

Review of the Application of Activated Carbon for Sewer Odour Abatement

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Executive Summary

Due to their excellent adsorptive activity and capability for a wide range of chemicals, activated carbon is the most widely used adsorbent in many industrial sectors including sewer odour control applications. This literature review was undertaken to provide a baseline summary of existing knowledge of activated carbon use in odour abatement, including abatement mechanisms, the importance of activated carbon properties and influence of operating conditions on the adsorption performance, and to identify existing knowledge gaps.

Sewer air consists of a wide range of compounds including H_2S and volatile reduced sulfur compounds (VSCs), ammonia, some amines and volatile organic compounds (VOCs). The diversity of chemical groups results in variable adsorption mechanisms with activated carbon materials, hence making complex adsorption processes in odour control applications. The adsorption performance is influenced by a range of variables such as natures of both the compound and activated carbon, reactivity of activated carbon surface, and operating conditions. The important effects of these variables on adsorption effectiveness are sometimes overlooked or not comprehended, resulting in unfavourable outcomes such as premature odour breakthrough, customer complaints and high on-going cost associated with frequent bed replacement.

Understanding removal mechanisms of the dominant odorous compounds in sewer air by activated carbon is essential to optimise the selection, design and operation for a particular odour control application. However, information on the removal mechanisms of most sewer air associated odorous compounds and VOCs are limited in the literature, with the exception of H_2S , whose adsorption mechanism has been intensively studied.

Activated carbon properties including particle size, surface area, porosity, surface chemistry, pH and nature of the adsorbate are found to affect the adsorption effectiveness. Since the properties of activated carbon have been seen to play important roles in adsorption processes, knowledge of these variables is essential to select the appropriate types of activated carbon and design effective adsorbers for a particular odour control application.

Operating conditions such as relative humidity, temperature, pressure, volumetric flow rates and adsorption competition also significantly influence the adsorption effectiveness of activated carbon. In current practices associated with sewer odour control applications, wastewater utilities and industrial partners are often aware of the importance of operating conditions to the performance of the activated carbon adsorbers, but have not completely comprehended their effects or effectively manipulate them for desirable performance outcomes. This is due to a lack of standard guidelines and specific research studies for determining appropriate operating parameters for a particular application.

Currently there is also no standard guideline available to support design and operation of fixed bed activated carbon adsorbers for odour control applications. The design procedures and operational considerations presented in this report are derived from various industrial-accepted practices and experiences. In sewer odour control applications, bed replacement is often based on empirical experience rather than the estimated lifespan suggested by the vendor.

Although activated carbon technology is expensive mainly due to the high on-going cost of replacing adsorbent materials, it is very effective for removal of a wide range of chemicals and highly robust against many operational failures than many other alternative odour control technologies such as biofiltration, biofilters and chemical scrubbers.

Key information identified in the existing literature about the use of activated carbon adsorption in odour control applications includes:

- Adsorption mechanisms of H_2S by various types of activated carbon were intensively studied, showing the conversion of H_2S to elemental sulfur or sulfuric acid as main pathways.
- Particle size affects the adsorption rate and the desirable carbon material should have the smallest particle size with sufficient ability to support bed weight and yield acceptable head losses.
- Surface area is directly related to the amount of adsorption sites on activated carbon, but not a sole factor determining the total adsorption capacity. Therefore it must be

considered in conjunction with other physical and chemical properties.

- Porosity with greater proportion of micropores is desirable for high adsorption capacity. Wide pore size distribution is favourable for adsorption of multiple-compounds of different sizes.
- Acidic surface functional groups favour adsorption of basic compounds while basic surface functional groups favour adsorption of acidic compounds. Increasing surface functional groups enhances adsorption of polar compounds.
- Different types of impregnations can be used to promote chemisorption of specific compounds on activated carbon surface, enhancing their adsorption capacities.
- Surface pH provides information about overall acidity/ basicity of surface chemistry.

Existing knowledge gaps related to the use of activated carbon for odour control applications are:

- Limited information about mechanistic removal/ kinetic of other sewer air malodorous organic compounds and VOCs.
- Lack of information about multicomponent competition for adsorption.
- Lack of full scale data to justify the effects of properties of activated carbon on actual service life and the effects of variations in operating conditions on the adsorber's performance.
- Lack of standard guidelines in design and operation of activated carbon.

To address these knowledge gaps, provide better odour abatement outcomes and improve the design of these systems, the following future works are recommended:

- (i) Identify the typical compositions of major odour causing compounds in sewer air associated with different wastewater sources.
- (ii) Study the adsorption mechanisms of other odorous compounds rather than H_2S , multicomponent adsorption and adsorption competition using equilibrium adsorption and kinetics experiments and analysis on changes of activated carbon properties.
- (iii) Compile information about the design, operations, issues and costs of activated

carbon adsorbers in odour control application from wastewater utilities and industrial partners (access to information is required).

- (iv) Evaluate the performance of full scale activated carbon adsorbers for the removal of odour and key odorants in sewer air.
- (v) Evaluate effects of the properties of activated carbon and operating conditions on the adsorption capacity based on the full scale data.
- (vi) Standardise the designing, operating and monitoring protocols to optimise the use of activated carbon adsorption and support the future practices.

The planned program of incoming experimental works and SP3 will contribute to address points (i), (ii), (iv), (v) and provide information to support point (vi).

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1.0 Introduction

1.1 Overview

Activated carbon is the most widely used adsorbent in many industrial sectors due to its excellent adsorptive properties. Activated carbon has high surface area, a microporous structure and a high degree of surface reactivity that allows it to effectively adsorb a variety of chemical compounds. Moreover, the chemical and physical properties of activated carbon can be modified to match the needs of a particular application by selecting different raw carbon materials, and employing different heat or chemical treatment during the carbonisation and activation processes.

Adsorption with activated carbon is one of most widely used technologies to control odours. With high operation and maintenance costs associated with replacement and regeneration, activated carbon is often used for low contaminant loads such as fouled air from sewers and wastewater treatment processes to ensure acceptable carbon life. Its advantages are consistent performance and mechanically simple processes. The use of activated carbon for controlling odorous emissions associated with sewer is the dominant odour abatement technique in Australia (Sivret and Stuetz, 2010).

Many wastewater utilities often express their concern about the high on-going cost of activated carbon for sewage odour abatement. For example, Sydney Water spent around AU\$ 750,000 per year on granular activated carbon replacement for odour abatement units (Sydney Water, 2009). One of the issues associated with the applications of activated carbon for sewage odour control is that premature odour breakthrough can occur and in some cases necessitate frequent bed replacement which can result in high costs for new material purchasing, labour, maintenance and disposal of exhausted carbon materials.

The composition of sewer air is complex and can contain a wide range of compounds including H_2S , malodorous gases and organic gaseous compounds in low concentrations (typically below 10 ppm). Vendors often cannot guarantee carbon lifespan in wastewater odour control applications. To ensure the selection of more appropriate adsorbent materials and increase the cost-effectiveness of abatement processes, there is a need to understand the

factors that control the level of adsorption of malodorous compounds in this complex humid gaseous matrix by activated carbon. This review supports these objectives by providing a baseline level of knowledge of adsorption mechanisms and the adsorbent operating parameters that influence the effectiveness of activated carbon as odour abatement technology.

This review will be presented in seven sections:

- Section 1 provides brief information on **current status of activated carbon market and its productions and applications**;
- **General principles of the gas adsorption theory** are represented in Section 2 to provide solid background for later discussions and critics on the use of activated carbon as adsorbent material for odour control applications;
- **Adsorption mechanisms for major malodorous compounds and volatile organic compounds present in sewer air** are reviewed in Section 3;
- **The key factors affecting adsorbent performance** (both adsorbent properties and operating conditions) are discussed in Section 4;
- Section 5 provides descriptions and discussion on the **analytical techniques** which are used **to characterise activated carbon properties**;
- In Section 6, the information about **process design, operation and costs** associated with sewer related odour abatement is reviewed; and.
- **Cost-performance analysis** between activated carbon and other available odour abatement methods is represented in Section 7.

1.2 Applications of Activated Carbon

According to BCC research report (2012), activated carbon is one of the major segments of the multibillion-dollar market of nanoporous and microporous adsorbents. The global activated carbon market was worth \$1.8 billion in 2011 and is estimated to reach \$3 billion by 2016 growing at a compound annual growth rate of 11.1% from 2011 to 2016. World demand for activated carbon is forecast to be around 1.7 million tons in 2014. Powdered and granular activated carbons account for 48% and 35% of the global activated carbon market respectively, while other forms of activated carbons (such as pellet, bead and

impregnated carbon) share the remaining portion. Adsorption of substances from liquids by activated carbon has been widely applied:

- in food productions and processing industries (e.g. removals of undesirable odours, colours, unwanted components to improve quality of food materials, preparation of alcoholic beverage, decolorisation of sugar, oils and fats);
- in chemical and pharmaceutical industries (e.g. purification, decolorisation of medicine products), in textile industries (e.g. removal of dyes);
- in petroleum industries (e.g. refining liquid fuels, separation); and
- in environmental sectors (e.g. spill clean-up, groundwater remediation, drinking water filtration).

While water treatment is currently the dominant application of activated carbon, its use for air purification is expected to grow at a fast pace over the next few years since regulatory authorities have increasingly implemented policies and regulations toward to the higher quality standards in air pollution control (BCC-Research, 2012). It is reported that up to 20% of the total production of activated carbon in industrialised countries is being used in gas-phase adsorption processes (Bansal and Goyal, 2005). Major gas phase applications include:

- removal of hazardous substances from industrial exhaust gases;
- odour and air quality control;
- purification of process gases from undesirable impurities; and
- recovery of solvents.

1.3 Production of Activated Carbon

Worldwide, the activated carbon industry produces more than 500,000 tonnes per year (Marsh and Rodriguez-Reinoso, 2006). Activated carbon is produced from solid carbonaceous based materials, such as wood, coconuts shells, fruit stones, lignites, petroleum coke, lignocellulosic biomass, peat and coals. Raw materials used for preparation of activated carbon often vary with their application (**Table 1.1**)

Table 1.1 Characteristics of typical raw materials used for activated carbon production
(Manocha, 2003)

Raw material	Carbon (%)	Volatile (%)	Density (g/cm ³)	Ash (%)	Typical Applications
Softwood	40-45	55-60	0.4-0.5	0.3-1.1	Aqueous phase adsorption
Hardwood	40-42	55-60	0.55-0.8	0.3-1.2	Aqueous phase adsorption
Lignin	35-40	58-60	0.3-0.4	-	Aqueous phase application
Nut shells	40-45	55-60	1.4	0.5-0.6	Vapour phase
Lignite	55-70	25-40	1.0-1.35	5-6	Wastewater treatment
Soft Coal	65-80	25-30	1.25-1.50	2.12	Aqueous & vapour phase adsorption
Petroleum coke	70-85	15-20	1.35	0.5-0.7	Gas-vapour phase adsorption
Semi hard coal	70-75	1-15	1.45	5-15	Gas-vapour phase adsorption
Hard coal	85-95	5-10	1.5-2.0	2.15	Gas-vapour phase adsorption

The raw material used is known to affect the adsorption properties of activated carbon (Yeganeh et al., 2006). Activated carbon with high ash content is often undesirable because the ash content reduces the mechanical strength and adsorption capacity of activated carbon. The surface area of activated carbon, to some extent, is inversely related to the ash content.

Bituminous coal and coconut shells are the oldest media type on the market and the most often used (Nagl, 1996). Coal based activated carbon has features of a wide range distribution of pore sizes including micropores, mainly mesopores and macropores. Meanwhile, the pore structure of coconut shell activated carbon is tighter and more microporous. VOC abatement and solvent adsorption for light molecular weight organics are a good fit for coconut shell activated carbon's microporous structure. Coconut shell based carbons also tend to have greater hardness, more resistance to abrasion and lower ash content than coal based activated carbons of similar grades. In Australia, there is a gradual development in coconut shell activated carbon market with approximately 6000 tonnes of coconut shell activated carbon imported annually from countries like India, Malaysia, Sri

Lanka and Philippines (BCC-Research, 2012). The coconut shell activated carbons from these countries are the best quality because good quality coconuts are harvested in these geographic regions (BCC-Research, 2012). Many of the applications where coal-based carbons have been traditionally used are potentially good applications for coconut shell-based carbon as well.

1.4 Carbonisation and Activation

To transform the raw material into activated carbon, a medium to high temperature treatment (thermal activation) with or without chemical addition (chemical activation) is used to remove solid mass while at the same time creating porous structure (i.e. the voids where removed mass was located). As the production of activated carbon from different source raw material and using different techniques have been discussed in detail in the book "*Active Carbon*" (Bansal et al., 1988), only a brief discussion of the effects of production processes on active carbon surface chemistry are covered and the reader is directed to that book for additional detail.

1.4.1 Heat treatment

Heat treatment is commonly used to transform the raw carbon materials into the activated form. The pore size distribution varies with the increasing heat treatment temperature (Marsh and Rodriguez-Reinoso, 2006). As temperature rises (typically above 280°C), nanometer sized voids start to develop and increase in size (length and breadth) with increasing temperature. However, accessibility to adsorbate gases decreases with increases in heat treatment temperature above 800°C as cross-linking of carbon atoms reduces the space between atoms and essentially closes off the porosity to adsorptive gas. Heat treatment alone produces the early-stage porous structure, but does not completely eliminate all impurities within carbon materials. Oxidising additives are needed during or after the heat treatment to remove further impurities from the voids and increase the porosity of the raw carbon materials. Oxidation processes can be applied using gas phases such as hot steam, carbon dioxide or oxygen or using a liquid phase such as H_3PO_4 , ZnCl_2 or KOH solutions.

Steam activation is the most widely used method for producing activated carbon in the

world. It is reported that significant increases in surface area of heat treated materials can be further achieved by steaming at approximately 900°C (Nagl, 1996). When an acceptable raw material with an initial ash content below 10% is used, steam activation easily yields specific surface areas above 1000 m²/g at a 50% activation conversion degree (Menendez-Diaz and Martin-Gullon, 2006).

It has been reported that activation with CO₂ produces similar micropore volumes as steam activation for the same starting material at similar activating conditions (Linares-Solano et al., 2000). However, the porosity developed during CO₂ activation is narrower with a greater proportion of micropores (below 0.7 nm width), while steam activation results in a development of wider porosity ranging from supermicropores to mesopores (Linares-Solano et al., 2000). Activated carbon with greater proportion of micropores is often suitable for VOC abatement and adsorption of light molecular weight organics.

Activation with oxygen produces highly microporous carbon with extraordinary high capacity molecular sieves and defined pore size distribution (Menendez-Diaz and Martin-Gullon, 2006). Although this method can result in outstanding products, its application is still not practical at industrial scale due to the difficulty in process control and expensive operational costs involved.

1.4.2 Chemical Treatment

Chemical activation using ZnCl₂ or H₃PO₄ is used for raw materials with high volatile content such as wood, almond shells and olive stones. The use of H₃PO₄ is preferred to ZnCl₂ in the current manufacturing of activated carbons because the ZnCl₂ activation method has several limitations including low recovery efficiencies, corrosion problems, the presence of residual zinc in the carbon products, and the need for stringent control of plant emissions (Menendez-Diaz and Martin-Gullon, 2006). Compared with thermal activation, the wood-based carbons activated with H₃PO₄ have lower density, lower abrasion resistance, a more developed mesoporosity and increasing macropore volume (Menendez-Diaz and Martin-Gullon, 2006).

Potassium hydroxide activation is a favourable method for raw materials with low volatile content but high carbon content such as high rank coals, previously devolatilised chars or petroleum coke. Activated carbon with surface area greater than 1500 m²/g can be obtained from the KOH activation process, and even some activated carbon were reported to have extremely high surface areas over 3000 m²/g (Wennerberg and O'Grady, 1987). Carbon activated with KOH often has extremely narrow range of microporosity and does not have mesopores (Menendez-Diaz and Martin-Gullon, 2006). Unlike other chemical activations, the porosity of carbons produced by KOH activation rises due to reactions between the carbon material with KOH that form solid and gaseous by-products that are subsequently burnt off compared to the oxidation or burn-off volatile content in other activation processes. KOH activation is usually carried out in inert atmosphere since the presence of air will result in excessive burn-off of the carbon material or the presence of carbon dioxide prohibits the development of carbon porosity (Lillo-Ródenas et al., 2003).

2.0 Gas Adsorption Theory

The adsorption of compounds in sewer air onto activated carbon follows a general vapour phase adsorption process wherein molecules of compounds in gas stream contact and adhere to a solid surface. The gas molecules being removed are referred to as the adsorbate, while the solid doing the adsorbing is called the adsorbent. The compound molecules or atoms can be either physically or chemically adsorbed, depending on the kind of the forces used to hold the odorants on the adsorbent surface (USEPA, 2008, Mikhalovsky and Zaitsev, 1997, Wynne and Spencer, 1982).

In physical adsorption (also referred as physisorption), the weak van der Waals forces of intermolecular cohesion may cause the gas molecules to bond to the solid surface or to condense into liquid on the solid surface. As a result, physisorption can be easily reversed by decreasing pressure or increasing temperature. In the case of chemical adsorption (also referred as chemisorption), a much stronger chemical bond known as chemical/ionic forces is formed between the adsorbate and the adsorbent. A sharing or exchange of electrons takes place and the process may be irreversible. Although both adsorption processes are exothermic reactions, physical adsorption is non-specific and can rapidly take place between any surface and any gas even at low temperatures, but chemisorption is specific and requires a chemical affinity between adsorbate and adsorbent as well as the availability of activation energy (Schnelle and Brown, 2001, Bansal and Goyal, 2005).

2.1 Physical Adsorption

Adsorption Mechanism

Physical adsorption in porous adsorbent takes place through a series of three steps described in **Figure 2.1**.

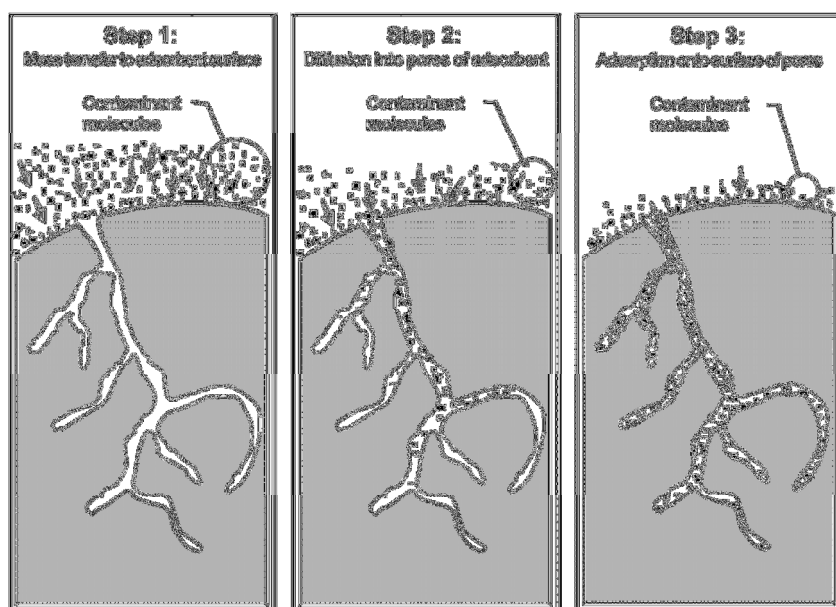


Figure 2.1 Mechanism of adsorption(USEPA, 2008)

In the first step, the adsorbate is transported from the gas phase to the external surface of the adsorbent particle. Interparticle mass transfer in the opposite direction (desorption process) also takes place at the same time, therefore any variations in operating temperatures and feed gas concentration can affect the adsorption-desorption efficiency. The rates of mass transfer are limited by a relatively thin film of comparatively stagnant gas phase immediately surrounding each of the adsorbent particles. In the second step, the adsorbate molecules from the external surface enter the porous structures within each adsorbent particle via molecular diffusion, the rate of which is dependent on the pore radii and molecular size of the adsorbed compounds. The bulk of adsorption occurs in these pores because the majority of the available surface area there. Finally, the adsorbate molecule adheres to the surface in the pore by the weak van der Waals forces of intermolecular cohesion. When the molecules adhere in the voids, they lose some energy in the forms of heat. Therefore, adsorption is exothermic.

Multiple layers of the adsorbed molecules referred as multimolecular layers are often formed on the surface of the adsorbent (Schnelle and Brown, 2001, Bansal and Goyal, 2005). Monomolecular adsorption between the adsorbate molecules and the surface of the adsorbent takes place first at low relative pressure (a ratio between partial pressure and saturation vapour pressure). After the completion of the first layer, second and subsequent layers can be formed as relative pressure increases. These subsequent layers are formed and

bound to the first layer by the forces similar to those in ordinary vapour condensation. That means the adsorbate molecules in the second and subsequent adsorption layers remain chemically unchanged from the gaseous phase.

An additional adsorption mechanism in physical adsorption is capillary condensation (Schnelle and Brown, 2001). According to these authors, the concept of capillary condensation is that adsorbate gas or vapour may condense to form a meniscus in the capillaries of the adsorbent as a result of the lowering of vapour pressure brought about by surface tension effects. Due to the increased number of van der Waal's interactions between the gaseous molecules in the confined space of the capillary, the condensation of gases takes place at the vapour pressure below the saturation vapour pressure of the liquid. The capillary condensation first fills up the smallest capillaries at the lowest vapour pressure and then fills larger capillaries as the pressure increases. The capillary condensation proceeds until saturation vapour pressure is reached and all pores are filled with liquid. In a given adsorbate-adsorbent system, unimolecular adsorption, multimolecular adsorption and capillary condensation can all take place, but unimolecular adsorption must precede the other two adsorption mechanisms.

Nature of Adsorption Forces

The forces active in physical adsorption are electrostatic in nature (USEPA, 2008, USEPA, 1999). These are the same forces of attraction which causes gases to condense and real gases to deviate from ideal behaviour. The specific electrostatic effects which produce the van der Waal's forces depend on the polarity of the both the adsorbent and the adsorbate (**Figure 2.2**). These effects can be classified into three groups: an orientation effect, dispersion effects and induction effects. For polar molecules, the attraction to each other occurs because of the orientation effect caused by the attraction between the dipoles. The adsorption of a nonpolar gas molecule onto a nonpolar surface is accounted for by the dispersion effect based on its oscillating dipole (momentary changes in electron distribution around the atomic nuclei). The attraction between a polar and nonpolar is caused by the induction effect. A molecule with a permanent dipole can induce or polarize a nonpolar molecule when they come in close contact, although this induction effect is very small compared to the orientation and dispersion attraction.

Since activated carbon is non-polar in nature due to the presence of many polar functional groups, all three electrostatic effects can occur on the activated carbon surface. This makes it a suitable adsorbent for removing many polar and non-polar compounds via physical adsorption in odour control applications.

