CHAPTER 1

INTRODUCTION

1.0 Introduction

1.1 Heavy Metals

Heavy metals belong to the sub-group of materials known as metals. Metals are defined as elements with metallic luster, are malleable and ductile, possess the capability to lose electron to form positive ion, form cation and have basic oxides, and the ability to conduct heat and electricity (Duffus, 2002). Metals are present in the environment naturally and mostly are found in soil, seawater, and freshwater. Heavy metals are classified based upon the density of the elemental form of the metals that are generally considered to be those metals with density exceeding 5 g/cm^3. (Inglezakis and Poulopoulos, 2006 ; Duffus, 2002). Heavy metals are also often used as a group name for metals and semimetals (metalloids) that have been associated with contamination and potential toxicity or ecotoxicity.

Characteristic examples of heavy metals are Cadmium (Cd), Mercury (Hg), and Lead (Pb) (Inglezakis and Poulopoulos, 2006). The natural or background levels of most heavy metals in seawater, drinking water, plants and animals are usually very low. But when the heavy metals are released into the environment by anthropogenic means which are human induced activities such as burning of fossil fuels, discharge of industrial effluence, mining and other actions, it leads to the development of higher than tolerable levels of metals in the environment. Of all commonly occurring heavy metal pollutants, mercury is the most toxic (Abbasi et al., 1998).

1.2 Mercury

Mercury (Hg) is the toxic heavy metal that is of significant concern as an environmental pollutant. Mercury and other noble metals were the first elements to be

discovered and utilized by humans because they exist in nature either in the free state or easily decomposable compounds (Carpi 2001). Mercury is a metal that is in liquid state at room temperature. Its boiling point and melting point is 356.7 ^{o}C and -38.87 ^{o}C, respectively.

Mercury occurs in three valence state in nature; elemental (Hg^{o}), monovalent (Hg^{+}) and divalent (Hg^{2+}) mercury (Berlin et al., 2007 ; Luo et al., 2010 ; Carpi, 1997). Elemental mercury (Hg^{o}) is relatively stable in the environment, volatile, only sparingly soluble in water and thus undergoes long-range transport in the atmosphere (Carpi, 1997). Of the two ionized states, monovalent and divalent mercury, the latter is more stable and thus more common in the environment. Divalent mercury (Hg^{2+}) can be associated with inorganic molecules such as chlorine, sulphur and hydroxyl ions.

In addition, mercury also exists in nature as organometallic compounds in which mercury is covalently bonded to carbon, in compounds of the types RHg^{+} and RHgR', where R and R' represent the organic moiety (Berlin et al., 2007). The inorganic mercury (divalent mercury) associate with organic molecules and produce organic complexes of mercury such as monomethylmercury and dimethylmercury. These organic compounds are of greatest concern in the ambient environment because they are the most toxic environmental mercury species and they are accumulated by a factor of up to 10^{5} in the aquatic food chain. Mercury is a highly mobile environmental pollutant that is toxic to both human and wildlife at extremely low levels. Because of its high mobility and toxicity, small environmental release of mercury can result in significant exposure, and emphasize the importance of understanding the source of mercury in the environment (Carpi, 1997).

1.2.1 Mercury Sources

Mercury has been known for years as both an anthropogenic contaminant and natural constituent in the environment.

1.2.1.1 Natural Sources

Mercury is circulated naturally in the biosphere, with 30,000 – 50,000 tons being released into the atmosphere by degassing from earth's crust and the oceans (Berlin et al., 2007). Recently, as reported by Pirrone and colleagues, an annual basis of the natural sources account for 5207 Mg of mercury released to the global atmosphere. This includes the contribution from re-emission process which is emissions of previously deposited mercury originating from anthropogenic and natural sources (Pirrone et al., 2010).

Table 1.1: Global mercury emission by natural sources to the atmosphere estimated for 2008.

Source Category	Mercury ($Mg\ yr^{-1}$)	Contribution (%)
Oceans	2682	51
Lakes	96	2
Forests	342	7
Tundra/Grassland/Savannah/ Prairie/Chaparral	448	9
Desert/Metalliferous/Non-vegetated Zones	546	10
Agricultural areas	128	2
Evasion after mercury depletion events	200	4
Biomass burning	675	13
Volcanoes and geothermal areas	90	2
Total	5207	100

Source: (Pirrone et al., 2010)

Mercury emission from the surface water which are lakes and ocean is driven by the concentration gradient of mercury between the top-water micro-layer and air above the surface water. As shown in Table 1.1, the total mercury evasion from ocean basin and lakes, account for 2778 Mg yr^{-1} of net gaseous mercury evasion to the atmosphere. Mercury emission from top soils and vegetation are influenced by meteorological conditions, historical atmospheric deposition and the type of vegetation and top soil. Mercury emissions from biomass burning have only recently been considered in regional and global estimates. The most recent estimates on the global mercury emission from biomass burning every year (annual average for the period 1997-2006) suggest a value about 675 Mg. The mercury emission from volcanoes varies over time depending whether they are in a degassing or eruption phase. The Hg/SO_2 mass ratio is generally adopted to estimate mercury emission from volcanoes. Mercury emission from calderas may also represent an important natural source of mercury. For example, the Phlegrean fields in Pozzuoli, Italy show fluxes of mercury as Hg-S complexes in the range of 0.9 to 19 g day^{-1} (Pirrone et el., 2010).

1.2.1.2 Anthropogenic Sources

Mercury has also been released into the environment each year (about 20,000 tons) by human activities. Yearly, approximately 2000 tons of mercury is produced for industrial use, a small part of which is used for synthesizing organic mercury compounds (Berlin et al., 2007). Recently, the anthropogenic sources, which include a large number of industrial point sources, are estimated to account for 2320 Mg of mercury emitted annually to the atmosphere (Pirrone et al., 2010). The major contributions for anthropogenic sources are described in Table 1.2.

