Reduction of Anthropogenic Volatile and Semi-Volatile Organic Compounds by Nanomaterials and Photolysis

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Abstract

Anthropogenic volatile organic compounds (VOCs) and semi-volatile organic (SVOCs) compounds are atmospheric pollutants contributing to the photochemical formation of tropospheric ozone. We combined adsorption and UV photolysis techniques for the removal and degradation of selected VOCs and SVOCs. For adsorption, we synthesized magnetite nanoparticles, a naturally occurring material, to avoid unknown detrimental impacts associated with new materials, as was the case with chlorofluorcarbons. The removal efficiency with magnetite was up to 98% for aromatics, and 30% for light alkanes. Magnetite nanoparticles were regenerated, characterized (TEM, XRD, BET), and reused with no decrease in reported removal efficiencies. Photolysis alone removed up to 30% of aromatics, and less than 20% of light alkanes. The combination of adsorption, and photolysis did not improve the removal efficiency. Adsorption was attributed to London dispersion interactions for light alkanes, and to acid-base properties for aromatics. Reductions by photolysis were attributed to reactive radicals.

Abrégé

Les composés volatiles et semi-volatiles organiques de sources anthropogéniques sont des polluants atmosphériques participant à la formation d’ozone troposphérique. Nous avons associé l’adsorption et la photolyse par rayons ultraviolets, pour enlever et détruire ces composés. Nous avons synthétisé des nanoparticules de magnétite, un matériel abondant dans la nature, afin d’éviter la création d’un autre problème de pollution comme il est parvenu avec l’utilisation des fluorocarburé chlorés. L’efficacité d’enlèvement par adsorption atteint un maximum de 98% pour les composés aromatiques et un maximum de 30% pour les alcanes légers. Les particules ont été regénérées, caractérisées (MET, XRD, BET), et réutilisées; aucune baisse en efficacité d’enlèvement n’est notée. Les expériences de photolyse atteignent une réduction maximale de 30% pour les composés aromatiques et de 20% pour les alcanes légers. Sous nos conditions expérimentales, aucune amélioration n’est notée par l’association des deux processus (adsorption et
photolyse). La réduction par adsorption est attribuée aux forces d’attraction London pour les alcanes et aux propriétés acides et basiques pour les aromatiques. La réduction par photolyse s’explique par la formation de radicaux réactifs.
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Chapter 1 - Introduction

1.1 Background

Changes in the chemical composition of the atmosphere due to anthropogenic activity have resulted in climate change and air pollution. Air pollution is defined as ‘a situation in which substances that result from anthropogenic activities are present at concentrations sufficiently high above their normal ambient levels to produce a measurable effect on humans, animals, vegetation, or materials’ [1]. Climate change is due to a change in the energy balance of the Earth [1], which can be positive or negative resulting in warming or cooling, respectively. The emissions of chlorofluorocarbons (CFCs), for example, have caused the increased depletion of the stratospheric Antarctic ozone. CFCs’ photolysis products react with other atmospheric components, as CH$_4$ and NO$_2$, producing in the presence of polar stratospheric clouds HCl and ClONO$_2$ that act as reservoirs of Cl$_2$ and ClOOCl and are released during the polar springs (October), catalyzing the reduction of O$_3$ in presence of light [1]. Another example is the increase of green house gases (GHG) as CO$_2$, O$_3$, CH$_4$ and N$_2$O that have been recognized for their role in warming [2] the Earth by 0.5 °C in the last century [1]. The most important GHG, CO$_2$, has increased by 35% in the atmosphere [2] since pre-industrial times; it absorbs reflected infrared radiation and re-emits it into the atmosphere [1]. Although models approximating climate change are associated with large uncertainties, energy change due to CO$_2$, CH$_4$ and N$_2$O was estimated to be +2.3 W. m$^{-2}$ [2] causing a warming effect. Ozone, resulting from reactions of nitrogen oxides and hydrocarbons in presence of light was estimated to cause a change of +0.35 W. m$^{-2}$ [2].

Aerosols are another class of compounds that have anthropogenic sources, and predominantly induce negative energy change by scattering (direct effect), or absorbing incoming solar radiation. They may also influence clouds microphysical properties by acting as cloud condensation nuclei, influencing the reflectivity, and abundance of cloud droplets also causing a negative change [2]. Volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) are organic liquids or solids with vapour pressures greater than 0.0007 atm, and maximum
boiling points of 260 °C [3]. They are emitted in the atmosphere as vapours [1]. Hydrocarbons are one type of VOCs that are emitted in the atmosphere; they are recognized for their role as photochemical oxidant precursor in the troposphere [1], and contribute to air pollution.

Volatile organic compounds are currently regulated by the Canadian Environmental Protection Agency (CEPA) for their role as precursors to ozone and PM$_{10}$ [4]. Figure 1 shows tropospheric reactions of VOCs; the example of propane oxidation, and its role in the formation of tropospheric ozone, and other photochemical smog components via the HOx/Ox cycle in presence of NOx and light is illustrated.

![Figure 1: The example of propane oxidation and role in tropospheric ozone production](image)

For hydrocarbons, VOCs include compounds with less than 12 carbons [3]. Other types of volatile organic compounds include alcohols, aldehydes, ketones, and esters [3].
VOCs’ global emission sources are represented in Figure 2, where 25% of total anthropogenic sources are due to the transport sector, which are mainly composed of hydrocarbons resulting from fuel incomplete combustion, or vaporization [1].

![Global Anthropogenic Non Methane Volatile Organic Carbon Estimated Emissions](image)

**Figure 2: Global anthropogenic non methane volatile organic carbon estimated emission. Based on data in [1].**

Current techniques aimed at lowering volatile organic compounds and semi volatile organic compounds emissions in the atmosphere can achieve high removal efficiencies, but are often challenged in one or many ways including:

- Energy requirements
- Expenses for large scale applications
- Selectivity limited towards certain compounds
- Generation of toxic by-products such as NO\(_x\) (NO\(_2\) and NO) and dioxin
- Non reusability
- Waste generation and need for disposal

Therefore, the need persists to develop means to remove these pollutants in an efficient, environmental friendly, and economical manner.
Adsorption processes for recovery of VOCs and SVOCs present many benefits:

- Facile use
- Reusability (ease of regeneration)
- No waste generation
- Natural material (magnetite nanoparticles) (no additional pollution burden)
- Recovery of pollutants
- Adaptability and tunability to cover a wider spectrum of compounds by using multiple surfaces with various properties (different materials and size range)

Adsorption processes have been combined with nanotechnology. Nanomaterials have the principal advantage of high surface areas, which present more active sites for the recovery of pollutants.

1.2 Objectives

The objective of the research was to develop a process to remove volatile organic compounds and semi volatile organic compounds with removal efficiencies comparable to current methods while addressing the challenges of cost, low energy requirements, and waste (non-) generation. We revisited the use of adsorption processes with naturally occurring nanomaterials such as magnetite, which has been previously used in water remediation [5]. We synthesized, characterized, and conducted a series of adsorption experiments using magnetite nanoparticles to test their ability to remove VOCs and SVOCs. We determined their efficiency in lowering concentrations of selected compounds at room temperature, and at 353 K. We also tested their lifetime for commercial application by determining the VOC removal efficiencies for regenerated particles. We combined the adsorption process with UV irradiation to test the improvement in the removal efficiency. We have also investigated their combined effect with activated carbon for reducing aromatics’ concentrations by coating the latter with magnetite nanoparticles.
Chapter 2 Literature Review

The first section of this chapter presents current remediation techniques, and their major limitations. The principles of adsorption are addressed in the second section. A description of common adsorbents follows in section three. In the last section, adsorbent regeneration techniques are discussed.

2.1 Current Remediation Techniques for VOCs and SVOCs in Air

Remediation methods typically involve the degradation of pollutants, their recovery, or a combination of both. Figure 3 represents the major techniques that are discussed in the following section.

Figure 3: VOCs Remediation Techniques
2.1.1 Destruction Techniques

- Thermal oxidation
- Catalytic oxidation
- Plasma
- UV and photocatalytic oxidation

2.1.1.1 Thermal Oxidation

VOCs are destroyed by oxidation at high temperature according to equation 1

\[ \text{C}_x\text{H}_y + (x + y/4)\text{O}_2 \rightarrow x \text{CO}_2 + y/2 \text{H}_2\text{O} \quad \text{[3]} \quad \text{(Equation (1))} \]

In practice, many intermediate steps and by-products are formed before complete mineralization.

The applied incineration temperature is higher than the pollutant’s auto-ignition temperature, the point where the rate of combustion in presence of \( \text{O}_2 \) is higher than that of heat loss of the compound [6]. In the range of 863-923 K, most organics are combusted; incinerators are designed to achieve more than 98% destruction when operated at 1143 K, but are generally operated around 1253-1473 K for complete destruction [6].

Destruction efficiency of 95% was reported for benzene and toluene at 1003-1233 K [7]. Thermal oxidation can be applied to concentrations ranging from 100 ppm to 2000 ppm [8] [7] but more energy is required to treat concentration below 1000 ppm, which raises the cost of operation [6]. In fact, smaller scale operation units, designed to treat low laden streams, are more expensive [6].

The major drawback, however, remains the high operating temperatures (even with furnaces designed to work at lower temperatures 1033-1083 K), which produce polluting by-products such as nitrogen oxides, \( \text{NO}_x \), dioxin, and furans [7].

\[ \text{N}_2 + \text{O}_2 \leftrightarrow 2 \text{NO} \quad \text{[3]} \quad \text{(Equation (2))} \]
$$\text{NO} + 0.5 \text{O}_2 \leftrightarrow \text{NO}_2 \ (\text{Equation (3)})$$

2.1.1.2 Catalytic oxidation

Heterogeneous catalytic combustion follows the same principle as thermal oxidation, but is designed to work at lower temperatures by using a catalyst to treat flue gas, as well as exhaust from vehicles. The polluted gas is heated to 593-753 K, and contacted with the hot catalyst, generally platinum or palladium at 813-948 K [9]. Heterogeneous catalysts consist of a solid carrier (porous, high surface area material, often inorganic, such as alumina, silica, titania, and zeolite) onto which catalytic materials as noble metals or metal oxides are deposited [10]. Noble metals supported on alumina are often used [9, 11] [12] for selectivity towards CO₂, and H₂O products [11], and for mechanical strength [9]. 75% of industrial applications for VOC removal employ supported noble metals [12].

\[
\begin{align*}
\text{CH}_4 \text{ (g)} & \rightarrow \text{CH}_3 \text{ (ads)} + \text{H} \text{ (ads)} \ (\text{Equation (4)}) \\
\text{CH}_3 \text{ (g)} & \rightarrow \text{CH}_2 \text{ (ads)} + \text{H} \text{ (ads)} \ (\text{Equation (5)}) \\
\text{CH}_2 \text{ (ads)} + \text{O} \text{ (ads)} & \rightarrow \text{CO} \text{ (ads)} + \text{H}_2\text{O} \ (\text{Equation (6)}) \\
\text{CO} \text{ (non-diss ad)} + \text{O} \text{ (ads)} & \rightarrow \text{CO}_2 \ (\text{Equation (7)}) 
\end{align*}
\]

The process is developed to provide up to 95 % VOC conversion at 723 K [9]. Up to 95% of toluene can be converted [7, 8]. The concentration range of polluted gas to be treated lies in the range 100-2000 ppm [8], and can be as low as 1 ppm [9]. As with thermal oxidation, operation cost increases for concentrations below 100 ppm [9] due to higher fuel usage [14].

By-products as dioxin or furan are not reported, but NOx is still generated [7]. In vehicle application, however, common three way catalytic converters (TWC) reduce NOx into N₂.

The most critical limitation to catalytic oxidation is the catalyst’s sensitivity to process conditions. High operating temperatures can cause phase transformation.
presence of poisoning, or blocking species, such as particulate matter [9] in the polluted streams, or side reactions may cause deactivation of the catalyst. Although it may be possible to regenerate a poisoned catalyst by heat treatment (desorption) or washing [10], deactivated catalysts require replacement and proper disposal [8]. Figure 4 summarizes the factors that reduce catalytic activity.

**Figure 4: Catalyst deactivation in heterogeneous catalytic oxidation**

An additional limitation pertinent to vehicle applications is cold start emissions, where exhaust must reach a light-off temperature, typically above 473 K [15] for the catalytic reactions to start [10]. In turn, during the cold start, the first two minutes of operation, 60-80% of hydrocarbons are emitted [10]. Attempts to trap hydrocarbons during the cold cycle with adsorbents, as zeolites, and release them at high temperatures (> 523K) were not successful as the temperature was too high to retain the hydrocarbons [10].

