Evaluation of Gas Phase Air Cleaners for Indoor Environmental Applications

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ABSTRACT

Evaluation of Gas Phase Air Cleaners for Indoor Environmental Applications

Golnoush Bolourani

While granular activated carbon (GAC) filters have been used extensively for removal of contaminants from industrial gas streams, little research has been done on their adsorption capacity for indoor environmental purposes where ventilation systems are used to remove volatile organic compounds (VOC) contaminants and may allow higher air recirculation. This research investigates the performance of GAC filters for indoor environments by challenging them with various VOCs and subsequently measuring their removal efficiencies and breakthrough times.

A small environmental, closed-loop, dynamic test chamber was designed, constructed and used to measure the performance of eight different GAC filter samples when they were exposed to cyclohexane, ethyl acetate and toluene at different humidity levels. Three of the filters were composed of virgin activated carbon with granules of different sizes and/or shapes. The remainder filters were impregnated with either phosphoric acid or potassium hydroxide.

The breakthrough times and removal efficiencies of the filters were analyzed. Within the concentration range examined and at 50% relative humidity (RH), toluene exhibited the highest adsorption capacity on the filters, followed by ethyl acetate and cyclohexane.

At 50% RH, the virgin filters were 25% more efficient in adsorbing the VOCs than the impregnated ones. For toluene, the 50% breakthrough times of filters 1A, 1B and 1C were 4, 0.13 and 0.03 hours, respectively, and the 80% breakthrough times were 5.60, 1.03 and 0.50 hours, respectively.

The effects of RH on adsorption of soluble (ethyl acetate) and insoluble (cyclohexane and toluene) VOCs on the performance of GAC filters were also investigated. The presence of water vapor in the chamber had little effect on the adsorption capacity of the toluene until about 50% RH. At 50% RH and above, an increase of 16.5% in adsorption capacity of ethyl acetate occurred, while the adsorption capacity of cyclohexane and toluene rapidly decreased. The 80% breakthrough times of filters 1A, 2A and 3A for toluene decreased on average, up to 33%, 38% and 25%, respectively, when the RH increased from 30% to 70%. Therefore, competitive adsorption of VOCs with water vapor molecules shortened the breakthrough times of the filters for toluene and cyclohexane as the RH level increased.

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1 Introduction

Scientists have been concerned about several different issues associated with indoor air quality (IAQ) for decades. The United States Environment Protection Agency (US EPA) has reported that most people spend up to 90% of their time indoors, and that the air within homes and other buildings can be more seriously polluted than it is outdoors (US EPA, 2007). Therefore, poor IAQ compromises human health, comfort and productivity. Headaches, fatigue, eye and mucous membrane irritation, respiratory problems, and unpleasant odors are the most commonly cited symptoms and complaints (Zhang, 2003).

Gaseous and particulate matter air pollutants are always and everywhere present in our daily lives. In past decades, the growth in IAQ-related illnesses has been the focus of study for many air quality researchers and health organizations. The actual causes of the symptoms remain largely unknown and usually disappear upon leaving a building.

Indoor air pollution is among the top five environmental risks to public health in the U.S. (US EPA, 2007). Respiratory illnesses, including the common cold, influenza, pneumonia, sinusitis and bronchitis affect more than 70% of all adults and contribute to the loss of 176 million work days and 121 million restricted-activity days each year (US Department of Health and Human Services, 1994). Additional studies indicate that workers with respiratory illnesses may suffer from as much as a 25% loss of productivity on the job (Fisk et al., 1998). Combined, absenteeism and lost productivity from IAQ-related health problems are estimated to cost businesses in the U.S. more than $60 billion annually (Fisk et al., 1998). Indeed, studies have shown that poor IAQ increases the probability of sick-leave for employees in the case of minor ailments and delays their return to work (Leyten et al., 2002). Two specific types of health problems are associated with poor IAQ:

a. Sick building syndrome: Symptoms include headaches, irritation of the eyes, mucous membranes and respiratory system, drowsiness, fatigue, and general malaise; however the source of the illness cannot be positively determined.

b. Building-related illnesses: These include specific infections, allergies or toxin-induced diseases with objective clinical findings related to building occupancy, such as Legionnaires' disease and hypersensitivity pneumonitis.

The earliest IAQ investigations were conducted in 1850 as part of the hygiene revolution (Sundell, 2004). During the 1960s, poor outdoor air quality was assumed to be responsible for many health problems (Sundell, 1994). It was not until the early 1970s that scientists started to investigate IAQ in response to the complaints about indoor working environments (Sundell, 1999). These issues are a major concern for industrialized countries, including Canada and the U.S. Yocom's (1982) research has found that indoor pollutant levels are often higher than found outdoors, sometimes exceeding ambient and even occupational standards.

Liu (1995) has categorized indoor air pollutants into four major groups: bioaerosols (microorganisms), respirable particles, gaseous contaminants and organic vapors (e.g. ethyl acetate, toluene). Bioaerosols are airborne particles that are present in outdoor air and can be carried indoors by HVAC systems and human activities. In the presence of nutrients and moisture, microorganisms can also develop in indoor mediums (Lu, 2005). Respirable particles have a diameter of less than 10 μm and can find their ways to the lower respiratory tract of human body They are principally the result of combustion and tobacco smoke (Lu, 2005). Gaseous contaminants including ozone, nitrogen oxides, carbon monoxide and sulfur dioxide are caused mostly through human activities and ventilation systems (Lu, 2005). Organic vaporous contaminants refer mainly to indoor contaminants, which are generated by indoor materials and human activities such as painting (Lu, 2005).

VOCs are the major types of organic vaporous contaminants. They typically occur in low concentrations in indoor environments (i.e. in parts per billion (ppb) ranges). Indoor VOCs usually arise from the infiltration of outdoor air, electronic and office equipment, carpets, solvents, building materials, human body effluents, tobacco smoke, cleaning products and ventilation systems (Sundell et al., 1993; Brown et al., 1994; Leovic et al., 1996; Zhang et al., 2003). Some of these compounds react with ozone and other oxidants to form secondary pollutants that can be more harmful than their initial formulation. Yu (1998) reported that more than 900 VOCs were detected during a US EPA survey of IAQ.

VOC sources can be permanent, temporary or intermittent, depending on the type of facilities and activities. Factors affecting their indoor concentrations include: building materials, human activities (such as cleaning, waxing, painting), combustion activities and environmental conditions such as RH, temperature, air velocity, ventilation rate and the efficiency of the air filter and local exhaust (Lu, 2005). The most commonly occurring indoor VOCs and their possible sources are presented in Table 1.1 (DiNardi, 2003).

Table 1.1: Common Indoor VOCs and Potential Sources (DiNardi, 2003)

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
Aromatic hydrocarbons (toluene, xylenes, ethylbenzene, benzene, stylene)	Combustion sources, paint, adhesives, gasoline, flooring
Chlorinated solvents (dichloromethane methylene chloride, trichloroethane etc.)	Upholstery and carpet cleaner or protector, paint, paint remover
Carboxylic acids (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
Ethyl Acetate	Varnish and lacquer and their removal, preparation of films and film plates
Cyclohexane	Perfumes, coating, paint, and varnish removers

Before the energy crisis of 1973, buildings had high ceilings and wide windows, and used natural ventilation systems. After the Arab oil embargo and the need to conserve energy, building design underwent drastic changes in order to become more energy efficient. Since then, scientists have been working hard to find solutions to optimizing energy conservation without sacrificing IAQ.

There are three methods of controlling undesirable indoor contaminants: source control, ventilation control and removal control. Ideally, the best way to deal with IAQ problems is to control or eliminate emission sources. Source control is always the first priority, because it is simpler to control the emitter than to eliminate the existing airborne contaminants themselves. However, it is not always possible to identify the sources readily, and even if the source is identifiable, it might not be feasible to remove it. So, one must consider a proper ventilation method and an efficient removal strategy at the same time. Increasing ventilation rates are not economically favored, because they consume more energy. Moreover, ventilation often involves the dilution of indoor air with possibly polluted outdoor air. Therefore, it is critical to employ an appropriate removal strategy in order to achieve an acceptable IAQ. Most recent research in building sciences focuses on improving IAQ by filtering pollutants out of indoor air environments and then re-circulating it (VanOsdell, 2006).

In dealing with IAQ problems, one should always seek an approach that is most appropriate and practical while also being economical and prioritizes all aspect of human health and comfort. For instance, even though copy machines are a source of contamination through the production of VOCs, they are an essential part of today's world and cannot be eliminated. Similarly, increasing air ventilation in buildings is unfeasible because of its impact on energy consumption. Thus, the role of removal control becomes crucial. New technologies offer various methods for removing airborne contaminants, such as thermal decomposition, bio-filtration, botanical air cleaning, photo catalytic oxidation (PCO), ultraviolet treatment and adsorption filters (Hunter and Oyama, 2000). Among the various adsorption filters commercially available, activated carbon is one of the most promising for its ability to treat air saturated with VOCs. Moreover, its high efficiency has been proven in industrial applications.

Using activated carbon is a popular way of filtering air, as other techniques tend to be either more expensive (e.g. thermal decompositions (Economy and Lin, 1976)) or too dangerous to be used in residential and office buildings (e.g. PCO which uses short wave of ultraviolet light (UVC) to kill viruses and bacteria and to reduce VOCs in ppb levels (Suzuki, 1994)). Despite the excellent performance of activated carbon in waste-water treatment and in the removal of pollutants from industrial gas streams, little research has been conducted on its adsorption capacity in removing VOCs from indoor air environments that rely on ventilation systems. In evaluating the activated carbon's efficiency, water vapor plays an important role. Water vapor is not a contaminant itself; however, due to its presence in the air, both outdoor and indoor, its effect on the adsorption capacity of filters requires further study. When using air filtration as a method of air purification in indoor environments, one should always consider the competition between water vapor and the challenged VOCs. Many studies claim, therefore, that elevated RH levels (RH>50%) negatively influence breakthrough time curves and the capacity of activated carbon to adsorb VOCs (Nelson et al., 1976b; Werner et al., 1985; Cal et al., 1997; Qi et al., 2000).

As mentioned above, the GAC filters have been used to control gaseous contaminants, even though their performance, lifespan and the impact of RH remains the subject of scholarly discussion (VanOsdell, 2006). Beds of GAC filters in ventilation system are the most common way to remove VOCs from indoor air.

Henschel (1998) reviewed the usage of GAC filters in residential and commercial environments and observed that there is still not enough data available on activated carbon applications to conclude how efficacious they are in removing indoor VOCs.

This thesis tests the ability and measures the capacity of GAC filters to remove VOCs at several humidity levels. The results of these experiments will provide a better understanding for the feasibility of using these filters in commercial and residential ventilation systems.

1.1 Objective

This research attempts to examine GAC in detail for use in the removal of indoor VOCs and in several RH levels for indoor air filtration applications. 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 GAC for reducing VOCs' exposures in indoor environments. This dissertation addresses three main objectives:

1. To characterize the GACs adsorption capacities for several VOC adsorbates (cyclohexane, ethyl acetate, and toluene).
2. To investigate competitive adsorption of VOC and water vapor in order to understand the effect of RH (30, 50, and 70% RH) on adsorption capacity of the GACs.
3. To measure GACs adsorption capacities and breakthrough times with challenge of VOCs at typical indoor conditions.

1.2 Outline of Thesis

Chapter 2 describes the fundamental of adsorption and reviews the literature available on IAQ problems, air filtration using different types of activated carbon and the prior research contributed to using GAC filter for air purification.

Chapter 3 describes the experimental methods and apparatus that were used to conduct the experiments and are required to support this research, including the development of a unique closed-loop test facility capable of accurately measuring concentration of VOCs with minimal sink effect and leakage, conducting the experiment in various conditions and sustaining steady operating parameters for long breakthrough tests.

Chapter 4 presents and discusses the results from breakthrough tests of VOCs and humidity levels. The resulting efficiency and breakthrough time curves are compared to literature and one another.

Chapter 5 provides concluding remarks and suggestions for further research.

2 Literature review

2.1 *Introduction*

GAC is a promising adsorbent for most organic materials and certain inorganic materials (e.g. iodine) (Muller, 1995). Most field and laboratory studies on removal of gas-phase contaminants by GAC filters suggest that their lifespan ranges from a few months to several years (Graham et al., 1990; Lui, 1990; VanOsdell et al., 1996; VanOsdell et al., 2006), while other studies report a much shorter lifespan (Ramanathan et al., 1988). There have been numerous studies on the industrial application of activated carbon, and more specifically GAC, but there is little literature available about its performance for indoor purposes. In this study, several experimental methods have been developed to evaluate the performance of air filters for gas-phase pollutants. Each method is briefly described and the test results are reported.

This chapter presents the fundamentals of adsorption, adsorption media and critical reviews of previous studies on the removal of gas-phase contaminants with an emphasis on GAC for removing VOCs from indoor air.

2.2 Adsorption Process

Adsorption is a process by which materials accumulate at the interface between two phases (Noll, 1991). These phases can occur in any of the following arrangements: liquid-liquid, liquid-solid, gas-liquid and gas-solid. The adsorbing part is called the adsorbent, and any substance being adsorbed is termed adsorbate.

The adsorption of gas onto (porous) solid adsorbents has major environmental significance. When solid and gas molecules interact, adsorption occurs. The adsorption process can be classified as either physical or chemical (chemisorption). Physical adsorption is caused when inter-molecular forces interact (Van der Waals forces), while chemisorption involves chemical reactions between the adsorbent and the adsorbate, in which a layer of compound between the adsorbate and the outermost layer of the adsorbent is formed (Ruthven, 1938).

Determining the amount of gas adsorbed onto a solid in a closed system can be done by measuring the degree to which either the adsorbate pressure within a known volume has decreased or the adsorbent mass has increased, due to the adsorbing gas molecules. Both approaches are frequently employed and provide precise results. Partial pressure (concentration) of the adsorbate, temperature of the system, the adsorbate and the adsorbent all directly affect the amount of gas adsorbed in moles per gram of solid. The most important factors in adsorption are as follows:

2.2.1 Adsorption Forces

Adsorption of gas onto a solid is caused by the attractive forces between the adsorbate and adsorbent molecules (Ruthven, 1938).

2.2.2 Pore Size

In porous materials, the size and shape of the pores of individual adsorbents can vary greatly. Pores are usually characterized by their width: either the diameter of a cylindrical pore or the distance between two sides of a slit-shaped pore. Pore size distribution of an adsorbent can be estimated by the Horvath-Kawazoe (HK) and Dublin-Stoeckli (DS) methods (Cal, 1995). Dubinin (1960) suggested a classification of pores which was later adopted by the International Union of Pure and Applied Chemistry (IUPAC, 1972), as shown in Table 2.1.

Table 2.1: Pore Classifications by Pore Width

Pore Classification	Pore Width
Micropores	Less than ~ 20 Å (2 nm)
Mesopores	Between ~ 20 and ~ 500 Å (2 and 5 nm)
Macropores	More than ~ 500 Å (5 nm)

Table 2.1 represents the classification of pores in porous materials. Micropores are prone to greater adsorption potential than mesopores and macropores. Their stronger interaction potential is the result of the proximity of their pore walls. In order to create enough adsorption force for an adsorbate molecule to attach itself to a micropore, a sequence of approximately ten surface atoms is required. The attractive forces on adsorbate molecules are a function of the distance between adsorbate and adsorbent atoms (pore size) and the polarity (permanent or induced) of adsorbate and adsorbent atoms (Marsh, 1987).

2.2.3 Adsorption Isotherms

The shape of an adsorption curve profile (called an adsorption isotherm) indicates the volume of adsorption sites with specific adsorption energies on an adsorbent. In fact, an adsorption isotherm plots the amount of chemicals adsorbed on an adsorbent versus gas concentration or partial pressure at a constant temperature. Adsorption first takes place in the higher-energy sites and gradually progresses to the lower ones. Numerous adsorption isotherms have been proposed, but the majority of them fall into five categories as classified by Brunauer, Deming, and Teller (BDDT) and as presented in Figure 2.1 (Gregg et al., 1982; Brunauer, et al., 1940).

Type I isotherm is a reversible process with a concave to P/P_0 axis. As P/P_0 approaches 1, variable n approaches a limiting value. It occurs during the physical adsorption of gases onto microporous solids. Type II isotherm, also a reversible process, results from the physical adsorption of gases on nonporous solids. The physical adsorption of gases by mesoporous solids occurs in type IV isotherms. Types III and V are the result of the adsorption of either polar or non-polar molecules, provided that the adsorbate-adsorbent force is relatively weak. It should also be noted that a type V isotherm possesses a hysteresis loop; water vapor adsorption on microporous activated carbon is an example of such an isotherm.

