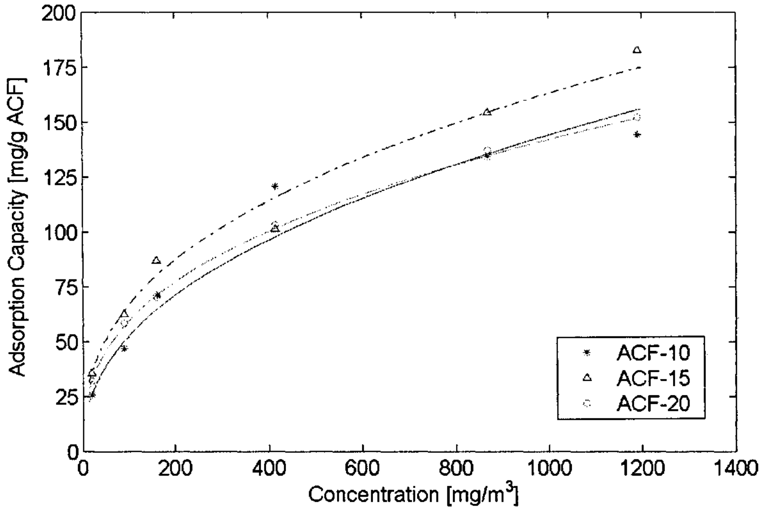


Figure 3.8 Experimental Adsorption Isotherms for Acetone and ACFs Based on the Freundlich Equation

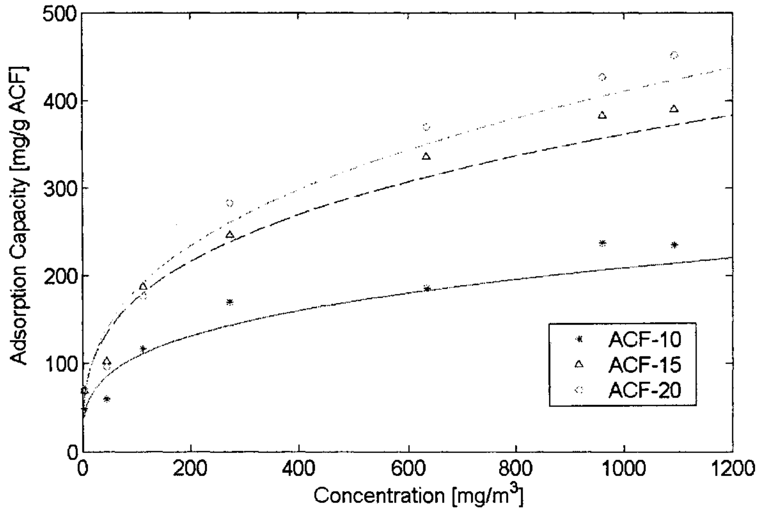


Figure 3.9. Experimental Adsorption Isotherms for Toluene and ACFs Based on the Freundlich Equation

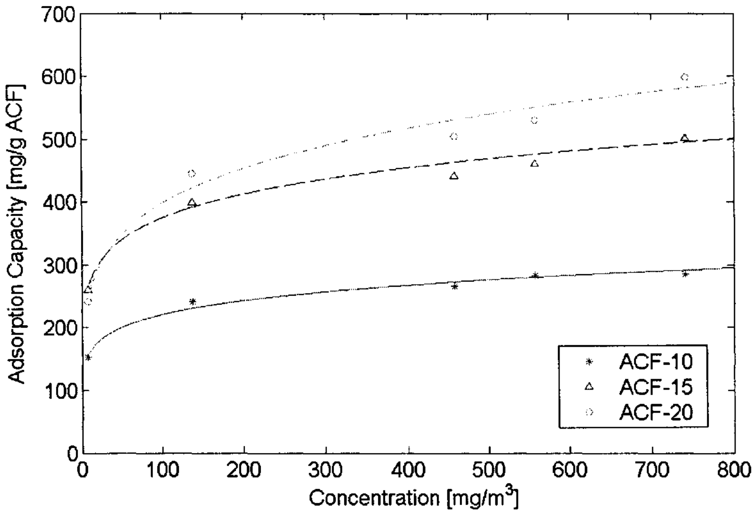


Figure 3.10 Experimental Adsorption Isotherms Limonene and ACFs Based on the Freundlich Equation

such as pore size distribution of microporous adsorbent, affinity of chemical, the size of molecules, chemical composition or surface chemistry of the adsorbent, and so on. It is difficult to quantify the contribution of each factor to the monolayer adsorption capacity without characterizing those factors.

The Freundlich Isotherm Equation

The Freundlich isotherm was used to interpret the adsorption capacities at untested concentration levels, using the experimental adsorption capacity data obtained in this project. Plots of the adsorption isotherms for each of the adsorbates and the three ACF samples are presented in Figures (3.8) through (3.10). The Freundlich parameters for the adsorption of acetone, toluene and limonene are provided in Table 3.4. The use of the Freundlich equation cannot guarantee that adsorption capacities for adsorbate at the high and low end concentrations can be estimated with good accuracy, nor can it provide information about the maximum adsorption capacity for each adsorbate. But it can give a very good estimation within the tested concentration range as stated in this project. For more accurate estimates, use of the Dubinin-Radushkevich equation as described in the following section can serve this purpose.

Table 3.4. Freundlich Parameters for VOC adsorbates and ACFs

	ACF-10	ACF-15	ACF-20
Toluene			
k	28.22	39.65	36.60
n	0.29	0.32	0.35
R^2	0.92	0.96	0.94
Acetone			
k	6.89	11.02	10.28
n	0.44	0.39	0.38
R^2	0.97	0.98	0.99
Limonene			
k	116.05	196.76	165.84
n	0.14	0.14	0.19
R^2	0.99	0.99	0.98

The Dubinin-Radushkevich (DR) Equation

Plots of the adsorption isotherms for each of the adsorbates and the three ACF species are presented in Figures (3.11) through (3.13). The Dubinin-Radushkevich parameters for the adsorption of acetone, toluene and limonene are presented in Table 3.5. As observed from R^2, experimental results fit the DR model very well for all of the three VOC adsorbates examined in this study. Because the DR equation is able to fit an entire type I adsorption isotherm which is applicable for activated carbon adsorption, where the Freundlich isotherm is only accurate over limited concentration ranges, if more accurate estimation is sought, the use of the DR equation is recommended (Cal, 1995). It can be seen from Table 3.5 that the maximum

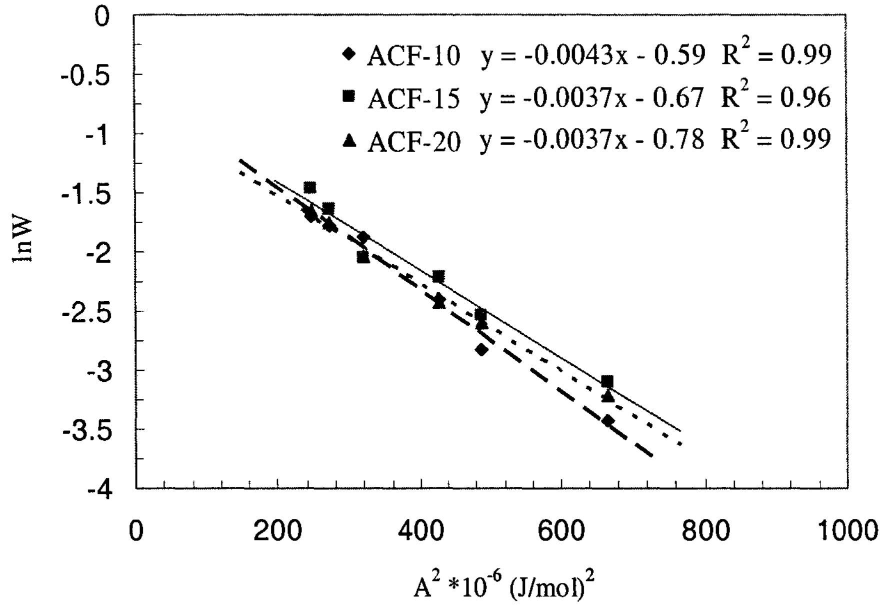


Figure 3.11 Experimental and DR Fitted Adsorption Isotherms for Acetone and ACFs

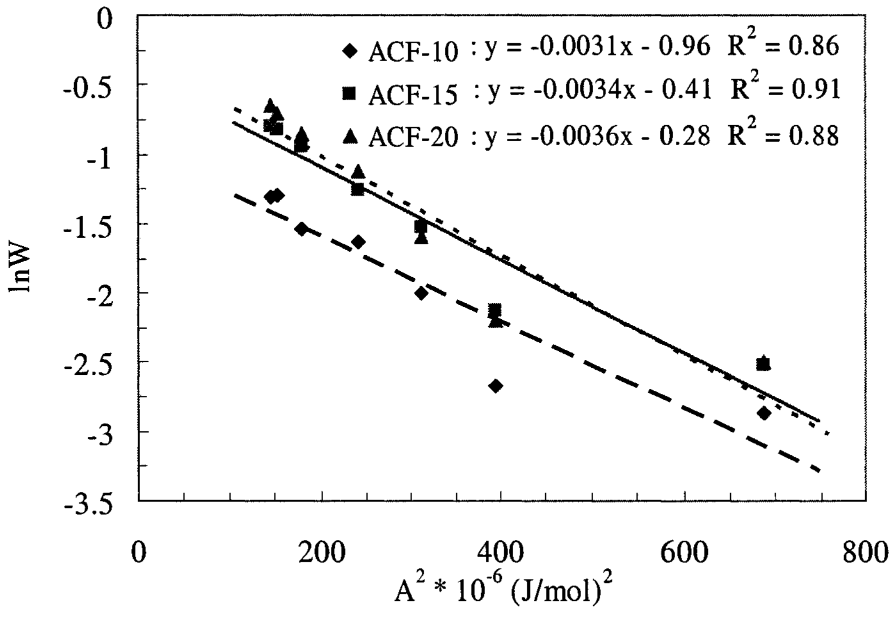


Figure 3.12. Experimental and DR Fitted Adsorption Isotherms for Toluene and ACFs

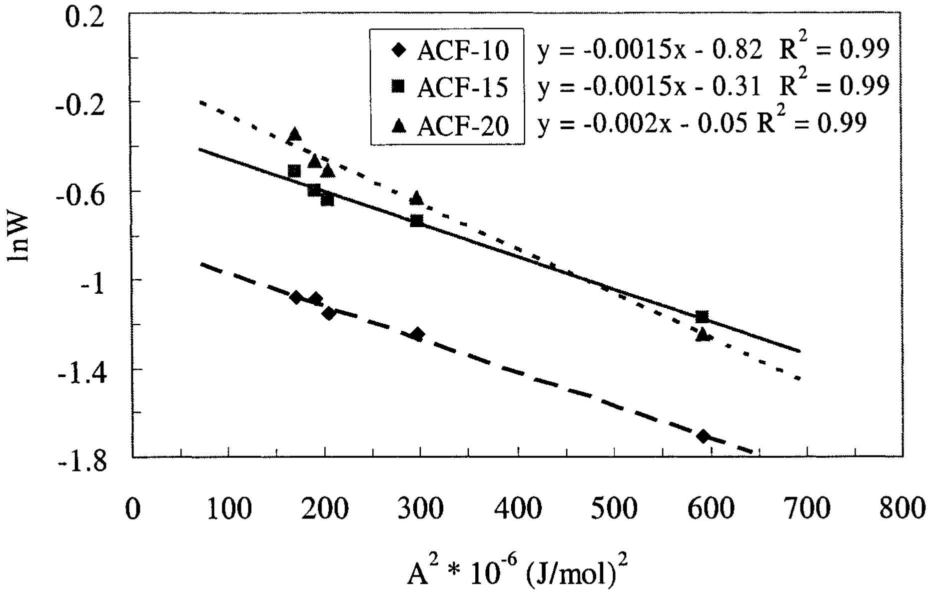


Figure 3.13 Experimental and DR Fitted Adsorption Isotherms for Limonene and ACFs

adsorption capacity (W_0) of ACF, regardless of species, for three tested VOCs, is in the order of acetone < toluene < limonene. Except for acetone, for both toluene and limonene, ACF-20 had a greater adsorption capacity than ACF-15, and ACF-15 had a greater adsorption capacity than ACF-10. When activation creates larger pores with greater surface, the number of smaller pores decreases. Thus, even though ACF-20 had greatest pore volume, due to weak affinity between ACF and acetone, some larger pores cannot be occupied. This probably is the reason why the ACF-20 which has the greatest specific surface area, adsorbed acetone the least. Table 3.5 also presents the adsorption energy (E_0) and the micropore half-width (x_0) obtained by using D-R equation. As indicated in Table 3.5, ACF for acetone had a larger slit-pore half-width and lower adsorption energy than for toluene and limonene. Usually, adsorbates with higher adsorption energy are easier to be adsorbed on the surfaces of adsorbent, and adsorbates with higher adsorption energy tend to displace adsorbates with lower adsorption energy.

Table 3.5. D-R Parameters for VOC Adsorbates and ACFs

	ACF-10	ACF-15	ACF-20
Toluene			
Max adsorbed weight W_0 [mg/g]	329.46	572.22	658.92
Total effective volume V_0 [cm^3/g]	0.38	0.66	0.76
Adsorption energy E_0 [KJ/mol]	15.09	14.41	14.00
Micropore half-width x_0 [nm]	0.80	0.83	0.86
$x_0\beta$ [nm]	0.95	0.99	1.02
R^2	0.86	0.91	0.88
Acetone			
W_0 [mg/g]	424.92	398.12	358.85
V_0 [cm^3/g]	0.54	0.50	0.45
E_0 [KJ/mol]	11.76	12.82	13.18
x_0 [nm]	1.02	0.94	0.91
$x_0\beta$ [nm]	0.63	0.58	0.56
R^2	0.99	0.96	0.99
Limonene			
W_0 [mg/g]	371.71	618.57	800.48
V_0 [cm^3/g]	0.44	0.74	0.95
E_0 [KJ/mol]	14.92	14.92	12.93
x_0 [nm]	0.80	0.80	0.93
$x_0\beta$ [nm]	1.39	1.39	1.61
R^2	0.99	0.99	0.99

Adsorption Capacity Prediction for Untested VOCs Using the Freundlich Parameters

The use of the D-R equation to predict adsorption isotherms of untested VOCs was explored in the literature (Cal, 1994, 1995) by changing the affinity coefficient in the D-R equation. The prediction was in reasonable agreement with experimental data. In contrast to the D-R equation, as indicated in the literature (Cal, 1995), the Freundlich isotherm has no predictive ability with regard to adsorption isotherms for similar adsorbates since no relationships is clearly presented in the constants of the Freundlich equation. However, after carefully examining the Freundlich isotherm parameters for all three adsorbates on ACFs, associations between Freundlich parameters and chemical properties do exist. For example, a linear relationship between lnK and $1/(P'\times VP^{0.5})$ for adsorbates on ACFs was observed as shown in Figure 3.14. A linear relationship between ln(n) and $\beta/P'^{0.5}$ for adsorbates on ACFs was also observed as shown in Figure 3.16. Evidence of these relationships was also observed in similar study in the following literature. After analysis of data from Cal (1995) (he used the term ACC to mean the same as the ACF used for this project) as shown in Table 3.6, it is interesting to see that the same relationships do exist in the active mode with air drawn through the test species as shown in Figures 3.15 and 3.17, which means that the associations not only exist in the passive adsorption mode, but exist in the active adsorption mode. In other words, the analysis from the literature is very supportive to the findings in this study.

The relationships described below indicate that it is possible to relate chemical properties to adsorption capacities at equilibrium for adsorbents. This finding is significant in so much as it suggests the possibility of being able to reasonably predict untested VOC adsorption capacities. However, because the relationships have not explicitly accounted for material properties, it may not be legitimate to extrapolate them to adsorbent specimens that differ significantly from the ACF used in this study. Based on findings of this study, the empirical constants of n and k for the Freundlich isotherm equation for untested chemicals can be estimated by the following equations:

For ACF-10: $$\ln k = 8.12\left(\frac{1}{p'\times VP^{0.5}}\right)+1.64 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(3.1)}$$

For ACF-15: $$\ln k = 8.28\left(\frac{1}{p'\times VP^{0.5}}\right)+2.05 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(3.2)}$$

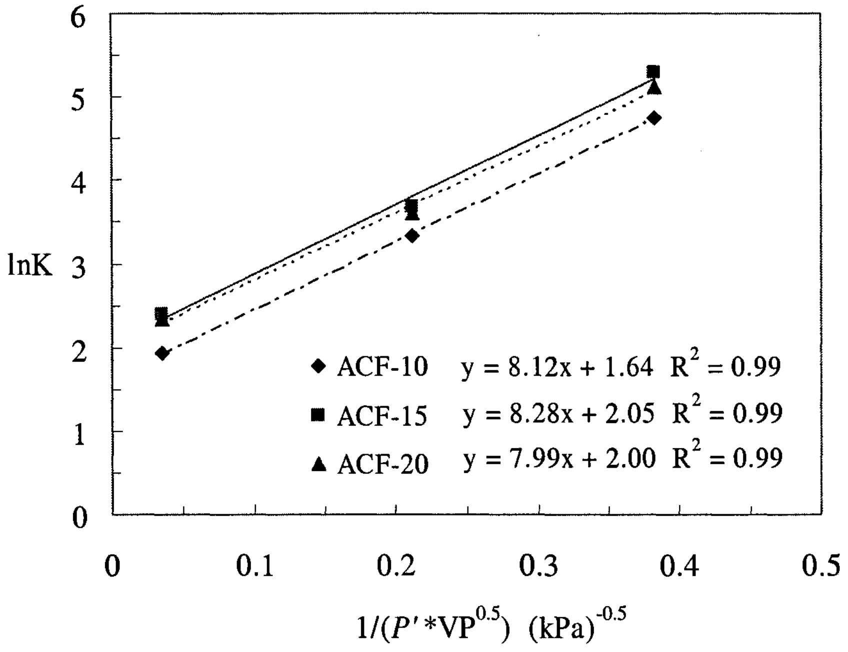


Figure 3.14 The Relationship Between K and Vapor Pressure and Polarity Index

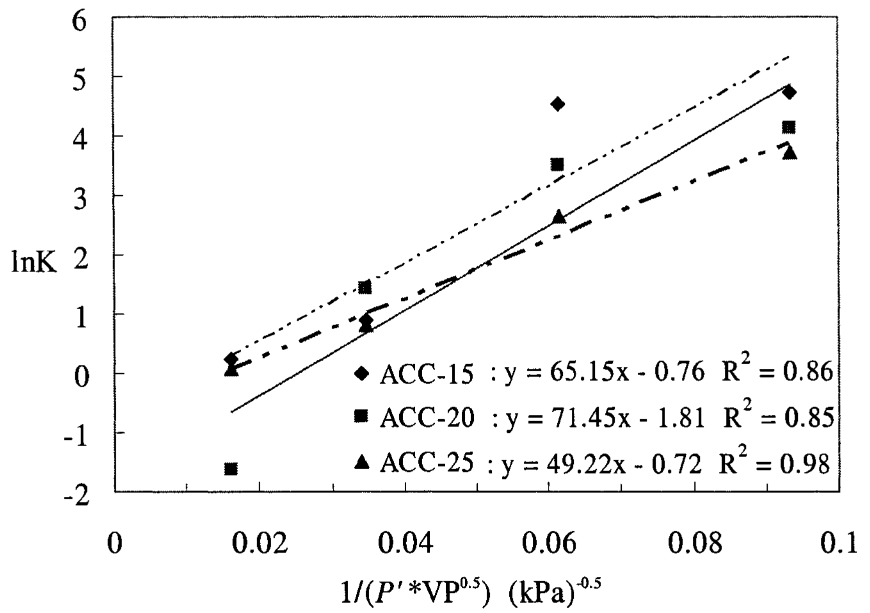


Figure 3.15 The Relationship Between K and Vapor Pressure and Polarity Index (Analyzed from Cal's Results, 1995)

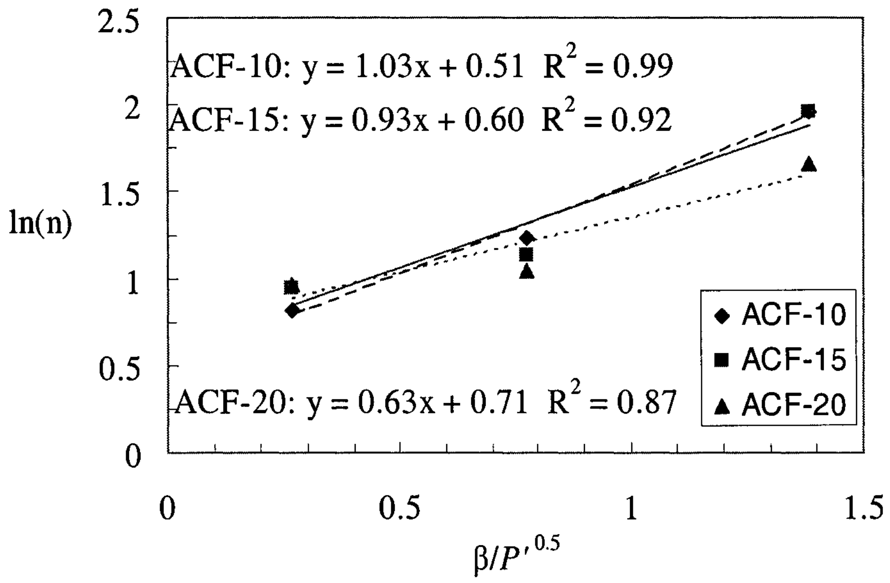


Figure 3.16 The Relationship Between n and β and Polarity Index

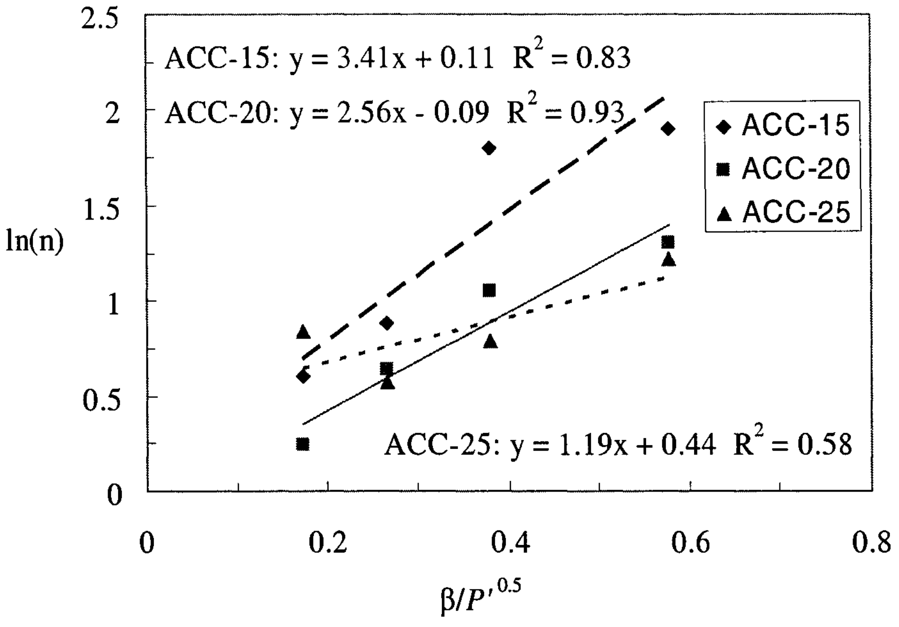


Figure 3.17 The Relationship Between n and β and Polarity Index (Analyzed from Cal's Result, 1995)

Table 3.6. Freundlich Parameters for VOC Adsorbates and ACC (Cal, 1995)

	ACC-15	ACC-20	ACC-25
Acetaldehyde			
k	1.270	0.198	1.080
n	0.546	0.781	0.432
Correlation Coefficient (R)	0.999	0.997	1.000
Acetone			
k	2.420	4.240	2.260
n	0.413	0.529	0.565
Correlation Coefficient (R)	0.995	0.994	0.995
Benzene			
k	112.000	62.300	41.400
n	0.149	0.272	0.294
Correlation Coefficient (R)	0.978	0.995	0.992
MEK			
k	92.600	33.900	14.100
n	0.165	0.350	0.455
Correlation Coefficient (R)	0.966	0.989	1.000

*Note: ACC: Activated Carbon Cloth

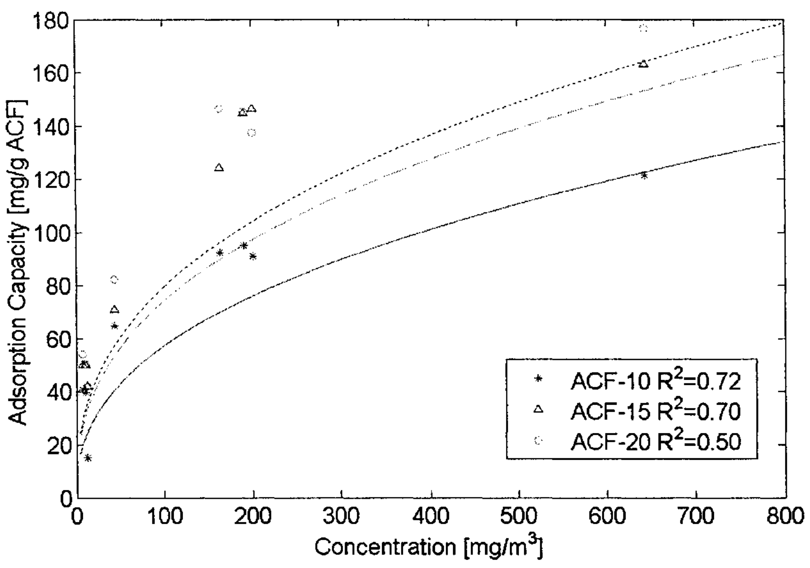


Figure 3.18 Experimental and Modeled Results for MEK

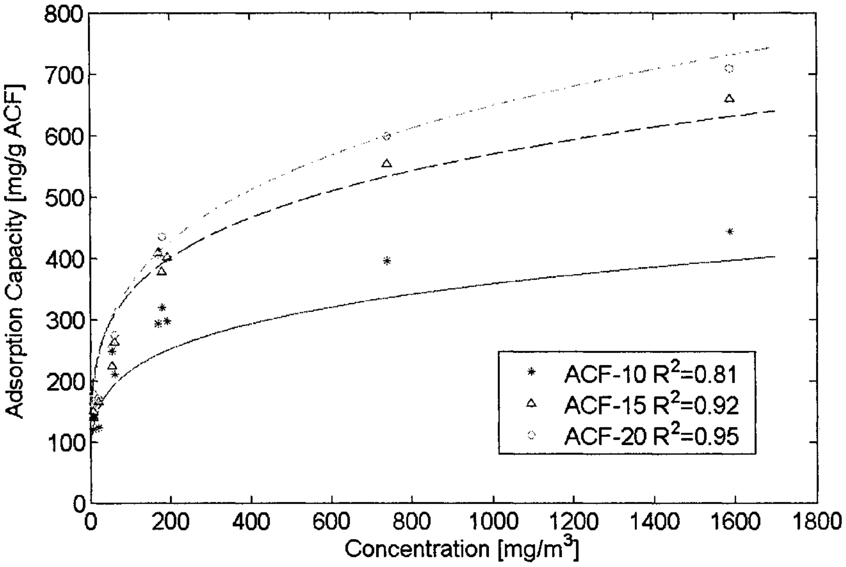


Figure 3.19 Experimental and Modeled Results for TCE

For ACF-20: $$\mathrm{Ink} = 7.99\left(\frac{1}{p'\times VP^{0.5}}\right)+2.00 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.3)$$

For ACF-10: $$\ln(\mathrm{n}) = 1.03\left(\frac{\beta}{p'^{0.5}}\right)+0.51 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.4)$$

For ACF-15: $$\ln(n) = 0.93\left(\frac{\beta}{p'^{0.5}}\right) + 0.60 \quad \text{.........................} \quad (3.5)$$

For ACF-20: $$\ln(n) = 0.63\left(\frac{\beta}{p'^{0.5}}\right) + 0.71 \quad \text{.........................} \quad (3.6)$$

The constants (n, k) of the Freundlich isotherm equation for each species of ACF can be determined by plugging values of polarity index (*P'*), vapor pressure (VP), and affinity coefficient (β) into the Equations 3.1 to 3.1. The chemical properties of trichloroethylene and methyl ethyl ketone are listed in Table 3.1. Based on the available constants of n and k for the Freundlich equation, one can obtain the adsorption isotherms for trichloroethylene and methyl ethyl ketone. The plots with predicted adsorption isotherms and experimental data for methyl methyl ketone and trichloroethylene are presented in Figures 3.18 and 3.19, respectively. As shown in Figure 3.18, the predicted adsorption isotherm underestimated the actual adsorption capacities for MEK for all three species of ACF at the lower concentration range (less than 600 mg/m^3). For concentrations around 600 mg/m^3, the predicted adsorption isotherm tended to agree better with experimental data. The reason for the poor predictability in the tested low concentration range is probably due to uncertainty involved in the determination of the constants of the Freundlich equation, since they were only based on three chemicals. A determination of the constants involving more chemicals may improve the effectiveness of the prediction. For TCE, the predicted adsorption isotherm slightly underestimated the adsorption capacities of ACF-10 only, but for ACF-15 and ACF-20, the predicted adsorption isotherm agreed very well with experimental data. Overall, the empirical models can predict the adsorption isotherms with reasonable accuracy for TCE and for MEK in higher concentrations in this study. They may be applied for predicting other chemical adsorption isotherms with success.