Catalytic oxidation has been combined with additional oxidizing agents providing removal efficiencies of 80-90% [16]. For example, injection of H₂O₂ or O₃ for the mineralization of VOCs has been tested [16]. The pollutants would be mineralized by OH
radicals resulting from the redox-electron transfer between bound \( \text{H}_2\text{O}_2 \) or \( \text{O}_3 \), and the catalyst surface (in this study FeOOH).

### 2.1.1.3 Plasma Techniques

VOCs can be decomposed by oxidation utilizing thermal and non thermal plasma (NTP). In thermal plasma, energy is supplied to heat all components including pollutant, background gas, ions, and free radicals to temperatures around 11 000 K [17]. The high electric potentials between a cathode and an anode heat, and ionize a gas as in a plasma torch. At those high temperatures, NOx can be produced in plasma flue gas [18].

In non thermal plasma, energetic electrons are produced [19] by acceleration in an electric field [17]. Non thermal plasma can be produced by electrical discharge or by electron beam irradiation [7]; the former is commonly used for environmental aims [17]. The high energy electrons (1-10eV) can then ionize the background gas by collisions resulting in reactive species mainly \( \cdot \text{O} \), \( \cdot \text{OH} \), and \( \cdot \text{H} \). These may react with other molecules, and produce secondary reactive species such as \( \text{O}_3 \), or collide with pollutant species dissociating them and/or producing other free radicals [17]. Depending on the number of alkyl groups formed, a series of reactions may take place, and lead to various by-products. Alkenes and alkynes result from H atom abstraction, while aldehydes result from an O atom addition, and dissociate to CO and \( \text{CO}_2 \) [20]. Some of the principal reactions for degradation of butane are depicted in Figure 5.

Concentration in the range 1-10 000 ppm can be treated [21]. However, efficiencies of NTP at ambient temperature are not generally competitive with other processes; specificity toward \( \text{CO}_2 \) remains low, and intermediates, as well as \( \text{O}_3 \) are produced [21].

A hybrid system combining plasma and a catalyst pushes the oxidation towards \( \text{CO}_2 \) production improving mineralization efficiencies, and reduces \( \text{O}_3 \) by-product [21]. For example, the mineralization of toluene in a plasma reactor combined with a catalyst
as activated carbon or zeolite did not generate O₃ or NOx; aerosols, however, were produced [7]. Other improved mineralization efficiencies with various catalysts are given in a recent review by Van Durme [21].

![Diagram of high voltage electrode and dielectric barrier](image)

**Figure 5: Non thermal plasma by electric discharge for the oxidation of n-butane**

**2.1.1.4 UV oxidation and photocatalytic oxidation.**

In this technique, high energy radiations such as vacuum ultra violet (VUV) and ultra violet – visible (UV-VIS) are used to photolyze VOCs into CO₂ and H₂O. Under irradiation with 254 nm and 185 nm, 10 % of toluene were converted in N₂ streams in absence of oxidative species (N₂ does not absorb above 125 nm) [22]. Direct photolysis of VOC with irradiation under 254 nm has not shown to be significant for alcohols, and other hydrocarbons [23].
Photocatalytic oxidation typically involves a photocatalyst capable of promoting redox reactions by absorbing radiation; TiO$_2$ is commonly used, and will be discussed in more details in upcoming sections. Photocatalysts absorb energy resulting in the excitation of an electron to the conducting band leaving a positive hole in the valence band. VOC mineralization can result from hole attack (h$^+$) [23] or from reactive hydroxyl and hydroperoxyl radicals resulting from hole reaction with OH$^-$ adsorbed on the photocatalyst (TiO$_2$) [24] [25] [26] [27]. Figure 6 represents the process for mineralization of toluene.

Photocatalytic activity is also combined with nanoparticles that can provide more active sites for VOC adsorption, and subsequent destruction [27].

Destruction efficiencies can reach up to 98% for a wide range of concentrations [7]. For example, 80 ppm of aromatic pollutants underwent complete oxidation [28]; photocatalytic mineralization of propane, n-butane and isobutane over ZrO$_2$-TiO$_2$ catalyst also reached 75-95% [29]. Reported degradation efficiencies are in the range of 66-99% for 17 VOCs by TiO$_2$ [23].

In analogy to catalytic oxidation, photocatalysts are also limited by operating conditions, and poisonous species. Limitations of TiO$_2$ will be discussed in upcoming sections.

### 2.1.2 Recovery Techniques

- Condensation
- Absorption
- Adsorption

#### 2.1.2.1 Condensation

VOCs can be recovered as liquids by condensation via heat transfer. A cooling substance, usually water above its freezing point, is indirectly contacted with the gas stream to
condense water vapour out; VOCs are condensed with refrigerants as liquid nitrogen [30], and can be recovered.

![Semiconductor Excitation](image)

**Figure 6: Mineralization of VOCs by photocatalysis**

2.2.1.2 Absorption

The recovery of VOCs can be achieved by exposing the gas stream to a liquid solvent in which the VOCs are more soluble [31]. In an absorber tower, liquid solvent absorbs soluble VOCs from polluted air upon contact via tower packing or liquid atomization [8]. Improved techniques, such as the rotating packed bed, have been developed to enhance gas-liquid mass transfer [32]; waste liquids used for the separation, and absorption of the pollutants, however, were still generated. The VOCs in the solvent are recovered by distillation.
Efficiencies are (within) 50-98% and depend on the VOC solubility in the solvent at concentrations ranging from 250 to 10 000 ppmv [33]. The process, however, necessitates the treatment of waste solvent [8], and the need to cool the gas to a temperature range within 277-311 K to prevent solvent evaporation, and decrease of absorption rate [33].

2.2.1.3 Carbon and zeolite adsorption

Adsorption has efficiently been used in VOC pollution control [34]. For separation and recovery, VOCs are usually physically adsorbed on adsorbent surfaces by London dispersion. Details about physical adsorption are addressed in Section 3 of this chapter. Activated carbon is commonly used for VOCs remediation because it has a large surface area (500 m$^2$ g$^{-1}$) capable of adsorbing organic compounds [8] [35].

Reported removal efficiencies fall within the range of 80-90% [7] for carbon [8]. Competitive adsorption with water [36] is one of the limitations of carbon as an adsorbent, as well as its flammability, and carbon losses, which are relevant to the regeneration process. The use of hot steam for regeneration may also decompose adsorbed compounds into more toxic species [37]. Details about flammability and regeneration limitations are provided in Sections 3 and 4 of this chapter.

Alternative adsorbents include hydrophobic zeolites (high silica) that are less prone to competition between water and VOC vapours [8]. They are thermally stable for temperatures up to 1123 K, and have removal efficiency of 90-96%. The disadvantage of zeolite, however, is their cost [8]; hydrophobic zeolites are more than 20 times the price of carbon 2$/lb [38]. Slow desorption at 100 °C may also result in additional cost during regeneration (usually achieved with hot steam) [39].

2.2.1.4 Membrane recovery

Membrane-based techniques allow separation and recovery of VOCs from polluted air [8] [7]. The polluted gas stream passes through the membrane where VOC
vapours are trapped, condensed, and recovered as liquids; the unpolluted air stream is re-circulated in the system [37].

Separation by membranes relies on selectivity and higher permeability of a gas (in a mixture) through the material. A simplified description of the process in terms of pressure gradient involves sorption of a gas from a high pressure medium followed by permeation through the membrane material, and desorption at the lower pressure side. Within the membrane, molecules are retained in the free-volume space, where electron density overlaps are reduced. This retention may depend on the size of the species, or on the condensation ability, both of which depend on the nature of gas/material system. Efficiencies as high as 99% were reported [8] [40], and the process favours high VOC concentration (5000 ppm) [37] [40].

Polymeric membranes are the traditional materials, and are used in their rubbery or glassy forms. Rubbery polymers such as PDMS, which have been used for VOC separation from exhaust air, show increased selectivity with increased condensation ability of the gases. For a certain polymeric material, however, there exists a maximal separation ability specific to each gas pair, and dependent on the gas’s permeability [41]. In turn, the separation of a mixture of gases may not be achievable with one type of polymer. Polymeric materials are also often limited by chemical instability at high temperature, and solubility in organic compounds, which can result in irreversible damages. Characteristics of different polymeric materials are illustrated in Table 1. Inorganic materials are also used for their higher temperature stability; their free-volumes, however, are lower. Carbon- based membranes such as carbon molecular sieves (CMS), and carbon nanotubes, have also been tested. CMS are size selective membranes with pores in the range 4-4.5 Å. The development of CMS technology is limited by its irrelevance to gas separations needed in industry, its sensitivity to high organics, which may cause pore blocking, and its cost, 1-3 times higher than polymer-based materials.
<table>
<thead>
<tr>
<th></th>
<th>Glassy-polyimides</th>
<th>Rubbery-PDMS</th>
<th>Microporous</th>
<th>Nanoporous-PTMSP</th>
<th>Perfluoropolymers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free-volume</td>
<td>Low</td>
<td>High</td>
<td>Very high</td>
<td>Very high</td>
<td></td>
</tr>
<tr>
<td>Selectivity - basis</td>
<td>Size</td>
<td>Condensation of gases</td>
<td>Extremely high</td>
<td>Extremely high-condensability of large molecules (blocking small ones)</td>
<td>Solubility</td>
</tr>
<tr>
<td>Chemical stability</td>
<td>Low</td>
<td>Low</td>
<td>Soluble in organic compounds, aging</td>
<td>High, insoluble in organic solvents</td>
<td></td>
</tr>
<tr>
<td>Mechanical stability</td>
<td>Higher than rubbery</td>
<td>Low</td>
<td></td>
<td></td>
<td>High</td>
</tr>
</tbody>
</table>

Carbon nanotubes are promising, but their commercialization is limited by the difficulty in synthesizing structures with specific vertical orientation relative to the gas stream. Other materials such as zeolite were also reported for their size selectivity, and show potential for the separation of light hydrocarbons. Mixed-matrix membranes combining the polymer phase with a coating of metal oxide or silica have been reported. In general, membrane separation is evolving with respect to materials used, as well as design, and implementation within a system. Details about CNTs and zeolite are given in section 2.3 of this chapter.
<table>
<thead>
<tr>
<th>Technique</th>
<th>Principle</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Direct Oxidation</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermal</td>
<td>$2C_6H_6 + 15O_2 \rightarrow 12CO_2 + 6H_2O$</td>
<td>95-99% [42, 7, 6, 8]</td>
<td>High temperature and energy requirement NOx, dioxin formation [43]</td>
</tr>
<tr>
<td>Catalytic</td>
<td>$\text{CH}_4 (g) \rightarrow \text{CH}_3 (\text{ads}) + \text{H} (\text{ads})$</td>
<td>95% [7, 8]</td>
<td>Catalyst deactivation: sintering, poisoning, blocking [10] [11]. Requires large thermal energy to decompose small concentrations [44]</td>
</tr>
<tr>
<td></td>
<td>$\text{CH}_3 (g) \rightarrow \text{CH}_2 (\text{ads}) + \text{H} (\text{ads})$</td>
<td>Lower temperature: 573K-923K °C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\text{CH}_2 (\text{ads}) + \text{O} (\text{ads}) \rightarrow \text{CO} (\text{ads}) + \text{H}_2\text{O}$</td>
<td>Lower Nox [42]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\text{CO (non-diss. ads)} + \text{O} (\text{ads}) \rightarrow \text{CO}_2 [13]$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catalytic + oxidizing agents</td>
<td>Additional oxidizing species: $\text{H}_2\text{O}_2, \text{O}_3$</td>
<td>80-95% [16]</td>
<td></td>
</tr>
<tr>
<td>VUV-UV</td>
<td>$&lt;180 – 300 \text{ nm} [22]$</td>
<td>10% [22]</td>
<td>Low oxidation efficiency</td>
</tr>
<tr>
<td><strong>Indirect Oxidation: Formation of Radicals</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrochemical (NTP)</td>
<td>RH oxidation $e^- \cdot \text{OH}^\bullet \cdot \text{O} (\text{''P}) \cdot \text{O} (\text{''D}) \rightarrow \text{CO}_2 + \text{H}_2\text{O}$</td>
<td>Atmospheric pressure and room temperature</td>
<td>NO and O$_3$ formation, N$_2$O and HNO$_3$, CO [45]</td>
</tr>
<tr>
<td></td>
<td>O$_3 + <em>$ $\rightarrow$ O$_2 + O^</em>$</td>
<td></td>
<td>High power input</td>
</tr>
<tr>
<td></td>
<td>O$^<em>$ + O$_3$ $\rightarrow$ O$_2 + O_2^</em>$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2O$^<em>$ $\rightarrow$ O$_2^</em>$ + $*$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>O$_2^<em>$ $\rightarrow$ O$_2 + ^</em>$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Photocatalytic oxidation</td>
<td>TiO$_2 + h\nu \rightarrow h^-\text{vb} + e^-\text{cb}$</td>
<td>98% [7]</td>
<td>Photocatalyst deactivation: aromatics, humidity effect 4-5% solar overlap</td>
</tr>
<tr>
<td></td>
<td>H$<em>2\text{O}</em>{\text{ads}} + h^-\text{vb} \rightarrow \text{OH}^&amp; + \text{H}^+$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>OH$^-\text{ads} + h^-\text{vb} \rightarrow \text{OH}^&amp;$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>O$_2^- + e^-\text{cb} \rightarrow$ O$_2^- +$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2 HO$^-\bullet \rightarrow$ H$_2$O$_2 +$ O$_2$ [47]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Membrane</td>
<td>Selectivity and permeability</td>
<td>90-99% [8]</td>
<td>Selectivity to VOC</td>
</tr>
</tbody>
</table>

$^*$ represents surface sites and adsorbed species on the surface
<table>
<thead>
<tr>
<th><strong>Condensation</strong></th>
<th>Selectivity to VOC. Efficient for small amounts of air (containing VOC) [8] and high concentration 5000ppm [40]</th>
<th>Wasted membranes Temperature and chemical sensitivity (polymeric) [40]</th>
<th>Wasted water [8]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apply low temperatures or high pressures</td>
<td>&gt;5000ppm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2.2 Gas-Solid Interactions: Principles of Adsorption

This section addresses theoretical basis of physical adsorption processes as it is often the preferred separation process for VOCs remediation [49].