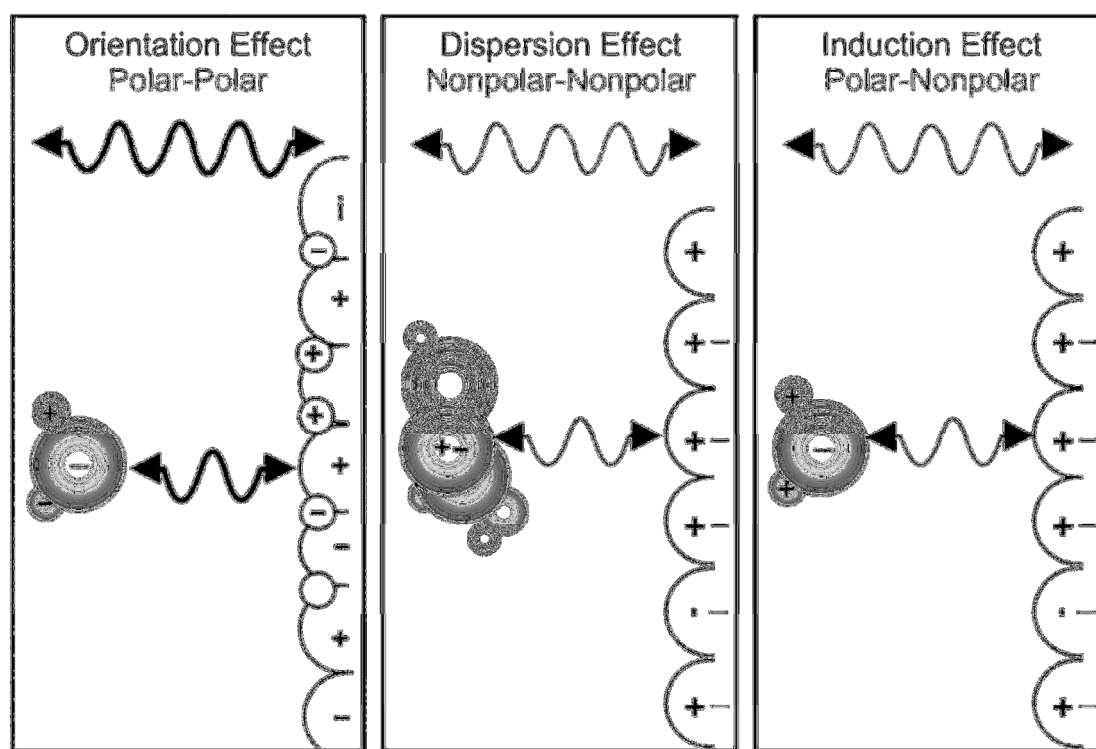


Figure 2.2 Effects of physical adsorption (USEPA, 1988)

Adsorption Equilibrium

The rate of physical adsorption depends on the equilibrium established between intermolecular interactions and the interaction of a molecule with the pore wall. This rate will vary for particular organic compounds being removed as well as for individual applications. Initially the rate of adsorption is large because the whole surface is available for adsorption. As adsorptive sites are occupied, the rate of adsorption can vary due to the occurrence of multi-layer adsorption following the formation of an adsorbate monolayer and due to competition of different compound molecules for the occupied sites. Parallel to this process, the rate of desorption (the rate at which the adsorbed molecules rebound from the adsorbent surface) increases. The equilibrium is reached when net adsorption is zero, i.e.

adsorption and desorption rate are equal. At the equilibrium, the chemical potentials of the free adsorbates equal that of the surface bound adsorbates.

Qin et. al. (2012) found that the time to achieve equilibrium (i.e. rate of adsorption) is significantly affected by the size of adsorbent particles. The smaller the particle size, the faster the equilibrium is reached. This is due to penetration of the adsorbate inside the adsorbent via internal diffusion and mass transfer being less restricted for smaller particles. For a given adsorbate-adsorbent system, the amount of the adsorbate adsorbed onto the surface of the adsorbent at the equilibrium depends on the pressure of the gas and the temperature of adsorption (Bansal and Goyal, 2005), with adsorption capacity increasing with increased pressure and decreased temperature.

Adsorption Selectivity

Physical adsorption of gases and vapour does not involve formation of chemical bonds. Instead, selective adsorption between adsorbates and adsorption sites (i.e. carbon surface) occurs during an entire adsorption process because adsorbates differ in molecular size and polarity from the surface of the adsorbent (Guo et al., 2007, Mikhalovsky and Zaitsev, 1997, USEPA, 2008). Non-polar adsorbents are preferable for nonpolar gaseous compounds while the polar adsorbents are primarily used for adsorbing water vapour and other polar compounds.

For microporous adsorbents, a strong pore filling effect occurs if the adsorbate molecules are similar in size to the micropores. This effect is governed by the overlapping adsorption potential of surrounding pore walls on the adsorbate molecules (Everett and Powl, 1976, Mangun et al., 1998). Small pores have higher overlapping potentials which hold adsorbate molecules of similar size tightly in the central position of the pore walls. In larger pores the overlapping potential is not strong enough for the adsorbate to fill the pores and thus the molecules are adsorbed onto the pore walls.

From an energetic view point, the progressive occupancy of adsorption sites is not a random process but one of selecting the next best available site. Not all gases are adsorbed equally and their adsorption may vary with different adsorbent materials. This implies that the

capacity of an adsorbent should be assessed against the least strongly adsorbed odorant because breakthrough of the less well adsorbed odorants occurs before those more strongly adsorbed (Smet et al., 1998).

2.2 Chemical Adsorption

Chemical adsorption (or chemisorption) results from the chemical interaction between the gas (adsorbate) and the solid (adsorbent). The gas molecules are held to the surface the adsorbate by the formation of a chemical bond. Oxidation of adsorbed odorant can occur due to catalytic reactive properties of the adsorbent surface or the action of impregnated oxidants.

Chemically adsorbed molecules lose their identity compared with those in the gas phase. The energy required to desorb compounds that have been chemically adsorbed is much higher than for those that have been physically adsorbed. Modified and impregnated adsorbents used for air treatment provide higher oxidative capacities than most virgin activated carbon, especially under high levels of humidity. The presence of humidity facilitates the oxidation reaction promoting effective removal (Adib, 2000). While physisorption may be a multimolecular process, the adsorbed layer in chemisorption is always unimolecular (Schnelle and Brown, 2001).

For adsorption onto activated carbon, physisorption tends to be the dominant mechanism. For any adsorbate, physisorption can occur on the unoccupied surface of the activated carbon and even on the layers of adsorbed molecules. In contrast, chemisorption depends on the availability of specific reactive sites on the activated carbon surface which can chemically react and/or bond with a given adsorbate. It implies that chemisorption can only take place on some solid surfaces for a given gas.

In a given adsorbate-adsorbent systems, the type of adsorption that takes place is governed by the nature of the adsorbate and adsorbent, the reactivity of the adsorbent surface, the surface area of the adsorbent, temperature and pressure of the adsorption. Therefore, it is often difficult to confirm whether the process of adsorption is either physisorption or chemisorption, or if both are occurring in appreciable proportions (Bansal and Goyal, 2005).

2.3 Adsorption Isotherm

Adsorption isotherms are commonly used to describe the equilibrium of adsorption of the adsorbate onto the surface of the adsorbent at a constant temperature. Adsorption isotherms describe how adsorbates interact with adsorbents and are critical in optimising the use of adsorbents (Steijns and Mars, 1977). The experimental adsorption equilibrium data is fitted into different isotherm models to find the suitable model. An adsorption isothermal curve is a plot of the adsorption equilibrium data as “capacity or loading” against fluid-phase concentration (or partial pressure for gas and vapour). For design purposes, adsorption isotherm can be used to determine amount of adsorbent required, which fixes the adsorber vessel volume and determines the adsorbent cost (Kent, 2008). Adsorption isotherms can also provide information on the adsorption mechanism associated with the interactions between the adsorbate and adsorbent molecules (Cook and Ross, 1973).

Several isotherm models exist, the most important being Freundlich, Langmuir, Brunauer-Emmet-Teller (BET) and Dubbin Equations. Detailed information about the isotherms and the multitude of equations can be found in several publications (Bansal and Goyal, 2005, Thomas and Crittenden, 1998, Schnelle and Brown, 2001, Kent, 2008). This section provides an overview of the important features of these isotherms.

Freundlich

The Freundlich isotherm equation is a purely empirical formula that is widely used for liquid and gaseous adsorption due to its simplicity. It is, however, valid only for unimolecular adsorption. The Freundlich isotherm can apply for both physical and chemical adsorption, although it is most applicable for the later.

Langmuir

The Langmuir isotherm equation was developed using thermodynamic and statistical approaches, focusing on the importance of dynamic adsorption equilibrium. Although the applicability of the Langmuir isotherm to experimental data in chemisorption and physisorption was investigated in many studies, only a few data fit this equation (Bansal and Goyal, 2005). The assumptions that (i) surface of the adsorbent is energetically uniform; (ii) there is no lateral interaction between the adsorbed molecules; (iii) all adsorption occurs

through the same mechanism; and (iv) only monolayer is formed are the limits of this model. The Langmuir isotherm is mainly used as a basis to derive more complex models.

Brunauer-Emmet-Teller (BET)

The BET Equation is a generalisation of the Langmuir concept to address the issue of multimolecular adsorption, but it is still bound to the other assumptions inherent in the Langmuir isotherm. In BET theory, only the first layer of the adsorbed molecules is formed by the interaction between the adsorbate and adsorbent (i.e. unimolecular adsorption). The subsequent layers are formed via a process similar to ordinary gas/vapour condensation. Bansal and Goyal (2005) point out that the BET equation provides reasonable values for the average enthalpy of adsorption in the first layer and satisfactory values for the monolayer capacity of the adsorbate which can be used to calculate the specific surface area of the solid adsorbent, but its applicability is limited to within the relative pressure range of 0.05 to 0.35. Outside this range, the effects of heterogeneity of the adsorbent surface and capillary condensation become significant and the BET equation loses its validity.

Dubinin

The Dubinin equation (derived from the potential theory of Polanyi) is widely used to describe the physical adsorption of gases in microporous materials, especially those of a carbonaceous origin. The Dubinin equation is valid over relative pressures from 1×10^{-5} to 4×10^{-1} , which corresponds to about 85 to 95% filling of the micropores (Bansal and Goyal, 2005). At relative pressures below 10^{-5} , ultra-fine micropores that are not accessible to larger molecules are filled.

Adsorption Isotherm Classification

Adsorption isotherms can be classified into five different types from I to V, illustrated in the **Figure 2.3**. The shape of each isotherm type can be explained by its adsorption characteristics (Thomas and Crittenden, 1998).

Type I isotherms are typically observed for the adsorption of gases on microporous materials whose sizes are not much larger than the molecular diameter of the adsorbate. This adsorption is limited to the pore filling mechanism and the completion of a single monolayer

of adsorbate at the adsorbent surface.

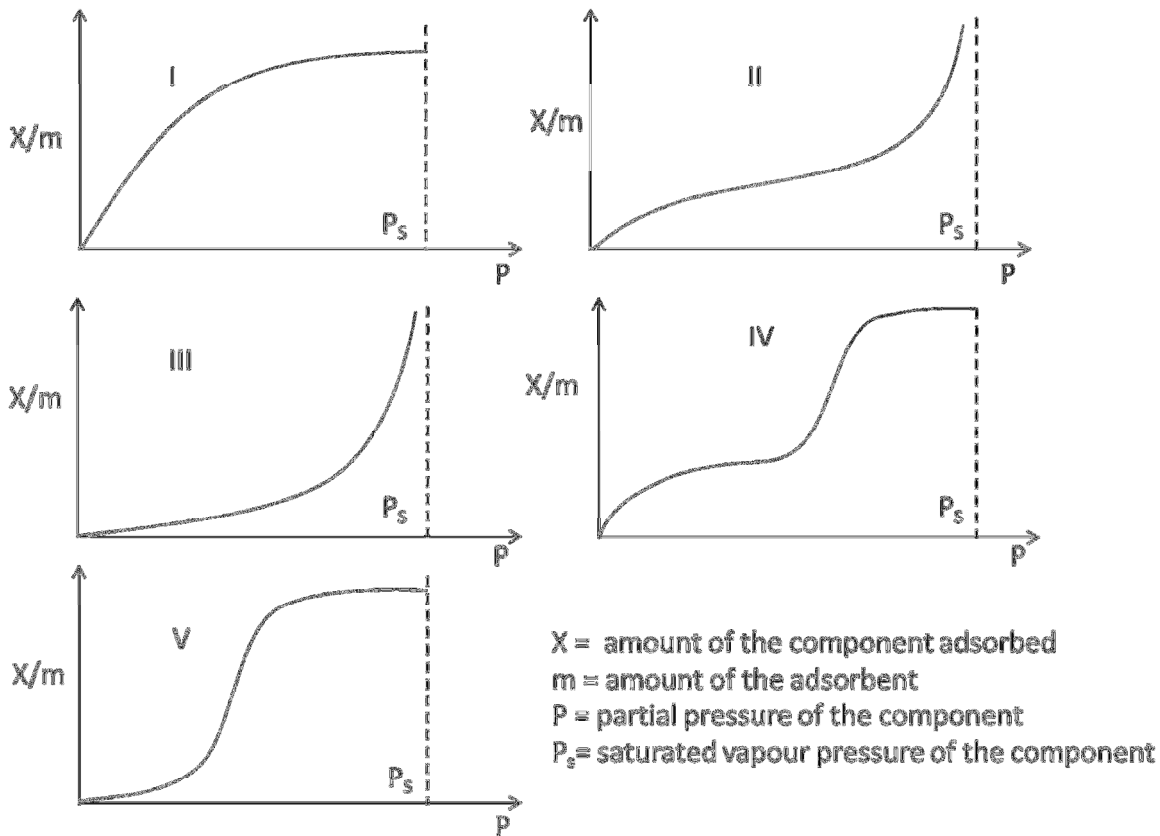


Figure 2.3 Typical shapes of the five types of adsorption isotherm

Type II isotherms do not exhibit the saturation limit and represent multilayer adsorption in which a monolayer adsorption occurs prior to the first point of inflection and then adsorption continues to occur in subsequent layers (i.e. condensation of adsorbate gases). Type II isotherms are observed for adsorbents that have a wide pore size distribution. The adsorbent displays a greater increase in its adsorption capacity as the adsorbate saturation vapour pressure is approached.

Similar to type II isotherms, Type III isotherms describe multilayer adsorption and show a steady increase in adsorption capacity with increasing relative pressure. However, the lack of a flat portion in the curve indicates that monolayer formation is missing.

Type IV isotherms are quite similar to Type II isotherms at the lower pressure region of the graph, explaining the formation of monolayer and subsequent multilayers. At the higher pressure region of the Type IV graph, capillary condensation occurs at pressure below the

saturation vapour pressure of the adsorbate.

Type V isotherms are similar to Type III isotherms (representing the multilayer adsorption) at low relative pressure, but are similar to Type IV isotherms at high relative pressure (capillary condensation). Hysteresis loops often occur in Type IV and Type V isotherms because of capillary condensation. Hysteresis occurs when desorption follows a different path from the adsorption, usually as a result of liquid filling pores in a certain way that is not the same as when they are removed (Kent, 2008). Although it is not common, hysteresis loops may be observed in isotherms of other types, providing useful information on the geometric shapes of pores in which vapour condensation occurs (Thomas and Crittenden, 1998).

The shape of an adsorption isotherm can provide important information about the adsorption of malodorous and volatile organic compounds such as if monolayer, multilayer and/or capillary condensation adsorption occurs at different partial pressures (i.e. concentration) of the compounds. At the time writing this report, there were no available adsorption isotherms between activated carbon and sewer related odorous compounds in the literature surveyed. As a result it is difficult to clearly understand mechanistic physical adsorption mechanisms between activated carbon and malodorous compounds in the sewer air.

2.4 Adsorption kinetics

Another conventional approach to investigate the mechanisms of adsorption involves kinetics-based modelling. Kinetic analysis helps to establish a rate of adsorption and determine the contact time required for an adsorption process, both important factors in adsorption system design (Rashidi et al., 2013, Ho, 2006). Adsorption kinetics also provide a baseline to determine the performance of adsorption systems.

Kinetic models can be classified as adsorption reaction models or adsorption diffusion models. The numerous kinetic based models used to describe kinetic process of the adsorption systems have been comprehensively reviewed (Ho et al., 2000, Ho, 2006, Qiu et al., 2009). Several kinetic models such as pseudo second order rate equation, Elovich's equation, and Ritchie's equation and intraparticle diffusion models were reported to be applicable for kinetic analysis of gas/solid adsorption. However, Qiu et al. (2009) concluded

that if the physical adsorption is mainly dominant, intraparticle diffusion models better represent the adsorption and provide insight into the adsorption mechanism than adsorption reaction models.

Adsorption is part of a continuous process and usually conducted at steady state conditions. In adsorption systems with very high adsorption rates, steady state could be viewed as an equilibrium state and understanding equilibrium adsorption means understanding the entire adsorption process. However, for most full scale applications steady state remains far apart from the equilibrium and additional knowledge about adsorption kinetics is essential for precisely describing the performance of an adsorption unit (Islam et al., 2004). While information about adsorption equilibrium (such as isotherms) completely defines the adsorption process in equilibrium state at a given temperature, kinetic analysis produces empirical values of parameters of adsorption processes and is valid only for a given set of conditions (i.e. initial solution concentration/partial gas pressure and amount of adsorbent used).

3.0 Adsorption of Odorous Compounds and Volatile Organic Compounds by Activated Carbon

Sewers are a potential source of odour emissions due to the presence of many malodorous compounds, including hydrogen sulfide, reduced sulfur compounds, ammonia and amines.

Table 3.1 shows typical malodorous compounds and their concentrations found near the facilities associated with wastewater treatment processes. Hydrogen sulfide, carbonyl sulfide, carbon disulphide, and ammonia are typically the most abundant compounds in the air around sewage associated infrastructure (Devai and DeLaune, 1999, Jeon et al., 2009). High levels of dimethyl sulfide, dimethyl disulfide and carbon disulfide are often found at the sludge handling infrastructure (Ras et al., 2008). Despite being less abundant, methyl mercaptan and trimethyl amine are significant odorants due to their low odour threshold along with dimethyl disulfide, dimethyl sulfide and hydrogen sulfide (Jeon et al., 2009).

While adsorption based odour abatement focuses on the removal of specific odorants, potential interaction between the adsorbent and the wide range of non-target compounds (odorous and non-odorous compounds such as VOCs, sulfur and nitrogen containing molecules) often occurs. Understanding of removal mechanisms of targeted odours compounds by activated carbon is important to enhance the selection of adsorbent materials, and design and operation of an odour abatement process in order to improve odour abatement outcome. Existing knowledge of adsorption mechanisms for major odorous and non-odorous VOCs found in sewer air is discussed in this section.

Table 3.1 Typical malodorous compounds and their concentration ranges near the facilities associated with wastewater treatment processes

Compound	Concentration range (mg/m ³)	Sampling location	Reference
H ₂ S	1.57 – 16+ ⁽¹⁾	Main intake	(Patria et al., 2001)
	34.8 – 47.1	Sewage creek	(Muezzinoglu, 2003)
	2.8 – 18.2	Inlet structure	(Al-Shammiri, 2004)
	37.2 – 66.5 ⁽¹⁾	Grit chamber outlet	(Cooper et al., 2001)
	0.04 – 0.76	Pump stations	(Dincer and Muezzinoglu, 2007)
	0.0001 – 0.033 ⁽¹⁾	Primary settling basin	(Jeon et al., 2009)
	0.00004 – 0.038 ⁽¹⁾	Aeration basin	(Jeon et al., 2009)
DMS	0.0007 – 0.0075	Primary treated sewage	(Ras et al., 2008)
	0.0004 – 0.61	Sludge handling facilities	(Ras et al., 2008)
	< 0.0016 ⁽¹⁾	Primary settling basin	(Jeon et al., 2009)
	< 0.01 ⁽¹⁾	Aeration basin	(Jeon et al., 2009)
	0.0034 – 0.037	Nearby WWTPs	(Leach et al., 1999)
DMDS	0.0087 – 0.040	Primary treated sewage	(Ras et al., 2008)
	0.0011 – 0.86	Sludge handling facilities	(Ras et al., 2008)
	0.00007 – 0.29 ⁽¹⁾	Primary settling basin	(Jeon et al., 2009)
	0.0018 – 0.033 ⁽¹⁾	Aeration basin	(Jeon et al., 2009)
	0.002 – 0.039	Nearby WWTPs	(Leach et al., 1999)
CDS	0.0003 – 0.42	Primary treated sewage	(Ras et al., 2008)
	< 0.66	Sludge handling facilities	(Ras et al., 2008)
MM	0.00001 – 0.01 ⁽¹⁾	Primary settling basin	(Jeon et al., 2009)
	< 0.0024 ⁽¹⁾	Aeration basin	(Jeon et al., 2009)
	0.0033 – 0.068	nearby WWTPs	(Leach et al., 1999)
TMA	< 0.004 ⁽¹⁾	Primary settling basin	(Jeon et al., 2009)
	< 0.001 ⁽¹⁾	Aeration basin	(Jeon et al., 2009)
Ammonia	0.48 – 1.47	Primary settling basin	(Jeon et al., 2009)
	0.069 – 0.39	Aeration basin	(Jeon et al., 2009)

(1) Converted from ppm to mg/m³

CDS: carbon disulfide

DMDS: dimethyl disulfide

DMS: dimethyl sulfide

MM: methyl mercaptan

TMA: trimethyl amine

3.1 Sulfur dioxide

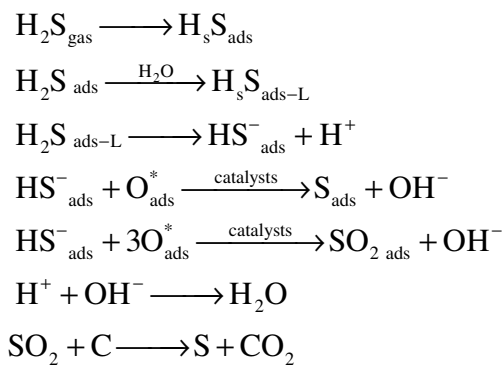
While not generally perceived as a sewer odorant, sulfur dioxide (SO₂) is abundant in the sewer headspace air and can cause severe corrosion problems due to its conversion to H₂SO₄. SO₂ is also an intermediate product in the oxidation process of several sulfur reduced malodorous compounds in the sewer air. According to Bandosz (2006), SO₂ can be removed from the gas stream by physical adsorption either on the walls of activated carbon or via the filling of micropores. Bandosz (2006) also found that sulfur dioxide inside carbon pores is further oxidised in the presence of moisture and oxygen to sulfuric acid, which is

accepted as the final product of the chemical immobilisation. Sulfuric acid is strongly retained in the pore system of the activated carbon, possibly by ionic bindings between the sulfate ions and positively charged activated carbon surface groups (i.e. basic functionalities). It has been observed that the greater degree of oxidation of SO₂ occurs, the greater the level of SO₂ adsorption (Raymundo-Piñero et al., 2000).

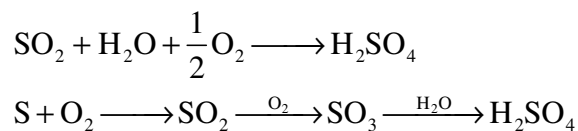
3.2 Hydrogen Sulfide

Due to the lower sulphur oxidation state in H₂S compared to that in SO₂, more complex catalytic oxidation of H₂S takes place on the surface of activated carbon (Bandosz and Ania, 2006). Removal of H₂S via chemical adsorption is either in the form of SO₄²⁻ and/or elemental sulfur. Surface oxidation reactions with adsorbed oxygen or catalysts (i.e. transition metals such as Fe, Zn and Cu in carbons) occur to form sulfur dioxide (SO₂) or elemental sulfur. Further oxidation of SO₂ to H₂SO₄ proceeds in the presence of water.