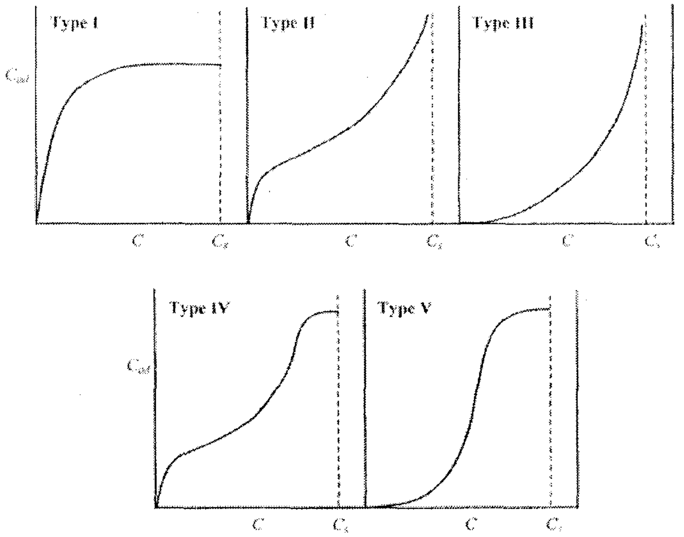

Figure 2.1: Brunauer's classification of adsorption isotherms (Adamson, 2000)

2.2.4 Theory of Volume Filling of Micropores

Dubinin has developed a widely used theory to explain physical adsorption of vapors onto microporous adsorbents that is known as "The Theory of Volume Filling Microporous (TVFM)" (Dubinin, 1975). Dubinin-Astakhov, Dubinin-Stoeckli and several other models are based on this theory. Before this, physical adsorption theories did not distinguish between adsorption on both porous and nonporous adsorbents. Instead, they only considered the formation of adsorption layers onto a surface. According to Dubinin's theory, adsorption in microporous space volume is volume filling rather than adsorption layer forming (Dubinin, 1991). Micropores in microporous materials are believed to be slit-shaped. After activation, these slits have variable widths. Usually, the longer the activation time, the wider the slit would be. Those slits or pores with smaller widths have higher adsorption energy due to the adsorption potentials of opposite pore walls (Carrott et al., 1991; Everett et al., 1976). This concept helps to explain the adsorption of low concentrations of gases onto microporous adsorbents, thus suggesting that highly microporous materials are the best option for the removal of low concentrations of VOCs (Dubinin, 1960; Dubinin 1991; Carrott et al., 1992; Cal et al., 1994).

2.3 Adsorption Medium

Commercial adsorbents are classified by the distribution of their micropore size, the structure of their surfaces and their chemical composition. Industrial adsorbents are highly porous materials with pore size distributions ranging from 20 to 500 angstroms. The most important properties of an industrial adsorbent over a period of time are its capacity, selectivity and stability. The adsorptive capacity is a function of adsorbent's specific surface area and porosity. Selectivity depends on the equilibrium properties of the system, diffusion rates. Polarity, chemical composition of the surface, and pore size distribution determine the ability of adsorbents to separate different gas molecules according to size, shape and polarity. The most frequently used adsorbents are silica gel, activated alumina, activated carbon and carbon molecular sieves (Ruthven, 1938). According to the American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE) fundamental handbook, gaseous contaminants with a higher relative molecular mass (such as a VOC) can be controlled and removed from ventilation systems with built-in activated carbon filters.

2.4 Activated Carbon

Activated carbon was selected as the air filter media in this study based on the suggestion of ASHRAE (1991) and because it is less selective in adsorbing VOCs than other materials (Zhang, 2000). Activated carbon or activated charcoal is a carbon based material derived from charcoal with a remarkably high specific surface area and large amounts of micropores. Activated carbons are produced in a two-step process in which carbonaceous materials such as wood, coal, coconut, etc. are first thermally decomposed in the absence of air and then activated (e.g. by CO_2 treatments) at elevated temperatures (above 250°C). Adsorption properties (specific surface area and pore size distribution) of the final products (activated carbons) highly depend on which carbonaceous material is used and the period of activation. Activated carbons are hydrophobic and organophilic by nature. Their wide range of applications from water purification, adsorption of gasoline vapors in automobiles and adsorption of organic vapors in air purification systems have been of interest to scientists for many years now (Ensor et al., 1988). There are various forms of activated carbon available commercially, such as powder activated carbon (PAC), activated carbon fiber (ACF) and granular activated carbon (GAC).

2.5 Experimental Methods and Results

Test methods available for removal of gaseous contaminants by adsorbents (Rivers, 1988) are (1) static tests where the adsorbent is brought into equilibrium with the challenged contaminants. Static tests concentrate on adsorbate/adsorbent interactions and provide little information about mass or energy transfer rate effects; and (2) dynamic or non-equilibrium tests in which adsorption of adsorbate on an adsorbent depends on various variables such as particle size, filter bed packing and pore size distribution (VanOsdell, 1994). Dynamic tests have been recommended by ASHRAE (Ostojic, 1985; VanOsdell, 1994, VanOsdell, 1996; VanOsdell, 2006). This method can be performed in a variety of systems: open-loop, closed-loop or partially closed-loop (Lee et al., 2006); however, it is simple to work with an open-loop system since upstream concentrations and RH can be controlled more easily. In a closed-loop system, by contrast, it is difficult to control upstream concentrations and/or RH since the air that passes through the filters is returned to the system, causing the concentration of upstream contaminants to increase continually. The dynamic closed-loop system is similar to the real-life practice of filters in HVAC systems, where the level of contaminants increases as the efficiency of the filters decreases (Lee et al., 2006).

There are two methods of measurement: one is to measure the concentrations (single bed (SB) method) (VanOsdell et al., 1995 and 1996) using a gas deletion instrument, such as a gas chromatography (GC) in the case of multiple gases or photoacoustic gas detection in case of individual gaseous compounds. The other is thermo-gravimetric analysis (TGA). This method requires the use of a Cahn gravimetric balance for measuring the total mass adsorbed by the activated carbon (Graham et al., 1990;

Ramanathan et al., 1988). The test specimen is placed on a balance and its weight gain during the adsorption of VOCs is monitored constantly until equilibrium is reached. This method does not provide sufficient information on the weight of gaseous compounds since other compounds, such as water vapor, are simultaneously adsorbed to the activated carbon.

In order to use the activated carbon for improving the quality of indoor environments, its lifespan and adsorption capacity should first be fully understood. Based on Foster's (1992) experiments on activated carbon, the 10% breakthrough times for adsorption of toluene with concentrations of 10 part per million (ppm) were determined to be 100 hours. Liu (1990) and Weschler et al. (1992) reported life-spans of a few months to several years for the activated carbon filters. They concluded that these life-spans were highly dependent on challenged VOCs. Using mathematical modeling, Liu (1991) determined a removal efficiency of 80% for GAC in a residence time of 0.06 seconds at challenge concentration of 100 ppb after 4000 hours.

Table 2.3 summarized the literature available on GAC when challenged with single compounds. As shown, Graham et al. (1990) exposed a specific weight of GAC (180 g) to benzene at different concentrations. They reported on average a 10% breakthrough time of 375 hours, when the average concentration of benzene was 1.456 ppm. They used the same method and set up as Ramanathan et al. (1988). In their study, the adsorption capacities of GAC for benzene were several orders of magnitude higher than that suggested by Ramanathan et al. (1988). None of the above studies monitored relative humidity of the systems.

VanOsdell's (1996) work showed that at concentrations of 1 ppm or less and when adsorption beds of GAC weighed approximately 25 grams, a 10% breakthrough time for toluene would be reached after 625 hours. These approaches for testing concentrations are considered to be economically inefficient since the experiments take so long to complete. In a research conducted by VanOsdell (2006), when GAC was challenged with five VOCs (mixture), a 10% breakthrough time of 135 hours was reported at 50% RH and toluene concentration of 1 ppm to 2 ppm. He admitted that the effect of relative humidity was particularly problematic.

Schmidt (2002) reported a 10% breakthrough time of 53.8 minutes for toluene at a concentration of 80 ppm and at 50% RH. He used a dynamic open-loop system and tested fibrous activated carbon (FAC). In the research of Scahill et al. (2004), a 10% breakthrough time for 123 mg of GAC exposed to toluene (2 and 909 ppb) occurred at approximately 73.8 minutes on average for toluene concentrations of 2 ppb and at 48.3 minutes on average for toluene concentration of 909 ppb at 25% RH. They used a very small GAC bed (with diameter of 0.48 cm and thickness of 1.04 cm).

Lee et al. (2006) tested FAC filters in a similar system with. They challenged four different FAC filters (A, B, C and D) with toluene at concentrations of 260 ppm at 25% RH. The injection rate was 4.32 μL/min and the tests were conducted at constant air velocity of 0.2 m/s: the residence time varied from 0.03 to 0.1 second. They reported the intial efficiencies of these filters to be 50-60%. The 80% breakthrough times of the filters were 2.02 hours for A, 1.03 hours for B, 2.68 hours for C and 5.98 hours for D. In their study they did not examin the FAC adsorption capacity in varous relative humidities

This thesis attempts to verify some of the earlier findings and to provide more data on the efficiency and lifespans of commercially available GAC filters in a closed-loop, dynamic environmental test chamber.

Table 2.2: Summary of literature review on GAC

VOC	Test Species	Air Flow (m^3/s)	Concentration (ppm)	Adsorption temperature (°C)	Residence Time (s)	Weight of GAC (g)	Adsorption Capacity (wt%)	Breakthrough time(10%) (hr)	RH (%)	Test Method	Reference
Acetaldehyde	Coal GAC	0.0472	0.119	N/A	N/A	0.15-0.2	0.0155	N/A	N/A	Dynamic (TGA)	Ramanathan, 1988
	Coal GAC	0.0472	0.153	N/A	N/A	0.15-0.2	0.044	N/A	N/A	Dynamic (TGA)	Ramanathan, 1988
Benzene	Cocounut GAC	0.0537	0.287	24	N/A	180	1.23	450*	N/A	Dynamic (TGA)	Graham, 1990
	Cocounut GAC	0.0179	0.862	24	N/A	180	2.83	275*	N/A	Dynamic (TGA)	Graham, 1990
	Cocounut GAC	*$4.786*10^{-3}$*	*3.218*	*24*	*N/A*	*180*	4.95	*400**	N/A	Dynamic (TGA)	*Graham, 1990*
	Coal GAC	0.0472	0.101	N/A	N/A	0.15-0.2	0.097	N/A	N/A	Dynamic (TGA)	Ramanathan, 1988
	Coal GAC	0.0472	0.119	N/A	N/A	0.15-0.2	0.498	N/A	N/A	Dynamic (TGA)	Ramanathan, 1988
	Coal GAC	0.0472	0.176	N/A	N/A	0.15-0.2	0.569	N/A	N/A	Dynamic (TGA)	Ramanathan, 1988
1,1-trichloroethai	Coal GAC	0.0472	0.115	N/A	N/A	0.15-0.2	0.153	N/A	N/A	Dynamic (TGA)	Ramanathan, 1988
	Coal GAC	0.0472	0.183	N/A	N/A	0.15-0.2	0.374	N/A	N/A	Dynamic (TGA)	Ramanathan, 1988
1,1-DCE	Cocounut GAC	0.000427	0.1	25	0.11	25	0.04	28	50	Dynamic (SB)	VanOsdell,1996
	Cocounut GAC	0.000427	1.1	25	0.11	25	0.36	13.3	50	Dynamic (SB)	VanOsdell,1996
	Cocounut GAC	0.000427	10	25	0.11	25	1.3	6.3	50	Dynamic (SB)	VanOsdell,1996
	Cocounut GAC	0.000427	116	25	0.11	25	5.7	3.1	50	Dynamic (SB)	VanOsdell,1996
	Cocounut GAC	0.000427	1100	25	0.11	25	12	0.55	50	Dynamic (SB)	VanOsdell,1996
Decane	Cocounut GAC	0.000427	0.665	25	0.11	25	15	628	50	Dynamic (SB)	VanOsdell,1996
	Cocounut GAC	0.000427	7.6	25	0.11	25	16	77	50	Dynamic (SB)	VanOsdell,1996
Toluene	Cocounut GAC	0.000427	0.44	25	0.11	25	6.6	625	50	Dynamic (SB)	VanOsdell,1996
	Cocounut GAC	0.000427	1.07	25	0.11	25	9.2	344	50	Dynamic (SB)	VanOsdell,1996
	Cocounut GAC	0.000427	9.18	25	0.11	25	16.2	72	50	Dynamic (SB)	VanOsdell,1996
	Cocounut GAC	0.000427	9.67	25	0.11	25	16.5	66	50	Dynamic (SB)	VanOsdell,1996
	Cocounut GAC	0.000427	71.7	25	0.11	25	18.8	11.9	50	Dynamic (SB)	VanOsdell,1996
	Cocounut GAC	0.000427	72.7	25	0.11	25	18	11.8	50	Dynamic (SB)	VanOsdell,1996
	GAC	0.001	0.002	25	N/A	0.1234	N/A	1.47	25	Dynamic	Scahill, 2004
	GAC	0.001	0.002	25	N/A	0.1225	N/A	1	25	Dynamic	Scahill, 2004
	GAC	0.001	0.909	25	N/A	0.1234	N/A	0.94	25	Dynamic	Scahill, 2004
	GAC	0.001	0.909	25	N/A	0.1225	N/A	0.49	25	Dynamic	Scahill, 2004
Hexane	Cocounut GAC	0.000427	0.4	25	0.11	25	3.2	376	50	Dynamic (SB)	VanOsdell,1996
	Cocounut GAC	0.000427	2.3	25	0.11	25	6	123	50	Dynamic (SB)	VanOsdell,1996
	Cocounut GAC	0.000427	10.6	25	0.11	25	10	37.9	50	Dynamic (SB)	VanOsdell,1996
	Cocounut GAC	0.000427	107	25	0.11	25	11	4.3	50	Dynamic (SB)	VanOsdell,1996
MEK	Cocounut GAC	0.000427	0.39	25	0.11	25	1.8	261	50	Dynamic (SB)	VanOsdell,1996
	Cocounut GAC	0.000427	2.3	25	0.11	25	3.5	86	50	Dynamic (SB)	VanOsdell,1996
	Cocounut GAC	0.000427	5	25	0.11	25	4.7	45.2	50	Dynamic (SB)	VanOsdell,1996
	Cocounut GAC	0.000427	34.3	25	0.11	25	8.2	9.7	50	Dynamic (SB)	VanOsdell,1996
	Cocounut GAC	0.000427	37.4	25	0.11	25	7.3	9.2	50	Dynamic (SB)	VanOsdell,1996

2.6 *Effect of Moisture on the Activated Carbon Adsorption*

When RH is above 50% the adsorption capacity of GAC filters is reduced (Nelson et al., 1976b; Owen et al., 1995). Water vapor is not a contaminant by itself, but it can affect the adsorption of gaseous contaminants. The adsorption of water on the activated carbon is a combination of strong water-water interactions and weak water-carbon interactions, producing hydrogen bonds with oxygenated functional groups on the carbon surface (Brennan, 2001). In Okazaki's (1978) study of water soluble compounds, the presence of moisture was held to be responsible for producing a film of liquid on the adsorbents (including activated carbon), since the presence of moisture promoted the adsorption of water-soluble vapors. However, in high concentration of VOCs (e.g. 20,000 ppm), moisture has less effect on their adsorption behavior (Delage et al., 1999). Biron et al., (1998) studied the condensation of water on activated carbon and its effect on eight VOCs (three water-miscible, three water-soluble and two insoluble) in conditions of high (73% and 89%) RH. Their performance showed that not all the water soluble VOCs (e.g. diacetone alcohol) are characterized by a higher uptake than insoluble ones (e.g. 1-hexanol). They concluded that the water solubility of VOCs is not a significant factor that influences the adsorption mechanism.

The adsorption behavior of the filters depends on the number and geometric arrangement of surface functional groups on the carbon surface (McCallum, 1999). At RH levels above 50%, the activated carbon fills up due to the capillary condensation of water within the pores. Cal et al. (1997) measured the adsorption capacity of the activated carbon fiber for the removal of VOCs in concentration ranges of 10–1000 ppmv and RH of 0% to 95%. In addition, he applied the Dubinin-Radushkevich method to predict equilibrium adsorption capacities in 100 ppbv to 10000 ppmv concentration ranges. The VOCs that were tested included: acetaldehyde, benzene, acetone and methyl ethyl ketone (MEK). At the above mentioned concentration ranges, these experiments showed that benzene had the highest adsorption capacity on the activated carbon (both theoretically and experimentally). Moreover, the authors observed that for RH below 50%, water vapor adsorption was insignificant. In another study, Cal et al. (1995) concluded that acetone (a water miscible compound) showed little decrease in its adsorption capacity on activated carbon cloths up to 90% RH, while at levels above 65%, the adsorption capacity of benzene (a water immiscible compound) was decreased. The VOC concentrations they tested were at 350 ppm to 1000 ppm.

Nelson et al. (1976b) examined the effect of humidity on adsorption of activated carbon at concentration of VOCs at 1000 ppm and humidity levels of 0% to 90%. They found that the effect of RH was minimal below 50% and above 50% RH the performance of the filter was reduced. Werner et al. (1985) measured breakthrough times for a VOC (trichloroethylene) at 50 ppm to 230 ppm concentrations and at 5% to 85% RH. They also reported a significant decrease in breakthrough times at levels above 50% RH. Owen et al. (1995) conducted similar tests on lower concentrations of toluene (1 ppm to 70 ppm) at various humidity levels (dry to 80% RH). Their results showed that all level of relative humidity had an adverse effect at low VOC concentrations.

Delage et al. (1999) investigated the effect of RH (0% to 60% RH) on the dynamic adsorption of VOCs (at concentrations of 0 to 20700 ppmv) on a GAC filter. They determined that RH levels did not affect adsorption capacities of the filters. They reported the 10% breakthrough time of GAC at dry condition to be 40.6 minutes where at presence of relative humidity it was 37.4 minutes.

