

COMPARISON OF ADSORPTION CAPACITIES OF NANOADSORBENTS WITH
CONVENTIONAL ACTIVATED CARBON FOR VOLATILE ORGANIC
COMPOUNDS

by

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ABSTRACT

COMPARISON OF ADSORPTION CAPACITIES OF NANOADSORBENTS WITH CONVENTIONAL ACTIVATED CARBON FOR VOLATILE ORGANIC COMPOUNDS

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This research explores the potential for using single wall carbon nanohorns (SWNHs) for adsorption of volatile organic compounds (VOCs) categorized as hazardous air pollutants and which contribute to ground level ozone smog formation. It also compares the adsorption capacity of conventional activated carbon and carbon nanohorns.

Carbon nanoadsorbents, with at least one dimension on the nanometer scale, can possess advantages over traditional activated carbon adsorbents in terms of binding energies or interaction potentials for physisorption. Nanotubes and nanohorns both have excellent adsorption properties due to high-energy adsorption sites in their interior

(internal pores) and in the region between adjacent nanotubes/nanohorns (interstitial channel). Nanohorns would be preferable for air pollutant removal applications because they self-assemble into spherical aggregates, with space between adjacent nanohorns large enough to accommodate small gas molecules and also are cheaper to manufacture as compared to nanotubes.

This research aims to:

1. Determine the adsorption capacity of open-end carbon nanohorns with heat treatment and densification and closed-end carbon nanohorns, with and without heat treatment and densification, for a variety of VOCs (alkanes and alkenes);
2. Determine which type of adsorbent gives the maximum adsorption capacity for a majority of the VOCs, and whether there are any trends in adsorption capacity vs. compound structure;
3. Determine the adsorption capacity of regular activated carbon for the same VOCs.

The experimental setup consisted of a gas chromatograph, gas tight syringes, 4mL clear glass vials with rubber septae and Tedlar bags. The compounds to be tested included the alkenes ethylene and propylene and the alkanes butane and hexane. The adsorbents used were closed-end nanohorns without any treatment, closed-end nanohorns with treatment (densification), open-end nanohorns with treatment (densification) and activated carbon pellets. Calibration curves were first created for each of the compounds on the GC software. Trial and error runs were conducted to determine the approximate minimum weight of nanohorns required for reasonably good

adsorption, the minimum time required for equilibrium and the maximum volume of compound that can be adsorbed by each type of adsorbent for each combination of compound and adsorbent.

The vials were filled with the minimum weight of adsorbent, which was found to be 0.03g, and a known volume of gas was injected into them. After the equilibrium time had passed, a sample was drawn out of the vial and injected into the GC to determine the residual concentration of gas in the vial after adsorption. Similar runs were conducted for each combination of gas and adsorbent with increments varying from 1 μ L to 10 μ L in volume. Adsorption isotherms were plotted with the residual concentrations in ppm obtained from the GC on X-axis and mass of volatile organic compound adsorbed per unit mass of adsorbent used in grams/grams on the Y-axis.

The results obtained indicated that activated carbon had much better adsorption capacity for all the chosen VOCs than nanohorns. Open-end nanohorns with treatment proved to have next highest adsorption capacity. Alkanes showed greater adsorption with the chosen types of adsorbents than alkenes.

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CHAPTER 1

INTRODUCTION

1.1 Ozone

The weather report on the radio or TV tells you that it is going to be sunny and hot and that an orange ozone alert has been issued. What is ozone? Why should you be concerned about it?

Ozone (O_3) is a gas composed of three oxygen atoms. It is found naturally in small concentrations in the stratosphere, a layer of Earth's upper atmosphere. Stratospheric ozone has been called "good" ozone because it protects the Earth's surface from dangerous ultraviolet light. Ozone can also be found in the troposphere, the lowest layer of the atmosphere. Tropospheric ozone (often termed "bad" ozone) is mostly human-made, a result of air pollution from internal combustion engines and power plants. Automobile exhaust and industrial emissions release a family of nitrogen oxide gases (NO_x) and volatile organic compounds (VOCs), by-products of burning gasoline and coal. NO_x and VOCs react in the presence of sunlight to form ozone, which is the reason for ozone levels increasing in sunny, high-temperature conditions of late spring, summer and early fall.

One of the solutions to prevent ozone from forming is to control the VOC concentrations in the atmosphere. This can be done in several ways. One of them is adsorption.

1.2 Hazardous air pollutants

Toxic air pollutants, also known as hazardous air pollutants, are those pollutants that are known or suspected to cause cancer or other serious health effects, such as reproductive defects or birth defects, or adverse environmental effects. Long-term exposure to these pollutants can cause damage to the liver, kidneys and central nervous system. Short-term exposure to volatile organic compounds can cause eye and respiratory tract irritation, headaches, dizziness, visual disorders, fatigue, loss of coordination, allergic skin reactions, nausea, and memory impairment. Many volatile organic compounds are hazardous air pollutants. (EPA website, 2005)

1.3 What is adsorption?

Simply put, adsorption is a process that uses special solids (called adsorbents) to remove substances (adsorbates) from either gaseous or liquid mixtures. Adsorption is effective for purifications, e.g. taking a contaminant ranging from 1 ppb to 1000 ppm out of a stream of gas or liquid. For the process of adsorption to be effective enough, proper selection of an adsorbent is important. The most important attributes of an adsorbent for any application are: *capacity*, *selectivity*, *regenerability*, *kinetics*, *compatibility* and *cost*. One of the most widely used adsorbents is activated carbon since it possesses most of the above mentioned attributes, mainly capacity and cost.

However, researchers have now developed a new form of carbon in the nano range. These are carbon particles in the scale of one-billionth of a meter (10^{-9}). Nanoadsorbents may have greater adsorption capacity per unit mass compared to conventional activated carbon, owing to high energy adsorption sites. Because of this,

they may prove effective in adsorbing compounds with high vapor pressure which are difficult to adsorb by conventional adsorbents.

1.4 Research objectives

1. To determine the adsorption capacity of open-end carbon nanohorns with heat treatment and densification and closed-end carbon nanohorns, with and without heat treatment and densification, for a variety of VOCs (alkanes and alkenes);
2. To determine which type of adsorbent gives the maximum adsorption capacity for a majority of the VOCs, and whether there are any trends in adsorption capacity vs. compound structure;
3. To determine the adsorption capacity of regular activated carbon for the same VOCs.

1.5 Overview of the report

The following chapter is the literature review which highlights various studies conducted related to this research. It summarizes conclusions from previous studies, shedding light on the findings and future prospects of nanoadsorbents. Chapter 3 describes the methodology that has been used, details of the apparatus and other necessary data. Chapter 4 includes experimental results and discussion. Chapter 5 contains conclusions and recommendations for further research.

CHAPTER 2

LITERATURE REVIEW

2.1 About adsorption

When a gas or vapor is brought into contact with a solid, part of it is taken up by the solid. The molecules that disappear from the gas either enter the inside of the solid or remain on the outside attached to the surface. Both of these phenomena are termed adsorption. The solid that takes up the gas is called the adsorbent and the gas or vapor taken up on its inside or outside is called the adsorbate.

Molecules and atoms can attach themselves onto the surfaces in two ways, viz; physisorption and chemisorption. In physisorption, there is a weak Van der Waal's attraction of the adsorbate to the surface. The attraction to the surface is weak but long ranged. During the process of physisorption, the chemical identity of the adsorbate remains intact, i.e. no breakage of the covalent structure of the adsorbate takes place. In chemisorption, the adsorbate sticks to the solid by the formation of a chemical bond with the surface. This interaction is much stronger than physisorption. The adsorbent regeneration in chemisorption though is a tedious and expensive process, with recovery being impossible in most cases.

Generally, the capacity of an adsorbent to adsorb a particular adsorbate is directly proportional to the molecular weight and inversely proportional to the vapor pressure of the adsorbate. The capacity of an adsorbent for a specific gas or vapor can

be presented as an isotherm. A point on an isotherm represents the mass of adsorbate per unit mass of adsorbent under equilibrium conditions at indicated temperature and gas-phase concentration.

2.2 About nanomaterials

Nanomaterials are substances which occur at the ultimate scale at which nature designs: the molecular scale. They are materials with structural features (particle size or grain size, for example) of at least one dimension in the range 1-100 nm. These materials, notable for their extremely small particle size or crystalline grain size, have the potential for wide-ranging industrial, biomedical, and electronic applications. Nanomaterials can be metals, ceramics, polymeric materials, or composite materials (www.csa.com, 2005). They have a wide range of potential applications from making sensors to chips. One promising potential application is adsorption.

Depending on the adsorbent and adsorbate, nanoadsorbents can possess advantages over traditional adsorbents in areas that impact adsorption capacity: surface area, pore size distribution, and surface chemistry (Shelly, 2003). Surface area determines the number of sites for gaseous pollutant molecules to attach to the solid adsorbent surface. The greater the surface area, more the sites available for adsorption and therefore less is the amount of adsorbent needed to adsorb a given quantity of pollutant. As regards to the pore size, it impacts not only the surface area, i.e. the greater the number of pores, the greater is the surface area, but also access to adsorption sites, i.e. smaller pore sizes may not accommodate larger molecules. Surface chemistry

affects binding sites for chemisorption, and binding energies or interaction potentials for physisorption and chemisorption.

The different forms of nanoadsorbents are:

2.2.1 Nanoparticles

These are collections of tens to thousands of atoms measuring 1-100 nm in aggregate diameter. Their surface area would be entirely external since creation of an internal pore structure in them would not likely be feasible. (Masciangioli and Zhang, 2003)

2.2.2 Nanotubes

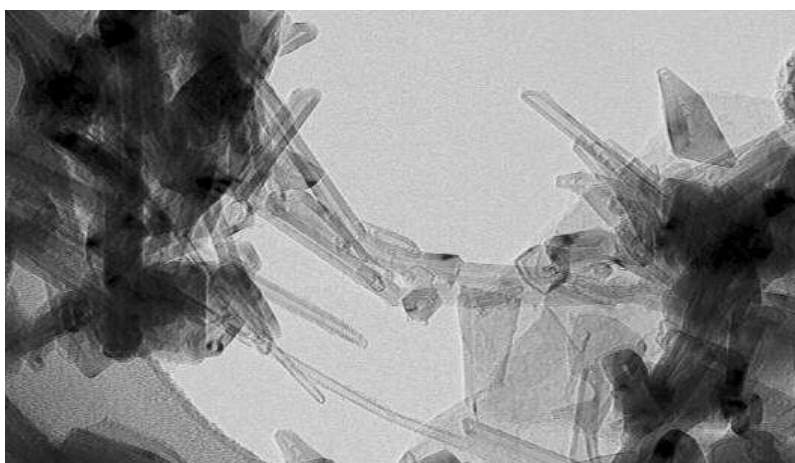


Fig. 2.1 TEM image of nanotubes

▪ *Single-Walled Nanotubes (SWNT)*

SWNTs, shown in Fig. 2.1, are envisioned as a graphene sheet rolled into a cylinder with diameter in the range of 1.2 – 1.4 nm and length ranging from tens of nm to tens of μm (Agnihotri, 2003). They have excellent adsorption properties due to high specific surface area and high-energy adsorption sites in their interior and in the region between adjacent nanotubes.

- *Multi-Walled Nanotubes (MWNT)*

MWNTs are arrangements of concentric SWNTs with an outer diameter ranging from 5 – 30 nm and length ranging from tens of nm to tens of μm (Agnihotri, 2003). Their advantage would be in higher sorption rates due to high-energy surface sites for compounds that are difficult to adsorb. Compared with SWNT, MWNT are advantageous in that they can be made with uniform lengths, known diameter distributions, without bundle formations, and with essentially no amorphous carbon which leads to “reproducible” adsorption isotherms. Both SWNTs and MWNTs are closed-end tubes.

2.2.3 Nanoscrolls

Nanoscrolls are just like nanotubes except that the sheets are curled up, without the caps on the ends, potentially allowing access to significant additional surface area. While nanotubes are normally made at high temperatures, nanoscrolls can be produced at room temperature. (Masciangioli and Zhang, 2003)

2.2.4 Nanohorns

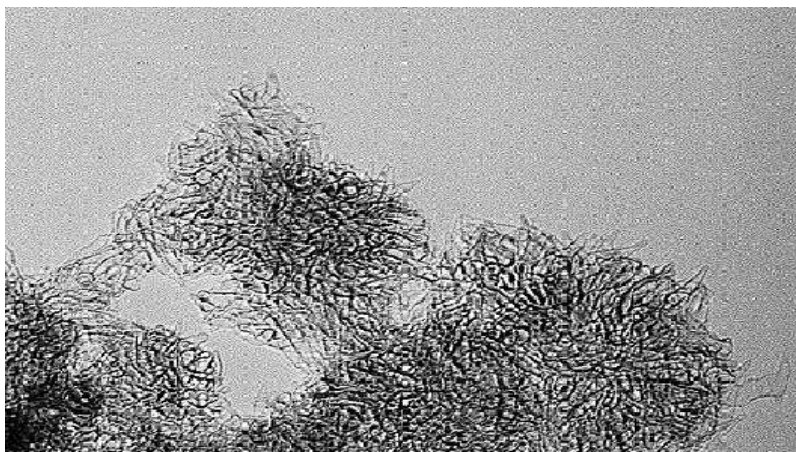


Fig. 2.2 TEM image of nanohorns

Nanohorns, shown in Fig. 2.2, have the same graphitic carbon atom structure as normal carbon nanotubes, but consist of a horn-shaped sheath aggregate of a single-wall graphene sheet. Typical nanohorns have a diameter of around 2 nm and a length of 30-50 nm, with the end of the tube closed by a conical cap with a cone angle of 20° (Masciangioli and Zhang, 2003). The intraparticle pores in the nanohorns can be opened with high-temperature treatment in O₂, resulting in a specific surface area of 1010 m²/g. Compression can further increase it to 1100 m²/g (Bekyarova et.al., 2003). Nanohorns self-assemble into spherical aggregates, with space between adjacent nanohorns large enough to accommodate small gas molecules.

2.3 Previous studies and ongoing research on nanoadsorbents

2.3.1 Studies on nanotubes

- ⇒ Smith et al. (2003) studied chemical activation of SWNT samples by mild oxidation with CO₂ followed by heat treatment in an inert atmosphere at 600°C. They examined the effect of the nanotube diameter distribution and packing on hydrogen uptake. It was concluded that the activation of SWNT samples can profoundly impact the adsorption of H₂.
- ⇒ Zhao et al. (2002) studied adsorption of various gas molecules (NO₂, O₂, NH₃, N₂, CO₂, CH₄, H₂O, H₂, Ar) on SWNTs and bundles using first principle methods. The equilibrium position, adsorption energy, charge transfer, and electronic band structures were obtained for different kinds of SWNTs. It was found that the gas adsorption on the bundle interstitial and groove sites is stronger than that on an individual nanotube.

- ⇒ Fujiwara et al. (2000) studied the adsorption properties of nitrogen and oxygen gases in single-walled carbon nanotube (SWNT) bundles by isotherm and X-ray diffraction (XRD). In the as-grown (AG) nanotubes with close-ended caps, both the gases were adsorbed only in the interstitial channels between triangular packed nanotubes. In the heat-treated (HT) nanotubes with open ends, the gases were adsorbed first in the inside of tubes, and next in the interstitial channels. The results indicated that the inside of nanotube had stronger affinity for gas adsorption than the interstitial channels of bundles.
- ⇒ Agnihotri et al. (2002) studied adsorption properties of water vapor and select organic vapors at 25°C on select SWNTs. The results were compared with granular activated carbon (GAC) and activated carbon filter cloth (ACFC). Organic vapors methyl ethyl ketone (MEK) and toluene were investigated. Isotherms were determined for adsorbate concentrations in the range of 0 to 0.95 P/P_o for water vapor and 30 to 5000 ppm_v for MEK and toluene. It was observed that the average diameter of nanotubes in the two samples, S95 and CS80, were consistent with the pore size distribution results. In conclusion, it was stated that when compared to activated carbons, SWNTs are less effective in removing pollutants present in concentration range of 10's to 1000's of ppm_v. The overall water adsorption capacity of SWNTs was found to be much less than that of activated carbons, which indicates that SWNTs are more hydrophobic than activated carbons. For organic vapors, S95 showed higher adsorption capacity for MEK and toluene than CS80. It was found that not all

porosity of SWNT samples is available for adsorption of MEK and toluene. Adsorption capacities of SWNTs were found to be only approximately $\frac{1}{2}$ of those of activated carbons for both water vapor and organic vapors. It was speculated that the capacities would increase at even lower gas-phase concentrations.

⇒ Hilding et al. (2001) studied the sorption mechanism for butane on MWNTs at room temperature and relative pressures ranging from 0 to 0.9. Three samples of MWNTs with similar lengths but different diameter distributions at 298.15K were used. Adsorption isotherms were modeled using a modified BET equation. It was seen that most of the butane was sorbed to the external surface of the MWNTs and only a small fraction of it condensed in the pores.

⇒ Yang et al. (2002) studied the purification of HiPco (High Pressure CO decomposition) single-walled carbon nanotubes (HPNTs) containing Fe by a one-step process with HCl-washing (D-method) and by a two-step process with HCl- washing after air oxidation (GD-method). The HPNT samples before and after purification were characterized using N_2 adsorption at 77K, thermogravimetric analysis (TGA), and X-ray photoelectron spectroscopy (XPS). The effects of purification on the adsorption properties of HPNT aggregates with regard to CH_3OH (methanol) and C_2H_5OH (ethanol) vapors were examined at 303K. It was seen that the purification greatly enhanced the adsorptivity for CH_3OH and C_2H_5OH vapors at 303K under a low relative

pressure, and this was associated with the enhanced microporosity and the oxygen-based functional groups introduced on the surface.

⇒ Long et al. (2001) studied dioxin removal using multi-walled carbon nanotubes (MWNTs). A technique based on temperature-programmed desorption (TPD) was used for studying dioxin adsorption. Carbon nanotubes were prepared using catalytic decomposition of methane. The obtained material was treated with nitric acid to dissolve the catalyst particles and then calcined at 400°C for 1 h in air. The amount adsorbed on carbon nanotubes is 10^{34} higher than that on activated carbon due to increased interaction potential between the two benzene rings of dioxin and the surface of nanotubes. Hence, significantly higher dioxin removal efficiency is expected with carbon nanotubes than that with activated carbon. It was seen that desorption temperatures, the desorption activation energy, and the Langmuir constant of dioxin on carbon nanotubes are much higher than those of activated carbon and γ -Al₂O₃. Carbon nanotubes exhibit strong oxidation resistance which was found to be beneficial for regeneration of dioxin at high temperatures.

Table 2.1 at the end of the chapter summarizes important information from the articles related to nanotubes.