Table 1.2: Global emission of total mercury from major anthropogenic sources to the atmosphere estimated for 2008.

Source Category	Mercury ($Mg\ yr^{-1}$)	Contribution (%)
Fossil-fuel (coal) fired power plants	810	35
Artisanal small scale gold mining	400	17
Non-ferrous metals manufacturing	310	13
Cement production	236	10
Waste disposal	187	8
Chlor-alkali (caustic soda production	163	7
Mercury production	50	2
Pig iron and steel production	43	2
Coal bed fires	32	1
Vinyl Chloride monomers production	24	2
Other	65	3
Total	2106	100

Source; (Pirrone et al., 2010)

Fossil fuel fired power plants primarily are one of the major anthropogenic mercury emission sources due to the huge consumptions of coal (Luo et al. 2009 ; Pirrone et al.,2010 ; Wang et al., 2009). Mercury is a trace element in coal. As shown in Table 1.2, fossil fuel fired power plants remain the largest sources of mercury emission to the global atmosphere annually, accounting for about 810 $Mg\ yr^{-1}$. During the combustion of coal, mercury in coal is volatized and converted to gaseous elemental mercury (Hg^o). Subsequent cooling of the flue gas and interaction of Hg^o with other flue gas constituents, such as chlorine occurs naturally in coal and unburned carbon, resulting in partial oxidation of the Hg^o to gaseous oxidized forms of mercury Hg^{2+} and particulate-bound mercury Hg^p. As a result, coal combustion flue gas contains varying percentages of Hg^p, Hg^{2+} and Hg^o (Carpi, 1997).

1.2.2 Problems with Mercury

1.2.2.1 Health Effect to Human

The toxicity of mercury is primarily associated with the cationic state (Hg^{2+}). However, absorption, tissue distribution and biotransformation are influenced significantly by the valence state of the metal. Exposure to mercury vapour leads to mercury accumulation in the brain which affect the central nervous system called neurotoxicity. This will give symptoms such as tremors, nervousness, insomnia, memory loss, muscle twitching and headaches. This normally happens to workers that are exposed to mercury through the manufacturing industries for example, fluorescents tube manufactures and chloralkali industries. The short term and high level exposure to mercury affect the respiratory system, causing symptoms such as cough, chest pains, respiratory distress and fibrosis. Besides, mercury also can cause acute renal failure that affect organs such as kidney and liver due to mercury concentration in blood and urine. The cardiovascular toxicity in humans has also been reported with increased blood pressure and heart rate (WHO, 2003; Berlin et al., 2007).

Mercury has gained the most notoriety because the world's first major case of metal pollutant, as also the most widely reported one, involved mercury poisoning. That was the Minamata case in which mercury uptake affected a large number of people living near the Minamata Bay in Japan. The case first came to light in 1953 but remained in public eye for several years because mentally retarded and physically deformed babies were born to mothers who were toxified by mercury. A research conducted found that the Minamata tragedy was caused by the methylmercury form in the bay from inorganic mercury discharged with industrial effluent. The mercury

absorbed from water by plant or precipitated from water into sediments that had found its way into fishes which were seriously contaminated with mercury. Then humans who eat the contaminated fish and plant had to deal with the worst impact of mercury poisoning at Minamata (Abbasi et al., 1998).

The World Health Organization (WHO) recommends the maximum mercury uptake by humans of 0.3 mg per week and the maximum acceptable concentration of 1µgL^{-1} in drinking water. The United States Environment Protection Agency (USEPA) limit for wastewater discharge for total mercury is 10 µgL^{-1} while the limit for drinking water is 2 µgL^{-1}. The Ministry of the environment of Japan has established even stricter limits at 5 and 0.5µgL^{-1}, respectively, for wastewater discharge and drinking water supplies (Zhu et al., 2009). As results of the mercury toxicity problems to human life, it is important to monitor and remove this heavy metal from aquatic environment.

1.2.2.2 Catalyst Poisoning

Catalyst poisoning refers to the effect that a catalyst can be poisoned if it reacts with another compound for example heavy metal that bonds chemically to the catalyst. But this catalyst poison does not chemically alter the catalyst, as it cannot participate in the reaction to be catalyzed. The catalyst poison is the substance that reduces the effectiveness of catalyst in a chemical reaction (Encyclopaedia Britannica, 2011). This catalyst poisoning normally happens in the petroleum industry from the refinery hydrocarbon feed stocks process. Typical examples of permanent poisons encountered when processing hydrocarbon feed-stocks would be contaminant metals such as nickel, copper, vanadium and in particular heavy metals such as lead, arsenic and mercury. All these metals have a significant deactivating effect on precious metal catalysts, but the

heavy metals have a particularly dramatic impact. This is so even at very low concentration, either present in the feedstock or accumulated on the catalyst. For instant, the catalysts consisting of palladium supported on alumina are widely used for the selective hydrogenation of acetylenes in petrochemical processing. Heavy metals that accumulate on this catalyst surface forms alloy through $d\pi - d\pi$ bonding. The result is to effectively remove active centres from the desired reaction scheme. Catalyst poisoning reduces yield and shortens catalyst life. It is therefore essential to reduce inlet mercury concentration to <5 ppb to achieve an economically acceptable service life (Dunleavy, 2006). Mercury poisoning, if left unchecked, may require an unplanned and premature catalyst change out with all its associated cost, including downtime.

For example, Campbell and Thomson have studied the effect of mercury poison on the nickel catalyst in the hydrogenation of cyclopropane and propylene processing by radiochemical techniques (Campbell & Thomson, 1958). They studied the effect of adsorption propylene, cyclopropane, hydrogen and mercury onto the nickel film catalyst at 25 ^{o}C. They found that, mercury poisoned the nickel film catalyst for the hydrogenation of cyclopropane, but not for that propylene. Mercury is first chemisorbed on the nickel film surface will displace the chemisorbed hydrogen. The multilayer mercury adsorption on a clean catalyst surface seems to block the surface for chemisorptions. Thus, the hydrogen, propylene and cyclopropane are not adsorbed on the surface covered with mercury. As a result, hydrogen is no longer chemisorbed in the presence of mercury, and cyclopropane hydrogenation is therefore inhibited.