The concentrations of VOCs in most of the literature are higher than usually found in indoor air concentrations. However, the breakthrough time of GAC filters at lower concentrations can be extrapolated from the results obtained at higher concentrations by using the Nelson-Harder correlation* (Scahill et al., 2004) to relate breakthrough times to upstream VOC concentrations:

$$t_2 = t_1 \left(\frac{C_2}{C_1} \right)^N \qquad (3)$$

Where C_1 and C_2 are upstream concentrations of VOCs at different known injection rates, t_1 and t_2 are the certain breakthrough times at which C_1 and C_2 were detected (respectively) and N is a constant for a given combination of the test's adsorbate and adsorbent. It can be calculated from a log-log plot of breakthrough times versus VOC concentrations.

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* This correlation is not applicable to this study, since only one injection rate was used to conduct the tests.

3 Experimental Setup and Methodology

3.1 *Introduction*

This chapter describes the experimental set-up and the methodology adapted for measuring the performance of the filters.

3.2 *Challenged Gas Selection and Tested GAC*

The representative VOCs for this study were selected according to ASHRAE guidelines and the following factors (VanOsdell, 1994) that:

- "VOCs should be found in indoor environments.
- VOCs thought to have potentially serious health effects be given priority.
- The chosen VOCs should be relatively easy to analyze and should not interfere with the analysis of other compounds.
- It should be possible to work safely with VOCs without having to take extraordinary personal safety precautions.
- The cost of test compounds should be reasonable."

Cyclohexane (HPLC grade manufactured by Fisher Scientific), ethyl acetate (HPLC grade manufactured by Fisher Scientific), and toluene (HPLC grade manufactured by Fisher Scientific), were selected because they have been classified among the most common indoor gaseous pollutants and/or air contaminants to pose significant health risks (Kingsley et al., 1999). These are three of a possible 113 contaminants that have been identified in investigated residential and commercial buildings (Spengler et. al., 1979; Grimsrud et al., 1984; Krause, 1987; Black et al., 1987; Bayer et al., 1988; Yuill et al., 1989; Daisey et al., 1994; Otson et al., 1994; Weschler et al., 1992; Ullrich et al., 1996; Hadwen et al., 1997). Moreover, they are easy to analyze, are not too expensive and do not require the use of extraordinary safety precautions.

The VOCs were also selected for their physico-chemical characteristics, such as: boiling point, polarity, vapor pressure and affinity coefficient[*]. Toluene has usually been adopted as a representative VOC in most previous studies (Lohse, 1995; Harbison, 1998). The US EPA Building Assessment Survey and Evaluation (BASE) study has detected toluene in the indoor air samples of 56 office buildings (Girman et al., 1999). VanOsdell (1994) suggested that toluene is one of the safest aromatic compounds and recommended its use as a representative VOC for IAQ studies. Toluene is a low-molecular weight aromatic compound that is often found in adhesives, wallpaper, joint compound, vinyl flooring, caulking, paint and chipboard. It has low water miscibility. However, even at low levels, toluene exposure can have narcotic effects on the central nervous system (Environment of Canada, July 2007).

Ethyl acetate has a low molecular weight, is water soluble and is often found in confectionaries, perfumes and fruits. Exposure to high levels of ethyl acetate can produce health problems, including narcosis and may cause liver and kidney damage (Environment of Canada, July 2007). Cyclohexane belongs to the cycloalkane family. Because it is not water miscible, it is often used as a solvent, in perfumes, coating, and paint and as a varnish remover. Health effects associated with exposure to this compound

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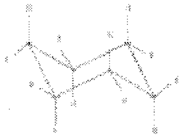
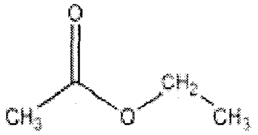
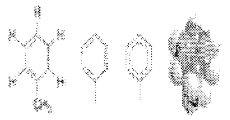
[*] Affinity between the VOC and activated carbon, Appendix A

vary from headaches to anesthesia, depending on the concentration and length of exposure (EPA, 2007).

While the selected VOCs are similar in terms of molecular weight and boiling point, their polarity and water solubility differ greatly. Table 3.1 shows the specifications of the selected VOCs.

Table 3.1: VOCs consumed in this study and their characteristics (Obtained from MSDS except where noted otherwise$^+$)

			
VOC	**Cyclohexane**	**Ethyl acetate**	**Toluene**
Polarity	**0**	**4.3**	**2.4**
Vapor Pressure	**95 (at 20°C)**	**76 (at 20°C)**	**22 (at 20°C)**
Molecular Weight (g/mol)	**84.16**	**88.11**	**92.14**
Solubility in Water	**Immiscible**	**8.3 g/100 ml (20 °C)**	**0.053 g/100 mL (20-25°C)**
Boiling Point (°C)	**80.74**	**77.1**	**110.6**
***Affinity for Carbon**	**1.058**	**0.851**	**1.186**
Henry's Law Constants	**$5.5\times10^{-3\bullet}$**	**$6.5^{\dagger}$**	**$1.6\times10^{-1\bullet}$**

+ Data are given for materials in their standard state (at 25 °C, 100 kPa) except where noted otherwise
***Affinity for carbon or affinity coefficient: is affinity between VOC and the surface of the adsorbent (Appendix A)**
•Yaws and Yang, 1992 †Meylan and Howard, 1991

This study used a 50 µL/min injection rate (continuously), based on trials and errors. Injection rates lower than this provided such low concentrations of challenged gas inside the environmental test chamber, that each test would have taken days – or even months – to complete. Because the test chamber was a closed-looped system, the concentration of the VOC inside the chamber would gradually increase and reach between 100 ppm and 500 ppm.

Eight different GAC were tested. Three of them were virgin activated carbons (group 1). One of the activated carbons was impregnated with 10% phosphoric acid. The third group consisted of four impregnated activated carbons; two of them had 5-10% and the other two 1-2% potassium hydroxide. Table 3.2 shows the GAC filters' physical characteristics and properties.

Table 3.2: GAC filters' identifications obtained from manufacturer

DATA / GAC	Activated Carbon (%)	Impregnated by	pH	Moisture maximum (wt%)	Hardness minimum (wt%)	Particle Diameter (mm)	Substrate CTC* minimum (wt%)	Substrate Surface Area (m^2/g)	Shape	Apparent Density (g/cm^3)	Ash Content maximum (%)
1A	100	N/A	8.9	2	95	3	70	1250	pellet	0.48	12
1B	100	N/A	8.9	2	95	4*3 mesh	60	1000	chips	0.48	4
1C	100	N/A	8.9	2	95	4	70	1250	pellet	0.48	12
2A	76	10% Phosphoric acid	2.5	15	95	3	70	1250	pellet	0.64	N/A
3A	75-85	5-10% Potassium hydroxide	9.5	15	95	3	70	1250	pellet	0.61	N/A
3B	75-85	5-10% Potassium hydroxide	9.5	15	95	4	70	1250	pellet	0.61	N/A
3C	90-95	1-2% Potassium hydroxide	9	4.5	98	3	70	1250	pellet	0.51	N/A
3D	90-95	1-2% Potassium hydroxide	9	4.5	98	4	70	1250	pellet	0.51	N/A

*The CTC is a standard test used to measure the porosity of activated carbon. The adsorptive capacity is determined by testing the activated carbon against saturated carbon tetrachloride (CCl_4) vapour. The result of this test are presented as ratio (expressed as percentage) of the weight of CCl_4 adsorbed by the activated carbon with respect to weight of activated carbon under saturated conditions.

3.3 *Chamber Design*

This dissertation attempts to provide a setting where GAC filters are used in mechanical ventilation systems to circulate indoor air while concentrations of upstream air constantly increase. A small scale, closed-loop, dynamic environmental test chamber was designed for this purpose: 1.5 m x1.5 m with a volume of 0.051 m^3 (Figure 3.1).

The chamber was made of galvanized steel ducts of 0.102 m diameter. An in-line fan with a diameter of 0.152 m was positioned in the system. A fan-controller knob was installed on the system to control the operation of the fan which could provide air velocity range of 0.1 to 1.33 m/s without the presence of any filters in the system. As it is illustrated in Figure 3.1, there were nine ports on the system.

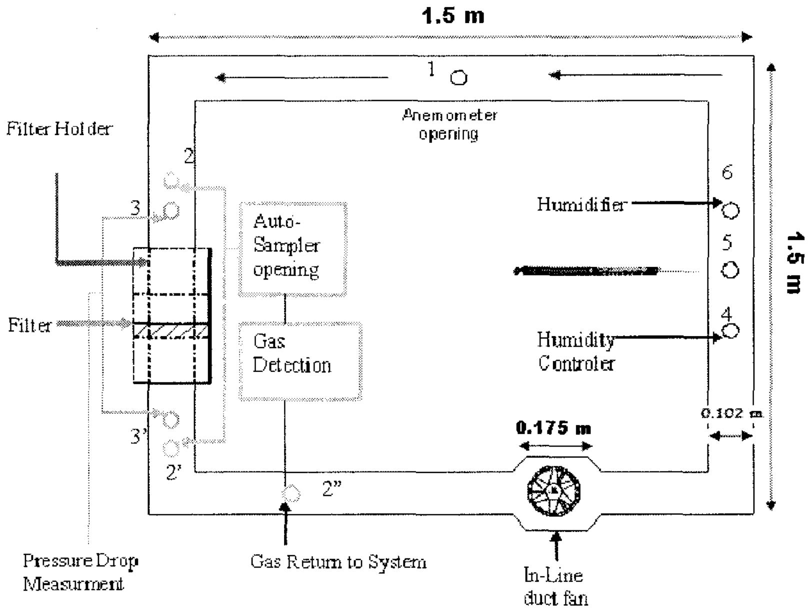


Figure 3.1: Design of the closed-loop, dynamic, small environmental test chamber:

1) Anemometer port 2) 2, 2',2'' Auto Sampler ports 3) 3, 3' Pressure Drop Measurement ports 4) Humidity Controller 5) Injection 6) Humidifier

Figure 3.2 shows that a cylindrically shaped filter holder with inner diameter of 0.127 m was used to hold the GAC filters horizontally. The filters were placed between two stainless steel, wire-mesh (of size 10 evenly). A ring, with a diameter of 0.127 m, held the second mesh on top the GAC filter and helped to reduce edge effect.

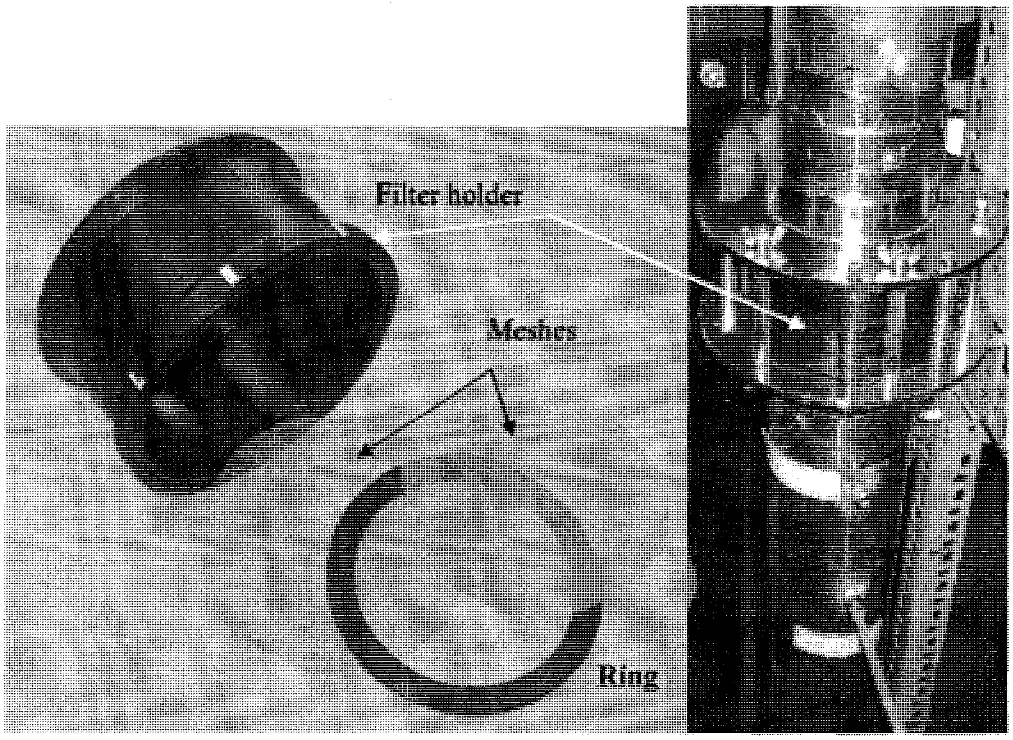


Figure 3.2: Filter holder (Left) and location of filter holder in the test chamber (Right)

3.4 Equipment

Auto-Sampler: A CAI Intelligent Sampling System MK2 was used for air sampling. Connected to a photoacaostic gas detector, it was programmed to take the sample alternatively from before (upstream) and after filter (downstream) (Figure 3.1, ports 2 and 2', respectively). The sampler had four channels, two of which were used for this study. The gas detector dictated time intervals for air samples to be taken from the test chamber. At each interval, a certain amount of air was sent to the photoacoustic gas detector for analysis.

Photoacoustic gas detector: The photoacoustic multi-gas monitor (Innova, AirTech Instruments 1312) was used to monitor up to seven different gases simultaneously. In this study, air samples were analyzed (with their concentrations being displayed on the gas detector monitor) before being returned to the chamber through port 2". After pumping an air sample through the auto-sampler, the photoacoustic gas detector irradiates it with a modulated, pulsating light of a pre-selected wavelength. Because the light is pulsating, the gas temperature increases and decreases causing an equivalent, directly proportional response in the gas pressure (an acoustic signal) in the closed cell. Two microphones mounted in the chamber wall measures this signal. This is repeated according to the number of gases being measured. The response times are down to approximately 13 seconds for one gas or water vapor and approximately 40 seconds if 7 gases and water vapor are measured together.

Micromanometer (Tsi, DP_CALC, Model No. 8702): The micromanometer was used to monitor pressure differences across the filter. As illustrated in Figure 3.1, the apparatus sensors were attached to ports 3 and 3', representing the pressure drop due to present of the filter.

Thermo-anemometer (VELOCICALC, Model No. 8346): This equipment measured the air velocity inside the chamber within a range of 0.05 m/s and 1.88 m/s. Its sensor (Figure 3.1, port 1) was located far enough away from the fan to eliminate any disturbance caused by air turbulence. The instrument's velocity sensor relies on a constant temperature thermal anemometer to detect the cooling effect of the moving airstream as it passes over a heated sensor (it is heated electrically by control circuitry in the electronics package).

Humidifier: An ultrasonic humidifier (ets, Model No. S612) produced moisture from distilled water. The probe (Figure 3.1, port 6) installed within the chamber controlled humidity levels as necessary.

Humidity Controller: An automatic humidity controller (ets, Model 514) monitored RH within the test chamber. It kept the RH constant at a pre-set level during testing. Its sensor was placed at port 4, as shown in Figure 3.1.

Syringe infusion pump (model Kd Scientific): This instrument injected VOCs continuously. It could provide an injection rate ranging from 0.001 μL/h to 14.33 mL/min.

Dial test indicator (model Starrett Test Dial Indicator 651 Series): A digital dial indicator was used to measure the thickness of the GAC filter beds when placed inside the filter holders. It measured the thickness in ranges of 1 (0.040") mm to 50 (2") mm by use of a plunger moving in and out.

3.5 Experimental Method and Procedure

Eight commercially available GAC filters were tested with individual VOCs. They were categorized into 3 groups based on their activated carbon content. Challenged gas was injected continuously at rate of 50 μL/min, increasing the VOC concentration from as much as 100 ppm to 500 ppm depending on the GAC filter and/or gas used. The moisture was maintained at a pre-adjusted level of RH (30%, 50% or 70%) during the experiments by humidifier and humidifier controller.

The auto-sampler was connected to a photoacoustic gas detector and collected air samples from upstream (before the filter) and downstream (after the filter) every one minute. Thus, every two minutes, the concentration of upstream or downstream air was displayed on the photoacoustic gas detector monitor. After photoacoustic analysis, the air samples were returned to the test chamber (Figure 3.1, port 2").

This study used a residence time of 0.1 seconds in order to verify some of the findings with the literature (Nelson, 1976a, b; VanOsdell, 1994; Cal, 1995; VanOsdell, 1996; VanOsdell 2006; Lee, 2006).

In order to maintain the residence time of 0.1 seconds, the GAC filters weighed 50 ± 0.5 grams. After placing them in the filter holders, their thickness was measured in nine different places (eight of them were 45° apart on the surrounding of circle[*] and one was at its center) as illustrated in Figure 3.3.

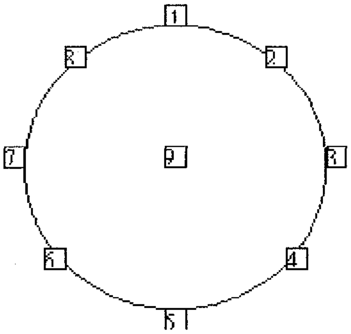


Figure 3.3: Locations of thickness measurements

The residence time was calculated as the ratio of average thickness of the GAC filter bed to the average air velocity, and the air velocity was monitored by a thermo-anemometer sensor that was fixed to the center of the duct at port 1 (see Figure 3.1). It was located far enough away from the fan, the filter, the injector and the humidifier to avoid any disturbance or turbulence. The pressure drop across a filter was measured using a micromanometer.