2.3.2 Studies on nanoscrolls

⇒ Viculis et al. (2003) reported a low-temperature, catalyst-free route to producing carbon nanoscrolls, a material analogous to multiwalled carbon nanotubes. It was found that short (1 hour), high-energy (500 W) sonication was necessary

for efficient carbon nanoscroll formation, converting over 80% of the dispersed carbon sheets into nanoscrollled material. Because the carbon nanoscrolls have greatly reduced van der Waals interactions compared with the starting graphite powder, a lowering of thermal stability was expected. The experiments that were conducted suggested that carbon nanoscrolls could have considerable surface area. TEM analysis showed that a typical scroll was made up of 40 ± 15 layers of carbon, based on an interlayer spacing of 3.4 Å. The carbon nanoscrolls had an average diameter of 40 nm. Therefore, the maximum number of layers per scroll would be 120, or 60 complete turns. Similar to activated carbons, carbon nanoscrolls were found to adsorb and retain solvents tenaciously. Therefore, these nanostructured forms of carbon could potentially be useful as adsorbents or perhaps even for hydrogen storage if an efficient method for removing residual solvent was developed. Because carbon sheets are one of the strongest materials known per unit weight, this low-density material may also be useful in composites for structural applications.

⇒ Braga et al. (2004) used molecular dynamics simulations to investigate carbon nanoscrolls formation, stability and structural effects due to charge injection. It was seen that CNS formation occurred automatically when a critical overlap between sheet layers was achieved for the partially curved sheets. Molecular dynamics simulations were used to investigate structural evolution for selected CNS configurations. Both neutral and charged CNSs were analyzed in order to investigate the effects of charge injection on scroll geometry. It was also stated in the study that because of the novel scroll topology, the CNS properties should

differ from those of either SWNTs or MWNTs. For example, in contrast to SWNTs and MWNTs, CNSs provide interlayer galleries that could be intercalated with donors and acceptors, and the nanotube diameter could expand to accommodate the volume of the intercalant. Results showed that the CNSs could have a lower energy than the precursor graphene and that scroll formation was a self-sustained curling process after a critical overlap area was reached. CNSs having an inner diameter smaller than about 20 Å were unstable with respect to an increase in this diameter, and conical scrolls could be trapped as a metastable state. It was found that charge injection caused unwinding of the CNSs, which might be important for the application of CNSs as nanomechanical actuators.

Table 2.2 at the end of the chapter summarizes important information from the articles related to nanoscrolls.

2.3.3 Studies on nanohorns

⇒ Bekyarova et al. (2001) studied budlike single-wall carbon nanohorns (SWNHs), which are capped hollow materials. They were oxidized by heating in O₂ to produce nano-order windows in the walls. The opening of budlike SWNHs was studied with transmission electron microscopy and N₂ adsorption at 77K. The adsorption isotherms showed an increase in porosity with increasing temperature of the SWNHs oxidation. The micropore volume of SWNH after oxidation in O₂ at 693K increased three times. It was concluded that the oxidation does not change the size and shape of the budlike SWNH

bundles but does increase the surface area available for adsorption by increasing access to inner sites. It is an effective way to produce SWNHs with a large micropore volume.

⇒ Murata et al. (2001) showed that the closed pores of SWNHs can be opened easily only by high-temperature treatment (HTT) in an oxygen atmosphere. The SWNHs were synthesized by CO₂ laser ablation of graphite under Ar gas at 101kPa. The SWNHs were treated in an oxygen atmosphere at 573, 623, 693 and 823K. The porosity of SWNH aggregates was determined volumetrically by the nitrogen adsorption isotherm at 77K after pretreatment at 423K and 1 mPa with the volumetric apparatus. The interaction potential function analysis showed the presence of three types of sites: interstitial sites, intraparticle monolayer sites, and intraparticle core sites. Adsorption on the intraparticle core sites occurred after primary micropore filling on the above strong sites. It was concluded that the interaction potential function analysis is helpful to understand the adsorption mechanism on SWNH assemblies.

⇒ Murakami et al. (2004) investigated the in vitro adsorption and release of the anti-inflammatory glucocorticoid dexamethasone (DEX) by as-grown SWNHs and their oxidized form, oxSWNHs. Adsorption analyses using [³H]-DEX determined the amount of DEX adsorbed by oxSWNHs to be 200mg for each gram of oxSWNHs in 0.5 mg/mL of DEX solution, which was approximately 6 times larger than that obtained for as-grown SWNHs. According to the adsorption kinetics, oxSWNHs had greater affinity for DEX than as-grown

SWNHs. It was then decided to conduct the experimentation with SWNHs without the oxygen groups. The oxSWNHs were treated at 1200°C under H₂, which removed the oxygen-containing functional groups on oxSWNHs. It was found that removal of the functional groups did not diminish the high affinity for DEX, suggesting that they have little contribution for the affinity. The study also concluded that the DEX-oxSWNH complexes exhibited sustained release of DEX into phosphate-buffered saline (pH 7.4) at 37°C and more rapid release into the culture medium. This study thus highlights the potential utility of SWNHs in drug delivery systems.

⇒ Bekyarova et al. (2002) studied the pore structure changes of single-walled carbon nanohorns (SWNHs) after oxidation with O₂ and CO₂ at different temperatures. Low temperature N₂ adsorption isotherms were analyzed to evaluate the parameters of both types of porosities present: interparticle pores and intraparticle cavities. The data obtained showed that O₂ opens significantly more nanohorns compared to CO₂. About 77% of the nanohorns were open in SWNH oxidized in O₂ at 693K. The highest percentage of pore opening with CO₂ was 45%.

⇒ Ohba et al. (2001) studied N₂ adsorption in the internal nanospace and the external surface of SWNH particles. The study involved detailed comparison of the simulated adsorption isotherm with the experimental isotherm in the internal nanospaces. Simulated isotherms for various values of width (*w*) of internal nanopore ranging from 2.5 nm to 3.3 nm were plotted. Actual adsorption

isotherms for internal nanospace and external surface were calculated over the relative pressure range of 10^{-6} to 1 from D (tube diameter) = 2.0 to 3.6 nm by every 0.1 nm. It was found that the simulated isotherm of $w = 2.9\text{nm}$ coincides with the experimental one of tube diameter $D = 3.2$ nm over the wide P/P_0 (relative pressure) region from 10^{-4} to 10^{-1} . Thus the average internal pore width of SWNHs is 2.9 nm.

⇒ A. J. Zambano et al. (2002) performed Xe adsorption studies on aggregates of SWNHs. The experiments were performed on two batches of SWNHs. Batch A had a small portion of open nanohorns and Batch B contained closed nanohorns. Isothermic heats of adsorption of Xe on SWNH samples were measured at low coverages. From these isothermic heat values, the binding energy of the highest-binding-energy sites for Xe on the SWNHs was determined. A value of 235meV was found for this quantity. This value was nearly 50% greater than the binding energy value for Xe on planar graphite, but was nearly 20% smaller than that for Xe on bundles of untreated, as-produced, commercially available single-wall carbon nanotubes. The specific surface area of the SWNHs was of the order of $250\text{m}^2\text{g}^{-1}$. It was concluded therefore that both the specific surface area and the highest-binding-energy values determined for the SWNHs indicated that this material had very highly desirable characteristics as an adsorbent.

⇒ Tanaka et al. (2002) measured the adsorption isotherms of H_2 and CH_4 on activated carbon fibers (ACF) and single-walled carbon nanohorns (SWNH) at vapor and supercritical conditions. It was found that H_2 and CH_4 are adsorbed

sufficiently on micropores of ACF and SWNH at the vapor conditions and their adsorption isotherms were described by the Dubinin-Radushkevich equation. The CH₄ molecules at 114K were adsorbed on ACFs with a micropore filling mechanism, same as N₂ molecules at 77K. However, the amount of CH₄ adsorption decreased remarkably with the increase of temperature. The adsorption of supercritical CH₄ was found to be more difficult than the adsorption of CH₄ vapor. H₂ vapors were also found to be adsorbed on SWNHs by micropore filling mechanism. The adsorption of CH₄ on ACF was greater than the adsorption of H₂ on SWNH. The H₂ vapor adsorption suggested the presence of physical adsorption sites having quite strong interaction potential. However, the adsorption of supercritical H₂ was not remarkable.

⇒ Murata et al. (2002) studied the exact physical adsorption amounts of supercritical hydrogen on SWNH assemblies at 77K, 196K and 303K. The fact that the adsorbed density of hydrogen in interstitial spaces was lower than that in internal spaces against the prediction from the interaction potential calculation was explained by the self-stabilization effect and self-locking mechanism. The interaction potential depths of interstitial and internal spaces were -1000K and -600K, respectively. However, hydrogen densities in both the interstitial and internal spaces were about 70gL⁻¹ at 77K at 5MPa, though the densities in the interstitial and internal spaces were 15 and 10gL⁻¹ at 303K and 6.5MPa. Similar enhancement was observed even at 196K. It was concluded that the self-stabilization effect and self-locking mechanism came from the

cluster formation by hydrogen molecules and the presence of strongly adsorbed molecules in the interstitial spaces, respectively.

⇒ Bekyarova et al. (2003) performed a study for methane storage using SWNHs that were compressed repeatedly at 50MPa to generate a nanocarbon material of high bulk density. The resulting nanostructured disordered carbon exhibited a high methane storage capacity of 160 cm³ of methane adsorbed / cm³ of nanocarbon at 3.5MPa and 303K. The experimental isotherms were compared with the simulation isotherms. The surface area (S) and micropore volume (V_{mi}) of the compressed SWNHs were estimated to be 1097 m²/g and 0.55 cm³/g, respectively. The corresponding values for uncompressed open SWNHs were S = 1030 m²/g and V_{mi} = 0.50 cm³/g. Thus the micropore volume and surface area increased after compression. The methane adsorption capacity of activated carbon measured in the same apparatus and under the same conditions as compressed SWNHs was 96 cm³/cm³ of adsorbent at 303K and 3.5MPa. It was thereby concluded that single-wall carbon nanomaterials with disordered structure could find application as storage media for methane and other supercritical gases.

Table 2.3 at the end of the chapter summarizes important information from the articles related to nanohorns.

2.4 Conclusion

From the above article summaries, the following conclusions related to potential air pollutant applications can be drawn:

For nanotubes –

- Heat treatment enhanced the adsorption properties of most of the nanotubes. The internal pores opened up due to intense heat, increasing the internal space for adsorption.
- The increase in micropore volume by heat-treatment is applicable to both nanohorns (SWNHs) as well as HiPco single-walled carbon nanotubes (HPNTs).
- Adsorption in the internal sites for open nanotubes was greater than interstitial sites, which in turn was greater than outer grooves. Adsorption on outer grooves was greater than that on outer surfaces due to increasing binding energy. Binding energy was least at the outer surface and greatest at the internal sites.
- Agnihotri et al. found that adsorption capacities of some SWNTs at 25°C for water and some organic vapors in the range of 10's to 1000's of ppmv were approximately $\frac{1}{2}$ of those for activated carbon which could be due to higher surface area and micropore volume of activated carbon. On the other hand, studies by Richard Long and Ralph Yang showed that the interactions of dioxins with carbon nanotubes (MWNTs) were much stronger than interactions with the current scrubber material of activated carbon. These stronger interactions were attributed to the unique structure and electronic properties of carbon nanotubes. Additionally, it was found that the dioxin molecule interacts with all surfaces on

the walls of nanotubes within the small pore, which resulted in overlapping of the interaction potentials, and thereby enhancing the potential.

Thus the work done so far on nanotubes proves that they can be very effective in adsorption applications related to air quality. With the enhancement of adsorption capacities with the help of the various treatments mentioned above, nanotubes prove to be promising in terms of adsorption capacity and low material requirements.

For nanoscrolls –

- Studies conducted by Viculis et al. on nanoscrolls concluded that these nanostructured forms of carbon could potentially be useful as adsorbents or perhaps even for hydrogen storage if an efficient method for removing residual solvent was developed.

For nanohorns –

- Oxidation does not change the size and shape of the budlike SWNH bundles but does increase the surface area available for adsorption by increasing access to inner sites. The micropore volume of SWNHs after oxidation in O₂ at 693K increased by a factor of three.
- The interaction potential function analysis conducted on high-temperature treated SWNHs showed the presence of three types of sites: an interstitial site, an intraparticle monolayer site, and an intraparticle core site. The adsorption on the intraparticle core sites occurred after primary micropore filling on the above strong sites.

- The dexamethasone adsorption capacity of oxSWNHs was 6 times greater than as-grown SWNHs. However, the presence of oxygen functional groups does not play any role in the enhancement of adsorption capacity of SWNHs.
- SWNH oxidation with O₂ at 693K opened 77% of the nanohorns as compared to SWNH oxidation with CO₂ at the same temperature, which opened only 45% of the nanohorns.
- Xe adsorption studies performed on SWNHs resulted in 50% greater binding energy value than that Xe on planar graphite, but was nearly 20% smaller than that for Xe on bundles of untreated, as-produced, commercially available single-wall carbon nanotubes. It was concluded that SWNHs had very highly desirable characteristics as an adsorbent.
- Tanaka et al. found that the amount of CH₄ adsorption on activated carbon fibers (ACF) decreased remarkably with the increase of temperature. The adsorption of supercritical CH₄ was found to be more difficult than the adsorption of CH₄ vapor. Both H₂ and CH₄ vapors were found to be adsorbed on SWNHs and ACFs, respectively, by micropore filling mechanism. The H₂ vapor adsorption suggested the presence of physical adsorption sites having quite strong interaction potential. However, the adsorption of supercritical H₂ was not remarkable.
- Study of physical adsorption of supercritical hydrogen on SWNH assemblies at 77K, 196K and 303K indicated that the self-stabilization effect and self-locking mechanism came from the cluster formation by hydrogen molecules and the presence of strongly adsorbed molecules in the interstitial spaces, respectively.

This explained the fact that the adsorbed density of hydrogen in interstitial spaces was lower than that in internal spaces against the prediction from the interaction potential calculation.

- Studies performed on compressed SWNHs for methane storage concluded that single-wall carbon nanomaterials with disordered structure could find application as storage media for methane and other supercritical gases.

It is clear from the above article reviews that not enough work has been done on adsorption of VOCs using carbon nanohorns, although they may have greater adsorption capacities than conventional adsorbents. Also it is seen that certain treatments alter the physical structure of nanoadsorbents improving their capacity and efficiency to adsorb. It is known that certain volatile organic compounds like ethylene are difficult to adsorb on conventional activated carbon due to greater vapor pressure. However, some studies show that nanoadsorbents could do a better job at adsorbing such volatile organic compounds. The main focus of this research therefore is to find out adsorption capacities of Nanohorns for these types of VOCs. Thus the ideas of exploiting the potential of Nanohorns, with and without treatment, for VOCs that are difficult to control via conventional adsorbents and in the process compare their capacities to conventional activated carbon, emerged.

Table 2.1 List of articles dealing with NANOTUBES

JOURNAL TITLE – <i>Journal of Physical Chemistry B</i> (2003), Vol. 107, pp. 3752-3760			
AUTHORS	TESTS	NANOTUBE TREATMENT(IF ANY)	CONCLUSION
Milton Smith, Jr., Edward Bittner, Wei Shi, J.Karl Johnson and Bradley Bockrath.	Chemical activation of SWNTs for hydrogen adsorption was studied.	SWNTs were oxidized in CO ₂ and then heat treated in an inert atmosphere.	Heat treatment enhanced the adsorption efficiencies of the SWNTs.
JOURNAL TITLE – <i>Nanotechnology</i> (2002), Vol. 13, pp. 195-200			
AUTHORS	TESTS	NANOTUBE TREATMENT(IF ANY)	CONCLUSION
Jijun Zhao, Alper Buldum, Jie Han and Jian Ping Lu.	Adsorption of various gas molecules (NO ₂ , O ₂ , NH ₃ , N ₂ , CO ₂ , CH ₄ , H ₂ O, H ₂ , Ar) on SWNTs was studied.	N/A	Gas adsorption on the bundle interstitial and groove sites between nanotubes is stronger than that on individual nanotubes.
JOURNAL TITLE – <i>Chemical Physical Letters</i> (2001), Vol. 336, pp. 205-211			
AUTHORS	TESTS	NANOTUBE TREATMENT(IF ANY)	CONCLUSION
Akihiko Fujiwara, Kenji Ishii, Hiroyoshi Suematsu, Hiromichi Kataura, Yutaka Maniwa, Shinzou Suzuki and Yohji Achiba.	Adsorption of nitrogen and oxygen gases on SWNTs was studied.	N/A	Inside of the nanotube has a stronger affinity for gas adsorption than the interstitial channels of the SWNT bundles.
CONFERENCE – (2002) 224 th American Chemical Society National Meeting, Boston, MA, August 18-24, p. 5 SESSION TITLE - Energy and Environmental Applications of Carbon Nanotubes.			
AUTHORS	TESTS	NANOTUBE TREATMENT(IF ANY)	CONCLUSION
Sandeep Agnihotri, Massoud Rostam - Abadi, Mark Rood and Robert Clarkson.	Adsorption of water vapor and select organic vapors at 25°C on select SWNTs was studied.	The SWNTs were specified to contain ~80 mass% SWNTs with remaining mass being catalyst (~12 mass% Fe) and other carbonaceous material. As specified, samples contained open-ended SWNTs.	When compared to activated carbons, SWNTs are less effective in removing pollutants present in concentration range of 10's to 1000's of ppmv. Adsorption capacities of SWNTs were found to be ~ ½ of those of activated carbon.
JOURNAL TITLE – <i>Langmuir</i> (2001), Vol. 17, pp. 7540-7544			
AUTHORS	TESTS	NANOTUBE TREATMENT(IF ANY)	CONCLUSION
Jenny Hilding, Eric Grulke, Susan Sinnott, Dali Qian, Rodney Andrews and Marit Jagtoyen.	Sorption of butane was studied on MWNTs at room temperature.	N/A	Most of the butane was sorbed to the external surface of the MWNTs and only a small fraction of it condensed in the pores.

Table 2.1 – continued

JOURNAL TITLE – <i>Journal of Physical Chemistry B</i> (2002), Vol. 106, pp. 8994-8999			
AUTHORS	TESTS	NANOTUBE TREATMENT(IF ANY)	CONCLUSION
Cheol-Min Yang, Hirofumi Kanoh, Katsumi Kaneko, Masako Yudasaka and Sumio Iijima.	Effects of purification on the adsorption properties of HPNT aggregates with regard to CH ₃ OH (methanol) and C ₂ H ₅ OH (ethanol) vapors were examined at 303K.	HPNTs containing Fe were purified by a one-step process with HCl-washing (D-method) and a two-step process with HCl-washing after air oxidation (GD-method).	It was seen that purification greatly enhanced the adsorptivity for CH ₃ OH and C ₂ H ₅ OH vapors at 303K under a low relative pressure, and this was associated with the enhanced microporosity and the oxygen-based functional groups introduced on the surface.

Table 2.2 List of articles dealing with NANOSCROLLS

JOURNAL TITLE – <i>Science</i> (2003), Vol. 299, Issue 5611, pp. 1361			
AUTHORS	TESTS	NANOSCROLL TREATMENT(IF ANY)	CONCLUSION
Lisa M. Viculis, Julia J. Mack and Richard B. Kaner.	The structure and formation of carbon nanoscrolls was studied using sonication and exfoliation techniques.	N/A	Nanoscrolls could potentially be useful as adsorbents or perhaps even for hydrogen storage if an efficient method for removing residual solvent was developed. They may also be useful in composites for structural applications.
JOURNAL TITLE – <i>Nano Letters</i> (2004), Vol. 4, No.5, pp. 881-884			
AUTHORS	TESTS	NANOSCROLL TREATMENT(IF ANY)	CONCLUSION
S.F. Braga, V.R. Coluci, S.B. Legoas, R. Giro, D.S. Galva and R.H. Baughman.	The formation, stability and structural effects of carbon nanoscrolls were studied.	N/A	Charge injection caused unwinding of the CNSs, which might be important for the application of CNSs as nanomechanical actuators.