1.2.2.3 Corrosion

Mercury is a naturally occurring trace component of natural gas, liquid associated with gas and crude oil. Elemental mercury is the dominant mercury species in gas after separation of produced water and condensate. Elemental mercury is the primary mercury species responsible for damage to equipment. In situations where mercury is a trace component of feed gas or liquid feeds to crackers, condensation of liquid or precipitation of solid, mercury can occur in heat exchanger passes, even with functional mercury removal systems in place. Deposition of liquid elemental mercury in aluminium heat exchangers (AHXs) can compromise their structural integrity. One mechanism by which this can occur is referred to as liquid metal embrittlement (LME) which has been responsible for a number of failures of aluminium equipment in the gas processing industry over the past 30 years. A second mechanism by which mercury can attack aluminium is amalgam corrosion (AMC), which requires both mercury and water in order to oxidized and thus degrade aluminium equipment (Wilhelm, 2008).

1.3 Heavy Metals Removal System for Water

In general, several methods and materials have been developed and used for the removal of heavy metals from water such as chemical precipitation, coagulation-flocculation, membrane filtration, electrochemical techniques, ion exchange, chelating agent and adsorption process (Zhu et al., 2009 ; Mamba et al., 2010). Unfortunately, some of these processes are often associated with drawbacks which make their use ineffective. High operational cost and inability of these processes to remove the heavy metals to the acceptable levels are the most common shortcoming of some of these processes (Mamba et al., 2010 ; Kurniawan et al., 2006). Nowadays, the adsorption

process is receiving increasing attention as a method for removing heavy metals from aqueous environment due to its eco-friendly characteristic.

1.3.1 Adsorption Process

Adsorption is a process whereby a substance (adsorbate or sorbate) is accumulated on the surface of a solid (adsorbent, or sorbent). The adsorbate can be in a gas or liquid phase. The driving force for adsorption is unsaturated forces at the solid surface which can form bonds with adsorbate. These forces are typically electrostatic or van der Waals interactions which are reversible. Stronger interactions involve direct electron transfer between the sorbate and the sorbent which are irreversible. The strength of this interaction dictates the relative ease or difficulty in removing (desorbing) the adsorbate regeneration and adsorbate recovery. The selective nature of the adsorbent is primarily due to the relative access and strength of the surface interaction for one component in the feed mixture. The solid is the mass-separating agent and the separating mechanism is the partitioning between the fluid and the solid phases.

An energy-separating agent, typically a pressure or temperature change, is used to reverse the process and regenerate the sorbent (Rodin, 2004). Adsorption in the liquid phase is influenced by many factors such as pH, type of adsorbent, solubility of adsorbate in the solvent and temperature as well as adsorptive concentration. The design of liquid-phase adsorptive separation process requires adsorption equilibrium data. These data have to be experimentally measured or calculated using various predictive multicomponent adsorption models or empirical correlations. The Langmuir and

Freundlich isotherms are the most widely used to correlate liquid phase adsorption data (Roque-Malherbe, 2007).

Adsorption process is used economically in a wide variety of separations in the chemical process industries. There are many environmental applications of adsorption in practice and many others are being developed (Rodin ,2004). Liquid phase adsorption, primarily onto carbon based materials, silica, zeolite and resins, provides a feasible technique and is one of the most extensively used technology for removal of organic and inorganic pollutants in industrial waste water (Roque-Malherbe, 2007).

The advantages of this technique are high removal efficiency, enables removal of refractory and/or toxic organic compound, possibility of compounds recovery, simple installation and maintenance, capability of system for fully automatic operation and a large variety of adsorbent available. The disadvantages of this technique are adsorbent deteriorate in capacity gradually, particulates in the feed can cause problems and high content of macromolecular compound decrease efficiency and may cause irreversible blockage of active sites. There are two general types of adsorption that are chemical and physical adsorption process (Inglezakis and Poulopoulos, 2006).

1.3.1.1 Chemisorptions

Chemisorption (chemical adsorption) occurs when the attraction between the adsorbent and the adsorbate can form a covalent bond, or when a chemical reaction occurs between the adsorbent and adsorbate. Chemisorption is the result of much stronger forces, comparable with those leading to the formation of chemical compounds. Normally, the adsorbed material forms a layer over the surface which is

only one molecule thick and the molecules are not considered free to move from one surface site to another (Chen et al., 2001). Usually, chemical adsorption will only allow a single layer of molecules (monolayer) to accumulate on the surface of the adsorbent (Rodin, 2004). When the surface is covered by the monomolecular layer, the capacity of the adsorbent is essentially exhausted. Also, chemical adsorption is seldom reversible (Chen et al., 2001; Rodin, 2004). The adsorbent must generally be heated to higher temperature to remove the adsorbed materials (Chen et al., 2001). Chemisorption is typically more specific, kinetically slower and has a larger heat of adsorption (Rodin, 2004).

1.3.1.2 Physisorptions

Physisorption is relatively nonspecific and occurs due to Van der Waals (dispersion) or electrostatic forces. This refers to the operation of weak forces of attraction or van der Waals' forces between molecules (Cheng et al., 2001; Rodin, 2004). The two forces involved are attractive forces and repulsive forces, with the net force depending on the distance between the surface and the adsorbate (Cooney, 1999). The Van der Waals or electrostatic forces include polarization forces, field-dipole interactions and field gradient-quadrupole interactions.