Conclusions

The adsorption of acetone, toluene and limonene, listed as indoor VOC pollutants, on the three species of ACF in the passive mode were investigated. All of the ACF studied showed encouraging uptakes of acetone, toluene and limonene in the passive mode. All these adsorption isotherms obey the Langmuir, Freundlich and Dubinin-Radushkevich isotherm equations as evidenced by convincing correlation coefficients between the fitted and experimental data, indicating the validity of using all three adsorption isotherm equations to model the adsorption isotherms over the concentration range of interest. The statistical models produced from the constants of the Freundlich isotherm equation predicted adsorption isotherms of each species of ACF for methyl ethyl ketone and trichloroethylene with reasonable accuracy. The relationships were also demonstrated in the literature in the same types of ACF. The statistical models may give a better prediction for untested VOCs if more VOCs are tested to reduce the errors involved in the determination of the constants of the statistical models. The excellent adsorption capacities of ACF indicate that the ACF has the potential as an adsorbent to effectively remove volatile organic compounds of sudden surges of concentration caused by spills, leaks, paint, waxing, or cleaning, etc.

References

Cal, M. P., Larson, S. M., Rood, M. J., Experimental and modeled resulted describing the adsorption of acetone and benzene onto activated carbon fibers, Environmental Progress, 13(1): 26-30, 1994

Cal, M. P., Characterization of gas phase adsorption capacity of untreated and chemically treated activated carbon cloths, PhD Thesis, UIUC, IL, 1995.

Federikse, H. P. R. and Lide, D. R., Handbook of Chemistry and Physics, CRC Publisher, 1973.

Foster, K.L., Fuerman, R. G., Economy, J., Larson, S. M., and Rood, M. J., Adsorption characteristics of trace volatile organic compounds in gas streams onto activated carbon fibers, Chem. Mater., 4: 1068-1073, 1992.

Liu, R. T., Use of activated carbon adsorbers in HVAC applications, Proceedings indoor air '93, pp. 209-217. Philadelphia, PA, American society of heating, refrigerating and air-conditioning engineers, Inc, 1993

Liu, R.; Filtration and indoor air quality: a practical approach, ASHRAE Journal, February, 18-23, 1995

Mangun, Charistian L., Richard D. Braatz, James Economy, et al. Fixed bed adsorption of acetone and ammonia onto oxidized activated carbon fibers, Ind. Eng. Chem. Res., 38: 3499-3504, 1999.

Mangun, C. L., DeBarr, J. A. and Economy, J., Adsorption of sulfur dioxide on ammonia-treated activated carbon fibers, Carbon, 39:1689-1696, 2001.

Maroni M., Seifert B., and Lindvall T., Indoor Air Quality: A Comprehensive Reference Book, pp 35, New York, Elsevier Science, 1995

Muller, C. O. and England, W. G. Achieving your indoor air quality goals: which filtration system works best? ASHRAE Journal, February, 24-32, 1995

Ramanathan K., Debler, V. L., Kosusko, M., and Sparks L.E., Evaluation of control strategies for volatile organic compounds I indoor air, Environmental Progress, 7(4): 230-235, 1988

Schwarzenbach, R. P., Gschwend, P. M. and Imboden, D. M., Environmental Organic Chemistry, New York, John Wiley & Sons, 1993.

Snyder, L.R. and Kirkland, J. J., Introduction to modern liquid chromatography, 2nd Edition, 258-260, John Wiley & Sons, Inc., 1979.

US Environmental Protection Agency (EPA). Report to congress on indoor air quality Vol. II. Assessmnet and control of indoor air pollution. Report No. EPA 400/1-89-001C. Washington DC. 1989

VanOsdell, D. W. and Sparks, L. E., Carbon Adsorption for indoor air cleaning, ASHRAE Journal, February, 34-40, 1995

Wenger, K., Lanning, J. A. and Anderson, L. G., Improving indoor air quality: a field assessment of gas phase filtration systems, the 89th Annual Meeting & Exhibition of Air & Waste Management Association, 1996.

Yu, C. and Crump, D., A review of the emission of VOCs from polymeric materials used in buildings, Building Environment, 33(6): 357-374, 1998

CHAPTER IV

EVALUATION OF AN INDOOR AIR QUALITY MODEL AND CHARACTERIZATION OF SORPTIVE KINETICS FOR ACTIVATED CARBON FIBER AND INDOOR SORPTIVE MATERIALS

Abstract

A series of sorption experiments was performed in a test chamber in order to evaluate the effectiveness of ACF for removal of indoor VOCs in the passive mode (i.e. air was not drawn through the test specimens of ACF). Three VOCs, toluene, acetone and limonene were examined in this study, and four indoor sorptive materials, carpet, cotton, polyester and gypsum board, were compared to the ACF. Tested VOC adsorption rates and adsorption capacities on ACF are greater than tested indoor sink materials by a factor of 1 to 3 orders of magnitude in the 10 to 1000 mg/m^3 concentration range and by a factor of 3 to 6 orders of magnitude in the 0.01 to 10 mg/m^3 concentration range, respectively. The experimental data for indoor materials and empty test chamber surfaces was found to be in good agreement in fitting the linear sink model based on the Langmuir adsorption process, while the experimental data for ACF was found to be very good in fitting the non-linear sink model based on the Freundlich adsorption process.

These experimental results on sorption kinetics of ACF in the passive mode appear to be promising for control of indoor VOCs, even considering the potential competition from indoor sorptive materials.

Introduction

Adverse health effects due to indoor VOCs are a concern in the non-industrial environment. High VOC concentrations are often encountered indoors with newly applied paint, wet materials, spills of chemicals, leaks, and household cleaners. In these scenarios, VOC concentrations can be as high as several hundred ppm (Yu et al., 1998) due to evaporation. When ventilation or other means are not available to reduce such local evaporative VOC emissions, passive adsorption by activated carbon may provide a feasible and cost-effective way to reduce the exposure during those activities; moreover, it may significantly reduce exposure due to secondary emissions from indoor sorptive materials such as carpet, cotton/polyester curtain, sofa, gypsum wallboard and so on. Activated carbon in the granular form (GAC) has been proven to be an efficient adsorbent for removing VOCs in the active mode in industrial scenarios for decades; however, much less is known about the effectiveness of activated carbon for removal of indoor VOCs in the passive mode, especially in the presence of indoor sink materials with large geometric areas.

The linear Langmuir indoor air quality (IAQ) model proposed by Tichenor et al. (1991) has been widely used for its simplicity and effectiveness. Tichenor indicated that the Langmuir isotherm applies to relatively flat, smooth surfaces (e.g., ceiling tile, wall-board), but it may be inappropriate for more complex surfaces (e.g., carpet and upholstery) of indoor sink materials. However, as shown in Figures 4.1, 4.2, and 4.3, through measurements of adsorption isotherms for toluene, 1,2-dichlorobenzene and 1,1,1-trichloroethane on polyacrylonitrile carpet fibers over the temperature range of 25

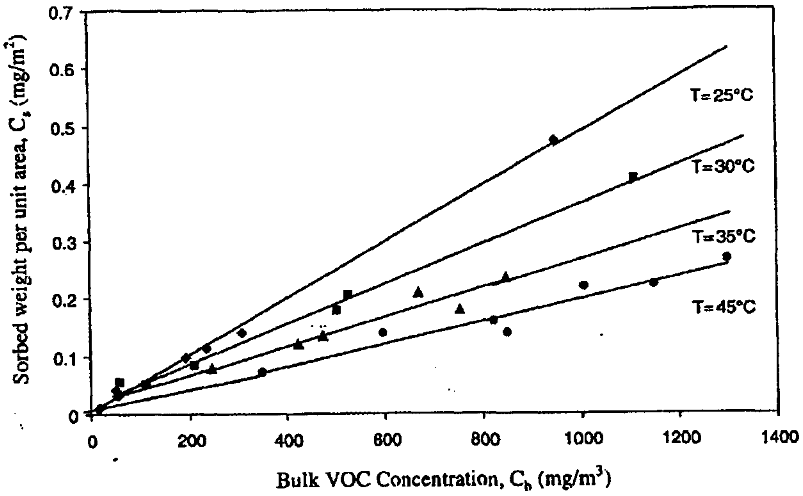


Figure 4.1. Sorbed Weight Per Unit Area Versus VOC Concentration for Toluene on Carpet Fibers at Different Temperatures (Elkilani et al., 2003)

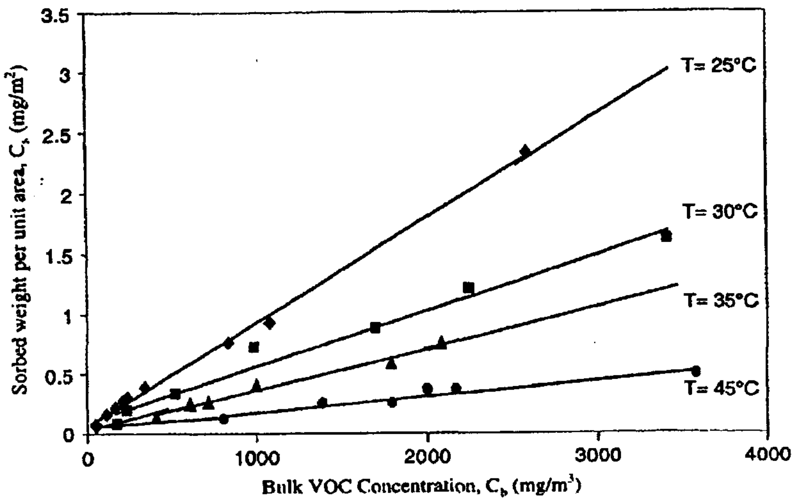


Figure 4.2. Sorbed Weight Per Unit Area Versus VOC Concentration for 1, 2-dichlorobenzene on Carpet Fibers at Different Temperatures (Elkilani et al., 2003)

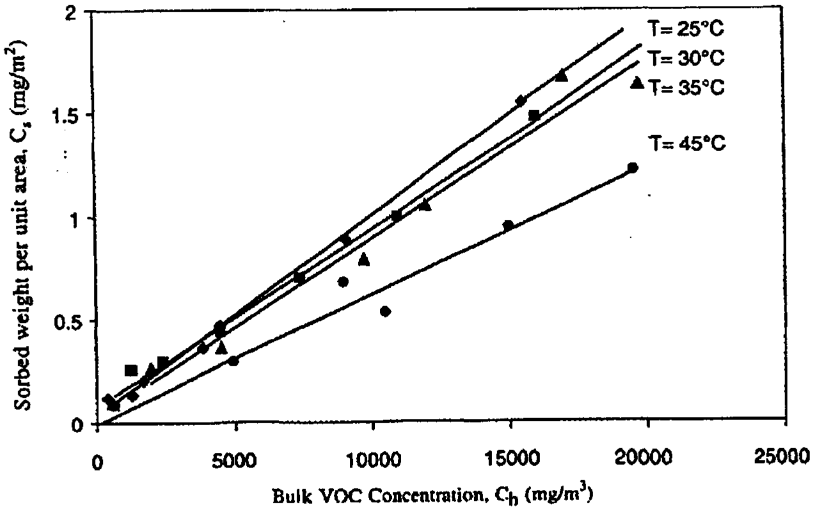


Figure 4.3. Sorbed Weight Per Unit Area Versus VOC Concentration for 1, 1, 1-tricholoethane on Carpet Fibers at Different Temperatures (Elkilani et al., 2003)

to 45 ^{0}C, Elkilani et al. (2003) reported that a linear relationship does exist between the equilibrium mass per unit area (mg/m^2), M_e, and the equilibrium concentration (mg/m^3), C_e, even at concentrations up to 20,000 mg/m^3. Moreover, Won et al. (2000, 2001) examined the adsorption of eight VOCs on three types of carpets and obtained sorptive parameters using the linear Langmuir adsorption IAQ model. In addition, through a series of sorptive experiments examining the relationship between adsorbed amount and VOC concentration in this study, linear Langmuir isotherms were also observed for the chamber surfaces for all three tested chemicals, acetone, toluene, and limonene as shown in Figure 4.4. Unlike the experiments performed by Elkilani et al. (2003), the experiments in this current study were conducted only at room temperature. All the tests, including the tests from the literature, were performed at concentrations up to thousands of mg/m^3, which is much higher than typical indoor concentrations (usually less than 10 mg/m^3), but still representing broad ranges of VOC concentrations with evaporative sources. If the adsorption profiles for carpet and the empty chamber surfaces follow the linear Langmuir isotherms at concentrations up to thousand of mg/m^3, it is likely that other indoor sink materials also follow the linear Langmuir isotherms. The reason is that carpets usually have a larger surface area than other indoor sink materials, such as wall board, cotton curtains, etc., followed by the empty chamber surfaces with the least surface area. Generally speaking, the larger the surface area of the adsorbent, the greater the amount of the adsorbed VOCs. Correspondingly, the stronger the interactions between molecules on the adsorbents as well as the more the deviation from the linear relationship would be expected. Thus, based on the results from the literature and this current study, it is reasonable to assume that the adsorption process for indoor sink materials follows the linear Langmuir isotherm, which means the amount adsorbed on the test material is linearly proportional to the equilibrium VOC concentration.

A series of adsorption studies of ACF in the passive mode in the test chamber was conducted in Chapter 3 to characterize the relationship between M_e and C_e after equilibrium was reached in order to determine whether VOC adsorption onto ACF follows the linear Langmuir sorptive mode. As shown in Figures 3.8-3.10, the adsorption isotherms on the ACF species tested, for acetone, toluene and limonene, actually followed the non-linear Freundlich sorption pattern. Thus, an exponential constant n associated with the Tichenor model equations (see Materials and Methods section) is needed to account for the non-linearity adsorption process for ACF. These experimental averaged values for n for three species of ACFs were 0.42, 0.31 and 0.16 (as shown in Table 3.4) for acetone, toluene, and limonene, respectively. Based on above discussion, the statement that the linear Langmuir isotherm is suitable for typical indoor applications is only partially true and therefore cannot be applicable for all sorptive materials. Therefore, the Langmuir isotherm may apply for some materials with weak adsorption properties while it may not be applicable for others with strong adsorption properties. The critical factor for the linear Langmuir isotherm application may be the amount of the adsorbate in the unit geometric area of surface or unit geometric volume of the sorptive material. The more adsorbed, the greater the repulsion forces, and the larger the isotherm may then deviate from the linear relationship. Although the ACF adsorption process

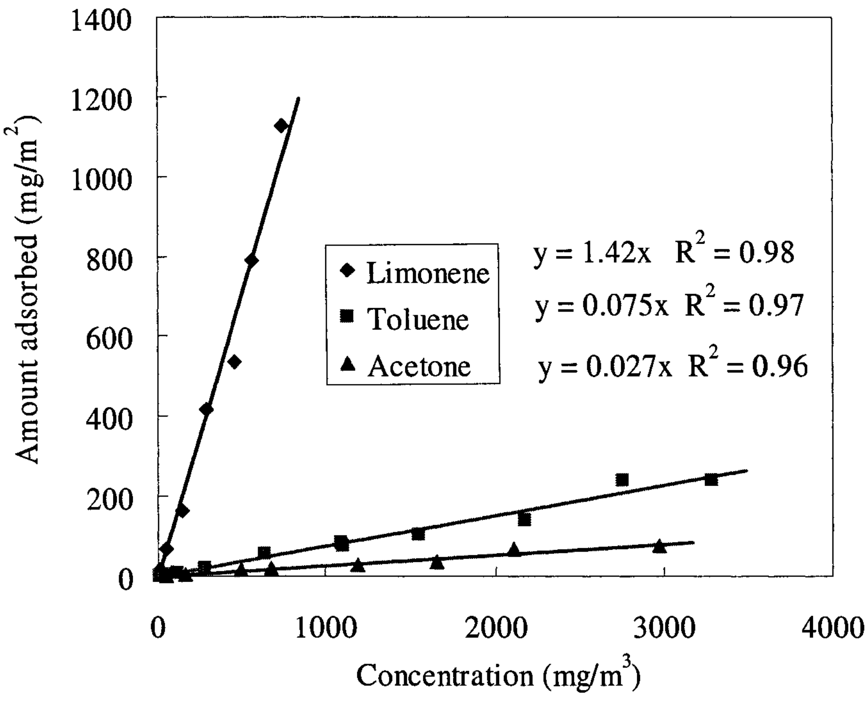


Figure 4.4 Adsorbed Weight Per Unit Area Versus VOC Concentrations in the Test Chamber for Acetone, Toluene and Limonene on the Empty Test chamber Surfaces.

appears to be non-linear, the desorption process is assumed to be linear, based on the fact that ACF has a strong affinity with VOCs and the assumption that desorption rate of ACF is small and comparable to that of indoor sink materials. In summary, both the adsorption and desorption processes were assumed to be the linear Langmuir sorption pattern for indoor sink materials, while the adsorption and desorption processes of ACF were assumed to be the non-linear (the Freundlich) pattern and the linear Langmuir pattern, respectively. The validity of these two assumptions is examined in the following sections of this chapter. The objectives of this phase of the study were: 1) to determine and compare sorptive kinetics of ACF and selected indoor sorptive materials based on selected VOCs, and 2) to evaluate an IAQ model based on the linear sink effects for indoor sorptive materials and the linear vs. non-linear sorptive effects for ACF.

Materials and Methods

Test Chamber

As shown schematically in Figure 4.1, the experiments were carried out in a 3 mm thick, 316 stainless steel rectangular test chamber with a volume of 51.7 L (50.2 cm × 39.7 cm × 26.0 cm). The chamber was maintained at a temperature of 23±1 °C. All components were made of 316 stainless steel, and included the inlet and outlet of the chamber, which were connected to a 20 cm long manifold tubing with 28 holes (hole diameter, 2 mm). A small computer case fan was installed at the center of chamber cover. Both the fan and the two manifolds were used for complete mixing. A Teflon® gasket was used as the chamber flange. A more detailed diagram of the test chamber is presented in Figure 4.6. The difference between inlet flow rate and outlet flow rate was less than 3% measured by two DryCal (BIOS, Model DC 1HC Rev. E) primary flow rate calibrators, indicating sufficient air tightness of the test chamber.

An oil filter and a particulate filter were used to pre-clean house air, followed by a Drierite gas drying jar to remove moisture and a zero air generator (Matheson Model MGEN-ZRC 3500, 3.5 L/min) to remove any excess organic compounds, resulting in purified air containing less than 0.1 ppm hydrocarbons measured as methane entering the test chamber. All the gas supplying and sampling lines were made of Tygon® tubing. Before each experiment, the test chamber was purged for more than 12 hours with purified air to remove moisture and trace organics in the chamber. The air tightness of the chamber was examined through air flow checking.

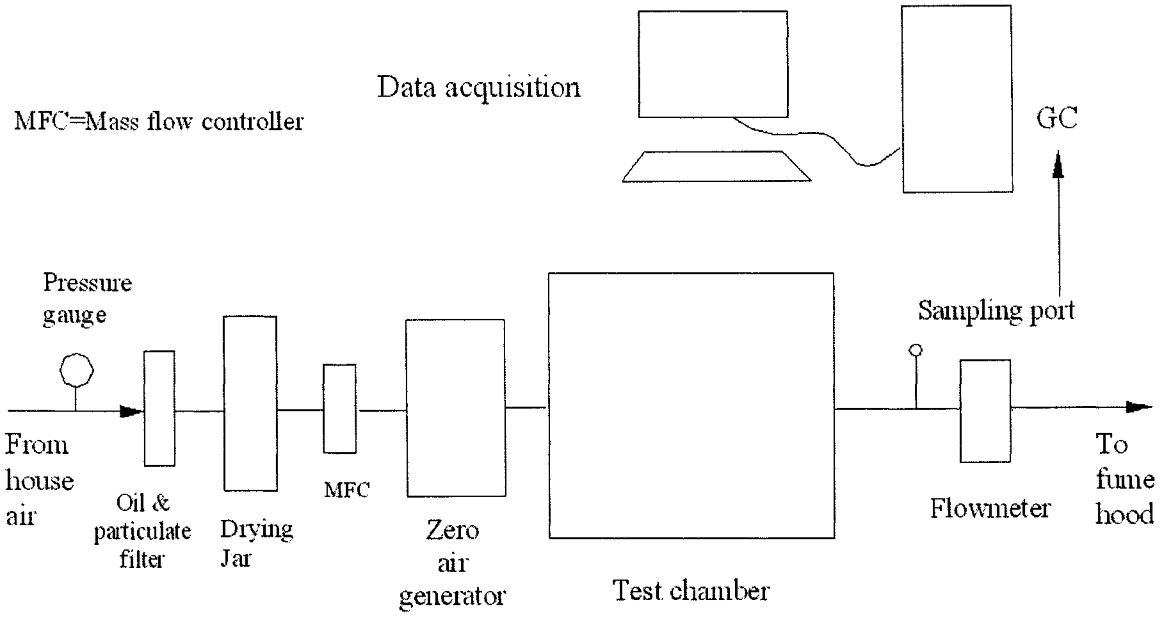


Figure 4.5. The Experimental Test System

Test Specimens

Three species of ACF (obtained from American Kynol), ACF-10, ACF-15, ACF-20, were tested. Each run was performed with equal sizes of three species of ACFs. The reported results in this study are the average of all three test species of ACF. The nominal specific surface areas for ACF-10, ACF-15, and ACF-20 are 1000 m^2/g, 1500 m^2/g and 2000 m^2/g, respectively. The same species (but not necessarily in the same batch) have been characterized in the literature (Foster et al., 1992; Cal et al., 1994; Cal, 1995; Mangun et al., 1999; Mangun et al., 2001) for their surface area and pore size distribution, with reported surface areas ranging from 730-760 m^2/g for ACF-10, 730-1670 m^2/g for ACF-15, and 1330-1610 m^2/g for ACF-20, respectively. The literature indicates that the pore size distribution range and mean increase with increasingly activated (higher surface area) ACF. The reported average pore width for ACF is from 0.81 to 1.34 nm. Four indoor sorptive materials (obtained from a local commercial outlet), gypsum board, carpet, polyester and cotton textiles, were also tested for comparison. Prior to use, the indoor sorptive materials were aged for two months in a well-ventilated, VOC-free office, as confirmed by real time samplings with MSA Passport VOC Analyzer, while ACF samples were dried in a desiccator for more than one month. The description of each material is detailed in Table 4.1. In order to eliminate adsorption of VOCs along the cut edges of the carpet and gypsum board, which may behave differently from their surfaces, their cut edges were sealed with sodium silicate and allowed to dry for two days in a well-ventilated laboratory before each test.