Table 2.3 List of articles dealing with NANOHORNS

JOURNAL TITLE – <i>Langmuir</i> (2002), Vol. 18, pp. 4138-4141			
AUTHORS	TESTS	NANO HORN TREATMENT(IF ANY)	CONCLUSION
E. Bekyarova, K. Kaneko, D. Kasuya, K. Murata, M. Yudasaka and S. Iijima.	Oxidation and porosity evaluation of budlike SWNH aggregates was done.	Capped hollow SWNHs were oxidized by heating in O ₂ to produce nano-order windows in the walls.	Oxidation does not change the size and shape of the budlike SWNH bundles but does increase the surface area available for adsorption by increasing access to inner sites.

Table 2.3 – continued

JOURNAL TITLE – <i>Journal of Physical Chemistry B</i> (2001), Vol. 105, pp. 10210-10216			
AUTHORS	TESTS	NANO HORN TREATMENT(IF ANY)	CONCLUSION
K. Murata, K. Kaneko, Steele, Kokai, Takahashi, Kasuya, Hirahara, Yudasaka and Iijima.	Molecular potential structures of heat treated SWNH assemblies were studied.	The SWNHs were synthesized by CO ₂ laser ablation of graphite under Ar gas at 101kPa and were treated in an oxygen atmosphere at 573, 623, 693 and 823K.	The interaction potential function analysis showed the presence of three sites: an interstitial site, an intraparticle monolayer site, and an intraparticle core site. It was concluded that the interaction potential function analysis is helpful to understand the adsorption mechanism on SWNH assemblies.
JOURNAL TITLE – <i>Molecular Pharmaceutics</i> (2004), Vol. 1, No.6, pp. 399-405			
AUTHORS	TESTS	NANO HORN TREATMENT(IF ANY)	CONCLUSION
Tatsuya Murakami, Kumiko Ajima, Jin Miyawaki, Masako Yudasaka, Sumio Iijima and Kiyotaka Shiba.	Adsorption and release of Dexamethasone in Vitro was studied.	SWNHs were treated in O ₂ to form oxSWNHs. For further research the oxSWNHs were treated at 1200°C to get rid of the oxy functional groups.	Removal of O ₂ functional groups did not diminish the high affinity for DEX, suggesting that they have little contribution to the affinity. DEX-oxSWNH complexes exhibited sustained release of DEX into phosphate-buffered saline (pH 7.4) at 37°C and more rapid release into culture medium.
JOURNAL TITLE – <i>Physica B</i> (2002), Vol. 323, pp. 143-145			
AUTHORS	TESTS	NANO HORN TREATMENT(IF ANY)	CONCLUSION
E. Bekyarova, K. Kaneko, D. Kasuya, K. Takahashi, F. Kokai, M. Yudasava and S. Iijima.	Pore structure and adsorption studies of SWNHs treated in different atmospheres were performed.	SWNHs were oxidized with O ₂ and CO ₂ at different temperatures.	The data obtained showed that O ₂ opens significantly more nanohorns compared to CO ₂ . About 77% of the nanohorns were open in SWNH oxidized in O ₂ at 693K. The highest percentage of pore opening with CO ₂ was 45%.
JOURNAL TITLE – <i>Nano Letters</i> (2001), Vol. 1, No.7, pp. 371-373			
AUTHORS	TESTS	NANO HORN TREATMENT(IF ANY)	CONCLUSION
T. Ohba, K. Murata, K. Kaneko, W.A. Steele, F. Kokai, K.Takahashi, D. Kasuya, M.Yudasaka and S. Iijima.	N ₂ adsorption in internal nanopores of SWNHs was studied.	N/A	Detailed comparison of the simulated adsorption isotherm with the experimental isotherm in the internal nanopores that provides 2.9nm of the average pore width.

Table 2.3 – continued

JOURNAL TITLE – <i>Nanotechnology</i> (2002), Vol. 13, pp. 201-204			
AUTHORS	TESTS	NANO HORN TREATMENT(IF ANY)	CONCLUSION
A.J. Zambano, S. Talapatra, K. Lafdi, M.T. Aziz, W. McMillin, G. Shaughnessy, A.D. Migone, M. Yudasaka, S. Iijima, F. Kokai and K. Takahashi.	Adsorption binding energy and adsorption capacity of Xe on SWNHs was studied.	N/A	The specific surface area of the SWNHs was of the order of $250\text{m}^2\text{g}^{-1}$. Both the specific surface area and the highest-binding-energy values determined for the SWNHs indicated that this material had very highly desirable characteristics as an adsorbent.
JOURNAL TITLE – <i>Molecular crystals and liquid crystals science and technology</i> (2002), Vol. 388, Issue 1, pp. 15-21.			
AUTHORS	TESTS	NANO HORN TREATMENT(IF ANY)	CONCLUSION
H. Tanaka, J. Miyawaki, K. Kaneko, K. Murata, D. Kasuya, M. Yudasaka, K. Kaneko, F. Kokai and K. Takaha	Comparative study on physical adsorption of vapor and supercritical H_2 and CH_4 on SWNH and ACF was conducted.	N/A	The adsorption of supercritical H_2 on SWNH was not remarkable. The amount of CH_4 adsorption on activated carbon fibers (ACF) decreased remarkably with the increase of temperature but was more than that of H_2 on SWNH. The adsorption of supercritical CH_4 was found to be more difficult than the adsorption of CH_4 vapor. Both H_2 and CH_4 vapors were found to be adsorbed on SWNHs and ACFs, respectively, by micropore filling mechanism.
JOURNAL TITLE – <i>Journal of Physical Chemistry B</i> (2002), Vol. 106, pp. 11132-11138			
AUTHORS	TESTS	NANO HORN TREATMENT(IF ANY)	CONCLUSION
K. Murata, K. Kaneko, H. Kanoh, D. Kasuya, K. Takahashi, F. Kokai, M. Yudasaka and S. Iijima.	Adsorption mechanism of supercritical hydrogen in internal and interstitial nanospaces of SWNH assembly was studied.	N/A	Self-stabilization effect and self-locking mechanism of SWNHs came from the cluster formation by hydrogen molecules and the presence of strongly adsorbed molecules in the interstitial spaces, respectively.

Table 2.3 – continued

JOURNAL TITLE – <i>Journal of Physical Chemistry B</i> (2003), Vol. 107, No. 20, pp. 4681-4684			
AUTHORS	TESTS	NANOHORN TREATMENT(IF ANY)	CONCLUSION
E. Bekyarova, K. Murata, M. Yudasaka, D. Kasuya, S. Iijima, H. Tanaka, H. Kahoh and K. Kaneko.	The possibility of SWNHs for carbon storage was tested.	The SWNHs were repeatedly compressed at 50MPa to generate a nanocarbon material of high bulk density.	The micropore volume and surface area increase after compression. It was thereby concluded that SWNHs with disordered structure could find application as storage media for methane and other supercritical gases.

CHAPTER 3

METHODOLOGY

Lab scale experiments were conducted to find out the kind of adsorbent that would achieve the best results for the selected hazardous air pollutants. It was decided to compare the adsorption capacities of conventional activated carbon and nanohorns in various physical states, for each of the pollutants and develop adsorption isotherms that would depict the maximum adsorption capacities for each type of adsorbent.

3.1 Description of equipment and apparatus



Fig. 3.1 Lab test experimental setup

The experimental setup is shown in Fig. 3.1 above. The equipment is described in detail below.

3.1.1 Volatile organic compounds



Fig. 3.2 Ethylene gas cylinder

The hazardous air pollutants selected for the research were alkanes - n-butane and n-hexane and alkenes - propylene and ethylene. Propylene and ethylene are classified as highly reactive VOCs regarding ground-level ozone formation. Hexane, in addition to forming ozone, is classified as a hazardous air pollutant.

The gases n-butane, hexane, ethylene and propylene were ordered from Matheson Tri-Gas in lecture bottles (LB), as shown in Fig. 3.2, with net weight ranging from 0.25 lbs to 0.6 lbs. These gases were research grade with purities ranging from 99.0% to 99.999%. The regulators for gas cylinders were of stainless steel and also ordered from Matheson Tri-Gas. VOC concentrations ranging from 3500 to 99,000 ppm were tested.

3.1.2 Nanohorns

Nanohorns were ordered from Nanocraft, Inc. They were made with a high temperature plasma process that used an electric arc to generate the plasma. Nanohorns condensed out of a carbon jet plume within the first 3 to 5 cm distance from the electric

arc. By 3 cm the nanohorns formed and within 5 cm the nanohorn clusters self assembled. The clusters were carried away by a vacuum and cooling system and were then captured in a bag. The bag was emptied to retrieve the powder. The jet plume of carbon vapor was generated from a carbon-graphite material heated to about 3000°C with 300 to 1000 amps at 5 to 20 volts. The parameters varied and were proportional to the anode cross section used. Each nanohorn was 2 to 3 nm in diameter and 30 to 50 nm in length. The clusters of nanohorns ranged in spherical diameter between 50 to 120 nm. Open-end and closed-end forms had the same dimensions. TEM images, as shown in Fig. 3.3, of open-end and closed-end nanohorns were very similar. The apparent density of the nanohorns before compaction was about 0.3 to 0.4 g/cu.cm. (Michael Pepka, President, Nanocraft, Inc., 2005)

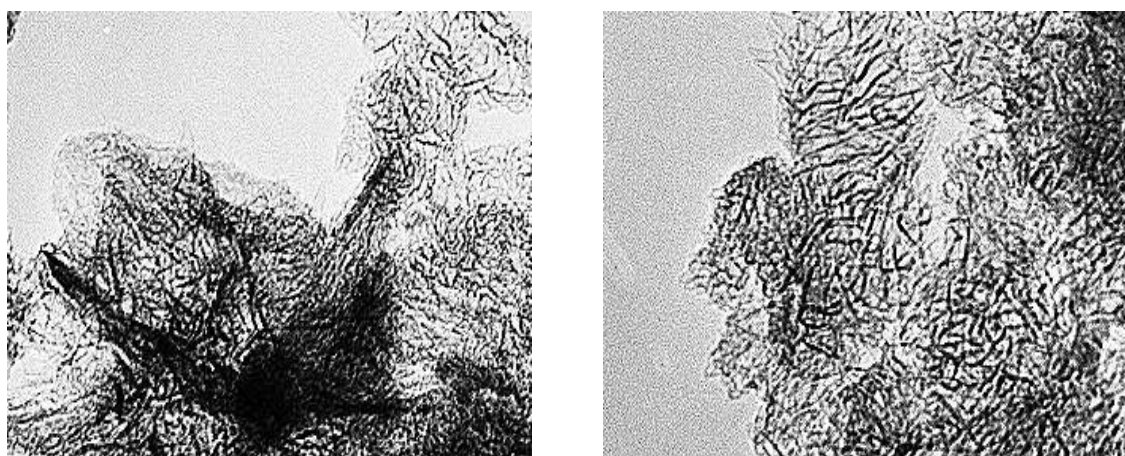


Fig. 3.3 TEM images of nanohorn clusters

The nanohorns ordered from the company were comprised of 10g of closed-end nanohorns without any treatment and 10g of open-end nanohorns with densification. Of the 10g of closed-end nanohorns, 5g were densified at UTA according to the following procedure. The nanohorns were mixed with acetone in the ratio of 20mL of acetone to

1g of nanohorns in a ceramic container. This mixture, with an ink-like appearance, was then placed at room temperature under a vented hood till the acetone had completely evaporated. It was then heated to 160°F for 8 hours in an oven. This process, termed densification, densified the nanohorns to 0.25g/cc. It made the nanohorns easy to handle and also increased their micropore volume.

3.1.3 Gas chromatograph (GC)



Fig. 3.4 Gas chromatograph

A gas chromatograph was used to determine the amount of gas adsorbed. The GC used for this research was an 8610C SRI Instrument, shown in Fig. 3.4, equipped with a flame ionization detector (FID), shown in Fig. 3.5. This detector detects compounds with at least one carbon-hydrogen bond.



Fig. 3.5 Flame ionization detector



Fig. 3.6 1/8" Packed column

The column used in the chromatograph, shown in Fig. 3.6, was a packed column, with high purity divinylbenzene (a good detector of alkanes, alkenes and alcohols) as packing material, diameter of 1/8" and length of approximately 3ft. The carrier gas used was helium and was supplied at a pressure of 6psi. Hydrogen was used as the combustion gas and was supplied at a pressure of 28psi. These gas cylinders, hydrogen – 76cf and helium – 77cf, were also ordered from Matheson Tri-Gas. The chromatograph was also equipped with an internal air compressor which eliminated the use of an external compressed air supply. The air pressure was maintained at 6psi.

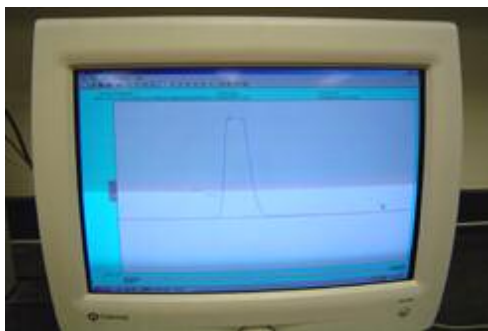


Fig. 3.7 PeakSimple software showing peak for ethylene

The chromatography software used was PeakSimple 3.29, shown in Fig. 3.7. The column oven temperature program was set through the software to ramp from 50°C to 250°C at the rate of 20°C/min. The peaks were classified by the software on the basis of the retention time of each compound, which also depended on the temperature program.

3.1.4 Miscellaneous apparatus



Fig. 3.8 Gas tight syringes, Tedlar bag and 4mL clear glass vial with rubber septa

Other apparatus used in the experiments are shown in Fig. 3.8. Gas tight syringes were used to introduce gases into the vials filled with a known weight of adsorbent and later into the GC for testing. The syringes were made of glass with 26 gauge removable needles. These syringes with different volumes like 25 μ L, 50 μ L, 100 μ L and 1mL were ordered from Cole Parmer. To test a particular compound, it was first injected into a Tedlar bag. These bags were fitted with a PTFE/silicone septum fitting in a polypropylene housing for use with hypodermic needle, the volume of the bags being 1.6L each, and dimensions being 9x9". Clear glass vials with screw thread cap and rubber septa were ordered from Cole Parmer. The vials were of 4mL volume and in a pack of 100.

3.2 Description of methodology employed

Altogether there were four types of adsorbents, viz. closed-end nanohorns without any treatment, closed-end nanohorns with treatment (i.e. densification), open-end nanohorns with treatment (they were densified at the time of manufacture) and VPR (raw) activated carbon pellets ordered from Calgon Carbon Corp. with a mesh size of 4 x 10. The VPR pellets are reactivated, primarily bituminous coal based.

The gas cylinder was fitted with an appropriate regulator. A small length of Teflon tubing, about 6 inches long, was fitted to the outlet of the regulator. The valve of the Tedlar bag was opened and fitted into the other end of the Teflon tube. A regulated flow of gas was then allowed into the Tedlar bag. The volume of gas collected into the bag was not fixed or known. After collecting a reasonable amount of gas, the bag was detached from the tube and the valve was closed. Another 6 inch long Teflon tubing was cut and fitted to the outlet of the filled Tedlar bag using a metal clamp. The other end of this tube was fitted with a plastic fitting having a septum. The valve of the bag was then opened by turning the tightly clamped tubing, and gas was allowed to fill into the tubing and the plastic fitting. The gas was then drawn out using the gas tight syringe.

Initially, for each combination of volatile organic compound and adsorbent, several trial and error runs were conducted to determine the maximum volume of compound that the adsorbent can completely adsorb. An approximate time of 10 minutes required to achieve adsorption equilibrium in the vial was also determined using these runs. The minimum quantity of the adsorbent was taken to be 0.03g in weight throughout, since it was difficult to measure and handle quantities below this value and also because it gave reasonably good adsorption.

Calibration curves were formed for each of the VOCs in order for the PeakSimple software to give the residual concentration values. For the calibration curves, first a shot of pure VOC of known volume (this chosen value was closest to the range of volumes to be used for the actual runs) was introduced into the GC and the

area count of the peak obtained was noted. The VOC was then diluted to a known concentration and the same volume of the diluted VOC was injected in the GC and the area count of the peak was noted. The calibration curve was thus formed using these data points. This procedure was followed to plot the calibration curves for all the VOCs to be tested.

Before each run each type of adsorbent was weighed to 0.03g using a digital weighing scale. The scale was calibrated in grams and gave readings up to four decimal places. It must be noted, though, that the scale possessed some degree of error and hence was not totally reliable. The glass vial was filled with the 0.03g of adsorbent. Increments in volume ranging from 1 μ L to 10 μ L for each run were chosen to be used throughout the research. Runs were carried out by injecting a known volume of VOC into the vials. After the time for equilibrium was passed, a sample of the same volume as that injected in the vial was drawn and injected into the GC. The software was initiated and the resultant concentration was noted. All runs were carried out at room temperature (70-80°F) and 59% humidity.

3.2.1 Formulae used in the calculations

- To calculate the initial concentration of VOC in the vial after injection

$$C_1 V_1 = C_2 V_2$$

Where,

C_1 = Concentration of VOC (without dilution) injected into the vial in
ppm

V_1 = Volume of VOC injected into the vial in μ L

C_2 = Concentration of VOC inside the vial after injection (with dilution by air inside the vial) in ppm

V_2 = Volume of headspace in the vial (total volume of the vial – volume occupied by nanohorns) in μL

- To convert the final concentration from ppm to mg/cu.m.

$$C_{mass} = \frac{MW \times C_{ppm}}{24.45}$$

Where,

C_{mass} = Concentration in mg/cu.m.

MW = Molecular weight of VOC in grams

C_{ppm} = Concentration in ppm

24.45 = Volume of a mole of gas in liters at STP conditions

- To calculate mass of VOC adsorbed in grams

The concentration in mg/cu.m. was first converted to g/L by multiplying it by 10^{-6} .

Mass of VOC adsorbed = Concentration of VOC adsorbed (i.e. total initial concentration of VOC in the vial – residual concentration obtained from the GC) in g/L x Volume of headspace in the vial (i.e. total volume of vial – volume occupied by nanohorns) in L.

The ratio of mass of VOC adsorbed in grams to the mass of adsorbent used in grams was calculated and a graph of the final concentration of VOC obtained from the

GC versus this ratio was plotted. The mass of VOC adsorbed per unit mass of adsorbent used gave a constant value after certain number of runs; this value was the adsorption capacity of the adsorbent for that VOC.

CHAPTER 4

RESULTS AND DISCUSSION

Once the data was collected from the runs for each combination of adsorbent and volatile organic compound, adsorption isotherms were plotted as mass of VOC adsorbed per unit mass of nanohorns versus equilibrium VOC concentration in ppm.