The attraction between molecules depends on the polar nature of the fluid component being adsorbed as well as that of the adsorbent. Van der Waals forces are directly related to the polarizability. An estimate of the relative strength of interaction is based on the sorbate size and polarizability (Rodin, 2004). The attractive force arises from rapidly oscillating dipole moments which occur in atoms and molecules due to lack of symmetry of the electron distribution around the nuclei. Even though, on a time

averaged basis, the electron distribution may be symmetrical, at any of time it is not, and this leads to transient dipole moments. The dipole moment of an adsorbate molecule near a solid surface induces a dipole moment in a surface atom or molecule, and the interaction of these two dipole moments causes a transient attractive force to exist (Cooney, 1999).

In addition to dipole-dipole interactions, one can have dipole-quadrapole interactions and quadrapole-quadrapole interactions, depending on the nature of the molecules. For example, SO_2 is symmetrical and therefore has no dipole, but it does have a quadrapole of the form $^{-}O–^{+}S^{+}–O^{-}$, and this can interact with a polar surface atom or molecules. The dipole-quadrapole and quadrapole-quadrapole interaction forces are much weaker than the dipole-dipole forces (Cooney, 1999). When an adsorbate molecule approaches a solid surface closely, its electron cloud will overlap with that of a surface atom or molecule and repulsive force will develop. Physisorption involves relatively weak forces and it is therefore reversible. Thus, desorption of adsorbed solute can occur. Physisorption is sensitive to temperature, relatively non-specific regarding sorbates, relatively fast kinetically and has low heat of adsorption. Multiple sorbate layers can form on the sorbate surface.

1.4 Active Materials for Adsorption

In the world of environmental science and technology, the removal of toxic heavy metals from wastewater by adsorption is receiving increasing attention over the currently used methodology because of the eco-friendly characteristic of the phenomenon (Das et al., 2008). The surface modification of various adsorbent has appeared as a very important field for enhanced specificity and desired surface

characteristic properties of the adsorbent materials. The specificities of these materials are for the cationic species adsorption. Chemical modification of adsorbent materials having desired functionality is an effective and feasible alternative for enhancing the adsorption capacity of the toxic cationic species. Therefore, there are several types of materials such as metal, natural and carbon based adsorbent used for heavy metal removal from the environmental.

1.4.1 Metal Based Materials

Water pollution by heavy metals is undoubtedly one of the major problems faced by the world today. Therefore, various methods are employed for the treatment of different metal pollutants. As discussed before, mercury is used widely despite its high levels of toxicity even at low dosages (Sumesh et al. 2011). Metal based adsorbent is one of the materials that has received a lot of attention for its efficiency and practical applicability on wide range of contaminant removal from air and water systems. There are several types of metal based adsorbent, such as metal sulphide (eg; CuS/C, CuS/Al_2O_3, FeS), metal oxide (eg; Ag/Al_2O_3), and metal nanoparticles (eg; Ag, Au) (Yan, 1996 ; Sumesh et al. 2011). The sulphide minerals have been recognized as important scavengers for metal ion such as gold, silver, palladium, uranium and copper. It is because of its property as a soft Lewis acid and thus its strong affinity for ligands containing sulphur, mercury sorbs onto sulphides and this sorption has been proposed as a method for removing this highly toxic element from aqueous media (Behra et al., 2001).

In 1996, Yan reported the removal of mercury from condensate and oil using metal sulphides based adsorption system. The choice of adsorbent were CuS/C,

CuS/Al_2O_3 and Ag/Al_2O_3. Since the mercury in spent adsorbent is mainly in the form of HgS, they were tempted to postulate that the reaction involved was;

$$CuS/\ support + Hg \longleftrightarrow Cu/support + HgS.$$

Besides, the mechanism of mercury adsorption by Ag/Al_2O_3, it is believed to be amalgamation process and the reaction of this mechanism as below;

$$Ag/support + Hg \longleftrightarrow Ag - Hg/support.$$

When a metal sulphide on support is used as adsorbent, the adsorption mechanism is dependent on adsorption temperature. As the adsorption temperature increased, physisorption will decreased while the chemisorptions will increase. Thus, by increasing the adsorption temperature, the mercury selectivity of adsorbent can be increased to a high level, leading to increased adsorption capacity. In the chemisorptions of mercury, chemical bonds are formed between the mercury and the metal sulphides on the support. From all three adsorption systems (CuS/C, CuS/Al_2O_3 and Ag/Al_2O_3), the CuS/C system is the most efficient in removing mercury from condensate and oil (Yan, 1996).

Numerous studies have reported the use of sulphides as ligand for mercury trapping in the various application systems. Iron element is the most common metal associated with sulphides that have been used as mercury trapping media (Brown et al., 1979 ; Jean et al., 1986 ; Behra et al., 2001; Jeong et al., 2007). Behra et al., 2001 conducted a study on the sorption of Hg^{2+} onto pyrite (FeS_2) in aqueous media. The Hg^{2+} was fully adsorbed onto the FeS_2 surface powder in the pH range of pH 4 – 12. Sorption of Hg^{2+} would probably be a surface complexation and a surface precipitation depending on the pH range. They have found that the sorption of Hg onto FeS_2 occurs on two types of surface sites which are pyritic surface functional groups, $\equiv S - H$ and Fe

oxyhydroxide groups, ≡O – H. At low pH, ternary surface complexes $\equiv S^{-1}$ – Hg – OH were formed. At high pH, they indicated the possible presence of a solid solution constituted of Fe(hydr)oxides and surface complexes between Hg and both oxides (≡O – H) and pyritic sulphur (≡S – H). Jeong et al., 2007 reported the use of synthetic nanocrystalline iron sulphides (FeS) also called Mackinawite, as mercury ion scavenger in aqueous systems. The possible sorption reactions of Hg^{2+} by iron sulphides include adsorption, precipitation as a discrete sulphides phase (HgS(s)), and solid solution formation with iron sulphides. In FeS removal systems, the Hg^{2+} sorption by precipitation is expected to be more favourable. The maximum adsorption capacity for Hg^{2+} ($q_{Hg,max}$) was 0.44 mmol/g in the pH range of pH 5.5 -6.0 (Jeong et al., 2007).