Table 4.1. Description of Test Material Samples

Test Specimen	Description	Storage	Size cmxcm	Density g/m^2	Thickness cm	Nominal surface area, m^2/g
ACF-10	Novoloid fibers	Desiccator	2x2	240	0.076	1000
ACF-15	Novoloid fibers	Desiccator	2x2	166	0.063	1500
ACF-20	Novoloid fibers	Desiccator	2x2	151	0.059	2000
Gyspum board	100% paper on the face	Ventilated office	30x40	N/A	1.270	N/A
Carpet	Hard back, 100% nylon	Ventilated office	30x40	N/A	1.490	N/A
Cotton	Commercial, 100% cotton	Ventilated office	30x40	N/A	0.039	N/A
Polyester	Commericial	Ventilated office	30x40	N/A	0.043	N/A

Test Chemicals

Target chemicals were chosen base on their physico-chemical property differences in boiling point, polarity, vapor pressure and affinity coefficient (affinity between VOC and the surface of the adsorbent). Acetone, toluene and limonene, which represent ketones, aromatics and terpenes, are often observed in many paints, adhesives, coatings and other indoor application products such as air-fresheners and cleaning agents, and are often detected in indoor environments. Their physico-chemical properties and sources are presented in Table 3.1 of Chapter 3.

Test Procedures

Before each experiment, the test chamber was soaked and cleaned with 2% Extran® (an alkaline agent) and then rinsed with distilled water several times. The test chamber was wiped by laboratory tissue and then dried by a hair-dryer. After a test specimen was placed on the floor of the test chamber and the chamber sealed, the chamber was then purged for 12 hours at two air changes per hour to remove any moisture and trace organics left in the chamber. Before each test, the background concentration of the chamber was determined by sampling for 30 minutes and was found to be negligible. Each chemical was injected as a liquid by syringe into a Teflon® Petri dish in the center of the test chamber. The fan was then started to ensure complete mixing. Moreover, in this study, each test specimen of ACF was well distributed on four equally divided sections of the floor of the test chamber as shown in Figure 3.2 of Chapter 3. The purpose of this spacing was to eliminate error due to non-uniform concentration distribution in the test chamber. For indoor sink materials, each test specimen was placed in the center of the floor of the test chamber and, because of its large size most of the chamber floor was covered by a single test specimen. Initially, the author examined the impact of the presence of ACF on indoor VOC emissions representative of evaporative sources, as compared to that of the presence of indoor sink materials. Toluene was used as a representative indoor VOC for these preliminary studies, and was evaporated from a glass vial 2 cm in diameter. As with the purging phase, once an experiment was begun, the air flow through the test chamber was maintained at 2 air changes per hour. After it was demonstrated that ACF had a significant impact and the tested indoor sink materials showed a comparatively insignificant impact on evaporative indoor VOCs through these preliminary studies, in order to quantitatively measure sorptive kinetics, additional experiments were conducted by initially allowing the test chemical to evaporate in the chamber and reach an equilibrium concentration statically before starting the airflow with an air change per hour range of 1 to 2. For these additional experiments, in order to expedite the evaporative process, a Petri dish with a diameter of 5 cm was used as the container of liquid chemical. When VOC concentrations from 3 or 4 successive air samples separated by at least 30 minutes had a variation of less than 10 %, the author regarded that the equilibrium between sorptive processes in the test chamber had been reached. The test chamber was then purged with purified air at a flow rate of approximately 1 L/min in order to determine desorption kinetics. In addition, the equilibrium partitioning coefficient, K_e, was determined experimentally, as described in the next section. Only one test material was tested per run. Surface adsorption of the empty test chamber was also characterized.

Sampling and Analysis of Chemicals

Air samples were collected through a sampling port on tubing connected to a manifold of the test chamber by SKC large activated coconut charcoal tubes with 400/200 mg charcoal in the front/rear sections. The sampling pump (SKC Pocket Pump® model 210-1002) was operated at a flow rate of 60-80 ml/min for 2 to 10 min. The charcoal tubes were desorbed with CS_2, and then analyzed by a Varian GC Analyzer Model 3900 equipped with flame ionization detector (FID) and with a CP-Wax 52CB (30 m*0.53 mm, ID, 1μm film) column.

Desorption efficiency of this method for ACF was validated by injecting an equivalent known amount of test VOC into desorption vials with the same amount of ACF as in each run in the experiments. The validation curves are presented in Appendix I. The adsorption results of each test VOC were adjusted according to its validation curve.

An Indoor Air Quality Model Proposed for This Study

As discussed in the previous section, the adsorption of some indoor sink materials was assumed to follow the linear Langmuir adsorption isotherm, while the adsorption process of ACF was found to follow the non-linear Freundlich isotherm even though the desorption process of ACF was assumed to be linear. Since the indoor air quality model proposed by Tichenor (1991) was based on the linear sorptive pattern, in order to estimate the sorptive parameters, any IAQ model must take this factor of linearity or non-linearity into account. Accordingly, the three IAQ model equations (Eqs. 2.28 and 2.29) proposed by Tichenor et al (1991) were modified in this current study by adding an exponential constant, n, for the concentration term. When n=1 as in the original Tichenor model, the sorption for indoor sink materials follows the linear Langmuir isotherm. But for the ACF, when n deviates from a value of 1 as described in the introduction of this chapter based on experimental data presented in Chapter 3, the

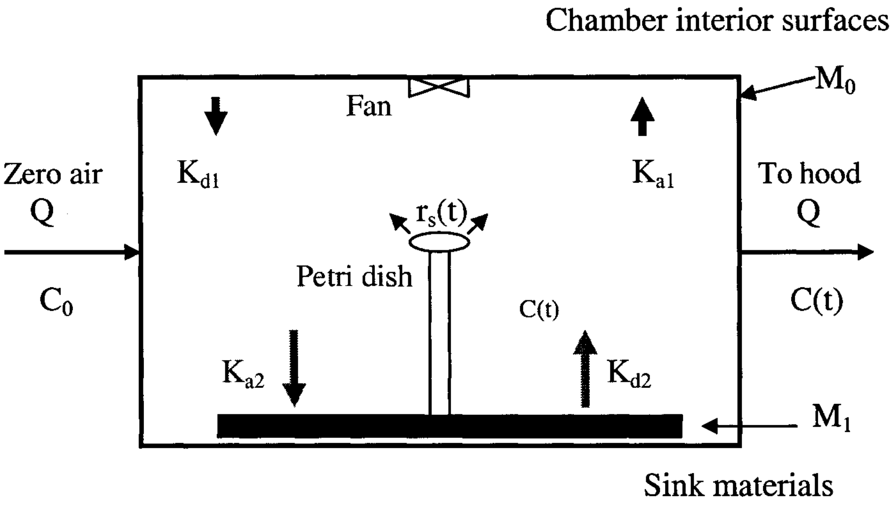


Figure 4.6 Schematic of the Sorption Process Based on the IAQ Models in This Study

modified equations may then allow the relationship to follow the non-linear Freundlich isotherm. Similar to Tichenor's IAQ model, which is based on the mass conservation of VOC in a well mixed test chamber as shown in Figure 4.6, the modified model may be represented as follows:

$$\frac{dC}{dt} = QC_{in} + R(t)\frac{A}{V} - NC - K_{a1}CL_0 + K_{d1}M_0L_0 - K_{a2}C^nL_1 + K_{d2}M_1L_1. \quad \text{....................(4.1)}$$

$$\frac{dM_0}{dt} = K_{a1}C - K_{d1}M_0 \quad \text{..(4.2)}$$

$$\frac{dM_1}{dt} = K_{a2}C^n - K_{d2}M_1 \quad \text{..(4.3)}$$

The above terms are defined as follows:

C and C_{in} : VOC concentrations in the test chamber and inlet, respectively, mg/m^3;

Q: the air flow rate through the test chamber, m^3/h;

R(t): the VOC emission rate, mg/h;

K_{d1}: the desorption rate of test chamber surfaces, h^{-1};

K_{d2}: the desorption rate of test material, h^{-1};

K_{a1}: the adsorption rate of test chamber surfaces, m/h;

K_{a2}: the adsorption rate of test material, (mg/m^3)$^{1-n}$ $*$ m/h for ACF, m/h for other test materials;

A: the test material geometric area, m^2;

N: the air exchange rate per hour;

V: the volume of the test chamber, m^3;

L_0 and L_1: the loading factors for test chamber and test materials, respectively, m^2/m^3,

M_0: the mass per unit area on the test chamber surface, mg/m^2;

M_l: the mass per unit area on the test material, mg/m^2; and

n: an empirical constant accounting for non-linearity in the adsorption process.

In this project, due to the removal of VOCs, oil and particulate from house air, the inlet VOC concentration is essentially zero. After complete evaporation of the test chemical in the Petri dish and the equilibrium of adsorption and desorption processes in the test chamber had been reached, the test chamber was purged with purified air. The chemical concentration in the test chamber experienced a decay profile from which the sorptive kinetics were determined. Since C_{in}, and R(t) at this point are both zero, Equation (4.1) can be simplified by dropping those two terms.

Determination of Parameters of the Model

The method of estimating sorptive kinetics was described by the literature (Tichenor, et al, 1991, Jørgensen, et al, 1999). In the literature, M_e for a test sink material was obtained by using the area-under-the-curve method; the M_e was then substituted into the models for M_l, and finally, the values for K_a and K_d were obtained by fitting the analytical solutions of Equations 4.1, 4.2, and 4.3 to experimental results by a non-linear regression curve fit routine. In this study, the equilibrium partitioning coefficient K_e values of the test chamber and test materials for each test chemical were directly determined experimentally. The K_e value for the empty chamber was first determined experimentally. When the adsorption and desorption processes reached equilibrium, the chamber /air partition coefficient K_e was determined with M_e divided by equilibrium concentration C_e as shown in Equation (4.4).

$$K_e = \frac{K_a}{K_d} = \frac{M_e}{C_e} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.4)$$

Since the amount of chemical injected in the chamber is known for each test, the amount of chemical adsorbed by the empty chamber surfaces can be determined by subtracting the amount in the air of the chamber and the amount adsorbed by ACFs from the amount injected. This series of experiments was performed in Chapter 3. Once K_e value for the empty chamber is known, M_0 can be determined at an equilibrium concentration by using Equation 4.4. M_e for each indoor sink material can then be obtained by subtracting the amount in the air of the chamber and the amount adsorbed by the chamber surfaces from the amount injected, and finally the K_e for each test specimen can be obtained by using Equation 4.4. Because indoor sink materials follow linear Langmuir isotherms, K_e is defined as in Equation (4.4). However, because ACF follows the Freundlich adsorption isotherm, the K_e is defined as:

$$K_e = \frac{K_a}{K_d} = \frac{M_e}{C_e^n} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.5)$$

Due to nonlinear effect of concentration, K_e and K_a for ACF have different units from K_e and K_a for indoor sink materials. The units for ACF are $m*(mg/m^3)^{(1-n)}$ for K_e and $m/h*(mg/m^3)^{(1-n)}$ for K_a, respectively. The kinetic parameters, in this case, the adsorption rate (K_a=K_e*K_d) and desorption rate (K_d), were obtained by fitting the experimental results to analytical solutions of simplified Equations 4.1, 4.2 and 4.3 by using a non-linear curve fit routine, in this case, Matlab R12.

The sorption kinetics can be determined either from the concentration buildup phase or from concentration decay phase. The uncertainty involved in the decay phase is lower than that of the buildup phase as reported by Jørgensen et al. (1999). It is likely that the problem occurred during parameter estimation by means of non-linear regression (Evans, 1996). In order to minimize the variation in estimating the parameters of the model, the sorption kinetics, K_a, K_d, were determined from the decay phase only in this current study.

Results and Discussion

Qualitative Evaluation of Sink Strength of ACF and Indoor Sink Materials

In order to qualitatively evaluate the effectiveness of ACF for removal of indoor VOC as concentration varied with time, a series of experiments was performed in an effort to observe the difference between the peak concentrations with and without the presence of ACF in the test chamber. Before characterizing the reduction of peak concentration caused by the presence of ACF, the empty chamber was also measured, followed by selected indoor sorptive materials as comparisons with ACF. All the selected materials, including the empty chamber, were tested separately. The test results are shown in Figure 4.2. If no sink effect occurred in the test chamber, the decay profile beginning with the peak concentration tested with the empty chamber only would follow the theoretical dilution curve as shown in Figure 4.2 (the dotted profile—"no-sink" curve). However, as shown in Figure 4.2, the decay profiles of indoor sink materials and even the empty chamber were higher than the "no-sink" curve, suggesting that the sink materials adsorbed toluene vapor and then reemitted it into the test chamber. It also indicated that indoor sink materials may act as secondary emitters and cause higher exposure than the chamber without those materials. This phenomenon again confirmed the sink effects of indoor sink materials and the importance of reducing the peak concentrations of VOCs. Obviously, if the peak concentrations of VOCs can be reduced, the exposure of residents would be significantly lessened in emission from freshly applied materials or human activities and from indoor sink materials because of the nature of indoor sink materials as potential secondary emitters. The impact from the presence of cotton or polyester on the concentration profile was relatively insignificant, and was in the same magnitude as that from the empty chamber surfaces. The gypsum board had a greater impact on the concentration profile than cotton and polyester. As expected, the carpet had the greatest impact on the concentration among the tested indoor sink materials because it has the largest surface area due to its roughness of surface. By comparing the peak concentrations of profiles in Figure 4.2 for the test chamber with ACF and the empty chamber, it suggests that ACF reduce the peak concentration by more than 50% even though the geometric area of ACF was only 4% of the cross-sectional area of indoor sink materials such as polyester, cotton, carpet, and gypsum board. In order to quantitatively measure the adsorbed VOCs, the area-under-the-curve method may be used to obtain the amount adsorbed by the test specimen. Thus, the adsorption capability of each material can be evaluated by comparing their adsorbed VOCs. However, this method cannot obtain information about the adsorption desorption rate constants of each material. Even though some attempts to determine the sorptive kinetics of carpets in a similar scenario were reported in the literature (Bouhamra and Elkilani, 1999; Elkilani et al., 2001), difficulties were encountered in two aspects: 1) it was difficult to find a model to accurately characterize the emission rate of the test chemical in the Petri dish or the glass vial if the buildup stage of the concentration profile was involved in the determination of the kinetics; 2) it was difficult to obtain the sorptive kinetics only based on the decay concentration profile if the method used by Tichenor (1991) was employed to determine the sorptive kinetics, because whether the equilibrium had been reached or not in the adsorption/desorption process in this test manner cannot be determined when the decay phase immediately follows the buildup phase. Thus, in order to obtain the sorptive kinetics and compare the sink strength quantitatively, a method used to achieve this is presented in the Materials and Methods Section of this Chapter.

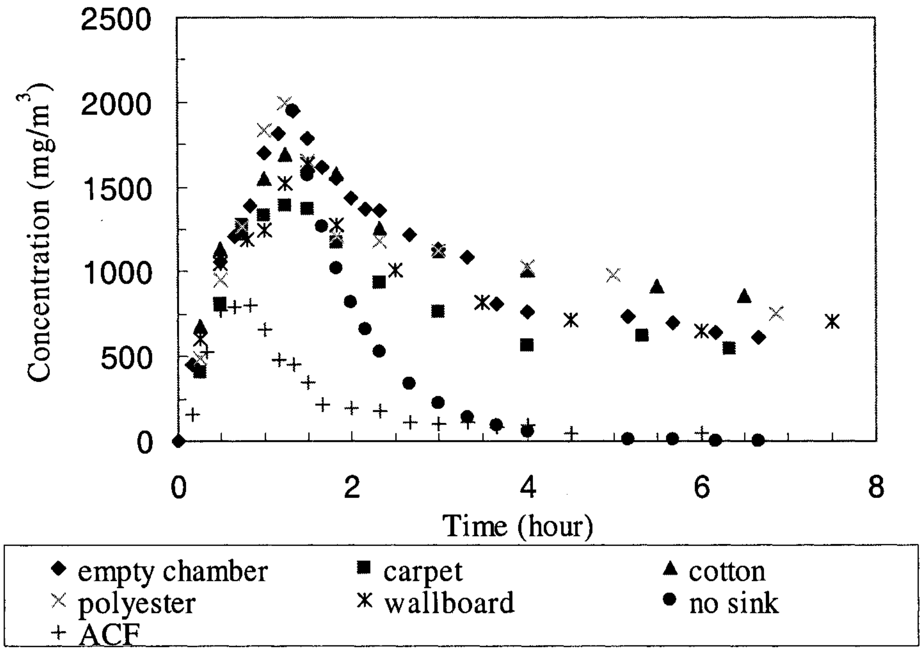


Figure 4.7. The Impact on Indoor Toluene Concentrations with the Presence of ACF or an Indoor Sorptive Material (Each Tested Separately).

Summary of Sorption Parameters and Modeling

The experimental results for all tested sink materials, including values for N, C_e, K_a, K_d, K_e, M_e, L_0, and L_1, are presented in Tables 4.2 - 4.4 for acetone, toluene and limonene, respectively. As indicated by Won et al. (2001), it is difficult to make inter-laboratory comparisons of sorption parameters, due to differences in test chemicals, test materials, and methods in estimating sorption parameters. The sorption parameters for toluene and carpet in this study ($K_a = 0.172$, $K_d = 0.169$) were in the range reported by Won et al. (2001), of from 0.11 to 0.49 for K_a, and from 0.16 to 0.65 for K_d. However, their value of K_a for toluene and gypsum board was 0.04, while 0.135 was obtained in this study. Jorgensen et al. (1999) reported a value of $K_a = 0.023$, $K_d = 0.308$ for toluene and cotton, respectively, the values of K_a and K_d obtained in this study are 0.071 and 0.2239, respectively, corresponding to a difference of 65% for K_a and 20% for K_d. The parameters for toluene and empty chamber were within an order of magnitude of those obtained in this current study. These kinds of differences are often seen in various publications. A special case is that the results for toluene and carpet reported by Bouhamra and Elkilani (1999) are significantly different from the results of this study and of others reported previously, which had a more than two orders of magnitude difference for K_a and more than an order of magnitude difference for K_d, respectively. The possible reason is that it may involve a large variation in characterizing the emission profiles and error involved in modeling of the emission profiles.

Table 4.2. Experimental Sorption Results --- Acetone and Sink Materials

	C_e mg/m^3	M_0 mg/m^2	M_1 mg/m^2	K_a m/h	K_d h^{-1}	K_e m	L_0 m^2/m^3	L_1 m^2/m^3	N h^{-1}	S_0 m^2	S_1 m^2
Empty chamber	10190	279	N/A	0.0046	0.168	0.027	18.25	N/A	1.45	0.94	N/A
Polyester	8109	222	1586	0.0056	0.028	0.196	15.97	2.28	0.95	0.83	0.118
Cotton	8081	221	1605	0.0056	0.028	0.199	15.97	2.28	1.3	0.83	0.118
Gypsum board	6670	183	3508	0.054	0.103	0.53	16.66	1.59	1.00	0.86	0.082
Carpet	8042	220	2154	0.0101	0.038	0.268	16.58	1.67	1.45	0.86	0.086
ACF	3111	85	57174	188.63*	0.089	2113.8#	18.06	0.186	1.2	0.93	0.010

*K_a for ACF: unit in m/h ×(mg/m^3)$^{1-n}$, #K_e for ACF: unit in m×(mg/m^3)$^{1-n}$

Table 4.3 Experimental Sorption Results --- Toluene and Sink Materials

	C_e mg/m^3	M_0 mg/m^2	M_1 mg/m^2	K_a m/h	K_d h^{-1}	K_e m	L_0 m^2/m^3	L_1 m^2/m^3	N h^{-1}	S_0 m^2	S_1 m^2
Empty chamber	3543	269	N/A	0.095	1.250	0.08	18.25	N/A	2.13	0.943	N/A
Polyester	5233	398	2282	0.065	0.150	0.43	15.98	2.27	1.14	0.826	0.117
Cotton	5121	402	2181	0.071	0.239	0.41	15.93	2.32	2.00	0.823	0.120
Gypsum board	4840	368	2398	0.135	0.273	0.50	15.68	2.57	1.28	0.810	0.133
Carpet	3751	285	3829	0.172	0.169	1.02	16.04	2.21	1.50	0.829	0.114
ACF	1556	118	70354	355*	0.049	7207#	18.06	0.18	1.75	0.934	0.010

*K_a for ACF: unit in m/h ×(mg/m^3)$^{1-n}$, #K_e for ACF: unit in m×(mg/m^3)$^{1-n}$

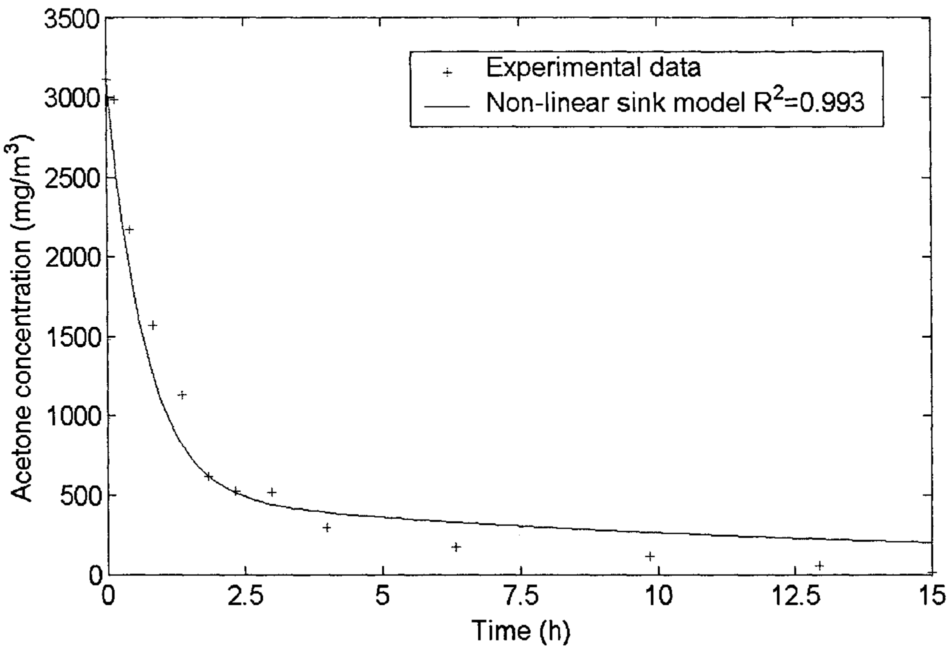
Table 4.4 Experimental Sorption Results --- Limonene and Sink Materials

	C_e mg/m^3	M_0 mg/m^2	M_1 mg/m^2	K_a m/h	K_d h^{-1}	K_e m	L_0 m^2/m^3	L_1 m^2/m^3	N h^{-1}	S_0 m^2	S_1 m^2
Empty chamber	538	764	N/A	0.28	0.197	1.42	18.25	N/A	2.17	0.94	N/A
Polyester	147	208	5294	1.03	0.028	36.11	15.98	2.26	1.89	0.83	0.117
Cotton	442	628	2188	0.66	0.133	4.95	15.97	2.28	2.18	0.83	0.118
Gypsum board	342	486	3177	0.41	0.044	9.28	15.93	2.32	2.17	0.82	0.120
Carpet	369	525	3973	1.70	0.158	10.75	15.75	2.50	1.87	0.81	0.129
ACF	175	249	58098	1947*	0.039	25422#	18.06	0.19	2.15	0.93	0.010

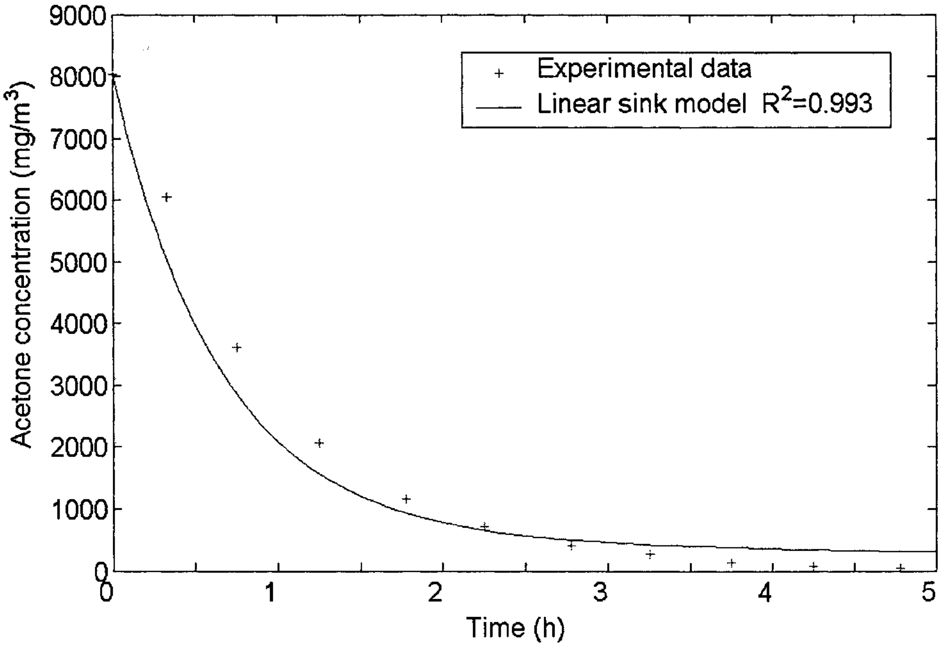
*K_a for ACF: unit in m/h×(mg/m^3)$^{1-n}$, #K_e for ACF: unit in m×(mg/m^3)$^{1-n}$