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[*] The filter holder cross section area was in a circular shape.

All the GAC filters were exposed to toluene with injection rate of 50* μL/min at 50% RH. One GAC filter was selected from each group as a representative for further tests, since the GAC filters in a group tended to show similar performance.

The 5 mL gas-tight Hamiltonian syringes were placed in the syringe infusion pump and injected the VOC into the test chamber at port 5 (see Figure 3.1) at the pre-set injection rate (50 μL/min).

3.6 Calibrations

The photoacoustic gas detector (Innova) and injector were calibrated to ensure that they were working properly for the conditions of this research.

3.6.1 Calibration of Photo-acoustic gas detector (Innova)

Innova was calibrated for three selected VOCs. Nitrogen gas from a compressed gas cylinder was used as the carrier gas (with a flow rate of 2.230 L/min) and continuously brought injected VOCs through Innova. Two Hamiltonian gas-tight syringes of 10 μL and 25 μL were used to inject these VOCs at rates of 1.30 μL/min, 1.40 μL/min, 1.50 μL/min, 1.60 μL/min, 1.70 μL/min and 1.80 μL/min. These injection rates were used to provide the concentration range of the VOCs (100–500 ppm) for this study. Figures 3.4–3.6 illustrate the calibration of Innova for individual VOCs at the mentioned injection rates.

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* All injections were continuously.

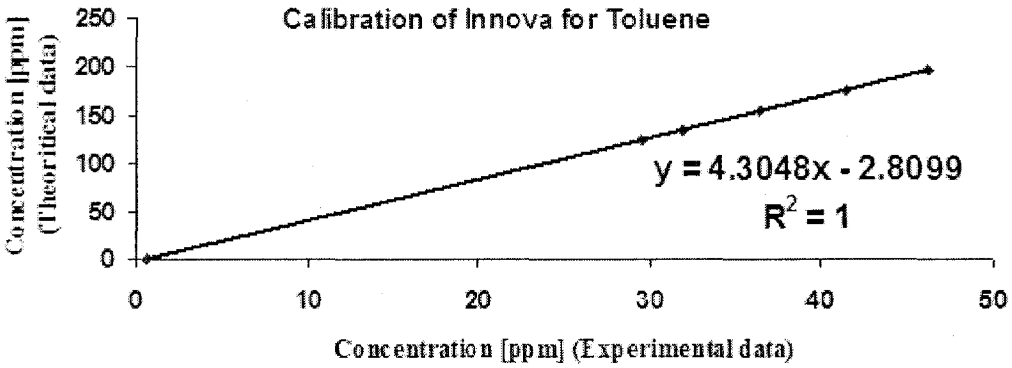

Figure 3.4: Calibration curve for toluene*

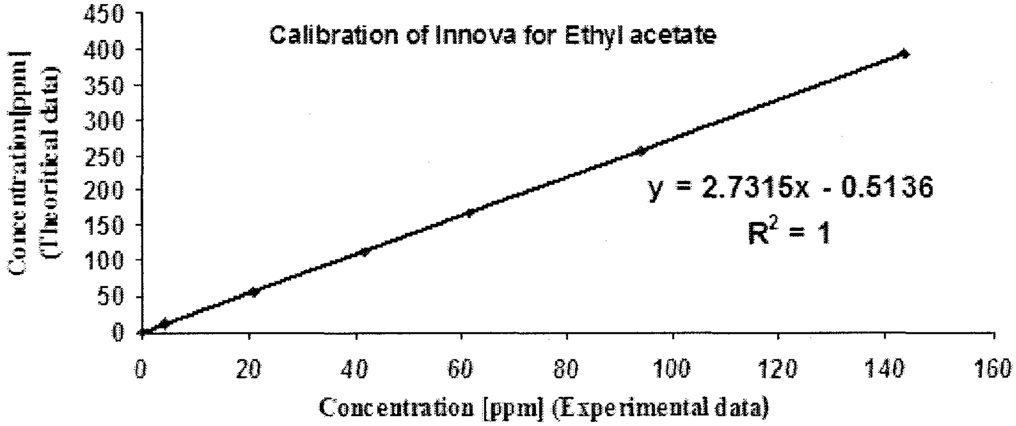

Figure 3.5: Calibration curve for ethyl acetate

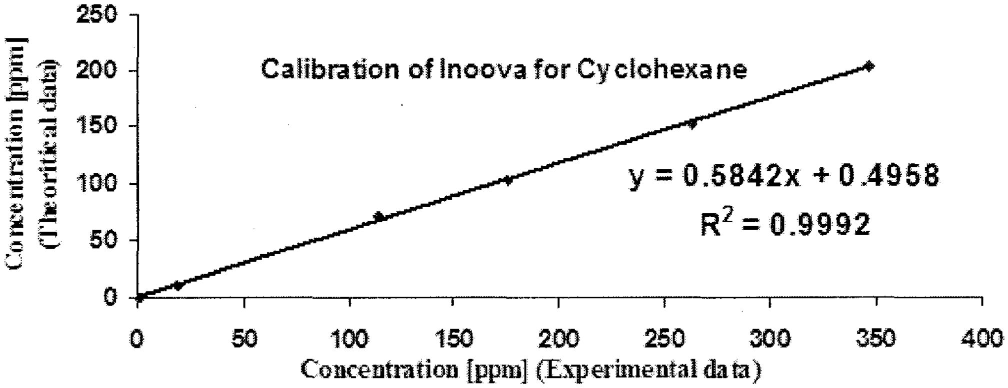

Figure 3.6: Calibration curve for cyclohexan

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* The theoretical data refers to the concentrations calculated based on the density, molecular weight, and the injection rate. The experimental data however, refers to the concentration obtained from Innova.

3.6.2 Calibration of Syringe Pump

The syringe infusion pump was calibrated, with injection rates for the tests being 10 μL/min, 20 μL/min, 50 μL/min and 100 μL/min. The syringe used for injection was a Hamiltonian gas-tight 5 mL. As illustrated in Figure 3.7, the coefficient of determination (R^2) equals 1.0 which means that all points lie exactly on a straight line, with no scatter. This linear regression shows that the empirical and theoretical values of injection rates were nearly identical.

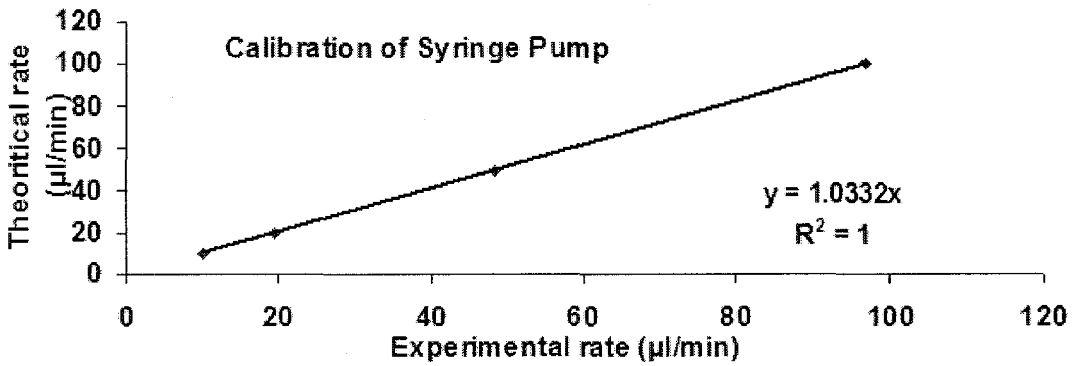

Figure 3.7: Calibration of syringe pump using a 5 mL Hamiltonian gas tight syringe

3.7 Chamber Leakage Test

The test chamber was sealed tightly using aluminum duct tape. A series of leakage tests was conducted using tracer gas techniques using sulphur hexafluoride (SF_6). The photoacoustic gas detector (Innova) was used to measure its concentration. As Figure 3.8 presents, the leakage rate was 7.08×10^{-5} m^3/s when the fan flow rate was 0.233 m^3/s. Thus, the leakage rate was 0.03% of the maximum flow rate provided by the fan.

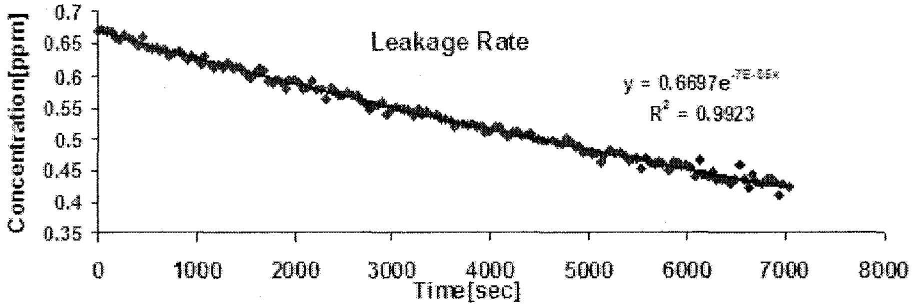

Figure 3.8: Leakage test curve

3.8 Blank Test

A test was conducted without a filter in order to measure the amount of VOC that would adhere to the surface of the test chamber. For this test, a 5 mL Hamiltonian gas tight syringe injected the VOC at a rate of 50 µL/min. Toluene was injected for 25 minutes and its upstream and downstream concentrations were monitored. Figure 3.9 shows these upstream and downstream concentrations.

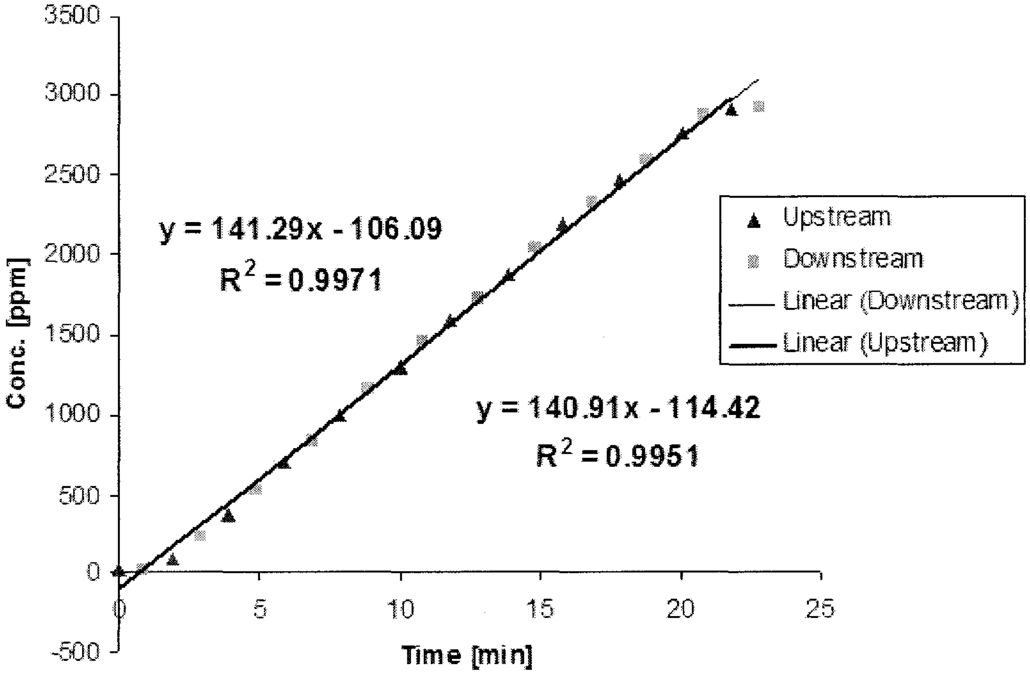

Figure 3.9: Blank test: toluene was injected at 50µL/min and 40% RH

During the injection period, the upstream and downstream concentrations increased at a linear rate (see Figure 3.9). The upstream concentration and downstream concentrations are aligned together. This demonstrated that the adsorption of VOCs inside the surface of the test chamber, between upstream and downstream sampling points, was negligible*. If there had been a significant adsorption of VOCs between the two ports, the downstream concentrations would have been lower than the upstream ones (similar to presence of filter). For this study, since both upstream and downstream concentrations were measured at the points similar to the blank test to gauge efficiency, the behavior of VOCs on the surface of the system between these two ports is most important. Therefore this blank test demonstrates that adsorption between these two points is insignificant.

Table 3.3 presents the mass of injected toluene and total mass adsorbed on the GAC filters from the start to end of injection time. It shows that the amount of injected toluene was very close to the value of toluene adsorbed on GAC filters. Both the maximum leakage rate of the system ($3.5x10^{-6}$ m^3/s) and sink effect were negligible.

Table 3.3: Mass balance for the system

GAC	RT(°C)	Calculated VOC (mg)	Injected VOC (mg)	Error
1A	25	18842.4	18855.08	0.07
1B	23	18045.24	18046.26	0.01
1C	25	17755.08	17771.45	0.09
2A	23	3673.68	3675.75	0.06
3A	23	915.57	917.18	0.18
3B	23	1145.69	1150.38	0.41
3C	24	14776.06	14814.45	0.26
3D	24	18269.73	18282.05	0.07

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[*] In this study, the bases for analysis relied merely on the concentrations of VOC right before and after the filter to evaluate the filter performance. So, adsorption on the fan or the rest of the duct is not important. The only important part is between the upstream and downstream ports, which have a relatively small surface area, especially compared to GAC specific surface area.

3.9 *Evaluation of Filter Performance*

Performances of filters were analyzed using efficiency and breakthrough curve concepts. The efficiency is the percentile ratio of the difference between upstream-downstream concentrations to the upstream concentration, and it decreases as time increases. Efficiency curves show the adsorption capacity of a filter as function of time. The breakthrough time is the time at which a filter reaches a certain level of efficiency (e.g. $t_{50\%}$: corresponds to a breakthrough time when a filter has reached 50% efficiency and $t_{80\%}$ corresponds to a breakthrough time when a filter has reached 20% efficiency). The analysis of the results was based on the the efficiency of filters, which is calculated from the data of both upstream and downstream concentrations as follows:

$$E = \left[1 - \frac{C_{downstream}}{C_{upsteam}}\right] \times 100 \qquad (1)$$

Where E is the efficiency [%], $C_{downstream}$ and $C_{upstream}$ are the concentrations downstream and upstream, respectively.

Since only one photoacoustic gas detector was used for this study, upstream and downstream concentrations could not be measured simultaneously. The concentrations of upstream, at the time that downstream concentrations were monitored were calculated through linear interpolation (Appendix B). Considering the higher VOC concentration in this study than a typical indoor environment, the 80% breakthrough time (defined as the time it takes to reach 80% of the challenge concentration exiting a filter) suggested a cost effective choice for GAC filter replacement and was, thus, used as an end point in this study. GAC filter performances varied considerably, so both 50% and 80% breakthrough times were used in this study's analysis. Figure 3.10 shows that as upstream and downstream concentrations for GAC filter 1C increased over time and the efficiency of the filter decreased (Figure 3.11 presents an efficiency profile of filter 1C).

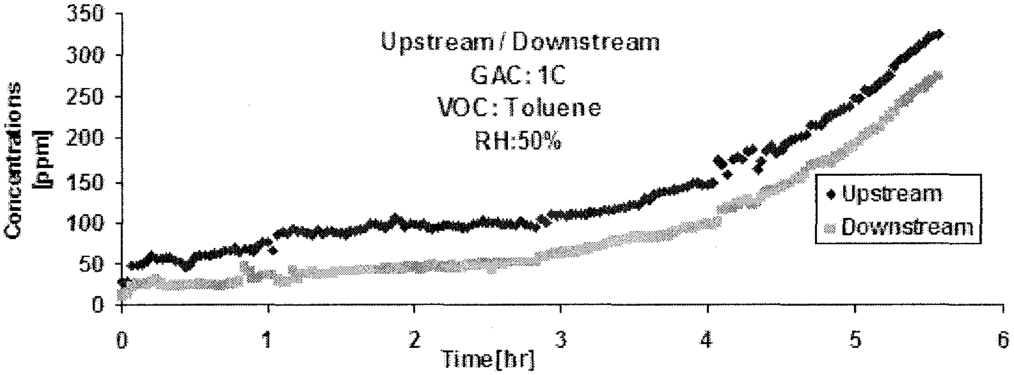

Figure 3.10: Profile of upstream and downstream concentration for GAC 1C filter

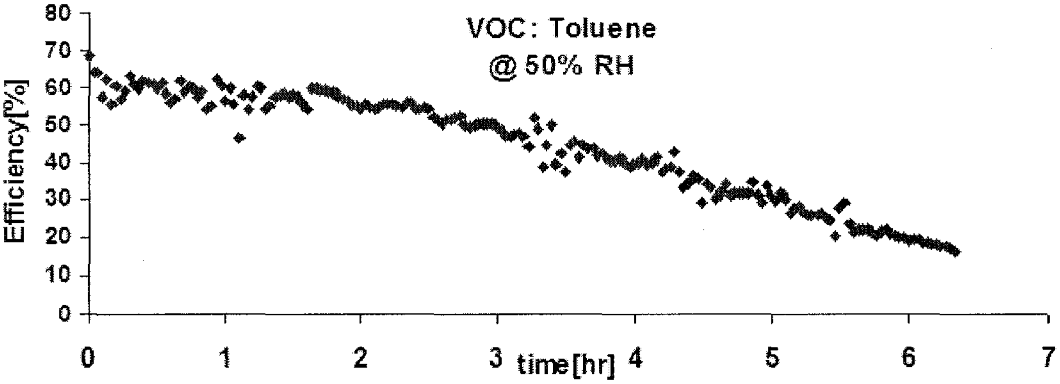

Figure 3.11: Efficiency profile for GAC 1C filter

In order to evaluate the repeatability of the test method, tests were carried out for two samples of filter 1C under identical test conditions. Figure 3.12 presents the efficiency profiles as a function of time for both tests; the results show good agreement. The 50% breakthrough times (of 2.03 hours (121.8 minutes) and 2.13 hours (127.8 minutes)) show an error of less than 5%.