As a gas molecule approaches the surface, it gains energy released from the vibrational [50] motion of the solid lattice; if it is able to release that energy while it is in the attractive region of the surface potential, adsorption will occur. In the opposite case, the molecule gets very close to the solid, within $k_bT$ at the top of the well, and acquires enough thermal energy to cause its escape. Adsorption is therefore favoured at lower temperatures [50]. The collision of a gas molecule with the solid surface results in different pathways that are represented in Figure 7.

Figure 7: Possible pathways following gas-surface collision. Based on [13]

Physisorption is characterized by weaker adsorption energies relative to chemisorptions; some reported values for physisorption are given in Table 3.
Table 3 Physical adsorption energies for various VOC-SVOC/adsorbent systems

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Adsorption Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene/activated carbon</td>
<td>36-64 kJ.mol⁻¹ [51]</td>
</tr>
<tr>
<td>Benzene/Al₂O₃</td>
<td>12.4 kcal.mol⁻¹ [52]</td>
</tr>
<tr>
<td>n-hexane/ Al₂O₃</td>
<td>10.1 kcal.mol⁻¹ [52]</td>
</tr>
<tr>
<td>Hexane on carbon nanotube</td>
<td>23.9 kJ.mol⁻¹ [53]</td>
</tr>
<tr>
<td>Benzene on carbon nanotube</td>
<td>22.9 kJ.mol⁻¹ [53]</td>
</tr>
<tr>
<td>VOCs/granular activated carbon</td>
<td>40 to 82 kJ.mol⁻¹ [54]</td>
</tr>
</tbody>
</table>

Recovery of physisorbed pollutants is therefore easier. On the other hand, chemisorption would require more energy to regenerate the adsorbent, as species are more strongly bound. In addition, regeneration processes may affect the surface properties of the adsorbent, as will be discussed in upcoming sections. The main characteristics of physisorption and chemisorption are represented in Table 4.

Table 4 Different characteristics of physisorption and chemisorption

<table>
<thead>
<tr>
<th></th>
<th>Physisorption</th>
<th>Chemisorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔHa</td>
<td>10 to 40 kJ.mol⁻¹</td>
<td>&gt;400 kJ.mol⁻¹</td>
</tr>
<tr>
<td>Binding</td>
<td>Attractive forces: mainly London dispersion but also electrostatic (polarization, field dipole and field gradient quadrupole)</td>
<td>Electron transfer—chemical bond formation</td>
</tr>
<tr>
<td>Specificity</td>
<td>Small due to dispersion and polarization</td>
<td>High due to dipole, quadrupole, π-bond [49]</td>
</tr>
<tr>
<td>Sorption</td>
<td>Layer by layer condensation</td>
<td>Monolayer coverage</td>
</tr>
<tr>
<td>Adsorption</td>
<td>Near boiling point of adsorbate at operating pressure</td>
<td>No restriction</td>
</tr>
<tr>
<td>Temperature</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Potential energy</td>
<td>None</td>
<td>If crossover is above zero-potential energy</td>
</tr>
<tr>
<td>barrier</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorption Isotherms</td>
<td>BET (multilayer adsorption)</td>
<td>Temkin</td>
</tr>
<tr>
<td>Theoretical models</td>
<td>Polanyi</td>
<td>Langmuir</td>
</tr>
<tr>
<td></td>
<td>Langmuir</td>
<td>Henry (low pressure limit of Langmuir)</td>
</tr>
<tr>
<td></td>
<td>Henry</td>
<td>Freundlich</td>
</tr>
<tr>
<td></td>
<td>Freundlich (low coverage)</td>
<td></td>
</tr>
</tbody>
</table>

Physisorption of a gas on a solid non polar surface is due to interaction forces characterized by an attractive, and a repulsive component, both dependent on intermolecular distance. At distances of a few angstroms [50], the attractive force, also called dispersion, is more important, and is mainly due to an induced dipole moment between the gas and the surface, which results from the instantaneous dipole moments

\[2 \text{ Cal} = 4.182 \text{J}\]
due to fluctuations in the electron cloud density about the nucleus for each molecule [55] [35].

The attractive component is also influenced by dipole-quadrupole, and to a lower extent by quadrupole-quadropole moments [35]. Quadrupole interactions arise for symmetrical molecules with different electronegativities atoms, and are responsible for adsorption on polar surfaces [35]. The sum of attractive and repulsive components is quantified by the Lennard-Jones equation:

$$U = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \quad (\text{Equation (8)})$$

The first term, $\phi_R$, represents the repulsive term, and the second represents the attractive term, $\phi_D$. $\varepsilon$ and $\sigma$ are constants available in the literature for many molecules; if unavailable, they are replaced by constants $A = 4\varepsilon\sigma^6$ and $B = 4\varepsilon\sigma^{12}$ giving equation:

$$U = \left[ -\frac{A}{r^6} + \frac{B}{r^{12}} \right] \quad (\text{Equation (9)})$$

$A$ and $B$ can be calculated by different models. The London model is described here

$$A_L = \frac{3}{2} * \alpha_1 \alpha_2 I \quad (\text{Equation (10)})$$

$$I = \frac{1}{I} = \frac{1}{I_1} + \frac{1}{I_2} \quad (\text{Equation (11)})$$

$\alpha$ and $I$ are the polarizability and ionization potentials of each molecule [49]. The polarizability, ionization potential, dipole moment values for selected VOCs and SVOCs are presented in Table 5.

For non polar molecules, such as paraffin hydrocarbons, only the non specific terms $\phi_D + \phi_R + \phi_P$ contribute to the potential energy.

For ionic adsorbents, additional contributions from polarization, dipole and quadrupole moments influence the interaction potential due to electrostatic energies. The overall potential for an ionic adsorbent is thus given by [49]:

$$\Phi = \phi_D + \phi_R + \phi_P + \phi_I + \phi_Q + \phi_s \quad (\text{Equation (12)})$$

$$\phi_P = -1/2 \alpha E^2 \quad (\text{Equation (13)})$$
\[ \phi_\mu = -\mu E \quad (\text{Equation (14))} \]

\[ \phi_Q = \frac{1}{2} Q \frac{dE}{dr} \phi_s \quad (\text{Equation (15))} \]

\( \phi_Q \) is the sorbate-sorbate interaction, \( E \) is the electric field, and \( Q \) is the quadrupole moment.

**Table 5** Dipole moment, ionization energy and polarizability values of selected VOCs and SVOCs

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \mu ): Dipole moment (D)</th>
<th>Ionization Energy (eV)</th>
<th>( \alpha ): Polarizability ( (10^{-24} \text{ cm}^3) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propane</td>
<td>0.084 ± 0.001 [56]</td>
<td>10.95 ± 0.05 [56]</td>
<td>6.29 [56]</td>
</tr>
<tr>
<td>2-Methypropane</td>
<td>0.132 ± 0.002 [56]</td>
<td>10.53 ± 0.10 [56]</td>
<td>8.14 [56]</td>
</tr>
<tr>
<td>Butane</td>
<td>0 [49]</td>
<td>10.32 ± 0.05 [56]</td>
<td>8.20 [56]</td>
</tr>
<tr>
<td>2-Methylbutane</td>
<td>0.13 ± 0.05 [56]</td>
<td>10.57 [56]</td>
<td>10.01 [56]</td>
</tr>
<tr>
<td>Benzene</td>
<td>0 [58]</td>
<td>9.24378 ± 0.00007 [56]</td>
<td>10.74 [56]</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.375 ± 0.010 [56]</td>
<td>8.8276 ± 0.0006 [56]</td>
<td>12.3 [56]</td>
</tr>
</tbody>
</table>

Desorption energy is a decisive parameter for the applicability of adsorption in large scale commercial use in the separation of gases. This is because the adsorbent has to be reusable for the process to be economical, so ease of desorption is desirable.

The time for desorption \( t_d \) is given by

\[ t_d = v^{-1} \exp(E_d/k_B T) \quad (\text{Equation (16))} \]

where \( v^{-1} \) represents the frequency of escape. As is illustrated, an increase in temperature allows shorter \( t_d \) [50]. The rate of desorption is given by

\[ r_d = vNa^m \exp (-E_d/RT) \quad (\text{Equation (17))} \]

where \( v \) is the pre-exponential factor of the desorption rate coefficient, \( Na \) is the number of binding sites of the ad molecules, \( m \) is the order of the desorption and \( E_d \) is the desorption activation energy. The rate of desorption increases with an increasing temperature; that is why thermal techniques are commonly used for adsorbent regeneration, as will be discussed in subsequent sections. The order will determine
whether surface coverage influences the rate. For zero order desorption, common for multilayer, the rate is independent of surface coverage. For first order desorption reaction, common for single species, the temperature at which the highest rate of desorption occurs is independent of surface coverage. On the other hand, for second order desorption reactions, where recombination of two adsorbates, and then evolution of one molecule occurs, the temperature at which highest rate of desorption occurs decreases with increasing surface coverage. Desorption of physisorbed species may also result from energy supplied by the solid adsorbent due to lattice thermal motion.

From an equilibrium approach, adsorption processes are generally favoured at lower temperature because the overall free energy of the system given by

$$
\Delta G = \Delta H - T\Delta S \quad \text{(Equation (18))}
$$

is lowered. For the process to be spontaneous ($\Delta G < 0$), and considering that going from a gas phase to an adsorbed state a molecule loses degrees of freedom decreasing the entropy of the system, the enthalpy change, $\Delta H$ has to be negative. Adsorption is therefore exothermic [13], and spontaneous at decreasing temperatures [59].

The magnitude of $\Delta H_a$, the adsorption energy ($\Delta H = -\Delta H_a$), determines the strength of binding, and may be experimentally determined by using the Clausius-Clapeyron equation:

$$
\frac{dnp}{d\left(\frac{1}{T}\right)} = \frac{-\Delta H_a}{R} \quad \text{(Equation (19))}
$$

The dependence of the amount of gas adsorbed on the equilibrium pressure of the gas at constant temperature is described by sorption isotherms [13]; shapes of which yield information on the mechanism of adsorption, and on the type of adsorbent (monolayer coverage or capillary condensation in pores).
2.3 Traditional and New Adsorbents for VOCs

2.3.1 Carbon-based adsorbents

Activated carbon (AC) is an amorphous carbonaceous material exhibiting high porosity, and surface areas ranging from 400-1600 m$^2$.g$^{-1}$[60] [61] [62]. It is prepared by pyrolysis of raw materials such as wood, peat, lignite, hard coal, oil products, charcoal, and coconut shells [61] in an inert atmosphere 1073 K, and activation at high temperatures (1223-1273 K) [60]. During carbonization, non carbon elements are volatilized leaving a stack of aromatic sheets consisting of randomly organized elemental carbon [60]. Activation empties these interstices filled with tarry matter, or by products from the decomposition of the original carbonaceous material filling, and results in a porous structure [60]. Chemical activation with KOH or NaOH [63] forms the powdered activated carbon (PAC) form, while gas phase activation with steam or CO$_2$ [63] forms the granular activated carbon (GAC) [61]. GAC has large internal surface areas and small pores, while PAC has small internal surface areas and large pore diameter [60]. Activated carbon is 85-95% carbon; the rest being hydrogen, nitrogen, sulphur and oxygen [60].