The pathway of H₂S oxidation on **virgin activated carbon** has been well described in the literature (Bagreev et al., 2000, Bandosz, 2002, Yan et al., 2002) and can be illustrated as follows:



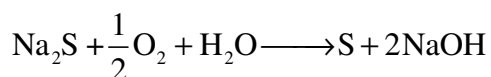
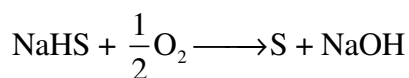
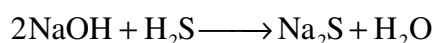
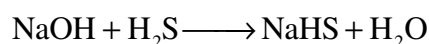
When the moisture is present, the following processes can occur:



Where the subscripts “gas”, “ads-L”, and “ads” refer to the presence of the reactants in gas, liquid and adsorbed states, respectively.

When the reaction occurs in very small pores, sulfuric acid is the dominant product because sulfur radicals in pores of this size are very susceptible to further oxidation to SO₂ and SO₃. The oxidation of SO₂ to SO₃ only takes place with the presence of O₂ in the gas phase and total SO₂ uptake is strongly influenced by the oxidation of SO₂ to SO₃ inside micropores (Raymundo-Piñero et al., 2000). It has been reported that more than 90% of H₂S reacts to form sulfuric acid (Dawson and Beyerlein, 1997). All the adsorption processes are exothermic; however the energy required extracting the adsorbate from the chemisorption surface is much higher than physical adsorption (Adib, 2000). The adsorption of sulfuric acid in the pore system is very strong and temperatures of higher than 673 K are often required to regenerate the catalysts (Bandosz and Ania, 2006).

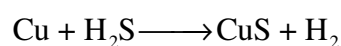
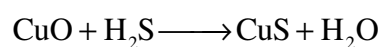
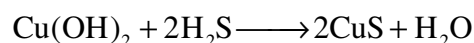
For **caustic impregnated activated carbons**, catalytic reactions of alkaline hydroxides and H₂S also occur to form products such as sulfites, sulfides and elemental sulfur. The alkaline oxidation pathway for NaOH impregnated carbon is as follows:



Alkaline oxidation from H₂S to elemental sulfur enhances the adsorption capacity of activated carbon. However, oxidation to products such as sulphites, sulfides or sulfates reduces the overall capacity because bulky alkali sulfides, sulfites and sulfates occupy a much larger portion of pore volume than elemental sulfur. Oxidation products from H₂S in alkaline media are non-volatile and the oxidation is irreversible, so a desorption does not occur (Turk et al., 1989).

Other oxidation catalysts such as metallic oxides or noble metals can also be impregnated on the carbon surface to encourage chemisorption, enhancing overall adsorption capacity. Formation of metal sulfide occurs when reduced sulfur compounds react with the impregnated salt or oxide of a suitable metal. The resulting sulfides are fixed on the carbon.

The oxidation reaction pathways depends on the metal impregnation. For example, in the case of copper impregnated activated carbon the oxidation pathways occur as follows:



Since the oxidation to elemental sulfur provides greater adsorption capacity than other oxidation products (e.g. sulfides, sulphites and sulfates), catalytically active ingredients such as Al_2O_3 , ZrO_2 and TiO_2 can be used to selectively oxidise hydrogen sulfide and other reduced sulfur compounds mainly to elemental sulfur and increase adsorption capacity (Graham, 2006, Steijns and Mars, 1977). These catalysts are added before the carbon activation process to become the integral parts of the carbon pore structure and will not be consumed during the oxidation of H_2S . Activated carbon with these incorporated catalysts is known as sulfur selective activated carbon. Other metal impurities in activated carbon such as oxides of Fe, Co, Mo, Ni and W have been observed to promote the direct conversion of H_2S into SO_2 (Cook and Ross, 1973, Ross and Jeanes, 1974, Steijns and Mars, 1977). The kinetic conversion of hydrogen sulfide to elemental sulfur tends to be slower than the non-selective oxidation to sulfuric acid (Graham, 2006). Therefore, sulphur selective activated carbon requires a longer retention time and slower superficial velocities to optimise the oxidation of H_2S to elemental sulfur. The adsorbed elemental sulfur can be extracted using ammonium sulfide (Stirling, 2000).

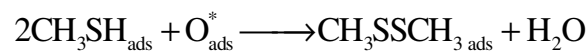
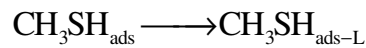
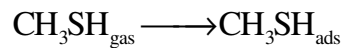
3.3 Methyl Mercaptan

Based on the results of a differential heat adsorption study, Tandaha and Boki (1978) concluded the adsorption of methyl mercaptan on virgin activated carbon is due to volume filling of micropores and the adsorption of monolayers or multilayers on transition pores. Catalytic oxidation of methyl mercaptan adsorbed in the carbon pores also occurs in wet conditions. According to Bashkova et al. (2002), the removal of methyl mercaptan follows two possible reaction pathways that are dependent on the pH of the system.

If the **pH is less than the pK_a** of methyl mercaptan ($\text{pK}_a = 10.3$), the adsorbed methyl

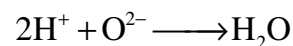
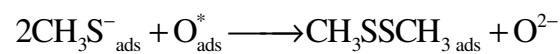
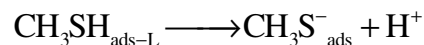
mercaptan is dissolved into the aqueous solution or oxidised into dimethyl disulfide which is then strongly adsorbed in carbon pores. Methyl mercaptan is readily oxidised to dimethyl disulfide on the carbon surface, with the almost doubled molecular weight yielding an increased capacity for physical adsorption (Turk et al., 1989).

At $\text{pH} < \text{pK}_a$



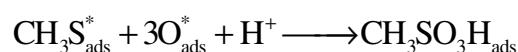
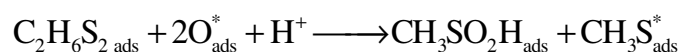
If the **pH is greater than pK_a** , the dissociation of methyl mercaptan into thiolate ions is dominant and concentrations of thiolate ions increase. Thiolate ions are then further oxidised to dimethyl disulfide, which is strongly adsorbed onto the activated carbon.

At $\text{pH} > \text{pK}_a$



Bashkova et al. (2002) also suggested that dimethyl disulfide is not the only product of the surface reactions, but can be further oxidised in the presence of water to form sulfinic acid and methane sulfonic acid. The formations of these strong acids, particularly sulphonic acid, are well associated with a significant reduction in pH of the system after methyl mercaptan adsorption.

Further oxidation of dimethyl disulfide



3.4 Other odorous sulfur compounds

Dimethyl disulfide

As mentioned previously, dimethyl disulfide, $[\text{CH}_3\text{SSCH}_3]$ is formed by the decomposition of methyl mercaptan and its formation is enhanced in the presence of water. It is believed that dimethyl disulfide is more strongly adsorbed on the surface of activated carbon than water; thus it possibly replaces water from the carbon surface as well as weakly adsorbed compounds (Bansal and Goyal, 2005).

Dimethyl sulfide

Besides physical adsorption, Goyal et al. (2008) suggested that the adsorption of dimethyl sulfide may also involve specific interactions between acidic surface groups and dimethyl sulfide molecules through chemical and quasichemical forces involving hydrogen bonding. They observed that the adsorption capacity is enhanced when the amount of the acidic oxygen-containing surface groups increased and decreased gradually when these surface groups are eliminated through increasing levels of heat treatment in a vacuum.

Carbonyl sulfide

Chemisorption of carbonyl sulfide is not clearly defined. The study by Sattler and Rosenberk (2006) demonstrated that the adsorption of carbonyl sulfide by activated carbon decreases in the presence of H_2S in the gas stream, implying carbonyl sulfide has a lower affinity toward activated carbon than hydrogen sulfide. The introduction of ammonia in the feed gas stream enhanced the effects on the adsorption of H_2S , but not carbonyl sulfide (Sattler and Rosenberk, 2006).

Carbon disulfide and dimethyl trisulfide

Carbon disulfide and dimethyl trisulfide are two other odorous reduced sulfur compounds commonly found in sewer air. Adsorption with activated carbon is reported to be a superior technique for removal of carbon disulfide since activated carbon has great affinity for carbon disulfide (Ross and Jeanes, 1974). The use of granular activated carbon to effectively remove dimethyl trisulfide in water was studied Zhang et al. (2011). Although there is no study in the surveyed literature specifically investigating the removal mechanisms of carbon disulfide in air by activated carbon, it is expected that sulfuric acids and elemental sulfur would be the

products formed after the binding of reduced sulfur compounds onto activated carbon (Bandosz, 2006).

3.5 Nitrogen Containing Compounds

Ammonia

Ammonia is removed by non-impregnated activated carbon through physisorption of gas molecules inside the carbon pores. For metal oxide impregnated activated carbon, the metal oxides (strong Bronsted acids) promote the protonation of ammonia into ammonium ions, which then interact with metal oxides or acidic surface groups by acid-base interactions (Le Leuch et al., 2010). The water in the adsorbent media also interacts with ammonia to give ammonium due to the Bronsted acidity of water, leading to similar acid-base interactions between ammonium and the activated carbon surface (Le Leuch et al., 2010). Other authors (Hitomi et al., 1993, Iyobe et al., 2004) have reported a correlation between adsorption of ammonia gas and the amount of acidic functional groups on the activated carbon surface.

Trimethyl amine

The adsorption pathways of trimethyl amine and other amines on activated carbon are quite similar as those of ammonia. Iyobe et al. (2004) point out that adsorption of trimethyl amine is effective on adsorbents with well-developed porous structure, large specific area and pore volume, and with dominant acidic groups on the surface.

Heterocyclic N-containing compounds

Indole, skatole and pyridines are other odorous heterocyclic N-containing compounds commonly found in sewer headspace air. It is well known in the air quality control industry that activated carbon has excellent adsorptive capacity for these compounds (El-Guendi, 1991). However, no studies on the mechanistic removal of these compounds by activated carbons in a gas phase were found in the surveyed literature. A few studies investigating the adsorption of these compounds in the aqueous phase were reviewed. A study on the adsorption of indole in an intestinal juice solution with activated carbon by Mintome et al. (2001) showed that activated carbons with appropriate mesopore size and a high amount of micropores are an effective adsorbent for indole removal.

3.6 Volatile Organic Compounds

Activated carbon has been long used in the many applications to remove and recover VOCs from gases and significant literature exists describing these adsorption processes (USEPA, 1988, Bansal and Goyal, 2005, Rafson, 1998, Vatauvuk et al., 1999). A brief overview of VOC adsorption onto activated carbon by provided and the reader is directed to the previous references for further detail.

Physisorption is believed to be the predominant mechanism in VOC adsorption by activated carbon (USEPA, 1988, Schnelle and Brown, 2001). VOC molecules diffuse from the gas phase across the boundary layer to strike the surface of the activated carbon; some rebound while others stick on the solid surface (Schnelle and Brown, 2001). Multi-molecular layers can build up during physical adsorption. Physical adsorption via capillary condensation may also occur as the adsorption forces reduce the vapour pressure in the capillaries present in the activated carbon structure.

Physical adsorption of the adsorbate is maximised in virgin activated carbon and in dry conditions since more adsorption sites are available for the target adsorbate to bind with via van der Waals attractive forces. At high temperature, chemisorption may take place through the formation of the strong chemical bonds between VOC molecules and the activated carbon. For example, the study by Chiang et al. (2001) about the adsorption of C_6H_6 , CCl_4 , $CHCl_3$ and CH_2Cl_2 onto various types of activated carbon indicated that physical adsorption was predominant in low temperature ranges (5°C to 30°C), while chemical interactions between activated carbon and VOCs took place at high temperature ranges (45°C to 80°C).

VOC compounds with high molecular weights and high boiling points a better adsorbed by activated carbon (USEPA, 2008). For nonregenerative activated carbon abatement systems, compounds having molecular weight greater than 50 and/or boiling points greater than 20°C can be effectively adsorbed (USEPA, 2008). **Table 3.2** shows the adsorption capacity of activated carbon (the amount of a compound that can be adsorbed on a unit weight of the activated carbon) for a representative list of organic compounds with respect to their boiling points and molecular weight. It should be noted that these results are material specific and may vary between different types/batches of activated carbon. In general, VOCs with greater

molecular weight and higher boiling point tend to have greater adsorption capacity with activated carbon. The compounds with boiling points above 110°C have an excellent adsorption capacity (greater than 20% weight of adsorbate per weight of activated carbon).

Table 3.2 Activated carbon adsorption capacity for volatile organic compounds

Adapted from (Shepherd, 2001)

Organic Compound	Molecular Weight	Boiling Point (°C)	Carbon Capacity (%)
Nitrobenzene	123	211	51
Tetrachloroethane	166	147	40
Tetrachloroethylene	165	121	35
Styrene	104	145	25
Xylene	106	138	21
Napthalene	128	217	20
Toluene	92	111	20
Benzene	78	80	12
MTBE	88	55	12
Hexane	86	68	7
Ethyl acrilate	100	57	5
Dichloroethane	99	99	7
Methyl ethylketone	72	80	4
Methylene chloride	84	40	2
Acrylonitrile	53	74	2
Acetone	58	56	0.8
Vinyl chloride	62	-14	0.7
Chloroethane	64	12	0.5
Bromotrifluoromethane	149	-58	0.13
Methane	16	-161	0.0003

Theoretically, activated carbon can be employed to remove any VOC compound from a gas stream provided that the amount of the adsorbent is sufficient for the concentration of the adsorbate in the gas stream. In practice, the use of activated carbon is not cost effective for low boiling point and molecular weight compounds such as methane, bromotrifluoromethane, chloroethane, vinyl chloride and acetone because adsorption capacities for these compounds are too low.

VOCs having molecular weights greater than 200 and boiling point greater than 175°C (e.g. long chain hydrocarbons +C₁₄, glycols, phenols, and amines) are often not desorbed because their affinity for the adsorbent is so strong that it is economically impractical to desorb these materials via any regeneration processes (USEPA, 2008). Other organic compounds (e.g.

organic acids, aldehydes, some monomers and ketones) having high chemical reactivity with carbon surface also exhibit the same constraint for regenerative systems.

4.0 Factors Affecting the Adsorption of Compounds by Activated Carbon

The adsorption of compounds by activated carbon is a complex process which depends on a range of variables such as the nature of the adsorbate and adsorbent, the reactivity of the adsorbent surface, the surface area of the adsorbent, and operating conditions. An understanding of these variables is essential to manipulate the process control parameters and provide favourable design outcomes. A review of the key factors affecting the adsorption of compounds by activated carbon is provided in the following subsections, in particular:

- activated carbon properties (section 4.1);
- nature of the adsorbate (section 4.2);
- operating relative humidity (section 4.3);
- operating temperature (section 4.4);
- operating pressure (section 4.5);
- volumetric flow rate (section 4.7); and
- the presence of adsorption competition (section 4.8).

4.1 Properties of Active Carbon

4.1.1 Overview

Carbon is the major constituent of activated carbon, accounting for 85-95% of the elemental composition. Activated carbon also contains other elements such as hydrogen (H), nitrogen (N), sulfur (S) and oxygen (O) that are derived from the source raw material or incorporated into the carbon during the activation and other preparation procedures. A typical activated carbon is made of 88% C, 0.5% H, 0.5 N, 1% S, 6-7% O with the remaining 3-4% as inorganic ash constituents (Bansal and Goyal, 2005).

The raw carbon material is nonpolar / hydrophobic in nature, making its surface attractive to a widely variety of organic and toxic compounds. Activated carbon can become increasingly hydrophilic if the amount of oxygen associated with the carbon surface increases via carbonisation, heat and/or chemical treatment processes in the presence of oxygen. Being nonpolar in nature and having polar surface functional groups due to carbonisation and

activation processes, activated carbon is a versatile adsorbent for many nonpolar and polar compounds as well as organic and inorganic chemicals. Physical and chemical properties of activated carbon such as particle size, surface area, porosity, surface chemistry, surface pH and presence of impregnated chemicals on the surface are most important factors influencing its adsorption performance.

4.1.2 Particle Size Distribution

In air purification applications, activated carbon is often manufactured in *granular*, *pelletized* and *bead* forms with typical particle size between 4 x 6 and 4 x 20 mesh (USEPA, 2008). The particle size distribution should be considered against pressure drops, which affects the operating energy cost. Powder activated carbon is often not suitable for gas treatment applications due to the potential pressure build-up inside the adsorption bed when handling high air flows. *Granular carbons* can be nearly spherical or have a flake shape with particle size ranging from 0.2 to 5 mm. *Pelletised carbons* are generally shaped like cylindrical rods with diameters ranging between 0.8 and 45 mm and with a length to diameter ratio ranging from 1 to 10. Because of its low pressure drop, high mechanical strength and low dust content, pelletized activated carbons is generally preferred over the granular activated carbon (Bansal and Goyal, 2005). *Activated carbon beads* are a more recent development. Their main benefit is a superior attrition resistance. They can promote better flow distribution than other shapes. Due to these benefits, activated carbon beads have been employed for fluidized bed adsorbers in gas purification and solvent recovery applications (Ayer, 2000).

Since mesopores and micropores make up the majority of total surface area, any variation in the particle size for activated carbon of the same quality does not significantly change the total surface area (i.e. total adsorption capacity). While the particle size may not affect the total adsorption capacity, it may affect the rate of adsorption kinetics because larger particle size implies greater restriction of molecular diffusion inside the particle structure and intraparticle mass transfer, meaning that it takes longer to reach adsorption equilibrium. This implies that the use of activated carbon with an excessively large particle size may require an adsorber bed with longer bed retention time, resulting in a higher capital costs. The optimal particle size should be just big enough to resist abrasion, support the weight of the bed, and minimise head loss across the bed.

4.1.3 Total Surface Area

An adsorbent's adsorption capacity is significantly influenced by its total surface area. This parameter is particularly important for physical adsorption because increases in total surface area will provide more adsorptive sites for the adsorbate molecules to bind with. Due to their microporous structure, most activated carbons have typical total surface areas ranging from 600 to 1600 m²/g (USEPA, 2008). Some "super" activated carbons produced from specific raw materials using special carbonisation and heat treatment processes have been reported to have surface areas up to 4000 m²/g (Menendez-Diaz and Martin-Gullon, 2006).

It should be noted that attempts to establish a direct relationship between activated carbon surface area and adsorption capacity have been inconclusive (Bandosz, 1999). Ros et al. (2007) claimed that enhancing the microporosity of the adsorbent directly related to the apparent surface area does not necessarily improve the H₂S retention ability in the absence of suitable inorganic composition and/or pH of the sorbent. Significant differences in adsorption capacity were sometimes seen for activated carbons with similar surface area (Bandosz, 1999) indicating the importance of considering a wide range of adsorbent characteristics in combination.

4.1.4 Porosity

The pore structure is one of the main physical properties used to characterise activated carbon. The pore structure is formed during the activation process and contains pores of several sizes. According to IUPAC recommendation (Bansal and Goyal, 2005), pore size distribution can be classified into three major groups:

- micropores with a pore width less than 2 nm;
- mesopores with a pore width from 2 to 50 nm; and
- macropores with a pore width greater than 50 nm.

Under the current (prevailing) model of the adsorption process for activated carbon (**Figure 4.1**), the micropores are the sites where the majority of adsorption takes place, with adsorbates travelling from the gas phase through the macropores (the entrance to the adsorption sites) and then through mesopores (the transportation passages or channels) to

reach the micropores. Pore size distribution plays an important role on the rate of adsorption by porous adsorbents. The suitability of a given carbon for a given application depends on the proportion of pores of suitable size for the adsorbate (Menendez-Diaz and Martin-Gullon, 2006).

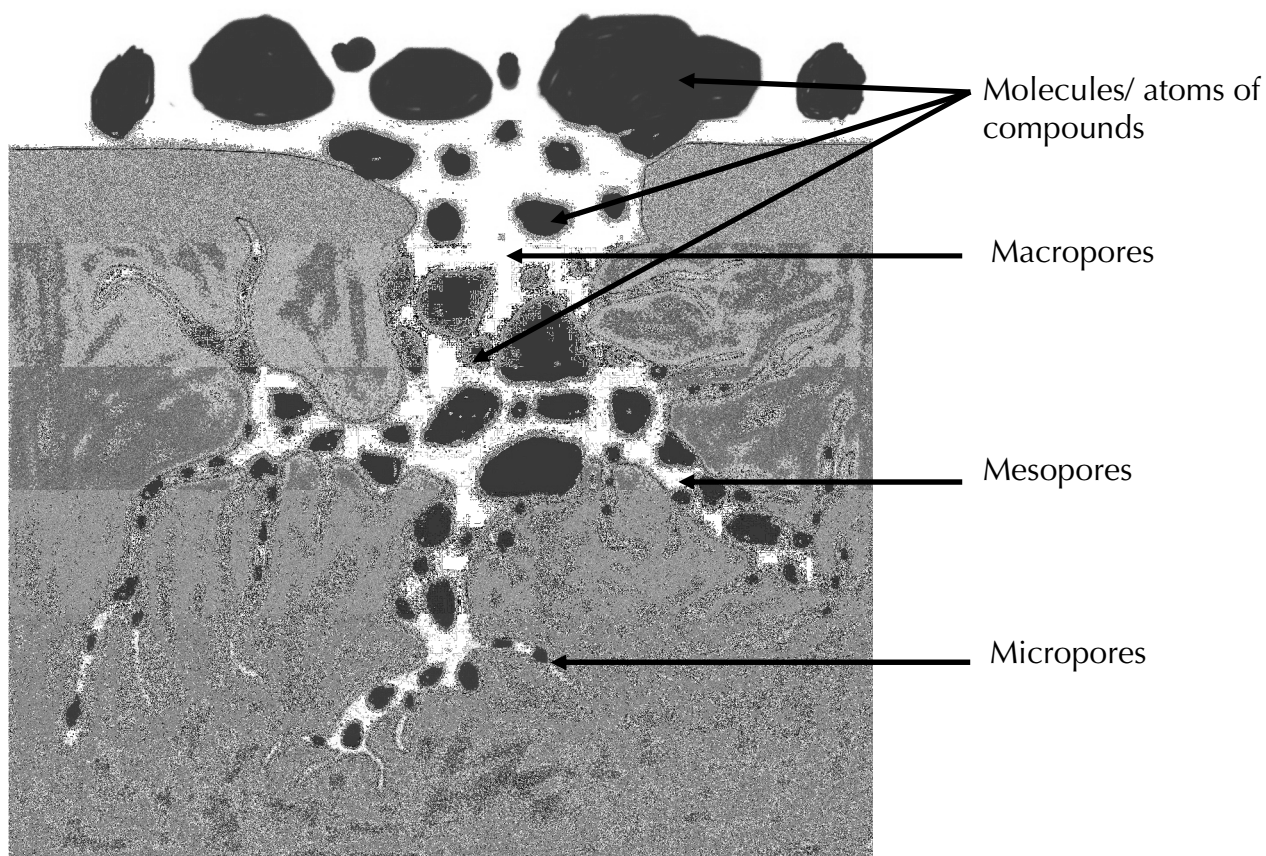


Figure 4.1 Illustration of the adsorption of chemical compounds onto activated carbon porous structure

Macropores have a very small contribution to the surface area of the adsorbent ($< 0.5 \text{ m}^2/\text{g}$) and hence are not considered to be not important for the adsorption process. Mesopores and micropores, on the other hand, contribute significant proportions to the total pore area of activated carbon. The surface area of the mesopores can account for up to 5% of total surface area of the carbon, while the specific surface area of micropores constitutes about 95% of the total surface area (Bansal and Goyal, 2005).