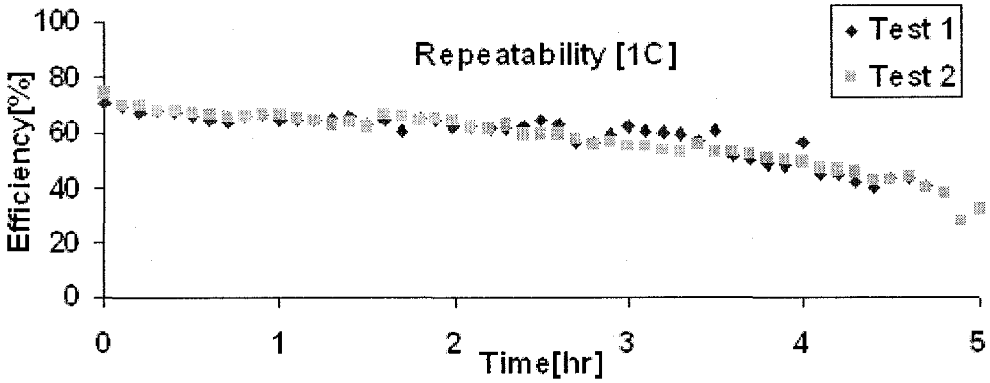

Figure 3.12: Repeatability tests for 1C under the same conditions using toluene as the challenged VOC at 50% RH

The 50% capacity (total mass of VOC adsorbed on the GAC filters until a 50% breakthrough time) was calculated by integrating the performance curve from start to 50% breakthrough time:

$$m_{50} = \int_{0}^{t_{50}} Q(C_{upstream} - C_{downstream})dt \qquad (2)$$

Where m_{50} is the total mass of VOC collected from start to the 50% breakthrough time, Q is the flow rate of the system, $C_{upstream}$ and $C_{downstream}$ are the concentrations detected before and after filtration, respectively. dt is the (hourly) time interval between sampling. The 50% capacity calculated by equation (2) was divided by the GAC bed mass to obtain a GAC capacity expressed as a percentage of VOC on the filter's bed. For instance, Figure 3.13 shows a 50% capacity divided by 49.903 grams of 1C. It shows that, when the filter reached its 50% breakthrough time, its capacity is 13.09% of GAC mass.

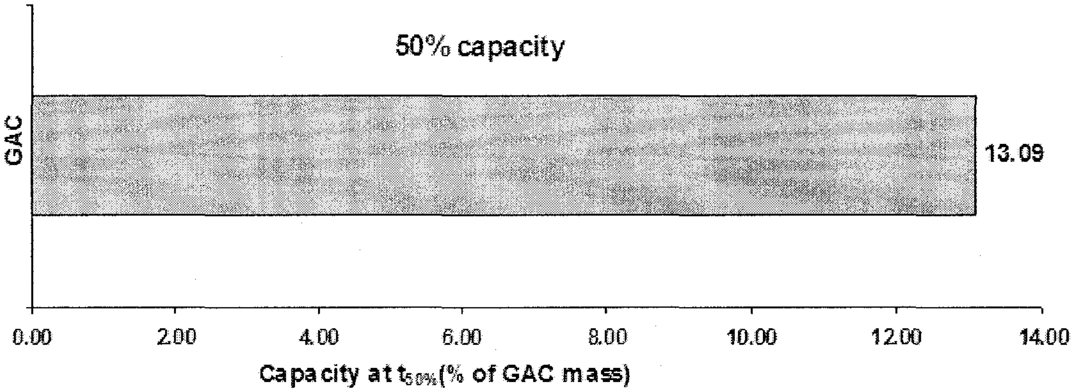

Figure 3.13: GAC 1C filter 50% capacity, challenged by toluene at RH 50%

4 Results and Discussion

This chapter presents and discusses the experimental results from the test chamber. Attempts were made to study the effect of RH and different VOCs on the performance of various GAC filters. After several initial trials, it was found that more than three weeks were required to complete an experiment at 1 ppm for toluene, when a GAC filter bed depth corresponding to a residence time of 0.1 second used. Thus, in order to complete each test in one day (maximum 12 hour), 50 μL/min was chosen as the injection rate in this study. The concentration of a VOC in the closed-loop test chamber increased constantly and reached 100 ppm to 500 ppm, depending on the VOC and/or GAC filter used. Since the breakthrough times of the filters tested at the higher concentrations could be extrapolated to calculate and predict correlating breakthrough times and filter behavior at lower concentration, it was more efficient (temporally and economically) to conduct these experiments at the higher concentration. A 50% and 80% breakthrough time ($t_{50\%}$ and $t_{80\%}$, respectively) were calculated for each test. 50% capacity (m_{50}) was calculated by integrating the performance curve from the beginning to a 50% breakthrough time (when a particular filter achieved 50% efficiency). The m_{50} was then divided by the GAC bed mass to obtain a GAC capacity value expressed as a percentage of VOC on the bed of GAC.

4.1 Toluene

All the GAC filters were tested with toluene. A residence time of 0.1 second, continuous injection of toluene at rate of 50 μL/min and the weights of 50 ± 0.5 g of the GAC filters were constant for all the tests.

4.1.1 GAC 1 filter series

This study used 3 virgin activated carbon GAC filters (1A, 1B, and 1C), which used pellets of different shapes. 1A and 1C had cylindrically shaped pellets with a diameter of 3mm and 4mm, respectively. 1B's irregularly shaped pellets (with a 4×3 mesh size). Nearly four continuous injections of 5mL were required before it was able to reach efficiency of 20%.

Table 4.1: GAC 1 Series tests conditions

GAC	Shape	AC (%)	Mass (g)	Velocity (m/s)	Pressure drop(in H2O)	RH (%)	Thickness (cm)	Residence time(s)
1A	pellet	100	50.344	0.12	0.014	50	1.18	0.098
1B	irregular	100	49.903	0.12	0.011	50	1.18	0.098
1C	pellet	100	49.992	0.12	0.007	50	1.19	0.099

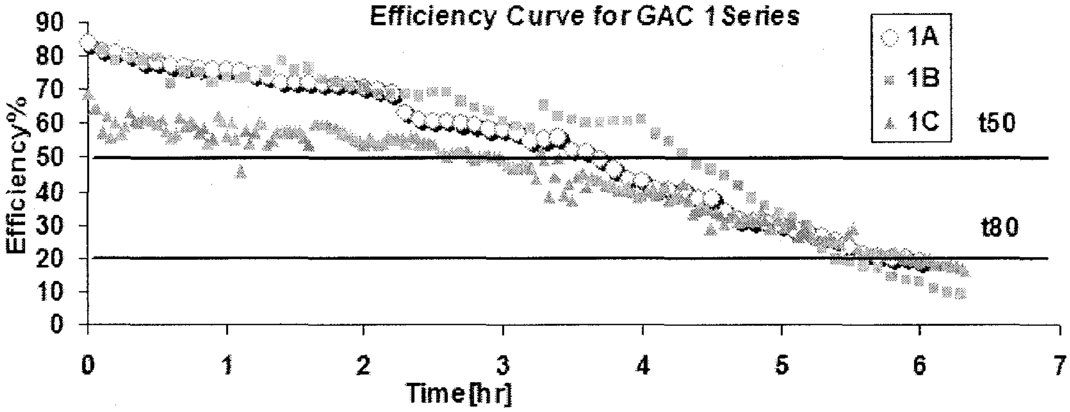

Figure 4.1: Efficiency curves for GAC 1 series, challenge by toluene at 50% RH (volumes of toluene injected were 21.75, 20.82, and 20.5 mL for 1A, 1B, and 1C respectively) *

Figure 4.1 shows the efficiency curves for GAC series 1 at 50% RH. The adsorption capacity of 1A and 1B were almost identical, but 1C was slightly less efficient in adsorbing toluene. The percentage of activated carbon used for this series was the same, with the only difference being the size of the granular. The 1C provided the lowest pressure drop (i.e., 0.007 inches of water gauge); this can be attributed to its larger grain size by comparison with the other two filters in its group. Being larger, they provided a less tightly packed bed and had more air voids, causing the filter to be less efficient in filtering VOCs. Table 4.2 shows a breakthrough time corresponding to 50% and 80% efficiency for this group. 1A and 1B took more time to reach 50% breakthrough times compared to 1C; but, 1C reached an 80% breakthrough time later than did 1A and 1B. Thus, while 1C had larger pellets, its capacity was comparable to 1A and 1B, even though 1A and 1B showed better performance from the onset, achieving full capacity faster than did 1C. GAC 1C reached 20% efficiency 22.6 minutes later than 1A did, and 28.2 minutes later than 1B did.

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* The volumes mentioned are the total injection and it does not represent the volumes necessary to reach 20% efficiency.

Table 4.2: 50% and 80% breakthrough times of GAC 1A, 1B and 1C for toluene

BT / VOC	t_{50} (h)	t_{80} (h)
1A	3.9989	5.5981
1B	4.3972	5.4967
1C	2.8311	5.9625

In a similar system (closed-loop dynamic environmetal chamber), Lee et al. (2006), tested four different fibrous activated carbon filters (FAC) for toluene. The injection rate was 4.32 μL/min, which is less than 1/10 of the injection rate used in this study. The test were conducted at constant air velocity of 0.2 m/s: the residence time varied from 0.03 to 0.1 second. The intial efficiencies of these filters were 50-60%. The 80% breakthrough times of the filters were 2.02 hours for A, 1.03 hours for B, 2.68 hours for C and 5.98 hours for D. Considering the fact that they had much lower toluene injection rate, the removal efficiencies of the GACs tested in this study are better than FAC tested by Lee et al. (2006).

4.1.2 GAC 2A filter

The 2A filters were made up of 76% activated carbon and 10% phosphoric acid. The average bed depth in the filter holder was 11.68 mm for 50.227 grams. The pressure drop was 0.008 in H_2O for an air velocity at 0.12 m/s, corresponding to a residence time of 0.1

seconds. As illustrated in Figures 4.2 and 4.3, the efficiency of this filter dropped from 90% to 40% within 0.2 hrs. Table 4.3 shows the test conditions for this filter.

Table 4.3: GAC 2A test conditions

GAC	Shape	AC (%)	Mass (g)	Velocity (m/s)	Pressure drop(in H2O)	RH (%)	Thickness (cm)	Residence time(s)
2A	pellet	76	50.227	0.12	0.008	50	1.16	0.096

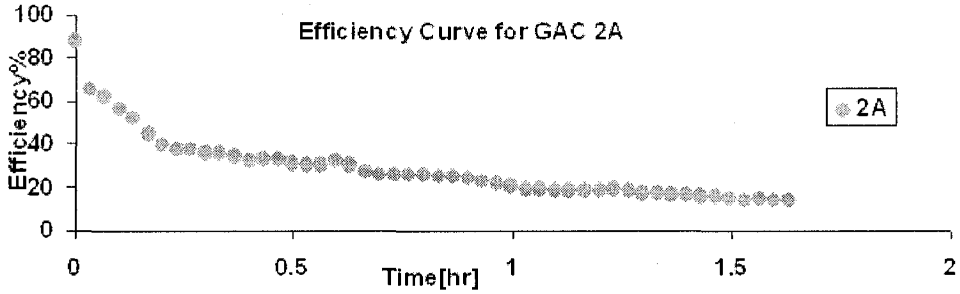

Figure 4.2: Efficiency curve for the GAC 2A challenge by toluene at 50% RH (volume of toluene injected was 4.23 mL)*

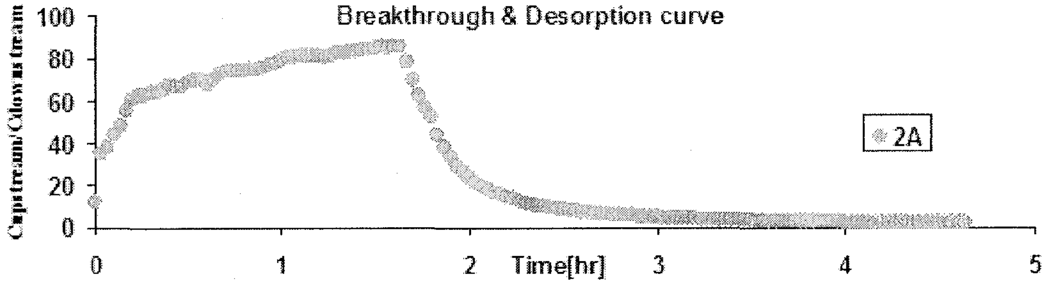

Figure 4.3: Breakthrough and desorption curve for the GAC 2A challenged by toluene at 50% RH

Once the efficiency of the GAC filter reached 20% or less, toluene was no longer injected. This filter reached 50% and 80% breakthrough times in 0.133 hours and 1.032 hours, respectively. Figure 4.3 shows the breakthrough time curve and desorption curve. Desorption occurs when adsorbed VOC is released from filter; the desorption curve, therefore, shows the speed at which the filters released the adsorbed contaminants. The

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* The volumes mentioned are the total injection and it does not represent the volumes necessary to reach 20% efficiency.

desorption process was started upon the termination of injection. The air was purged through the system by a flow rate of 3.055 L/min through a port on the chamber. Toluene was desorbed from GAC 2A filter in approximately 1.24 hours.

4.1.3 GAC 3 filter series

This group comprised four GAC filters with regularly shaped pellets of different diameters. Series 3 filters were composed of activated carbon and potassium hydroxide. Filters impregnated with potassium hydroxide are useful in treating acidic pollutant gases, such as SO_2. However, an impregnated activated carbon is less efficient for adsorbing organic compounds than a virgin one.

For GAC 3A and 3B, the percentage of activated carbon and potassium hydroxide was between 75%–85% and 5%–10%, respectively. 3B pellets were larger in diameter than 3A, thus causing a lower pressure drop for 3B. 3C and 3D had equal compositions of 90% to 95% activated carbon and 1% to 2% potassium hydroxide. 3C had a smaller pellet diameter than did 3D.

Table 4.4: GAC 3 filter series test conditions

GAC	Shape	AC (%)	Mass (g)	Velocity (m/s)	Pressure drop(in H2O)	RH (%)	Thickness (cm)	Residence time(s)
3A	pellet	75-85	50.448	0.12	0.006	50	1.07	0.089
3B	pellet	75-85	50.402	0.12	0.005	50	1.17	0.097
3C	pellet	90-95	50.161	0.12	0.007	50	1.18	0.098
3D	pellet	90-95	49.863	0.12	0.005	50	1.17	0.097

Table 4.4 shows the conditions of the tests and Figure 4.4 presents the efficiency profiles of the tested filters. GAC filters 3C and 3D were better at removing toluene than filters 3A or 3B. While 3A and 3B had 50% breakthrough times of only 0.033 hours and

0.068 hours, respectively, the 50% breakthrough times for 3C and 3D were 0.966 hours and 1.032 hours, respectively. It would seem that 3C and 3D performed better than the GAC 3A and 3B because of the higher concentration of activated carbon in their compositions and therefore, the 80% breakthrough time was reached approximately five times faster for 3A and 3B than for 3C and 3D. Table 4.5 presents the 50% and 80% breakthrough times of the filters.

Table 4.5: 50% and 80% breakthrough times of GAC 3A, 3B, 3C, and 3D for toluene

BT / VOC	t_{50} (h)	t_{80} (h)
3A	0.0331	0.4997
3B	0.0681	0.7661
3C	0.9658	4.5297
3D	1.0325	4.2636

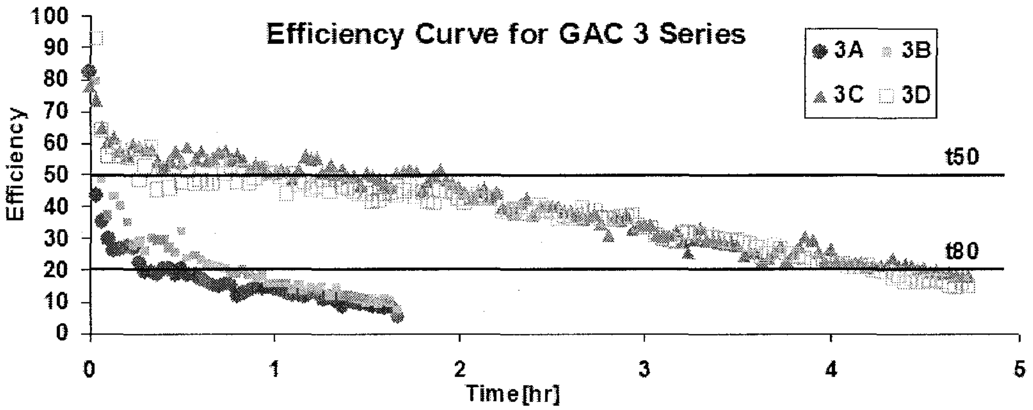

Figure 4.4: Efficiency curves for GAC 3 series, challenge by Toluene at 50% RH (volumes of toluene injected were 1.06, 1.33, 17.1, and 21.1 mL for 3A, 3B, 3C, and 3D respectively)[*]

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[*] The volumes mentioned are the total injection and it does not represent the volumes necessary to reach 20% efficiency.