Adsorption of organics and other non-polar compounds [61] occurs on the predominately hydrophobic sites of AC [60]. At relative humidity above 60%, however, competitive adsorption with water vapour may result [8].

Flammability at high temperatures is the major drawback for activated carbon. Self-ignition temperatures for various activated carbon materials were determined to range from 548 K to higher than 643 K [64]. Increased temperature may result from oxidation [65] initiated by oxygen on the surface, and is accompanied by further temperature increase resulting in CO$_2$ and CO if sufficient oxygen is adsorbed [66], or if external heating is applied [64].

*Carbon nanotubes and fibers*
Carbon fibers (micrometer scale) are made of graphite sheets that are arranged in various directions fibers [67]. Activated carbon fibers (ACF) are prepared from the carbonization and gas activation of polymeric fibers [68]. Their properties include:

- higher surface areas ranging from $1000 \text{ m}^2\text{.g}^{-1}$ to $2000 \text{ m}^2\text{.g}^{-1}$,
- pore size distribution ranging from 8-10 Å,
- small and uniform fiber diameter,
- inflammable up to 1273 K,
- versatility in shapes due to high strength and elasticity [68]

Carbon nanotubes are nanostructured materials in the forms of single wall carbon nanotubes (SWNT) having one carbon layer with cylindrical crystalline pores in the microporous range. Multiwalled carbon nanotubes (MWNT) have two layers in the mesoporous range [69]. They are grown from the decomposition of hydrocarbons or CO, where the carbon dissolves into a metal catalyst such as Fe, Co, or Ni on a support material like SiO$_2$, Al$_2$O$_3$, MgO, Al$_2$O$_3$-SiO$_2$, zeolite and clay [68]. They have a hollow structure and their surface area is greater than $1500 \text{ m}^2\text{.g}^{-1}$[70].

Carbon fibers and nanotubes are limited by low oxidative stability, and CO$_2$ release has been reported [67]. The adsorption efficiency of ACF for low concentrations of VOCs is still low, and the development of mixed ACF to address competitive adsorption in mixtures of VOCs remains challenging [71]. Figure 8 shows a high resolution transmission electron microscopy image of carbon nanotubes.
2.3.2 Zeolite and alumino-silicates

A zeolite is a microporous material as well as a molecular sieve; the size of the pores will affect the effective diffusion of molecules, and restrict access to the internal surface [13]. Shape selectivity can be specific to:

- reactant (only some reactant can pass through catalyst pores to active sites)
- product (only those small enough to escape the pores can diffuse out- this is one of the ways bulky product can deactivate a catalyst by blocking the pores)
- transition state (only transition states small enough can be formed) [73]

Natural zeolites are hydrophilic and characterized by a silicon/aluminum ratio [38]. Hydrophobic zeolite such as Y, also known as faujasite, are dealuminated zeolites; Al is chemically replaced with Si resulting in high Si/Al = 300 [38, 68], and surface areas are in the range 400-800 m².g⁻¹[74]. Low VOC concentration were treated in the presence of humidity [39].

2.3.3 Siliceous Mesoporous Materials
Silica gels are mesoporous materials (pores > 20 Å) [68] with surface areas in the range of 750-850 m$^2$.g$^{-1}$ [34, 68]. The gel is formed by polymerization of hydrated SiO$_2$ prepared by mixing a sodium silicate solution with an acid (H$_2$SO$_4$ or HCl) [68]. The gel is then dried and activated. Silica gels can also be synthesized by sol-gel with the hydrolysis of an alkoxide.

Adsorption occurs on surface hydroxyl, or silanol Si-OH [68] to remove VOCs as benzene and toluene [75].

2.3.4 Ordered Mesoporous Silicas

Nanostructured materials can be synthesized by using block copolymer as templates (defined in the appendix); they have surface areas comparable to those of activated carbon (up to 1000 m$^2$. g$^{-1}$) [76] as well as high pore volume; they may be promising adsorbents [39]. However, low interaction potential is expected within the pores for gas solid processes [68]. The weak nature of the bonding, however, may still be advantageous as it would allow facile regeneration, and they have been reported in VOC removal applications [68].

MCM-41 [76], SBA-15, and SBA-16 [69] are ordered mesoporous silicate/aluminosilicate molecular sieves [69]. MCM-41 form by the condensation of a silica gel onto a template’s walls. Typical pore sizes are within 20-100 Å, and depend on the template’s properties. Different pore sizes and adsorption properties [68] can be obtained by changing synthesis parameters.

SBA-15 and SBA-16, synthesized in acidic media on triblock polymer structures have surface areas of 850 m$^2$.g$^{-1}$ and 740 m$^2$.g$^{-1}$, respectively [77]. SBA-15 has large pores of 30 nm, but owes its high surface area to the additional microporosity within its walls; it is also thermally, and hydrothermally stable [77]. Selectivity can be tuned by controlling pore sizes (15-300 Å) via thermal treatment [76] [77]. For instance, alkene selectivity is tuned with higher microporosity compared with alkanes [69]. Different
forms as fibers, monoliths, spheres, rods, and nanoparticles can also be synthesized [69] [77]. SBA-15 has reported selectivity for aromatics (benzene, toluene) [78].

2.3.4 Alumina

Activated alumina, Al$_2$O$_{(3-x)}$(OH)$_{2x}$, is a porous material used primarily as an adsorbent, catalyst, or support material for catalysts [79]. The calcination of aluminum hydroxides such AlO(OH) (boehmite) and α-Al(OH)$_3$ (also known as gibbsite and accounting for 90% of natural bauxite), causes volatilization of OH groups forming a porous structure. Calcination temperature is the principal factor affecting phase, and surface area of the activated alumina; for boehmite precursors, however, initial particle size and surface area also affect the final product [79]. High surface area alumina nanoparticles can be prepared from gels synthesized by alkoxide hydrolysis [80] or by reaction of soluble aluminum salts and aluminates [79].

Activated alumina is hydrophilic, and is commonly used for water vapour removal [79], fluorides and arsenic from water [79], and can adsorb aromatics as o-xylene [62], benzene [81] [52] as well as alkanes as hexane [52] and ethane and other hydrocarbons [82]. Alumina owes its surface reactivity to the acidic and basic properties of its surface components Al and O$_2^-$ and OH groups, respectively [79].

2.3.5 Iron Oxide

Iron oxide is a transition metal oxide that exists in nature; the common phases are magnetite (Fe$_3$O$_4$-Fe$^{2+}$Fe$^{3+}$$_2$O$_4$), maghemite (γ-Fe$_2$O$_3$), hematite (α-Fe$_2$O$_3$), goethite (α-Fe(O)OH) [83] [84]. Magnetite (10-100 nm) exists naturally [83] in sediments [85]. Magnetite particles smaller than 10 µm are also emitted as industrial dust from steel production, and from combustion processes [83].

Iron oxide nanoparticles can be synthesized by co-precipitation [86], from hydrolysis and precipitation of alkoxides [87], or from thermal decomposition of an iron
precursor [88]. Magnetite can also be formed by heating haematite, Fe$_2$O$_3$, at 1673 K, or by partial oxidation of FeO [89].

Magnetite nanoparticle have reported chemical stability [88] towards oxidation at room temperature, however, phase change to maghemite [90] starts to occur upon heating at 378 K [91].

Magnetite has acidic and basic sites due to Fe$^{2+}$/Fe$^{3+}$ and O$^{2-}$ from hydroxyl groups (5 groups per nm$^2$) [83], respectively. Magnetite has been reported for removal of arsenic [92], chlorinated organic compounds, and toxic metals in water [5]. In the gas phase, it has been used for n-butane [93], benzene [81], and styrene [83] adsorption, and has been combined with H$_2$O$_2$ for heterogeneous catalytic oxidation of n-butyl chloride [94].

Finally, magnetite nanoparticles are biodegradable and non-toxic [95] making their use environmental friendly. Their small size in nature, however, causes respiratory problems [83].

2.3.6 Photocatalysts: TiO$_2$

Available as a mineral in nature in the anatase, rutile, and brookite phases [96], TiO$_2$, a semiconductor, has recently become popular for the photocatalytic degradation of VOCs [23] [27] [24]. TiO$_2$ nanoparticles can be synthesized by alkoxide hydrolysis and precipitation followed by calcination at high temperatures [97] [98].

Anatase has a superior photocatalytic activity compared with rutile due to higher crystallinity [99], and slower positive hole-electron recombination process [26]; both phases are superior to amorphous structures [99], where crystal defects cause recombination of electrons and holes [100]. With a band gap of 3.23eV, anatase can absorb wavelengths in the UV range 380 nm [101] [26] [102] and up to 387.5 nm, which represents 4-5% of solar radiation [101] [103]. To maximize overlap with solar radiation, lowering of the band gap energy [104] [103] by doping with metal or non-metal [104] such as nitrogen, sulphur, fluorine or carbon [105] has been carried out. The resulting material has shown increased degradation of pollutants [103].
As the most abundant specie in contact with TiO$_2$ surface in the gas phase is the pollutant, higher surface area generally resulted in higher degradation as long as particle size was not too small to affect crystallinity, and result in amorphous particles [106]. It is suggested that nanoscale TiO$_2$ have enhanced photocatalytic activity compared to larger bulk particles due to faster diffusion of electron and positive hole to the catalyst surface, which slows down electron hole recombination process, one of the limitation of TiO$_2$ [106].

Water presence affects the photocatalytic degradation of various VOCs differently; enhancement at small H$_2$O concentration [106], while inhibition [107] or slowing down [108] at higher concentrations [106] were noted. The latter was reported to be due to competitive adsorption between target pollutant and water vapour on the TiO$_2$ surface [106]. On the other hand, the former was explained by the presence of a thin layer of OH$\bullet$ adsorbed on TiO$_2$, which capture holes, and increase the oxidation reaction rate [109] [110] [25].

In absence of humidity, benzene cracks at the surface of the TiO$_2$ [110], while toluene forms strongly bound intermediates [23] [24]; both cause the reduction in activity [110]. So, controlling humidity levels in air streams is required, and may be a challenging limitation.
<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Surface Area</th>
<th>Adsorption</th>
<th>Limitations</th>
<th>Pollutant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial P25 Degussa TiO₂ powder</td>
<td>50± 15 m².g⁻¹ [23] [106]</td>
<td>h⁺ + OH → OH•</td>
<td>Humidity [108] aromatic poisoning [23] [106] [24]</td>
<td>VOCs [23] Acetylene [108]</td>
</tr>
<tr>
<td>Thin film TiO₂</td>
<td>150 – 359 m².g⁻¹ [111], [99]</td>
<td>Same</td>
<td>Same</td>
<td>1-butene [106], benzene [96], toluene [24] [27]</td>
</tr>
<tr>
<td>Alumina pellets</td>
<td>161 -340 m².g⁻¹ [52] [75, 112]</td>
<td>Al and O₂⁻ and OH [79]</td>
<td></td>
<td>VOC[112], o-xylene [62], benzene and hexane [52]</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>800-1500 m².g⁻¹ [60]</td>
<td>Non polar [39]</td>
<td>Flammable [8], water competition [8], sensitive (aldehydes, ketones, esters) [8]</td>
<td>VOCs [8] [113]-</td>
</tr>
<tr>
<td>Activated carbon fiber</td>
<td>1000-2000 m².g⁻¹ [68] [61]</td>
<td>Microporous [114]</td>
<td>Degassing, low oxidative stability [67] High cost [68]</td>
<td>VOC (xylene)[114]</td>
</tr>
<tr>
<td>Carbon nanotubes</td>
<td>2500 m².g⁻¹[115]</td>
<td>Active sites inside and outside tube [115]</td>
<td>Same</td>
<td>VOC [116] aromatics [117]</td>
</tr>
<tr>
<td>Zeolite</td>
<td>400-800 m².g⁻¹ [74] [69] [39]</td>
<td>Size-molecular sieving</td>
<td>10 times more expensive than activated carbon [62]</td>
<td>VOC [8, 39]</td>
</tr>
<tr>
<td><strong>Silica Gels</strong></td>
<td>Mesoporous 750-850 m².g⁻¹ [34], 76 m².g⁻¹ (3-5 mm) [75]</td>
<td>Polarity [118]</td>
<td></td>
<td>VOC [78], high affinity and capacity for aromatics [75]</td>
</tr>
<tr>
<td><strong>Ordered Mesoporous Silicas</strong></td>
<td>740 -1000 m².g⁻¹ [76, 77]</td>
<td>Versatile pore size 15-300 Å [76]</td>
<td></td>
<td>VOC [69], [77], light HC, benzene, toluene ethylene [78]</td>
</tr>
</tbody>
</table>
2.4 Regeneration techniques

Owing to the equilibrium state of adsorption processes, regeneration methods often aim at reversing the process by disrupting this equilibrium. Some methods apply heat or reduce relative pressure of the pollutant. Other techniques displace adsorbates by exploiting adsorbent properties such as selectivity while others focus on the chemical properties of the adsorbates such as solubility in a particular medium. The following section illustrates how adsorbents are commonly regenerated.