4.1 Data obtained

Table 4.1 Data for ethylene and closed-end nanohorns without treatment

Data for ethylene and closed-end nanohorns without treatment									
Calibration file	Run	Amount of nanohorns before adsorption		Volume of VOC injected into the vial (μL)	Volume of VOC injected into the GC (μL)	Initial conc. of VOC in the vial (ppm)	Final conc. from GC (ppm)	Mass of VOC adsorbed (g)	(Mass of VOC adsorbed)/ (Mass of nanohorns) (g/g)
		Weight (g)	Volume (mL)						
Ethy17μL.CAL	1	0.03	0.25	17	17	4533	2790	0.00000749	0.00025
Ethy17μL.CAL	2	0.03	0.25	18	17	4800	2956	0.00000792	0.00026
Ethy17μL.CAL	3	0.03	0.25	19	17	5067	3109	0.00000841	0.00028
Ethy17μL.CAL	4	0.03	0.25	20	17	5333	3226	0.00000905	0.00030
Ethy17μL.CAL	5	0.03	0.25	21	17	5600	3298	0.00000989	0.00033
Ethy17μL.CAL	6	0.03	0.25	22	17	5867	3480	0.00001025	0.00034
Ethy17μL.CAL	7	0.03	0.25	23	17	6133	3594	0.00001091	0.00036
Ethy17μL.CAL	8	0.03	0.25	24	17	6400	3713	0.00001154	0.00038
Ethy17μL.CAL	9	0.03	0.25	25	17	6667	3806	0.00001228	0.00041
Ethy17μL.CAL	10	0.03	0.25	26	17	6933	4057	0.00001235	0.00041
Ethy17μL.CAL	11	0.03	0.25	27	17	7200	4322	0.00001236	0.00041

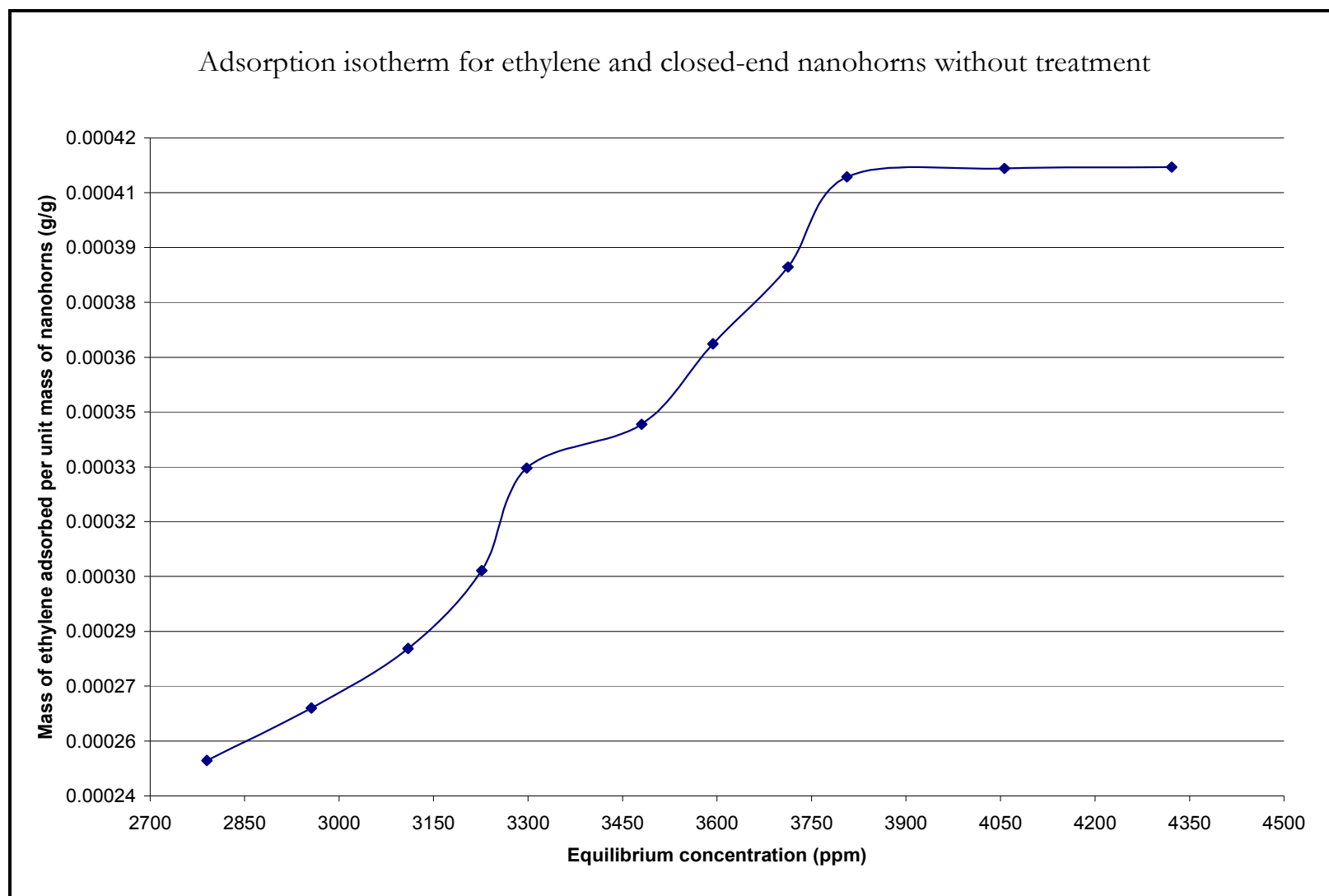


Fig. 4.1 Adsorption isotherm for ethylene and closed-end nanohorns without treatment

Table 4.2 Data for ethylene and closed-end nanohorns with treatment

Data for ethylene and closed-end nanohorns with treatment									
Calibration file	Run	Amount of nanohorns before adsorption		Volume of VOC injected	Volume of VOC injected	Initial conc. of VOC in the vial	Final conc. from GC	Mass of VOC adsorbed	(Mass of VOC adsorbed)/ (Mass of nanohorns)
		Weight (g)	Volume (mL)	into the vial (μL)	into the GC (μL)	(ppm)	(ppm)	(g)	(g/g)
Ethy17μL.CAL	1	0.03	0.0625	16	17	4063	3127	0.0000042	0.00014
Ethy17μL.CAL	2	0.03	0.0625	17	17	4317	3272	0.0000047	0.00016
Ethy17μL.CAL	3	0.03	0.0625	18	17	4571	3429	0.0000052	0.00017
Ethy17μL.CAL	4	0.03	0.0625	19	17	4825	3556	0.0000057	0.00019
Ethy17μL.CAL	5	0.03	0.0625	20	17	5079	3727	0.0000061	0.00020
Ethy17μL.CAL	6	0.03	0.0625	21	17	5333	3910	0.0000064	0.00021
Ethy17μL.CAL	7	0.03	0.0625	22	17	5587	4016	0.0000071	0.00024
Ethy17μL.CAL	8	0.03	0.0625	23	17	5841	4247	0.0000072	0.00024
Ethy17μL.CAL	9	0.03	0.0625	24	17	6095	4504	0.0000072	0.00024
Ethy17μL.CAL	10	0.03	0.0625	25	17	6349	4755	0.0000072	0.00024

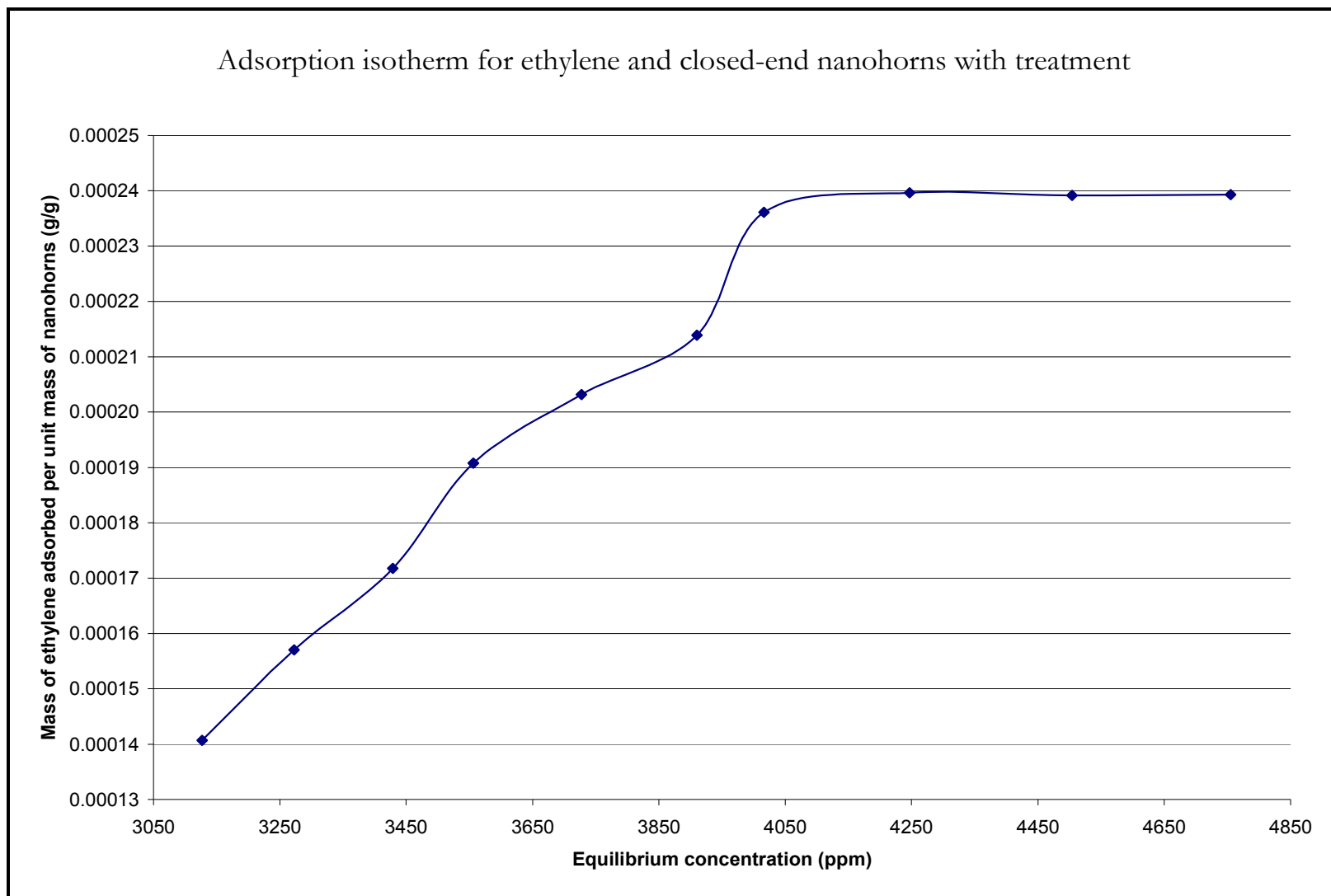


Fig. 4.2 Adsorption isotherm for ethylene and closed-end nanohorns with treatment

Table 4.3 Data for ethylene and open-end nanohorns with treatment

Data for ethylene and open-end nanohorns with treatment									
Calibration file	Run	Amount of nanohorns before adsorption		Volume of VOC injected into the vial (μL)	Volume of VOC injected into the GC (μL)	Initial conc. of VOC in the vial (ppm)	Final conc. from GC (ppm)	Mass of VOC adsorbed (g)	(Mass of VOC adsorbed)/ (Mass of nanohorns) (g/g)
		Weight (g)	Volume (mL)						
Ethy17μL.CAL	1	0.03	0.0625	17	17	4317	3687	0.0000028	0.000095
Ethy17μL.CAL	2	0.03	0.0625	18	17	4571	3931	0.0000029	0.000096
Ethy17μL.CAL	3	0.03	0.0625	19	17	4825	4169	0.0000030	0.000099
Ethy17μL.CAL	4	0.03	0.0625	20	17	5079	4398	0.0000031	0.000102
Ethy17μL.CAL	5	0.03	0.0625	21	17	5333	4611	0.0000033	0.000109
Ethy17μL.CAL	6	0.03	0.0625	22	17	5587	4812	0.0000035	0.000116
Ethy17μL.CAL	7	0.03	0.0625	23	17	5841	5055	0.0000035	0.000118
Ethy17μL.CAL	8	0.03	0.0625	24	17	6095	5309	0.0000035	0.000118
Ethy17μL.CAL	9	0.03	0.0625	25	17	6349	5563	0.0000035	0.000118

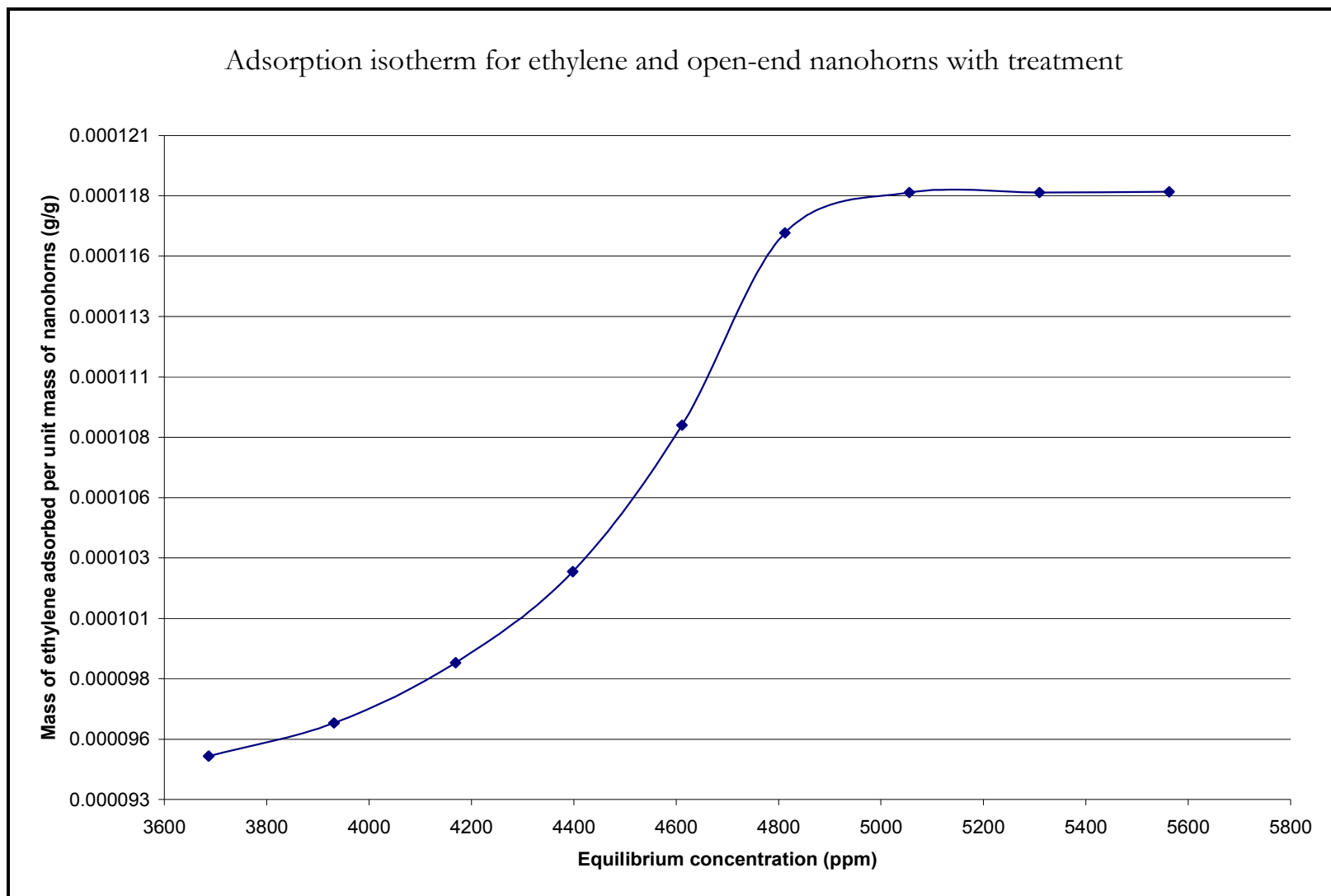


Fig. 4.3 Adsorption isotherm for ethylene and open-end nanohorns with treatment

Table 4.4 Data for ethylene and activated carbon pellets

Data for ethylene and activated carbon pellets									
Calibration file	Run	Amount of nanohorns before adsorption		Volume of VOC injected into the vial (μL)	Volume of VOC injected into the GC (μL)	Initial conc. of VOC in the vial (ppm)	Final conc. from GC (ppm)	Mass of VOC adsorbed (g)	(Mass of VOC adsorbed)/ (Mass of nanohorns) (g/g)
		Weight (g)	Volume (mL)						
Ethy17μL.CAL	1	0.03	0.0625	22	17	5587	2614	0.00001341	0.000447
Ethy17μL.CAL	2	0.03	0.0625	23	17	5841	2823	0.00001361	0.000454
Ethy17μL.CAL	3	0.03	0.0625	24	17	6095	3024	0.00001385	0.000462
Ethy17μL.CAL	4	0.03	0.0625	25	17	6349	3254	0.00001396	0.000465
Ethy17μL.CAL	5	0.03	0.0625	26	17	6603	3478	0.00001409	0.000470
Ethy17μL.CAL	6	0.03	0.0625	27	17	6857	3723	0.00001413	0.000471
Ethy17μL.CAL	7	0.03	0.0625	28	17	7111	3977	0.00001413	0.000471
Ethy17μL.CAL	8	0.03	0.0625	29	17	7365	4231	0.00001413	0.000471