Mesopores primarily act as conduits leading the adsorbate molecules to the micropore cavity. With a capillary structure (i.e. networks of conduits), mesopores play an important role in the adsorption via capillary condensation, which enhances the overall adsorption

capacity.

While mesopores are filled at high relative pressure with the occurrence of capillary condensation, micropores are filled at low relative vapour pressure before the capillary condensation starts to occur in the mesopores (Bansal and Goyal, 2005). The adsorption in micropores is through pore space filling, not capillary condensation. The adsorption energy in micropores is much greater than that in mesopores or on the nonporous surface because of overlapping adsorption forces. Small pores similar in size to the adsorbate molecules cause overlapping of the adsorption potential, resulting in an enhancement of adsorption forces. Micropores have been identified in several studies to be the most favourable pores for the adsorption of gaseous pollutants onto activated carbon. Tanada et al. (1978) found the amount of methyl sulfide and methyl disulfide adsorbed were linearly related to the volume of micropores with a radius less than 20 Å (equivalent to 2 nm). The study conducted by Adib et al. (1999) indicated that the H₂S breakthrough capacity decreases in the same order as the volume of micropores decreases, although their linear correlation coefficient was only 0.6829. Similarly, greater adsorption and breakthrough capacity of methyl mercaptan for activated carbons with greater micropore volume was reported by Baskiva et al. (2002). Many studies such as those reported by Adib et al. (2000) also indicated that the volume of micropores in the exhausted activated carbon is significantly smaller compared to that in the original carbon, and micropores are important adsorption sites for gaseous pollutants.

The porosity of an activated carbon often varies in terms of entrance dimensions, which limit the accessibility of different adsorbates to the adsorption sites (Marsh and Rodriguez-Reinoso, 2006). Molecular sieve effects may occur either because the pore width is narrower than the adsorbate molecules or because the shapes of the pores do not allow the molecules of the adsorbate to penetrate into the micropores (Menendez-Diaz and Martin-Gullon, 2006). Activated carbons with greater porosity and a relatively high proportion of small micropores is open to molecules of smaller size than to molecules of larger size and the reverse holds for lower porosity activated carbons with more mesopores and larger micropores. Tanada and Boki (1978) observed that the adsorption rate of methyl mercaptan on adsorbents with a range of pore sizes is faster than those containing mainly micropores of radii of less than 7.5 Å.

The average micropore size is also important for adsorption as it governs the specific adsorption energy which is related to adsorption strength (Bashkova et al., 2002). Due to the overlapping adsorption potential, micropores exert stronger attraction towards adsorbates whose molecular sizes are similar to the pore size of the micropores. This is the case for SO₂ (a product of the oxidation of reduced sulfur malodorous compounds after being adsorbed onto activated carbon), where activated carbon with a wide micropore size distribution has been found to have less SO₂ adsorption capacity (Raymundo-Piñero et al., 2000). Raymundo-Piñero et al. (2000) claimed that decreases in pore size favours the oxidation of SO₂ to SO₃ inside the micropores because the degree of oxidation is determined by the adsorption potential inside the pores which is strongly influenced by the pore size. However, since oxygen is needed for the oxidation process to occur, the effect of pore size on SO₂ adsorption capacity is subject to the presence of the oxygen in the gas phase. Furthermore, it has been reported that the high extent of pore filling of SO₂ is due to the strong overlapping adsorption potential of pore walls that occurs in activated carbon with small pore sizes (Wang and Kaneko, 1998). Their study showed that the most favourable pores for the adsorption of SO₂ are those with widths smaller than 0.8 nm since the diameter of SO₂ is estimated to be about 0.43 nm.

4.1.5 Surface Chemistry

Studies show that the adsorption capacity of adsorbents with similar pore structures can be very different (Radovic and Rodríguez Reinoso, 1996). This is because the pore structure is an important factor but not the sole factor determining the adsorption capacity of activated carbon. Another essential factor influencing adsorption by activated carbon is the nature of the surface chemistry (including types and abundance of specific functional groups) which determines the degrees and types of interactions between the carbon and adsorbate molecules or atoms. Menedez-Diaz and Martin-Gullon (2006) admit that although surface sites associated with functional groups represent a small proportion of total surface area, small variations in the chemical nature of an activated carbon may produce important changes in its adsorption capacity.

The regular network of covalent C-C bonds on the surface of raw carbon material is broken

with reactive carbon sites (in the forms of unsaturated atoms) present at the edges of the basal planes (Boehm, 2008). The surface functional groups are a result of the unsaturated carbon atoms bonding with heteroatoms such as oxygen, hydrogen, sulfur, nitrogen and halogens during the carbonisation and activation processes. X-ray diffraction studies (Bansal and Goyal, 2005) have shown that these heteroatoms are bonded to the edges and corners of the aromatic sheets or to carbon atoms at defect positions, giving rise to carbon-oxygen, carbon-hydrogen, carbon-nitrogen, carbon-sulfur, and carbon-halogen surface functional groups that are incorporated within the carbon layers forming heterocyclic ring systems.

Oxygen containing surface functional groups

The most abundant element in the activated carbon structure beside carbon is oxygen. As a result, the most common and perhaps most important types of surface functional groups on the surface of activated carbons are oxygen containing functional groups including carboxyl, hydroxyl, ether, carbonyl, lactone, quinone, amide, chromene-like or pyrone-like functional groups. It is believed that oxygen containing surface functional groups are formed by oxidation of the unsaturated outer-layer carbon atoms either with oxygen or other oxidising gases such as ozone, nitrous oxide, carbon dioxide or oxidising solutions like nitric acid or hydrogen peroxide (Menendez-Diaz and Martin-Gullon, 2006). The oxidation process with oxygen requires heat treatment to accelerate the formation of these surface functional groups, but can occur at room temperature for carbon previously treated at high temperatures (Menendez-Diaz and Martin-Gullon, 2006). Activated carbon also has a tendency to extend the layer of carbon-oxygen surface compounds, making it capable of neutralising oxidising gases such as ozone and oxides of nitrogen, and reacting with adsorbed oxygen at temperature below 400°C (Bansal and Goyal, 2005). Above 400°C, the gasification of carbon and decomposition of the surface functional groups becomes dominant.

According to Bansal and Goyal (2005), there are three types of oxygen containing surface functional groups (acidic, basic and neutral) on activated carbon that are formed via reactions between surface carbon and oxidising agents under different temperatures, pressures and treatment procedures. The majority of oxygen containing surface functional groups are acidic since they can easily be formed by heating carbon in the presence of oxygen at temperatures up to 400°C or treating carbon with oxidising agents at room

temperature. Acidic oxygen containing surface functional groups are well characterised and postulated to be carboxylic, lactones and phenolic groups. These acidic functional groups contribute to hydrophilic and polar characteristics of the carbon surface. Neutral functional groups are formed by the irreversible chemisorption of oxygen at unsaturated sites of ethylene-type structure present on the carbon surface. Basic functional groups are only obtained when the carbon surface is heated in vacuum or in inert atmosphere at 1000°C to free all surface oxygen groups, subsequently cooled to room temperature, and then contacted with pure oxygen gas. The structures of basic surface oxygen groups are proposed to be pyrone-type structure, but to date this has not been clearly defined or accepted.

Oxygen containing surface groups govern the surface characteristics of activated carbon including wettability, polarity, and acidity, as well as its catalytic, electrical, and chemical reactivity. For example, although carbon is nonpolar in nature, the presence of oxygen-containing surface groups can increase its polarity. This implies that formation of hydrogen bonds between polar functional surface groups and molecules of water or other polar adsorbates can occur on carbon surface. It has been reported that the adsorption of polar and polarised compounds such as water vapour, methanol, ethanol, ammonia, amines, dyes and surfactants are related to the amount of oxygen containing surface groups in the activated carbon (Bansal and Goyal, 2005).

The increase in hydrophilicity associated with oxygen containing surface groups is also important for the preparation of carbon supported catalysts (impregnation) from aqueous solutions as well as for the adsorption of polar adsorbates in a gas stream (such as H₂S) that can dissociate in aqueous solutions (Banosz and Ania, 2006). During the H₂S oxidation-adsorption process the presence of carbonate groups on the carbon surface was found to favour the formation of sulfur polymers that are insoluble in water and cannot be removed from micropores by washing (Adib et al., 2000). Davini (1994) observed that SO₂ can be adsorbed on the surface of activated carbon by forming strong bonds between SO₂ and oxygen containing surface functional groups with a basic nature. However, increasing hydrophilicity comes with a cost of a reduction in the adsorption capacity of the activated carbon for nonpolar compounds. Studies by Puri et al. (1973) and Bansan and Dhami (1980) have shown that while the presence of acidic oxygen-carbon surface functional groups

enhances the activated carbon's hydrophilicity, it suppresses the adsorption of benzene (a nonpolar compound).

Nitrogen containing surface functional groups

Other significant surface functional groups on activated carbons are basic nitrogen containing functional groups which can be introduced by treatment with ammonia, melamine or urea during the activation process (Menendez-Diaz and Martin-Gullon, 2006, Shen et al., 2008). The presence of nitrogen containing surface functional groups in the carbon matrix was found to enhance oxidation of hydrogen sulfide during adsorption (Mikhalovsky and Zaitsev, 1997). It was also reported that the H₂S adsorption capacity of activated carbon with high amounts of basic nitrogen containing surface functional groups can be greater than the adsorption capacity of caustic impregnated activated carbon (Bandosz, 2006). Bandosz (2006) also noted that the greater adsorption capacity of activated carbon is a result of its nitrogen containing surface functional groups being highly dispersed in the small pores, contrary to alkaline hydroxides being in abundance in the liquid phase inside the pores of caustic impregnated carbons. The presence of basic nitrogen containing surface functional group in the carbon structure enhances the amount of adsorbed anions (such as HS⁻) and increases the polarity of carbon surface and the amount of water adsorbed (Bandosz, 2006). In addition, the nitrogen containing surface functional groups provide direct contact of HS⁻ ions with the carbon matrix, promoting the immediate creation of active sulfur radicals which are readily oxidised to other sulfur species and sulfuric acid (Bandosz, 2006). The oxidation reactions first occur in the smallest pores and once they are filled up with acid the large pores start to play a role. H₂S is gradually oxidised in pores of increasing size until all pores are filled and the pH is low enough to suppress the dissociation of H₂S (Bandosz, 2006).

The presence of nitrogen containing surface functional groups also enhances the removal of SO₂ (Bandosz and Ania, 2006). The basic surface functional groups present on the surface of activated carbon have also been found to contribute to SO₂ oxidation to H₂SO₄ which is then strongly fixed in the pore system (Raymundo-Piñero et al., 2000, Mochida et al., 1997). In the case of methyl mercaptan, the basicity of activated carbon is reported to enhance removal by increasing the concentration of thiolate ions that are further oxidized to dimethyl

disulfide (which is strongly adsorbed in the micropores of activated carbon) (Bashkova et al., 2002).

4.1.6 Carbon Impregnations

The impregnation of caustic chemicals such as alkaline hydroxides onto the surface of activated carbon can significantly enhance the uptake capacity for H_2S mainly via the oxidation-adsorption processes.

Alkaline Impregnation

A study of H_2S adsorption/oxidation on sodium hydroxide impregnated activated carbon observed that at least 3 moles of H_2S are adsorbed per mole of NaOH (Bagreev and Bandosz, 2002). Chiang et al. (2000) also investigated the adsorption of H_2S and CH_3SH by virgin carbon and alkaline activated carbons (including NaOH , Na_2CO_3 , KOH , and K_2CO_3 impregnations). The authors observed that all types of alkaline impregnated activated carbon had better adsorption capacities for both H_2S and CH_3SH than the virgin activated carbon despite the impregnated activated carbons having smaller the surface areas, micropore areas and pore volumes than virgin carbon. This implies significant chemical adsorption between the alkaline impregnates and reduced sulfur compounds. The impregnated activated carbon were ranked as follows for H_2S adsorption capacity; $\text{NaOH} > \text{Na}_2\text{CO}_3 > \text{KOH} > \text{K}_2\text{CO}_3$. Compared to the virgin activated carbon sample, NaOH impregnated activated carbons had 3.2 and 2.2 times the adsorption capacity for H_2S and CH_3SH , respectively.

Metal Impregnation

Metallic oxides or noble metals can be impregnated onto the activated carbon surface to enhance chemisorption, thus enhancing overall adsorption capacity. Oxidation of reduced sulfur compounds often yields significantly enhanced adsorption capacity in comparison to physical adsorption alone (Turk et al., 1989). Further oxidation of metal sulfides to elemental sulfur also takes place in the presence of oxygen, further increasing the overall H_2S adsorption capacity (Bandosz, 2006) due to the bulky sulfides occupying a much larger portion of activated carbon pore volume than that occupied by elemental sulfur. Copper and iron impregnations have been found to enhance the H_2S adsorption capacity of activated carbon fibre cloth (Le Leuch et al., 2010). The authors also observed that zinc impregnation

had a negative effect on the adsorption capacity despite of the zinc oxides being known to react with H_2S in an oxidation reaction.

Side effects of impregnation on adsorption capacity

The use of impregnation for improving the adsorption of specific odorous compounds may lessen the activated carbon's adsorption capacity for other gases because the surface areas and pore volume available for physical adsorption are reduced (Smet et al., 1998, Turk and Bandosz, 2001). Laboratory measurements using accelerated adsorption tests with 1% H_2S concentrations (ASTM-D6646 – 01 standard) often show that impregnated activated carbon can have higher breakthrough capacities than virgin carbon, by a factor of 10 times or more in some cases (Smet et al., 1998). These promising results have not always translated to improvements in the field performance, where activated carbon media is usually exposed to much lower concentrations of H_2S and other competitive odorous and non-odorous gases. Field testing (Bandosz et al., 2000a) has demonstrated that the performance of impregnated activated carbon may not be as great as those obtained in the laboratory and virgin activated carbons can in some cases outlast impregnated activated carbon.

Bagreev and Bandosz (2001) observed that H_2S adsorption capacities of virgin and caustic-impregnated carbons measured by the ASTM-D6646 – 01 standard test with 1% H_2S concentration are not comparable because the ASTM results for virgin activated carbon are usually underestimated due to the slower kinetics of H_2S oxidation on their surface. The study by Koe and Tan (1987) also showed that non-impregnated carbon outperformed impregnated activated carbon in the treatment of off-gas from a surplus activated sludge dissolved air floatation unit whose odour was characterised by a low H_2S concentration. The occupation of adsorption sites by the impregnate chemicals reduces adsorption via physical binding. When comparing the performance of alkali-impregnated carbon and non-impregnated carbon for sewerage odour treatment, Koe and Tan (1990) observed that alkali-impregnated activated carbon had a significantly greater capacity to remove H_2S than the virgin activated carbon, but their final odour concentrations were comparable. The treatment cost of non-impregnated activated carbon is generally lower than that of alkali-impregnated activated carbon and impregnation also increases the fire risk during operation because impregnated activated carbons tend to have lower ignition temperatures. It is therefore

critical to understand the compounds responsible for odour and select an adsorbent material that is optimal for removing them in order to achieve efficient and cost-effective odour control solutions.

4.1.7 Surface pH

The average activated carbon surface pH (resulting from the local environment or arrangement of surface functional groups) has a significant effect on the adsorption of odorous compounds. Surface pH governs the dissociation of H_2S into hydrogen sulfide ions along with its subsequent oxidation and adsorption onto the carbon surface (Adib et al., 1999, Yan et al., 2004). Basic conditions on the carbon surface increase the dissociation rate of H_2S and correspondingly the concentration of HS^- ions. When HS^- ions are adsorbed into the small pores, they will be oxidised by oxygen in the system to highly dispersed elemental sulfur. Increasing HS^- concentrations forces the created elemental sulfur atoms to be close to each other, resulting in the formation of polysulfides that are trapped in the activated carbon pores. Chemisorption is the dominant process in activated carbons with basic surface pH (Yan et al., 2004).

If the pH becomes acidic, the concentration of HS^- and elemental sulfur in the pores is low. With the presence of the oxygen and water in the system, sulfur atoms are susceptible to further oxidation to SO_2 , SO_3 and H_2SO_4 because the probability of isolated sulfur atoms meeting each other is low. After H_2S adsorption the pH of the carbon gradually decreases due to the formation of H_2SO_4 , slowing the adsorption rate. The increasing formation of H_2SO_4 will gradually suppress the dissociation of H_2S and immobilise hydrogen sulfide. While basic and mildly acidic surfaces increase the H_2S adsorption capacity, more acidic surfaces below pH 4.0 will have reverse effect (Adib, 2000). Yan et al. (2004) suggested that physical adsorption mostly dominates when carbon surface is below pH 4.5. Published data from studies on H_2S adsorption by alkaline impregnated activated carbon shows carbon surface pH along the exhausted carbon beds (from outlet to inlet) decreased while sulfur content in the corresponding carbon portions increased (Yan et al., 2004). The surface pH of exhausted carbons are commonly low because some of the elemental sulfur trapped in micropores has been converted to sulfuric acid (Adib, 2000).

Investigating the effect of carbon characteristics on the adsorption of methyl mercaptan with four different virgin activated carbons, Bashkova et al. (2002) found the amount of methyl mercaptan adsorbed depends on surface chemistry of the adsorbents. They observed decreasing methyl mercaptan adsorption onto the activated carbon as carbon surface pH decreased. Low pH condition may mimic the dissociation of methyl mercaptan to dimethyl disulphide, eventually reducing the removal efficiency of methyl mercaptan. As previously discussed in **Section 3.3**, the removal of methyl mercaptan is greater via dissociation to dimethyl disulphide, which is strongly adsorbed onto the activated carbon at room temperatures.

4.2 Properties of Adsorbates

Physical adsorption is also dependent upon the nature of the adsorbate species. Since carbon is a nonpolar material, nonpolar adsorbates such as organic compounds are adsorbed in preference to polar inorganics. The molecular weight and boiling point of a compound also affects the physical adsorption.

As previously discussed in **Section 2.1**, adsorbates with greater molecular weight are more strongly adsorbed than those with smaller molecular weight. Organic compounds with molecular weight over 45 are expected to be successfully adsorbed by any activated carbon based adsorbent (Petrov, 2008). There is a practical limit to the increases in adsorption associated with increases in molecular weight. Increases in molecular weight often mean an increase in molecular size, and if the molecular size of the adsorbate is larger than the size of the activated carbon micropores the adsorbate cannot penetrate to fill the pore space and will not be adsorbed.

Higher boiling point compounds have a stronger affinity for activated carbon because rebound and expulsion of adsorbed species (from the surface and from inside activated carbon, respectively) are less vigorous (Kent, 2008). High molecular weight and boiling point compounds also tend to react chemically on the carbon surface, forming solid or polymerisation products that are extremely difficult to desorb (USEPA, 2008).

The concentration of adsorbate in the feed stream often varies in odour abatement applications. At a constant flow rate, increases in adsorbate concentration mean a greater

adsorbate partial pressure that enhances the rate of adsorption to the adsorbent and correspondingly increases the adsorption capacity of the activated carbon. However, the adsorption capacity increase will not be large enough to completely offset the increase in mass loading (USEPA, 1988), with a net effect moving the active mass transfer zone towards the outlet of the odour abatement processes. As long as the mass transfer zone remains within the activated carbon bed, the outlet odorant concentration is independent of the inlet odorant concentration. As a result, the effects of short-term variations in inlet odorant concentrations on abatement performance are generally negligible.

4.3 Relative Humidity

Relative humidity increases the adsorption capacity of some sulfur compounds because the presence of water encourages oxidation, absorption and subsequent dissociation of the sulfur compounds in water. Water vapour promotes the basic pH on the activated carbon surface required for dissociation of H_2S into HS^- , and HS^- ions will be oxidised into sulfuric acid or elemental sulfur by the oxygen present in the system.

While studying the breakthrough capacity of different activated carbon materials with dry and wet (80% humidity) air flows, Bandosz et al. (2000b) observed that the presence of humidity significantly increased (up to 100 times) the adsorption capacity of activated carbon for H_2S . The adsorption capacity at dry conditions is often very small and mainly physical adsorption takes place in the small pores of the activated carbon. The presence of a high level of humidity in the gas stream is a necessary condition for the adsorption of H_2S via oxidation and chemical adsorption. These findings have been supported by Chiang et al. (2000), who measured the adsorption capacity of NaOH impregnated activated carbon for H_2S to be 6-7 times greater with humidified feed stream than that with a dry feed stream. However, Chiang et al. (2000) observed that the adsorption capacity for H_2S decreased as the relative humidity increased from 50% to 80%. The study undertaken by Le Leuch et al. (2003) also indicated that activated carbon having basic functional groups or basic catalysts has an optimal humidity of around 60% with respect to H_2S adsorption capacity.

According to Bandosz (2006), although water is a very important factor in the process of H_2S adsorption by activated carbon, excess water was reported to decrease adsorption from the gas phase onto the activated carbon due to small pores filling with the condensed water

vapour, limiting direct contact of HS⁻ with carbon surface in the smallest pores. Furthermore, the wetted surface and the presence of oxygen groups favour the formation of H₂SO₄, which eventually suppresses the dissociation of subsequent H₂S adsorbates. These findings imply that water vapour does not only enhance chemical adsorption of H₂S, but also competes with H₂S for adsorption sites, thus excessive relative humidity above 60% may not be optimal for H₂S adsorption.

Above 100°C, the effect of humidity on the adsorption capacity of the activated carbon is insignificant due to the very low partial pressure of water and correspondingly low amount of water deposited onto the carbon surface (Steijns and Mars, 1974). The activated carbon surface is hydrophobic in nature and often has a low affinity for water due to the high degree of aromatisation and the presence of graphene-like sheets (Bansal et al., 1988, Leon y Leon and Radovic, 1992).

Pre-humidifying activated carbon using clean air with humidity similar to that in the gas stream to be treated is found to enhance the adsorption capacity for H₂S by some activated carbon materials (Yan et al., 2002, Bagreev and Bandosz, 2001, Adib et al., 1999). This finding indicates that some features on surface carbon that significantly influence H₂S adsorption will only be activated by water. The results from the study on the effects of pre-humidification on the H₂S adsorption of various carbons showed that H₂S adsorption capacities of pre-humidified activated carbon is two to six times higher than that of the same material on an as-received basis (Bagreev and Bandosz, 2001).

Humidity also enhances the adsorption of methyl mercaptan by activated carbon by initially facilitating the dissociation of methyl mercaptan into dimethyl disulfide which is then adsorbed onto the carbon surface (Bashkova et al., 2002). As mentioned previously, water content is important for the oxidation of methyl mercaptan into dimethyl disulphide, which is more strongly adsorbed by activated carbon at the room temperature than methyl mercaptan due to the difference in their physiochemical properties.