2.4.1 Thermal regeneration

As adsorption of gases is an exothermic process, heat application is a common way for desorbing adsorbates to regenerate the adsorbent [35], [119], [120], [121]. Heating the adsorbent can be accomplished by:

- Hot steam
- Hot air or inert gas
- Electrothermal heating

2.4.1.1 Hot steam

Steam at 373-513 K flows through, or over the adsorbent to remove adsorbates [34] [122] [123] [124]. The condensation of the steam releases more heat, and improves desorption [34]. The desorbed species are recovered by condensation, and separated by gravity decantation, or distillation [34], if they are miscible in water.
The condensed water may require treatment due to possible solubility of the adsorbate [121]. Another drawback is the need for adsorbent drying [125].

Strongly bound adsorbates may require additional heating steps. Figure 9 represents the case of activated carbon [3].

![Figure 9: Activated Carbon Regeneration](image)

The residual (char) from the pyrolysis of non volatile adsorbates may clog pores; the adsorbent is reactivated with CO\textsubscript{2} or steam gasification. Despite new pore formation, 5-20% loss of activated carbon is inevitable [126] [123], [120], and reduction in adsorption capacity results [124].

### 2.4.1.2 Hot gas

Exposing the adsorbent to hot air or inert gas such as N\textsubscript{2} at 413 K desorbs the species, and [125] prevents their hydrolysis [123]. On the other hand, the large volumes of air or N\textsubscript{2} required, due to their low specific heat, [125] dilutes the desorbate [123] requiring further treatments [125].

### 2.4.1.3 Electrothermal heating
Electrothermal heating is accomplished by:

- Joule effect: alternating current to heat the saturated adsorbent (423 K) [121]
- Infrared and microwave radiation [123].

Electromagnetic induction: an induced current heats the adsorbent to 373-473K [123]. The desorbed species are flushed out with an inert gas, and condensed in a cold trap [123]. Activated carbon [122], carbon cloths, and hydrophobic zeolites [123] were regenerated with electrothermal techniques.

### 2.4.2 Chemical Regeneration: extractive and reactive

Extractive regeneration:

- Organic solvent
- Surfactant solution
- Supercritical and subcritical fluids (CO$_2$ and water)

Extraction with organic reagents depends on solubility [127] [128] of the adsorbed specie [126] [120] [35]. Extracted desorbed species require subsequent treatment, and the use of chemicals can affect adsorbent porosity reducing adsorption capacity after a few cycles [121]; incomplete regeneration, and reagent cost are other limitations to the technique [128].

Extraction in a surfactant solution [120] proceeds by partitioning of the organics, and concentration in the hydrophobic interior shielded with a hydrophilic exterior [129]. For example, toluene was removed from activated carbon using sodium dodecyl sulphate (SDS), and resulted in minimal decrease in adsorption capacity [130]. The surfactant aggregate also requires treatment for separation of organics [120].
Alternative solvents include fluids such as hot water and CO\textsubscript{2} under subcritical and supercritical conditions, respectively. Hot water at 473-573 K [120] and 120 bars \textsuperscript{3} [124, 128] is passed through the adsorbent, and extracts organic compounds due to changes in physical properties including lower dielectric constant, viscosity, density and surface tension [128]. Under these conditions, access to pores is facilitated, and organics miscibility in water is possible. For example, at 648 K and 215 atm, water and benzene are miscible [128]. At ambient conditions, the fluid goes back to its initial state, as a gas or a liquid, for solvent and solute recovery [121].

Up to 95\% recovery of initial adsorbent capacity was reported with hot water extraction [122]. Another advantage is the smaller energy requirement compared with thermal regeneration [128].

The supercritical conditions for CO\textsubscript{2} are at 304 K and 73 bar [121]. The miscibility of toluene and benzene in supercritical CO\textsubscript{2} allowed regeneration of activated carbon [131]. Limitations include the need for large amounts of CO\textsubscript{2}, incomplete regeneration, and the cost of supercritical units [120]. Loss of adsorption capacity (activated carbon) also occurs, but remains lower than that due to thermal regeneration [132].

Reactive regeneration

Another approach involves the reaction between the solvent and the adsorbed species resulting in a less adsorbed product [133]. For example, reaction of sodium hydroxide with phenol adsorbed on activated carbon formed sodium phenoxide, which has different adsorption capacity [133]. NaOH and HCl were used to regenerate maghemite nanoparticles [134]. This method depends on specificity and selection of a solvent, and on the nature of the adsorbed species.

\textsuperscript{3} Pressure units: 1 atm = 1.01325 bars
2.4.3 Pressure-Swing Adsorption (PSA) and Vacuum-Swing Adsorption (VSA)

Pressure swing adsorption, PSA, and vacuum swing adsorption, VSA, involve lowering pressure ratios, and altering the adsorption equilibrium [49].

In PSA, the adsorbent is regenerated by decreasing the total pressure, and purging with a fraction of the desorbate at a lower relative pressure (200-500 torrs\(^4\) [123]) [49] [135] and constant temperature [34]. The adsorbent capacity is reduced due to a shift in the equilibrium between the adsorbed phase, and the purging stream. The desorbed specie is then recovered [126]. The efficiency of the system is limited to a high loading of adsorbed pollutant [126]. PSA is used for the removal of very volatile organic compounds, and other adsorbates having weak adsorption energies [123]; desorption of gasoline vapors and light HC was reported [126]. Regeneration by VSA operates by the same principle as PSA, but the desorption pressure is at sub-atmospheric conditions (0.25-0.35 atm) [49].

2.4.4 Electrochemical

Electrochemical regeneration consists in applying a current to desorb the adsorbate, and then degrade it by electrochemical oxidation [136]. For a system in NaCl, Na\(^+\) ions go to the cathode, where the saturated adsorbent is fixed, and facilitate the desorption of the adsorbed specie; electrochemical oxidation with chloride or oxygen follows at the anode [136]. Regeneration efficiencies up to 95% are achievable with the increase in regeneration current and time [137] [138].

2.4.5 Oxidation Techniques

Oxidation techniques overlap with remediation techniques. A catalyst or photocatalyst (combined with irradiation) may be used to adsorb, and decompose the

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\(^4\) 1 atm = 760 torrs
adsorbed species [120] [139, 140]. The regeneration efficiency is dependent on the relative rates of destruction, and desorption of pollutants from the adsorbent [120], it is lower when the rate of desorption is slower than that of degradation [141].

2.4.6 Ozone

A stream of ozone-oxygen mixture goes through the adsorbent at 298 K; direct ozonation, or generation of OH radicals decomposes the sorbed species [142]. As much as 80% of GAC was recovered [142].

2.4.7 Inert purge gas stripping

Lowering the pressure of the contaminant in the gas phase by a stripping action with an inert gas at constant temperature and pressure reverses the concentration gradient, and removes sorbed species. The technique is usually applied for weakly sorbed pollutants whenever recovery is not required [34, 49].

2.4.8 Displacement

Displacement of the adsorbate by another species is useful if the adsorption equilibrium can be reversed by a change in feed composition. The adsorbate and desorbent must have similar affinity towards the adsorbent such that both be easily adsorbed, and desorbed depending on the feed composition. The technique is used when thermal desorption is not applicable due to adverse effects on the adsorbent, or possible reactions with the adsorbed species [49].
<table>
<thead>
<tr>
<th>Technique</th>
<th>Principle</th>
<th>Advantages</th>
<th>Recycling</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal</td>
<td>Desorption at 973-1273 K in the presence of inert gas or oxidizing gases [120] [123]</td>
<td>Desorbs weakly and strongly bound adsorbates [126]</td>
<td>No recovery [35]</td>
<td>Adsorbent treatment [35] and reduced activity [123] [120] [124] [119]</td>
</tr>
<tr>
<td>Steam regeneration</td>
<td>Steam at 378-513 K [123, 124]</td>
<td>Lower temperatures</td>
<td>Recovery by distillation or condensation [34] [35] [123]</td>
<td>Water treatment [123] Adsorbent drying [125]</td>
</tr>
<tr>
<td>Hot gas</td>
<td>Hot air or inert gas [123] (N₂) at 413 K [125]</td>
<td>Prevents hydrolysis of desorbed solvent [123]</td>
<td>Recovery by condensation [125]</td>
<td>Large volumes of air and N₂ Þ desorbate dilution [123]</td>
</tr>
<tr>
<td>Electrothermal heating</td>
<td>Joule effect [123] [121], infrared and micr-wave radiation [123], Electromagnetic induction [123]</td>
<td>Higher desorbate concentrations [143]</td>
<td>Recovery of condensed vapours [123] [144]</td>
<td>Uniformity of electric current challenge [144], hot spots (ignition in presence of O₂ ) [143], conducting adsorbents needed</td>
</tr>
<tr>
<td>Pressure swing</td>
<td>Lower pressure 200-500 mm Hg [123] [34]</td>
<td>Very volatile organic compounds [123]</td>
<td>Recovery by condensation in cold trap [123]</td>
<td></td>
</tr>
<tr>
<td>Hot water</td>
<td>473- 573K and 120 bars [120][124][128]</td>
<td>Small carbon mass and structure losses [124],</td>
<td>Recovery</td>
<td></td>
</tr>
<tr>
<td>Supercritical fluid regeneration</td>
<td>CO₂ extraction [120]</td>
<td>Lower loss of surface [132]</td>
<td>Recovery [121]</td>
<td>Incomplete removal of organics [120]</td>
</tr>
<tr>
<td>Surfactant enhanced regeneration</td>
<td>organics partitioning in a surfactant solution [120]</td>
<td>Low adsorption capacity loss (activated carbon) [130]</td>
<td>Recovery and recycling [120, 130]</td>
<td>Surfactant removal from adsorbent and treatment [130]</td>
</tr>
<tr>
<td>Inorganic and organic reagents</td>
<td>Inorganic oxidizing agents reaction resulting in less adsorbed product or organic solubilising agents [121, 127]</td>
<td></td>
<td></td>
<td>Adsorbent chemical sensitivity [121], incomplete regeneration [128] Solvent separation, treatment and disposal [132] [126]</td>
</tr>
<tr>
<td>Inert purge gas stripping</td>
<td>Lower partial pressure of adsorbate [34] at constant temperature and pressure [145]</td>
<td></td>
<td>Inefficient due to dilution [49]</td>
<td>Weakly adsorbed species [146] [49]</td>
</tr>
<tr>
<td>Displacement cycle</td>
<td>Preferential adsorption by other species [34]</td>
<td>Heat sensitive adsorbate [34]</td>
<td>Recovery</td>
<td>Desorption of displacement agent [145]</td>
</tr>
<tr>
<td>--------------------</td>
<td>-----------------------------------------------</td>
<td>-------------------------------</td>
<td>----------</td>
<td>---------------------------------------</td>
</tr>
<tr>
<td>Electrochemical</td>
<td>Desorption at cathode and oxidation at the anode [137] [138]</td>
<td>Fast (10 min) and high regeneration (up to 95%) [137] [138]</td>
<td>No recovery</td>
<td></td>
</tr>
<tr>
<td>Oxidation</td>
<td>Injection of O₃ [142], catalyst or photocatalyst + UV [120] [141]</td>
<td></td>
<td>No recovery</td>
<td></td>
</tr>
</tbody>
</table>
Chapter 3- Methodology