GAC 2A filter (with 50% capacity of 0.59% of GAC mass) was less efficient than 3C and 3D (with 50% capacity of 10.05% and 10.92% of GAC mass, respectively). Filter 2A's capacity was approximately the same as for 3A and 3B as shown in Figure 4.6. The reason for this behavior of 2A was the percentage of activated carbons (76%) in its composition that was nearly the same as percentage of activated carbons in 3A and 3B. Figure 4.6 shows that GAC 1 series had the best adsorption capacity. As the percentage of activated carbons was reduced in the GAC filters, their adsorption capacity for adsorbing toluene decreased.

The adsorption capacities were higher for filters with higher percentage of activated carbon. The average $t_{80\%}$ for virgin activated carbon was 5.68 hours for toluene concentrations of 300 ppm at 50% RH, and the $t_{80\%}$ impregnated GAC 2A, 3A and 3B filters was around 1 hour.

Figure 4.5 shows the 50% capacity of GACs for toluene (m_{50}: the mass of toluene adsorbed on the GAC filter from the initial injection to 50% breakthrough time and then divide it by the mass of GAC and present the result in percentage). If tested GACs were ranked based on the 50% capacity, the result would be as follow: 1B>1A>1C>3D>3C>3B>2A>3A.

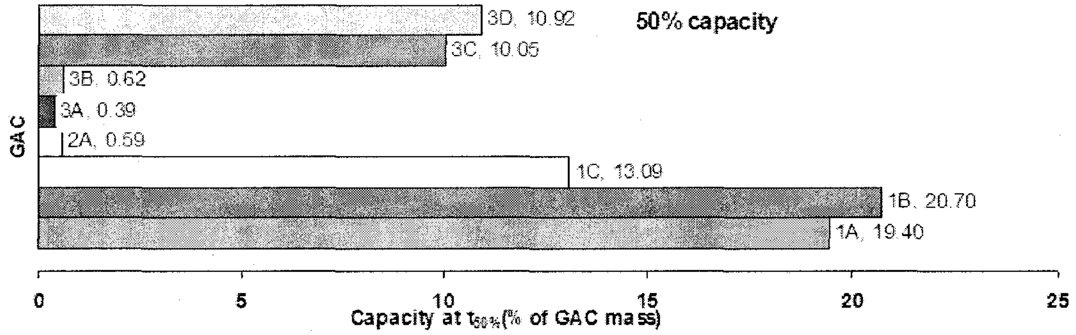

Figure 4.5: Adsorbed VOC mass at 50% breakthrough per GAC filter mass, challenged with toluene at RH 50%

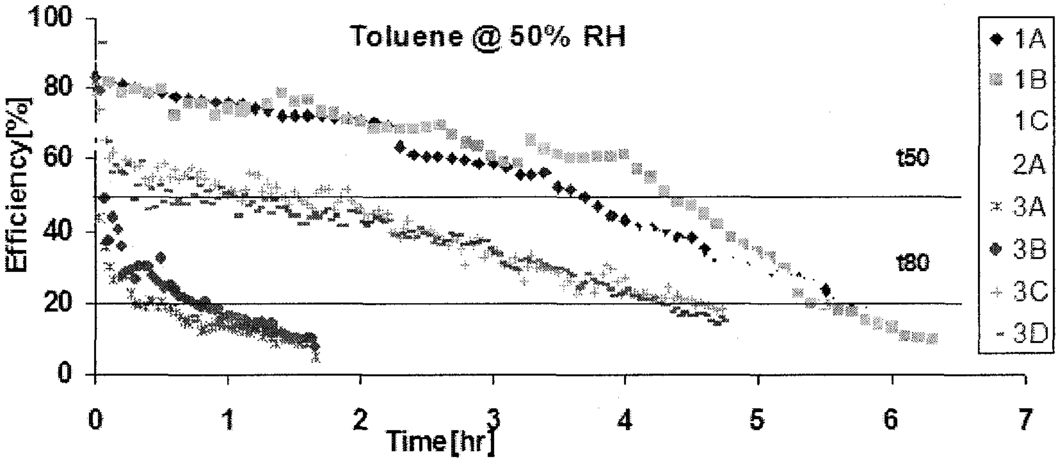

Figure 4.6: Efficiency profile of the GAC filters when challenged by toluene

4.2 Cyclohexane

Toluene test results showed similarity in efficiency curves for each of the GAC filter groups. 1A, 2A and 3A filters were selected for further study and were exposed to cyclohexane at 50% RH. Figure 4.7 shows that 1A was the most efficient one for removing cyclohexane, while 2A and 3A had similar adsorption capacities. The 1A was a virgin activated carbon filter and its significantly higher adsorption capacity for cyclohexane was the result of having more pore sites available to adsorb cyclohexane than the other two impregnated GAC filters. Table 4.6 presents the conditions of tests for this VOC.

Table 4.6: GAC filter series test conditions challenged by cyclohexane

GAC	Shape	AC (%)	Mass (g)	Velocity (m/s)	Pressure drop(in H2O)	RH (%)	Thickness (cm)	Residence time(s)
1A	pellet	100	50.042	0.13	0.004	50	1.42	0.10
2A	pellet	76	50.543	0.12	0.006	50	1.23	0.10
3A	pellet	75-85	50.195	0.11	0.007	50	1.18	0.10

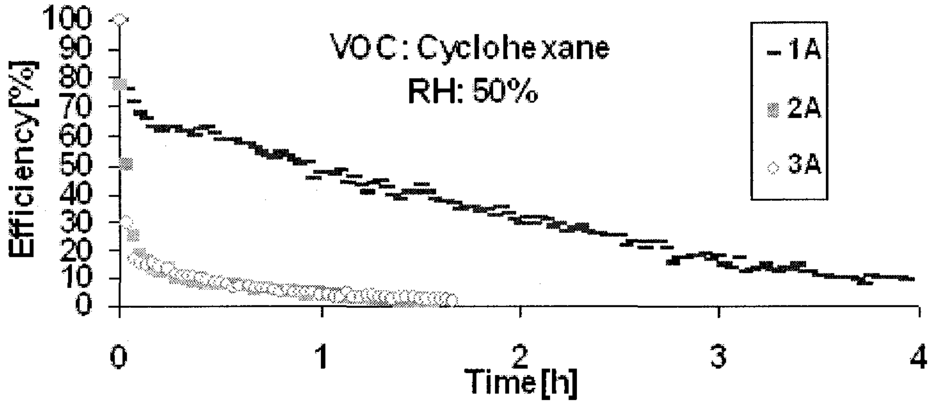

Figure 4.7: Efficiency profile for GAC filters challenge by cyclohexane (volumes of cyclohexane injected were 11.35, 2.67, and 3.31 mL for 1A, 2A, and 3C respectively)[*]

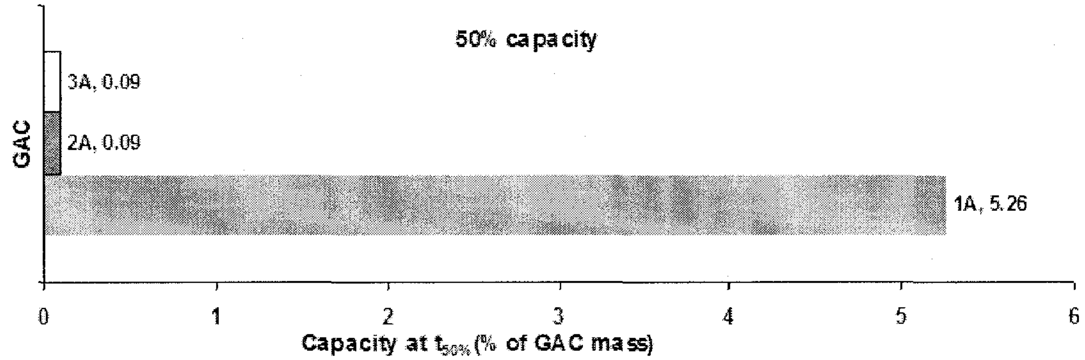

Figure 4.8: Adsorbed VOC mass at 50% breakthrough per GAC filter mass, challenged with cyclohexane at RH 50%

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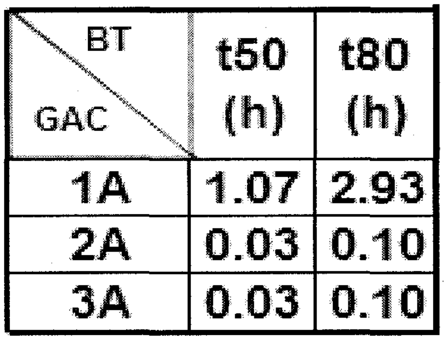
[*] The volumes mentioned are the total injection and it does not represent the volumes necessary to reach 20% efficiency.

Figure 4.8 shows the 50% capacity of the GAC filters for cyclohexane. 1A had the highest capacity, while 2A and 3A had similar, but much lower, capacity. Table 4.7 shows the corresponding breakthrough times of $t_{50\%}$ and $t_{80\%}$ for the filters when challenged by cyclohexane.

Table 4.7: 50% and 80% breakthrough times of GAC 1A, 1B and 1C for cyclohexane



BT GAC	t50 (h)	t80 (h)
1A	1.07	2.93
2A	0.03	0.10
3A	0.03	0.10

4.3 Ethyl acetate

GAC filters 1A, 2A and 3A were exposed to ethyl acetate. The conditions of the tests are illustrated in Table 4.8 and the removal efficiencies of the filters are illustrated in Figure 4.9. 1A showed the best performance among those filters with lower percentages of activated carbons because it had more pores to adsorb ethyl acetate. 2A and 3A had a lower adsorption capacity for ethyl acetate than did 1A due to impregnation and lower availability of pores sites. The 50% capacities of the three filters are shown in Figure 4.10.

Table 4.8: GAC filter series test conditions challenged by ethyl acetate

GAC	Shape	AC (%)	Mass (g)	Velocity (m/s)	Pressure drop(in H2O)	RH (%)	Thickness (cm)	Residence time(s)
1A	pellet	100	49.816	0.12	0.006	50	1.19	0.992
2A	pellet	76	50.189	0.11	0.006	50	1.19	1.082
3A	pellet	75-85	50.267	0.12	0.006	50	1.17	0.975

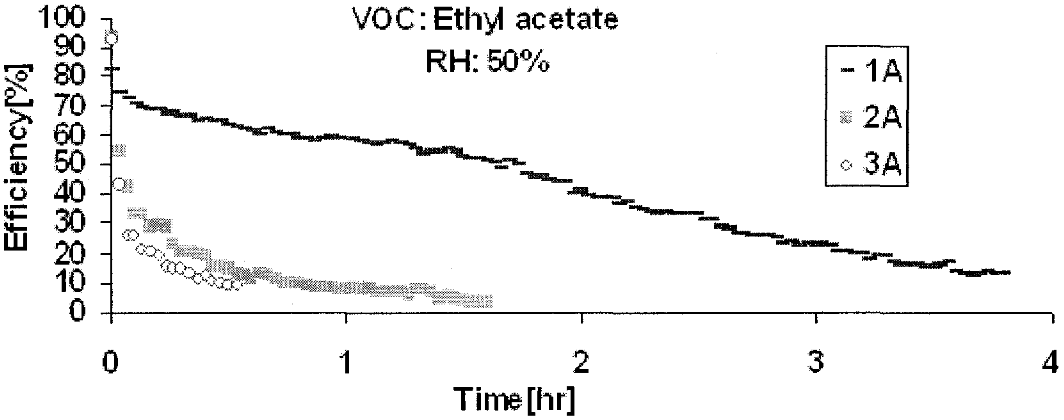


Figure 4.9: Efficiency profile for GAC filters challenge by ethyl acetate at 50% RH (volumes of ethyl acetate injected were 15, 3.5, and 1.4 mL for 1A, 2A, and 3C respectively)[*]

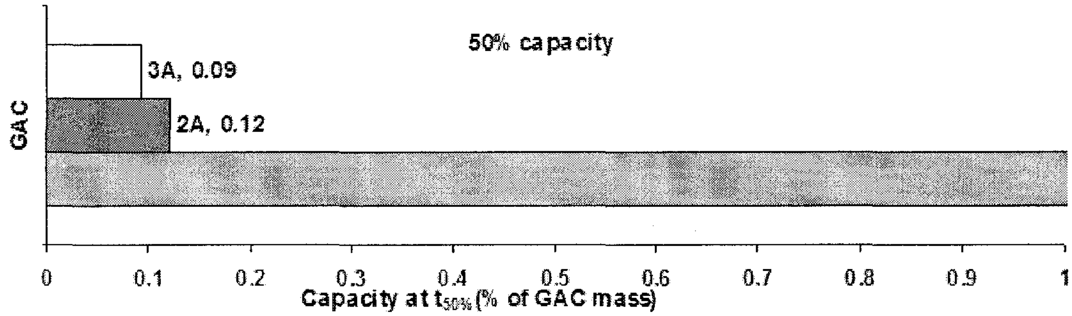


Figure 4.10: Adsorbed VOC mass at 50% breakthrough per GAC filter mass, challenged with ethyl acetate at RH 50%

Table 4.9 shows the corresponding breakthrough times of t_{50} and t_{80} for the filters when challenged by ethyl acetate.

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[*] The volumes mentioned are the total injection and it does not represent the volumes necessary to reach 20% efficiency.

Table 4.9: 50% and 80% breakthrough times of GAC 1A, 1B and 1C for ethyl acetate

BT GAC	t50 (h)	t80 (h)
1A	1.07	2.93
2A	0.03	0.10
3A	0.03	0.10

4.4 Effect of different VOCs on the removal efficiency of GACs

This section seeks to investigate the adsorption capacity of the GAC filters (1A, 2A and 3A) when exposed to different VOCs. Figure 4.11 illustrates the efficiency curves of filter 1A when it was exposed to the three selected VOCs at 50% RH. 1A presented the highest adsorption capacity for toluene, but had the lowest capacity for ethyl acetate and cyclohexane. 1A's efficiency curve for ethyl acetate (water miscible) appeared slightly higher than efficiency curve of cyclohexane (water immiscible) due to presence of moisture in the system. Filters 2A and 3A had performed similarly as demonstrated in Figures 4.12 and 4.13.

The comprehensive study on adsorption of indoor air contaminants by GAC filters by VanOsdell et al. (1996) was conducted in a humid environment (50% RH) with the concentration of VOCs varying from 1 ppm to 80 ppm and with the flow rate being fixed to correspond to 0.1 second residence time. Their results showed that toluene 10% breakthrough times were almost twice longer than MEK at same challenge concentration. MEK is a water miscible compound with affinity coefficient and boiling point almost similar to ethyl acetate. The conclusion of their results is similar to the result of toluene and ethyl acetate tests at 50% RH as illustrated in Figure 4.11 (toluene 80% breakthrough time is 5.43 hours and ethyl acetate 80% breakthrough time is 3.51 hours).

The filters all performed best when they were challenged with toluene. Table 3.1 shows that toluene has the highest affinity coefficient (The affinity between VOCs and the surface of the adsorbent, see Appendix A) for activated carbon. The high adsorption capacity of GAC filters for toluene is also related to its highest boiling point, lowest vapor pressure and highest molecular weight among tested compounds. Although it was expected that the filters would perform better when tested with cyclohexane than with ethyl acetate, all filters showed opposite results (at 50% RH): a slightly higher adsorption capacity for ethyl acetate than for cyclohexane. The presence of moisture increased the adsorption capacity of the filters for the water miscible ethyl acetate. By contrast, cyclohexane is water immiscible and therefore it was less adsorbed by filters in presence of moisture than did ethyl acetate (the water molecules tend to block the pores that would have otherwise served as adsorption sites for cyclohexane).