Adequacy of the IAQ Model

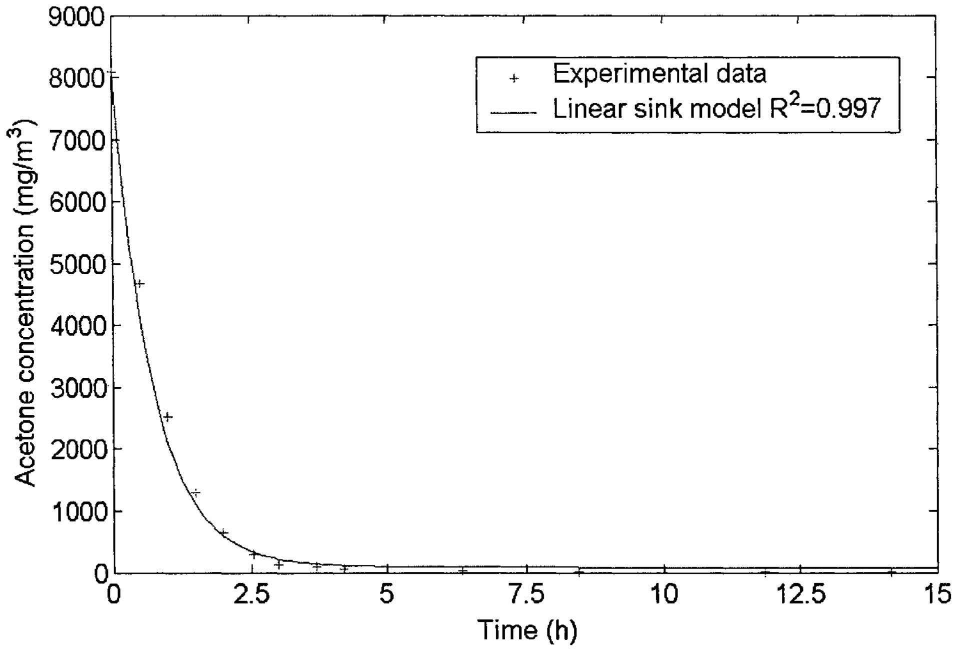
An et al. (1999) reported that a linear sink model based on the Langmuir adsorption process was found to be acceptable in fitting the experimental data for a wide range of K_e values. Tichenor (1991) suggested that the Langmuir assumption appears to be applicable to flat, smooth surfaces (e.g., ceiling tile, wallboard), but may be not suitable for surfaces with great roughness and irregularities (such as carpet). However, as shown in Figures 4.8 – 4.10, for all test indoor sorptive materials and chamber surfaces, the linear sink model fit the experimental results very well (R^2>0.96), which may indicate that the model is adequate to describe the results. For ACF, as characterized in the passive adsorption section in Chapter 3, the adsorption process does not follow the linear Langmuir isotherm, while the Freundlich adsorption isotherm is more appropriate for ACF in this study. The reason for this may be due to molecular interactions of adsorbates on the ACF surface; in other words, because ACF has a much greater adsorption capacity in a much smaller geometric area, and the distances among adsorbed molecules are not as great as those on weak sink materials. Thus, the repulsion forces may not be negligible. If more molecules will be adsorbed on the ACF surface, they must overcome the repulsion forces even though the first layer of the surface is not totally covered. However, the desorption process for ACF was assumed to be linear to its concentration on ACF (or the amount of VOC adsorbed in the adsorbent). The assumption is validated since the desorption rates of ACF for three tested chemicals are in the same order of magnitude as those of indoor sink materials. The linear desorption process was assumed in the original Tichenor IAQ model and was successfully applied for various VOCs on many indoor sink materials. Similarly, together with the non-linear adsorption process,



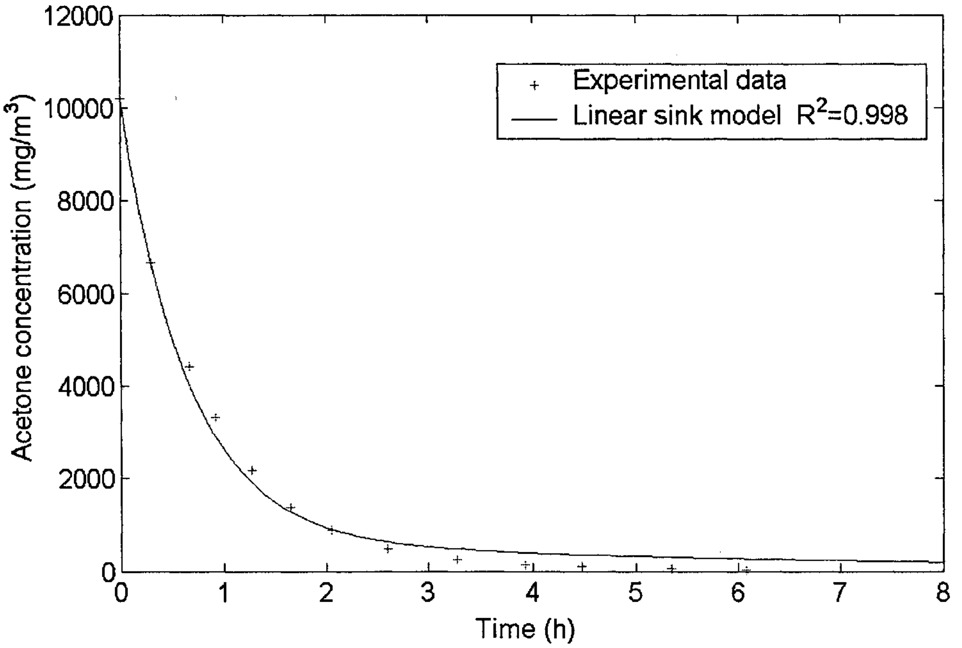
a) Acetone on ACF



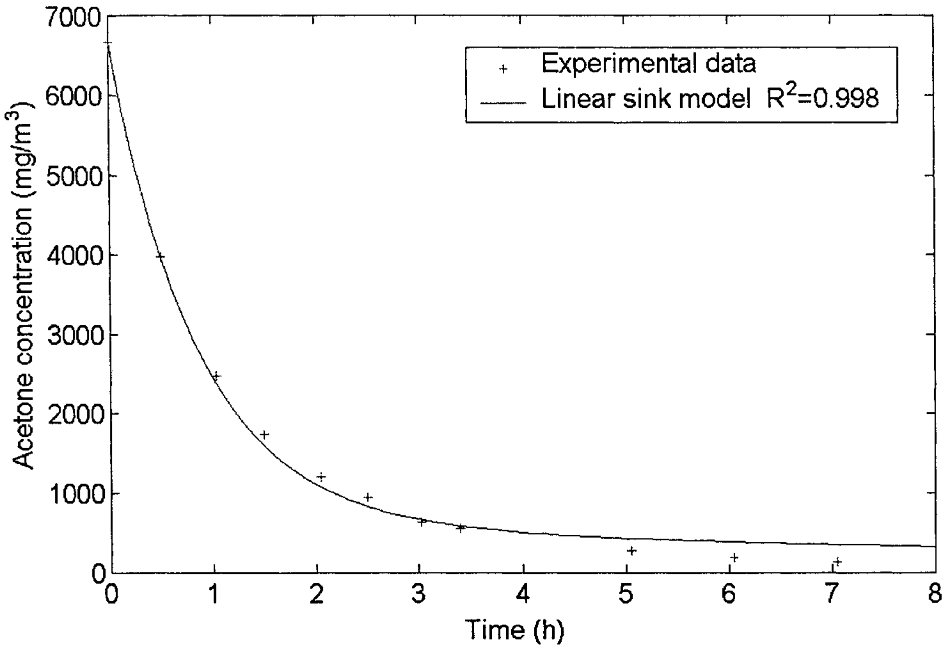
b) Acetone on Carpet



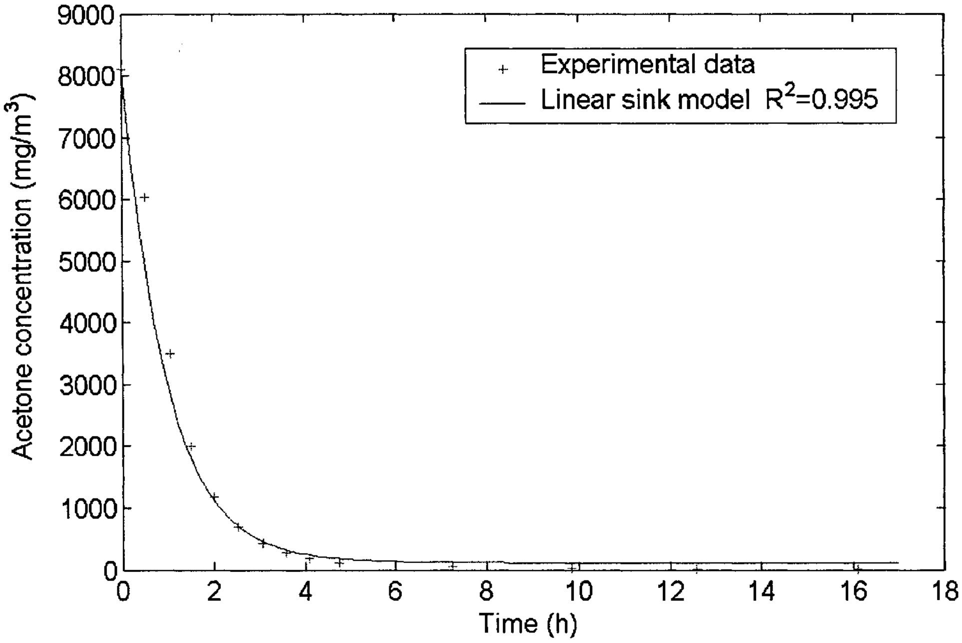
c) Acetone on Cotton



d) Acetone on Empty Chamber

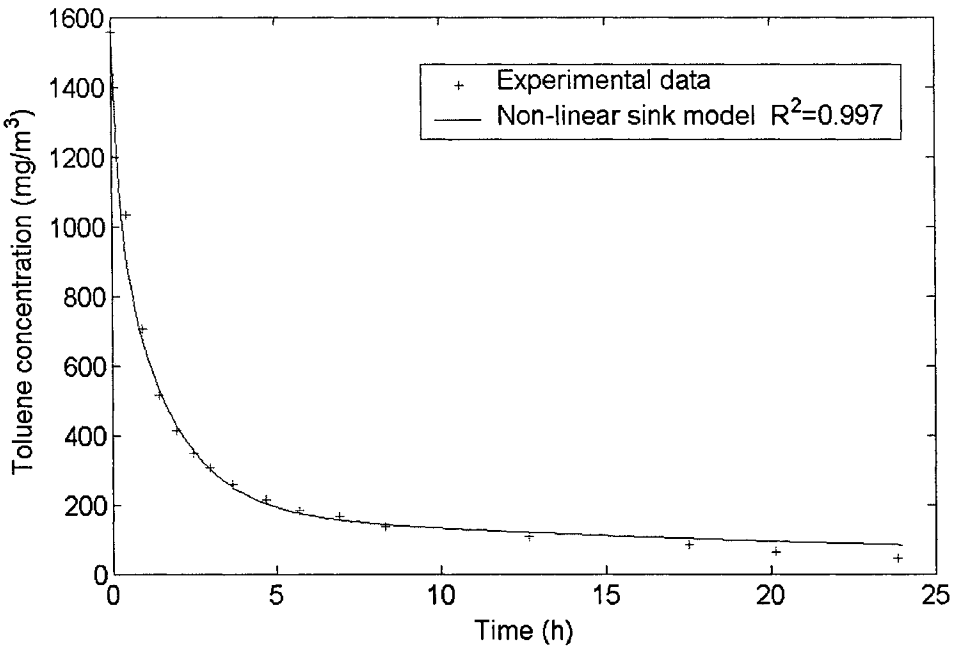


e) Acetone on Gypsum Board

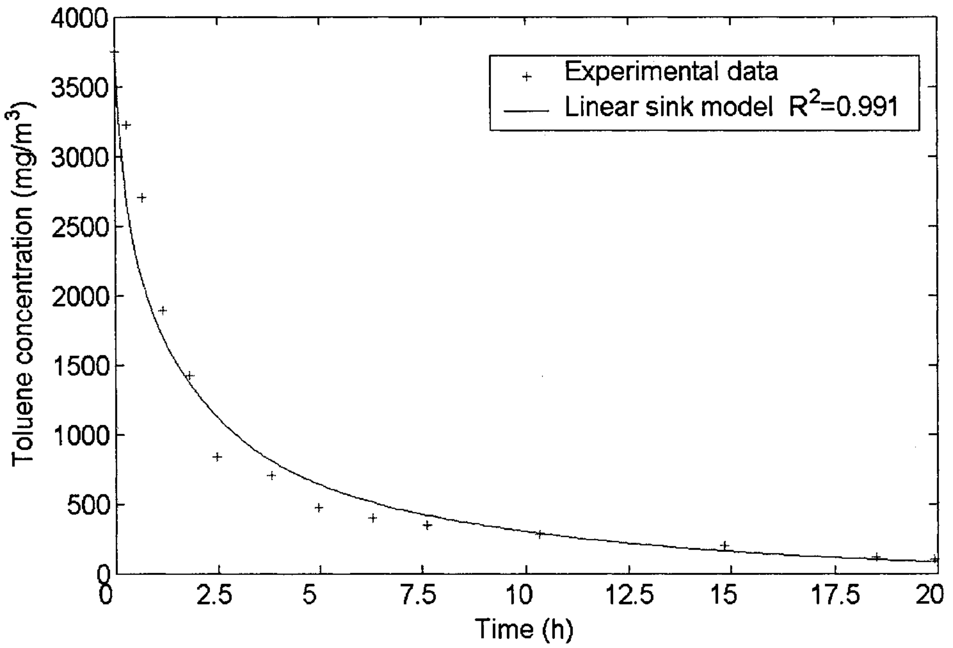


f) Acetone on Polyester

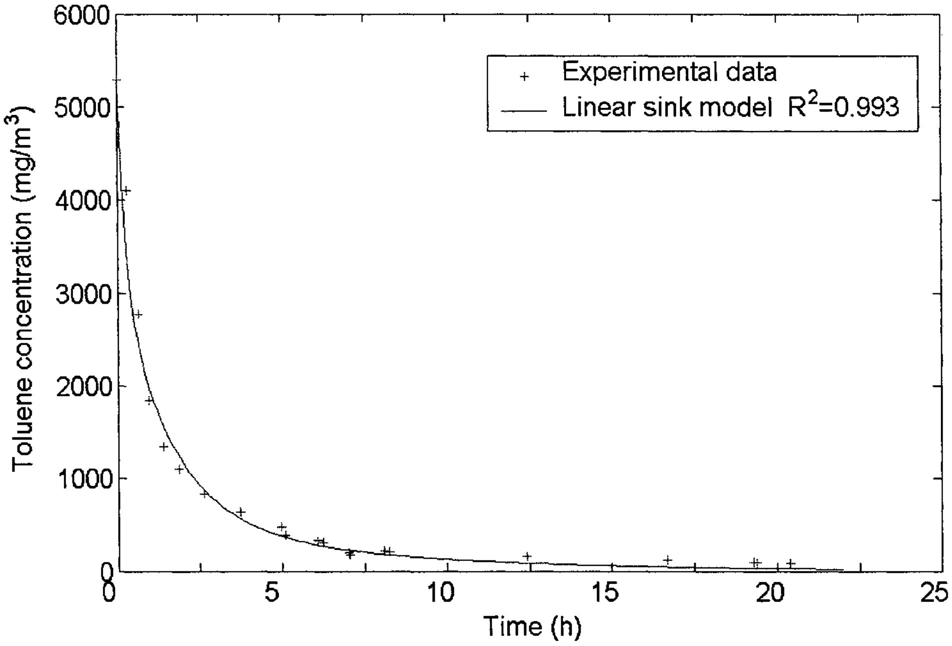
Figure 4.8 Measured Acetone Decay Profiles and IAQ Modeled Results



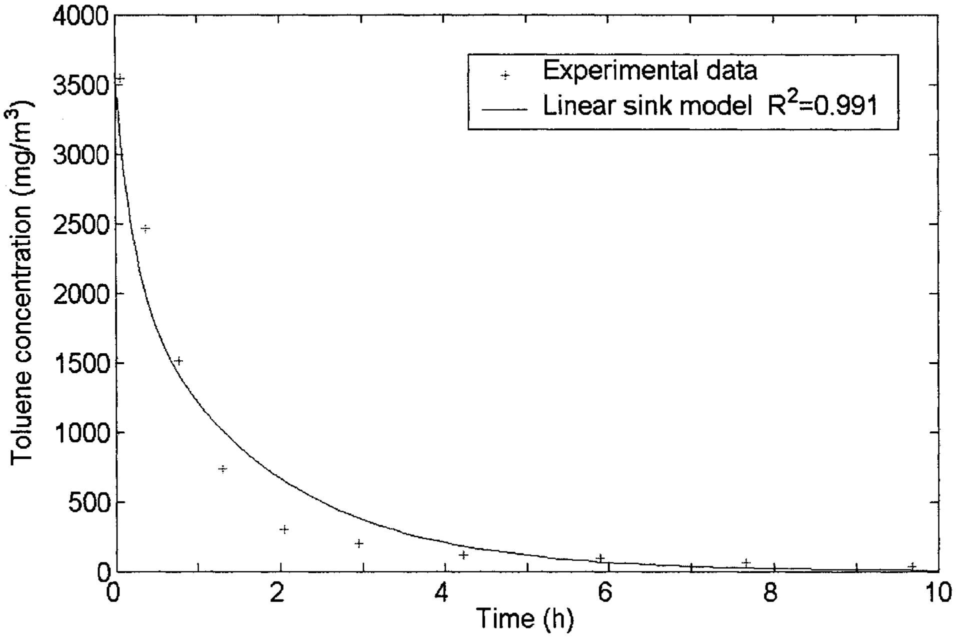
a) Toluene and ACF



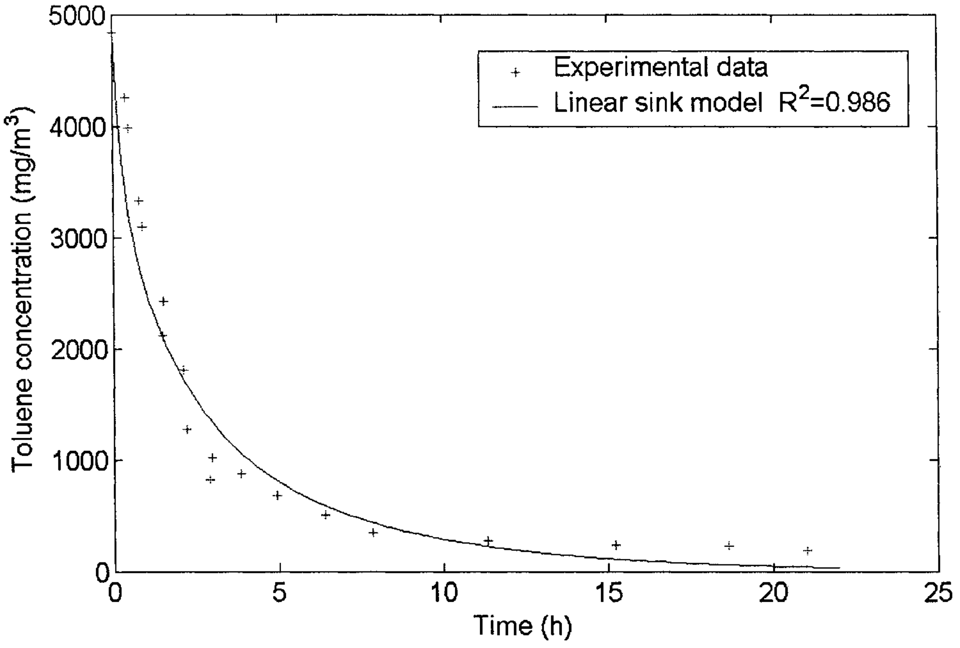
b) Toluene on Carpet



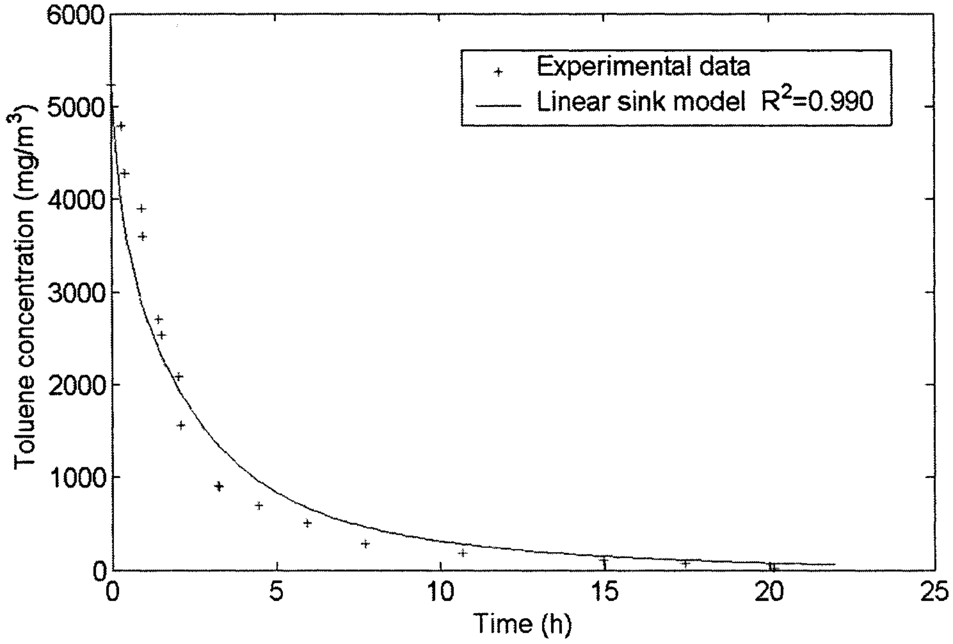
c) Toluene on Cotton



d) Toluene and Empty Chamber

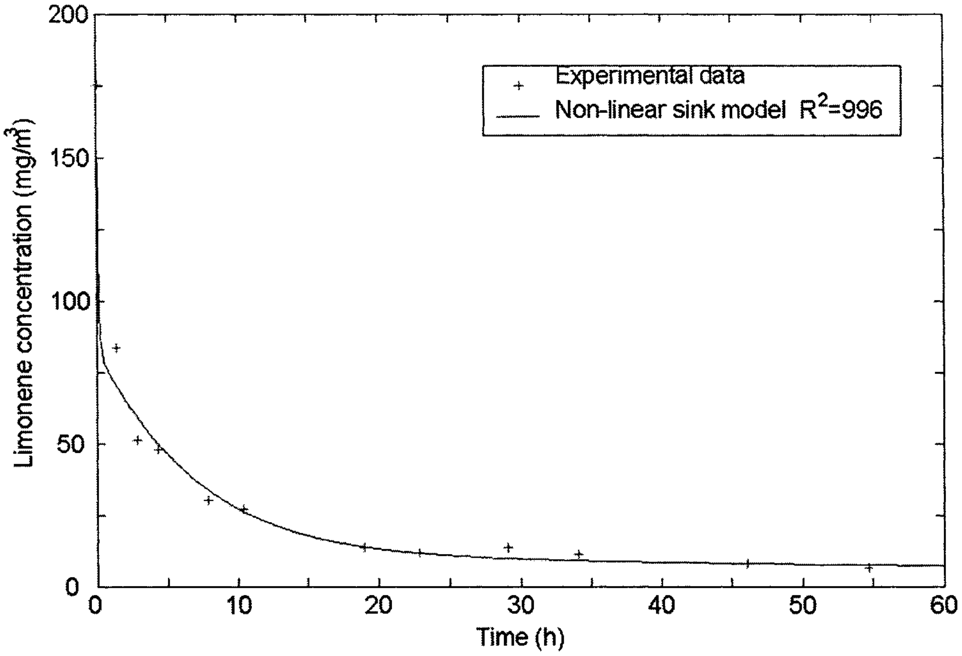


e) Toluene on Gypsum Board

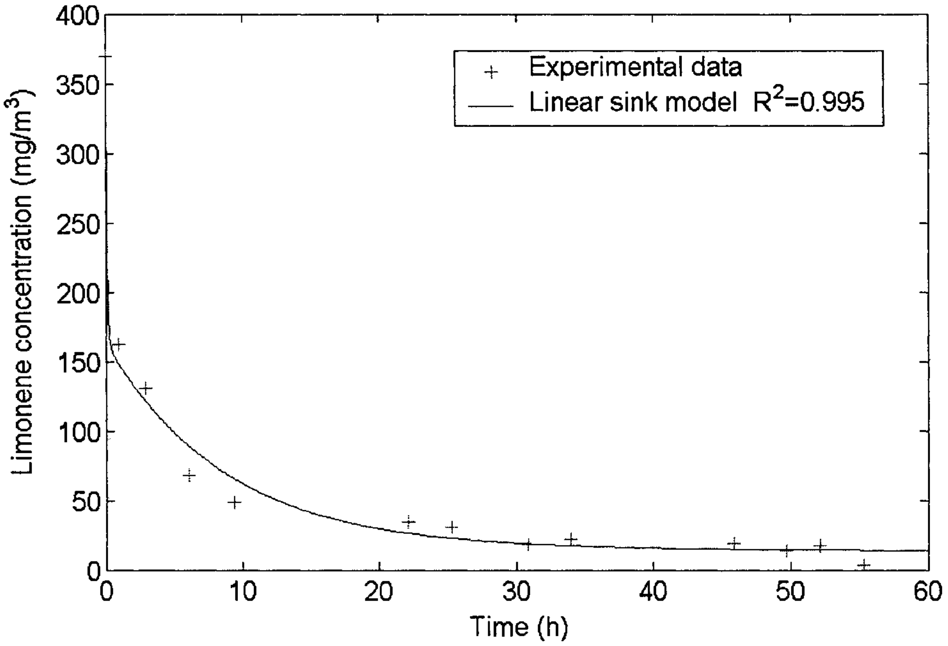


f) Toluene on Polyester

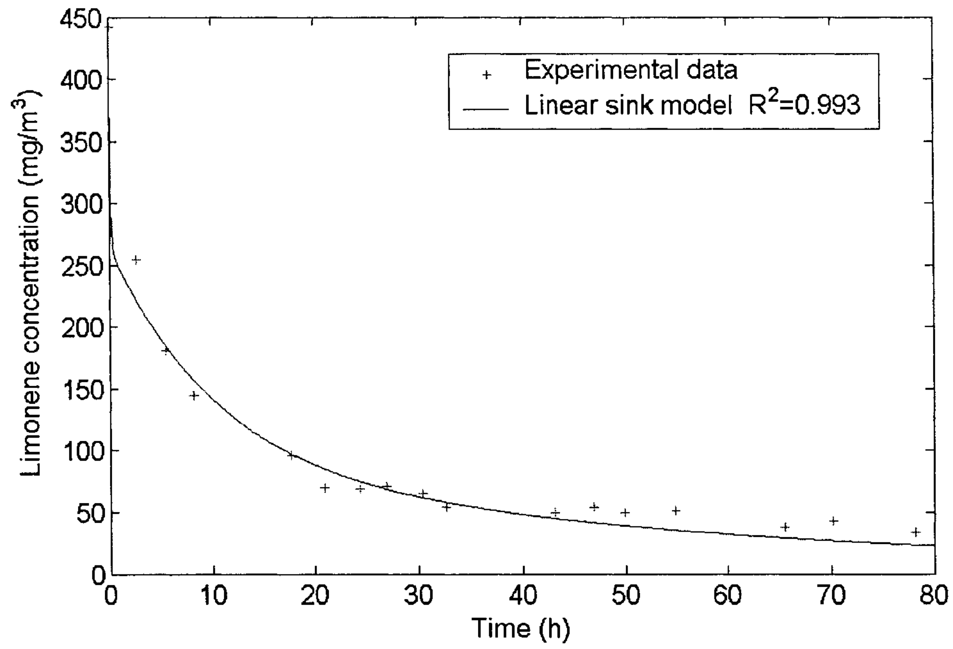
Figure 4.9 Measured Toluene Decay Profiles and IAQ Modeled Results