Besides, the use of silver and gold as adsorbent for mercury ion have also been reported earlier (Mercer, 1979; Katsikas et al., 1996 ; Morris et al., 2002; Fan et al., 2009). Recently, Sumesh and colleagues reported the use of silver nanoparticles of 9±2 nm and 20±5 nm core diameter, protected by mercaptosuccunic acid (MSA) and supported on activated alumina (Ag@MSA) for the removal of mercuric ions present in contaminated waters (Sumesh et al., 2011). The Ag@MSA nanoparticles show the existence of carboxylate ion on the nanoparticles that originates from the MSA compound. From the infra red (IR) analysis, they have found that the carboxylate groups of MSA are bonded to the Hg^{2+} ion. This finding was in agreement with the X-ray photoelectron spectroscopy (XPS) that showed the complexation of mercuric ions with the carboxylate groups of MSA (Sumesh et al., 2011).

1.4.2 Natural Materials

The use of inexpensive biological materials such as algae, plant, fungi and bacteria for removing and recovering heavy metals from wastewater has emerged as a potential alternative method to conventional techniques (Zeroual et al., 2003 ; Fabre et al., 2003 : Das et al., 2008 ; Eom et al., 2010). The marine algae are one of the natural materials that have attracted the attention of many researchers as organism to be investigated and tested as potential adsorbent for metal ions. Marine algae are renewable natural biomasses that proliferate ubiquitously and abundantly in the littoral zones of world oceans often posing environmental nuisance.

The study of the removal of mercury ion from synthetic mercurial water in fixed-bed column using marine algae named *Ulva lactuca* as biosorbent has been reported by Zeroul and colloquies. They determined that the sorption rate of mercury ion onto *Ulva lactuca* is divided into two stages which are a fast initial rate followed by a much slower sorption rate. The fast initial mercury sorption was attributed to the surface binding by natural particles and the following slower sorption was attributed to the interior penetration. They reported that more than 90% of mercury uptake occurs within 20 minutes and equilibrium was reached in 40 minutes. The maximum uptake capacities (q_{max}) of mercury ion onto Ulva lactuca drops from 149.25 to 27.24 mg/g when pH decreases from pH 7 to 3.5 (Zeroual et al., 2003).

Other types of plant have also been reported as potential mercury adsorbent, such as garlic (*Allium sativum* L.), garlic vine (*Pseudocallyma alliacium*), garden pea (*Pisum sativum* L.), spring wheat (*Triticum aestivum* L.), sugar beet (*Beta vulgaris* L.), oil-seed rape (*Brassica napus* L.) and rice seeding (*Oryza sativa* L.) (Eom et al., 2010 ;

Feng et al., 2004 ; Du et al., 2005 ; Greger et al., 2005 ; Papandreou et al., 2007). Recently, Eom and co-workers reported the use of dry garlic (*Allium sativum* L.) as biosorbent for mercury ion removal from aqueous solution. Garlic was used in this study because of the presence of organosulfur compounds. They reported that, the garlic powder has a good adsorption capacity for mercury with the maximum amount of mercury adsorbed (q_{max}) 0.6497 mg/g, where the mercury concentration of the solution has a significant impact on the adsorption capacity of the biosorbent (Eom et al., 2010).

Das and colleagues reported the adsorption characteristics of mercury on functionalized *Aspergillus versicolor* mycelia by using Atomic force microscopy (AFM) technique. (Das et al., 2008). This study is the first to report on the alteration of the nanomechanical properties of fungal cell wall following by the chemical functionalization process. They attempted to study the characterization of functionalized mycelia and their adsorption characteristics with respect to mercury following by the introduction of xanthate group on the surface of *Aspergillus versicolor* mycelia by covalent linkage of sulphur groups. The adsorption of mercury ion on the xanthate functionalized mycelia suggested that the adsorption mainly follows ion exchange mechanism processes. They reported the maximum adsorption capacity of xanthate functionalized mycelia for Hg^{2+} aqueous is found to be 256.5 mg/g, where for nonfunctionalized mycelia the corresponding values is 80.71 mg/g.

Green-Ruiz et al. reported that the use of bacteria for removing mercury is an effective technology for the treatment of industrial wastewater and can become an effective tool for the remediation of man-impacted coastal ecosystem with this metal. The study on the mercury removal onto nonviable biomass of *Bacillus sp*. was

conducted to investigate the potential of this microbial biomass serving as biosorbent material. From the study, it was found that the removal of mercury from the solution appeared to be more efficient at lower mercury concentration (92.0 % for 0.2 mgL^{-1}) than at higher (68.1 % for 10 mgL^{-1}). Therefore, the estuarine *Bacillus sp*. used was suitable biosorbent for mercury ion and that in term of percentage of mercury biosorbed, this process was more efficient at lower concentration of mercury. This is an important fact because, alternative conventional techniques may be ineffective when the metal content in the aqueous solution is very low (<100 mgL^{-1}) (Green-Ruiz, 2006).