Sattler and Roseberk (2006), however, found that the adsorption of carbonyl sulfide by activated carbon was reduced as the relative humidity increased with the presence of H₂S in

the gas stream. The authors claimed that the low solubility of carbonyl sulfide compared with hydrogen sulfide is a possible reason for the less effective removal of carbonyl sulfide by activated carbon via dissociation in water. It is possible that amount of water adsorbed during pre-humidification will increase as a result of the increase in hydrophilicity and reduced quantity of available adsorption sites.

Many studies (James, 2003, Schnelle and Brown, 2001, Chou and Chiou, 1997, Keener and Zhou, 1990) have pointed out that relative humidity in the gas stream is often undesirable for the removal of VOCs because water vapour can compete with these adsorbates for the activated carbon adsorption sites. Relative humidity above 50-60% severely affects the adsorption capacity of activated carbon for VOCs (James, 2003, Schnelle and Brown, 2001, Chou and Chiou, 1997, Keener and Zhou, 1990). Reductions in relative humidity to below 50% is recommended for both non-regenerative and regenerative beds (Schnelle and Brown, 2001). Increases in relative humidity are also reported to cause early breakthrough and broaden the breakthrough curve for VOCs (Gong and Keener, 1993, Jonas et al., 1985). According to the design guideline of the US Army Corp of Engineers (2001), adjusting the relative humidity to between 40% - 50% is often the best compromise.

The effect of humidity on VOC adsorption is, however, often insignificant if the initial concentrations of VOCs in the gas stream exceed 500 ppm (Keener and Zhou, 1990, Delage et al., 1999). Delage et al. (1999) reported that prehumidification of the activated carbon adsorbent without causing water condensation can reduce excessive heating of the bed while not affecting the VOC adsorption capacity. This is due to activated carbons having a greater affinity for organic VOCs than for water, with weakly adsorbed water vapour on carbon surface from prehumidification being desorbed and replaced by VOCs. If the water condensation occurs, the water will block the access of VOCs to the available adsorption sites and reduce the adsorption capacity.

Heat exchangers are sometimes used to remove moisture as liquid waste and control the relative humidity in gas streams to an optimal range. This can be done either through raising the gas temperature to lower the relative humidity (relative humidity can drop 15-20% when air temperature is heated by 2-3°C) or lowering the temperature in order to force

condensation. Increasing gas temperature to reduce relative humidity comes at the costs of reduced adsorption capacity because the adsorption process is exothermic. The condensation of moisture, on the other hand, results in the need to deal with low pH liquid waste that can be highly corrosive due to the reduced sulfur compounds forming sulfuric acid.

In Australia it is a common practice to maintain humidity of inlet sewer air to activated carbon adsorbers above 80%. The clear reason is unknown, but it is possible due to the fact that sewer air is often completely saturated and a significant reduction in humidity implies a need of extra facilities to deal with large amounts of corrosive moisture condensation. Consequently, the removal effectiveness of activated carbon adsorbers may be reduced by sub-optimal operating conditions.

4.4 Temperature

The adsorption capacity of an adsorbent decreases as the temperature within the adsorbent bed increases (**Figure 4.2**). The mechanism responsible is that increasing operating temperature results in increases in the vapour pressure of the adsorbate and the energy level of adsorbed molecules (USEPA, 2008), with a portion of the adsorbed molecules gaining sufficient energy to overcome the weak van de Waal's attraction and rebound into the gas phase (effectively desorbing). Increases in operating temperature have been observed to shift the breakthrough curve to the left (toward the outlet of the odour control unit), resulting in a shorter lifespan (USEPA, 1988). The **Figure 4.3** illustrates a typical breakthrough curve for activated carbon adsorption.

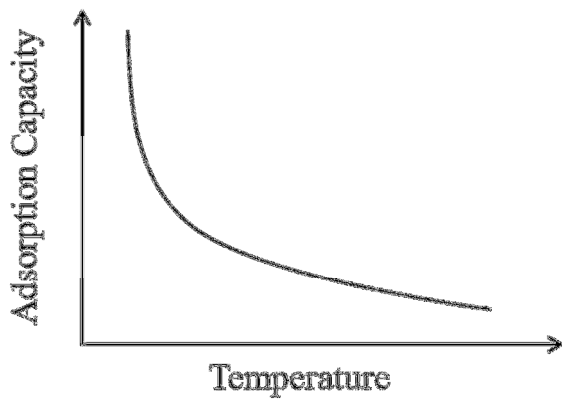


Figure 4.2 Activated carbon adsorption capacity versus adsorber temperature

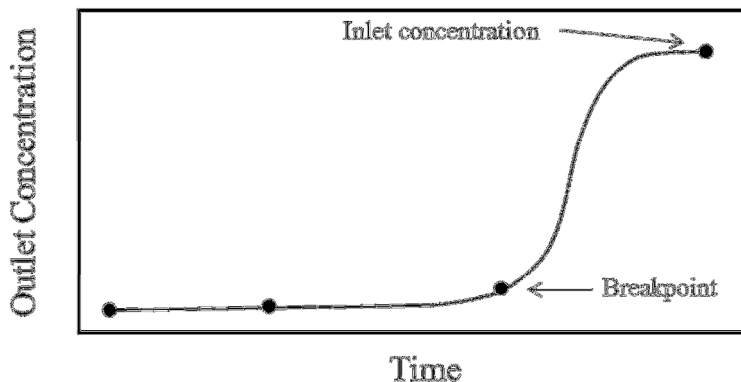


Figure 4.3 Typical breakthrough curve

The operating temperature of an adsorber can vary significantly due to changes in the feed stream temperature and exothermal reactions occurring inside the adsorber (USEPA, 1988). Changes in the feed stream temperature directly contribute to changes in the adsorber operating temperature. Increases in the adsorbate loading can result in greater heat of adsorption and heat up the adsorber. The heating is much more significant if the concentration of the adsorbate is extremely high, the gas flow rate through the carbon bed is relatively low, and the carbon is dry. It is, therefore recommended to continuously monitor temperature and other operating parameters which directly affect the temperature to minimise fire hazards.

4.5 Pressure

It is widely accepted that an increase in the partial pressure of the adsorbate increases the adsorption capacity. As the partial pressure of the adsorbate is proportional to the total pressure of the system, increases in operating pressure increase the adsorption capacity. This

occurs because molecules are packed more tightly together at higher pressure, increasing the probability that they hit the available adsorption sites. No studies assessing the effects of operating pressure on adsorption of the sewer-associated odorants were found in the surveyed literature. However, if the adsorption isotherm between a particular compound and a specific activated carbon is available, the changes in the adsorption capacity due to variations in partial pressure could be estimated.

4.6 Volumetric Flow Rate

Volumetric flow rate or superficial bed velocity directly affects the removal efficiency. As the superficial velocity increases, the carbon particles are exposed to the adsorbate for shorter time periods, and the number of adsorbate molecules removed from the feed stream at a given point decreases. In contrast, the lower the superficial velocity through the bed (i.e. the longer contact time) the greater the probability that the adsorbate molecules reach the adsorption sites.

During design, the size of activated carbon based adsorber is estimated by multiplying the volumetric flow rate by the empty bed contact time. For a given removal efficiency and operating conditions, an increased bed contact time gives a higher degree of carbon saturation and increased activated carbon requirements. The carbon loading increases rapidly in the initial stage with an increase of the contact time and then gradually increased (i.e. reaching steady state) until equilibrium. There is, however, an increasing cost associated with the greater amount of adsorbent media required to increase bed contact time. The optimal bed contact time is the minimum time that allows steady state conditions to be reached. The appropriate empty bed contact time is selected based on experience or data from pilot scale studies so that the lowest concentration odorants can be removed to the desired levels. There is no standard available for determining these variables. Some suggestions provided by the industry are currently accepted as practical guidelines and will be described later in **Section 6.4**.

4.7 Adsorption Competition

It is expected that the adsorption competition exists for feed streams containing multiple adsorbates due to the finite number of adsorptive sites in the activated carbon. This competition results in selective/preferential adsorption between the activated carbon and molecules of different polarities, molecular weights, sizes, volatilities and chemical reactivities. For example, Sattler and Rosenberk (2006) found that adsorption of carbonyl sulfide by activated carbon decreases in the proportion to the percentage of H₂S in the gas stream. In addition, many VOCs emitted from sewage treatment plants may affect odorant removal via competition. For example, ketones have been identified as particularly reactive compounds that can quickly bind onto the surface of activated carbon via strong chemical reactions (USEPA, 1988). Even polar water vapour molecules, which exhibit stronger attractions for each other rather than activated carbon, can compete with the non-polar hydrocarbon molecules when the relative humidity is high (Bandosz, 2006).

Conversely, the presence of some compounds in the feed gas stream may actually enhance adsorption of the other compounds. For instance, ammonia vapour present in the gas stream can enhance the adsorption capacity of activated carbon for reduced sulfur compounds (Turk et al., 1989, Sattler and Rosenberk, 2006). The adsorption capacity of virgin activated carbon for hydrogen sulfide, methyl mercaptan and heavier vapours increased considerably with the continuous injection of a small side stream of ammonia gas to the odorous gas stream and outperformed caustic impregnated carbon (Turk et al., 1989, Sattler and Rosenberk, 2006). This was due to ammonia acting like a catalyst to encourage the rapid oxidation of these reduced sulfur compounds to elemental sulfur (Turk et al., 1989).

Limited information in the surveyed literature is available to evaluate the effects of multi-adsorbates on the performance of the activated carbon used for odour control applications and is an area requiring further research.

4.8 Summary

The adsorption of compounds by activated carbons is significantly influenced by a range of variables including adsorbate and adsorbent properties and the process operating conditions. In order to manipulate the adsorption during the design and operation of activated carbon

based adsorption processes to provide effective and efficient odour control solutions, it is critical to comprehend the effect of these variables on the adsorption of compounds by activated carbon. **Table 4.1** summarises information about the key factors affecting the adsorption of compounds by activated carbon which have been discussed the previous sections.

Table 4.1 Summary of key information about factors affecting the adsorption of compounds by activated carbon

Factors	Relation to adsorption by activated carbon	Remarks
Particle size	<ul style="list-style-type: none"> • Affects the adsorption rate • Particles size governs the access of intraparticle mass transfer and molecular diffusion inside the particle structure 	<ul style="list-style-type: none"> • Smallest particle size with a sufficient abrasive resistance, the ability to support bed weight, and an acceptable head loss
Surface Area	<ul style="list-style-type: none"> • Directly related to the amount of adsorption sites on activated carbon • Greater surface area potentially produces greater adsorption capacity 	<ul style="list-style-type: none"> • Not the sole (dominant) factor determining the total adsorption capacity • Need to consider in conjunction with other properties
Porosity	<ul style="list-style-type: none"> • Macropores – entrance to the adsorption sites • Mesopores – transportation passage where adsorption via capillary condensation can occur • Micropores – main adsorption sites where majority of physical and chemical adsorptions take place • Amount of micropores volume is related to the adsorption capacity 	<ul style="list-style-type: none"> • Greater porosity with high proportion of small micropores is favourable to molecules of smaller size • Less porosity with more proportion of mesopores and larger micropores is favourable to molecules of larger size • Activated carbon with high proportion of small micropores is probably a good fit for the removal of reduced sulfur compounds (oxidised to elemental sulfur)

Surface Chemistry	<ul style="list-style-type: none"> Functional surface groups governs wettability, polarity, acidity, and catalytic, electrical and chemical reactivity of activated carbons 	<ul style="list-style-type: none"> Acidic functional surface groups favour adsorption of basic compounds while basic groups favour adsorption of acidic compounds Increasing hydrophilicity enhances adsorption capacity of polar compounds and reduces adsorption capacity of non-polar compounds
Impregnations	<ul style="list-style-type: none"> Promotes chemisorption and enhance adsorption capacity for specific compounds 	<ul style="list-style-type: none"> Reduces adsorption capacity of non-targeted compounds by physisorption Increases fire hazard (need better temperature monitoring)
Surface pH	<ul style="list-style-type: none"> Determine the degree of chemisorption 	<ul style="list-style-type: none"> High surface pH (basic) favours the adsorption of reduced sulfur compounds
Properties of Adsorbates	<ul style="list-style-type: none"> Molecular weight and boiling point affects physisorption Compounds with greater molecular weight and/or higher boiling points often have stronger affinity onto activated carbon 	<ul style="list-style-type: none"> Compounds with large molecular weight have restricted access to adsorption sites due to their size possibly being bigger than the sizes of the activated carbon pores.
Relative humidity	<ul style="list-style-type: none"> Water vapour promotes basic pH condition on activated carbon surface, activates functions of some surface groups or catalysts and allows adsorbate molecules to move from gas phase to liquid phase, and to be oxidised. 	<ul style="list-style-type: none"> Water can compete with the targeted adsorbates for adsorption sites Optimum humidity is around 60% and below 50% for the adsorption of sulfur-reduced compounds and VOCs respectively by activated carbon
Operating temperature	<ul style="list-style-type: none"> Temperature is inversely related to adsorption capacity 	<ul style="list-style-type: none"> Lack of specific research studies and operation standards
Operating pressure	<ul style="list-style-type: none"> Pressure is proportionally related to adsorption capacity 	<ul style="list-style-type: none"> Lack of specific research studies and operating standards
Volumetric flow rates	<ul style="list-style-type: none"> Flow rates are associated with bed retention time Directly affect removal efficiency 	<ul style="list-style-type: none"> Lack of operating standards Industry-accepted guidelines available
Adsorption competitions	<ul style="list-style-type: none"> Co-presence of compounds can enhance or suppress the adsorption of target compounds onto activated carbon 	<ul style="list-style-type: none"> Literature information on adsorption competition is very limited

Although very important, information about the impacts of these variables on adsorption is often limited or unavailable. Product specifications provided by vendors only include a few variables such as surface area, pore volume, pH and adsorption reactivity toward certain representative compounds such as H₂S, iodine, methylene blue, carbon tetrachloride or butane. There are no standardised lists of characteristic parameters to be provided in activated carbon specifications, nor are there guidelines for determining the operating parameters of the activated carbon based odour abatement units. As a result, it is difficult to optimise the adsorption efficiency unless further experiments or studies are carried out to fill the knowledge gaps.

5.0 Techniques to Characterise Activated Carbon Properties

The physical and chemical properties of activated carbon play an important role in adsorption processes. Knowledge of these characteristics is crucial for selecting appropriate activated carbon types along with the effective design of activated carbon adsorption system. Activated carbon can be characterised by a wide range of physical, chemical and computational techniques (Bandosz et al., 2003, Yasuda et al., 2003). Several common analytical methods used for the characterisation of activated carbon are summarised in the **Table 5.1** along with data for given materials and their availability from vendors. There is no single method to completely characterise the properties of the activated carbon. Each method has its limitations; therefore they are often used in combination to provide comprehensive information on the physical and chemical properties of activated carbon.

Table 5.1 Analytical methods available for the characterisation of carbons

Properties	Methods	Information typically provided by vendor
Surface pH	Reflux Condenser and Titration (ASTM D3838-05)	Yes (sometimes)
pK _a of functional groups	<ul style="list-style-type: none"> • Computer simulation, • Potentiometric titration 	No
Chemical content	<ul style="list-style-type: none"> • X-Ray florescence, • Elemental analysis 	No
Surface group functionality	<ul style="list-style-type: none"> • Calorimetry, • Fourier transform infrared spectroscopy, • X-ray photoelectron spectroscopy 	No
Surface area, molecular sieve properties, and pore-size distributions	<ul style="list-style-type: none"> • Gas adsorption (BET) , • Butane activity (ASTM D5742-95), • Iodine number (ASTM D4607-94), • Carbon tetrachloride activity (ASTM D3467-04) • Calorimetry, • Small angle X-ray scattering 	Yes
Pore characterisation and porosity	<ul style="list-style-type: none"> • Scanning tunnel microscopy, • Transmission electron microscopy, • Scanning electron microscopy, • Optical microscopy 	No
Average polarity	Calorimetry	No
Crystallite sizes, carbon-carbon distribution functions	X-ray diffraction (wide-angle X-ray diffraction)	No
Molecular structure, element containing functionalities	Nuclear magnetic resonance	No
Atomic scale structure visualisation	Scanning tunnelling microscopy	No
Adsorption activity and capacity	<ul style="list-style-type: none"> • Constructing an adsorption isotherm for a particular adsorbate-adsorbent system • H₂S adsorption (ASTM D3838) 	No Yes
Particle Size Analysis	Standard sieving method (ASTM D2862-97)	Yes
Total Ash Content	Standard Combustion method (ASTM D2866-11)	Yes
Ball-Pan Hardness	Standard method (ASTM D3802-10)	Yes
Apparent Density	Standard method (ASTM D2854-09)	Yes

5.1 Activated Carbon pH and acidic/basic function groups

Activated carbon pH is often referred as the pH of an aqueous slurry of carbon and provides a useful information of the nature of the functional groups present on the activated carbon surface. In solution, acidic groups on the carbon surface tend to donate protons and become negatively charged while basic groups adsorb protons from the solution and become positively charged. Oxygen containing functionalities usually behave as acids and donate proton in aqueous solution, lowering the pH (Bandosz and Ania, 2006). The standard measurement procedure for activated carbon pH, *ASTM D3838-05*, was developed by the American Society for Testing Materials (2011).

Boehm titration is also used to determine the type and the amount of acidic groups on the carbon surface (Contescu et al., 1997, Salame and Bandosz, 2001). The method, first developed by Boehm (Boehm, 1966), is based on the selective neutralisation by equilibrium with a series of bases of increasing strength. Bandosz and Ania (2006) claimed that Boehm titration is very reliable, simple, fast and is usually a reproducible method to evaluate the general trends in surface acidity. However, they point out that the technique is limited to the determination of acidic groups such as carboxylics, lactones, and phenols and is based on an assumption that all functional groups (including nitrogen, phosphorus or sulfur containing groups) on sample surface are oxygen containing acids. This means that the correlation between the estimation by Boehm titration and the actual acidity of the samples depends on whether or not the heteroatoms (N, P and S) are significant.

Potentiometric titration is an alternative approach to estimate the acidic properties of carbon surfaces in terms of their proton affinity distribution. This technique has some limitations including slow establishment of ion exchange equilibria, and interferences by the sample particle size and rate of titration (Bandosz and Ania, 2006, Contescu et al., 1997). It has been reported that activated carbon acidity measured by potentiometric titration and by Boehm titration have similarities and differences (Salame and Bandosz, 2001, Contescu et al., 1997).

The successful uses of *immersion and flow adsorption calorimetry* to characterise surface chemical properties (nature of surface groups, hydrophobicity/hydrophilicity, acid/base properties) of different carbon materials are reviewed by Menendez (1998). Immersion and

flow adsorptive calorimetry is based on the measurement of heat of adsorption released by a sample which is immersed either in a liquid or in a stream of a carrier liquid containing a probe compound.

5.2 Surface area, pore size distribution and pore characterisation

The specific surface area and pore size distribution of the activated carbon is often determined by applying *Brunauer-Emmett-Teller* (BET) theory to the isotherms generated by adsorption tests conducted using N₂ at 77 K or CO₂ at 273 K. BET theory is based upon the assumption that the monolayer is located on surface sites having uniform adsorption energy and multilayer build-up occurs via a process analogous to condensation of the liquid adsorbate. To obtain information on the surface area and the pore size distribution, the results of BET adsorption can be processed by various procedures such as the Dubinin-Radushkevich plot, Barrett-Joyner-Halenda method, Horvath-Kawazoe method, or density functional theory method.

BET analysis has a number of limitations including molecular sieve effects and molecular shape selectivity due to constrictions in microporous structure, along with diffusion effects due to insufficient kinetic energy for liquid N₂ adsorbate to penetrate all the micropores at a low temperature of 77 K (Menendez-Diaz and Martin-Gullon, 2006). Due to these limitations, the surface area measured by the BET method with N₂ adsorption at 77 K may be up to 40% larger than the true area if the sample contains relatively large micropores, or smaller if there is a high proportion of ultramicropores (Inagaki and Tascon, 2006). Higher temperature CO₂ adsorption (273 K) can be used to overcome these limitations for micropores less than 1 nm width, while N₂ adsorption is suitable to test larger pores (Menendez-Diaz and Martin-Gullon, 2006). It should be noted that the BET isotherm is only applicable in the relative pressure range 0.05 to 0.35 (Bansal and Goyal, 2005). At lower relative pressures it is not usually valid because the influence of surface heterogeneity becomes significant. At higher pressures the BET isotherm loses its validity because adsorption by capillary condensation takes place along with a physical adsorption via filling of volume pores.

Immersion and flow adsorption calorimetry is an alternative technique to determine surface

areas and pore size distribution. This method assumes proportionality between surface area and the enthalpy of saturation adsorption. The main advantages of this technique over the BET procedure are that measurements can be conducted at room temperature and small samples are required (<0.4 g) (Saluja et al., 1987).

Determination of butane activity, iodine number and carbon tetrachloride activity in accordance with the published ASTM standard methods are commonly carried out by the vendors to assess the activation level of activated carbon. *Butane activity* is defined as the ratio (in percent) of the mass of butane adsorbed by an activated carbon sample to the mass of the sample, when the carbon is saturated with butane under specific conditions (ASTM D5742-95). *Iodine number* is the amount of iodine adsorbed (in milligrams) by 1 g of carbon under specified conditions (ASTM D4607-94). *Carbon tetrachloride activity* is defined as the ratio (in percent) of the weight of carbon tetrachloride adsorbed by an activated carbon sample to the weight of the sample when the activated carbon is saturated with carbon tetrachloride under specified conditions (ASTM D3467-04). These variables are neither absolute nor relative measures of the effectiveness of the tested activated carbon for other adsorbates or at other operating conditions than the specified conditions of the test. Instead, butane activity, iodine number and carbon tetrachloride activity are only indicators of micropore volume, surface area and pore volume of activated carbon sample, respectively.

Visualisation of extrinsic pores on the surface of carbons can be conducted using various microscopy techniques such as *scanning tunnelling microscopy (STM)* (Donnet et al., 1994, Paredes et al., 2003, Paredes et al., 2002), *transmission electron microscopy (TEM)* (Endo et al., 1998) and *scanning electron microscopy (SEM)* (Oshida et al., 1996, Inagaki and Suwa, 2001). *STM* is based on the interaction of an ultra-sharp tip with the sample surface to obtain an image of the localised surface area. With resolution down to atomic/molecular levels, the *STM* technique can provide useful information on the outermost surface of the samples down to the micropore scale. *STM* requires samples with atomically flat and crystalline surface in order to acquire good resolution images and can only produce the image on the external porosity in the material. Meanwhile, *TEM* measures the scattering pattern of a high powered electron beam shooting through the sample surface and records pores in white and pore walls in black on micrographs. These micrographs are then quantitatively analysed with

the aid of image processing tools to provide information on pore size distribution and the smoothness of pore walls. Unlike TEM, the *SEM* technique does not use a concentrated electron beam to penetrate the object, but instead scans the beam across the object. The lost energy of the beam is measured to create a three-dimensional picture of the surface of the sample. Although SEM is not as powerful as TEM, it can produce comprehensive information on the distribution and characterisation of large size pores such as pores inside the worm-like particles, crevice-like pores on worm like particles and pores formed by complicated entanglement of these fragile worm-like particles.