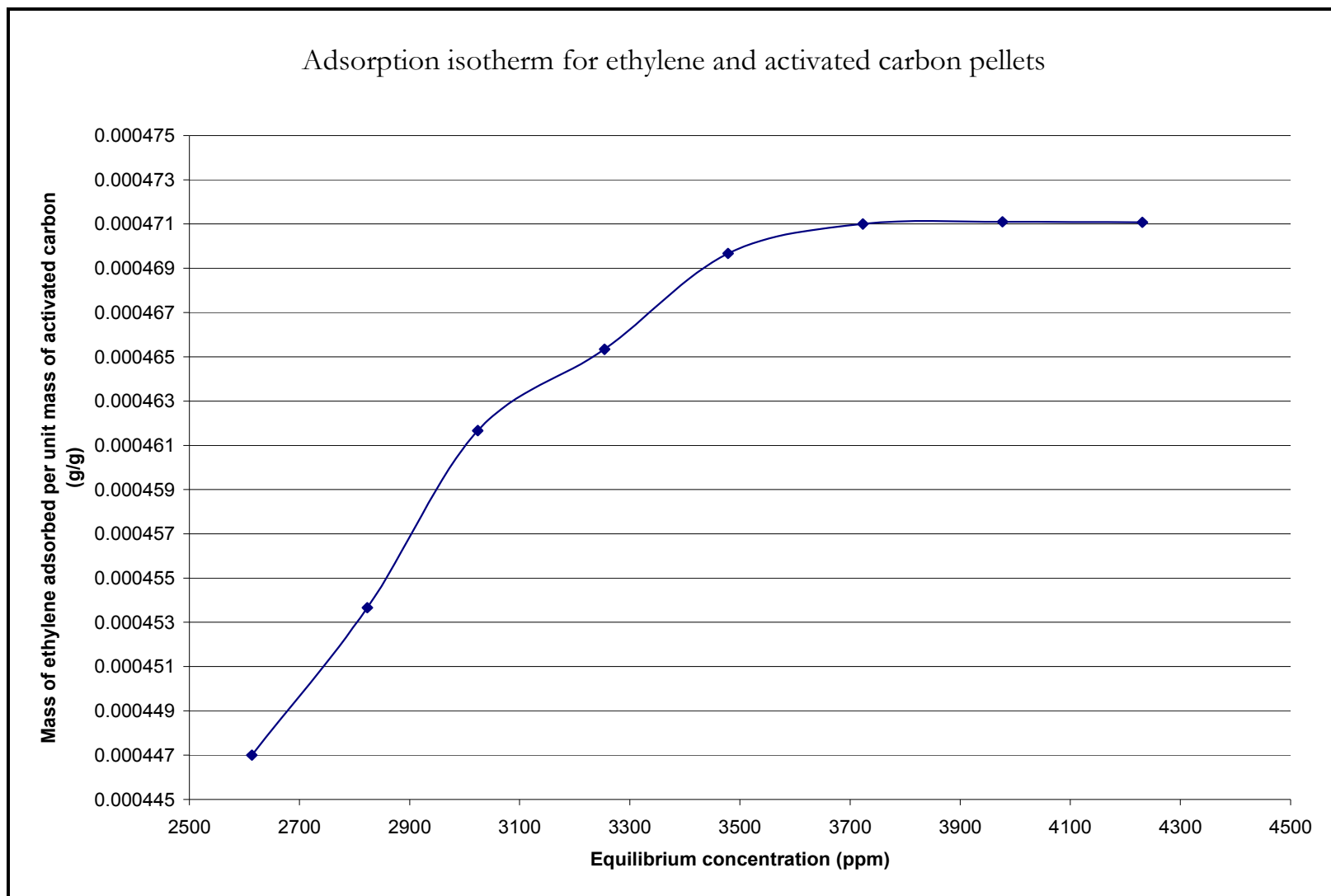


Fig. 4.4 Adsorption isotherm for ethylene and activated carbon pellets

Table 4.5 Data for propylene and closed-end nanohorns without treatment

Data for propylene and closed-end nanohorns without treatment									
Calibration file	Run	Amount of nanohorns before adsorption		Volume of VOC injected into the vial (μL)	Volume of VOC injected into the GC (μL)	Initial conc. into the vial (ppm)	Final conc. from GC (ppm)	Mass of VOC adsorbed (g)	(Mass of VOC adsorbed)/ (Mass of nanohorns) (g/g)
		Weight (g)	Volume (mL)						
Prop17μL.CAL	1	0.03	0.25	16	17	4265	2318	0.0000125	0.000418
Prop17μL.CAL	2	0.03	0.25	17	17	4532	2509	0.0000130	0.000434
Prop17μL.CAL	3	0.03	0.25	18	17	4799	2715	0.0000134	0.000447
Prop17μL.CAL	4	0.03	0.25	19	17	5065	2912	0.0000139	0.000462
Prop17μL.CAL	5	0.03	0.25	20	17	5332	3037	0.0000148	0.000493
Prop17μL.CAL	6	0.03	0.25	21	17	5598	3136	0.0000159	0.000529
Prop17μL.CAL	7	0.03	0.25	22	17	5865	3243	0.0000169	0.000563
Prop17μL.CAL	8	0.03	0.25	23	17	6131	3377	0.0000177	0.000591
Prop17μL.CAL	9	0.03	0.25	24	17	6398	3673	0.0000176	0.000585
Prop17μL.CAL	10	0.03	0.25	25	17	6665	3897	0.0000178	0.000594

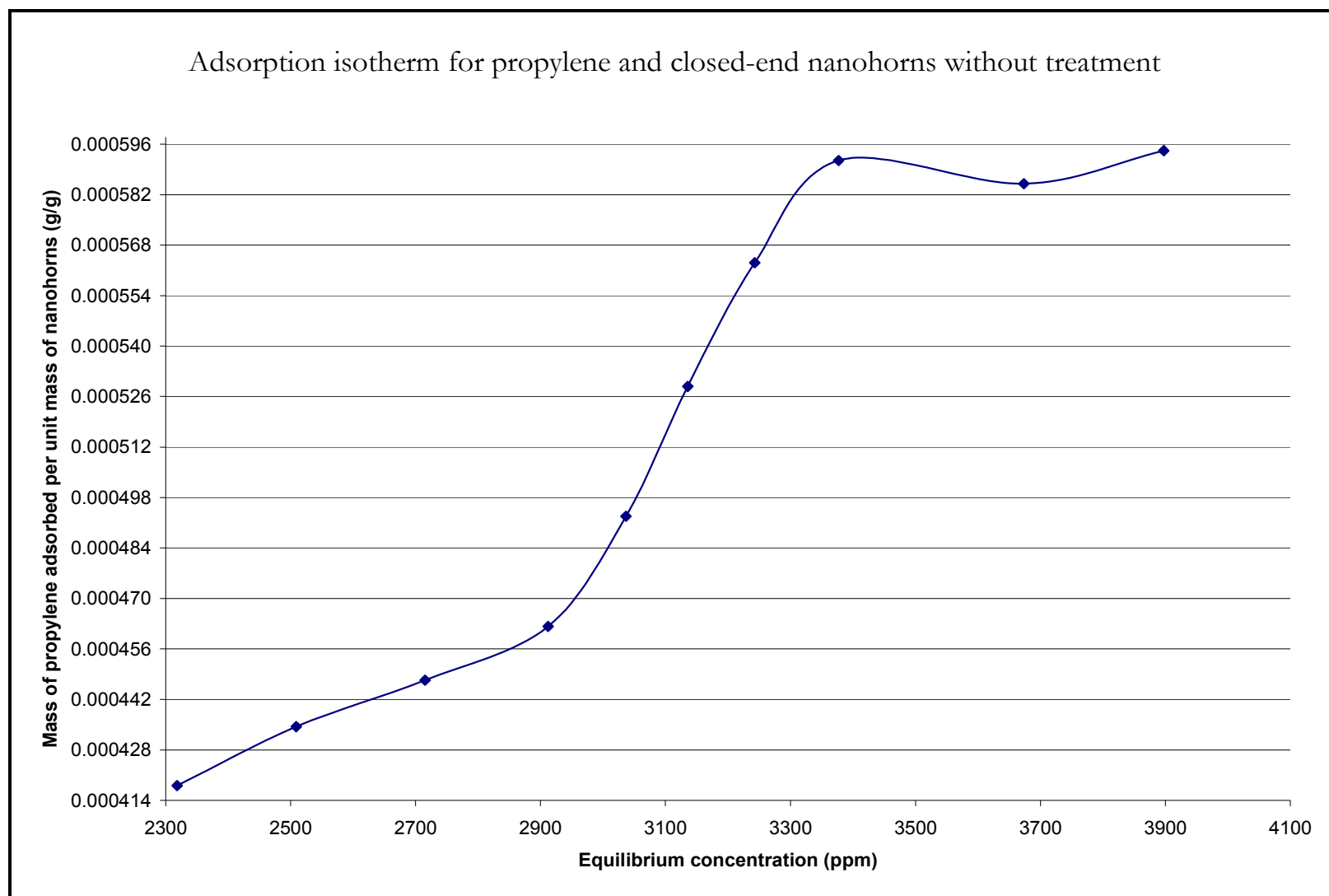


Fig. 4.5 Adsorption isotherm for propylene and closed-end nanohorns without treatment

Table 4.6 Data for propylene and closed-end nanohorns with treatment

Data for propylene and closed-end nanohorns with treatment									
Calibration file	Run	Amount of nanohorns before adsorption		Volume of VOC injected into the vial (μL)	Volume of VOC injected into the GC (μL)	Initial conc. into the vial (ppm)	Final conc. from GC (ppm)	Mass of VOC adsorbed (g)	(Mass of VOC adsorbed)/ (Mass of nanohorns) (g/g)
		Weight (g)	Volume (mL)						
Prop17μL.CAL	1	0.03	0.0625	14	17	3554	2759	0.0000054	0.000179
Prop17μL.CAL	2	0.03	0.0625	15	17	3808	2917	0.0000060	0.000201
Prop17μL.CAL	3	0.03	0.0625	16	17	4062	3093	0.0000066	0.000219
Prop17μL.CAL	4	0.03	0.0625	17	17	4316	3256	0.0000072	0.000239
Prop17μL.CAL	5	0.03	0.0625	18	17	4570	3462	0.0000075	0.000250
Prop17μL.CAL	6	0.03	0.0625	19	17	4824	3615	0.0000082	0.000273
Prop17μL.CAL	7	0.03	0.0625	20	17	5078	3788	0.0000087	0.000291
Prop17μL.CAL	8	0.03	0.0625	21	17	5332	3930	0.0000095	0.000316
Prop17μL.CAL	9	0.03	0.0625	22	17	5586	4100	0.0000100	0.000335
Prop17μL.CAL	10	0.03	0.0625	23	17	5840	4360	0.0000100	0.000334
Prop17μL.CAL	11	0.03	0.0625	24	17	6093	4597	0.0000101	0.000337

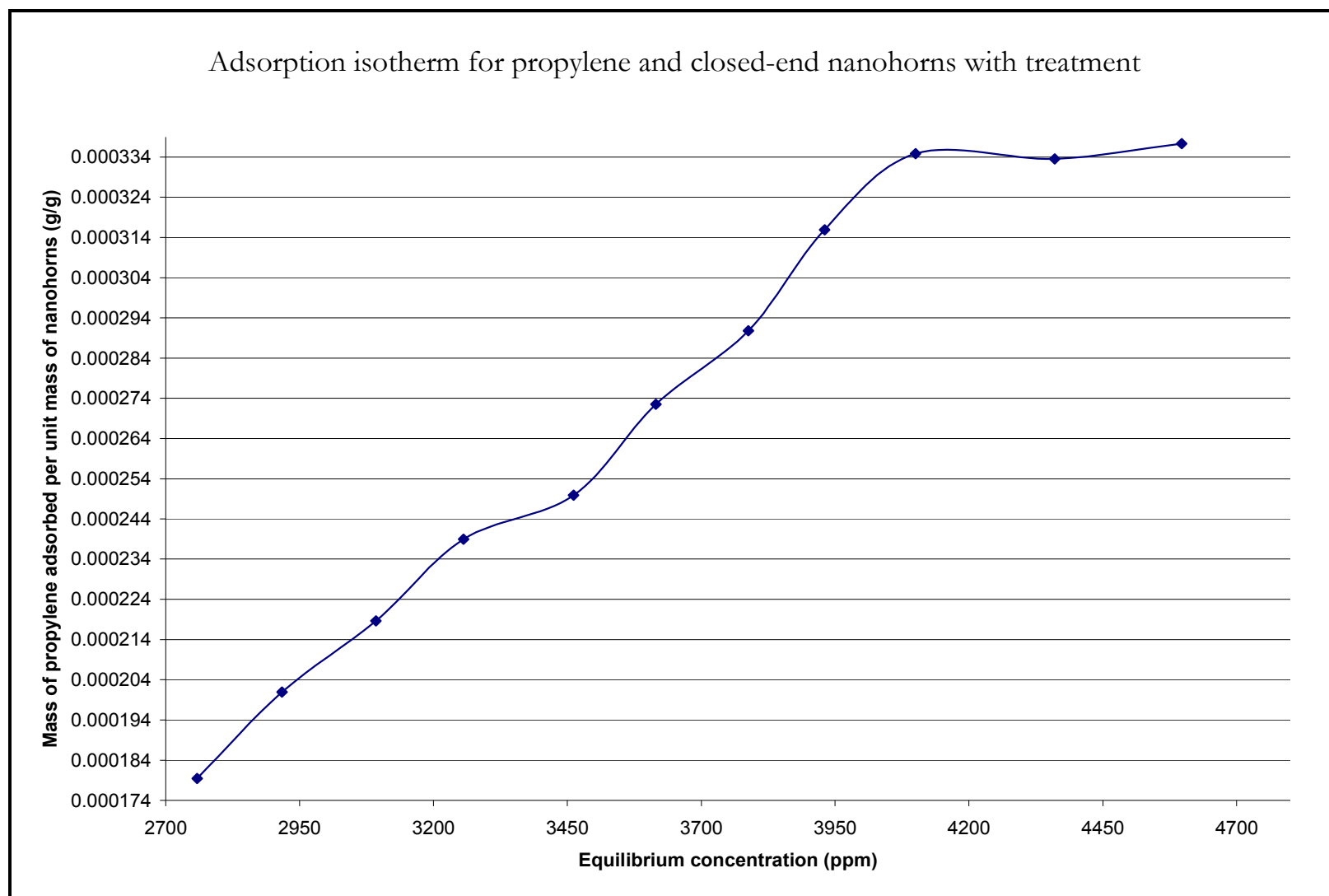


Fig. 4.6 Adsorption isotherm for propylene and closed-end nanohorns with treatment

Table 4.7 Data for propylene and open-end nanohorns with treatment

Data for propylene and open-end nanohorns with treatment									
Calibration file	Run	Amount of nanohorns before adsorption		Volume of VOC injected into the vial (μL)	Volume of VOC injected into the GC (μL)	Initial conc. into the vial (ppm)	Final conc. from GC (ppm)	Mass of VOC adsorbed (g)	(Mass of VOC adsorbed)/ (Mass of nanohorns) (g/g)
		Weight (g)	Volume (mL)						
Prop17μL.CAL	1	0.03	0.0625	15	17	3808	1731	0.0000140	0.000468
Prop17μL.CAL	2	0.03	0.0625	16	17	4062	1932	0.0000144	0.000480
Prop17μL.CAL	3	0.03	0.0625	17	17	4316	2119	0.0000149	0.000495
Prop17μL.CAL	4	0.03	0.0625	18	17	4570	2315	0.0000153	0.000508
Prop17μL.CAL	5	0.03	0.0625	19	17	4824	2522	0.0000156	0.000519
Prop17μL.CAL	6	0.03	0.0625	20	17	5078	2735	0.0000158	0.000528
Prop17μL.CAL	7	0.03	0.0625	21	17	5332	2938	0.0000162	0.000540
Prop17μL.CAL	8	0.03	0.0625	22	17	5586	3180	0.0000163	0.000542
Prop17μL.CAL	9	0.03	0.0625	23	17	5840	3435	0.0000163	0.000542
Prop17μL.CAL	10	0.03	0.0625	24	17	6093	3684	0.0000163	0.000543

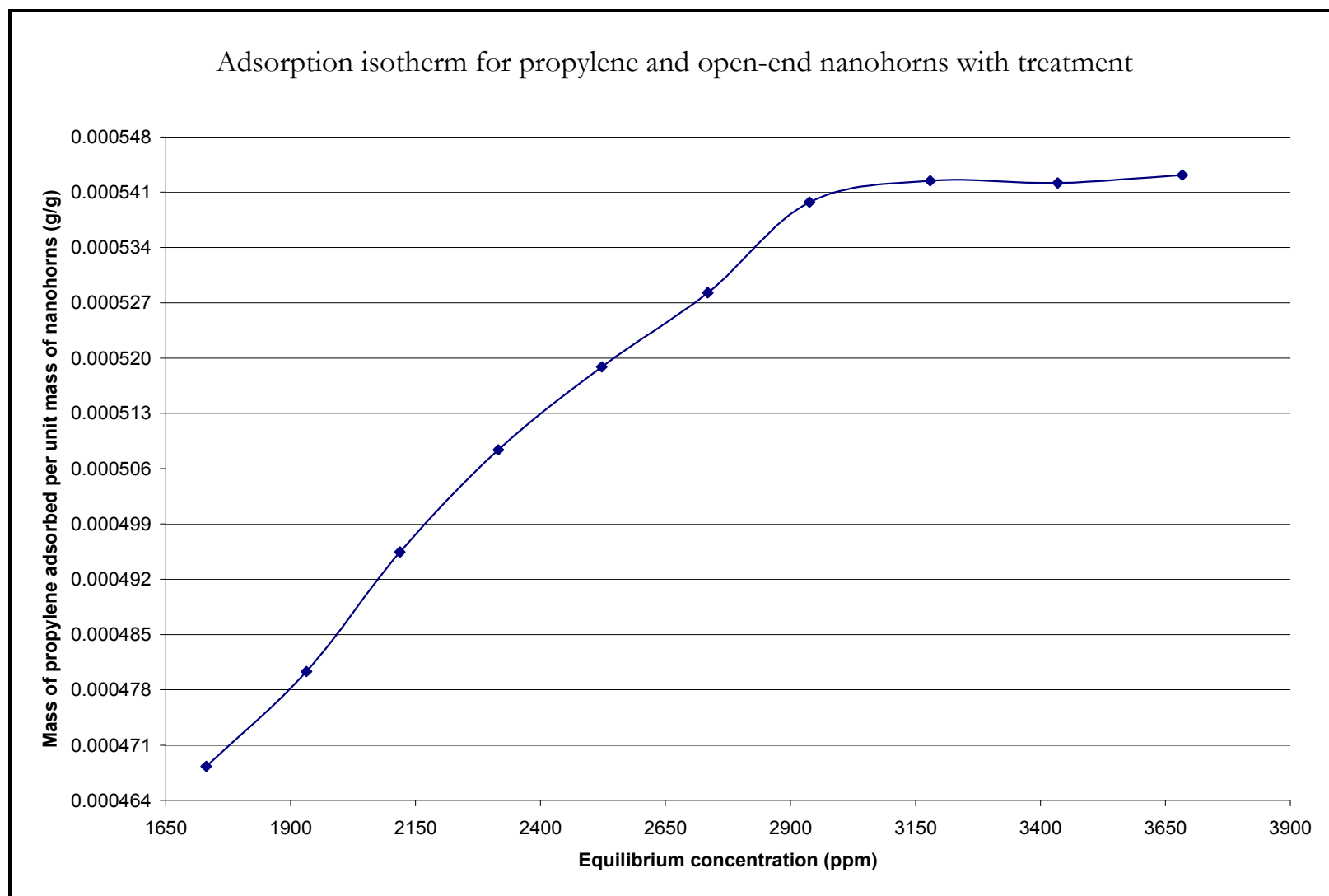


Fig. 4.7 Adsorption isotherm for propylene and open-end nanohorns with treatment

Table 4.8 Data for propylene and activated carbon pellets

Data for propylene and activated carbon pellets									
Calibration file	Run	Amount of nanohorns before adsorption		Volume of VOC injected into the vial (μL)	Volume of VOC injected into the GC (μL)	Initial conc. into the vial (ppm)	Final conc. from GC (ppm)	Mass of VOC adsorbed (g)	(Mass of VOC adsorbed)/ (Mass of nanohorns) (g/g)
		Weight (g)	Volume (mL)						
Prop17μL.CAL	1	0.03	0.0625	44	17	11171	1321	0.0000666	0.00222
Prop17μL.CAL	2	0.03	0.0625	45	17	11425	1344	0.0000682	0.00227
Prop17μL.CAL	3	0.03	0.0625	46	17	11679	1496	0.0000689	0.00230
Prop17μL.CAL	4	0.03	0.0625	47	17	11933	1614	0.0000698	0.00233
Prop17μL.CAL	5	0.03	0.0625	48	17	12187	1726	0.0000708	0.00236
Prop17μL.CAL	6	0.03	0.0625	49	17	12441	1806	0.0000719	0.00240
Prop17μL.CAL	7	0.03	0.0625	50	17	12695	1899	0.0000730	0.00243
Prop17μL.CAL	8	0.03	0.0625	51	17	12948	2156	0.0000730	0.00243
Prop17μL.CAL	9	0.03	0.0625	52	17	13202	2408	0.0000730	0.00243