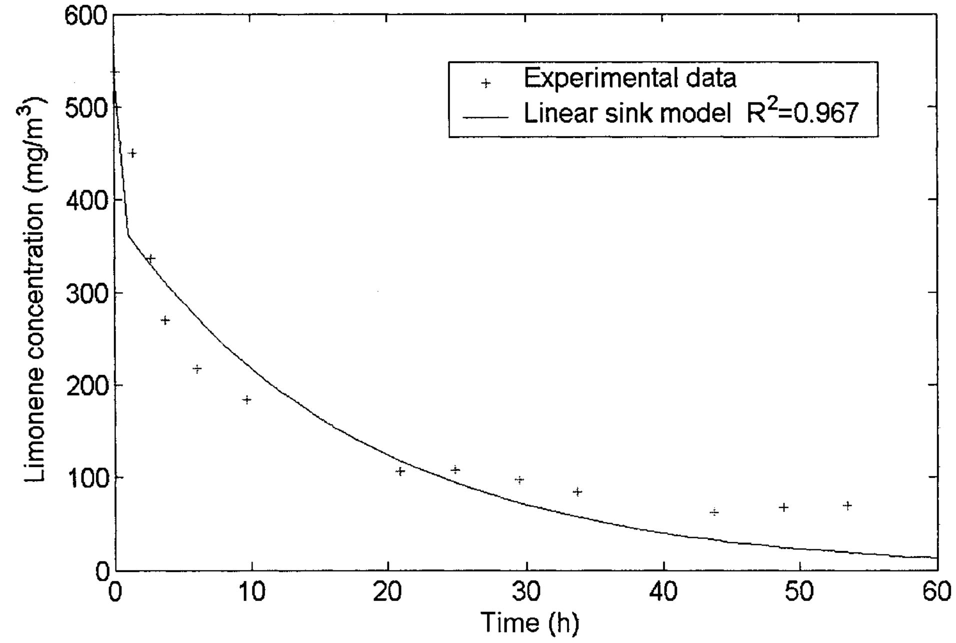
a) Limonene on ACF



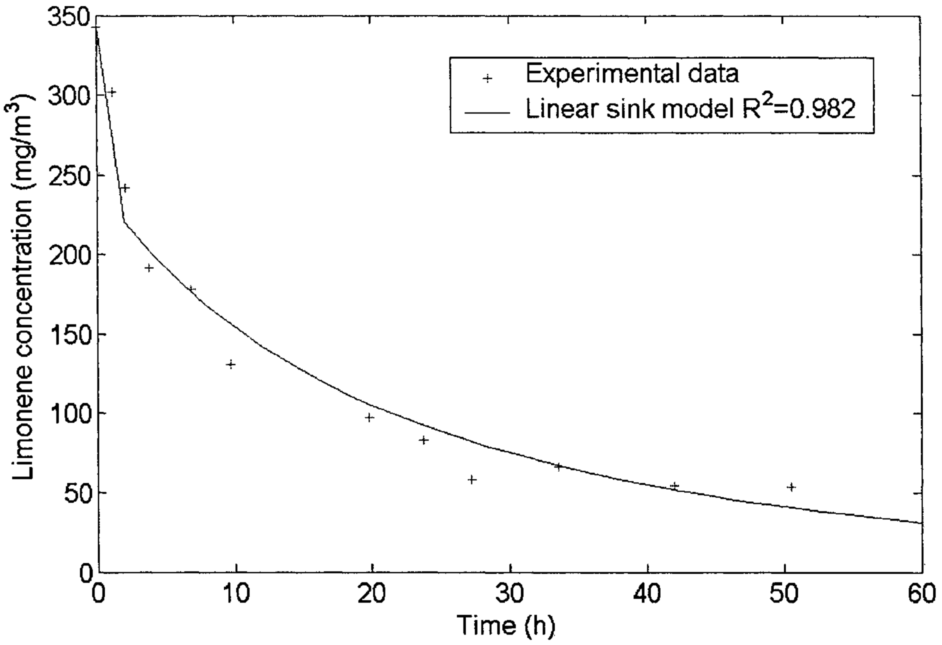
b) Limonene on Carpet



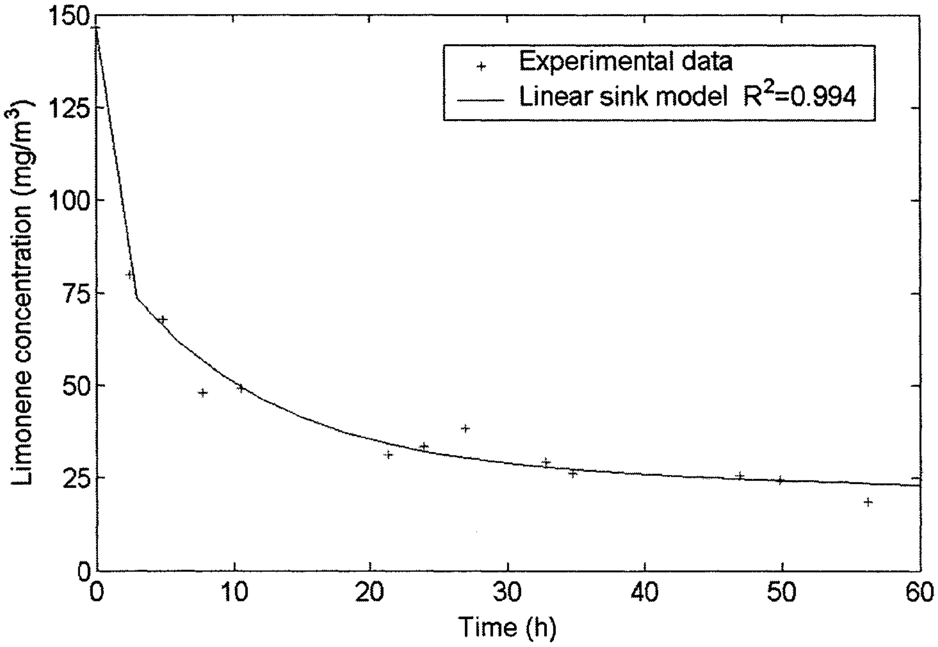
c) Limonene on Cotton



d) Limonene on Empty Chamber



e) Limonene on Gypsum Board



f) Limonene on Polyester

Figure 4.10 Measured Limonene Decay Profiles and IAQ Modeled Results the modified IAQ model with this assumption fit experimental results very well for ACF (R^2>0.99), Moreover, the linear Langmuir model was also attempted to be used for ACF, and it was found that the linear sink model was not able to converge to generate sorptive kinetics or was not able to generate reasonable results in the non-linear fit routine. Thus, the assumption of the non-linear adsorption process and the linear desorption process for ACF is appropriate for this study.

Comparison of Sorptive Kinetics of ACF and Indoor Sink Materials

As referenced to Figures 4.1-4.4, the adsorption isotherms measured in this study and in literature are linear, it can inferred that the K_a and K_e for indoor sink materials, are constants at indoor concentration levels; in other words, they are independent of concentrations. However, as indicated by their units, the K_a and K_e for ACF are associated with ambient concentration of the test chemical. Since the K_a and K_e terms for non-linear adsorption materials such as ACF do not have the same units as linear adsorption materials, direct comparison would not have clear physical significance. Therefore, the K_a and K_e must be adjusted by canceling out the concentration term, defining new terms K_a' and K_e' as:

$$K_a' = K_a / C^{1-n}, \quad K_e' = K_e / C^{1-n} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.6)$$

After converted with the unit conversion factors in Table 4.5 for C^{1-n} term, the K_a' and K_e' terms for ACF, in units of m/h, and m, respectively, decrease with increasing concentration as shown in Figures 4.11 and 4.12. This interesting finding explains why the ACF experienced a faster uptake rate in lower concentrations but a slower uptake rate in higher concentrations as observed in Figures 3.8-3.10. Note that the figures 4.11 and 4.12 are used for illustration purpose and only show a segment of indoor concentration range just because the values of K_a' and K_e' are too large at lower concentrations (i.e., < 0.1 mg/m^3) so that the difference between the lines for these three chemicals cannot be distinguished. Once converted to be in the same

Table 4.5. The Unit Conversion Factors for C^{1-n} at Various Concentrations.

	Conc. (mg/m^3)		
	0.01	**10**	**1000**
Acetone	0.07	3.8	55
Toluene	0.04	4.8	110
Limonene	0.02	6.9	331

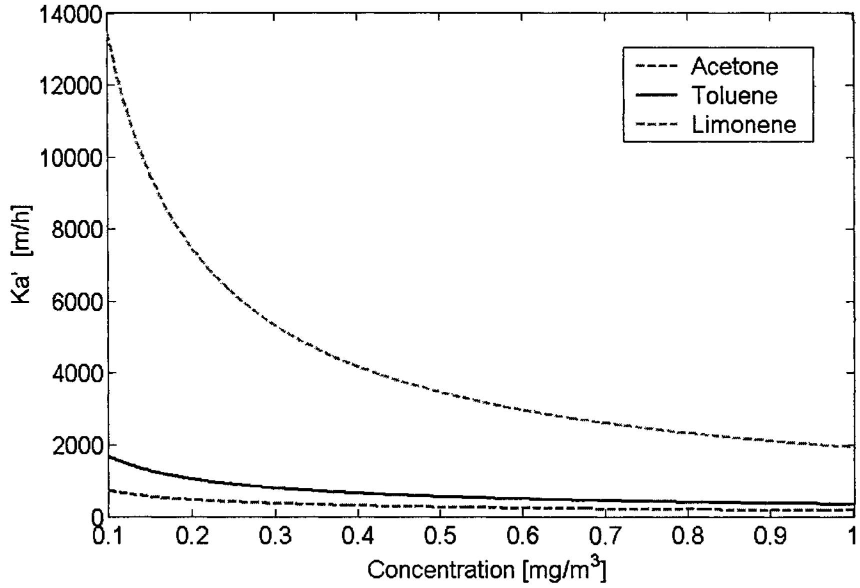


Figure 4.11. Representative Segment of K_a' at Various Concentrations

units as those for indoor sink materials, the results therefore are comparable. The tested VOC adsorption rates and adsorption capacities on ACF are greater than tested indoor sink materials by a factor of 1 to 3 orders of magnitude in the 10 to 1000 mg/m^3 concentration range, and by a factor of 3 to 6 orders of magnitude in the 0.01

to 10 mg/m^3 concentration range, respectively. However, because of limited applicable range of the Freundlich isotherm equation, it may not be legitimate to extrapolate the relationship to a concentration region greater than the tested range in this study. This caveat is particularly important for higher concentrations. Comparison of adsorption capacities between indoor sink materials and ACF at higher concentration (e.g., 50,000 ppm) based on K_e for indoor sink materials and K_e' for ACF would lead to erroneous conclusions. First, the linear Langmuir isotherm may no longer be followed at such high concentration for indoor sink materials. Second, ACF may not follow the Freundlich isotherm because of its limited concentration range of applicability.

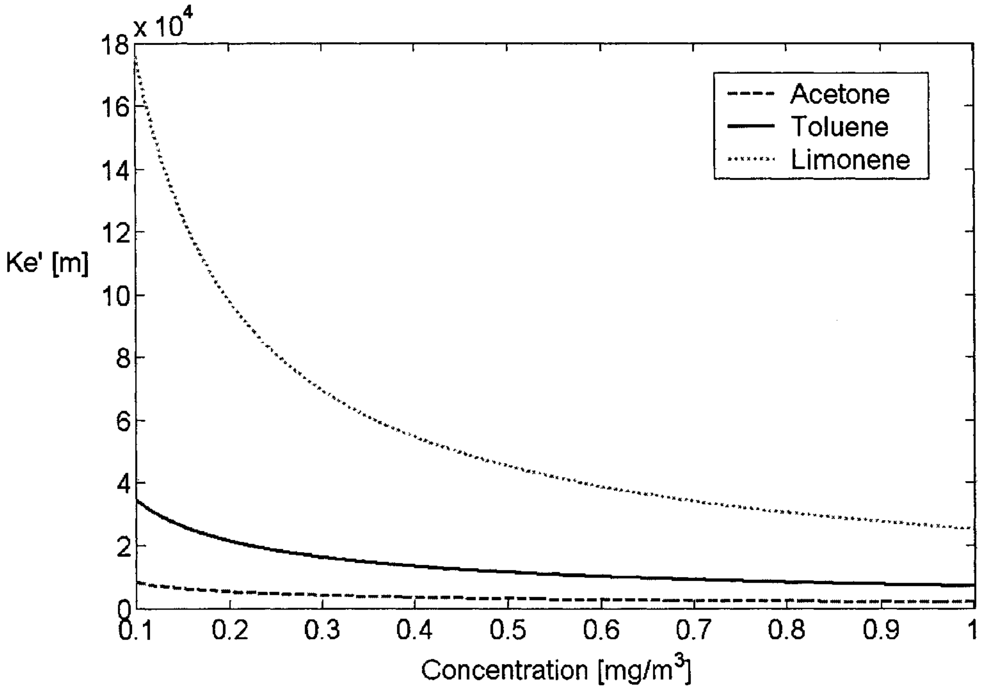


Figure 4.11. Representative Segment of K_e' at Various Concentrations

As referenced to the definitions of K_a and K_e, the uptake rate of an indoor sink material depends on K_a, the larger the K_a, the greater the uptake rate. But the adsorption capacity of an indoor sink material depends on K_e, the larger the k_e, the greater the adsorption capacity. For ACF, the uptake rate depends on K_a', the greater the K_a', the greater the uptake rate of indoor VOCs. The adsorption capacity of ACF depends on K_e'. The larger the K_e', the greater the adsorption capacity. As stated earlier, the K_a' and K_e' for ACF are several orders of magnitude greater than those of indoor sink materials, thus, even though the competitive effect of indoor sink materials was not investigated in this study, it can be stated that the majority of indoor VOCs would be adsorbed by ACF even in the presence of indoor sink materials at typical concentrations encountered indoors. These outstanding adsorption properties for ACF in the passive mode suggest it may be useful for removing indoor VOCs, and thus, reducing both immediate exposures and secondary emissions from indoor sink materials. The applications of ACF could include confined spaces, commercial or residential buildings, offices, space craft air quality improvement, shelter-in-place situations in environmental chemical exposures (whether from accidents or terrorism), etc.

The extent of adsorption of VOCs is highly dependent on test sink materials (adsorbent). When the linear Langmuir adsorption process applies, the adsorption capacity of a sink material is best represented by equilibrium partitioning coefficient, K_e. The higher the K_e value, the greater the mass adsorbed on the sink material at a given concentration. For acetone, the K_e values of different sink materials increase in the following order: test chamber surfaces < polyester < cotton < carpet < gypsum board < ACF. This order is true for toluene except that carpet has a higher K_e than gypsum board. However, for limonene, the increasing sequence in K_e follows: test chamber surfaces < cotton < gypsum board < carpet < polyester < ACF.

For all three test chemicals, the steel test chamber surfaces did show some sink effects, with the strongest sink effect observed for limonene, and weaker sink effects observed for acetone and toluene. The K_e values for these three VOCs range from 0.017 m to 1.42 m. These results indicate that sink effects of the test chamber surfaces may need to be considered in estimating the sorptive kinetics of the test materials as the results are similar to those of indoor sink materials. Polyester and cotton have very similar adsorption behaviors for acetone and toluene. The adsorption rate K_a, desorption rate K_d, and K_e for acetone and toluene for these two materials are nearly the same. However, the adsorption performance for limonene for those two materials differs significantly from that for acetone and toluene. For example, the K_e for polyester is five times more than for cotton. This is probably due to the differences in the interaction between limonene and the two test materials.

Gypsum board has the strongest sink effect among four tested indoor sorptive materials for acetone, while carpet has the strongest effect for toluene. Overall, gypsum board and carpet have higher sink effects than cotton and polyester. However, polyester has a surprisingly high sink effect for limonene, much higher than the other tested materials except ACF. Obviously, the adsorption surface area of polyester is not higher than that of carpet, or even cotton. Thus, it appears that surface chemistry may play an important role in the unusual adsorption behavior of polyester. For building materials exhibiting higher adsorption and equilibrium partition coefficients, they would be expected to reach adsorption/desorption equilibrium more quickly, have a greater impact on reductions in VOC concentrations for short-term sources like spills, newly painted/cleaned houses, etc., and reemit the adsorbed VOCs into the air later, acting as secondary emitters. The larger the K_d, the faster the VOCs reemit into the air, the higher the exposure would be expected. In order to minimize re-emissions from indoor sink materials, those materials could be removed or covered by ACF with much stronger sink effects during a surge of short-term VOC emission.

For a given material, the extent of adsorption was observed to be very sensitive to the test chemicals. As shown in Table 3.1, in general, these three VOCs differ greatly in boiling point, polarity, affinity. As indicated by K_e listed in Tables 4.2 – 4.4, adsorption capacities of all tested materials, including ACF, decrease with polarity and increase with affinity and boiling point. In other words, all test materials are able to adsorb non-polar VOCs easier than polar VOCs, as evidenced by the fact that limonene has much greater adsorption kinetic constants for all test materials than toluene and acetone. The observations presented in this study are consistent with those presented by Won et al. (2000, 2001), An et al. (1999), and Van der wal et al. (1998), who reported that the extent of sorption to a specific material is generally proportionally related to polarity.

Conclusions

The four indoor sorptive materials and the empty test chamber surfaces adsorb all three chemicals tested. The tested VOC adsorption rates and adsorption capacities on ACF are greater than tested indoor sink materials by a factor of 1 to 3 orders of magnitude in the 10 to 1000 mg/m^3 concentration range, and by a factor of

3 to 6 orders of magnitude in the 0.01 to 10 mg/m^3 concentration range, respectively. The excellent adsorption performance in the passive mode compared to indoor sink materials suggests that ACF is promising in removing indoor VOCs in the passive mode even in the presence of and in competition with other indoor materials. Results predicted using an IAQ mathematical model based on linear sink effects for indoor sorptive materials, and non-linear sink effects for ACF, respectively, were in very good agreement with the results observed.

References

An Y., Zhang J. S., and Shaw C.Y., Measurements of VOC adsorption/desorption characteristics of typical interior building materials, HVAC & R Research, 5(4): October 1999.

Elkilani, A.S. et al, Development of model for the estimation of indoor volatile organic compounds concentration based on experimental sorption parameters, Environmental Science & Technology, 33(12): 1999

Elkilani, A.; An indoor air quality model that includes the adsorption of VOCs on fabrics, Trans. IchemE., 79(7B): 233-243, 2001

Elkilani, A.S. et al, Sorption of volatile organic compounds on typical fibers, Environment International, 29: 575-585, 2003.

Evans, W.C., Linear systems compartment modeling, and estimability issues in IAQ studies, In: Tichenor, B.A. (ed.) Characterizing Sources of Indoor Air Pollution and Related Sink Effects, Philadelphia, PA, American Society for Testing and Materials, (ASTM STP 1287), pp. 239-262, 1996.

Jørgensen R.B. and Bjørseth O., Sorption behavior of volatile organic compounds on material surfaces-the influence of combinations of compounds and materials compared to sorption of single materials, Environment International, 25(1):17-27, 1999.

Tichenor B. A., Guo Z., Dunn J.E., Sparks L.E. and Mason M. A., The interaction of vapor phase organic compounds with indoor sinks, Indoor Air, 1: 23-35, 1991.

Van der wal, J. F., Hoogeveen, A.W. and van Leeuwen, L., A quick screening method for sorption effects of volatile organic compounds on indoor materials, Indoor Air, 8: 103-112, 1998.

Won D., Corsi R. L. and Rynes M., New indoor carpet as an adsorptive reservoir for volatile organic compounds, Environmental Science & Technology, 34(19): 4193-3198, 2000

Won D., Corsi R. L. and Rynes M., Sorptive interactions between VOCs and indoor materials, Indoor Air, 11:246-256, 2001.

Yu C. and Crump D., A review of the emission of VOCs from polymeric materials used in buildings, Building Environment, 33(6): 357-374, 1998

CHAPTER V

EVALUATION OF ACTIVATED CARBON FIBER (ACF) FILTERS FOR REMOVAL OF SINGLE VOLATILE ORGANIC COMPOUND (VOC) AND VOC MIXTURES IN INDOOR AIR

Abstract

This study evaluated the effectiveness of ACF that could be used as in-duct ventilation filters for removal of indoor VOCs at subppm levels. Two common indoor VOCs, toluene and acetone, were chosen to represent typical indoor VOCs with a wide range of polarity and boiling points. One species of ACF with a nominal surface area of 2000 m^2/g was tested in this study. The test chamber consisted of a tube-shaped adsorption column, which was maintained at a temperature of 23±1 ^0C. The flow rate of the challenge VOC stream was 1 L/min, corresponding to a face velocity of 0.21 m/s.

The tested ACF species in the active mode exhibited an adsorption capacity of 0.75% to 6.5% weight of test species for acetone in the 0.30 to 7.67 ppm concentration range, and 5.1% to 41.4% weight of test species for toluene in the 0.06 to 13.09 ppm concentration range, respectively. The experimental data fit very well for the two tested chemicals with all three adsorption isotherm equations (R^2>0.96): the Langmuir, Freundlich and Dubinin-Radushkevich, which may be used to predict adsorption

capacities for untested concentrations in the tested concentration ranges. Experimental data indicated that the ACF filter with a residence time of 0.1 second at 60 ppb levels may have a 50% breakthrough lifetime of 4.5 months for toluene, while it may only have 1 month for acetone. Analysis of experimental results indicates that breakthrough times of ACF filters for different challenge VOCs may be extrapolated from high concentrations to low concentrations with good accuracy. VOC mixture adsorption on ACF showed a competitive effect at all tested concentration levels, from 0.33 to 11.6 ppm. For the mixtures of toluene and acetone, due to competitive adsorption effects, the individual VOC adsorption properties on ACF were reduced, but toluene was affected to a lesser extent than acetone.

Introduction

Indoor air quality (IAQ) is an issue of rising concern in the United States. Concern about IAQ is driven mainly by health problems that are thought to be attributable to indoor air pollutant exposure. Building and furnishing materials and consumer products are important sources of VOCs such as toluene, acetone and numerous others in the indoor environment (DiNardi, 2003). While exposure to any one specific pollutant, such as toluene, at levels typically found in IAQ situations, does not cause clinically identifiable symptoms, the combined effects of various compounds found indoors have been associated with a number of symptoms, such as headache, irritation of the eyes and of mucous membranes, irritation of the respiratory system, drowsiness, fatigue and general malaise, collectively referred to as sick building syndrome (SBS) or tight building syndrome (TBS) (Hines et al., 1993).

Three methods of VOC control most commonly employed are source control, ventilation control and removal control. Source control is not always practical; for example, photocopy machines are a necessity in a modern office, and cleaning is very common in buildings--both introduce VOCs into the indoor environment. Increased ventilation can lead to increased energy usage, making this a more costly option. Thus, practical methods need to be developed for the removal of VOCs from indoor environments. Adsorption, absorption, incineration, and catalytic conversion are all removal techniques for VOCs. All have demonstrated applicability in conventional pollution control applications. However, adsorption on activated carbon seems to be the most popular technique currently in use for indoor applications (Ramanathan, 1988). ACF, a new form of activated carbon, offers a number of advantages over granular activated carbon (GAC), which include greatly improved contact efficiency with adsorbates leading to greater rates of adsorption, and superior adsorption capacity and adsorption properties especially at low concentrations of contaminants (Yue and Economy, 2001). Thus it seems that it may offer encouraging solutions for the removal of indoor VOCs, but its performance in indoor applications has not been sufficiently tested.

High VOC concentrations are often encountered indoors with newly applied paint, wet materials, spills, leaks, and household cleaning. The dominant mechanism is evaporation. Research on activated carbon passive adsorption in this scenario was investigated and the results presented in Chapters 3 and 4. The results indicated that ACF is an effective material in removal of VOCs in the passive mode even in the presence of indoor sorptive materials in indoor environments.

Low VOC concentrations are present indoors with dry materials such as particle board, gypsum board, or any off-gassing materials with very low emission rates. For activated carbon application in this scenario, although adsorption of indoor VOCs onto GAC has recently been addressed by some literature (Graham, 1990; Liu, 1995; Muller,1995; Ramanathan, 1988; VanOsdell, 1994, 1995, 1996), Henschel's review (1998) of GAC usage indicates that there still are insufficient data on activated carbon applications for removal of indoor VOCs.

Two important characteristics of activated carbon application for indoor environments are not clear. First, the life span of activated carbon for VOC adsorption in indoor environments remains controversial. Liu (1990) and Weschler (1992) suggested that the life spans of GAC adsorption devices range from a few months to several years based on anecdotal field experience and extrapolations from laboratory studies. Liu (1991) also predicted that GAC had a removal efficiency of 80% with a contact time of 0.06 second at the challenging concentration of 100 ppb after 4000 hours based on the prediction of a mathematical model. In contrast, Graham (1990) reported that the activated carbon breakthrough time for benzene at 287 ppb was 450 hours. Foster (1992) reported ACF breakthrough times for adsorption of benzene and acetone individually at concentrations of approximate10 ppm are around 100 hours. Ramanathan (1988) reported that breakthrough would occur immediately upon after installation of a 15 cm thick granular carbon filter based on his simulation results. His results indicated that GAC may not be suitable for indoor VOC removal.