Small-angle X-ray scattering (SAXS) is used to determine pore size distribution and surface roughness at boundaries of pores by measuring the intensity of the scattering beam and the way in which this varies with the scattering angle (Nishikawa, 2003). One advantage of SAXS over the conventional adsorption methods is its access to ultramicropores and closed pores that are not accessible to adsorption based techniques.

5.3 Chemical content

Elemental analysis is used to assess heteroatoms (e.g. hydrogen, nitrogen, and sulfur) present in the activated carbon. Samples are combusted in high temperature in a stream of oxygen to completely convert all carbon compounds into carbon dioxide, hydrogen into water vapour, and sulfur into sulfur dioxide, while nitrogen containing compounds in the sample is reduced to N_2 by copper turnings (Bandosz and Ania, 2006). Specific detection techniques vary with the commercial instruments, although thermal conductive or infrared detectors are often used. The oxygen content may be estimated as the difference between 100% and the percentage of other measured components present (C, H, S, N).

X-ray photoelectron spectroscopy (XPS) can also be used to provide additional information on the chemical composition of material surfaces and has been employed to characterise chemical properties of various activated carbon samples (Mangun et al., 2001, Chingombe et al., 2005, Moreno-Castilla et al., 2000). This technique uses X-ray photons to excite electrons and then measures the kinetic energy of the ejected electrons as they try to return to their original stable energy state. Since the kinetic energy of the ejected electron is dependent on the specific binding energy of a given chemical element, different chemical elements can be

identified. Each element will have a characteristic set of peaks in the photoelectron spectrum and its abundance is related to the intensity of the peaks. It should be noted that the exterior surfaces of many samples are often more strongly oxidised than the inner core, thus the results of XPS are reliable for the characterisation of the surface of materials only (Bandosz and Ania, 2006). Samples must be dried and XPS must be carried out in ultrahigh vacuum to minimise collisions between foreign molecules/atoms and flying electrons.

X-Ray fluorescence (XRF) is commonly used for the qualitative and quantitative determination of elements with atomic number greater than that of oxygen (Bandosz and Ania, 2006). It is based on the principle in which elements in the samples get excited after absorbing the energy of primary X-Ray beam and emit their own characteristic fluorescence X-Rays. The main applications of XRF are to determine the inorganic constituents of activated carbons as a result of activation method (Hines et al., 2004), or are deposited on the surface as a product of surface reactions (Bagreev et al., 2004). Quantitative determination using XRF for solid samples is not easy and requires special calibration precautions such as uniform dispersion of the target element, uniform matrix particle size, and a constant matrix volume in order to achieve the accurate and reproducible analysis (Bandosz and Ania, 2006).

5.4 Surface functional groups

Fourier transform infrared (FTIR) spectroscopy has widely applied for qualitative and quantitative analysis of surface functional groups in activated carbon following modification treatments and under different operating conditions (Chingombe et al., 2005, Lu et al., 2012, Mangun et al., 2001, Moreno-Castilla et al., 2000, Romanos et al., 2013, Yang and Lua, 2006, Yan et al., 2004). In FTIR, the adsorption of the infrared beam passing through a sample at different wavelengths is measured. The degree of adsorption depends on the presence of various molecules in the sample. Infrared adsorption bands on activated carbon surfaces corresponding to various functional groups have been reported in previous studies (Fanning and Vannice, 1993, Lazar and Lazar, 2003).

FTIR analysis is, however, subjected to sample handling difficulty due to the fact that many activated carbons are too opaque for infrared beam to transmit through (Bandosz and Ania, 2006). The traditional sample preparation with KBr pellet, which is often used to dilute

activated carbon samples in an appropriate transparent medium, is time-consuming. Grinding conditions, difficulty in controlling sample moistures, radiation loss, and shifting of spectra baseline in high frequency bands due to particle light scattering all impact on the performance of FTIR (Breger and Chandler, 1969). The use of alternative sampling methods such as specular reflectance, diffuse reflectance, photoacoustic spectroscopy, or total internal reflectance can overcome these limitations and have been used in many studies to characterise surface chemistry of carbon materials (Moreno-Castilla et al., 2000, Fanning and Vannice, 1993, Cimadevilla et al., 2003)

Nuclear magnetic resonance (NMR) is a spectroscopic technique based on measurement of absorption of electromagnetic radiation by nuclei of the atoms which develop energy states in an intense magnetic field of the frequency between 4 - 900 Mhz. Isotopes of many elements (e.g. ^1H , ^2H , ^6Li , ^{10}B , ^{11}B , ^{13}C , ^{14}N , ^{15}N , ^{17}O , ^{19}F , ^{23}Na , ^{29}Si , ^{31}P , ^{35}Cl , ^{129}Xe , etc.) can be used as a NMR probe. Although NMR is not used commonly to study the surface of activated carbon, this technique has been employed to evaluate the fractions of aromatic and aliphatic functional groups in the activated carbon structure with ^{13}C spectra (Haghseresht et al., 1999), and to determine changes in surface density of functionalities and arrangements of heteroatoms on the activated carbon surface with ^{23}Na , ^{31}P and ^{11}B spectra (Harris et al., 1999, Bourbigot et al., 1995, Shirasaki et al., 2000).

5.5 Adsorption Capacity

Adsorption Isotherms

As discussed previously in **Section 2.3**, every type of activated carbon has a specific adsorption isotherm at a certain operating temperature. Adsorption isotherms can be used to estimate performance in full scale treatment processes. For example, the adsorption isotherm provides useful information about whether it is possible to reach a desired removal level with the selected activated carbon, particularly when multiple compounds are present and one or more compounds are poorly adsorbed. Carbon loading (i.e. adsorption capacity) can be directly obtained from the isotherms for a designed inlet concentration and desired removal efficiency. Adsorption isotherms can also be used to compare the relative performance of different types of carbon. The adsorption isotherm should be constructed in the conditions that are as similar as the actual conditions encountered in the odour control application. If

adsorption competition is believed to be significant, competitive adsorption isotherms should be obtained using a combination of several of the dominant compounds present in the gas to be treated.

Choosing the appropriate model is the most difficult task in constructing adsorption isotherms for a specific adsorption application (Seidel-Morgenstern, 2004). Adsorption isotherms can only be determined experimentally by comparing the experimental data with the results of model simulations produced by different isotherm models. The determination of experimental data for isotherm curve can be time-consuming and labour-intensive due to difficulty in determining the precise amount of adsorbent and uncertainty concerning the time needed to reach equilibrium.

Accelerated adsorption capacity methods

The use of an accelerated adsorption capacity method (referred as a short-cut method) is an alternative way to estimate the adsorption capacity of activated carbon for a specific adsorbate. In sewer odour control applications, the standard test method (determination of the accelerated hydrogen sulfide breakthrough capacity of granular and pelletized activated carbon - ASTM D6646-03) is widely performed by vendors to illustrate the adsorption effectiveness of their activated carbon because H_2S is often assumed to be the dominant odorous compound present in sewer headspace air. This method determines the adsorption capacity of the tested activated carbon at the breakthrough point under the specified laboratory test conditions using a controlled temperature of around 25°C, a humidified air stream (relative humidity around 80%), containing 1% H_2S (by volume), and with a contact time of 4.8 sec. The air stream is passed through a carbon bed until 50 ppmv breakthrough of H_2S is observed (representing 99.5% removal efficiency) and then the H_2S adsorption capacity of the carbon per unit volume is calculated.

Advantages of this method are that it is a straightforward and standardised testing protocol with all calculation procedures clearly described. In comparison with adsorption isotherms, this method is less time/labour intensive and does not require any complex modelling.

The accelerated adsorption capacity method has several limitations. First, the method only

assesses the adsorption of a single compound (H_2S) in isolation. It does not assess the ability to adsorb other odorants nor does it assess the potential of multi-compound adsorption effects which discussed previously in **Section 4.7**. Secondly, the test does not simulate actual operating conditions used for full scale systems. Due to the use of a high H_2S concentration for accelerated adsorption test (1% H_2S) compared to typical concentrations ranging from sub-ppm to hundreds of ppm in sewer air, the mass transfer zone in the bed column used in this test is proportionally much larger than that used in full scale systems. Such difference favours activated carbon with rapid removal of H_2S over carbons with slower kinetics.

Due to differences between operating conditions, the actual lifespan of the activated carbon in full scale odour abatement systems are sometimes significantly different from the expected lifespan (Smet et al., 1998, Bandosz et al., 2000a), sometimes leading to premature odour breakthrough and the need for unscheduled media replacement.

5.6 Other common measurable properties of activated carbons

Total ash content, particle size, hardness and density are commonly measured using standard methods developed by the American Society for Testing Materials (see **Table 5.1**) Information about these properties is often provided by vendors for any particular activated carbon product. Although these variables cannot be used on their own to identify which activated carbon has the optimal adsorption capacity for particular odour control applications, they are important factors in the selection process. As previously discussed, ash content provides an indication of overall activity and reactivation efficiency of activated carbon. Particle size distribution affects the rate of adsorption kinetics and pressure drops. Hardness is an important indicator of activated carbon to maintain physical integrity and withstand frictional impacts during a whole lifespan of the system. Higher density implies greater volume activity.

5.7 Remarks

As previously discussed in **Section 4**, understanding the physical and chemical properties of activated carbon is essential to evaluate and select the optimal activated carbon products for odour control applications. However, most product specifications provided by vendors of activated carbon contain only basic activated carbon properties. Information on properties

such as pore size distribution, surface functional groups, elemental content and adsorption isotherm are often not available unless being obtained via independent studies. Since odour control applications deal with a complex matrix of sewer air containing thousands of malodorous and volatile organic chemicals, making a selection based only on the vendor's product specification may lead to the use of sub-optimal adsorbent. The need exists for a standardised list of properties that provides the information necessary to effectively select these materials. A summary of key properties of activated carbon and testing methods recommended for applications controlling specific odorants in sewer air are presented in **Table 5.2**. It should be noted that although information about these key properties could not be used to derive the quantitative adsorption capacity of the specific odorants, they indicate the potential adsorption capacity which can be used to support the selection of activated carbon.

Table 5.2 Key properties and testing methods recommended to support activated carbon selection for specific odour abatement applications

Property	Analytical methods	Recommended when selecting activated carbon to remove:			
		H ₂ S	H ₂ S & reduced sulfur compounds)	Polar compounds	VOCs
Surface pH	Titration	✓	✓	✓	-
Oxygen containing functional groups	Fourier transform infrared & X-ray photoelectron spectroscopy	-	-	✓	-
Average polarity	Calorimetry	✓	✓	✓	✓
Chemical content	Elemental analysis; & X-Ray fluorescence	-	✓	-	-
Detailed pore size distribution (porosity)	BET adsorption; calorimetry; microscopies; & small-angle X-ray	✓	✓	✓	✓
Surface Area	Calorimetry & BET adsorption	✓	✓	✓	✓
Adsorption capacity	ASTM D3838	✓	-	-	-
Adsorption activity & capacity	Studying adsorption isotherm & kinetics	✓	✓	✓	✓

6.0 Full Scale System Design

Both system design and operation are important to achieve high odour removal efficiencies on a continuous basis. This section will focus on the design of activated carbon based adsorption systems commonly applied for odour abatement in sewer networks.

6.1 Characteristics of Feed Stream

The design of a full scale system often begins with the determination of feed stream characteristics including: the specific compounds present in the feed stream, their concentrations (range and average), flow rate, temperature, pressure (range and average), and relative humidity. Knowledge of these data is essential for subsequent design steps such as a selection of the adsorption system configuration, selection of the adsorbent material, and other design calculations.

6.2 System Configuration - Fixed Bed Adsorber

Activated carbon bed adsorbers vary in size from small static cartridges or skid mounted drums for handling air flow of 50-1000 m³/hr to large activated carbon adsorption systems with capacities in excess of 100,000 m³/s. Small disposable units are usually used for odour control and treatment of relatively low VOC concentrations, while large fully automated regenerative carbon adsorption systems can handle VOC's from few ppm to tens of thousands ppm concentrations. For sewer odour control applications dealing with reduced sulfur odorants, nonregenerative activated carbon fixed bed adsorbers are usually used since a regenerative system coupled with either solvent recovery process or incineration is often not cost-effective. This section will focus only on the design and configuration of a fixed bed adsorber.

Fixed bed adsorbers are typically a vessel that may or may not be compartmented and has inlet and outlet ducting for the gas feed and a distributor plate at the bottom supporting the granular or pelletised activated carbon media. The layout of fixed bed adsorbers can be either horizontal or vertical. Typical configurations are shown in **Figure 6.1**. The feed gas stream usually passes through the adsorber in a downward direction to avoid the fluidisation of the adsorbent media.

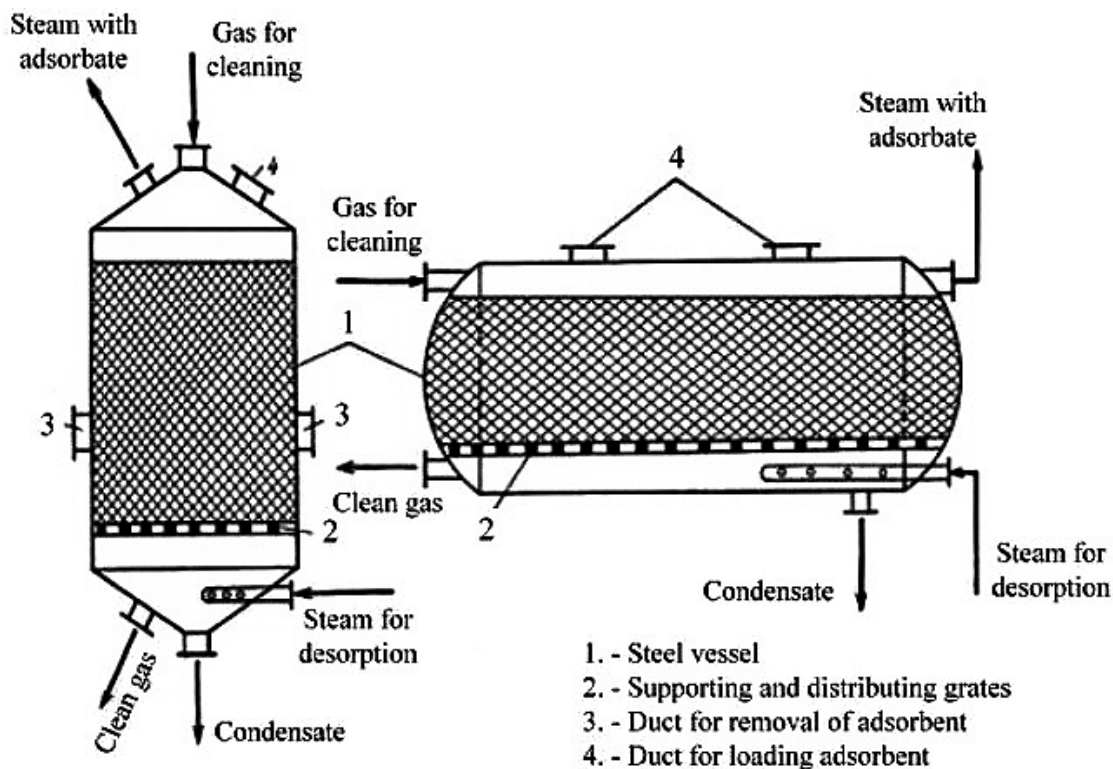


Figure 6.1 Schematic of vertical (left) and horizontal (right) fixed bed adsorbers (Thomas and Crittenden, 1998)

A fixed bed system adsorbs increasing amounts of adsorbates in an unsteady-state process until the bed is saturated. In operation, the stationary bed can be divided into three approximate zones including the saturated zone in which carbon pores are completely filled with the adsorbates, followed by the adsorption zone where the current adsorption are actually occurring, and the final zone where the activated carbon has little or no adsorbed compounds. The size and location of these zones within the bed will change with time. As the gas stream passes through the adsorbent bed, the amount of adsorbed components will increase until reaching equilibrium, resulting in a saturated zone ("a front") moving through the depth of the bed. Eventually, the mass transfer front of agent chemical (e.g. sulfur) will progress along activated carbon bed during the operation (**Figure 6.2**).

Within a short distance from the bed inlet, the mass transfer zone becomes stable and its shape remains unchanged as it progresses through the bed (a constant pattern mass transfer). When the mass transfer front nears the outlet, the pollutant concentration reaches the breakthrough concentration (i.e. maximum acceptable concentration) and the activated carbon filter has reached the end of its useful life.

The shape of the breakthrough curve is defined by the actual rate and mechanism of the adsorption process, the nature of the adsorbents, the gas superficial velocity, the concentration of the solute in the stream, and the bed depth (Schnelle and Brown, 2001). The breakthrough time generally decreases with decreased bed depth, increased particle size of adsorbents, increased rate of gas flow through the bed, and increased adsorbate concentrations in the feed. The breakthrough points may be sharply defined in some cases, and in others poorly defined. The design consists of, in part, the determination of the breakthrough curve using either a pilot scale system or standard accelerated methods.

For a fixed bed system with single-use activated carbon, the exhausted material is emptied out at the end of the operating life and the bed is refilled with fresh material. The used activated carbon should be disposed in accordance with local, state or national regulations. In Australia, activated carbon waste from odour control applications (not containing free liquid) is classified as a general solid waste provided it passes a leachate test (Gupta et al., 1992, Airguard Research and Technical Center, 2013). Spent activated carbon is commonly disposed in Australia via landfill.

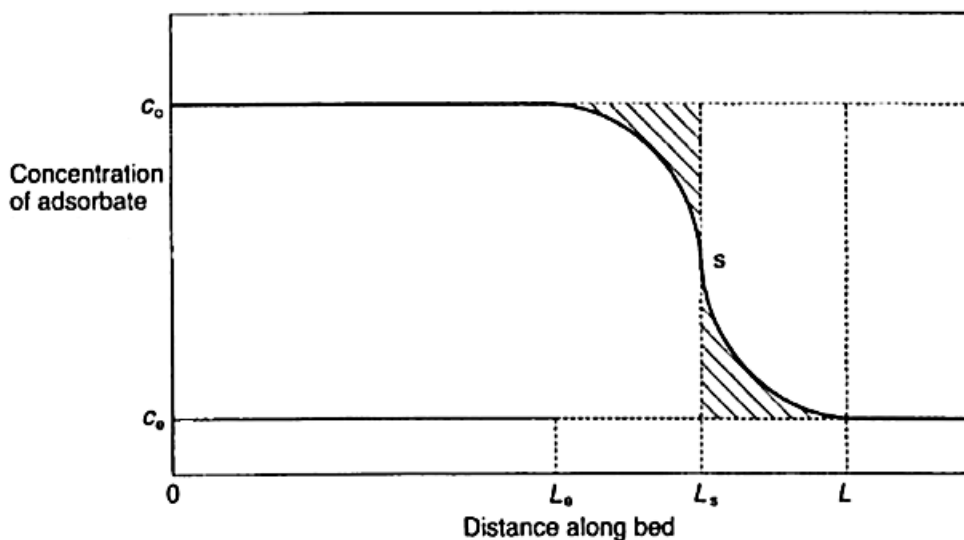


Figure 6.2 Mass transfer zone in a activated carbon bed (Thomas and Crittenden, 1998)

6.3 Material Selection

Material selection is an application specific decision that considers the type and concentrations of specific compounds in sewer headspace air along with the sewer air flow rate. Selection of an appropriate activated carbon material for a given application is based on the following general criteria:

- Possibility to yield desirable operational performance in terms of adsorption capacity and selectivity, kinetics, and durability (i.e. chemical and thermal stability, high mechanical strength and hardness);
- Low in inorganic materials (which are non-porous and reduces the adsorption capacity measured per mass unit); and
- Availability (i.e. stable supply) and prices of activated carbon materials since it is a significant component of the total cost of the adsorption system and ongoing operating cost.

Rarely will a single activated carbon product be optimal with regards to all of these aspects, although it is possible to narrow the choice to one or two types of activated carbon. The final decision should be made based on the characteristics of the particular adsorbent, which must be experimentally measured. To the knowledge of the author at the time writing this report, there is no existing uniform guidance for helping select the appropriate activated carbon materials. Customers have to make the selection based on their own experience, results from pilot scale trials or research studies if available, or rely on information given by the vendors.

6.3.1 Types of Activated Carbon

Many types of activated carbon are available including virgin, water regenerative, chemically impregnated, sulfur selective and molecular sieve activated carbon. **Table 6.1** provides a brief comparison of the common activated carbon media used for odour control applications. Molecular sieve activated carbon is not included in the list since it is mainly used for gas separation rather than odour control. Information on molecular sieve activated carbon can be found in the book “*Activated Carbon Adsorption*” (Bansal and Goyal, 2005).

It should be noted that the adsorption capacity of activated carbon can vary between batches due to the inconsistencies in raw material. Yan et al. (2002) tested six different production batches of an activated carbons and found that the adsorption capacity varied between 5.2 ~ 21.1 % weight of H₂S per weight of activated carbon.

Table 6.1 Comparison of activated carbons used for odour control.

Adapted from (Graham, 2006)

	Virgin	Impregnated	Water-regenerative	Sulfur-selective
Apparent density, g/cm ³	0.50	0.55	0.56	0.40
Impregnates	None	NaOH/ KOH	None	None
Fate of H ₂ S	Sulfur/H ₂ SO ₄	Sulfur/H ₂ SO ₄	H ₂ SO ₄	Sulfur
H ₂ S adsorption capacity, by weight (%)	4-7	20-25	14-18	65-75
Ignition temperature	~380°C	~150°C	~420°C	~540°C
pH of exhausted carbon	Acidic	Acidic	Acidic	Neutral
Applications (main targeted pollutants)	Ammonia, sulfur malodorous and volatile organic compounds	H ₂ S and odorous sulfur organic compounds	H ₂ S	H ₂ S and sulfur organic compounds

Virgin Carbon

Different from activated carbon used for liquid phase adsorption, activated carbon used for gas phase adsorption has a larger number of small pores. Virgin activated carbon produced from coal or coconut shell raw material is similar in hydrogen sulfide removal capacity but different in adsorption of organic odours (Graham, 2006). Coconut shell based activated carbon typically has lower ash content, greater hardness, and a tighter, more microporous pore structure than coal based activated carbon. The average pore diameter of coconut shell based activated carbon is often less than 2 nm, whilst a smaller portion of pores in coal-based activated carbon is in the lower micropore diameter size (Schnelle and Brown, 2001). Due to the difference in microporosity, coconut shell based activated carbon is a good fit for the removal of light molecular weight VOCs while coal based activated carbon is more suitable for low-molecular weight hydrocarbons, chlorinated organics and high-molecular weight compounds like pesticides (Schnelle and Brown, 2001). Bagreev and Bandoz(2001) claimed that coconut-based activated carbon is superior to coal-based carbon for the

adsorption/oxidation of H_2S . Virgin activated carbon can be thermally reactivated and restored to near its original adsorptive capacity (Rafson, 1998).