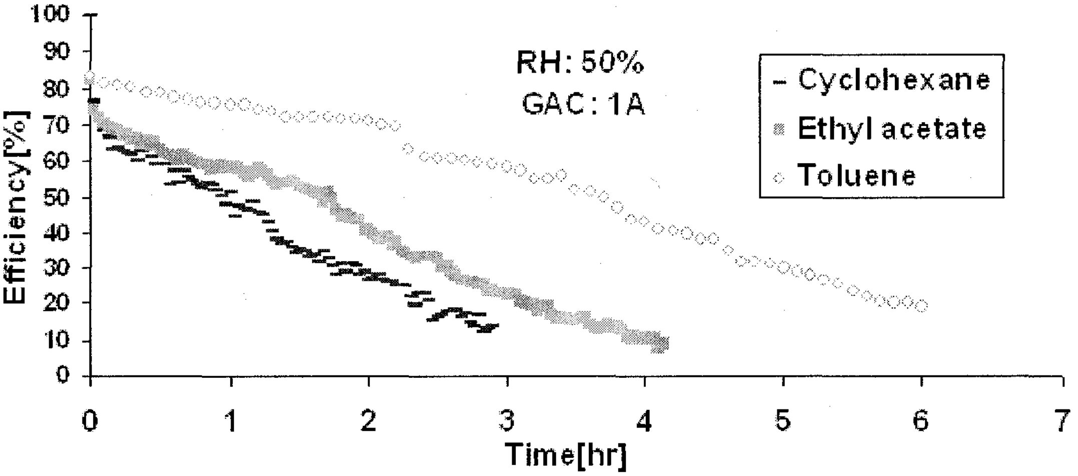

Figure 4.11: Efficiency profile for 1A for different VOCs at 50% RH (volumes of VOC injected were 11.35, 15, and 20.82 mL for cyclohexane, ethyl acetate, and toluene respectively)*

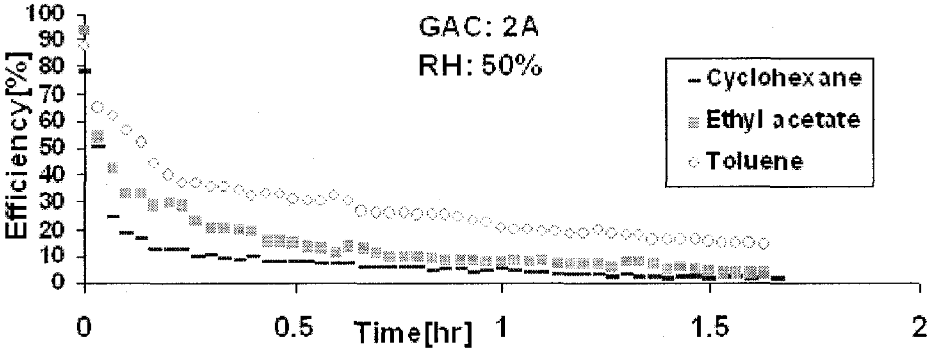

Figure 4.12: Efficiency profile for 2A for different VOCs at 50% RH (volumes of VOC injected were 6.67, 3.5, and 4.23 mL for cyclohexane, ethyl acetate, and toluene respectively)*

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[*] The volumes mentioned are the total injection and it does not represent the volumes necessary to reach 20% efficiency.

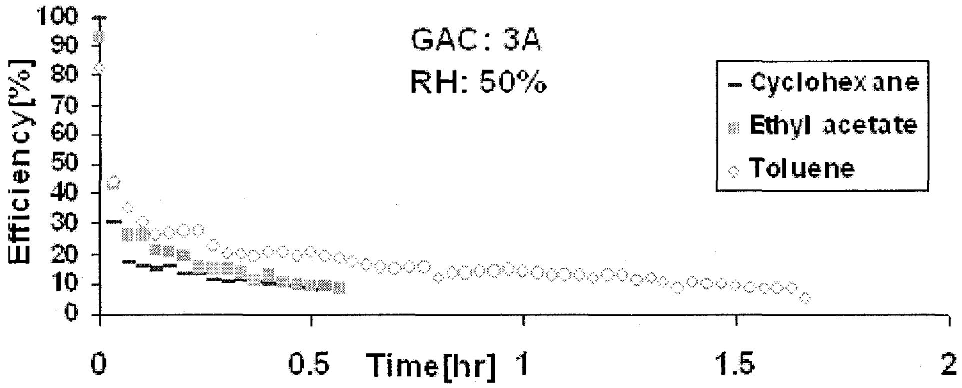

Figure 4.13: Efficiency profile for 3A for different VOCs at 50% RH (volumes of VOC injected were 3.31, 1.40, and 1.06 mL for cyclohexane, ethyl acetate, and toluene respectively)*

Table 4.10 shows the 50% capacity of all the filters. Toluene adsorption capacity of GAC 1A was 2.5 times higher than ethyl acetate and 3.7 times higher than cyclohexane at 50% RH. Toluene adsorption capacity of GAC 2A was 4.9 times higher than ethyl acetate and 6.6 times higher than cyclohexane. Toluene adsorption capacity of GAC 3A was 4.3 times more for both cyclohexane and ethyl acetate.

Table 4.10: 50% Capacity† (% of GAC mass) at 50% RH

VOC / GAC	Adsorbed Cyclohexane (%)†	Adsorbed Ethyl acetate (%)†	Adsorbed Toluene (%)†
1A	5.26	7.75	19.40
2A	0.09	0.12	0.59
3A	0.09	0.09	0.39

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* The volumes mentioned are the total injection and it does not represent the volumes necessary to reach 20% efficiency.

† adsorbed mass of VOC (g) per mass of GAC (g), expressed in percentage

4.5 Effect of Humidity Level on Adsorption of VOCs

The purpose of this section of study was to investigate the efficiency of GAC filters in humid environments. Thus, the GAC filters' adsorption capacity was measured at three selected humidity levels: 30± 5%, 50± 5% and 70± 5% RH. Filters 1A, 2A and 3A were challenged by toluene at these different humidity levels. The injection rate was 50 μL/min (continuously), and the tests were conducted at room temperature [24 ± 1°C].

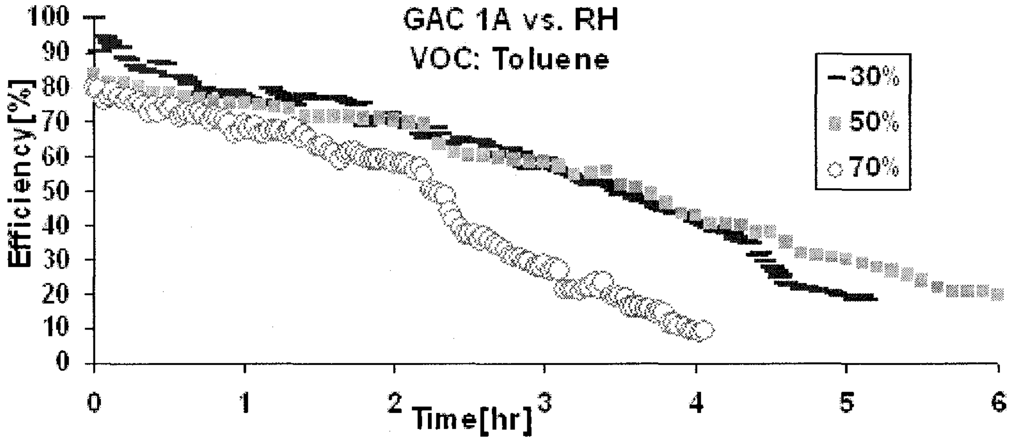

Figure 4.14: Efficiency profile for the 1A for various relative humidity, challenged by toluene (volumes of toluene injected were 25, 20.82, and 19 mL for 30, 50, and 70% respectively)[*]

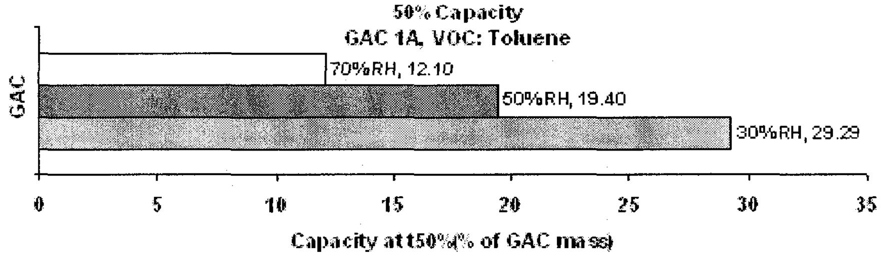

Figure 4.15: Adsorbed VOC mass at 50% breakthrough per GAC 1A filter mass, challenged with toluene at different RH

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[*] The volumes mentioned are the total injection and it does not represent the volumes necessary to reach 20% efficiency.

Figure 4.15 shows the 50% capacity of the GAC 1A when challenged by toluene. It shows that the 50% capacity of toluene was decreased by 33.7% and 37.6% when humidity increased from 30% RH to 50% and from 50% to 70% RH respectively.

Figures 4.14, 4.16 and 4.18 show the efficiency profile of filters 1A, 2A and 3A when tested with toluene at selected RH levels. In Figure 4.14 the curves demonstrate that as the RH level increased, the adsorption capacity of the 1A for toluene decreased. As RH increases, the competition to fill the micropores between water molecules and toluene molecules intensifies (Cal et al., 1995). Because toluene molecules are semi-polar, they are not water-soluble. Thus, the water molecules already adsorbed tend to attract other water molecules (due to strong dipole-dipole attractions of water molecules) rather than attracting semi-polar molecules like toluene. As such, water molecules clog the pores. While the 80% breakthrough time of 1A decreased by 40% when humidity increased from 50% to 70% RH, a much shorter reduction (13.3%) in the 80% breakthrough time was observed when humidity elevated from 30% to 50% RH. The same results were reported by Nelson (1976b), when GAC filters were tested with toluene at concentrations of 1000 ppm and at 0% to 90% RH. They reported a decrease in efficiency of the filters for the adsorption of toluene at 50% RH and higher. Owen et al. (1995) measured breakthrough times for toluene (1 ppm to 70 ppm) at various humidity levels (dry to 80% RH). They showed that humidity below 50% RH had negligible impact and that significant reductions in breakthrough times occurred at higher RH levels (75% RH).

In contrast the impregnated GAC filters showed much better performance at 30% RH compare to 50% and 70% RH. As illustrated in Figure 4.16, when the relative humidity increased from 30% to 50% RH, the efficiency of 2A dropped 30%. As the relative humidity increased from 50% to 70% RH, the 2A efficiency dropped 16%. GAC 3A also had a significant decrease in efficiency when relative humidity increased from 30% to 50% RH (see Figure 4.18).

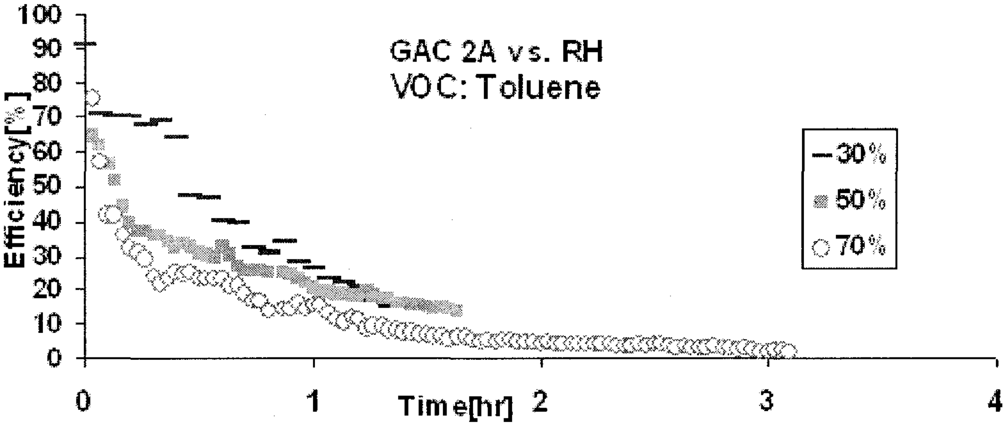

Figure 4.16: Efficiency profile for the 2A for various relative humidity, challenged by toluene (volumes of toluene injected were 4.75, 6.67, and 3.15 mL for 30, 50, and 70% respectively)*

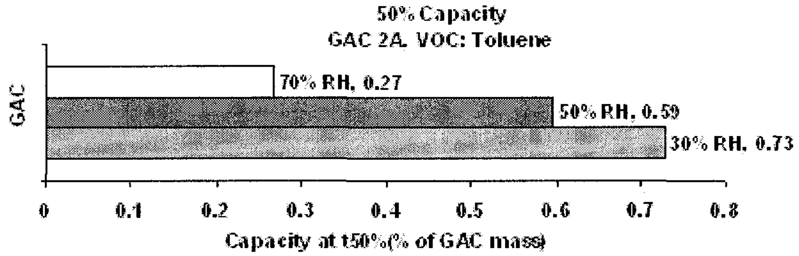

Figure 4.17: Adsorbed VOC mass at 50% breakthrough per GAC 1A filter mass, challenged with toluene at different RH

Figure 4.17 shows the 50% capacity of toluene when GAC 2A was used an air cleaner. The 50% capacity of toluene was reduced by 19% when relative humidity

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* The volumes mentioned are the total injection and it does not represent the volumes necessary to reach 20% efficiency.

increased from 30% to 50%. When relative humidity increased from 50% to 70%, the decrease in 50% capacity of toluene was 54%.

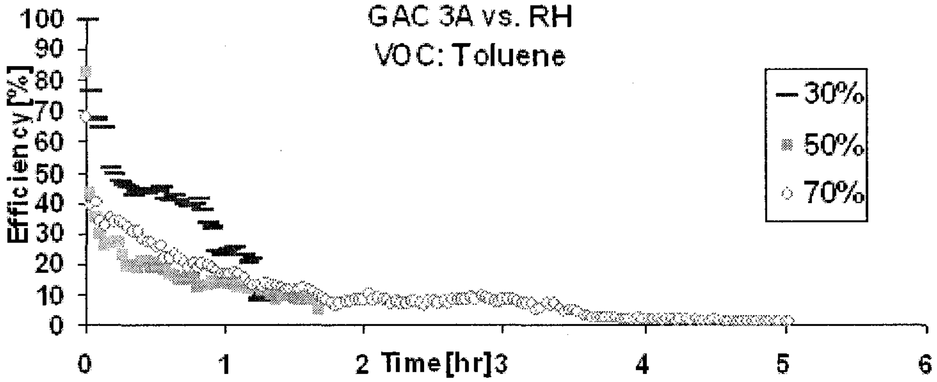

Figure 4.18: Efficiency profile for the 2A for various relative humidity, challenged by toluene (volumes of toluene injected were 4.75, 6.67, and 3.15 mL for 30, 50, and 70% respectively)*

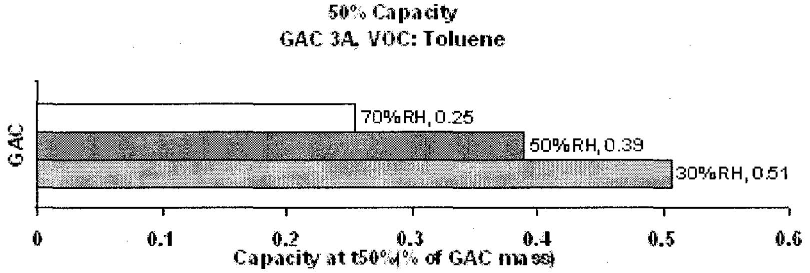

Figure 4.19: Adsorbed VOC mass at 50% breakthrough per GAC 1A filter mass, challenged with toluene at different RH

The 50% capacity of GAC 3A when it was challenged with toluene is illustrated in Figure 4.19. The 50% capacity of GAC 3A decreased 23% for toluene when humidity increased from 30% to 50%. As humidity elevated from 50% to 70% RH the capacity lowered 35%.

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* The volumes mentioned are the total injection and it does not represent the volumes necessary to reach 20% efficiency.

Figure 4.20 illustrates the efficiency profiles of filter 1A when tested with cyclohexane. The injection rate was 50 μL/min (continuously), and the tests were conducted at room temperature [24 ± 1°C]. The adsorption efficiency of 1A was significantly higher at 30% RH than at either 50% or 70% RH, because more pore sites were available to the water immiscible cyclohexane molecules at 30% RH. The 80% breakthrough times of 1A reduced 60% when humidity increased from 30% to 70% RH. Under the same conditions, ethyl acetate showed exactly opposite results (Figure 4.22). The highest adsorption capacity was seen at 70% RH; and as RH increased, the adsorption capacity also increased. The reason is believed to be due to the fact that as ethyl acetate is extremely water soluble, its molecules in a gas phase can be not only adsorbed on the pores of the filter, but also absorbed by water molecules already adsorbed to the filter. The 80% breakthrough time of the filter increased by 40% when relative humidity elevated from 30% to 70%.

The results show that the elevated humidity levels have negative impact on adsorption capacity of non-polar VOCs while they enhance adsorption capacity of polar ones.

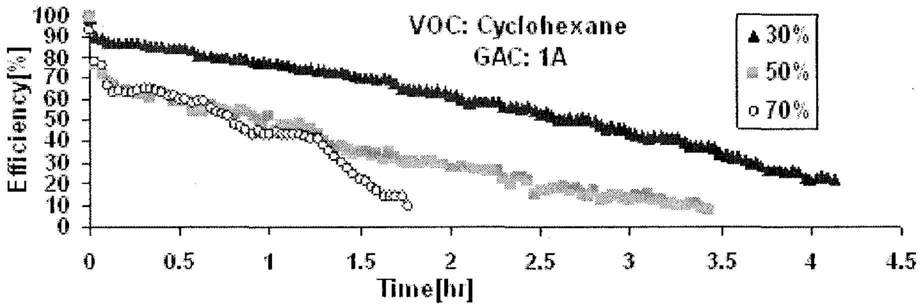

Figure 4.20: Efficiency profile for GAC 1A filter at different relative humidity levels, challenged by cyclohexane (volumes of cyclohexane injected were 13.5, 11.35, and 8.8 mL for 30, 50, and 70% respectively)[*]

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[*] The volumes mentioned are the total injection and it does not represent the volumes necessary to reach 20% efficiency.