1.4.3 Carbon Based Materials

Carbon is the sixth element of the periodic table and has the lowest atomic number of any element in column IV of the periodic table. Each carbon atom has six electrons which occupy $1s^2$, $2s^2$, and $2p^2$ atomic orbitals. The $1s^2$ orbital contains two strongly bound core electrons. Four more weakly bound electrons occupy the $2s^2 2p^2$ valence orbitals. In the crystalline phase, the valence electrons give rise to $2s$, $2p_x$, $2p_y$, and $2p_z$ orbitals which are important in forming covalent bonds in carbon materials. Since the energy difference between the upper $2p$ energy levels and the lower $2s$ level in carbon is small compared with the binding energy of the chemical bonds, the electronic wave functions for these four electrons can readily mix with each other, thereby changing the occupation of the $2s$ and three $2p$ atomic orbitals so as to enhance the binding energy of the C atom with its neighbouring atoms. The general mixing of $2s$ and $2p$ atomic orbitals is called hybridization, whereas the mixing of a single $2s$ electron with one, two, or three $2p$ electrons is called sp^n hybridization with n = 1, 2,3. Thus three possible hybridizations occur in carbon: sp, sp^2 and sp^3, while other group IV elements such as Si and Ge exhibit primarily sp^3 hybridization. Carbon differs from Si

and Ge insofar as carbon does not have inner atomic orbitals, except for the spherical 1*s* orbitals, and the absence of nearby inner orbitals facilitates hybridizations involving only valence *s* and *p* orbitals for carbon. The various bonding states are connected with certain structural arrangements, so that *sp* bonding gives rise to chain structures, sp^2 bonding to planar structures and sp^3 bonding to tetrahedral structures (Dresselhaus & Endo, 2001).

Carbon based materials are most commonly used as adsorbent and catalyst. This is due to their high surface area and high volume of pores and also the variety of chemical properties of their surfaces (Bandosz, 2008). In adsorption on carbon based materials, the type of carbon materials plays an important role since carbon has a complex porous structure with associated energetic as well as chemical heterogeneities. The energetic and chemical homogeneities are determined by the variety of surface functional groups, irregularities, and strong nonuniformity. This heterogeneity significantly influences the process of physical adsorption (Roque-Malherbe, 2007).

In addition, for the reactive adsorption process, the chemical environment of carbon materials plays an important role. The chemical environment provides structure that will be developed sufficiently for dispersion of active chemical species and for accommodation of molecules to be adsorbed or undergo a targeted chemical reaction (Bandosz, 2008). The chemical nature of the internal surfaces created when carbon based material is activated, is such that the surface has an attraction for certain molecules if they are present in the liquid phase which fills the pores (Cooney, 1999).

Carbon based materials are the main adsorbent used in the case of liquid-solid adsorption system. This is due to their uniquely powerful adsorption properties and the ability to readily modify their surface chemistry. The surface chemistry refers to the functional groups present on the carbon surfaces that can be classified as acidic and basic surface properties. The acidic functional groups include carboxyl, carbonyl, phenolic, hydroxyl, lactone and anhydride. The basic functional groups are chrome and pyrole like structures. Despite being a small fraction of the overall carbon surface, the oxygen groups are, however very active exhibiting a significant influence or adsorption capacity. The adsorption capacity on carbon depends on the nature of the adsorbent and adsorbate, and also the solution condition, for example, pH, temperature and ionic strength (Roque-Melherbe, 2007).

For the physical adsorption, the porous structure is the most important feature. The pore volume represents the total volume of the pores in a carbon particle per unit weight of the carbon. Pore size distribution is useful in selecting carbons with high adsorptive capacities for particular types of contaminants. For the removal of large molecule size material from liquid, carbon with large pores (>20Å) are needed. For gas adsorption, small pores (<10Å) are best suited (Cooney, 1999).

1.4.3.1 Activated Carbon

Activated carbon, also called activated charcoal, is charcoal that has been treated with oxygen to open up millions of tiny pores between the carbon atoms (Encyclopaedia Britannica). There are two types of activated carbon used in the industry as adsorbent, which are granular activated carbon (GAC) and powdered activated carbon (PAC) made usually by carbonization and chemical activation (USEPA, 1997). Activated carbons,

both powdered and granular, are made from a wide variety of carbonaceous starting materials such as coal, wood, peat and coconut shell (Cooney, 1999).

Activated carbon are the most widely used industrial adsorbent for removing contaminants and pollutants from gaseous, aqueous and nonaqueous streams (Roque-Melherbe, 2007). This is due to their high surface area, high volume of pores and the variety of chemical properties on their surfaces (Bandosz, 2008). The selectivity of activated carbon for adsorption is dependent on their surface chemistry as well as on their pore size distribution. Besides, micropores (<2nm) located between carbon (graphene) layers, activated carbon may consist of mesopores (2 nm > and <50 nm) and macropores (>50 nm) in different portions (Daud & Houshamnd, 2010). This characteristics are important in the adsorption process because the adsorption capacity for specific adsorbate depend on accessibility of the adsorbate molecules into pores and consequently on the size of pores and of adsorbate. Activated carbon was reported to have the BET surface area range 500 to 3000 m^2/g (Radovic, 2009). The surface of activated carbon is hydrophobic which has region containing diverse functional groups. These groups are called heteroatoms such as oxygen, nitrogen, hydrogen, phosphorus and sulphur that can be categorized to acidic, basic and neutral functional groups (Daud & Houshamnd, 2010; Bandosz, 2008).

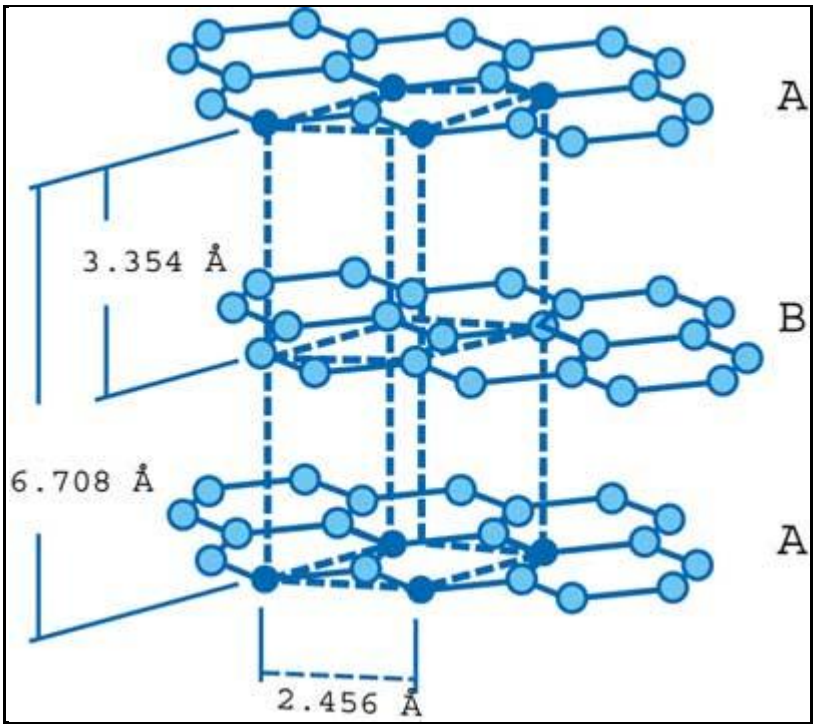
1.4.3.2 Carbon Nanotubes (CNTs)