3.1 Materials and Supplies

<table>
<thead>
<tr>
<th>Materials and Supplies</th>
<th>Purity</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultra high purity He</td>
<td>99.999 %</td>
<td>MEGS</td>
</tr>
<tr>
<td>Extra dry air</td>
<td></td>
<td>MEGS</td>
</tr>
<tr>
<td>Hydrogen</td>
<td></td>
<td>MEGS</td>
</tr>
<tr>
<td>Ultra high purity N\textsubscript{2}</td>
<td>99.999 %</td>
<td>MEGS</td>
</tr>
<tr>
<td>Ethane</td>
<td>99 + %</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Propane</td>
<td>99 %</td>
<td>Aldrich Chemical Company</td>
</tr>
<tr>
<td>n-Butane</td>
<td>99%</td>
<td>Aldrich</td>
</tr>
<tr>
<td>2-Methylpropane</td>
<td>99 %</td>
<td>Aldrich Chemical Company</td>
</tr>
<tr>
<td>2-Methylbutane</td>
<td>&gt;95.0%</td>
<td>Fluka Chemika</td>
</tr>
<tr>
<td>Benzene</td>
<td>Certified ACS</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>Toluene</td>
<td>HPLC Grade</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>Ethanol ACS Grade</td>
<td>95%</td>
<td>Commercial Alcohols</td>
</tr>
<tr>
<td>Dimethyldichlorosilane (DMDCS)</td>
<td>5% DMDCS in toluene</td>
<td>Sigma-Aldrich Chemie GmbH</td>
</tr>
<tr>
<td>Nitric acid concentrated</td>
<td>ACS Reagent</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>Ammonium hydroxide (25% NH\textsubscript{3}.H\textsubscript{2}O)</td>
<td>ACS PLus</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>FeCl\textsubscript{3}.6H\textsubscript{2}O</td>
<td>Reagent grade &gt; 98%</td>
<td>Sigma-Aldrich Chemie GmbH</td>
</tr>
<tr>
<td>FeCl\textsubscript{2}.4H\textsubscript{2}O</td>
<td>Minimum 99%</td>
<td>Sigma-Aldrich Chemie GmbH</td>
</tr>
<tr>
<td>Gas tight syringes 5000 µl, 250 µl</td>
<td>Not applicable</td>
<td>Hamilton Co., Reno Nevada</td>
</tr>
<tr>
<td>Septa (15 mm Dia)</td>
<td>Not applicable</td>
<td>Hamilton</td>
</tr>
<tr>
<td>Hg Lamp, 100W</td>
<td>Not applicable</td>
<td>Oriel, New Port</td>
</tr>
<tr>
<td>SPME Car/PDMS fiber</td>
<td>Not applicable</td>
<td>Sigma-Aldrich</td>
</tr>
</tbody>
</table>

3.2 Analytical Techniques

3.2.1 Gas Chromatography-Flame Ionization Detector (GC-FID)

We quantified volatile and semi volatile organic compounds using a gas chromatograph equipped with a flame ionization detector (FID) (HP 6890). The FID,
commonly used for hydrocarbon analysis [147], [148], [149], consists of a flame that combusts the incoming analytes producing ions that are collected on an electrode, and providing an electrical signal that varies proportionally with the total mass of carbon and hydrogen atoms of the compound injected [150].

**Operating conditions**—The GC-FID conditions for all experiments were as follows: oven temperature started at 50 °C with a hold time of 1 min, ramped up to 132°C at 15 °C.min\(^{-1}\) followed by an increased ramp to 220 °C at a rate of 20 °C.min\(^{-1}\), and a hold time of 8 minutes. The GC was equipped with a PLOT column (HP-Plot Al\(_2\)O\(_3\) “S” deactivated), and operated in the splitless mode. The injector port, and FID temperatures were set at 290, and 300 °C, respectively. The helium (column flow), air, and hydrogen flows were 2.3, 300, and 40 mL/min, respectively. The helium make up flow was 15.0 mL/min.

The oven temperature program, including ramps and hold time, was varied until retention times specific to each compound were obtained. Some of the challenges with other temperature programs included signal overlaps, broadly shaped peak areas, and tailing.

**Limit of detection**—The limit of detection for the FID is 0.001 ppm of sample gas in a mixture [151]. The concentrations in all experiments were 100 ppm, and above this limit.

**3.2.2 Solid-Phase Micro-extraction (SPME)**

Sampling of target compounds was carried out using SPME, frequently used to for the extraction, and quantification of volatile and semi-volatile organic compounds from gas mixtures [152] [153]. Upon contact with the fiber, the analytes are adsorbed on the adsorptive Car/PDMS coating, recommended for C\(_2\)-C\(_{10}\) compounds, and then volatilized in the GC injector port. SPME was selected as a sampling technique because it is solventless, and does not produce waste, nor does it require extra materials such as liquid
nitrogen (which would be required for cryo-focusing); it is also re-usable over a particular lifetime.

**SPME extraction conditions**—To carry out quantitative and qualitative analyses with SPME, the fiber was conditioned for 2 hours at 300 °C in the GC injector port, as prescribed by the supplier (Supelco). Extraction conditions were optimized to minimize competitive adsorption noted for Car/PDMS coated fibers. With increased extraction times, lighter compounds such as ethane were displaced by molecules with higher distribution constants such as toluene, yielding inconsistent peak area values. To avoid competitive adsorptions on Car/PDMS, the extractions were carried out under non-equilibrium conditions by fixing the extraction time at 2 min, and keeping the stirring rate constant. After extraction, the SPME fiber was desorbed for 6 min in the GC injector port, retracted, and removed for subsequent analyses. Figure 10 represents the extraction and desorption steps.

![Figure 10: Adsorption experiments set-up](image)

Challenges with SPME: fibers with the same coating coming from the same lot had different extraction profiles for the fixed conditions. Therefore, comparison between
2 fibers from the same lot was not always possible. Their lifetime was shortened due to fiber coating stripping off (partial or complete). This happened as a result of pieces of septa ending up in the liner, and coming into contact with fiber.

3.3 Experiments

3.3.1 Stock and Gas Mixtures Preparation

All flasks used for stock or gas mixtures were washed, silanized, and dried overnight at 393 K.

**Stock mixture**—Individual gas mixtures were prepared for each compound in separate flasks. The clean flasks, and gas cylinders were connected to a vacuum line, evacuated down to $8.5 \times 10^{-3}$ torrs, and filled to 76.0 torrs with the required gas. For semi-volatiles, the flasks were evacuated, and placed in a dewar filled with liquid nitrogen. A maximum of 1 mL of liquid was injected through the septum; the liquid immediately crystallized. The flask was then removed from the liquid nitrogen, and gradually heated back to room temperature. The pressure of vaporized SVOCs was recorded to one decimal place. Ultra high purity nitrogen gas was used to fill up all flasks to 760.0 torrs.

**Gas Mixtures**—All 100 ppm gas mixtures were freshly prepared from stock mixture of individual compounds. The flasks were evacuated, flushed, and then filled with $N_2$ to 760.0 torrs. For adsorption experiments, the particles were added followed by evacuation, and flushing with $N_2$. The required concentration of each gas was calculated according to

$$ ppm = \frac{\rho_{gas} \cdot V_{gas} (\mu L) \times 24.45 \ (dm^3 \ mol^{-1}) \times 1000}{V_{flask} (mL) \times 10^{-6} \times MW_{gas} (g \cdot mol^{-1})} $$

(Equation (20))

To account for the dilution of stocks, $V_{gas}$ is divided by the dilution factor.
3.3.2 Adsorption Experiments

The experimental design consisted in comparing a pair of gas mixtures identical in initial concentration, but differing in that one contained 4.00 g of adsorbent. The stirring was turned on for 20 minutes prior gas injection, and fixed at a constant level. Once all gases were injected, the mixture was left to stir for another 5 minutes before sampling was started.

3.3.3 Photolysis Experiments

The effect of irradiation at 254 nm (Oriel 6281 100 W Hg lamp) on the reduction of VOCs and SVOCS was tested. Experiments were conducted by comparing pre and post irradiation concentrations for a freshly prepared gas mixture in N₂. The glass flask was fitted with a quartz unit to allow UV radiation penetration. The flask was placed in a chamber covered with aluminum foil to maximize reflections. The irradiation time was 2 hours. In addition, the effect of the medium was tested by carrying out the experiments in pure air. Figure 11 shows the experimental set-up for the photolysis tests.

3.3.4 Adsorption and Photolysis Experiments

The effect of photolysis combined with iron oxide was also carried out. Pairs of samples with and without iron oxide were irradiated for 40 min. Sampling was performed pre and post irradiation for each flask.
3.3.5 Adsorbent synthesis: iron oxide nanoparticles

Magnetite nanoparticles were prepared based on the method already described in [86], where 11.68 g of FeCl$_3$.6H$_2$O and 4.30 g of FeCl$_2$.4H$_2$O were dissolved in 200 mL of deoxygenated distilled water at 358 K. Under vigorous stirring, 15 mL of NH$_4$OH were slowly added to the dissolved solution, and resulted in a black precipitate. The mixing was sustained for 5 min while purging with N$_2$. The precipitate was set aside to settle, and the liquid was decanted. The precipitate was washed with deoxygenated water 4-5 times, collected on a magnetic bar, and dried at 323 K. Prior use the dried particles were evacuated for 4 hours, and flushed twice with ultra pure nitrogen.

To coat granular activated carbon with magnetite nanoparticles, the carbon was treated with 1M HNO$_3$ for 4 hours followed by overnight drying at 393 K. For the coating
process, the treated carbon was transferred into the magnetite solution, and gently stirred for 1 hour. The coated carbon was then dried in the oven at 323 K.

3.5 Adsorbent Characterization: TEM, XRD and SA

3.5.1 Transmission Electron Microscopy

Transmission Electron Microscopy (Philips CM200 TEM) was used to determine the size, and shape of the magnetite particles. All samplings for size and morphology observation were done by dipping carbon coated copper grid into the powdered sample, spraying with anti-dust, and taking electron micrographs of the particles retained on the grid.

3.5.2 X-Ray Diffraction

An X-Ray Diffractometer (Siemens D5000 equipped with a Gobel mirror) was used to determine the crystal phase of the synthesized nanoparticles. The powdered samples were layered on a glass slide, and placed in the sample holder. Cu- rays K alpha with \( \lambda = 1.5418 \text{ Å} \) was used for scanning at 2 theta. A graphite monochromator was used to eliminate K beta (1.39Å).

3.5.3 Surface Area Analyzer (BET)

The nitrogen adsorption and desorption isotherms at 77 K were measured using a surface area analyzer (Micromeritics Flow Sorb II 2300) after samples were degassed for 1 hour at 393 K. The specific surface area (SSA) was calculated from the average of 3 readings from \( \text{SSA} = \frac{\text{Surface Area (measured)}}{\text{sample weight}} \).

Figure 12 represents a summary of the methodology
3.6 Error analysis

Errors associated with data collection included: (a) FID carbon response, (b) reproducibility due to human errors, and (c) reproducibility due to miscellaneous events.

(a) FID carbon response
Reproducibility in peak areas depended on the FID response to provide the same signal for the same concentration of a compound. The FID is carbon mass selective, and the peak area increases with the mass of carbon injected. To verify precision of the detector response, different concentrations of compounds were extracted with SPME, and injected. Figure 13 represents the response to different concentrations of toluene.

![Detector Response for Toluene](image)

**Figure 13: FID response to toluene**

The FID response also increases with carbon number. It must be noted, however, that injected amounts were pre-concentrated on the SPME fiber, which had different extraction profiles for the selected compounds due to different affinity to the adsorptive phase (keeping all other conditions constant). For example, with the Car/PDMS fiber, and under our extraction conditions, butane exhibited higher peak areas compared with those of benzene.

Retention times for selected compounds must be reproducible and avoid overlaps. The variation in retention times for the tested compounds are represented in Figure 14. Table 8 shows the retention times for the compounds analyzed.
Figure 14: Retention time reproducibility of selected compounds

Table 8 Retention times of tested compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Average retention time (min) (n=6)</th>
<th>Relative Standard deviation %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>3.137± 0.002</td>
<td>0.074</td>
</tr>
<tr>
<td>Propane</td>
<td>5.417±0.006</td>
<td>0.109</td>
</tr>
<tr>
<td>Methylpropane</td>
<td>8.661±0.009</td>
<td>0.104</td>
</tr>
<tr>
<td>n-Butane</td>
<td>9.023±0.010</td>
<td>0.106</td>
</tr>
<tr>
<td>Methylbutane</td>
<td>12.426±0.011</td>
<td>0.090</td>
</tr>
<tr>
<td>Benzene</td>
<td>20.007 ± 0.018</td>
<td>0.091</td>
</tr>
<tr>
<td>Toluene</td>
<td>24.154±0.042</td>
<td>0.173</td>
</tr>
</tbody>
</table>

(b) Reproducibility influenced by human errors

Human errors affected the precision of the peak area obtained and depended on:

✓ Injection technique: coordination between injection and the start of the run (press ‘Start’ button)
✓ Sampling: extraction time reading with a stopwatch, elapsed time between removal of the fiber from the sampling flask, and injection in the GC.

Figure 15 shows the reproducibility of injection of several compounds at the same concentration.

![Peak Area Reproducibility](image)

**Figure 15: Reproducibility of injections. Error bars represent standard deviation**

All data collected (peak areas) for treatment had a relative standard deviation ((Standard deviation /Average peak area) * 100) less than 5% calculated from a minimum of 3 readings for the same concentration.