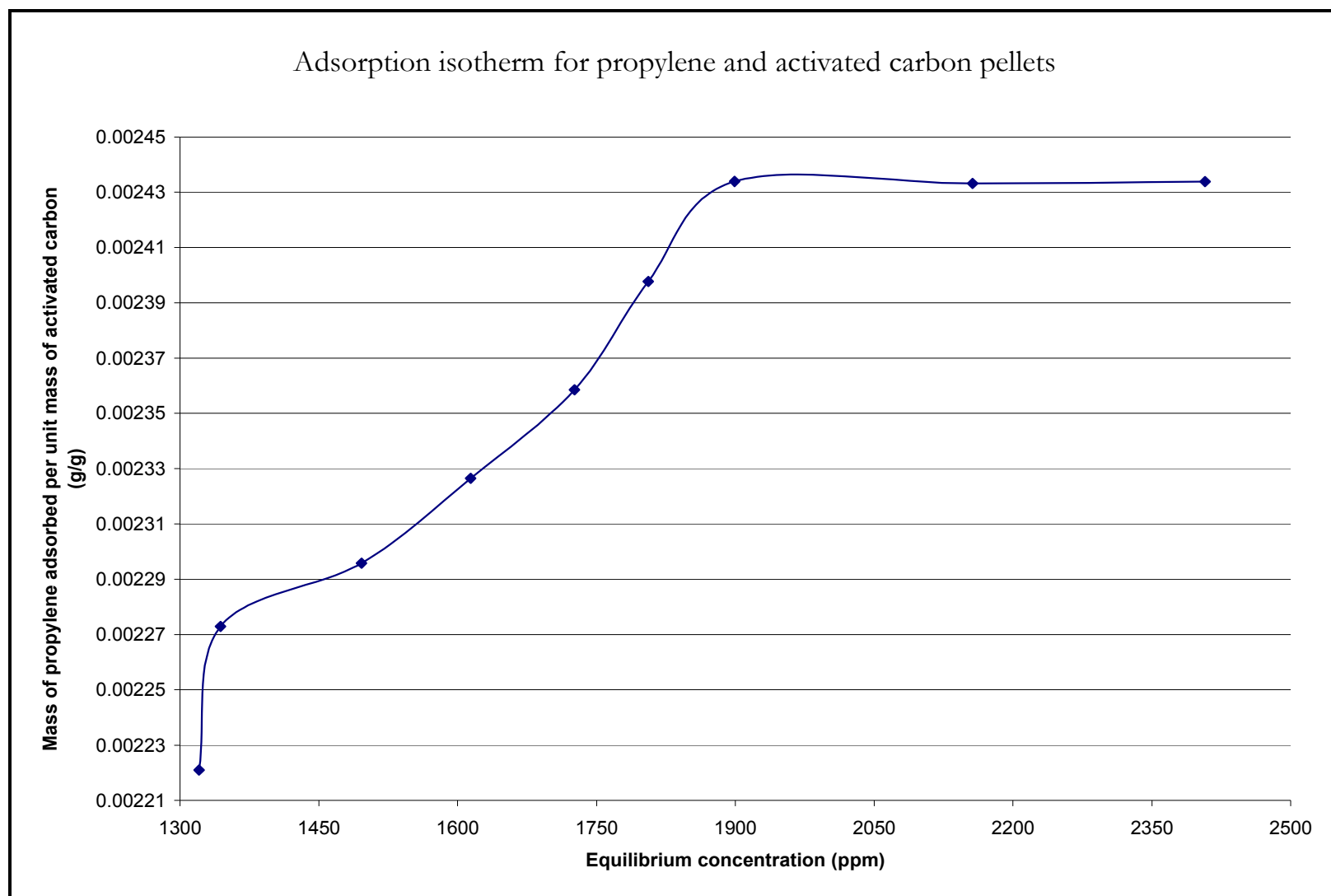


Fig. 4.8 Adsorption isotherm for propylene and activated carbon pellets

Table 4.9 Data for butane and closed-end nanohorns without treatment

Data for butane and closed-end nanohorns without treatment									
Calibration file	Run	Amount of nanohorns before adsorption		Volume of VOC injected	Volume of VOC injected	Initial conc. into the vial	Final conc. from GC	Mass of VOC adsorbed	(Mass of VOC adsorbed)/ (Mass of nanohorns)
		Weight (g)	Volume (mL)	into the vial (μL)	into the GC (μL)	(ppm)	(ppm)	(g)	(g/g)
But17μL.CAL	1	0.03	0.25	15	17	4000	1566	0.0000216	0.000721
But17μL.CAL	2	0.03	0.25	16	17	4266	1816	0.0000218	0.000727
But17μL.CAL	3	0.03	0.25	17	17	4533	2020	0.0000224	0.000745
But17μL.CAL	4	0.03	0.25	18	17	4800	2268	0.0000225	0.000751
But17μL.CAL	5	0.03	0.25	19	17	5066	2477	0.0000230	0.000768
But17μL.CAL	6	0.03	0.25	20	17	5333	2679	0.0000236	0.000787
But17μL.CAL	7	0.03	0.25	21	17	5599	2894	0.0000241	0.000802
But17μL.CAL	8	0.03	0.25	22	17	5866	3162	0.0000241	0.000802
But17μL.CAL	9	0.03	0.25	23	17	6133	3428	0.0000241	0.000802

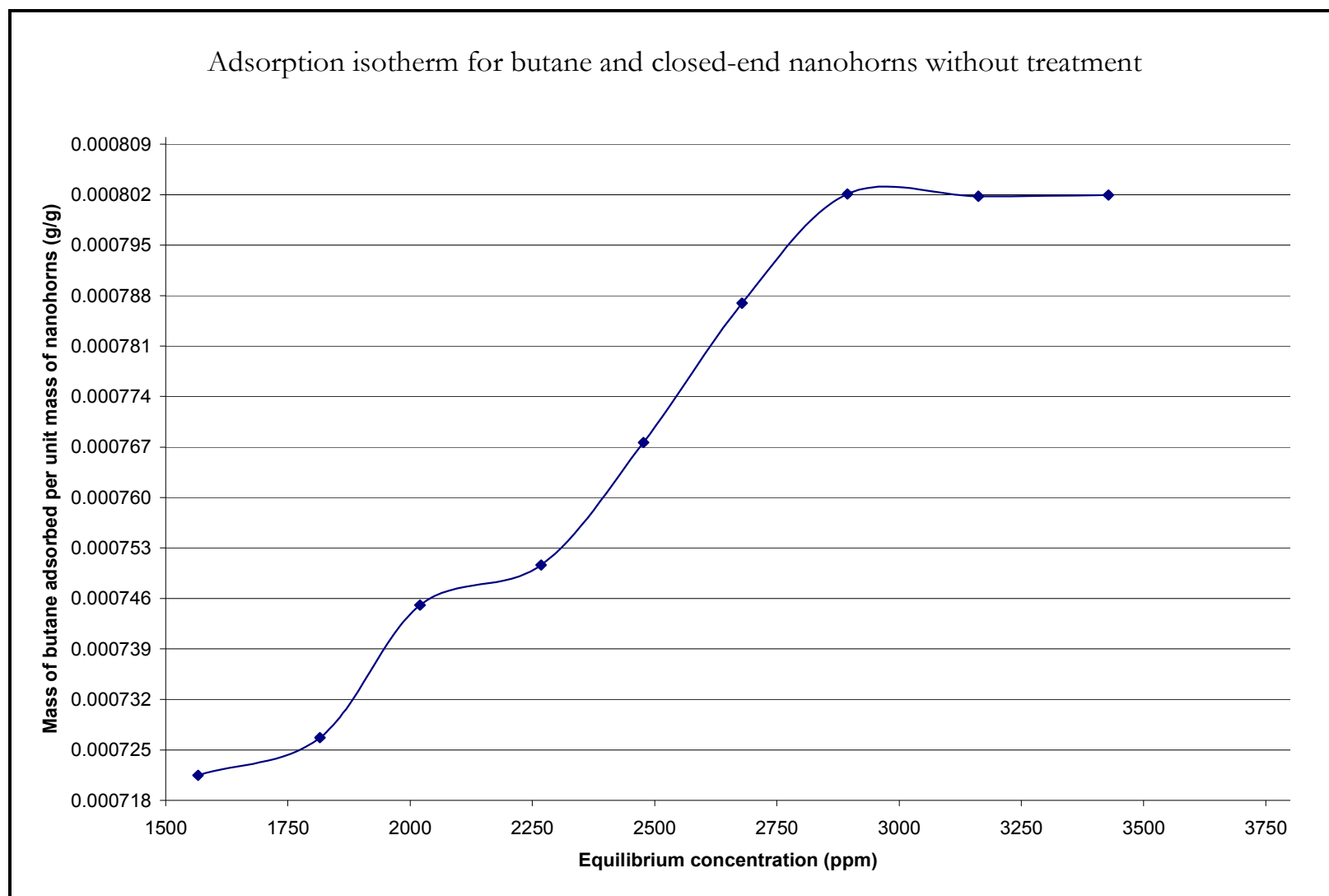


Fig. 4.9 Adsorption isotherm for butane and closed-end nanohorns without treatment

Table 4.10 Data for butane and closed-end nanohorns with treatment

Data for butane and closed-end nanohorns with treatment									
Calibration file	Run	Amount of nanohorns before adsorption		Volume of VOC injected	Volume of VOC injected	Initial conc. into the vial	Final conc. from GC	Mass of VOC adsorbed	(Mass of VOC adsorbed)/ (Mass of nanohorns)
		Weight (g)	Volume (mL)	into the vial (μL)	into the GC (μL)	(ppm)	(ppm)	(g)	(g/g)
But17μL.CAL	1	0.03	0.0625	18	17	4571	1270	0.0000308	0.001028
But17μL.CAL	2	0.03	0.0625	19	17	4825	1510	0.0000310	0.001032
But17μL.CAL	3	0.03	0.0625	20	17	5079	1731	0.0000313	0.001042
But17μL.CAL	4	0.03	0.0625	21	17	5333	1965	0.0000315	0.001049
But17μL.CAL	5	0.03	0.0625	22	17	5587	2203	0.0000316	0.001054
But17μL.CAL	6	0.03	0.0625	23	17	5841	2451	0.0000317	0.001055
But17μL.CAL	7	0.03	0.0625	24	17	6095	2705	0.0000317	0.001055
But17μL.CAL	8	0.03	0.0625	25	17	6349	2959	0.0000317	0.001055

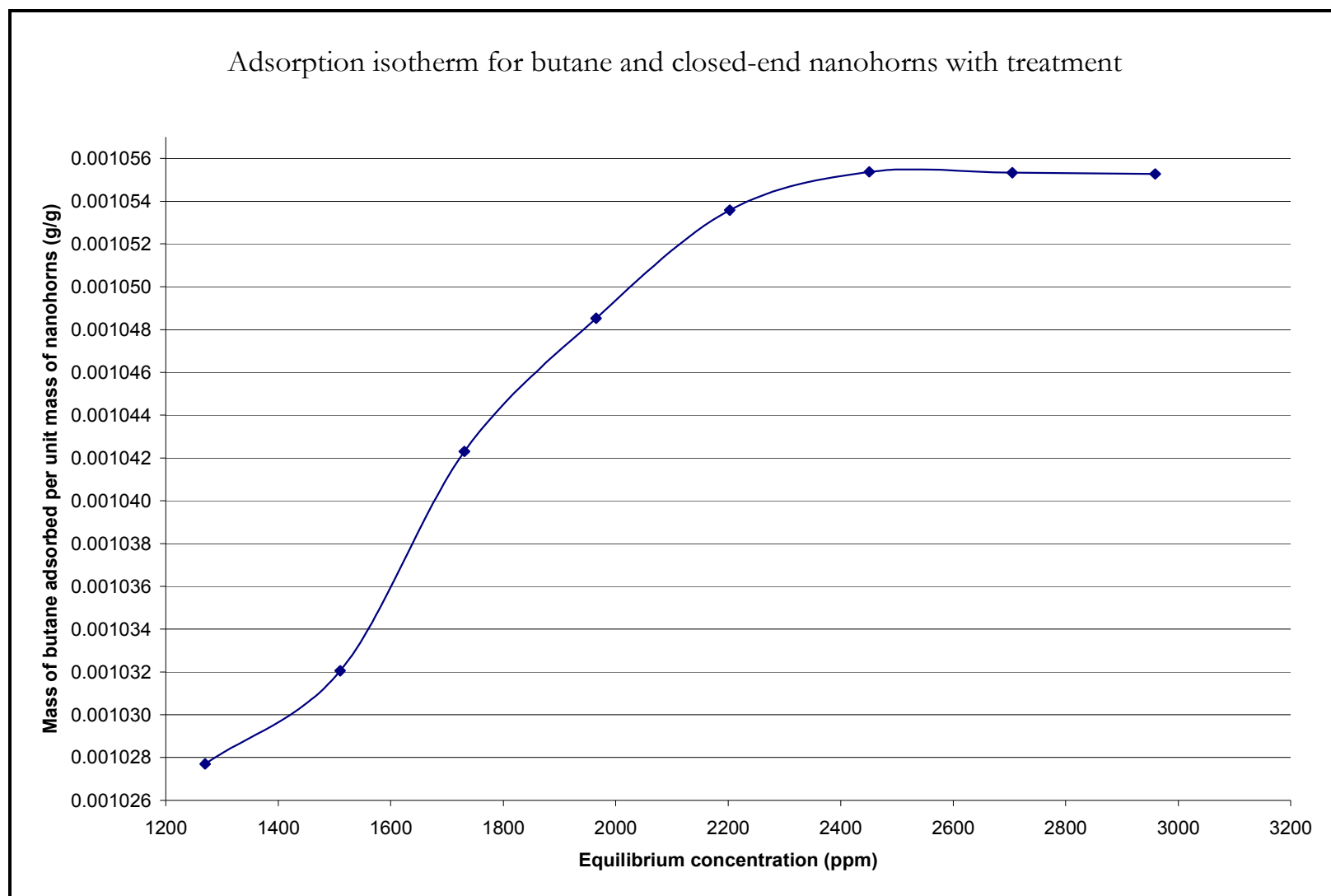


Fig. 4.10 Adsorption isotherm for butane and closed-end nanohorns with treatment

Table 4.11 Data for butane and open-end nanohorns with treatment

Data for butane and open-end nanohorns with treatment									
Calibration file	Run	Amount of nanohorns before adsorption		Volume of VOC injected into the vial (μL)	Volume of VOC injected into the GC (μL)	Initial conc. into the vial (ppm)	Final conc. from GC (ppm)	Mass of VOC adsorbed (g)	(Mass of VOC adsorbed)/ (Mass of nanohorns) (g/g)
		Weight (g)	Volume (mL)						
But17μL.CAL	1	0.03	0.0625	60	17	15237	1038	0.0001326	0.00442
But17μL.CAL	3	0.03	0.0625	62	17	15744	1099	0.0001368	0.00456
But17μL.CAL	4	0.03	0.0625	64	17	16252	1232	0.0001403	0.00468
But17μL.CAL	5	0.03	0.0625	65	17	16506	1287	0.0001422	0.00474
But17μL.CAL	6	0.03	0.0625	66	17	16760	1325	0.0001442	0.00481
But17μL.CAL	7	0.03	0.0625	68	17	17268	1482	0.0001475	0.00492
But17μL.CAL	8	0.03	0.0625	70	17	17776	1804	0.0001492	0.00497
But17μL.CAL	9	0.03	0.0625	72	17	18284	2275	0.0001495	0.00498
But17μL.CAL	10	0.03	0.0625	74	17	18792	2780	0.0001496	0.00499

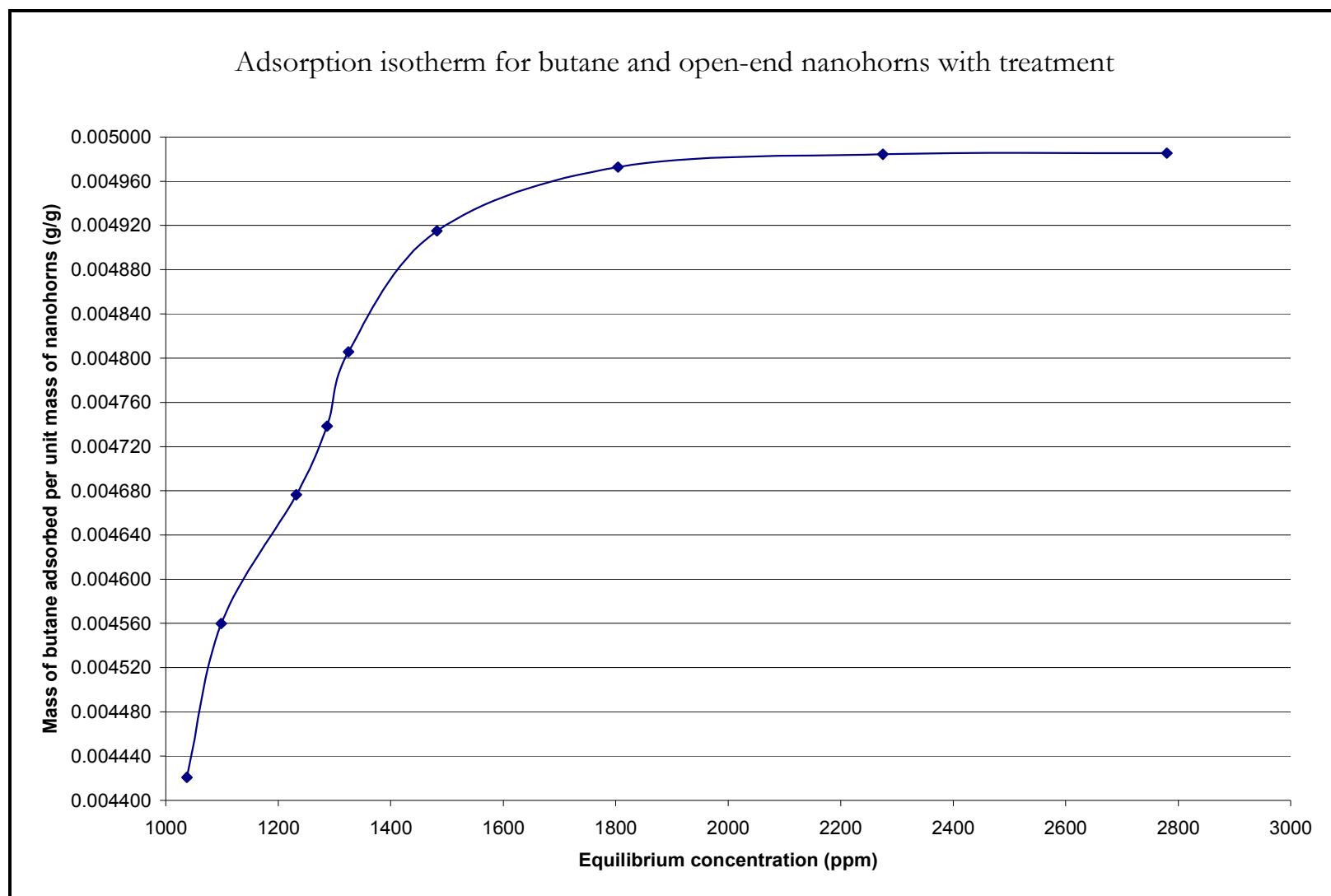


Fig. 4.11 Adsorption isotherm for butane and open-end nanohorns with treatment

Table 4.12 Data for butane and activated carbon pellets

Data for butane and activated carbon pellets									
Calibration file	Run	Amount of nanohorns before adsorption		Volume of VOC injected into the vial (μL)	Volume of VOC injected into the GC (μL)	Initial conc. into the vial (ppm)	Final conc. from GC (ppm)	Mass of VOC adsorbed (g)	(Mass of VOC adsorbed)/ (Mass of nanohorns) (g/g)
		Weight (g)	Volume (mL)						
But17μL.CAL	1	0.03	0.0625	300	17	76183	1453	0.000698	0.0233
But17μL.CAL	2	0.03	0.0625	320	17	81262	1705	0.000743	0.0248
But17μL.CAL	3	0.03	0.0625	330	17	83801	1884	0.000765	0.0255
But17μL.CAL	4	0.03	0.0625	340	17	86341	2073	0.000787	0.0262
But17μL.CAL	5	0.03	0.0625	350	17	88880	2518	0.000807	0.0269
But17μL.CAL	6	0.03	0.0625	360	17	91419	3044	0.000825	0.0275
But17μL.CAL	7	0.03	0.0625	370	17	93959	3787	0.000842	0.0281
But17μL.CAL	8	0.03	0.0625	380	17	96498	5757	0.000848	0.0283
But17μL.CAL	9	0.03	0.0625	390	17	99038	8295	0.000848	0.0283