A carbon nanotube is rolled from a single graphene layer, which is a hexagonal network of carbon atoms to form carbon nanotubes. Since nanotubes can be rolled from a graphene sheet in many ways, there are many possible orientations of the hexagons on the nanotubes, even though the basic shape of the carbon nanotube wall is a cylinder

(Dresselhaus & Endo, 2001). Carbon nanotubes can be thought of as one or more planar sheets of graphite rolled into a cylinder or several concentric cylinders closed seamlessly. Carbon tubes are normally closed at both ends (Ebbesen 1996). However, the end caps may be removed (Tsang et al 1994). The revelled hollow centre falls into the range of micropores and mesopores. Also due to the curvature of the pore wall, adsorption energy in carbon nanotubes is expected to be higher than in porous carbons. Thus, carbon nanotubes may find applications as adsorbents.

Graphite is composed of layers of carbon atoms that are arranged in 6-membered hexagonal rings. These rings are attached to one another on their edges. Carbon atom in these ring arrays are in the sp^2-hybridized state. In the sp^2 molecular orbital model each carbon atom is attached to three other species, three other carbon atoms in the case of graphite (Terrones, 2003). As shown in Figure 1.1, graphite structures consists of layers in which carbon atom are arranged in an open honeycomb network containing two atom per unit cell in each layer, labelled as A and B. The stacking of the graphene layers is arranged, such that the A and other A atoms on consecutive layer are on top of one another, but the B atoms in one plane are over the unoccupied centres of the adjacent layers, and similarly for the other B atom on the other plane. This gives rise to two distinct planes, which are labelled by A and B. These distinct planes are stacked in the 'ABAB' Bernal stacking arrangement with a very small in plane nearest neighbour distance C – C of 1.421Å. The unit cell dimensions are the lengths of the imaginary line connecting in-plane carbon atoms, along cell edges that are parallel with the graphite layers, *a*, and the length of the imaginary line connecting between-plane carbon atoms, *c*, between the first and third layer (the edge perpendicular to the graphene layer). These dimensions are: a= 2.462 Å, c= 6.708 Å. Since the distance between two layers, *c*, is

6.708 Å, the distance between any two adjacent layers (interplanar distance) is 3.354 Å, (Dresselhaus & Endo, 2001).

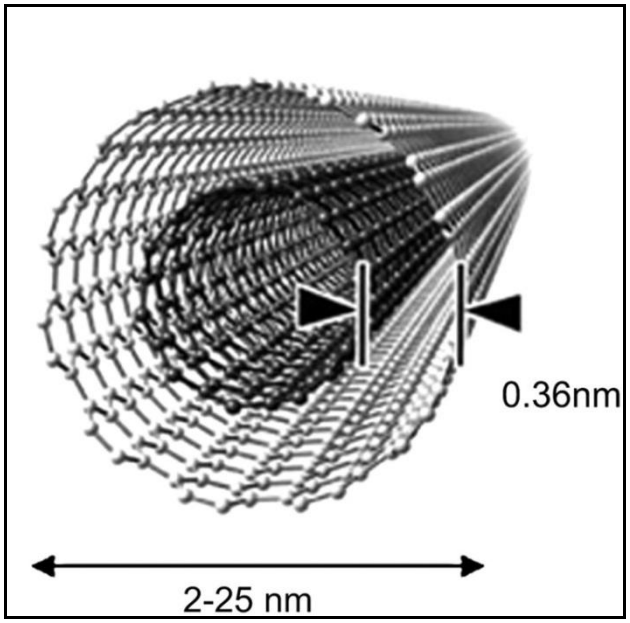


(Source: Norley, 2001)

Figure 1.1: The crystal structure of hexagonal single crystal graphite, in which the two distance planes of carbon hexagons called A and B planes are stacked in an ABAB sequence.

Carbon nanotube is divided into two forms that is Multiwalled Carbon Nanotube (MWCNTs) and Singlewalled Nanotubes (SWCNTs). The first carbon nanotubes molecule of fullerene family was synthesized by Harry Kroto, Richard Smalley and their colleagues in 1985 (Haris, 2009). Since then, research in carbon material has expanded rapidly by the beautiful images of multi-walled carbon nanotubes (MWCNTs) shown first at a meeting at Richmond, Virginia in October 1991 and published in *Nature* a month later by Sumio Iijima (Haris, 2009; Naseh et al., 2009; Tessonnier et al., 2009). MWCNTs consisting of a nested coaxial array of single-wall nanotube constituents, separated from one another by approximately 0.36 nm (3.6 Å) of the

interlayer distance of graphite, see Figure 1.2 (Dresselhaus & Endo, 2001). These multilayer nanotubes were firstly produced using an arc-discharge evaporation method similar to that used for fullerene synthesis, the needles grow at the negative end of the electrode used for the arc discharge. Each needles comprising of coaxial tubes of graphitic sheets, are typically composed of 2 to 50 concentric cylindrical shells ((Iijima, 1991). On each tube, the carbon atom hexagons are arranged in a helical fashion about the needle axis. The helical pitch varies from needle to needle and from tube to tube within a single needle. It appears that this helical structure may aid the growth process. The formation of these needles ranged from a few nm to a few tens of nm in diameter (Iijima, 1991; Kiang et al., 1995). Each shell has the structure of a rolled up graphene sheet with the sp^2 carbons forming a hexagonal lattice (Kiang et al., 1995). However, Kiang and co-workers studied three MWCNTs with different inner diameter and number of shells using HRTEM and found that interlayer spacing could vary from 3.4 Å to 3.9 Å and increase with increasing shell diameter (Kiang et al., 1998).