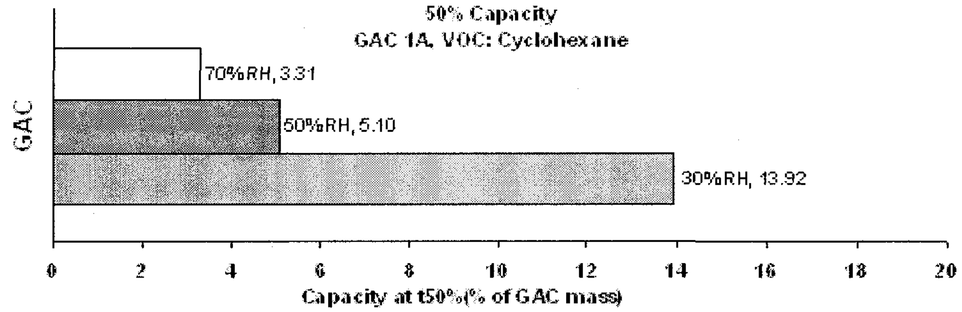

Figure 4.21: Adsorbed VOC mass at 50% breakthrough per GAC 1A filter mass, challenged with cyclohexane at different RH

Figure 4.21 illustrates the 50% capacity of GAC 1A filter when exposed to cyclohexane at different humidity levels. The 50% capacity decreased significantly as humidity increased. A 63% decrease was observed when relative humidity increased from 30% RH to 50% RH. The reduction in 50% capacity was 35% when relative humidity increased from 50% to 70% RH.

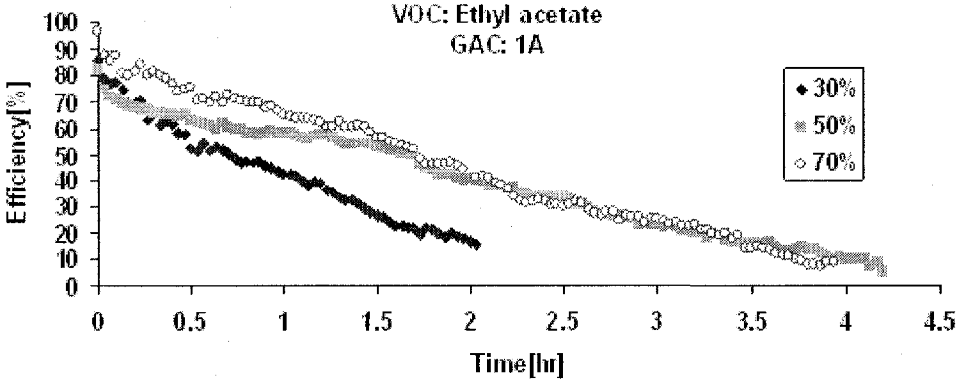

Figure 4.22: Efficiency profile for GAC 1A filter at different relative humidity levels, challenged by ethyl acetate (volumes of toluene injected were 15.3, 15, and 17.5 mL for 30, 50, and 70% respectively)*

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* The volumes mentioned are the total injection and it does not represent the volumes necessary to reach 20% efficiency.

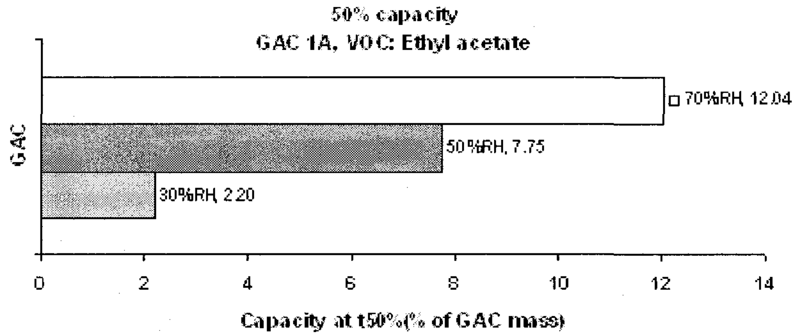

Figure 4.23: Adsorbed VOC mass at 50% breakthrough per GAC 1A filter mass, challenged with ethyl acetate at different RH

When GAC 1A was exposed to ethyl acetate, its 50% capacity increased as humidity increased (see Figure 4.23). The increase in 50% capacity of ethyl acetate on 1A was 55.3% and 72% when relative humidity increased from 50% to 70% RH and from 30% to 50% RH.

Figures 4.24 and 4.25 show the performance of 1A when challenged by different VOCs at 30% and 70% RH. As previously explained (see Figure 4.11), significantly larger amounts of toluene were adsorbed by comparison with the other two VOCs at 50% RH. Between cyclohexane and ethyl acetate, cyclohexane was expected to adsorb better (due to its slightly higher affinity coefficient for activated carbon and boiling point than that of ethyl acetate, see Table 3.1) but, instead, the results showed the opposite effect at 50% (see Figure 4.11) and 70% RH (see Figure 4.25). However at 30% RH (see Figure 4.24), cyclohexane had higher adsorption capacity than ethyl acetate. At 70% RH, the efficiency profile of ethyl acetate almost reached that of toluene (Figure 4.25). The high solubility of ethyl acetate in water is believed to be the principal factor for this result. Therefore, at a high RH levels (50% and 70%), ethyl acetate was adsorbed more efficiently than cyclohexane.

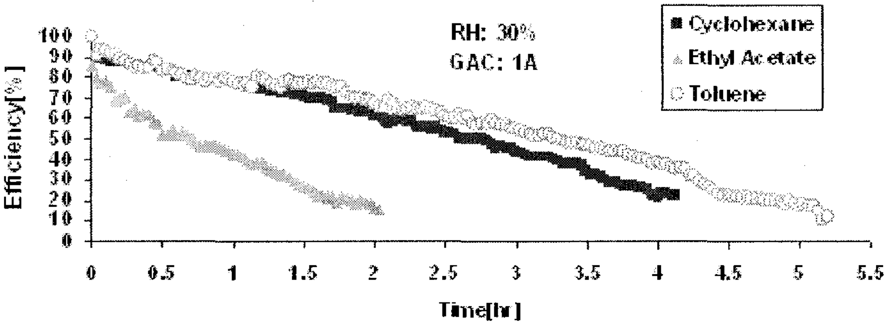

Figure 4.24: Efficiency profile for the GAC 1A filter at 30%RH challenged with selected VOCs (volumes of VOC injected were 15.3 13.5, and 25 mL for cyclohexane, ethyl acetate, and toluene respectively)*

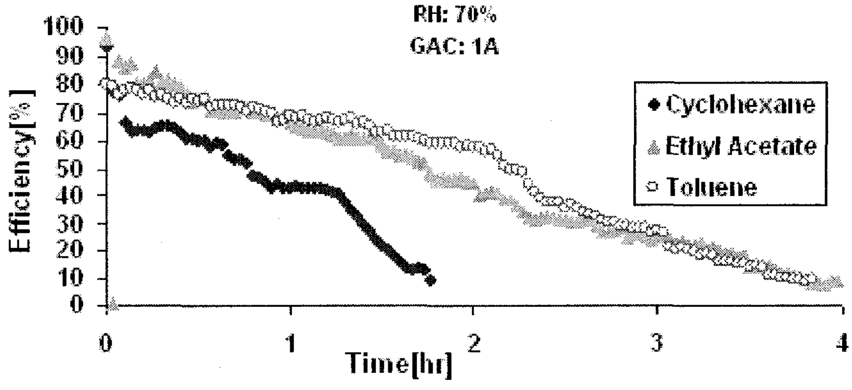

Figure 4.25: Efficiency profile for the GAC 1A filter at 70%RH challenged with selected VOCs (volumes of VOC injected were 8.8, 17.5, and 19 mL for cyclohexane, ethyl acetate, and toluene respectively)*

The results show that at 50% RH and above, the present of moisture can significantly increase the breakthrough time of water soluble compounds and decrease efficiency of non-soluble ones. Cal (1996) reported that significant changes in capacity of GAC occurred at 90% RH for miscible and at 65% RH for immiscible VOCs.

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* The volumes mentioned are the total injection and it does not represent the volumes necessary to reach 20% efficiency.

4.6 Summary

This study investigated the efficiency of various GAC filters when exposed to VOCs. The results revealed that filters with a higher percentage of activated carbon performed better than those with a lower percentage. For instance, GAC 1 series (virgin activated carbon) had the best adsorption capacity for all the tested VOCs (cyclohexane, ethyl acetate and toluene). Toluene was the best adsorbate for the tested filters due to its high affinity coefficient to activated carbon.

The filters were also tested at three levels of RH: 30%, 50% and 70%. It was found that as RH increased, the adsorption capacity of filters for cyclohexane and toluene decreased. The filters were more efficient at filtering ethyl acetate at elevated levels of RH, due to the high solubility of the compound in water. The 50% capacity of 1A for ethyl acetate increased up to 81%, while it showed 76% and 59% decrease for adsorbing cyclohexane and toluene, respectively, when the relative humidity level increased from 30% to 70%.

Filters 1A and 1B had a remarkably better adsorption capacity for toluene than the other GAC filters tested in this study (50% capacity of 19.4% and 20.7% of GAC mass, respectively). The percentage of activated carbon in the filters was significant in determining the adsorption capacity. Thus, the higher the percentage of activated carbon, the higher the adsorption capacity of VOCs would be.

GAC 1 series (virgin activated carbon) showed the best efficiency results. The percentage of activated carbon was equal in this group. The only difference was the shape of the active carbon pellets, which had an impact on pressure drops for each of the filters (1A: 0.014 inches of water gauge, 1B: 0.011 inches of water gauge and 3A: 0.007 inches of water gauge). This result shows the possible diverse applications for all the filters. The $t_{50\%}$ of 1C (time required to achieve 50% efficiency) was faster for 1A and 1B, but it reached $t_{80\%}$ 1.14 times more slowly. Filter 1C had larger pellets, but its capacity was comparable with that of 1A and 1B. 1A and 1B performed better from the beginning and therefore reached their 20% adsorption capacity faster than did 1C. As such, $t_{80\%}$ was longer for 1C because it took longer for the filter to reach 20% adsorption capacity. 1C reached 20% efficiency 22.6 minutes later than did 1A, and 28.2 minutes later than did 1B.

Since the impregnated GAC filters have lower capacities, their t_{80} was shorter than for the group 1 filters. Filters 2A, 3A and 3B performed poorly when challenged with toluene at 50% RH. They reached 80% breakthrough times in 1.03 hours, 0.5 hours and 0.77 hours respectively. Due to the high percentage of impregnated materials and low percentage of activated carbons, pores that would otherwise be occupied by VOC molecules were blocked.

Filters 3C and 3D had similar efficiently trends. Their adsorption capacities were closer to the group 1 filters because they had a lower percentage of impregnated materials and a higher percentage of activated carbon. They reached 80% breakthrough times in 4.53 hours and 4.26 hours respectively.

5 Conclusions and Recommendations

5.1 *Conclusions*

GAC filters have been used to treat drinking water, waste water and industrial gas streams for decades, proving its efficacy in removing undesired contaminants. However, its performance for indoor air environments and for ventilation systems in buildings and residences is still unknown. As such, this study sought to evaluate the removal efficiency of GAC filters for VOCs in indoor environments. The effect of humidity on the adsorption of VOCs was also tested. Seven types of commercially available filters were tested, and were categorized according to their carbon content and size. The efficiency of their filtration capacity was tested with three VOCs (cyclohexane, ethyl acetate and toluene) at 30%, 50% and 70% RH. The breakthrough times and efficiency curves of these tests were also analyzed.

It was the first time any of these GAC filters had been tested for their adsorption capacity of VOCs. The first group of filters (with virgin activated carbon) performed the best, while the second and third groups (with impregnated activated carbon) had lower adsorption capacities for the challenged VOCs. Toluene exhibited the highest adsorption capacity, followed by ethyl acetate and cyclohexane at 50% RH. As activated carbon is hydrophobic, non-polar VOCs (e.g. toluene) are better at adsorbing on activated carbon (Delage et al., 1999). This study found that the best adsorbed VOC by GAC filters was toluene agreed with the findings of VanOsdell et al. (1996) and Lee et al. (2006).

At the concentration tested, the 80% breakthrough time of the first group was 6 hours on average, proving that these filters had good removal efficiency for VOCs. GAC filters in groups 2 and 3 were less efficient by 25%, as a result of impregnation.

Water vapor has been reported to be problematic in the study of indoor air gaseous contaminant removal. Water levels in indoor air exist at concentrations far above those of VOC contaminants and do affect the adsorption capacity of GAC filters. An attempt, therefore, was made to characterize the effect of humid air on the adsorption of soluble (ethyl acetate) and insoluble (cyclohexane) compounds. Efficiency curves showed a decreased in adsorption for cyclohexane and toluene up to 40% and 30%, respectively, as the humidity level increased. However, ethyl acetate's efficiency increased by 16.5% as RH increased because of its water miscible nature. When the virgin activated carbon were tested at 30% RH, their adsorption capacity was higher for cyclohexane than ethyl acetate, but as the RH levels (50% and 70%) increased, the adsorbability of cyclohexane dropped below that of ethyl acetate. The efficiency of filters 1A, 2A, and 3A for the adsorption of toluene decreased up to 33%, 38% and 25%, respectively, when the RH increased from 30% to 70%. These results agreed with Nelson (1976b), Werner (1985) and Cal (1995). This study, however, rejects the conclusions of Delage et al. (1999), who concluded no significant difference in the adsorption capacity for water soluble and non-soluble compounds when humidity increased.

The results of this thesis can be applied in the design of adsorption systems that utilize GAC filters to improve and/or preserve IAQ. Moreover, these conclusions can also contribute to a better understanding of the performance of GAC filters in HVAC systems and organic sampling devices.

5.2 Recommendation for Future Work

Based on the findings of this study, recommendations for future research on the application of GAC filters for the removal of indoor VOCs are as follows:

1. Evaluation of the adsorption capacity of the GACs for the removal of indoor VOCs with the presence of indoor sink materials to determine their actual efficiency.
2. Investigation of breakthrough times and adsorption capacities of the GAC filters for various VOC mixtures.
3. Examination of the performance of GACs for the removal of indoor VOCs at real-life ppb concentrations.
4. Determination of the actual adsorption capacities of GAC filters for VOCs from evaporation sources (when concentration varies with time).

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7 Appendix

7.1 Appendix A

Affinity Coefficient (β) is the ratio of the electronic polarizations, P_e (cm3/mol) (Reucroft et al., 1971). The electronic polarization and affinity coefficient are represented as:

$$P_e = \frac{(n_r - 1)M}{(n_r + 2)\rho}$$

$$\beta = \frac{p_e}{(P_e)_{ref}}$$

where n_r, is the refractive index of the liquid adsorbate, M is the molecular weight of the adsorbate (g/mol), and p is the density of the liquid adsorbate (g/cm^3). Benzene is used as reference.

VOC	**M_W**	**Density(ρ)***	**n_r^{20**}**	**n_r^{25***}**	**P_e**	**B**
Cyclohexane	**84.16**	**0.779**	**1.427**	**1.425**	**27.610**	**1.058**
Ethyl acetate	**88.12**	**0.897**	**1.372**	**1.370**	**22.207**	**0.851**
Toluene	**92.14**	**0.867**	**1.496**	**1.494**	**30.925**	**1.186**
Benzene(ref)	**78.11**	**0.879**	**1.501**	**1.50**	**26.081**	**1**

*Density (ρ): density of liquid (g/cm^3) from MSDS datasheet at 25°C
**n_r: refractive index from CRC Handbook of Chemistry and Physics 1973/74 at 20°C
***n_r: refractive index calculated from equation 7.1

The refractory index is temperature dependant, the n_r at 25°C (test condition temperature) was obtained from equation 7.1. According to O'Neil (2006), the index of refraction of organic compounds decreases by approximately 0.00045 ± 0.0001 for every 1 °C increase in temperature.

(Reflective index (RI) at Temperature T_1)-(T_1-T_2)(0.00045)= RI at T_2 Equation 7.1

7.2 Appendix B

Polynomial interpolation:

Consider table of values below:

x	x_1	…	x_n
y	y_1	…	y_n

And assume that the x_i's form a set of n distinct points. The table presents n points in the Cartesian plane, and we want to find a polynomial, which is defined for all x, that takes on the corresponding values of y_i for each of the n distinct x_i's in the table. A polynomial p for which $p(x_i)=y_i$ when $1 \le i \le n$ is said to interpolate the table. Polynomial depends on n. when n=2, since a line can pass through two points, a linear function is capable of solving the problems.

$$p(x) = y_1 + \left(\frac{y_2 - y_1}{x_2 - x_1} \right) (x - x_1)$$

Sample calculation for application of this thesis (the value are just example and might not have real experimental value):

The air sample before the filter was taken at 19:28:53 and after the filter air sample was taken at 19:29:53. To figure out the concentration of VOC before the filter at 19:29:53, a simple linear interpolation was applied.

	x	y		
	time	Concentration Before	time	Concentration After
1	19:28:53	54.4	19:29:53	36.1
2	19:30:53	56.8	19:31:55	37.6

Concentration **(VOC before the filter at 19:29:53)** =

$$54.4 + \left(\frac{56.8 - 54.4}{19:30:53 - 19:28:53} \right) ([19:29:53 - 19:28:53) = 55.6 \text{ ppm}$$