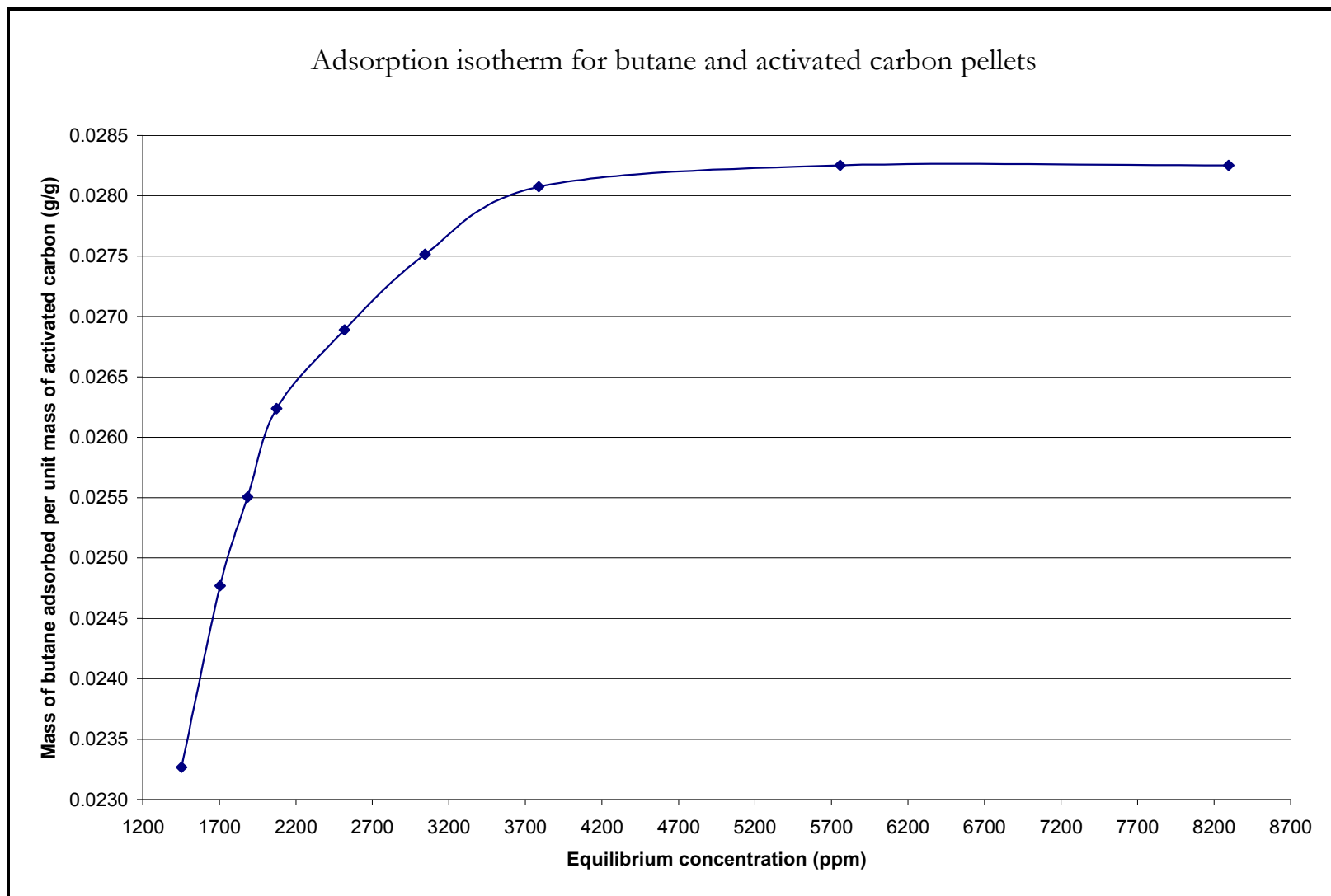


Fig. 4.12 Adsorption isotherm for butane and activated carbon pellets

Table 4.13 Data for hexane and closed-end nanohorns without treatment

Data for hexane and closed-end nanohorns without treatment									
Calibration file	Run	Amount of nanohorns before adsorption		Volume of VOC injected into the vial (μL)	Volume of VOC injected into the GC (μL)	Initial conc. in the vial (ppm)	Final conc. from GC (ppm)	Mass of VOC adsorbed (g)	(Mass of VOC adsorbed)/ (Mass of nanohorns) (g/g)
		Weight (g)	Volume (mL)						
Hex17μL.CAL	1	0.03	0.0625	13	17	3432	2268	0.0000154	0.00051
Hex17μL.CAL	2	0.03	0.0625	14	17	3696	2357	0.0000177	0.00059
Hex17μL.CAL	3	0.03	0.0625	15	17	3960	2471	0.0000196	0.00065
Hex17μL.CAL	4	0.03	0.0625	16	17	4224	2595	0.0000215	0.00072
Hex17μL.CAL	5	0.03	0.0625	17	17	4488	2675	0.0000239	0.00080
Hex17μL.CAL	6	0.03	0.0625	18	17	4752	2826	0.0000253	0.00084
Hex17μL.CAL	7	0.03	0.0625	19	17	5016	2961	0.0000271	0.00090
Hex17μL.CAL	8	0.03	0.0625	20	17	5280	3110	0.0000286	0.00095
Hex17μL.CAL	9	0.03	0.0625	21	17	5544	3236	0.0000304	0.00101
Hex17μL.CAL	10	0.03	0.0625	22	17	5808	3479	0.0000308	0.00103
Hex17μL.CAL	11	0.03	0.0625	23	17	6072	3736	0.0000308	0.00103

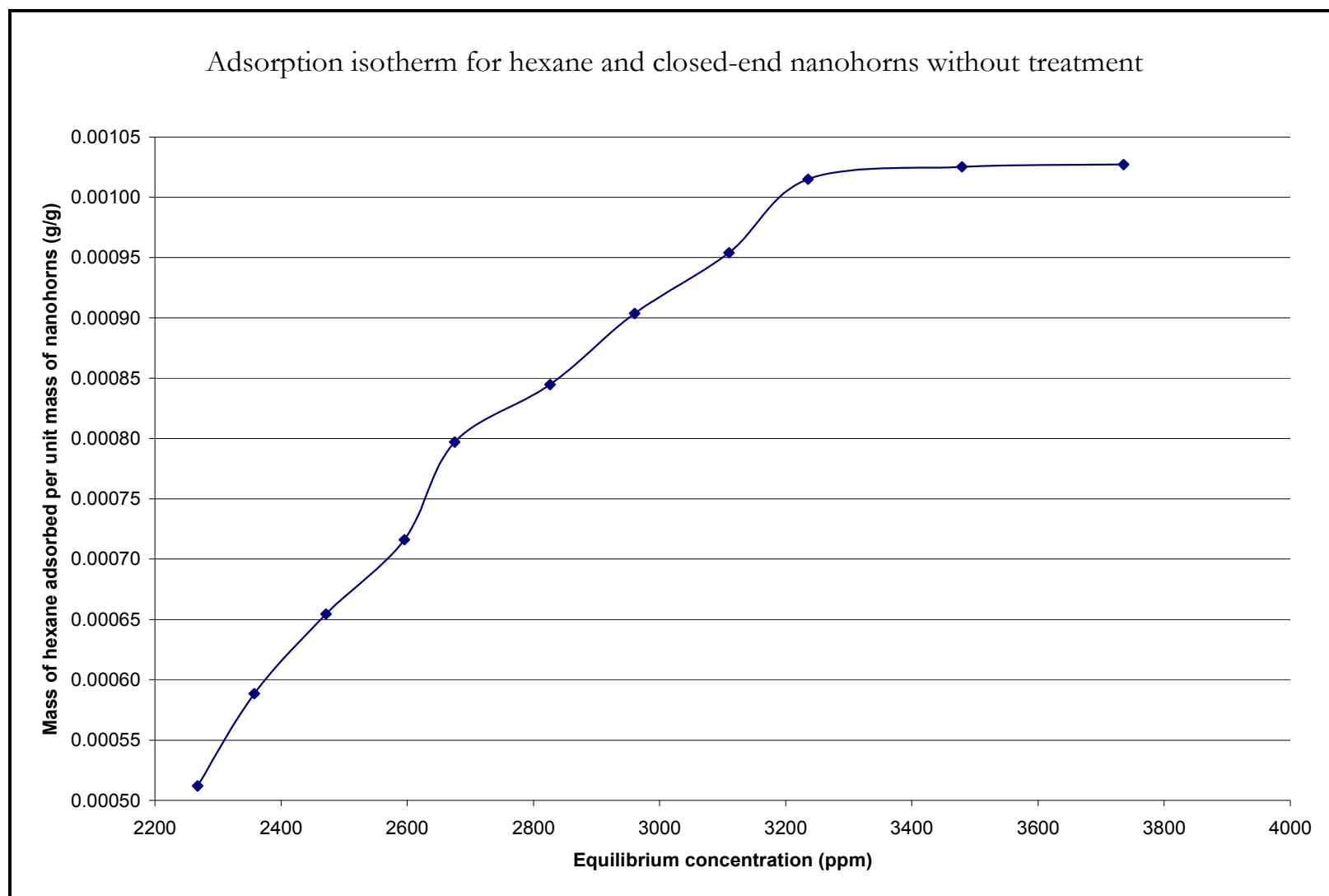


Fig. 4.13 Adsorption isotherm for hexane and closed-end nanohorns without treatment

Table 4.14 Data for hexane and closed-end nanohorns with treatment

Data for hexane and closed-end nanohorns with treatment									
Calibration file	Run	Amount of nanohorns before adsorption		Volume of VOC injected into the vial (μL)	Volume of VOC injected into the GC (μL)	Initial conc. in the vial (ppm)	Final conc. from GC (ppm)	Mass of VOC adsorbed (g)	(Mass of VOC adsorbed)/ (Mass of nanohorns) (g/g)
		Weight (g)	Volume (mL)						
Hex17μL.CAL	1	0.03	0.0625	16	17	4023	2344	0.0000233	0.000775
Hex17μL.CAL	2	0.03	0.0625	17	17	4274	2542	0.0000240	0.000800
Hex17μL.CAL	3	0.03	0.0625	18	17	4526	2748	0.0000246	0.000821
Hex17μL.CAL	4	0.03	0.0625	19	17	4777	2967	0.0000251	0.000836
Hex17μL.CAL	5	0.03	0.0625	20	17	5029	3206	0.0000252	0.000841
Hex17μL.CAL	6	0.03	0.0625	21	17	5280	3422	0.0000257	0.000858
Hex17μL.CAL	7	0.03	0.0625	22	17	5531	3659	0.0000259	0.000864
Hex17μL.CAL	8	0.03	0.0625	23	17	5783	3886	0.0000263	0.000876
Hex17μL.CAL	9	0.03	0.0625	24	17	6034	4141	0.0000262	0.000874
Hex17μL.CAL	10	0.03	0.0625	25	17	6286	4387	0.0000263	0.000876

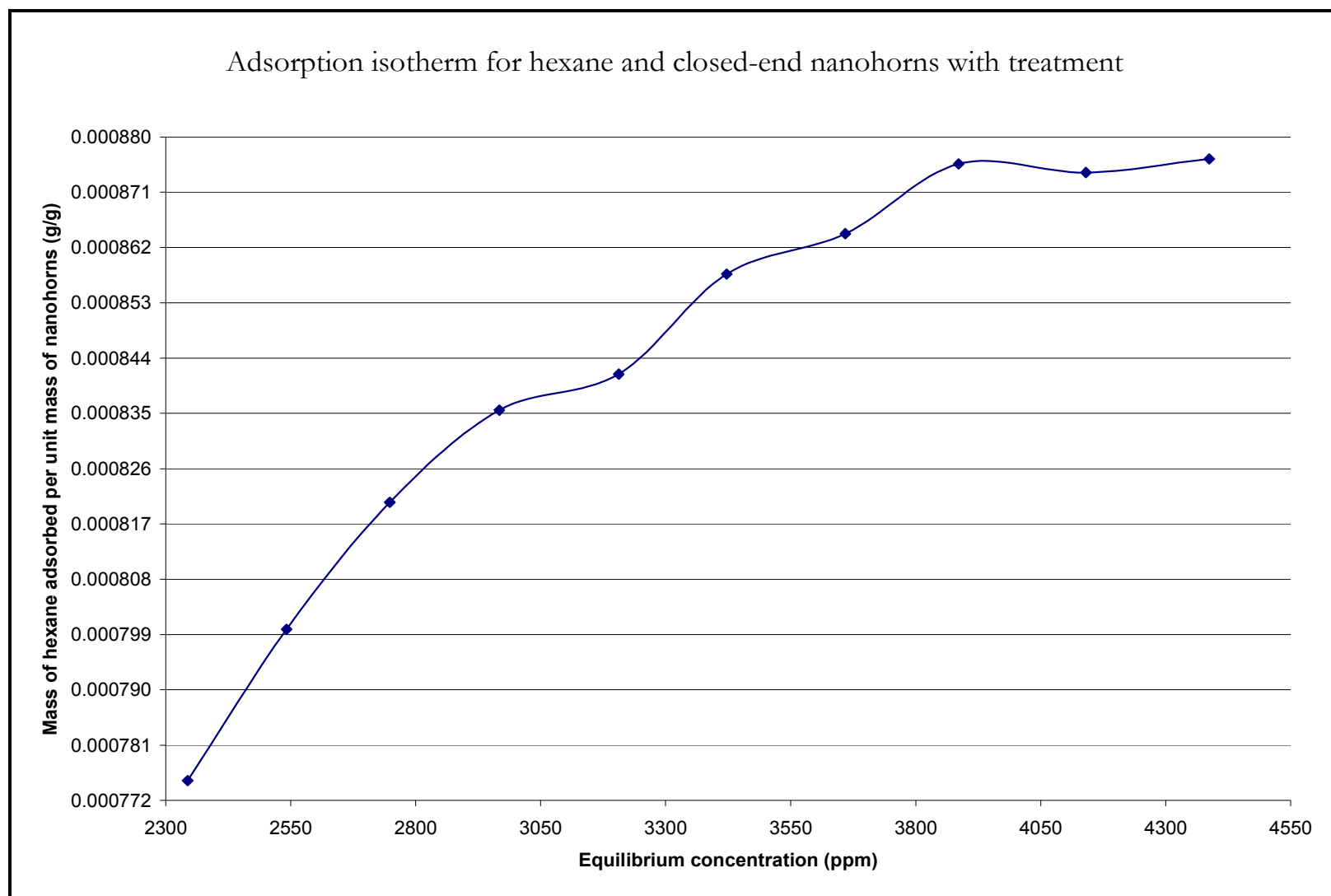


Fig. 4.14 Adsorption isotherm for hexane and closed-end nanohorns with treatment

Table 4.15 Data for hexane and open-end nanohorns with treatment

Data for hexane and open-end nanohorns with treatment									
Calibration file	Run	Amount of nanohorns before adsorption		Volume of VOC injected into the vial (μL)	Volume of VOC injected into the GC (μL)	Initial conc. in the vial (ppm)	Final conc. from GC (ppm)	Mass of VOC adsorbed (g)	(Mass of VOC adsorbed)/ (Mass of nanohorns) (g/g)
		Weight (g)	Volume (mL)						
Hex17μL.CAL	1	0.03	0.0625	17	17	4274	2199	0.0000287	0.00096
Hex17μL.CAL	2	0.03	0.0625	18	17	4526	2411	0.0000293	0.00098
Hex17μL.CAL	3	0.03	0.0625	19	17	4777	2620	0.0000299	0.00100
Hex17μL.CAL	4	0.03	0.0625	20	17	5029	2848	0.0000302	0.00101
Hex17μL.CAL	5	0.03	0.0625	21	17	5280	3065	0.0000307	0.00102
Hex17μL.CAL	6	0.03	0.0625	22	17	5531	3253	0.0000316	0.00105
Hex17μL.CAL	7	0.03	0.0625	23	17	5783	3498	0.0000316	0.00105
Hex17μL.CAL	8	0.03	0.0625	24	17	6034	3747	0.0000317	0.00106
Hex17μL.CAL	9	0.03	0.0625	25	17	6286	3996	0.0000317	0.00106