Second, the results on adsorption capacities of activated carbon in indoor concentrations appear to also be inconclusive. Foster (1992) reported that adsorption capacities of different types of ACF vary from 0.5% to 20 wt % for benzene and acetone individually at concentrations of approximate 10 ppm which are not typical concentrations of indoor VOCs. Graham (1990) reported adsorption capacities for benzene several orders of magnitude higher (in the range of 4-15 wt% of GAC for the concentration range of 0.28-3.2 ppm) than those of Ramanathan's results (in the range of 0.001-0.006% wt% for the concentration range of 0.1-0.17 ppm. Thus, the adsorption capacity of GAC or ACF needs to be more accurately determined in indoor environments.

In addition, mathematical modeling on ACF for indoor applications is not well addressed although some modeling attempts for ACFs were reported (Lordgooei, 2001; Mangun, 1999). While modeling to predict granular activated carbon adsorption capacity and breakthrough time application in industries is documented (Tien,1994; Ruthven, 1984), most of the reported models are too complex to be used from a practical standpoint. A statistical model based on extrapolation from high concentrations to low concentrations would be helpful to predict the lifetime of ACF materials used as in-duct filtration systems. Such a model would allow users to estimate the necessary change-out schedule without involving complicated calculations.

VOCs are often encountered in indoor environments as mixtures, involving several to several hundred chemicals in each scenario. The presence of a VOC mixture presents a two-fold challenge: first, from a health standpoint, the additive or synergistic effect of VOCs could make it difficult to estimate the health risk even though each individual VOC concentration is much below its allowable exposure limits such as permissible exposure limits (PELs) by OSHA, or threshold limit values (TLVs) by

ACGIH. Second is the difficulty of remediation and removal of VOC mixtures. A method that collects efficiently for a single VOC does not necessarily work effectively for a VOC mixture. In order to determine a replacement schedule for activated carbon filters, it is critical to know how the VOC mixture affects breakthrough times and adsorption capacities of individual indoor VOCs, and how differently it affects individual VOCs with different properties. Literature on VOC mixture adsorption properties onto ACF at indoor concentration levels has not been found. It is desirable to characterize how one VOC's presence influences the ACF adsorption property on other VOCs at indoor levels.

This research focuses on examining the applicability of indoor VOC adsorption onto activated carbon fibers. The goals of this research were: 1) to characterize and model adsorption capacities for the selected VOCs on the ACF; 2) to establish a statistical model to predict breakthrough time for untested indoor concentration levels; and 3) to characterize competitive adsorption profiles of the binary mixture and predict each component's adsorption capacities by using the Ideal Adsorbed Solution Theory (Vahdat et al., 1994).

Materials and Methods

In this study, in order to obtain the challenge VOC in the 60 ppb to 13 ppm concentration range, the VOC from the acetone gas cylinder of 100 ppm and the toluene gas cylinder of 118 ppm was diluted with purified house air. The purification process involved a particulate filter and an oil filter for removal of house air contaminants, and a zero air generator (Matheson Model MGEN-ZRC 3500, 3.5 lpm) for eliminating any excess hydrocarbons to below 0.1 ppm hydrocarbons measured as methane. Rotameters were used for flowrate measurement. The challenge VOC concentration desired was obtained by adjusting flowrate ratio of dilution air to VOC from calibrated cylinders.

Considering polarity and boiling point effects on activated carbon adsorption, three very common indoor VOCs with different polarities and boiling points (as shown in Table 5.1): toluene, limonene and acetone (ranging from low to moderate polarity) - were initially chosen for use in the project. However, the author found that limonene was not stable above room temperature if permeation devices were used as the source of the VOC (Zhang, 2001); moreover, a limonene cylinder was not commercially easily available, and thus, limonene was not used in this project. In spite of its elimination in the project, toluene and acetone still can represent a broad spectrum of polarities and boiling points of VOCs.

Table 5.1: Selected VOCs' Physicochemical Properties

Characteristics	Chemical Name		
	Limonene	Toluene	Acetone
Chem. class	Terpene HC	Aromatic HC	Ketone
Formula	$C_{10}H_{16}$	$C_6H_5CH_3$	CH_3COCH_3
Molecular weight	136.24	92.1	58.08
Vapor pressure, kPa @25^{0}C	2.67	3.85/2.93	28.6/30.9
Boiling point, ^{0}C	175-177	110.8	56.2
Water solubility, mg/L	1.80	526.00	1000000.00
Polarity	———	———	——→
Refractive index	1.47	1.50	1.36
Density of liquid, g/cm^3	0.84	0.87	0.79
Affinity coefficient	1.73	1.18	0.62

To simulate a scaled down version of an in-duct ACF filtration system, ACF was placed in one end of a test chamber. It consisted of a tube-shaped adsorption column with a diameter of 1.0 cm. A GC o-ring was used to fasten the ACF to the supporting end which has many small holes to let the air pass through. The challenge flow rate was fixed at 1 lpm with a corresponding face velocity at the surface of the ACF at 0.21 m/s, which falls into the 0.1-1.0 m/s face velocity range for in-duct ventilation filters. Each piece of ACF cloth has a thickness of 0.59 mm with a density of 151g/m^2, and a nominal surface area of 2000 m^2/g. Adsorption capacities and breakthrough times of activated carbon for toluene and acetone were investigated in the concentration range of 50 ppb to 13 ppm. Adsorption properties of activated carbon for VOC mixtures were also tested in this project.

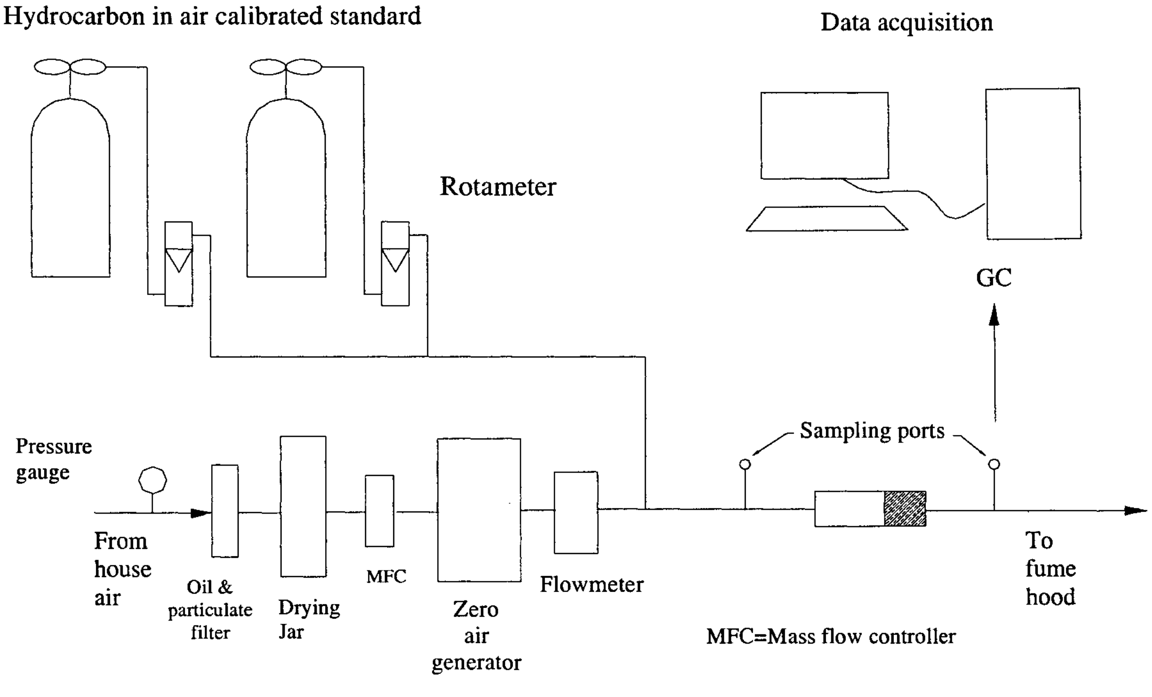


Figure 5.1. Experimental Setup Diagram

The diagram above (Figure 5.1) shows the basic configuration of the test system. This setup was housed in a room maintained at a temperature of 23±1 ^{0}C. Air samples were collected by Supelco charcoal sampling tubes (Cat. No.20267-U) at two sampling ports (upstream for inlet concentration, downstream for outlet concentration) in front of and after the adsorption column. The sampling flow rate ranged from 100 to 200 ml/min. Sample collection was followed immediately by CS_2 desorption and analysis by a Varian GC (Model 3900) using a flame ionization detector (FID) with a HP-1 capillary column (dimensions of 30 m*0.53 mm, I.D 1.5 μm).

Results and Discussion

Determination of ACF Bed Depth

After several initial trials, the author found that it took more than three weeks to complete an experiment at 1 ppm for toluene if an ACF bed depth corresponding to residence time of 0.1 second was used. If the breakthrough times of the ACF filters tested at a longer bed depth were able to be extrapolated from the results tested at shorter bed depth, much time could be saved to accomplish experiments. Thus, the relationship between breakthrough times and adsorption length of ACF filters was examined in this study. Different studies used various definitions of breakthrough time. Considering the low VOC concentrations in typical indoor environments, 50% breakthrough time, defined as time to reach 50% of the challenge concentration exiting the ACF filter, would be a cost effective choice for ACF filter replacement, therefore, it was used in this study. For convenience, different amounts of ACF filter disks were stacked in the adsorption column to provide different adsorption bed depths and residence times. For this test purpose, the challenge concentrations for toluene and acetone were 13 ppm and 7.7 ppm, respectively. Experimental results showed that the adsorption capacities of ACF for toluene and acetone remained constant (coefficient of variance less than 12.3%), but breakthrough time was linearly related to adsorption length as shown in Figure 5.2. Therefore, in order to expedite the experiment process, all experiments were performed thereafter with the use of 4 pieces of ACF in each test.

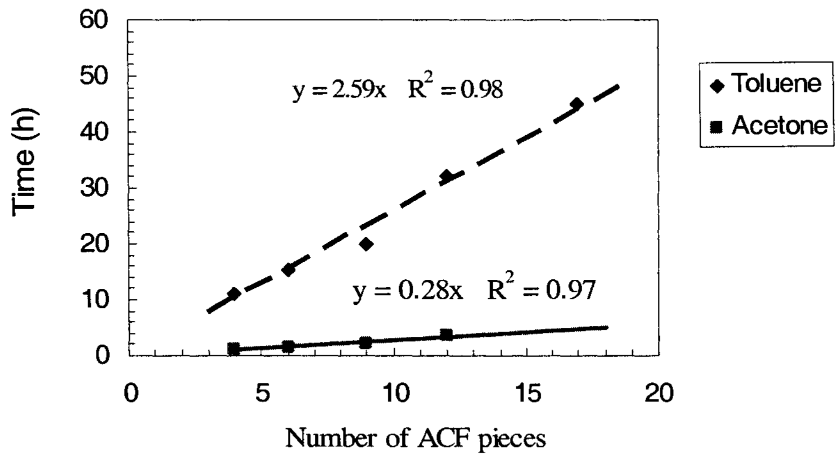


Figure 5.2 The Relationship Between Breakthrough Time and the Number of ACF Pieces, (◆) Toluene, 13.1 ppm; (■) Acetone, 7.7 ppm.

Table 5.2. Adsorption Capacities and Breakthrough Time of VOC Adsorbates on the ACF

	Concentration ppm	Adsorption Capacity mg VOC /g ACF	50% breakthrough time, h	Number of experiments, N
Acetone	0.30	7.50	18	1
	1.38	20.1±3.03	9	3
	3.83	32.90	3.3	1
	7.67	59.5±7.33	1.1	6
Toluene	0.06	51.10	362	1
	0.26	136.93	119	1
	2.52	274.6±14.53	35	3
	3.62	298.98	32	1
	9.94	364.89±9.21	12	3
	13.09	413.60	11	1

The experimentally determined adsorption capacities and breakthrough times for toluene and acetone as a function of concentration are summarized in Table 5.2. As shown in Table 5.2, adsorption capacities increase with concentration for both toluene and acetone, while breakthrough times decrease with concentration. However, ACF has a greater adsorption capacity and much longer breakthrough time for toluene than for acetone.

Adsorption Isotherms

There are various adsorption isotherms describing the relationship between adsorption capacity and adsorbate concentration. Among them, the Langmuir equation is the simplest and one of the most frequently used monolayer theoretical adsorption models, which apply to cases where there is no interaction among adsorbate molecules on the surface of an adsorbent. Considering indoor VOC concentrations are usually in the subppm levels, the Langmuir equation may work very well in this concentration region.

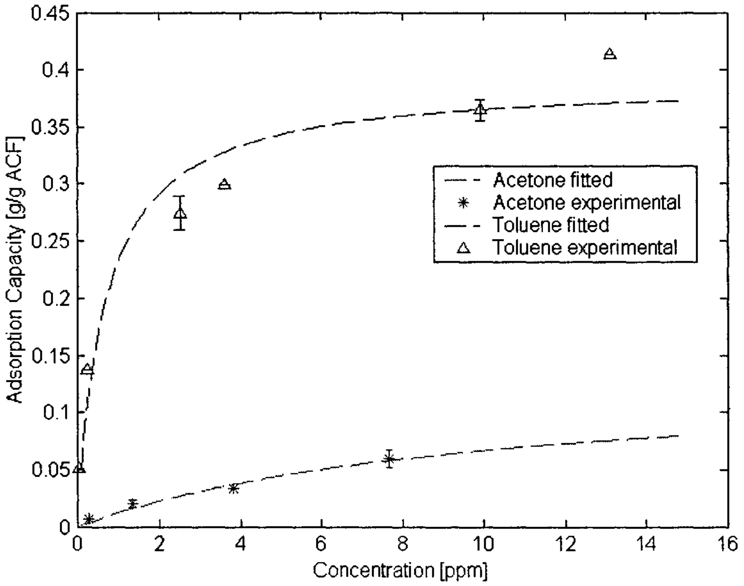


Figure 5.3 Correlations of the Langmuir Equation for Acetone and Toluene adsorption on ACF, (Δ) Toluene R^2=0.99; (∗) Acetone R^2=0.99.

The Langmuir equation can be expressed as:

$$q = \frac{mkC}{1 + kC} \quad \text{...} \quad (5.1)$$

where q is the adsorption capacity (g/g), C is the adsorbate equilibrium concentration (ppm), and m and k are adsorption constants, in the units of g/g and ppm^{-1}, respectively. The constants m and k are specific for each chemical and can be obtained from a SAS nonlinear regression of q vs. C for each set of experimental data. The adsorption constants determined through this method are shown in Table 5.3. As indicated in Table 5.3 and shown in Figure 5.3, the Langmuir equation can be reasonably fitted by the experimental data with good correlation ($R^2 = 0.99$). The shape of acetone adsorption isotherm in the test concentration region appears to be close to a straight line, while toluene adsorption isotherm exhibits as a curve. When the kC term becomes very small, it can be ignored, and the Lagmuir isotherm equation can be reduced to a linear form. It can be seen from Table 5.3, the k value for acetone is much smaller that for toluene. Thus, the adsorption isotherm of acetone appears to be linear in the test concentration region.

Table 5.3 Langmuir Parameters for VOC Adsorbates and ACF

	Acetone	Toluene
m (g/g)	0.13	0.39
k (ppm^{-1})	0.10	1.45
R^2	0.99	0.99

The Freundlich isotherm is an empirical equation and may be derived by assuming that an adsorbent has a heterogeneous surface composed of different pore sizes of adsorption sites. Based on the Freundlich expression, the amount adsorbed increases infinitely with increasing concentration. The Freundlich equation may be represented as:

$$q = kC^n \quad \text{...} \quad (2)$$

When a challenge adsorbate concentration approaches zero, the Langmuir equation reduces to a linear form, frequently identified as the Henry's law equation, while the Freundlich equation does not reduce to a linear form, if n is not close to unity. Therefore, one should be cautious about using the Freundlich equation when it applies to indoor air pollutants (Hines, 1993). Moreover, the Freundlich is only useful for limited adsorbate concentration ranges (Cal, 1995), which are dependent on the combination of adsorbate and adsorbent. Thus, how well the Freundlich equation would work for the current study is examined here. Since there is a linear relationship between adsorption capacity and adsorbate concentration (or partial pressure), when this expression is plotted on log-log scales as shown in Figure 5.4, k and n can be obtained from the intercept and

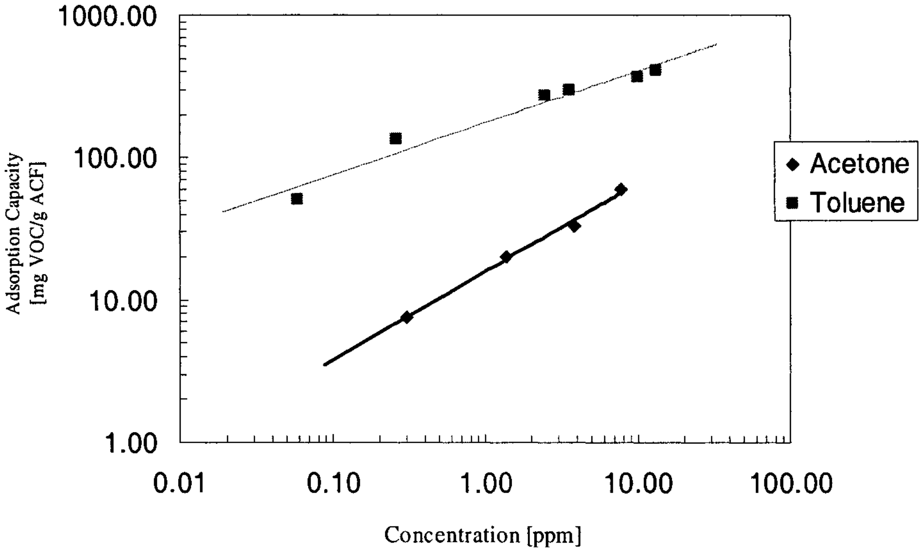


Figure 5.4 Correlations of the Freundlich Equation for Acetone and Toluene Adsorption on ACF, (◆) Acetone R^2=0.96; (■) Toluene R^2=0.99.

slope of the linear regression plot. Usually, n has a value less than unity (Tsai, 1999). The Freundlich parameters, k and n were thus determined for toluene and acetone and are presented in Table 5.4. As indicated by the coefficient of determination (R^2), the Freundlich model predictions were in good correlation with the experimental data; in other words, the Freundlich equation works very well in the tested concentration ranges for both toluene and acetone.

Table 5.4 Freundlich Parameters for VOC Adsorbates and ACF

	Acetone	Toluene
k	15.80	175.91
n	0.62	0.36
R^2	0.96	0.99

The Dubinin-Radushkevich (D-R) isotherm is one of the equations proposed by M.M. Dubinin based on the theory of volume filling of micropores (TVFM). Dubinin proposed that adsorption is characterized by volume filling within the adsorption space instead of forming adsorption layers in a porous adsorbent. On the basis of the potential theory, Dubinin and his co-workers proposed the Dubinin-Radushkevich equation as follows:

$$\ln W = \ln W_0 - \left(\frac{1}{\beta E_0}\right)^2 A^2 \quad \text{..........................} \quad (5.3)$$

Where: W----Volume of the adsorbate adsorbed at temperature T, cm^3/g

W_0---- Total volume of micropores of ACF, cm^3/g

$A = RT \times \ln(P_0/P)$, the maximum differential molar work, needed to transport one mole of the adsorbate from the liquid or gas phase to a surface of an infinitely large amount of the adsorbent, J/mol, P_0, saturation vapor pressure; P, partial pressure of adsorbate at equilibrium

β ---- Affinity coefficient and is the ratio of adsorption potentials of the adsorbate to a reference adsorbate, with respect to benzene in this project

E_0----Characteristic adsorption energy

The plot of the adsorption isotherms for each of the adsorbates and the ACF is presented in Figure 5.5. The Dubinin-Radushkevich parameters obtained for the adsorption of acetone and toluene are presented in Table 5.5. As observed from the coefficient of determination (R^2), experimental results fit the DR model very well for the two VOC adsorbates examined in this study. Because the DR equation is able to fit the entire range of type I adsorption isotherm which is applicable for activated carbon adsorption, where the Freundlich isotherm is only accurate over limited

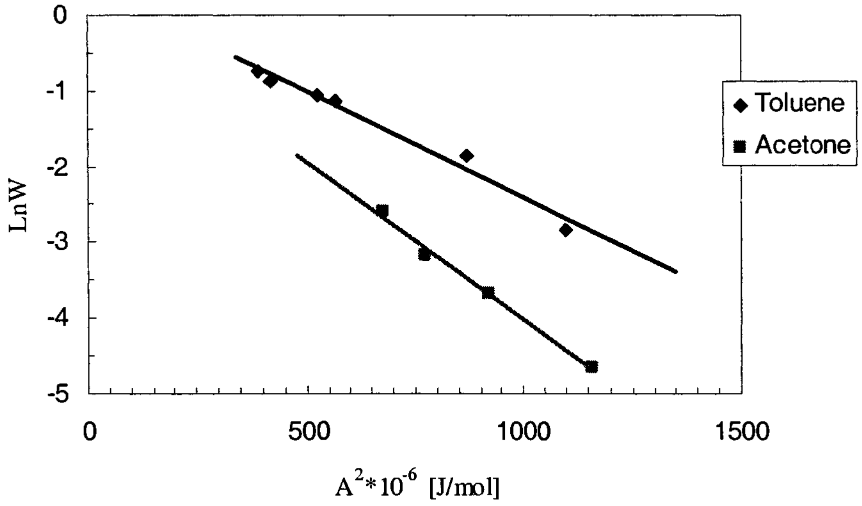


Figure 5.5 Correlations of the Dubinin-Radushkevich Equation for Acetone and Toluene Adsorption on ACF, (◆) Toluene R^2=0.96, (■) Acetone R^2=0.98.

concentration ranges, if a more accurate estimation is sought, the use of DR equation is recommended (Cal, 1995).

Table 5.5 DR Parameters for VOC Adsorbates and ACF

	ACF-20	
Compound	Toluene	Acetone
Max adsorbed weight W_0 [mg/g]	1283.16	900.49
Total effective volume V_0 [cm^3/g]	1.48	1.14
Adsorption energy Eo [KJ/mol]	22.49	16.13
Micropore half-width x_0 [nm]	0.53	0.74
$x_0\beta$ [nm]	0.63	0.58
R^2	0.96	0.98

Breakthrough Time

It is time-consuming and expensive to test the breakthrough times for activated carbon filters at subppm levels that are routinely found indoors. If breakthrough times measured at higher concentration levels can be extrapolated to low levels, then it would be a much more convenient process in terms of cost and time to predict the replacement time for activated carbon filters applied indoors. In this study, the breakthrough times of ACF filters for both toluene and acetone at various concentrations were characterized as shown in Figures 5.6 and 5.7. All curves exhibited asymmetrically sigmoid shapes with longer breakthrough times at lower concentrations. For a given ACF and contaminant, plotting the breakthrough times at a given percent at various concentrations:

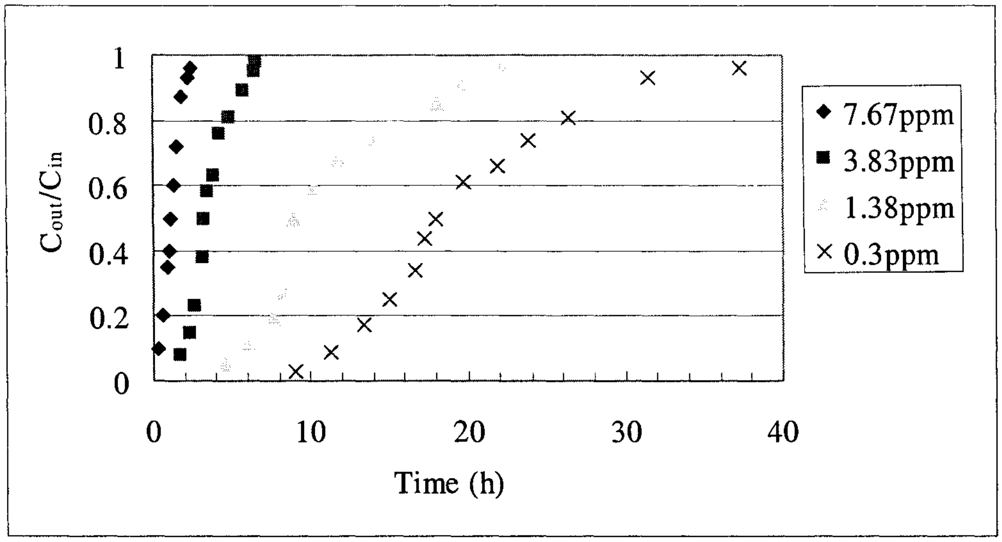


Figure 5.6 Breakthrough Curves for ACF-20 at Various Concentrations of Acetone

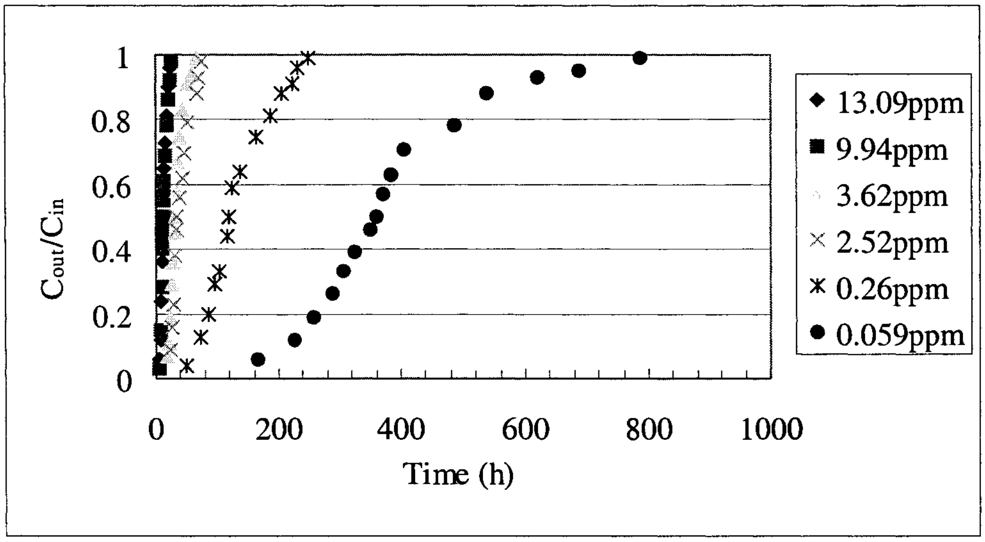


Figure 5.7 Breakthrough Curves for ACF-20 at Various Concentrations of Toluene

in logarithmic scales formed a family of straight lines. In this case, the 50% breakthrough times for both toluene and acetone vs concentrations were plotted in logarithmic coordinates as shown in Figure 5.8. The breakthrough times at lower concentrations can then be extrapolated from the results of higher concentrations.