As previously mentioned, the predominant adsorption process between VOCs and adsorbents is physisorption. Virgin activated carbon with high total surface area are a desirable adsorbent material for the removal of VOCs. The desirable activated carbon material should also have the pores larger than the molecular sizes of the VOCs to be adsorbed so that the gas molecules can penetrate and fill the pore space. According to USEPA (1988), selecting an activated carbon with a majority of micropores smaller than approximately twice the diameter of the adsorbate molecules will result in the greatest adsorptive forces.

Water regenerative activated carbon

Water regenerative activated carbon removes hydrogen sulfide from gas streams by almost exclusively oxidizing the hydrogen sulfide into sulfuric acid with little or no elemental sulfur formed (Graham, 2006). The functional groups on the carbon's surface (formed by adding an amine-based compound into coal char during the activation process at high temperature and in the absence of oxygen) allow these activated carbons to be regenerated by water washing. Due to its high solubility in water, the sulfuric acid that is initially formed and stored in the carbon's pore structure can be leached from the carbon by water-washing. Although minimal handling is required for water regenerative carbons, care is required in discharging the water wash because the initial water wash can be very acidic with a pH well below 2 (Rafson, 1998).

Sulfur selective catalytic activated carbon

Like virgin activated carbon, sulfur selective catalytic activated carbon is manufactured from coal, but have catalytically active ingredients added during the activation process to oxidise hydrogen sulfide and other reduced sulfur compounds to elemental sulfur and minimise the formation of sulfuric acid (Graham, 2006). Since the molecular size of sulfur is less than one-third the molecular size of sulfuric acid, more sulfur can be stored in the same carbon pore volume space than can be stored as sulfuric acid. The removal capacity of hydrogen sulfide is expected to significantly increase in comparison with other types of activated carbon

(**Table 6.1**). Exhausted sulfur selective activated carbon is less hazardous for handling and disposal because it is pH neutral. Sulfur selective activated carbon tends to require longer bed contact and slower superficial velocity due to the slower kinetic conversion of sulfur-reduced compounds to elemental sulfur compared to the conversion to sulphuric acid.

Impregnated Activated Carbon

Chemically impregnated activated carbon has been available for nearly 20 years (Graham, 2006). Activated carbon can be chemically impregnated to enhance the removal of specific odorants such as H_2S . Impregnation chemicals such as salts, oxides of metals, neutralising or oxidising agents can increase catalytic property of the original activated carbon, and may greatly increase the removal capacity of the activated carbon bed. To control high concentration of H_2S in wastewater associated processes, alkaline hydroxide impregnated activated carbon is often used. It should be noted that caustic impregnated activated carbon with pH in the range of 8.5-9.5 has been observed to hardly remove any ammonia (Kolton-Shapira, 1995).

Modified and impregnated adsorbents used for air treatment have higher oxidative capacities, especially under high levels of humidity. Some types of impregnated activated carbon can be regenerated to restore their adsorption capacity by immersing in sodium hydroxide or potassium hydroxide, which removes the elemental sulfur and sulfuric acid (Bandosz, 2006). The full adsorptive capacity of the original carbon cannot be regenerated as some loss in capacity is incurred during each regeneration cycle.

6.3.2 Selection based on the Adsorbent Characteristics

It is often assumed that the larger the surface area the better the adsorption of compounds by activated carbon. However, as previously discussed, surface area does not always correlate with capacity. Even when it does, adsorption kinetics and other factors may have a more significant effect on the overall cost and performance than adsorption capacity (Kent, 2008).

Selection of activated carbon requires data on a range of properties such as densities, particle size, porosity, adsorption capacity, selectivity, regenerability, kinetics, and cost. Vendors

may have charts and tables available, although vendors' data are often generic (not batch specific) and are seldom guaranteed to be valid for the design purpose. Some adsorption equilibrium data can be found in published books such as "Adsorption Equilibrium Data Handbook" and "Carbon Isotherms for Toxic Organics" (Valenzuela and Myers, 1989, Dodds and Cohen, 1980) as well as relevant journal articles from *Adsorption*, *Carbon*, *Chemical Engineering Science*, *Langmuir* etc. Despite of a multitude of sources, data correctly matched for a particular adsorbent-adsorbate in the temperature and pressure range of interest are seldom found. The use of these resources implies the risk of suboptimal design. Obtaining the experimental data for the particular adsorbent-adsorbate system can reduce this risk and improve design.

Density data (including bulk, particle and solid densities) are used in calculations of total adsorbent cost, vessel dimensions from the amount of adsorbent, and for conversion between adsorption capacities per unit mass and adsorption capacity per unit volume. Void fractions are used in pressure drop calculations and material mass balance equations (Kent, 2008).

Adsorption capacity (or activated carbon loading) is the amount of adsorbate taken up by the adsorbent per unit mass (or volume) of the adsorbent. Since adsorption capacity data are used to determine the amount of adsorbent required and also the volume of the adsorber vessels, these data have a significant impact on the capital cost. The capital cost can be significantly higher if a low adsorption capacity adsorbent is selected. It is more convenient to compare alternative adsorbents with respect to their capacities on a per unit volume basis because total volume of adsorbent needed directly determines the cost of the vessels, pipes and other equipment.

Equilibrium adsorption data provides information on the adsorption capacities of the adsorbent in the temperature and pressure ranges of interest. For gas phase applications, adsorption isotherm plots of adsorption capacity for a particular adsorbate against the partial pressure of the adsorbate at each fixed temperature can also provide useful information on the potential performance of the activated carbon with Type I, II or IV isotherms representing favourable performance and Type III or V isotherms representing unfavourable performance (Kent, 2008). Additionally, hysteresis loops indicate possible adverse impacts on adsorption

kinetics and regenerability. Other types of equilibrium adsorption data such as isosteres and isobars can also provide information about the adsorption capacity.

In addition to adsorption isotherms, other properties such as surface area, pore size distribution, carbon tetrachloride activity, iodine number and butane activity also provide indications of the adsorption capacity. These data are often provided by vendors to describe activated carbon, although they can only indicate the potential adsorption of the activated carbon. Quantitative adsorption capacity information for a particular adsorbate-adsorbent system are obtained from the adsorption isotherm and kinetic adsorption tests.

Selectivity can be defined as a tendency and capacity of the adsorbent to attract one component over another. Adsorbents with the most desirable selectivity are those which do not adsorb the major components (e.g. carrier gas), but mainly remove the target components (e.g. toxic and odorous compounds). The target components may be selectively adsorbed by the adsorbent at different degrees due to their difference in polarity, molecular size and reactivity. Selectivity of the adsorbent is also affected by the nature of its surface chemistry and impregnation. For the applications with multiple dominant odorants, the adsorption performance of an activated carbon material should be evaluated against the least strongly adsorbed odorant because the breakthrough of less well adsorbed odorants occurs before those that are more strongly adsorbed (Smet et al., 1998).

Mass transfer kinetics (i.e. rate of adsorption kinetics) is related to intraparticle mass transfer resistances and plays an important role in defining cycle time and the size of the equipment in the fixed bed adsorption process (Kent, 2008, Thomas and Crittenden, 1998). Mass transfer kinetics are demonstrated by the shape of the breakthrough curve (a plot of the effluent concentration versus time). If the adsorption is efficient, the effluent concentration would be zero until the time (breakthrough time) at which the effluent concentration suddenly increases to the value of the feed concentration. At this point, the bed would be completely saturated. Fast kinetics is often supported by the existence of a sharp breakthrough curve, while slow kinetics results in a distended breakthrough curve.

Adsorbent costs can vary with time, supplier and other factors. The adsorbent cost can be

very high if their production requires the expensive raw materials, special treatment processes, and/or expensive chemicals for impregnation or incorporation of oxidation catalysts. Price is also sensitive to the quantity in the order. This factor should also be taken into account when selecting the adsorbent material.

6.4 Design Approach

Full scale adsorbers can be designed using either rigorous solution of the conservation, transport and thermodynamic equations or through short-cut empirical techniques based on laboratory scale, pilot scale, and industrial scale data (Thomas and Crittenden, 1998). These methods are comprehensively described by Thomas and Crittenden (1998), and this section briefly summarizes the important features of these approaches.

In the rigorous approach, it is desirable to conduct predictive mathematical modelling of the heat, mass and momentum transfer processes that occur in both the adsorption and desorption stages of a process. This helps to avoid the need to carry out expensive and time-consuming experiments. A certain amount of experimental data is, however, required for modelling and must be obtained from the experimental work or the literature. Prediction accuracy will be related to the accuracy and availability of fundamental data as well as the number and importance of assumptions and approximations made in order to obtain the solution. No general analytical solution exists and computational resources are often required to determine the numerical solution of the full set of equations. Several adsorption design and simulation software are commercially available, such as AdDesignS[™] and Aspen Plus[®] that support the evaluation and design of fixed bed adsorption processes for the removal of contaminants from air and water.

Many designs of activated carbon adsorbers, particularly fixed beds, employ empirical short cut methods. This approach is extensively used not only due to its simplicity, but also due to the complex nature of the more rigorous alternatives. These methods include the (i) length or weight of unused bed, (ii) the mass transfer zone depth, (iii) the empty bed contact time, (iv) the bed depth service time, (v) the transfer unit approach, and (vi) the capacity at breakthrough point. The detailed description of these short-cut methods are presented in the book *“Adsorption Technology & Design”* (Thomas and Crittenden, 1998). All empirical short

cut methods involve the design of small-scale experiment in order to obtain data for the design of the full size plant. The accelerated adsorption test with 1% H₂S concentrations (ASTM D6646 – 01), which is used to estimate the breakthrough capacity of the activated carbon, is an example of a short cut method for designing fixed bed activated carbon adsorbers in wastewater odour control applications.

These design methods are simple and straight forward because the data obtained from the small-scale experiments can be directly used to determine the required flow rate and dimensions of the full-scale bed. Special attention needs to be paid to the choice of the length, diameter and flow rate in the small scale experiments so that flow dynamics and the dispersion characteristics in the small-scale experiments are similar to those in the full-scale system. For example, a small-scale column bed should be long enough to retain several mass transfer zone lengths. The constant pattern mass transfer zone must be achieved in the small-scale column if a full-size design is based on the breakthrough curve. In multicomponent systems, non-adiabatic systems, or in cases where there are unfavourable adsorption isotherms, the full-scale bed length should be equal to the pilot scale bed length which gives the required performance.

The following procedure based on the guideline of the US Army Corps of Engineers (2001) can be used to estimate design parameters of the conventional nonregenerative fixed bed adsorber:

- determine initial parameters such as flow rate of air phase entering the air blower, temperature of the vapour feed, designed run time between carbon changes, required number of carbon vessels, atmospheric conditions (ambient temperature and pressure), adsorbate components and their concentrations;
- estimate the superficial velocities based on vendors' literature;
- calculate the partial pressure of each component from its concentration and total pressure;
- determine the adsorption capacity of the activated carbon from the isotherm data for each component corresponding to its partial pressure at the operating pressure and temperature or from short cut empirical methods;

- estimate the quantity of carbon required to adsorb these components over the designed run time;
- estimate the diameter of the carbon adsorption vessels from flow rate and superficial velocity;
- estimate the depth of the vessels from the carbon density, quantity of carbon required, and cross sectional area of the vessel;
- calculate the total pressure drops through the units in the process train;
- determine the size and type of blower based on the flow rate and total pressure required (using manufacturers' pump curve);
- determine the size and type of heat exchanger; and
- estimate the budget.

6.5 Design and Operation Considerations

Although there are no standard design criteria for gas phase adsorption, the following guidelines are considered to be industry-accepted practices for vapour phase – granular/pelletized activated carbon fixed bed systems:

- flow velocity: 0.15 to 0.45 m/s
- carbon bed depths: 0.6 – 2.0 m
- maximum adsorber diameter: 3.6 m
- empty bed contact time: 2 – 4 s
- Common performance requirements for removal of VOCs in industry:
 - 90-95% using steam regenerable activated carbon
 - 99% using virgin activated carbon respectively
- Typical design requirements for removal of H₂S:
 - at least two stages each at efficiency of 90-95% to reach the overall removal 99-99.5%, or
 - one stage at the efficiency of 99%

In order to estimate the amount of adsorbate passing through an activated carbon bed, it is recommended to assume 90% capture of VOCs per bed. The 90 percent capture is the minimum performance capability required in a design of activated carbon adsorber and typical figure guaranteed by suppliers. These will be conservative estimates, and it is

expected that the actual operation of an activated carbon unit can result in higher capture rates.

From rules of thumb, surface loading rate (or superficial velocity) should not be greater 30 m/min in order to achieve 90% or more removal efficiency (USEPA, 2008). It is also recommended that lower limit of the gas velocity is 6 m/min to avoid flow related problems such as channelling.

It is essential to ensure that the adsorption bed is well packed and the flow is well distributed. Poorly packed beds can develop channels (i.e. open areas through which air can pass) that short-circuit the adsorbent bed, resulting in elevated outlet odorant concentrations. If the channelling is small, the system may be able maintain the required removal efficiency, however if the channelling is significant the removal efficiency will severely drop. Channelling can be minimised using the rule of thumb that the ratio of bed diameter to the particle diameter should be greater than 20 (Thomas and Crittenden, 1998).

If the adsorption vessels and the spent carbon storage vessel will be pressurised or put under vacuum they must be designed, fabricated, tested and marked in accordance with the applicable Australian standards such as AS 1200: 2000 Pressure Equipment, AS 1210: 1997 Pressure Vessel, or ASME – International Boiler and Pressure Vessel Code. Furthermore, pressure safeguards such as rupture disks must be incorporated. Carbon loading and unloading piping should avoid long runs, areas of low velocity, radical bends, low spots without cleanouts, line restrictions and restrictive bends. Some activated carbon materials become corrosive when wetted, thus the vessel and piping must be made from corrosion resistant materials with additional protective coatings. Typical protective linings are vinyl ester, fibreglass polyethylene, Teflon and kynar (US Army Corps of Engineers, 2001). Wet drained activated carbon adsorbs oxygen from the air, thus all adsorption and storage vessels must include ventilation and all inspection manways should be designed to support confined space entry procedure. The activated carbon bed should have velocity and sampling ports at inlets and outlets for air quality monitoring purposes. The port locations should be chosen in accordance with the US EPA standard methods in the *“Quality Assurance Handbook for Air Pollution Measurement Systems –Volume III Stationary Source-Specific Methods”* (Shigehara et al., 1994). Additional ports for gas and sample extraction can also be added, often at

25/50/75% of bed depth to assist the determination of remaining service life of the adsorber during its operation.

Bed fouling is another consideration in adsorber design. Fouling gradually reduces the carbon adsorption capacity and can occur when non-target compounds in the gas stream bind with the adsorbent and will not desorb from the bed. These compounds can be solid particles, high molecular weight compounds, or compounds which chemically react on the surface of the carbon. Approaches to compensate for bed fouling include increasing the volume of carbon beyond the minimum required to achieve the desired adsorption time, or increasing the amount of water used to regenerate the bed in cases of the water washable activated carbon (USEPA, 1988).

For vapour phase applications, activated carbon adsorbers may not be able to maintain the desired level of performance when high levels of dust and moisture are present (Williams, 1995). Dust or lint greater than 3 µm in size can cover the surface of the adsorbent and reduce the surface area available to gas molecules for adsorption (USEPA, 2008). A particulate matter filter can be installed prior to the blower to minimise the effect of dust on the adsorbent. Flooding of sewer pump station air exhausts can also shorten the life of activated carbon beds as sewage will clog all carbon adsorption sites. If the activated carbon is contaminated by a substance that damages it irreversibly, it must be disposed of and replaced.

One issue faced during the use of activated carbon for vapour phase applications is the development of bed hot spots during operation. Hot spots occur in the area of activated carbon bed where temperature increases to the point at which oxidation occurs. The heating in the bed is mainly from the exothermic reaction of gas species with the activated carbon material that only occurs in the mass transfer zone where the gas species are absorbed by the media or reacted with chemical compounds impregnated on the carbon media. VOC concentrations greater than 500 ppmv can present a fire risk in activated carbon beds due to the significant heat release from adsorption (Soelberg et al., 2011). It has been observed in some installations that heat from adsorption of VOCs has actually built up and ignited bed fires (Shelley, 1994). VOC concentrations in sewer air are typically lower than 500 ppmv;

therefore, a fire risk associated with adsorption of VOCs is negligible. However, if caustic impregnated carbons are used, the impregnation decreases the ignition temperature of the carbon, increasing the hazard of self-ignition (Bandosz et al., 2000b, Turk and Bandosz, 2001). Some oxidation processes such as that of hydrogen sulfide to sulfur either directly or indirectly via (dissociation to HS^-) also releases significant heat (Bandosz, 2006) and can contribute to the risk of bed self-ignition. The operating conditions that increase the hotspot fire risk are uneven-distribution flow, low gas velocities, presence of sufficient oxygen and high reactivity between gas species at high concentrations with adsorbent material.

Hotspots can be detected and controlled by monitoring in-bed, and bed outlet gas temperatures as well as carbon monoxide concentrations. Internal sprinklers can be installed in the carbon vessel as an additional fire protection measure if there is a high probability of bed ignition. Other alternatives to minimise fire hazard in the activated carbon adsorber are pre-conditioning and pre-wetting of the activated carbon bed. Since adsorption reactions can lead to temperatures of up to 120°C in new activated carbon, pre-conditioning carbon beds with gas stream of relatively low concentrations of solvents (called “heel”) is recommended to reduce the adsorption exotherm to temperature below 30°C (James, 2003). Pre-wetting the carbon beds is an alternative approach to reduce exothermic activity and minimise flammability hazard during start-up. Pre-wetting has the additional benefit of preventing dust cloud formation (occupational hygiene hazard) when loading the carbon into the beds. Similar to pre-humidification, pre-wetting activated carbon may also improve the adsorption capacity for H_2S via dissociation, but affects adsorption performance for other non-polar compounds.

As previously discussed in **Section 4**, high operating temperatures and relative humidity decrease adsorption capacity. As general rule, the temperature should be kept below 53°C to ensure the adequate adsorption capacity (USEPA, 2008). For relative humidity, it is recommended to maintain the operating value around 50% for optimal adsorption efficiency. Relative humidity is essential in the chemical oxidation of reduced sulfur compounds, but high relative humidity will affect the physical adsorption capacity for these compound and VOCs.

In gas phase applications, headloss varies significantly depending on piping configuration, carbon particle size and surface loading rate. A typical pressure drop through an activated carbon based treatment system is from 83 mm to 330 mm of water column (0.8 - 3.2 kPa) per meter of carbon bed (US Army Corps of Engineers, 2001). High pressure drop during operation may result in improved bed loading near the bed entrance, but it may also cause condensation (Thomas and Crittenden, 1998) and increase the process operating cost.

6.6 Monitoring Considerations

For nonregenerative activated carbon fixed bed adsorbers, the bed replacement is based on empirical experience because vendors do not often guarantee carbon life (Estrada et al., 2011). Often vendors only provide “generic information” about the H₂S adsorption capacity of activated carbon product intended for use in sewage odour control applications. Since sewage related emissions also contain other odorous gases and VOCs, the estimate of carbon life based on the data of H₂S adsorption capacity is usually unreliable.

Any adsorption system using nonregenerative activated carbon is very robust during its operation. Throughout its service life, the removal efficiency is stable against fluctuating operating conditions within an acceptable range of design values. Any significant drops in removal efficiency are due to either the activated carbon reaching the end of its lifespan, facing undesirable operating conditions, or bed cracking or channelling.

To maintain the desirable performance with uninterrupted service, it is necessary to determine the remaining service life of the adsorber by monitoring the progress of the adsorbed phases profile through the carbon bed (Wynne and Spencer, 1982). Remaining service life can be determined using a test element attached to the influent face of one of the system's cell. Before the estimated service life passes, the test element is removed from the cell and sent for analysis to determine the remaining adsorption capacity of the cell. The test element also provides the indication of any potential problems such as plugging, excessive vapour condensation, and physical deterioration of carbon pellets or carbon fibre materials.

Alternatively, the performance of the adsorption system can be evaluated by measuring the outlet concentration of the adsorbate. In activated carbon based adsorption systems, the exit

VOC concentration tends to be constant and relatively independent of the inlet VOC concentration, thus the efficiency tends to drop as VOC concentration in the feed stream drops (Riser-Roberts, 1998). Hence changes in the outlet concentration should be carefully monitored since the increasing outlet concentrations may indicate possibilities of varying operating conditions that are outside the designed range, or that the process is reaching the breakthrough point.

Monitoring is conducted using on-line instruments that draw samples from the outlet gas stream on the frequent basis. Different instruments can be used for measuring VOCs concentrations such as flame ionisation detectors, catalytic combustion detectors, photoionisation detectors, while sulfur compounds can be monitored using electrochemical sensors (e.g. OdaLog®, Jerome®). The major advantage of on-line monitoring is that prompt corrections can be undertaken to address any issues associated with the performance of each bed. This approach is however, reactive and not predictive. It should also be noted that the commercially available electrochemical sulfur sensors focus on H₂S, but are cross-sensitive to other sulfur containing compounds (Sivret et al., 2010). Furthermore, operators should be aware of a variety of problems associated with the sampling lines which may occur and affect the accuracy of the monitoring data. These problems include, but are not limited to, air infiltration due to leaking connection or corroded parts, adsorption and absorption of samples drawn from the outlet stream due to low temperature and water condensation (a particularly important issue for sewer and wastewater treatment facilities), reduced sample gas flow rate due to plugging of tubes between the sampling inlet and the monitoring instrument, and inoperative control valves or mass flow controllers.

Other operating parameters such as relative humidity, inlet gas temperature, and static pressure drop, and volumetric flow rate should also be monitored frequently since these factors are known to influence the adsorption capacity as discussed in previous sections. The *relative humidity* should be monitored frequently and promptly adjusted to ensure that it mostly remains within the optimal range. Gas inlet temperatures should be compared with typical period baseline values. Elevated inlet temperatures may lead to inadequate performance.

Static pressure drops across the adsorber bed are usually much lower than the designed values and any changes in pressure drop from baseline levels are often associated with conditions that may worsen performance. If the gas flow rate remains constant, increases in pressure drop indicate the accumulation of dust and particulate matter on the inlet side of the bed while decrease in pressure drops indicate the development of channelling, or partial or complete collapse of the fixed bed due to the corrosion of the support grid.

Any observation of *gas flow rates* above the design ranges may imply premature breakthrough. Increasing gas flow rates can be noted by increased pump motor current, increased bed pressure drop, or increased static hood pressure. The reverse holds for decreasing gas flow rates. Decrease in gas flow rates also indicates potential problems such as the increasing fugitive emission from the process (i.e. gas leaking possibly due to corrosion and rupture of the adsorber's structure, ducts and pipes).

6.7 Process Economics

Information on investment and operating costs for full-scale activated carbon odour abatement processes is limited due to the reticence of vendors to provide the economic data of their processes to academic researchers. Most of economic information available in the literature (European Commision, 2003, US Army Corps of Engineers, 2001, Ruddy and Carroll, 1993, Smet et al., 1998) is based on old data (prior to 1998). The most recent economic analysis of the odour treatment technologies were conducted by Estrada et al. (2012, 2011) based on 2007-2010 data on the investment and operating costs of full-scale systems which had been obtained from odour-treatment technologies vendors in Spain and Australia. The investment and operating costs of activated carbon technology from the 2007-2010 data (Estrada et al., 2011) are quite comparable with the costs reported prior to 1998 (Smet et al., 1998).