(c) Reproducibility due to miscellaneous events

Miscellaneous events included:

✓ Synthesis of different batches of heterogeneous particles, which showed variation in the interactions with different compounds
Variability in output of the two lamps that were used for irradiation in the photolysis experiments

Overall precision for all data collected was based on a minimum of 3 peak areas with RSD < 5%.

Errors associated with data treatment

The calculated removal percentages of all compounds display non normal distributions; histograms are presented in the appendix. Statistical analysis was carried out using the Wilcoxon signed-rank test with a rejection p-value of < 0.05 on the difference values between the control and the treatment flasks mean peak areas. More than 5 sets of difference values are treated for each compound. The p-value was calculated for pairs of each compound using SPSS. The assumption is the null treatment (p > 0.05).

The accumulated error associated with data collection is $\sqrt{x^2 + y^2 + z^2}$, and is due to the challenges stated above namely human errors (x), GC-precision (y), and random miscellaneous errors (z).

3.7 Removal efficiency calculations

Removal efficiency was calculated by comparing a control with a test sample containing the adsorbent, subject to UV irradiation or containing the adsorbent and subject to irradiation. The example of toluene removal efficiency is given below.

<table>
<thead>
<tr>
<th>Sample</th>
<th>GC-FID peak area (pA.s)</th>
<th>Average peak area (pA.s)</th>
<th>Standard deviation</th>
<th>Relative standard deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>965</td>
<td>982.3</td>
<td>918.6</td>
<td>32.9</td>
</tr>
<tr>
<td>Test</td>
<td>16.4</td>
<td>17.5</td>
<td>17.5</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Removal efficiency % = (955.3-17.1)/955.3 * 100 = 98.2 %
Chapter 4 Results and Discussion

4.1 Adsorbent Characterization

4.1.1 TEM

The transmission electron microscope provides crystallite size of the nanoparticles prepared by co-precipitation of iron chloride salts. The TEM image in Figure 17 shows a spherical crystalline structure with diameters ranging from 5-20 nanometers.

Figure 17: TEM of magnetite
Figure 18: Electron diffraction of magnetite

The electron diffraction pattern in Figure 18 reveals crystallography of the synthesized iron oxide; concentric rings with well resolved spots indicate the particles are polycrystalline made up of large crystallites
4.1.2 XRD

Figure 19 shows the X-ray diffraction pattern of an fcc crystal with reflections in the \{111\}, \{220\}, \{311\}, \{400\}, \{422\}, \{511\}, \{404\}, and \{535\} planes. These reflections are characteristic of magnetite [83].

![X-ray diffraction pattern of magnetite](image)

Figure 19: X-ray diffraction pattern of magnetite

4.1.3 Surface Area

The BET surface area was measured for the magnetite nanoparticles, and is 79.89±0.64 \(\text{m}^2\cdot\text{g}^{-1}\).

4.2 Adsorption Experiments

4.2.1 Room temperature

The ability of magnetite nanoparticles to remove common VOCs and SVOCs by adsorption was tested for potential use as a clean, and practical remediation technology for outdoor air pollution. The removal % of selected compounds by magnetite nanoparticles is represented in Figure 20.
Figure 20: Removal of VOCs and SVOCs by magnetite (n=5)

Figure 21: Average removal efficiency. Error bars represent standard error
In the presence of magnetite nanoparticles at room temperature, benzene and toluene were reduced by 80-90% and 90-98%, respectively. Lighter compounds removal are much lower; methylbutane, butane and methylpropane were removed by 20 %, 15% and 15%, respectively. A comparison with other remediation techniques is illustrated in Table 9.

Table 10 Comparison of removal efficiencies for common remediation techniques and magnetite nanoparticles

<table>
<thead>
<tr>
<th>Remediation Technique</th>
<th>Removal Efficiency</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_3$O$_4$ (surface area 80 m$^2$.g$^{-1}$)</td>
<td>Methylpropane less than 15%</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>n-Butane less than 15%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Methylbutane 20%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Benzene more than 80%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Toluene 95%</td>
<td></td>
</tr>
<tr>
<td>Thermal oxidation</td>
<td>Up to 95-99%</td>
<td>[42], [7], [6], [8]</td>
</tr>
<tr>
<td>Catalytic oxidation</td>
<td>95%</td>
<td>[9] [7, 8]</td>
</tr>
<tr>
<td>Photocatalytic oxidation</td>
<td>98%</td>
<td>[7]</td>
</tr>
<tr>
<td>Activated carbon (surface areas 1000 m$^2$.g$^{-1}$)</td>
<td>80-90%</td>
<td>[7]</td>
</tr>
<tr>
<td>Hydrophobic zeolite (Surface area 850 m$^2$.g$^{-1}$)</td>
<td>90-96%</td>
<td>[8]</td>
</tr>
<tr>
<td>Membrane Separation</td>
<td>90-99% [8]</td>
<td>[8]</td>
</tr>
</tbody>
</table>

Factors influencing the removal efficiency include, and are not limited to, the nature of the surfaces, the chemical properties of the adsorbed molecule, i.e., polarity, the kinetics of adsorption and desorption processes, and the surface area of the adsorbent. The chemical and physical nature of both the surface and the adsorbate plays a crucial role in determining the removal efficiency and the adsorption/desorption rates.

One of the possible explanations for the superior removal of aromatics is the fact that aromatics can interact strongly with the surface through their electron donating and accepting capability. This type of interaction has been observed between compounds such as styrene and ethylbenzene, which display similar molecular orbitals to benzene and toluene [154] [81]. The stronger interaction with Fe$_3$O$_4$ was attributed to unoccupied 3d states in Fe$^{2+}$ that interact with the HOMO of the aromatics. The concurrent back donation of electrons to the resulting LUMO of the aromatics from the occupied 3d of Fe$_3$O$_4$ has also been considered [154]. In our work, it is suggested that Fe$^{2+}$/ Fe$^{3+}$ of
magnetite act as acidic sites that interact with the \( \pi \) electrons of the aromatics acting as basic sites. The enhanced removal of toluene compared with benzene can also be due to its higher electron delocalization and polarity. Aliphatic alkanes on the other hand, which exhibit much lower electron donating ability, show much lower removal efficiencies. It is also known [49] that the interaction potential of paraffins is dependent on the non specific interactions, and its magnitude is dependent on the polarizability of the sorbed species, where higher polarizability corresponds to stronger binding. In our experiments, the higher removal efficiency of methylbutane, followed by n-butane and finally methylpropane agrees with the increasing polarizability values (Table 5).

It is possible that the different removal efficiencies of the tested compounds relate to the adsorption and desorption rates. In our system, all experimental quantities were measured after an adsorption equilibrium was reached. Therefore, the contribution of the adsorption and the desorption rate to the removal efficiency cannot be ascertained at this stage. Further investigation such as the measurement of adsorption isotherms is essential to determine the rate constants of both processes and is the subject of the future direction of this project.

### 4.2.2 High temperature

The effect of increased temperature on adsorption and subsequently on removal efficiency was tested to determine applicability of the magnetite nanoparticles at different conditions. Experiments carried out at 353 K are represented in Figures 22 and 23. Benzene and toluene are removed by 50-65\%, and 60- 95 \%, respectively, and that methylbutane, methylpropane and n-butane were removed by 0—17\%, 0-30\%, and 0-30 \%, respectively.
Figure 22: Removal efficiencies at high temperature

Figure 23: Average removal efficiencies (n=4 for toluene, benzene, and methylbutane; n=3 for n-butane, methylpropane). Error bars represent standard error.
The decrease in removal % shows adsorption is not as efficient at higher temperature for the tested compounds, the decrease being more significant for light hydrocarbons compared with aromatics. The variability is larger for all compounds especially methylpropane.

This can be explained by lower adsorption energies of physisorbed compounds, which are more sensitive to an increase in temperature; hence desorb more easily. In fact, the desorption by temperature swing exploits the reversibility of physisorption allowing regeneration of adsorbent. The lower effect on aromatic-adsorbent interaction can be attributed to the stronger binding due to the specific acid–base properties characteristic of their binding to magnetite; the acid-base interactions allow them to bind more strongly, and have higher adsorption energies, which would require higher temperature for desorption or renders their desorption more difficult than that of alkanes.

Adsorption is therefore favoured at lower temperatures. In practice, exhaust or flue gas temperature will be lowered by a turbulence cooling system, which our group has developed; application with magnetite nanoparticles will be the subject of future work.

4.2.3 Adsorption with activated carbon coated with magnetite nanoparticles

The efficiency of granular activated carbon coated with magnetite nanoparticles (935.2 m². g⁻¹) for the removal of benzene and toluene at concentrations of 20 ppm was tested, and compared with ordinary activated carbon (1117.4 m². g⁻¹). Toluene is removed by 94% and benzene by 85% and 86% for coated and uncoated carbon, respectively, and is within the experimental uncertainty errors. Figure 24 shows the removal efficiency for coated and uncoated activated carbon. As previously mentioned, factors influencing the removal efficiency also include the surface area. In the case of activated carbon vs coated activated, the indifference in removal efficiency of benzene and toluene was not a coincidence. The heterogeneity of the magnetite coating does not allow surface area and nature of sites’ (π interactions with magnetite acidic sites) to be singled out. To determine
which factor has a greater influence on the removal efficiency, a controlled surface coverage with monodisperse particles is needed.

![Graph showing removal efficiency by magnetite coated (dark) and uncoated activated carbon (white). Error bars represent propagation of errors. This is the result for one run only.](image)

**Figure 24:** Removal efficiency by magnetite coated (dark) and uncoated activated carbon (white). Error bars represent propagation of errors. This is the result for one run only.

The coated carbon was tested in an external facility (Concordia University) for the removal of 10 ppm toluene from indoor air streams. The removal efficiency was 70%, 20% lower than that achieved with uncoated carbon. The test was carried out presence of humidity, which decreased suggesting competition for the sites on magnetite. For practical applications, water removal will be required; one way would be to use multiple interfaces for removal of water before contact with the magnetite surfaces.

### 4.3 Regeneration of magnetite nanoparticles

Regeneration of adsorbent is essential for commercial use. A common challenge for current techniques is the difficulty in regenerating surfaces, which may get poisoned
or degraded by working conditions such as high temperatures and/or presence of poisoning species.

Magnetite nanoparticles were regenerated 4 times by overnight drying at 323 K; removal efficiencies are presented in Figure 25. The removal efficiencies for benzene, toluene and methylbutane remain comparable from the 2\textsuperscript{nd} to the 4\textsuperscript{th} use of the particles, 80-90\%, 90-98\% and 20-25\%, respectively. For light compounds, removal efficiencies remain comparable for 2\textsuperscript{nd}, 3\textsuperscript{rd} 4\textsuperscript{th} uses, but are lower for the first use. Values as high for butane and methylpropane, and as low for benzene and toluene were not reproduced for other first uses so the comparison in terms of removal efficiency is limited to 2\textsuperscript{nd}, 3\textsuperscript{rd} and 4\textsuperscript{th} usage of the particles. The TEM images show that the crystalline structure, and shape of the particles are maintained throughout multiple use/regeneration cycles. X-ray diffraction patterns also show that no phase change had occurred, which confirms the removal efficiency values obtained for 2\textsuperscript{nd}, 3\textsuperscript{rd} and 4\textsuperscript{th} uses. Figure 25 and 26 shows XRD and TEM for fresh and used particles, respectively. The regeneration experiment under those conditions was performed once. The lower efficiency for n-butane and methylpropane can be attributed to the variability noted in the adsorption of those compounds.

Studies report sintering, and reduction of surface areas for regenerated adsorbents such as TiO\textsubscript{2}, and activated carbon due to high temperature conditions. In our case, high temperatures were not required as the compounds were only weakly adsorbed, and therefore easily desorbed.

Regeneration by washing with distilled water, and drying at 323 K was also carried out. Since particles regenerated once by each technique achieved similar results, subsequent regenerations were carried out by drying only. No recycling was attempted since the particles still achieve removal efficiencies after multiple regenerations. New particles were synthesized because with each experiment some would remain stuck on the walls of the flask due to the stirring- water alone did not remove them, but they were easily dissolved in concentrated HCl.
Figure 25: XRD for fresh (left) and magnetite nanoparticles regenerated 4 times (right)

Figure 26: TEM for fresh particles, 2nd and 4th regenerations (from left to right)
4.4 Photolysis Experiments

Irradiation with UV-Vis light was carried out both in the presence, and absence of nanoparticles, and in two different media, pure air and ultra pure N₂, to determine if removal efficiency % could be improved. Photolysis alone (hv=254nm) reduced the concentration of all tested compounds in N₂ and air, but the reduction in the air medium was higher for all compounds.

Figure 27: Photolysis of selected compounds in air (white stripes) and N₂ (black stripes) for 2 hours. Error bars represent 3 standard deviations.