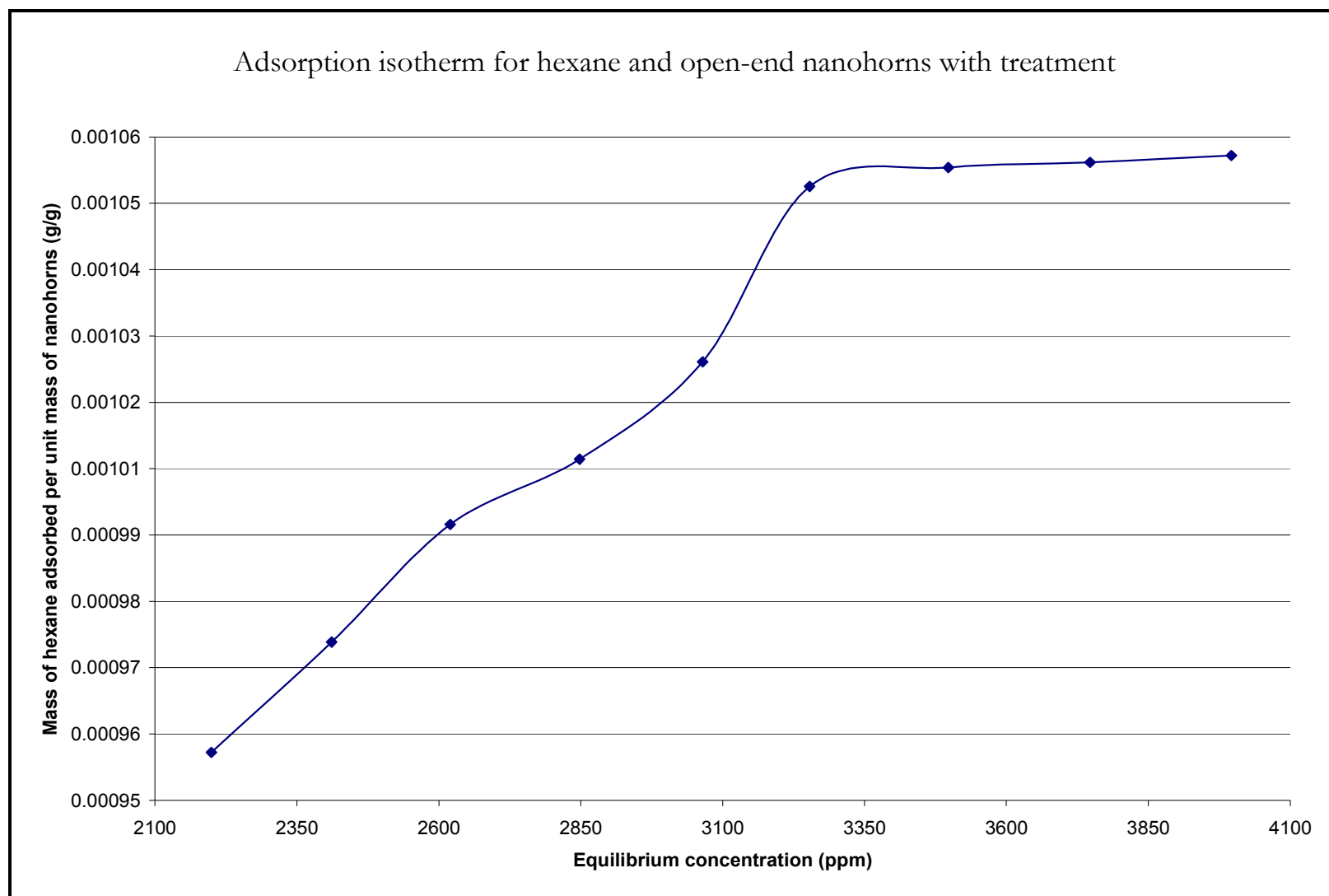


Fig. 4.15 Adsorption isotherm for hexane and open-end nanohorns with treatment

Table 4.16 Data for hexane and activated carbon pellets

Data for hexane and activated carbon pellets									
Calibration file	Run	Amount of nanohorns before adsorption		Volume of VOC injected into the vial (μL)	Volume of VOC injected into the GC (μL)	Initial conc. in the vial (ppm)	Final conc. from GC (ppm)	Mass of VOC adsorbed (g)	(Mass of VOC adsorbed)/ (Mass of nanohorns) (g/g)
		Weight (g)	Volume (mL)						
Hex17μL.CAL	1	0.03	0.0625	90	17	22629	1973	0.0002861	0.0095
Hex17μL.CAL	2	0.03	0.0625	100	17	25143	3413	0.0003010	0.0100
Hex17μL.CAL	3	0.03	0.0625	110	17	27657	5387	0.0003084	0.0103
Hex17μL.CAL	4	0.03	0.0625	120	17	30171	7327	0.0003164	0.0105
Hex17μL.CAL	5	0.03	0.0625	130	17	32686	9532	0.0003207	0.0107
Hex17μL.CAL	6	0.03	0.0625	140	17	35200	12015	0.0003211	0.0107
Hex17μL.CAL	7	0.03	0.0625	150	17	37714	14526	0.0003211	0.0107
Hex17μL.CAL	8	0.03	0.0625	160	17	40229	17040	0.0003211	0.0107

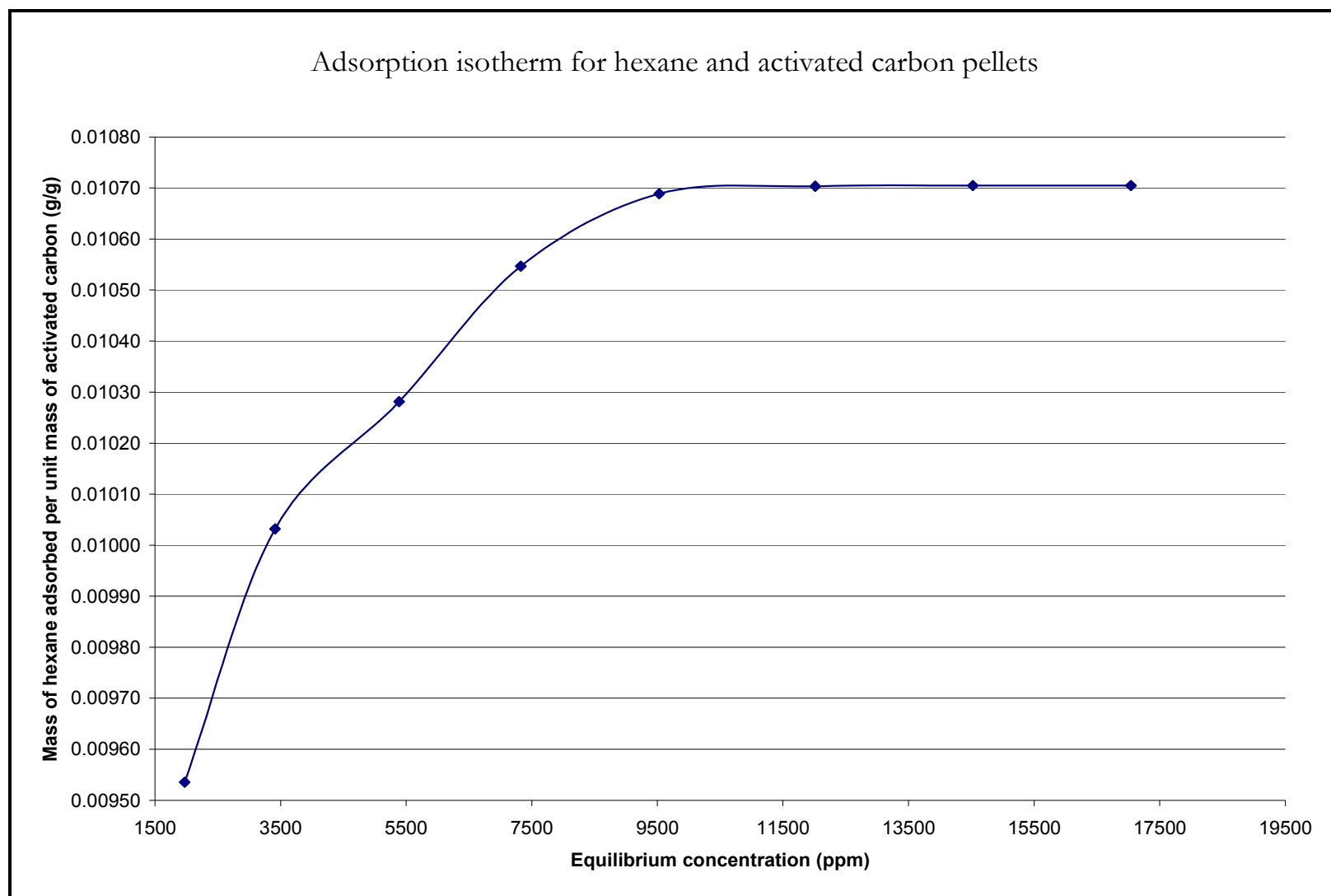


Fig. 4.16 Adsorption isotherm for hexane and activated carbon pellets

4.2 Summary of results

Following is the summary table showing the maximum adsorption capacity for each combination of adsorbent and volatile organic compound.

Table 4.17 Summary of maximum adsorption capacities of adsorbents (g/g)

Compound	Type of adsorbent			
	Closed-end NH without treatment	Closed-end NH with treatment	Open-end NH with treatment	Activated carbon pellets
Ethylene	0.00041	0.00024	0.00012	0.00047
Propylene	0.00059	0.00033	0.00054	0.0024
Butane	0.00080	0.0011	0.0050	0.028
Hexane	0.0010	0.00087	0.0011	0.0110

4.3 Discussion of results obtained

It can be seen from the above table that activated carbon has higher values of adsorption capacity for each of the VOCs as compared to the nanohorns. Hence it can be said to be a better adsorbent as compared to the nanohorns for the chosen volatile organic compounds. Agnihotri et. al. (2004) similarly found that the adsorption capacity of single-walled nanotubes for MEK and for toluene was lower than that of activated carbon.

Activated carbon possessing greater adsorption capacity than nanohorns does not prove that it has greater total surface area than nanohorns, although it likely has greater accessible surface area. Adsorption of a particular compound by a particular adsorbent depends on a number of things like volume and size of micropores, vapor pressure or volatility of the compound being adsorbed and surface area of adsorbent.

- Volume and size of micropores – Micropores are spaces formed inside and between adjacent nanohorns. It is in these spaces that adsorbate molecules get lodged during adsorption. Therefore the size of adsorbate molecule and the size of micropores play a key role in effective adsorption. If the molecule is too big to fit into the micropore, the adsorption capacity is reduced. The treatment performed on the adsorbent alters the arrangement of the micropores, thereby altering their size and volume.

Considering ethylene and propylene from the table above, it is seen that the closed-end nanohorns without any treatment have greater adsorption capacity than the closed-end nanohorns with treatment. This may be explained

by the fact that the treatment employed, being densification, densifies the nanohorns, resulting in smaller pore sizes between the nanohorns. The size of the pores may be so small that the molecules of ethylene and propylene are too big to be lodged into the pores. Activated carbon, likely to be having greater pore size and thus greater accessible surface area, shows greater adsorption as compared to closed-end nanohorns with treatment and without treatment. Adsorption capacity of closed-end nanohorns without treatment for ethylene and propylene being greater than that of open-end nanohorns with treatment may also be explained by the reduction in pore size of open-end nanohorns due to the densification treatment. Since ethylene and propylene adsorb in greater amounts to closed-end nanohorns without treatment as compared to open-end nanohorns with treatment, it can be inferred that ethylene and propylene preferentially adsorb to sites between nanohorns (access to which would be reduced via treatment), compared with sites within the nanohorns (that could only be accessed when ends were open). On the other hand, butane and hexane preferentially adsorb in nanohorns, since the open-end nanohorns have a greater adsorption capacity for alkanes, with or without treatment.

These preferences for adsorbing between nanohorns for alkenes and within nanohorns for alkanes are in both cases more pronounced for the smaller molecule (ethylene and butane). Adsorption capacities for closed-end nanohorns without treatment and open-end nanohorns with treatment are comparable for propylene and hexane.

- Vapor pressure/volatility and molecular weight of the VOC – Mass of VOC adsorbed is directly proportional to molecular weight and inversely proportional to vapor pressure/volatility. In terms of molecular weight, the compounds rank as, hexane > butane > propylene > ethylene. In terms of volatility, the compounds rank as, hexane < butane < propylene < ethylene. This means that we would anticipate, based on molecular weight and volatility alone, adsorption capacity to follow the order, hexane > butane > propylene > ethylene. This order is indeed followed except that the capacities of butane and hexane are reversed for all adsorbents except closed-end nanohorns without treatment. This may be due to the fact that hexane is a larger molecule than butane and thus has more limited access to smaller pores. All four types of adsorbents show greater adsorption for alkanes, which might be due to the fact that alkanes have low vapor pressure as compared to alkenes and therefore are more effectively bound to the adsorbents.

Ethylene is known to possess the highest vapor pressure among the chosen VOCs. High vapor pressure implies that the compound is more inclined towards staying in the vapor phase than any other phase. To bind this kind of compound, very high binding energies may be required. Nanohorns are known to have greater binding energy than activated carbon, which would explain why in the case of ethylene the nanohorns adsorption capacity (closed-end without treatment) is almost as high as for activated carbon. The high binding energy of

the nanohorns offsets their likely lower accessible surface area, compared with activated carbon.

The open-end nanohorns do not have caps at the tube ends which, if present, might have provided extra binding energy to bind the ethylene molecule. This might explain the lower value of adsorption capacity of open-end nanohorns for ethylene as compared to the closed-end nanohorns.

- Surface area of adsorbent – Considering only the nanohorns, propylene is better adsorbed by open-end nanohorns with treatment as compared to closed-end nanohorns with treatment. This may be because open-end nanohorns possess greater accessible surface area than closed-end nanohorns. For butane and hexane, the open-end nanohorns with treatment seem to have greater adsorption capacity than the other two types of nanohorns. This also may be explained by the greater accessible surface area within the nanohorns possessed by open-end nanohorns as compared to the closed-end nanohorns, especially when both the open and closed-end nanohorns have been treated, which reduces the accessible surface area between the nanohorns. The adsorption capacity of closed-end nanohorns with treatment for hexane is less than that of the other two types of nanohorns. This might be due to the fact that the treatment reduces the pore size, and also the open-end nanohorns possess greater accessible surface area than the closed-end ones. The greater surface area and higher binding energy of open-end nanohorns with treatment might explain the finding that open-end nanohorns

with treatment have greater adsorption capacity than closed-end nanohorns with and without treatment.

Activated carbon has a surface area that ranges from 600 – 1400 m²/g (Cooper and Alley, 2002). Bekyarova et. al (2003) found that a maximum nanohorn surface area of 1100 m²/g could be created using heat treatment at 693K in oxygen. In contrast, the nanohorns in this research were only heated to a temperature of 344K (160°F) in air; thus, their surface area was considerably less than 1100 m²/g. If the activated carbon used in this research had a surface area near the high end of the activated carbon range (600 – 1400 m²/g), it would help explain the greater adsorption capacity of activated carbon. The activated carbon may not only have had greater surface area but may also have had a larger fraction of the surface area accessible to the VOCs tested.

4.4 Common trends observed from the results

- All four types of adsorbents show greater adsorption of alkanes than alkenes.
- Activated carbon has greater adsorption capacity than nanohorns for each of the VOCs, likely due to greater accessible and total surface area.
- For alkenes, the second best type of adsorbent is the closed-end nanohorns without treatment, indicating that the alkenes preferentially adsorb onto sites between the nanohorns.
- For alkanes, the second best type of adsorbent is the open-end nanohorns with treatment, indicating that the alkanes preferentially adsorb onto sites within the nanohorns.

- For ethylene, the adsorption capacity of closed-end nanohorns without treatment is very close to that of activated carbon. This might be because the higher binding energy of the nanohorns is more important for ethylene, which is very volatile, and helps offset the lower accessible surface area of the nanohorns.
- For propylene, the adsorption capacity of closed-end nanohorns without treatment is very close to the adsorption capacity of open-end nanohorns with treatment.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

After reviewing the results and the discussion that followed, the following conclusions can be drawn:

1. Alkanes are better adsorbed in case of all four types of adsorbents than alkenes.
2. Activated carbon possesses higher adsorption capacity than the nanohorns in the case of both alkanes and alkenes, likely due to greater total and accessible surface area. However, the adsorption capacities of activated carbon and closed-end nanohorns without treatment are comparable in the case of ethylene, the most volatile of the compounds tested. Higher energy binding sites of the nanohorns are more important for ethylene since it is very volatile.
3. After activated carbon, open-end nanohorns with treatment seem to be the best adsorbent for alkanes, and closed-end nanohorns without treatment for alkenes. This indicates that alkanes preferentially adsorb within the nanohorns, while alkenes adsorb between nanohorns.

This research has showcased quite a few aspects on which the adsorption phenomenon, in the case of nanohorns and VOCs, depends. As seen from the results and discussion, molecular weight and volatility play a very significant role in the

successful and effective adsorption of volatile organic compounds. Surface area of the adsorbent, although being a prominent aspect, is some times overshadowed by factors such as these. Treatments such as densification increase the surface area of adsorbents but may not assure effective adsorption since the increased surface area may not be accessible by the adsorbate molecules as needed. The physical properties of the compounds to be adsorbed hold great significance in the adsorption process. In many cases, they govern the adsorption process as much as the more basic parameters like surface area and pore sizes and volumes.

5.2 Recommendations

A lot of work can still be done on this topic to help produce a better and efficient application for the industry. The following are a few recommendations for further research.

1. To better explain the results obtained, a finding of the actual accessible surface area of all four adsorbents can be carried out by determining the N₂ adsorption isotherm for each of the adsorbent.
2. Since open-end nanohorns with treatment are seen to have the next greater adsorption capacity after activated carbon for these compounds, it would be interesting to find out the adsorption capacities of open-end nanohorns without any treatment for the same group of compounds.
3. Other classes of compounds such as alcohols and mixture gases such as methyl chloride can be tested to check which adsorbent has greater adsorption capacity for them.

4. One of the potential advantages of nanohorns in terms of adsorption is their hydrophobicity; at high humidities, nanohorn adsorption sites may not fill with water vapor molecules as quickly as those of activated carbon. Adsorption of ethylene onto closed-end nanohorns without treatment should be tested versus activated carbon at higher relative humidities.
5. A nanohorn sample should be heated to 693K, following the method of Bekyarova et. al. (2003) to increase “windows” to allow access to interior adsorption sites. This sample should then be tested for ethylene adsorption.

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BIOGRAPHICAL INFORMATION

Born in the city of Vadodara, India on July 18th, 1980, Miss. Namrata B. Deshmukh's earliest memories are of her father, who has always been a constant source of inspiration in her life with his words of wisdom and encouragement. Upon completion of high school, her inclination for science led her to pursue a Bachelor's degree in the field of Construction Engineering from Shah and Anchor Kutchhi Engineering College, affiliated with the University of Mumbai. Namrata's undergraduate degree only served to stroke the burning desire to pursue higher education from a reputable University which resulted in her decision to come to the University of Texas at Arlington for a Master's degree in Environmental Engineering.

She started her degree program at UTA in the spring of 2003. During the first year of her degree program she developed a growing interest in, and a strong understanding of, the subject of Air Quality. Dr. Melanie Sattler's offer to work on a research topic under her supervision was both a decisive moment and an incredible opportunity in Namrata's professional career. Her research broadly dealt with Adsorption but took a step further by trying to exploit the potential of Nanoadsorbents. What made it more challenging to her was that not much work had been done in this particular area.

During this period she was also given the opportunity to work as a Graduate Teaching Assistant for Dr. Sattler for two semesters and as a Graduate Research Assistant for one semester towards the completion of her degree program. She was also

initiated into Chi Epsilon – The National Civil Engineering Honors Society and was presented with a valuable opportunity to present her research paper to the 230th National Conference of the American Chemical Society in the field of Environmental Nanotechnology.