Activated carbon is one of the most expensive odour treatment technologies due to the high investment cost, high operating cost, large land area and potentially problematic disposal of spent media. The price of material, the size and type of adsorption processes constitutes the investment cost of the activate carbon adsorber. Designed empty bed retention time is a key parameter for determining the total cost because longer retention time means a larger vessel and more volume of activated carbon required. The adsorber vessels and activated carbon

materials can comprise from 50% to nearly 90% of the total initial investment costs (Vatavuk et al., 1999). Auxiliary equipment such as blowers, pumps, and internal piping also contribute to the cost of these systems. Additional investment may also be required for the installation of heat exchange or particulate filter for moisture and dust control. Activated carbon adsorbers often have a large footprint, thus the investment cost could be significantly higher if the land available is limited or the price of land is relatively high. **Table 6.2** and **Table 6.3** provide an example of a typical breakdown of investment and operating costs respectively for a fixed bed activated carbon system (Vatavuk et al., 1999).

Table 6.2 Typical capital investment breakdown for a fixed bed activated carbon adsorber

Cost Item	Factor
Initial Investment Cost	
Purchased equipment costs:	
• Adsorber + auxiliary equipment	= A
• Instrumentation	= 0.10 A
• Sales taxes	= 0.03 A
• Freight	= 0.05 A
Total purchased equipment costs	= B = 1.18 A
Direct installation costs:	
• Foundation and supports	= 0.08 B
• Handling and erection	= 0.14 B
• Electrical	= 0.04 B
• Piping	= 0.02 B
• Insulation	= 0.01 B
• Painting	= 0.01 B
Total direct installation costs	= 0.30 B
Site preparation cost	= C
Buildings	= D
Indirect installation costs	
• Engineering	= 0.10 B
• Construction and field expenses	= 0.05 B
• Contractor fees	= 0.10 B
• Start-up	= 0.02 B
• Performance test	= 0.01 B
• Contingencies	= 0.03 B
Total indirect installation costs	= 0.31 B
<i>TOTAL Capital Investment</i>	<i>= 1.90 A + C + D</i>

Table 6.3 A typical breakdown of the annual operating costs for a nonregenerative activated carbon adsorber

Cost Item	Factor
Initial Investment Cost	
Direct annual costs:	
Operating labour	
• Operator	= E
• Supervisor (15% of operator)	= 0.15 E
Maintenance	
• Labour	= E
• Material (100% maintenance labour)	= E
Media replacement	
• Replacement labour	= G
• Media cost	= H
Utilities	
• Electricity	= I
Total direct annual costs	$= 3.15 E + G + H + I$
Indirect annual costs:	
• Overhead (60% of sum of operating labour and maintenance)	= 1.89 E
• Administration charge (2% of total capital investment)	= $0.02 \times (1.90 A + C + D)$
• Property tax (1% of total capital investment)	= $0.01 \times (1.90 A + C + D)$
• Insurance (1% of total capital investment)	= $0.01 \times (1.90 A + C + D)$
Total direct installation costs	$= 1.89 E + 0.04 \times (1.90 A + C + D)$
<i>TOTAL Annual Cost</i>	$= 5.04 E + G + H + I + 0.04 \times (1.90 A + C + D)$

The investment cost per unit flow rate for nonregenerative activated carbon fixed bed adsorbers (with capacities < 50000 m³/h) varies in the range of €2.5 – €14 (equivalent to \$3.5 –\$20, at a rate of €1 = \$1.4) per m³/h (Estrada et al., 2011). The investment cost per unit

flow rate decreases with increased design flow rate. Costs of packing materials, energy consumption, and work (including labour, transport and handling, disposal and maintenance) are key components of the operating cost. Due to relatively short lifespan of the activated carbon (i.e. need for frequent bed replacement), 66% of the overall operating cost was contributed by the packing of material while work and energy accounted for 25% and 9% respectively (Estrada et al., 2012). The European Commission reported the annual operating costs per unit flow rate ranged from €5 to €200 (equivalent to from \$7 to \$208) per m³/h for activated carbon systems in wastewater and gas treatment/ management applications (European Commision, 2003). Estrada et al. (2012) also estimated an annual operating cost of €7.2 (equivalent to \$10) per m³/h for an activated carbon adsorber controlling odour emissions of 50,000 m³/h from a WWTP in Germany. Disposal costs as hazardous wastes were €120 and €320 (equivalent to \$168 and \$448) per m³ of spent activated carbon for landfill and incineration, respectively. Transport and handling costs were €432 (equivalent to \$605) per m³ of activated carbon.

The overall treatment costs are also strongly dependent on other factors such as geographic location, design removal efficiency, design flow rate, and concentration and the nature of target adsorbates. From the analysis of several full scale odour abatement systems, Estrada et al. (2011) reported that differences in removal efficiencies for H₂S (from 90 to 99%) and odour removal (from 70 to 95%) leads to a significant difference in both investment and operating costs. Indeed, the requirement for higher removal efficiencies often implies a need for longer bed retention time which leads to a larger adsorber and higher quality adsorbent materials which are often more expensive. Estrada et al. (2011) also observed that investment costs per unit flow rate treated decreased exponentially with increasing flow rates regardless of the technology, implying the relevance of the economies of scale in odour abatement. Wage levels, price levels, energy price, and disposal method of spent carbon according to the national regulations vary with geographic location, thus both investment and operating costs can vary significantly between countries. Variations in adsorbate concentrations can lead to substantial increases in treatment costs. Kraakman and Cesca (2012) observed that the activated carbon is the most cost-effective option for relatively low flow (7,500 m³/h) odorous emissions containing less than 7.5 ppmv of H₂S, but become economically unfavourable when the H₂S concentration exceeds approximately 20 ppmv. The costs of

treating acidic odour streams are generally higher because caustic impregnation is often needed to enhance adsorption (Atkinson et al., 1997). In contrast, the treatment cost for basic odour streams is generally cheaper since most activated carbon by default have predominantly acidic oxygen-containing groups on their surface.

7.0 Comparison with Other Odour Control Technologies

Besides activated carbon adsorption, other processes commonly applied for the treatment of odours include incineration, chemical scrubbers, biofilters, and biotrickling filters. A comparison of the land, energy and water use, as well as investment and operating cost of different odour treatment technologies is presented as **Table 7.1**.

Table 7.1 Comparison of common odour treatment technologies with respect to design flow rate, resource usage, investment and operating costs per unit flow rate

(Estrada et al., 2012, Estrada et al., 2011, Atkinson et al., 1997, Smet et al., 1998)

	Incineration	Activated Carbon ^(a)	Chemical Scrubber	Biofilter	Biotrickling filter
Design flow rate $\times 10^3$ (m ³ /h)	2 – 200	0.1 – 50	1 - 100	0.1 - 100	1 - 100
Relative land use (%) per m ³ /h	0.5	19	3	100	13
Relative investment cost (%) per m ³ /h	100	30	25	56	85
Relative energy input (%) per m ³ /h	100	1.5	1.5	1.5	0.5
Relative water use (%) per m ³ /h	0	0	66 ^(b)	46 ^(c)	100 ^(b)
Relative operating cost (%) per m ³ /h	100	40	24	18	10

(a) Nonregenerative activated carbon system

(b) Potable water consumption

(c) Secondary effluent

With the highest investment and operating costs per unit of design flow rate, *incineration* is the most expensive option for odour treatment applications. The main factors contributing to the high costs of the incineration are the significant energy consumption required to thermally destroy odorous gases and the installation of specialised infrastructure suitable for high temperature processes.

Activated carbon adsorption has a lower investment cost and operating cost per unit flow rate, which are 30% and 40% of those of incineration, respectively. The investment and operating costs per unit flow rate of activated carbon are, however, relatively high due to the large footprint required and the need for frequent material replacement due to the short

lifespan.

Chemical scrubbers are a cheaper option with the relative investment and operating costs of 25% and 24%, respectively in comparison with incineration. The highest contribution to chemical scrubber operating costs is the purchase of the chemicals. The requirement for potable water consumption and treatment of contaminated effluent add the operating costs.

For *biofilters* and *biotrickling filters*, the investment costs are usually high due to the large ground area and expensive media packing procedure, respectively. However, these two technologies have relatively low operating costs because the energy consumption is low and secondary treated wastewater can be used instead.

The influence of utility prices and design parameters on the total costs over the design lifetime can be significantly different among these technologies. Sensitivity analysis conducted by Estrada et al. (2012) had the following key findings:

- the investment costs per unit design flow rate decreased exponentially with the increasing design flow rates regardless of the technology, highlighting the relevance of the economies scale in odour treatment;
- increase in empty bed retention time significantly affects the total costs over the design lifetime of biofilters, chemical scrubbers and biotrickling filters, but not activated carbon adsorbers;
- packing material price and packing cost affect the operating costs of activated carbon adsorbers and biofilters much more than the other technologies;
- activated carbon is not cost-effective for the odour treatment applications with high inlet concentrations of H_2S (above 20 ppmv), while biotechnologies are the most effective for treating high H_2S concentration gas stream; and
- use of media with a short lifespan is less cost-effective for activated carbon and biofilters because frequent media replacement will incur substantial material packing and labour costs.

Total cost comparison should not only take into account investment and operational cost,

but also include the costs of complying with appropriate storage, treatment, disposal, and transportation regulations for the spent activated carbon. Project costs estimating software, for example the Micro Computer Aided Cost Estimating System (MCACES) or Remedial Action Cost Engineering Requirements (RACER™) System, can be used to estimate the life cycle costs of systems and to compare alternatives. These application software provide cost estimation for environmental projects, technologies and processes based on generic engineering solutions which were derived from historical project information, industry data, government laboratories, construction management agencies, vendors, contractors, and engineering analysis.

Table 7.2 summarises the removal effectiveness of these technologies for different groups of compounds. Both activated carbon and incineration are broadly applicable since they are proven effective for removing various gaseous types of compounds including hydrophilic, hydrophobic, acidic and basic chemicals. For chemical scrubbers, biofilters and biotrickling filters, the target gaseous compounds must be dissolved in liquid phase to interact with the chemical reagent solution or biologically active media. Therefore, these technologies are only effective for compounds that are soluble in water. Acidic odour streams are not effectively treated by biofilters and biotrickling filters since the low pH in the biofilm inhibits biological activity. The most common type of treatment for highly acidic odours is chemical scrubbing. In addition, multi-stage chemical scrubbers can be used to effectively deal with odour streams of different pH ranges.

Table 7.2 Removal performance of common odour treatment technologies for each group of compounds (Estrada et al., 2011, Atkinson et al., 1997)

	Incineration	Activated Carbon	Chemical Scrubber	Biofilter	Biotrickling filter
Low hydrophobic	E	E	E	E	E
Medium hydrophobic	E	E	A	A	A
High hydrophobic	E	E	P	P	P
Acidic	E	E*	E	P	P
Basic	E	E	E	A	A

E: Effective (removal efficiency RE >95%); A: Acceptable (90% < RE <95%); P: Poor (RE < 90%)

*Caustic impregnated/ specific selective activated carbon is needed.

The semi-quantitative robustness is evaluated by considering both degrees of impacts and probability of occurrence of a number of operational disorders, upsets and interruptions (**Table 7.3**). Activated carbon and incineration are the most robust technologies, while biotechnologies have robustness comparable to that of chemical scrubbers. Biofilters, biotrickling filters and chemical scrubbers have average levels of the robustness, with the sensitivity to operational failures approximately double that of activated carbon. Biotechnologies are prone to upset caused by changes in operational parameters such as water and food supply, temperature and concentrations of toxic chemicals in the feed stream. Meanwhile, the performance of a chemical scrubber is governed by the chemical dosing, and the presence of a continuous water and chemical supply.

Table 7.3 Semi-quantitative robustness evaluation of common odour treatment technologies(Estrada et al., 2012)

	Activated Carbon	Chemical Scrubber	Biofilter	Biotrickling filter
	Degrees of impacts × (Probability of Occurrence in brackets)			
Water supply disorder	1 × (1)	4 × (3)	3 × (4)	3 × (3)
Energy supply interruption	1 × (2)	3 × (2)	2 × (2)	3 × (2)
Chemical dosing disorder	1 × (1)	4 × (2)	1 × (1)	1 × (1)
Feed air supply interruption	1 × (2)	1 × (2)	2 × (2)	2 × (2)
Fluctuation of inlet concentrations	1 × (4)	2 × (4)	2 × (4)	2 × (4)
Higher inlet concentrations	4 × (1)	1 × (1)	2 × (1)	1 × (1)
Fluctuation of inlet temperature	1 × (3)	1 × (3)	2 × (3)	1 × (3)
Meteorological conditions	1 × (5)	1 × (5)	1 × (5)	1 × (5)
Sensitivity to operational failures	22	45	42	37
Overall Robustness	High	Average	Average	Average

Degree of Impacts: 1 - Insignificant; 2 - Low; 3 - Moderate; 4 - High; 5 - Catastrophic

Probability: (1) - Very unlikely; (2) - Low; (3) - Occasional; (4) - Probably; (5) - Frequent

8.0 Conclusion

This review of adsorption process identified knowledge gaps in current practices associated with the application of activated carbon for sewer odour abatement. A summary of key findings and knowledge gaps is provided in the **Table 8.1**.

Table 8.1 Summary of key findings and knowledge gaps

Key findings	Knowledge gaps
<ul style="list-style-type: none">• Intensive study of the adsorption mechanisms of H₂S by various types of activated carbon has been done.• Importance of physical and chemical properties of activated carbon to removal capacity/ performance for particular odour control applications.• Importance of relative humidity, temperature, pressure and contact time to the performance of an activated carbon adsorber .• Non-hazardous waste classification for the disposal of used activated carbon.• High operation cost due to replacement of activated carbon beds.• Highly robust against operating failures and effective (>95% and > 99%) for removing odour and chemicals.	<ul style="list-style-type: none">• Mechanistic removal/ kinetics of other wastewater associated malodorous organic compounds and VOCs.• Competition in multicomponent adsorption.• Lack of full scale field data to justify the effects of properties of activated carbon on actual service life as well as the effects of variations in operating conditions on adsorber performance in field applications.• Lack of standard guidelines for design and operation of activated carbon adsorbers for odour control applications.

Understanding the removal mechanisms of the dominant odorous compounds in sewer air by activated carbon is essential to optimise process selection, design and operation for a particular odour control application. However, only limited information about the removals mechanisms for most odorous compounds and VOCs is available in the literature, with the exception of H₂S, whose adsorption mechanism has been intensively studied. Key points from the review of odorant adsorption mechanisms are:

- Complex catalytic oxidation of H₂S takes place on the surface of activated carbon to form either elemental sulfur and/or sulfuric acid which is then strongly bound within the micropores of the activated carbon. Alkaline hydroxides (e.g. NaOH/ KOH) or metallic oxides (e.g. CuO) can be impregnated on surface carbon to

encourage chemisorption of H_2S via its oxidation to products like sulfides, sulphites, sulfates and elemental sulfur. Conversion to elemental sulfur leads to much greater adsorption capacity and is more desirable due to the smaller portion of activated carbon pore volume occupied by elemental sulfur.

- Adsorption of methyl mercaptan is through volume filling of micropores and adsorption via the formation of monolayers or multilayers on transition pores. In wet conditions, methyl mercaptan adsorbed in pores or on the activated carbon surface can be further oxidised to dimethyl disulfide, sulfinic acid and methane sulfonic acid. The oxidation to dimethyl disulfide yields increased adsorption capacity than other oxidation products.
- Adsorption mechanisms for other odorous compounds have not been comprehensively studied. Although their adsorption mechanisms are not clear, it is well known that activated carbon has excellent adsorptive capacity for a wide range of odorous compounds including dimethyl disulfide, dimethyl sulfide, carbonyl sulfide, carbon disulfide, dimethyl trisulfide, ammonia, trimethyl amine, idole and skatole.
- Activated carbon has a long history of use to remove or recover a wide range of volatile organic compounds in gas phase applications. VOC compounds having molecular weight greater than 50 and boiling points greater than 20°C are known to be effectively adsorbed by activated carbon. Physical adsorption is the predominant adsorption mechanisms, but some chemisorption may take place at elevated temperature (e.g. $> 45^\circ\text{C}$). The information about VOC adsorption is quite general and specific data on the removal performance for dominant VOCs in sewer air are limited.

Many factors including activated carbon properties and the nature of the adsorbate affect adsorption effectiveness in a particular application:

- Particle size distribution influences the rate of adsorption kinetics, pressure drops across the bed, and the ability to support the bed weight. Particle size determines the access of intraparticle mass transfer and molecular diffusion inside the particle structure.

- The total surface area indicates adsorptive sites available for the adsorbate molecules to bind with, especially via physisorption. Most activated carbons have total surface area between 600 and 1600 m²/g. Increasing total surface area may produce greater adsorption capacity, but direct relationship is inconclusive.
- The pore structure is comprised of micropores (width <2nm), mesopores (width 2-50nm) and macropores (>50nm) which are important in providing adsorption sites, transportation passage, and entrances for adsorbates, respectively. A pore size distribution with high proportion of small micropores favours adsorbate molecules of smaller size, while one with greater proportion of mesopores and larger micropores favours larger adsorbates.
- Surface chemistry governs wettability, polarity, acidity, and catalytic, electrical and chemical reactivity of the activated carbon. Impregnations play an important role in promoting chemisorption and enhance adsorption capacity for specific adsorbates.
- Surface pH determines the degree of chemisorption with respect to physisorption.
- Properties of adsorbates such as molecular weight, boiling point, and polarity are important because they govern the affinity and accessibility of the molecules to activated carbon.

Since the properties of activated carbon play important roles in adsorption processes, this information is essential to select the appropriate types of activated carbon and design the effective activated carbon adsorber for a particular application. A wide range of physical, chemical and computational techniques are available to characterise physical and chemical properties of activated carbon and there is no single test to comprehensively characterise activated carbon, and a range of tests must be used in conjunction to provide comprehensive information. Currently, a limited range of activated carbon properties are presented in the product specifications provided by manufacturers/vendors, other properties must be obtained from independent experiments.

Most odorous and organic compounds in sewer headspace air are physically adsorbed by activated carbon. These chemicals are therefore weakly adsorbed and decreasing partial pressure or increasing temperature may release the adsorbed compounds from the activated

carbon, contributing to premature odour breakthrough.

Operating conditions such as relative humidity, temperature, pressure, volumetric flow rates and adsorption competition significantly affect the effectiveness of activated carbon:

- Relative humidity increases the adsorption capacity of some sulfur compounds; however too much moisture will suppress physisorption. Optimal humidity is recommended to be around 60% and below 50% for the adsorption of sulfur-reduced compounds and VOCs, respectively.
- Increasing temperature often has negative effects on activated carbon adsorption, particularly where physisorption is a dominant process although some chemical reactions may require a certain minimum temperature to initiate. Increasing bed temperature may occur during adsorption process and hot spots must be monitored and controlled to avoid the ignition of carbon materials. Temperature should be kept below 53°C to ensure the adequate adsorption capacity.
- Any increase in the partial pressure of the adsorbate increases the adsorption capacity. If the varying partial pressures are still less than designed partial pressure, the desirable removal efficiency should always be maintained.
- The volumetric flow rate directly affects the removal efficiency. Increasing velocity leads to shorter exposure of carbon particles to the adsorbate while decreasing velocity results in the longer exposure. Volumetric flow rate is inversely proportional to empty bed contact time. Superficial velocity is recommended not greater than 30 m/min in order to achieve >90% removal efficiency and not less than 6 m/min to avoid flow problems such as channelling.
- Adsorption competition may exist in the presence of multiple adsorbates due to the finite number of adsorption sites. This competition results in selective/preferential adsorption between the activated carbon and molecules of different polarities, molecular weights, sizes, volatilities, and chemical reactivities. In some cases, the presence of non-target compounds enhances the adsorption capacity for the target compound(s).

In current practices associated with sewer odour control applications, wastewater utilities

and industrial partners are aware of the importance of operating conditions on the performance of activated carbon adsorbers, but have not completely comprehended their effects or effectively manipulate them for desirable performance outcomes. This is likely due to a lack of industry guidance and specific research studies to determine optimal operating parameters for particular applications. There is a need to undertake research studies, laboratory experiments and field testing in order to develop a standard guideline for sewer odour control applications.

Currently, there are no standard guidelines available to assist the design and operation of fixed bed activated carbon adsorbers for odour abatement applications. The design procedures and operational considerations presented in this report are derived from various industrial-accepted practices and experiences. For a particular application, the selection of activated carbon material must be based on data associated with certain properties of the adsorbent such as densities, porosity, adsorption capacity, selectivity, regenerability, kinetics and costs. These data must be obtained from vendor's database, library, textbooks or even from independent laboratory testing.

Either adsorption isotherms or short cut testing methods such as capacity at breakthrough point can be used to derive data on adsorption capacity. Each technique has its own advantages and disadvantages. Field data on the design, operation and performance of activated carbon adsorbers is mostly not accessible to the public, making it difficult to evaluate and compare these methods.

In sewer odour control applications, the adsorbent bed replacement is often based on empirical experience rather than estimated lifespan suggested by the vendor. The actual service time of the adsorbers should be frequently monitored. From industrial experience, several approaches can be used including analysing a test element, monitoring outlet concentrations and static pressure drop:

- The test element analysis will provide information about the remaining adsorption capacity and other potential problems such as plugging of carbon pellets due to particulates, excessive vapour condensation or physical deterioration of the materials.

- Any changes in outlet concentrations imply potential premature breakthrough or improper operations because outlet concentrations should be relatively constant and independent from variation in inlet concentration.
- With the constant gas flow, changes in static pressure drop during typical operation are good indications for problems inside the adsorber.

The cost of activated carbon technology (i.e. non-regenerative fixed bed adsorber) is dominated by the cost of the adsorbent media. A vessel and activated carbon media can account for up 90% of the start-up cost. Meanwhile, replacing used activated carbon (purchasing new adsorbents & packing) can contribute 66% of total annual operating costs, while work and energy are liable for rest of the cost. Activated carbon is cost-effective for dealing with sewer air stream containing low concentrations of pollutants (e.g. <7.5 ppm H₂S) and flow rate (< 50000 m³/h). However, activated carbon is very effective for the removal of a wide range of chemicals and highly robust against many operational failures than many other alternative odour control technologies like biotrickling filters, biofilters, and chemical scrubbers.

To address the knowledge gaps identified in this review, following future work is recommended:

- (i) Identify the typical compositions of major odour causing compounds in sewer air associated with different wastewater sources;
- (ii) Study the adsorption mechanisms of other odorous compounds rather than H₂S, multicomponent adsorption and adsorption competition using equilibrium adsorption and kinetics experiments and analysis on changes of activated carbon properties;
- (iii) Compile information about the design, operations, issues and costs of activated carbon adsorbers in odour control application from wastewater utilities and industrial partners (access to information is required);
- (iv) Evaluate the performance of full scale activated carbon adsorbers for the removal of odour and key odorants in sewer air;
- (v) Evaluate effects of the properties of activated carbon and operating conditions on

- the adsorption capacity based on the full scale data; and
- (vi) Standardise the designing, operating and monitoring protocols to optimise the use of activated carbon adsorption and support the future practices.

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