Benzene and toluene decreased by 22% and 32%, respectively. Propane, butane, methylpropane, and methylbutane decreased by 12%, 12%, 15%, and 17%, respectively. Removals for the selected compounds in both media are presented in Figure 27. No reduction was reported in absence of UV irradiation. However, the reduction % was much higher when gases were exposed to iron oxide nanoparticles in N₂ medium, as illustrated in the previous section. The reduction in our studies can be due to the direct or indirect photolysis routes, where reactive species are formed, and can decompose the selected compounds. Direct photolysis of alkanes as ethane, propane, methylpropane, n-butane,
isobutane, has been reported at wavelengths in the vacuum UV at wavelengths less than 185 nm and presented in Table 10. The range required for their destruction is far more energetic than the output of the lamp used in our experiments (254nm). Therefore, photolysis alone is not a favoured pathway to remove volatile organic compounds.

Table 11 Photolysis wavelengths for selected hydrocarbons

<table>
<thead>
<tr>
<th></th>
<th>Wavelength nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propane</td>
<td>&lt;160 [155]</td>
</tr>
<tr>
<td>n-butane</td>
<td>&lt;185 [156] [157]</td>
</tr>
<tr>
<td>Methylbutane</td>
<td>&lt;147 [158]</td>
</tr>
<tr>
<td>Methylpropane</td>
<td>&lt; 170 [159]</td>
</tr>
<tr>
<td>Benzene</td>
<td>&lt; 200 [160]</td>
</tr>
<tr>
<td>Toluene</td>
<td>253.7 [161]</td>
</tr>
</tbody>
</table>

In contrast, direct photolysis of toluene has been reported at 253.7 nm [161]

\[
C_7H_8 + h\nu \rightarrow CH_3\cdot + C_6H_5\cdot \quad (\text{Equation (21)})
\]

\[
\rightarrow C_6H_5CH_2\cdot + H \quad (\text{Equation (22)})
\]

\[
\rightarrow C_6H_4CH_3\cdot + H \quad (\text{Equation (23)})
\]

The alternative mechanism to explain the reductions in the alkanes subject to UV radiation is through the formation of reactive radicals. The experiments carried out in N\textsubscript{2} contained <2 ppm O\textsubscript{2} as impurity and < 3 ppm H\textsubscript{2}O, while the second set was carried out in air with 20% O\textsubscript{2}. Possible radical formation may be initiated by the photolysis of O\textsubscript{2} or toluene (reactions 21, 22, and/or 23). The former occurs by reaction (24) forming reactive atomic oxygen species, which may then form O\textsubscript{3} by reaction (25). The greater reduction when experiments were carried out in air compared with N\textsubscript{2} suggests O\textsubscript{2} plays a role. Furthermore, reactions carried out in 20% O\textsubscript{2}, and in absence of UV radiation reveal no reduction in any of the compounds. The photolysis of O\textsubscript{3} is known to occur at wavelengths between 240-320 nm [1] therefore the formation of O (\textsuperscript{1}D) by reaction (26) can be anticipated.
O$_2$ + $hv$ (< 243 nm) $\rightarrow$ O ($^1$D) + O ($^3$P)  (Equation (24)) [162]

O ($^3$P) + O$_2$ + M $\rightarrow$ O$_3$ + M  (Equation (25)) [162]

O$_3$ + $hv$ $\rightarrow$ O ($^1$D) + O$_2$ (at 254 nm)  (Equation (26)) [163]

The reactive atomic oxygen may then oxidize the hydrocarbons. The photo-oxidation of toluene by reactive O ($^1$D) has been observed and suggested to occur by reaction (27)

$18$ O ($^1$D) + C$_7$H$_8$ $\rightarrow$ CO$_2$ + H$_2$O  (Equation (27)) [164]

The complete oxidation has not been achieved and intermediates as formic acid and some aldehydes were detected [164].

If the oxidation of toluene by reaction (27) is plausible, the formation of OH• may occur by reaction (28). OH• is a known powerful oxidant formed by reaction (8) and can decompose VOCs according to reaction (9). 2OH• may also lead to the formation of H$_2$O$_2$ by self-reaction.

H$_2$O + O ($^1$D) $\rightarrow$ 2OH•  (Equation (28))

RH + OH• $\rightarrow$ R• + H$_2$O for alkanes (Equation (29))

In the case of aromatics such as benzene and toluene, oxidation occurs by OH• addition by reaction (30 and 31, respectively)

C$_6$H$_6$ + •OH $\rightarrow$ C$_6$H$_7$O• [R•]  (Equation (30))

C$_7$H$_8$ + •OH $\rightarrow$ C$_7$H$_7$O• [R•]  (Equation (31))

or by abstraction for toluene: C$_6$H$_5$CH$_2$• + H$_2$O [1, 165]

These R• may then form RO$_2$• by reaction (32)

R• + O$_2$ + M $\rightarrow$ RO$_2$• + M  (Equation (32))
In the case of toluene, \( \text{RO}_2 \cdot \) forms a bicyclic radical, which reacts with \( \text{O}_2 \) forming a bicyclic peroxy radical \([1]\). Toluene may also react with \( \text{O}_2 \) by reaction (33)

\[
\rightarrow \text{o-cresol} + \text{HO}_2\cdot \quad \text{(Equation (33))}
\]

These radicals may terminate by reactions 34 and 35:

\[
\text{HO}_2\cdot + \text{HO}_2\cdot \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad \text{(Equation (34))}
\]

\[
\text{HO}_2\cdot + \text{RO}_2\cdot \rightarrow \text{ROOH} + \text{O}_2 \quad \text{(Equation (35))}
\]

The radical formation may re-start by photolysis of \( \text{H}_2\text{O}_2 \) yielding 2 \( \text{OH}\cdot \), which can decompose the hydrocarbons. An alternative or concurrent route with reaction (8), which may explain the reductions in hydrocarbons is by \( \text{CH}_3\cdot \) and \( \text{C}_6\text{H}_5\cdot \) reaction with \( \text{O}_2 \) by reaction (32) followed by reaction (36)

\[
\text{RO}_2\cdot + \text{RH} \rightarrow \text{ROOH} + \text{R}\cdot \quad \text{chain propagation \ (Equation (36)) \ [165]}
\]

If no other oxidizing specie is available (\( \text{HO}_2\cdot \)), \( \text{RO}_2\cdot \) may undergo self reactions. An alternative mechanism for the reduction of the other compounds is from

\[
\text{O}_2 + \text{RH} \rightarrow \text{HO}_2\cdot + \text{R}\cdot \quad \text{(Equation (37)) \ [166]}
\]

However, reactions carried out in 20\% \( \text{O}_2 \) and in absence of UV radiation reveal no reduction in any of the compounds. Therefore, the initiation reaction is not likely to occur via reaction (37). To conclude on the definite mechanism by which compounds are reduced, product studies are needed. A recap of possible mechanism is presented in Figure 28.
4.5 Adsorption combined with photolysis

When photolysis was combined with adsorption no improvement was noted under our conditions. The combined effects of adsorption and photolysis are represented in Figure 29.

Figure 28: Summary of possible mechanism for reduction of VOCs by UV irradiation in N₂ and pure air

Figure 29: Removal efficiency of magnetite combined with 40 min irradiation. Error bars represent 3 standard deviations (n=3 for all compounds except benzene, n=2). Values outside 3 standard deviations were omitted.
Irradiation in this set of experiments was carried out for 40 min and with a different lamp. The decrease due to photolysis alone is lower for all compounds compared with data presented in the previous section. The lamp from the first set was damaged and had to be replaced. The output was supposed to be equivalent to that of the new lamp yet discrepancies were noted. Unfortunately, the radiant power was not experimentally determined for the first lamp. Under these new conditions (new lamp), no improvement was noted for the combination of adsorption and photolysis. The combined effect remained within the error bars of experimental uncertainty.

4.6 Data analysis

For the adsorption experiments, the p-values for the set of runs of all compounds were calculated and are tabulated in Table 11

<table>
<thead>
<tr>
<th>Compound</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>0.003</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.005</td>
</tr>
<tr>
<td>Methylbutane</td>
<td>0.003</td>
</tr>
<tr>
<td>n-Butane</td>
<td>0.015</td>
</tr>
<tr>
<td>Methylpropane</td>
<td>0.041</td>
</tr>
</tbody>
</table>

For toluene, benzene and methylbutane, the p-values are very low and disprove the assumption of non treatment or no difference between the pairs. The higher values for light compounds show more support for the assumption of the non treatment, and can be associated with variability in the gas-solid interactions (Section 4.2). In short, the higher p-values of light compounds do not allow a definite conclusion about whether they can be efficiently removed by magnetite under our experimental conditions.

5 The lamp used for the first set to compare photolysis in N₂ and air and represented in Figure 26 was damaged. The replacement achieved lower decreases for all compounds, and was used for the combined experiments of adsorption.
5.1 Conclusion

Aromatics’ adsorption on iron oxide achieves high removal efficiencies comparable to existing high energy techniques. Alkanes were not as efficiently adsorbed, and this was suggested to be due to their lower electron donating ability, which made non specific attractive London forces the sole adsorbing force. In addition to surface interactions, other factors such as adsorption/desorption kinetics and surface area can influence removal efficiencies. Additional experiments to determine adsorption and desorption rate constants and to synthesize monodisperse particles are required to understand what factors that mostly influence removal efficiency.

The experiments did not require additional energy, special maintenance or operating conditions, or disposal of the adsorbents. Magnetite can be a potential adsorbent for aromatics removal at room temperature.

The removal efficiency was found to decrease for all compounds especially alkanes when adsorption was carried out at 353 K. Toluene was the least affected at the high temperature. This was suggested to be due the weaker interactions that bind alkanes to the surface, and make them more easily desorbed. Adsorption conditions should be maintained at room temperature for best removal efficiency as higher temperature showed unfavourable to adsorption of some compounds.

Regenerated nanoparticles did not show any decrease in removal efficiencies for the selected compounds. Magnetite nanoparticles were characterized after each use confirming phase and sizes of the particles had not changed between regenerations, and suggesting these particles may be viable for practical applications.

Direct photolysis was suggested to be possible only for toluene. The reduction of other VOCs was attributed to the formation of radicals most likely from ozone photolysis. They are either attacked by the radicals formed from the toluene decomposition, or from atomic oxygen resulting from the ozone photolysis or from OH•. Product studies are needed to conclude on the most definite mechanism of reduction.
5.2 Future work

The adsorption of light compounds should be tested in a different experimental design that would increase contact between the gases and the nanoparticles. One such system may be a closed loop circular system through which the polluted gas would circulate. Another area worth investigating is the effect of humidity on the adsorption by the magnetite nanoparticles. Other adsorbents have shown that the concentration of relative humidity affects adsorption of gases. So, adsorption at different concentration of water vapour should be carried out. Another continuation of this work may be the study of the effect of polycrystalline structure on the adsorption of pollutants by considering surface energies, identifying the most active sites, and looking at the orientations of sorbed molecules. To conclude on the photolysis pathway of the various compounds, the identification of various intermediates and products should be carried out.

Future work may also include testing anthropogenic magnetite powders released from industrial sources (steel production) for adsorption of VOCs.

Also the effect of other classes of pollutants such as SO$_2$ and NO$_2$, also present in flue and vehicle exhaust, on adsorption of VOCs should be studied in order to determine the application conditions of magnetite as competitive adsorption for VOCs sites may occur. In this case, the study of multiple surface sites for interactions would be needed to remove possible competitors from the stream, if any. This can be accomplished by incorporating different adsorption surfaces for various pollutant removals.
References


Appendix

Definitions

Part per million

\[ ppm = \frac{1 \text{ gas volume (or mole) - identical for ideal gas at 1 atm}}{10^6 \text{ air volume (or mole)}} \]

\[ 1 \text{ ppm (gas)} = \frac{1 \mu L (\text{gas})}{1 L (\text{air})} = \frac{V_m}{MW} \times \frac{1 \mu g}{m^3} \]

\( V_m \) is the ideal gas standard molar volume [reference, #429]

Polarizability

“The polarizability of an atom or molecule describes the response of the electron cloud to an external field. The atomic or molecular energy shift \( \Delta W \) due to an external electric field \( E \) is proportional to \( E^2 \) for external fields which are weak compared to the internal electric fields between the nucleus and electron cloud. The electric dipole polarizability \( \alpha \) is the constant of proportionality defined by \( \Delta W = -\alpha E^2/2 \). The induced electric dipole moment is \( \alpha E \)” [56].

Block copolymer

A polymer composed of more than one type of monomer arranged into distinct segments, or blocks [167].
Histograms computed by SPSS and showing non normal distribution

- Benzene
- Toluene
- n-Butane
- Methylpropane
- Methylbutane