Mathematically, the relationships can be represented as the following empirical equations (Eqs. 5.4 and 5.5):

For toluene:

$$\log(t_b) = -0.63\log(C) + 1.77 \quad \text{......................} \quad (5.4)$$

For acetone:

$$\log(t_b) = -0.83\log(C) + 0.92 \quad \text{......................} \quad (5.5)$$

Generally,

$$t_b = AC^B \quad \text{..................................} \quad (5.6)$$

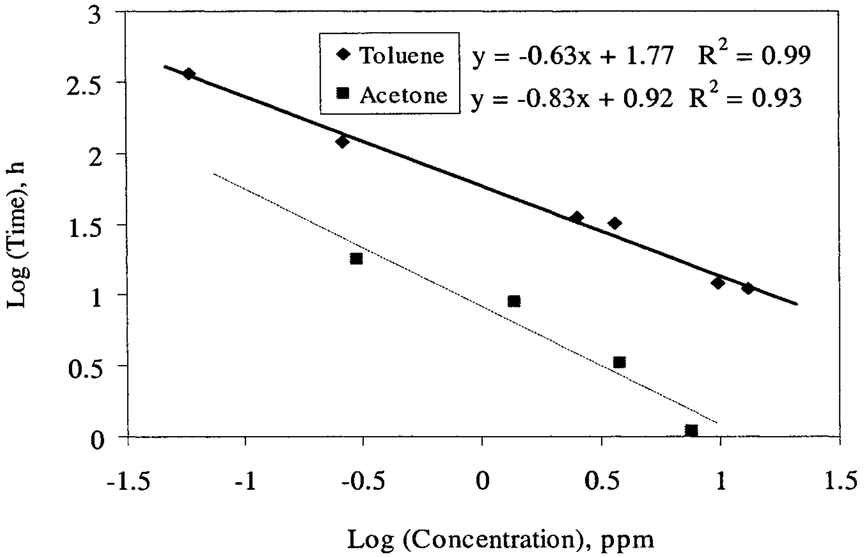


Figure 5.8 Correlations of Breakthrough Time and Challenge Concentration in Log Scale for Acetone and Toluene Adsorption on ACF, (◆) Toluene R^2=0.99, (■) Acetone R^2=0.93.

where t_b is the breakthrough time, C is the concentration, and A and B are constants for a given combination of test chemical and test adsorbent. Taking the ratio of two breakthrough times with different concentrations for a given combination of test chemical and test adsorbent, the following relationship is obtained:

$$\frac{t_{b,\ low\ conc.}}{t_{b,\ high\ conc.}} = \left(\frac{low\ concentration}{high\ concentration}\right)^{B} \quad \text{..........................} \quad (5.7)$$

Nelson and Harder (1976) reported an averaged B of -0.67 with a standard deviation of ±0.17 based on nine solvent vapors tested in the range of 50 to 3000 ppm, which included acetone, benzene, carbon tetrachloride, hexane, diethylamine, isopropyl alcohol, methyl chloroform, methyl acetate and dichloromethane vapors. The results obtained in this current study agree very well with the literature, which means that the relationship that breakthrough time is inversely proportional to challenge concentration in log-scale is valid for both concentration at industrial levels and concentration at indoor levels. This relationship allows us to extrapolate the breakthrough time for indoor VOC filters based on results from higher concentrations at which ACF breakthrough time has been tested.

Adsorption of VOC Mixtures on ACF

Adsorption Profile Characterization

Indoor VOC pollution does not normally result from a single compound. In most cases, tens or hundreds of VOCs can be found in typical indoor environments. Yu (1998) reported that more than 900 VOCs were detected during a US EPA survey of indoor air quality. However, the properties of ACF adsorption for VOC mixtures is not clear; in other words, how one compound's presence influences another compound's adsorption onto ACF is not known at indoor concentration levels. The adsorption of mixtures of acetone and toluene on ACF at different concentrations has been investigated in this

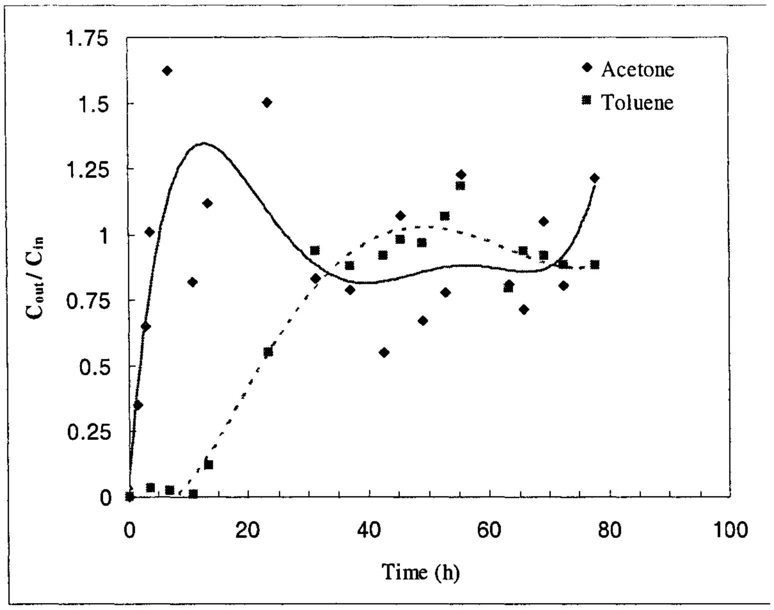


Figure 5.9 Adsorption Profiles of Acetone and Toluene Mixture on ACF, (♦) Toluene, Concentration = 2.8 ppm, (■) Acetone, Concentration = 2.5 ppm.

study. Figure 5.9 presents the adsorption profiles of an acetone-toluene mixture onto ACF.

As shown in Figure 5.9, competitive adsorption was present immediately upon initiation of the adsorption experiment. Both acetone and toluene were competing for smaller microporous sites which possess higher adsorption potential. Adsorption first takes place in the higher-energy sites and progressively fills the lower-energy sites. The forces on adsorbate molecules are a function of distance between adsorbates and adsorbent atoms (pore size) and polarity (permanent or induced) of the adsorbate and adsorbent atoms (Marsh, 1987). Due to toluene's non-polar nature, toluene usually has a larger adsorption force with adsorption sites; thus, toluene can displace part of the adsorbed acetone which may lead to effluent concentration of acetone greater than challenge concentration at a later time. Moreover, the competitive adsorption process was dynamic and interactive which was manifested by the presence of both adsorption and desorption simultaneously. The face velocity of VOC filters may play an important role in adsorption equilibrium. Even though the effect of face velocity has not been investigated in this study, it is generally believed that increasing face velocity would decrease adsorption capacity of the adsorbent and increase the turbulence of the adsorption process and thus may carry away some weakly adsorbed molecules (Yoon and Nelson, 1984).

Binary Mixture Effect on Individual Component Breakthrough Times

The atmosphere in indoor environments usually contains more than one VOC. As a result, the effect of a VOC mixture on ACF breakthrough time needs to be investigated in order to estimate change-out time for in-duct ventilation VOC filters. Table 5.6 presents the breakthrough times (BT) of individual components and binary mixture for both acetone and toluene. As shown in Figures 5.10 and 5.11, the presence of toluene has much a greater impact on the breakthrough time of acetone than that of acetone on toluene, especially at lower concentrations. Compared to the results of single compounds, the breakthrough times of acetone in mixtures are reduced by 35% to 64%,

Table 5.6. Breakthrough Time (BT) of Single Component and Binary Mixture for Acetone and Toluene

n	Acetone			Toluene		
	Conc., ppm	BT--single, h	BT--mixture, h	Conc., ppm	BT--single, h	BT--mixture, h
3	10.2	1.2	0.76 ± 0.07	11.6	12.5	9.8 ± 0.45
1	4.9	2.2	1.2	5.4	20.4	17.1
3	2.4	3.9	2.3 ± 0.15	2.8	30.8	23.4 ± 0.82
2	0.75	10.6	4.1	1.69	42.3	39.8
3	0.33	20.9	7.0 ± 0.5	1.1	55.5	53.5 ± 0.95

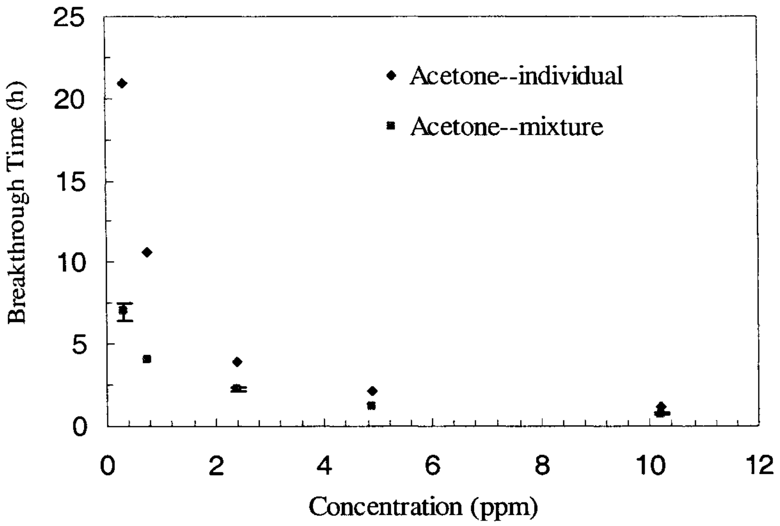


Figure 5.10 Breakthrough Time of Individual Component and Binary Mixture for Acetone.

while the breakthrough times of toluene in mixtures are reduced in a much smaller scale, from 2.7% to 20%. This was commensurate with the mixture effect on adsorbate adsorption capacity onto ACF, that is, mixture effect on ACF adsorption capacity of acetone was much greater than that of toluene. However, the effects of a binary mixture on both adsorption capacity and breakthrough time for acetone and toluene do have a characteristic in common, namely, the presence of another compound will decrease ACF adsorption properties of individual components.

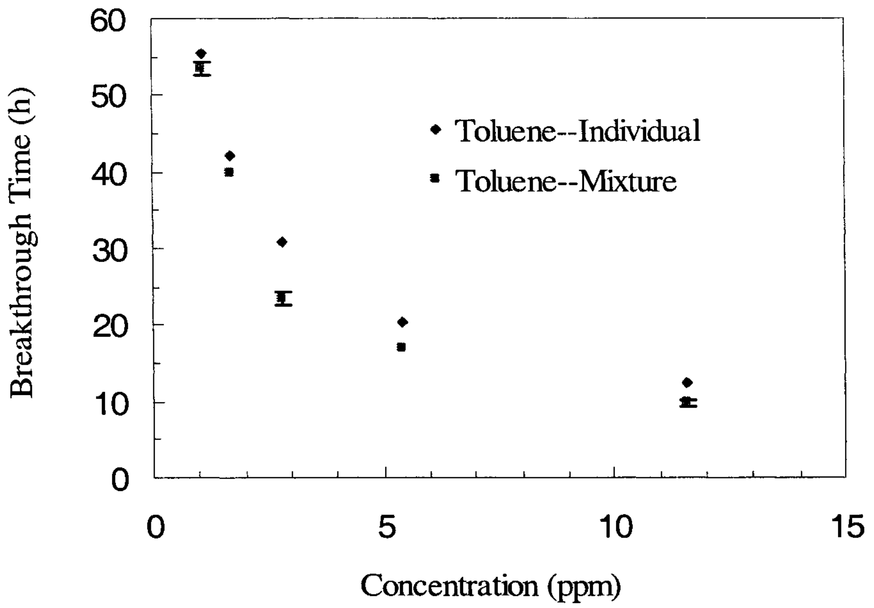


Figure 5.11 Breakthrough Time of Individual Component and Binary Mixture for Toluene.

Adsorption Prediction of A Binary Mixture on ACF

Experimental data on the adsorption of vapor mixtures on activated carbon are limited, since it is difficult to obtain data for complete breakthrough curves for different concentrations of VOCs in each vapor mixture / adsorbent system (Vahdat et al., 1994). Indoor air represents an extreme example of multi-component adsorption, because several hundred organic compounds may be present. A method that can predict the adsorption performance of adsorbents in the presence of VOC mixtures based on the performances of the individual components would reduce the need to collect extensive experimental data. Several methods have been proposed as listed in a review written by Ruthven (1984) and include Bering et al., Grant and Manes, Myers and Prausnitz (Bering et al., 1972; Grant and Manes, 1966; Myers and Prausnitz, 1965). After evaluating different methods, the Ideal Adsorbed Solution Theory (IAST) seemed to be practical to this current study. Thus, only IAST proposed by Myers and Prausnitz was examined.

In IAST, the following basic equations are used to predict multi-component isotherms from single-component adsorption isotherms:

$$X_1 = \frac{py_1}{p_1^0(\Pi)} \qquad X_2 = \frac{py_2}{p_2^0(\Pi)} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5.8)$$

where: X_1, X_2 : mole fractions of components in adsorbed phase.

y_1, y_2: mole fractions of components in the gaseous mixture,

p: the total pressure of the test system [Pa],

$p_i^0(\Pi)$: partial vapor pressure of adsorbate in standard state [Pa],

Π is the spreading pressure of the adsorbed phase [N/m], which corresponds to the difference in surface tension between a clean surface and an adsorbate-covered surface.

ψ_i^0 is surface potential of the adsorbent of ith component at standard state [mol/kg], which can be expressed as:

$$\psi_i^0 = \frac{\Pi A}{RT} = \int_0^{p_i^0} \frac{W_i^0}{p} dp \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5.9)$$

where: A : the specific surface area [m^2/kg],

R : the gas constant [8.3145 J/(mol-K)],

T : temperature [K], and

W_i^0 : adsorption capacity of single component i, mol/g.

Adsorption capacity of single component W_i^0 can be characterized by the Langmuir isotherm, which is given by:

$$W_i^0 = \frac{m_i k_i P_i^0}{1 + k_i P_i^0} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(5.10)}$$

where m_i and k_i are Langmuir constants for component i. They are available in Table 5.3.

At equilibrium, the spreading pressure should be the same for all compounds (Myers and Prausnitz, 1965), for this study, we have:

$$\Pi_1 = \Pi_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(5.11)}$$

Combining Equations 5.9, 5.10 and 5.11 yields:

$$m_1 \ln(1 + k_i p_1^0) = m_2 \ln(1 + k_2 p_2^0) \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(5.12)}$$

Based on mole fraction of binary mixture in this study, we have:

$$X_1 + X_2 = 1 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(5.13)}$$

Substitution of Equation 5.8 into Equation 5.13 yields:

$$\frac{py_1}{p_1^0} + \frac{py_2}{p_2^0} = 1 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(5.14)}$$

Combining Equations 5.8 and 5.14, p_1^0 and p_2^0 can be obtained. Thus, X_1 and X_2 will be obtained also. The total amount adsorbed can be calculated from the following equation (Myers and Prausnitz, 1965):

$$\frac{1}{W_t} = \frac{X_1}{W_1^0} + \frac{X_2}{W_2^0} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(5.15)}$$

The adsorption capacity for the individual components can be found from the following expression:

$$W_1 = W_t X_1 \qquad W_2 = W_t X_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(5.16)}$$

where: W_1^0, W_2^0 = adsorption capacity of single component 1 and 2, respectively (mol/g),

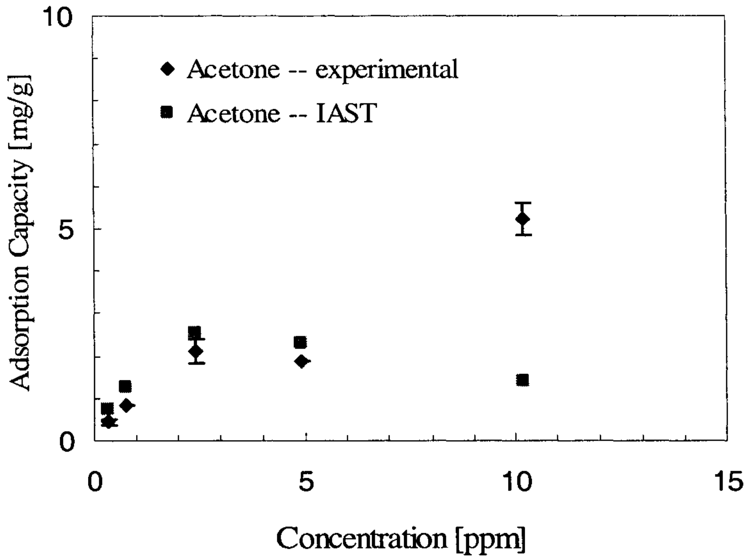


Figure 5.12 ACF Adsorption Capacity of Acetone Based on Experiments and Prediction by IAST

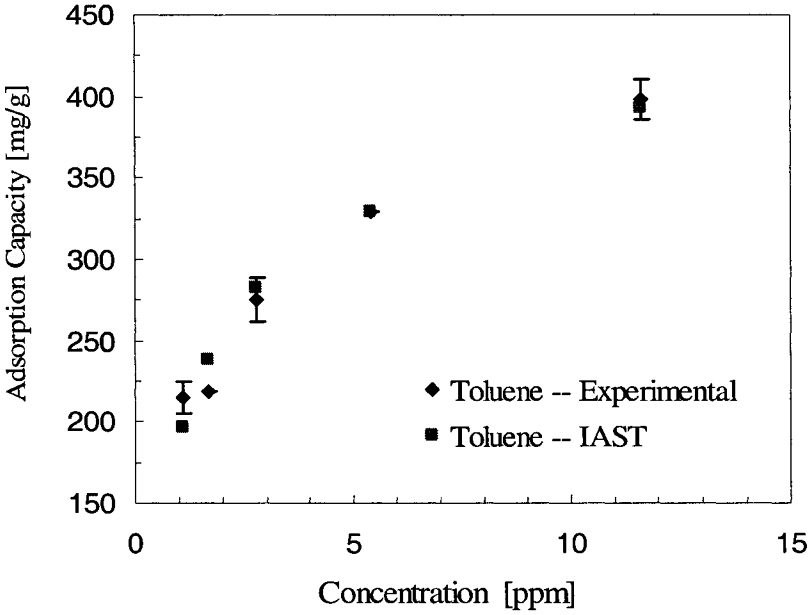


Figure 5.13 ACF Adsorption Capacity of Toluene Based on Experiments and Prediction by IAST

Table 5.7 Adsorption Capacities of Single Component and Binary Mixture for Acetone and Toluene Based on Experimental and IAST.

n	Acetone			Toluene		
	Conc., ppm	Experimental, mg/g	IAST, mg/g	Conc., ppm	Experimental, mg/g	IAST, mg/g
3	10.2	5.25 ± 0.37	1.4	11.6	398.39 ± 12.63	393.7
1	4.9	1.88	2.3	5.4	329.1	329.4
3	2.4	2.12 ± 0.3	2.53	2.8	275.58 ± 13.82	282.7
2	0.75	0.83	1.27	1.69	219.38	238.2
3	0.33	0.45 ± 0.08	0.75	1.1	214.7 ± 9.94	196.4

W_t = total adsorption capacity (mol/g),

W_1, W_2 = adsorption capacities of the components in a binary mixture (mol/g)

For binary mixtures of acetone and toluene, the adsorption capacities from experimental results and IAST are presented in Table 5.7. As shown in Figures 5.12 and 5.13, IAST predicted results agree visually very well with experimental results, indicating that IAST may be a good method to estimate ACF adsorption capacities of VOC mixtures at indoor levels.

Conclusions

ACF has very good adsorption capacities for VOCs even at indoor concentration levels. The Langmuir, Freundlich and Dubinin-Radushkevich equations can be used to predict adsorption capacity. Experimental data indicated that the ACF filter with a residence time of 0.1 second at 60 ppb levels may have a 50% breakthrough lifetime of 4.5 months for toluene, while it may only have 1 month for acetone. Extrapolation of breakthrough time from high challenge concentrations to low challenge concentrations can be achieved with good accuracy. Competitive adsorption in a VOC mixture is present, which shortens breakthrough times for each component in the mixture, and reduces adsorption capacities. The effectiveness of the Ideal Adsorbed Solution Theory has been demonstrated in predicting individual adsorption capacities for the experimental acetone-toluene mixtures.

References

Being, B. P., Sperpinskii, V. V. and Surinova, S. I., Acad. Sci. USSR Bull.,Div.Chem. Sci., (2):381, 1972

Cal, M. P., Characterization of gas phase adsorption capacity of untreated and chemical treated activated carbon cloths, Doctoral Thesis, UIUC, Illinois, 1995

DiNardi, S. R. The Occupational Environment: Its Evaluation, Control and Management, AIHA press, Second edition, 2003

Foster, K.L., Fuerman, R. G., Economy, J., Larson, S. M., and Rood, M. J., Adsorption characteristics of trace volatile organic compounds in gas streams onto activated carbon fibers, Chem. Mater., 4:1068-1073, 1992

Graham, J., and Bayati, M., The use of activated carbon for the removal of trace organics in the control of indoor air quality, Proceedings of Indoor Air '90, Toronto, Canada, 133-138, 1990

Grant, R. J. and Manes, M., Correlation of some gas adsorption data extending to low pressures and supercritical temperatures, Ind. Eng. Chem. Fundam., 3(3):221-224, 1964

Henschel, D. B., Cost analysis of activated carbon versus photocatalytic oxidation for removing organic compounds from indoor air, Journal of the Air and Waste Management Association, 48: 985-994, October, 1998

Hines, A. L., and Cliffs, E., Indoor Air Quality and Control, PTR Prentice-Hall, Inc, 26-257, 1993

Liu, R., Removal of volatile organic compounds in IAQ concentrations with short carbon bed depths, Proceedings Indoor Air '90, 177-182. Atlanta: American Society of Heating, Refrigerating and Air-Conditioning Engineers, Inc., 1990

Liu, R.T., Modeling activated carbon adsobers for the control of volatile organic compounds in indoor air, Far East Conference on Environmental Quality, 1991, Hong Kong, ASHRAE , Nov.,5-5, 1991,

Liu, R., Filtration and indoor air quality: a practical approach, ASHRAE Journal, February, 18-23, 1995

Lordgooei, M., Rood, M. J., and Rostam-Abadi, M., Modeling effective diffusity of volatile organic compounds in activated carbon fiber, Environmental Science and Technology, 35: 613-619, 2001.

Mangun, C. L., Braatz, R. D., Economy, J., and Hall, A. J., Fixed bed adsorption of acetone and ammonia onto oxidized activated carbon fibers, Ind. Eng. Chem. Res., 38: 3499-3504, 1999.

Marsh, H., Adsorption methods to study microporosity in coals and carbons—a critique, Carbon, 25(1): 49-58, 1987

Meininghaus, R., Diffusion and adsorption of volatile organic compounds in building materials-impact on indoor air quality, Environment Science Technology, 34:3101-3108, 2000

Muller, C. O., and England, W. G. Achieving your indoor air quality goals: which filtration system works best? ASHRAE Journal, February, 24-32, 1995

Myers, A. L. and Prausnitz, J. M., Thermodynamics of mixed gas adsorption, AIChE Journal, 11:121 (1965)

Nelson, G., and Harder, C., "Respirator cartridge efficiency studies: VI. Effect of concentration." AIHAJ, 37(4): 205-216,1976

Ramanathan K., Debler, V. L., Kosusko, M., and Sparks L.E., Evaluation of control strategies for volatile organic compounds I indoor air, Environmental Progress, 7(4): 230-235, 1988

Ruthven, D., Principles of Adsorption and Adsorption Processes, John Wiley and Sons: New York, 1984

Tien, C., Adsorption Calculations and Modeling, Butterworth Heinemann, Washington, 1994.

Tsai, W., Chang, C., Ho, C., and Chen, L., Adsorption properties and breakthrough model of 1,1-dichloro-1-fluoroethane on activated carbons, Journal of Harzardous Materials, B69: 53-66, 1999.

Vahdat, N., Swearengen, P. M., and Johnson, J.S., Adsorption prediction of binary mixtures on adsorbents used in respirator cartridges and air-sampling monitors, Am. Ind. Hyg. Assoc. J. (55)/ October 1994.

VanOsdell, D.W. Evaluation of test methods for determining the effectiveness and capability of gas-phase air filtration equipment for indoor air applications-phase I: literature review and test recommendations, ASHRAE Transactions: Research, 100: 511-523, 1994

VanOsdell, D. W., Carbon Adsorption for indoor air cleaning, ASHRAE Journal, February, 34-40, 1995

VanOsdell, D. W., Owen, M. K., and Jaffe, L. B., VOC removal at low contamination concentrations using granular activated carbon, Journal of the Air and Waste Management Association, 46: 883-890, September, 1996

Weschler, C.J., Shields, H. C., and Naik, D. V., An evaluation of activated carbon filters for the control of ozone, sulfur dioxide, and selected volatile organic compounds, environments for people: IAQ92: October 119-21, San Francisco USA, 1992

Yoon, Y. H., and Nelson, J.H., Application of gas adsorption kinetics I. a theoretical model for respirator cartridge service life, Am. Ind. Hyg. Assoc. J., 45(8): 509-516, 1984

Yu, C., and Crump, D., A review of the emission of VOCs from polymeric materials used in buildings, Building Environment, 33(6): 357-374, 1998

Yue, Z.; and Economy, J., Removal of chemical contaminants from water to below USEPA MCL using fiber glass supported activated carbon filters, Environment Science Technology, 35(13): 2844-2848, 2001

CHAPTER VI

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

Summary

Activated carbon, commonly in palletized, granular, powered, or molded form, has been used for decades in removing undesired contaminants in waste water, drinking water, and industrial gas streams. While activated carbon has demonstrated its effectiveness in industrial applications, its efficiency in removing VOCs generated from indoor environments, typically at lower air concentration, remains less clear. In this study, activated carbon fiber (ACF) is evaluated for its applicability in collecting indoor VOCs in both the passive mode (without air drawn through) and the active mode (with air penetrating through ACF).