(Source: Reilly, 2007)

Figure 1.2: Structure of MWCNTs.

A single wall nanotube rope, which is a nanocrystal consisting of 10–100 single-wall nanotubes (SWCNTs), whose axes are aligned parallel to one another, and are arranged in a triangular lattice with a lattice constant that is approximately equal to *d*t + *c*t, where *d*t is the nanotube diameter and *c*t is approximately equal to the interlayer lattice constant of graphite, see Figure 1.3 (Dresselhaus & Endo, 2001). The physical reason why these nanostructures form is that a graphene layer (defined as a single 2D layer of 3D graphite) of finite size has many edge atoms with dangling bonds, index dangling bonds and these dangling bonds correspond to high energy states. Therefore the total energy of a small number of carbon atoms is reduced by eliminating dangling bonds, even at the expense of the strain energy, thereby promoting the formation of closed cage clusters such as fullerene and carbon nanotubes (Dresselhaus & Endo, 2001).

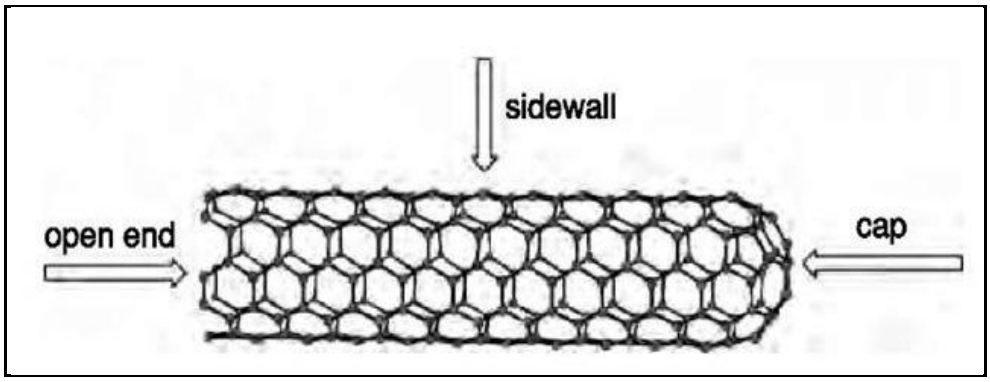


Figure 1.3: Structure of SWCNTs.

In 1993, two groups independently found ways to produce SWCNTs in the microscopic quantities (Iijima & Ichihashi, 1993; Bethune et al., 1993). These methods both involved co-vaporizing carbon and transition metal catalyst, and produced single layer nanotubes approximately 1 nm in diameter and up to several micron long. In one case, Iijima and Ichihashi produced single-layer nanotubes by vaporizing graphite and Fe in an Ar/CH_4 atmosphere. The tubes were found in the deposited soot (Iijima &

Ichihashi, 1993 ; Kiang et al., 1995). On the other hand, Bethune et al., vaporized Co and graphite under helium buffer gas, and found single layer nanotubes in both the soot and in web-like material attached to the chamber walls (Bethune et al., 1993; Kiang et al., 1995).

Generally, carbon nanotubes have been shown to exhibit a variety of interesting properties. They have high electrical conductivity that can be useful in constructing nanotubes –based electronic devices. They also show high mechanical strength with the Young's modulus of the best nanotubes as high as 1000 GPa, approximately five times higher than steel. The crystalline carbons also display the highest measured thermal conductivities. Thermal conductivity of CNTs with values of greater than 3000 $Wm^{-1}K^{-1}$ at room temperature has been reported. Carbon nanotubes possess good chemical stability in aggressive media (Haris, 2009; Naseh et al., 2009; Tessonnier et al., 2009). It has been demonstrated that C – C covalent bond in the graphene layer is one of the most stable chemical bonds (Sun & Gao, 2003). Carbon nanotubes have exhibited great potential in applications such as composite reinforcements, field emitters for flat panel display, sensors, energy storage and energy conversion devices, and catalysts support phases, because of their extraordinary mechanical, electrical, thermal and structural properties (Li et al., 2007).

1.5 Significant of Study

Mercury pollutant has significant impact at local, national, regional and global levels as it can cause harm to living organism and failure in oil and gas industries. For example, it causes diseases such as irreversible neurological damage, tremors, loss of sensation in extremities, vision and hearing loss to human. Mercury present in the hydrocarbon feed

will deposit in the cryogenic equipment causing cracking of welded aluminium heat exchangers and cause cold box failure in steam cracking ethylene plant. Among several methods for the mercury removal from aqueous solution such as precipitation, ion exchange and membrane separation, adsorption proves to be an efficient and cost effective method. Recently, MWCNTs have become a new adsorbent material with great potential as a trapping media for mercury in aqueous environment. MWCNTs exhibit specific adsorption properties in comparison with activated carbon due to their peculiar morphology, the role of defects and the probability of opening or closing of the tubes which are believed to induce cooperative interaction between mercury and MWCNTs phase.

1.6 Objective of Study

The objectives of this study are; (1) to chemically modify MWCNTs with oxygen and sulphur-containing functional group for mercury adsorption, (2) to study the efficiency of mercury adsorption by the chemically modified MWCNTs.