Adsorption isotherms were measured for acetone, toluene and limonene and three species of ACF. For the 3 to 1200 mg/m^3 concentration range examined in the passive mode, limonene exhibited the highest adsorption capacity of all three ACF species, followed by toluene, and acetone. The adsorption capacities of three species of ACF vary with their different specific surface areas and pore size distributions. For the 60 ppb to 13 ppm concentration range examined in the active mode, toluene exhibited a higher adsorption capacity than acetone. Limonene was not examined in this test mode because of difficulty in generating a stable gas concentration. It is believed that limonene has the greatest adsorption capability in the three tested chemicals. The adsorption capacity for a compound tested in the active mode may differ from that tested in the passive mode even if they are tested at the same concentration levels. The reason is that the air velocity may play a role in the adsorption process.

The Langmuir, Freundlich and Dubinin-Redushkevich adsorption isotherm equations were used to predict the adsorption capacities at untested concentrations for the three adsorbates and three ACF species in both the passive adsorption mode with the concentration range of 3 to 1200 mg/m^3 and the active adsorption mode with the concentration range of 60 ppb to 13 ppm. Both concentration ranges were defined for two categories of indoor environments with VOCs generated from different mechanisms. Empirical statistical models based on the Freundlich equations were established and evaluated by comparison made between experimental results and predicted results for trichloroethylene and methyl ethyl ketone. They can be used to predict untested VOC adsorption capacities on the tested ACF species with reasonable accuracy.

Sink materials, such as carpet, gypsum board, cotton drapes, sofa, and furniture, are often seen in indoor environments and can act as sink reservoirs as well as secondary emitters. Sorption experiments were performed in order to determine the sorptive kinetics of ACF, cotton, polyester, gypsum board, carpet and empty chamber surfaces for acetone, toluene and limonene. ACF has greater adsorption capacities and greater adsorption rates than other materials by a factor of 3-6 in the 0.01-10 mg/m^3 concentration range, with a factor of 6 at 0.01 mg/m3 and a factor of 3 at 10 mg/m3, regardless of the tested chemicals, while the desorption rates of ACF are comparable to those of the tested indoor sink materials. Generally speaking, carpet has the greatest sorptive kinetics among the tested indoor sink materials, and for a sink material, it has the greatest sorptive kinetics with limonene, followed by toluene and acetone. The linear Langmuir sink model was examined for indoor sink materials and was found to be suitable, while the non-linear sink model, with the assumption that the adsorption process follows the non-linear isotherm and the desorption process follows the linear isotherm, was successfully applied for ACF.

The breakthrough time of ACF filters was examined in the concentration range of 60 ppb to 13 ppm. The relationship of breakthrough time at different concentration levels was established and the breakthrough time of ACF filters at lower concentrations can be extrapolated from the results obtained at higher concentrations. When an acetone-toluene mixture was tested, it was found that competitive adsorption of indoor VOCs shortens the breakthrough time of ACF filters and reduces their adsorption capacities on each individual VOC. The Ideal Adsorbed Solution Theory was examined for its effectiveness for predicting adsorption capacity of each chemical in a binary mixture. The prediction agrees quite well with experimental results.

The sorptive kinetics for ACF and indoor sink materials obtained in this study can be used by modelers to predict the impacts of sorptive materials on indoor air quality, and on occupant exposures to VOCs. Especially, the experimental results for ACF presented in this study clearly demonstrate its superior sorption capacity and indicate a very promising potential for ACF as a sorptive medium to reduce occupant exposures to indoor VOCs. The practical applications of ACF could include confined spaces and shelter-in-place situations for controlling exposures from accidental or intentional release of VOCs, and more common settings such as commercial or residential buildings, offices, and space craft air quality improvement for reducing exposures from indoor VOCs at typical concentration levels.

Conclusions

Based on the results presented in Chapters 3, 4 and 5, the following conclusions can be made:

1. ACF has demonstrated its effectiveness in removing indoor VOCs from evaporative sources in the passive mode. The adsorption capacity is correlated to the polarities of VOCs, with higher adsorption capacities for non-polar VOCs, and lower adsorption capacities for polar VOCs.
2. The established statistical models based on the Freundlich equation can be used to predict untested VOC adsorption capacity with reasonable accuracy for ACF in both the active mode and the passive mode. The Langmuir equation, the Freundlich equation, and the Dubinin-Radushkevich equation can be applied for prediction of VOC adsorption capacity onto ACF at untested concentration levels in the whole concentration range tested in this study.
3. ACF has greater adsorption rates for tested VOCs than tested indoor sorptive materials by a factor of 1 to 3 orders of magnitude in the 10 to 1000 mg/m^3 concentration range, and by a factor of 3 to 6 orders of magnitude in the 0.01 to 10 mg/m^3 concentration range, respectively, while desorption rates are comparable. Thus, even in the presence of indoor sink materials, ACF still has very good potential in reducing peak concentrations of VOCs.

4. The linear Langmuir sink model is appropriate for indoor sink materials, including, gypsum board, cotton, polyester, and carpet, at indoor concentration levels, while the non-linear Langmuir sink model characterizes the sorption of ACF better. The assumptions that the adsorption of ACF follows the non-linear process while the desorption of ACF obeys the linear relationship between the amount of VOC in the sink material and VOC concentration in bulk air are suitable in this study.
5. Breakthrough time of ACF filters at lower concentration levels can be extrapolated from the results obtained at higher concentrations. The linear relationship between VOC concentration and time in log scale works in both indoor concentration levels and industrial concentration scenarios. ACF filters with a residence time of 0.1 second can last months if challenged with single VOC at low ppb levels. Polar VOCs have a shorter breakthrough time than non-polar VOCs.
6. Adsorption is competitive in VOC mixtures at typical concentration levels. The competitive effect reduces individual VOC adsorption capacity and shortens individual VOC breakthrough time. The Ideal Adsorbed Solution Theory can be used to predict individual VOC adsorption capacity in binary mixtures.

Limitations of the Current Work

1. Due to limitations of the time and facilities available for the study, only five VOCs have been tested, and the empirical statistical models for predicting adsorption capacities for untested VOCs are only based on three tested VOCs. As

described in Chapter 1, hundreds of VOCs are present indoors. The examined VOCs only cover a vapor pressure range of 2 to 100 kPa. Thus, they cannot represent the entire range of VOCs encountered indoors. Testing with additional VOCs would result in more accurate correlations between the Freundlich isotherm constants and properties of VOCs, and would also provide a better understanding of untested VOCs' adsorption properties on ACF.

2. Ozone's presence in indoor environments may initiate chemical reactions. In this study, the house air was purified and therefore ozone should not have been present in the test system. Thus, chemical reactions were not considered in this current study. However, under certain circumstances, chemical reactions of indoor VOCs may need to be considered in future studies.
3. Adsorption isotherms for indoor sink materials were not measured in this study. In order to determine the applicable range of the linear Langmuir IAQ model, those adsorption isotherms need to be characterized.

Recommendations

Based on the current findings, recommendations for future research on ACF application for removal of indoor VOCs are as follows:

1. In the passive mode, the effectiveness of ACF for removal of indoor VOCs with the presence of indoor sink materials should be evaluated in order to determine the real efficiency of ACF for removal of VOCs.

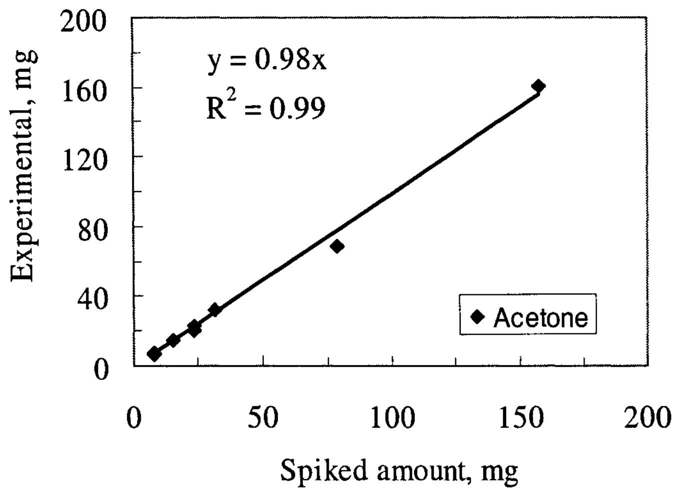
2. The effectiveness of ACF for removal of indoor VOCs at subppm levels in the active mode needs to be evaluated in order to explore its application in indoor environments at normal concentrations.
3. Field study of ACF filters is needed to evaluate the breakthrough times and adsorption capacities with various VOC mixtures.
4. More VOCs are needed to be tested in order to establish more robust statistical models based on the Freundlich equation for predicting adsorption capacities of untested VOCs.
5. As concentration varies with time, the actual adsorption capacities of ACF for VOCs from evaporative sources needs to be determined.

APPENDICES

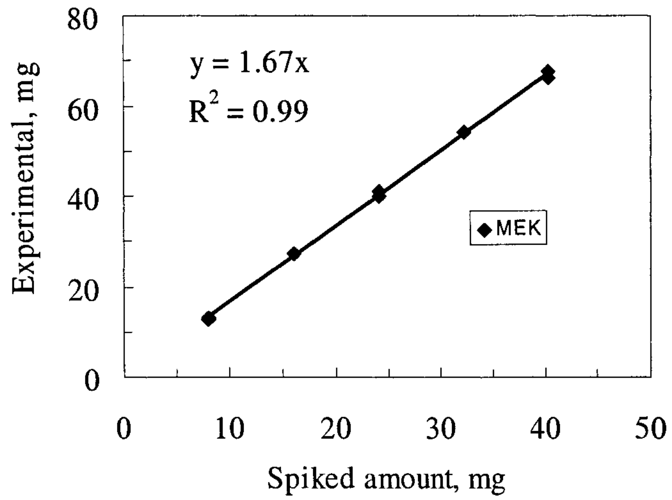
Appendix A

The Use of Gas Chromatography and Validation of Sampling with Charcoal Tubes

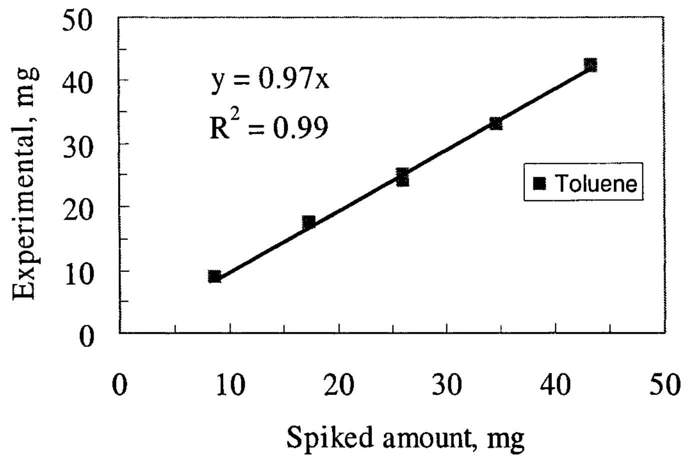
Graphs in Figure A1 were used for calibration of desorption efficiency for ACF by using CS_2 in this study. Figure A2 was used as a sample of day-to-day calibration of the gas chromatograph. Tables A1.1 and A1.2 are representative checks for reproducibility of peak area and linear calibration curve characterization, respectively. Validation of sampling with charcoal tubes for selected chemicals was performed by using NIOSH Manual of Analytical Methods (NMAM), Fourth Edition, 1994. Method 1300 was used for acetone, 1501 for toluene, and 1552 for limonene.



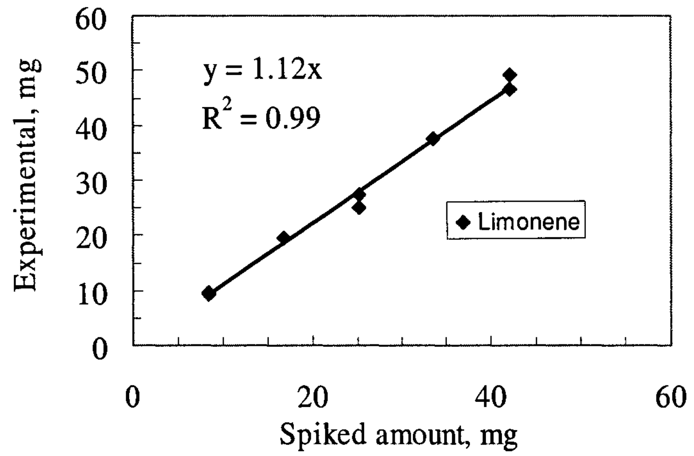
(a) Acetone and ACF



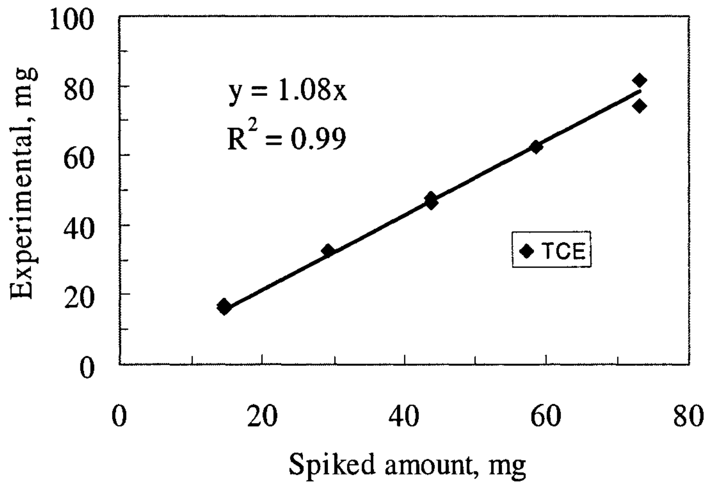
(b) Methyl Ethyl Ketone and ACF



(c) Toluene and ACF



(d) Limonene and ACF



(e) Trichloroethylene and ACF

Figure A1.1. Calibration Curves of Desorption Efficiencies with CS_2 for ACF

Table A1.1 Reproducibility Check with 250 ppm Stock Solution of Toluene

	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10
	77254	82835	80585	84237	84892	78252	85596	80946	78927	78115
Mean	81163.9									
SD	3059.2									
CV	3.77%									

Table A1.2 GC Linearity Calibration for Toluene

Conc.	2	10	100	200	300	500	700	1000
Peak area	589	2781	27040	55271	90827	140410	186739	271435

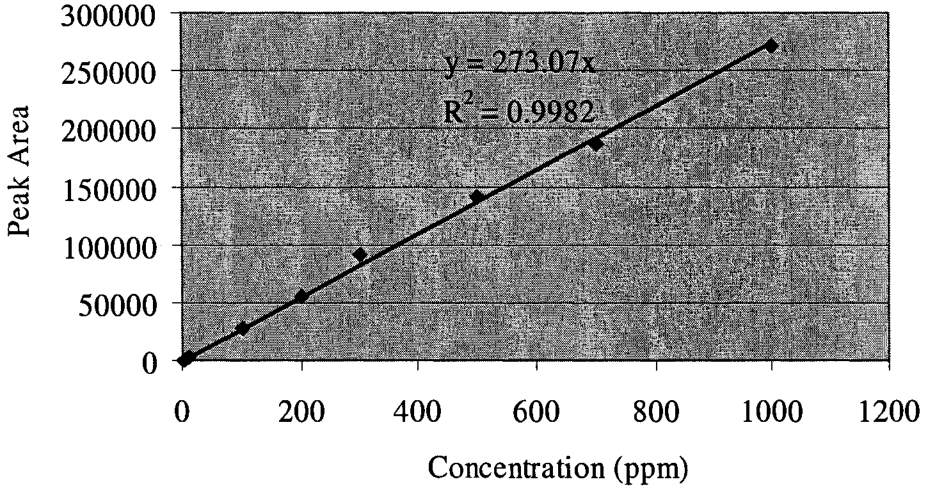


Figure A1.2 Calibration Curve Between Concentration and Peak Area for Toluene

Appendix B

Data Analysis Programs

Sample Matlab Program for Determination of K_a/K_d and Generation of Graphs.

Main program

```
clear all;
global c0;
global m0;
global m1;
global beta;
global CompoundNo;

FileName='gp3nw2';
y=load([FileName '.dat']);
t=y(:,1);
i=2
CompoundNo=i-1;
beta=88;

c=y(:,i);
c0=3111.82;
m0=85.26;
m1=57174.02;

[betahat f J]=nlinfit(t,c,'ODESolutionw',beta);
betahat

betaci=nlparci(betahat,f,J)
R=corr2(c,c+f);
result(i-1,1)=R;

t1=[0:0.1:15]';
c1=ODESolutionw(betahat,t1);
plot(t,c,'+r',t1,c1);
legend('Experimental data','Non-linear sink model')
xlabel('Time (h)');
ylabel ('Acetone concentration (mg/m3)');

result
fid=fopen([FileName 'Lan.dat'],'w');
fprintf(fid, '%f ','ResultOutput');
fclose(fid);
```

Subroutine of the IAQ model (ODESolutionW.m)

```
function dy=Langmuir_Background(t,y)
global CompoundNo;
global beta;
global c0;
global m0;
ka2=beta;
ke2=2113.8;
L=0.186;
N=1.2;

BackgroundData=[0.0046 0.168];
ka1=BackgroundData(1);
kd1=BackgroundData(2);
L1=18.06;
a=0.41;

dy=zeros(3,1);
dy(1)=-N*y(1)-ka1*L1*y(1)+kd1*y(2)*L1+L*(ka2/ke2)*y(3)-L*ka2*(y(1))^a;
dy(2)=ka1*y(1)-kd1*y(2);
dy(3)=ka2*(y(1))^a-(ka2/ke2)*y(3);
```

Subroutine of solving ordinary differiential equations using Runge-Kutta method (Langmuir_Background.m)

```
function y=ODESolutionW(betaInput,tspan)
global beta;
beta=betaInput;
options = odeset('RelTol',1e-4,'AbsTol',[1e-6 1e-6 1e-6]);
[T,Y] = ode45('Langmuir_Background',tspan,[3111.82 85.26 57174.02],options);
y=Y(:,1);
```

gp3nw2.dat

```
0.10   175.15
1.38    83.60
2.90    51.41
4.38    48.09
7.88    30.40
10.40   27.12
19.03   13.64
22.86   11.74
29.11   13.73
34.13   11.49
```

```
46.16   8.07
54.66   6.38
```

The following program is used for acetone in the Freundlich non-linear fitting in the passive adsorption mode (Chapter 3):

```
clear all;
k1=6.89;
m1=0.44;
c1=15:0.5:1200;
cm1=[20.2 91.00 160.85 413.04 868.33 1190.27];
wm1=[25.53 46.92 71.16 120.88 134.25 144.21];

k2=11.02;
m2=0.39;
c2=15:0.5:1200;
cm2=[20.2 91.00 160.85 413.04 868.33 1190.27];
wm2=[35.61 62.54 86.59 101.27 154.27 182.75];

k3=10.28;
m3=0.38;
c3=15:0.5:1200;
cm3=[20.2 91.00 160.85 413.04 868.33 1190.27];
wm3=[31.89 58.27 69.85 103.26 137.27 152.02];

w1=k1*c1.^m1;
w2=k2*c2.^m2;
w3=k3*c3.^m3;

figure (1)
h=plot(cm1,wm1,'b*',c1,w1,'b--',cm2,wm2,'r^',c2,w2,'r--',cm3,wm3,'go',c3,w3,'g--');

legend(h([1,3,5]),'ACF-10','ACF-15','ACF-20');
xlabel('Concentration [mg/m^3]');
ylabel('Adsorption Capacity [mg/g ACF]');
```

The following program is used for concentration correction of K_a for ACF by C^{1-n} (Chapter 4)

```
clear all;
k1=188.6;
n1=0.41;
c1=0.1:0.001:1;

k2=354.6;
```

```
n2=0.32;
c2=0.1:0.001:1;


k3=1947.4;
n3=0.16;
c3=0.1:0.001:1;

w1=k1*c1.^(-1+n1);
w2=k2*c2.^(-1+n2);
w3=k3*c3.^(-1+n3);

figure (1)
h=plot(c1,w1,'b--',c2,w2,'r--',c3,w3,'g--');

legend(h([1,2,3]),'Acetone','Toluene','Limonene');
xlabel('Concentration [mg/m^3]');
ylabel('Ka [m/h]');
```

The following program is used for concentration correction of K_e for ACF by C^{1-n} (Chapter 4)

```
clear all;
k1=2113.8;
n1=0.41;
c1=0.1:0.001:1;

k2=7207.3;
n2=0.32;
c2=0.1:0.001:1;

k3=25422.4;
n3=0.16;
c3=0.1:0.001:1;

w1=k1*c1.^(-1+n1);
w2=k2*c2.^(-1+n2);
w3=k3*c3.^(-1+n3);

figure (1)
h=plot(c1,w1,'b--',c2,w2,'r--',c3,w3,'g--');

legend(h([1,2,3]),'Acetone','Toluene','Limonene');
xlabel('Concentration [mg/m^3]');
ylabel('Ke [m]');
```

The following program is used for Methyl ethyl ketone adsorption capacity prediction (chapter 3):

```
clear all;
k1=8.66;
n1=0.41;
c1=5:0.5:800;
cm1=[12.20 10.81 8.02 43.60 191.17 200.84 163.51 643.61];
wm1=[15.17 39.68 40.70 64.82 95.30 91.16 92.57 121.57];

k2=13.18;
n2=0.39;
c2=5:0.5:800;
cm2=[12.20 10.81 8.02 43.60 191.17 200.84 163.51 643.61];
wm2=[42.26 50.11 50.04 70.89 144.89 146.55 124.49 163.25];

k3=12.31;
n3=0.39;
c3=5:0.5:800;
cm3=[12.20 10.81 8.02 43.60 191.17 200.84 163.51 643.61];
wm3=[42.24 50.53 54.32 82.36 145.57 137.66 146.48 176.79];

w1=k1*c1.^n1;
w2=k2*c2.^n2;
w3=k3*c3.^n3;

figure (1)
h=plot(cm1,wm1,'b*',c1,w1,'b--',cm2,wm2,'r^',c2,w2,'r--',cm3,wm3,'go',c3,w3,'g--');

legend(h([1,3,5]),'ACF-10','ACF-15','ACF-20');
xlabel('Concentration [mg/m^3]');
ylabel('Adsorption Capacity [mg/g ACF]');
```

The following program is used for tricholoethylene adsorption capacity prediction (chapter 3):

```
clear all;
k1=78.40;
n1=0.22;
c1=5:0.5:1700;
cm1=[8.56 20.73 7.61 54.78 63.06 179.65 194.18 171.73 741.26 1588.95];
wm1=[120.62 122.62 140.14 248.97 211.56 320.47 297.68 293.50 395.79 444.51];
```

```
k2=124.64;
n2=0.22;
c2=5:0.5:1700;
cm2=[8.56 20.73 7.61 54.78 63.06 179.65 194.18 171.73 741.26 1588.95];
wm2=[149.74 165.73 139.42 224.78 262.86 379.05 401.86 409.68 554.95 660.11];

k3=107.58;
n3=0.26;
c3=5:0.5:1700;
cm3=[8.56 20.73 7.61 54.78 63.06 179.65 194.18 171.73 741.26 1588.95];
wm3=[178.50 170.57 161.38 257.27 274.84 435.16 401.33 406.07 599.26 709.50];

w1=k1*c1.^n1;
w2=k2*c2.^n2;
w3=k3*c3.^n3;

figure (1)
h=plot(cm1,wm1,'b*',c1,w1,'b--',cm2,wm2,'r^',c2,w2,'r--',cm3,wm3,'go',c3,w3,'g--');

legend(h([1,3,5]),'ACF-10','ACF-15','ACF-20');
xlabel('Concentration [mg/m^3]');
ylabel('Adsorption Capacity [mg/g ACF]');
```

The following program is used in estimation of the Freundlich constants for acetone with three species of ACF (chapters 3 and 5):

```
clear;
Title" Acetone Freundlich parameter determination";
data a1;
input c m @@;
cards;
20.20   25.53
91.00   46.92
160.85  71.16
413.04  120.88
868.33  134.25
1190.27 144.21
;
run;
data a2; set a1;
logc=log(c);
logm=log(m);
run;
proc reg data=a2;
model logm=logc;
run;
```

```
data a1;
input c m @@;
cards;
20.2     35.61
91.0     62.54
160.85   86.59
413.04   101.27
868.33   154.27
1190.27  182.75
;
run;
data a2; set a1;
logc=log(c);
logm=log(m);
run;
proc reg data=a2;
model logm=logc;
run;

data a1;
input c m @@;
cards;
20.2     31.89
91.0     58.27
160.85   69.85
413.04   103.27
868.33   137.27
1190.27  152.02
;
run;
data a2; set a1;
logc=log(c);
logm=log(m);
run;
proc reg data=a2;
model logm=logc;
run;
```

VITA

VITA

Huajun Lu was born on January 25, 1971 in Hubei province, People's Republic of China. Huajun graduated from Jiangxi University of Science and Technology (of China) where he earned a Bachelor of Science in Safety Engineering in July of 1993. Upon completing his undergraduate education, Huajun immediately enrolled in Northeastern University (of China) where he obtained a Master of Science in Safety Technology and Engineering in March of 1996. Prior to beginning his doctoral studies at Purdue University in August of 2001 Huajun worked as environmental, health and safety supervisor in Guangzhou, China. Huajun completed his doctoral studies in December of 2005.