CHAPTER 2

LITERATURE REVIEW

2.0 Literature review.

2.1 Mercury removal system from water.

The commonly used conventional methods for mercury removal from water systems include chemical precipitation, magnetic filtration and ion exchange techniques. Chemical precipitation is the method of causing contaminants that either dissolved or suspended in solution to settle out of solution as a solid precipitate, which then can be filtered, centrifuged or separated from the liquid portion. Precipitation is assisted through the use of coagulant, an agent which causes smaller particles suspended in solution to gather into larger aggregates. An example of chemical precipitation is the aqueous mercury treatment operation by using sulphide precipitation method. Sulphide precipitation is one of the common method for removal of inorganic mercury from wastewater. In this process, sulphide (eg ; sodium sulphide or another sulphide salt) is added to the wastewater stream to convert the soluble mercury to the relatively insoluble mercury sulphide form. The example mechanism of this process is as follows; $Hg^{2+} + S^{2-} \rightarrow HgS$ (s) (USEPA, 1997). For example, the S-based precipitation via organosulphur compound was used as coagulant in chemical precipitation. The organic precipitant agent TMT (trimercoptotriacin: trimercapto-S-triazine-trisodium) is very stable and can form precipitate in the presence of complexing agents which bind mercury and prevent formation of H_2S with N_2S (Essa et al., 2005).

Magnetic filtration of soluble species such as ionic metal is accomplished by forming a magnetic precipitate through coagulation and magnetic seed addition, and then passing wastewater through a filter made with ferromagnetic wires which represent a magnetic field. The magnetic precipitate can be rapidly and efficiently removed by magnetic filtration, even if the precipitate is quite fine. This occurs because of the strong magnetic forces that act on the magnetic particles as they move through the magnetic field. The magnetic particles are captured on the filter matrix by the magnetic force, which overcomes other competing forces of gravitation, hydrodynamics and inertia. Terashima and colleagues reported the mercury removal in a bench scale magnetic filtration unit fed gas scrubbing waste water from municipal solid waste incineration plant. This technique is combined the process of chemical coagulation, magnetic seeding and high gradient magnetic filtration (HGMF). The calcium polysulphide (CaSx) and ferric chloride ($FeCl_3$) are used as coagulant for chemical precipitation. For an influent mercury concentration of 15.0 mg/L, effluent mercury concentrations of 0.003 to 0.117 mg/L were achieved (Terashima et al., 1986).

Ion exchange is a versatile separation process with potential for broad application in the wastewater purification. Ion exchange is a reversible chemical reaction wherein ion from solution is exchanged for similar charged ion attached to an immobile solid particle (USEPA, 1981). This solid ion exchange particle is called resins. Ion exchange resins are classified as cation exchangers, that have positively charged mobile ion available for exchange, and anion exchangers, whose exchangeable ions are negatively charged. For example, mercury in the form of anionic complexes, such as $HgCl^{-}_3$, can be treated by anion exchange resins. The thiol resin, Duolite GT-73, is reported to be selective for mercury in any of its oxidation states. The Duolite GT-73 contains the thiol (-SH) group and reacts with ionic mercury. The thiol functional group has a high selectivity for mercury as well as a strong tendency to bind certain other metal ions such as copper, silver, cadmium and lead. The disadvantages of this technique include spent regenerant brine that must be disposed of, can yield variable effluent quality and cannot typically be used for waters with a high total dissolved solid content (USEPA, 1997; Ritter & Bibler, 1992).

Among all of the conventional methods, the adsorption process has become increasingly attractive to many researchers because of its advantages that include cost effectiveness, simple operation and environmental friendliness. Up to now, a variety of adsorbents have been developed and reported as materials for the adsorption of heavy metals from water and wastewater system. For example, metals oxides, biometerials, polymer, and activated carbon. However these adsorbent suffer from low adsorption capacities of metal ions and cannot be regenerated. The presence of high amount of mercury in water systems causes serious effects on human health. Thus, this issue puts the scientific community under pressure to develop new materials for removal and elimination of mercury ions from water in an efficient and economically viable method. In accordance to this, the carbon based material such as activated carbon and carbon nanotubes have been found to be efficient adsorbent in removing of organic and inorganic contaminant from water and wastewater system.

2.2 Functionalization of carbon based materials.

Carbon based materials, primarily activated carbon and carbon nanotubes, have received great attention as the media for mercury trapping in water based systems. Due to its hydrophobic properties, the chemical and physical functionalization on carbon has been studied for years to modify the carbon surface to achieve hydrophilic characteristics.

2.2.1 Activated carbon

Activated carbon is extensively used as catalyst, catalyst support and also adsorbent in various industrial applications. Activated carbon are usually non selective and their surfaces suffer from lack of enough reactive groups. This drawback can be improved by various types of modification. There are various methods of modification reported by many researchers that study the textural characteristic, surface chemistry and thermal stability of modified activated carbon (Daud & Houshamnd, 2010; Biniak et al, 1997; Castilla et al., 2000; Puente et al., 1997). Oxidation is one of the famous methods for modification and pre-modification used by many researchers in order to introduce oxygen- containing functional groups on the carbon surfaces.

Beniak and colleagues modified the activated carbon at different treatment conditions, such as high temperature treatment (1000K) under vacuum, oxidation with concentrated nitric acid and ammonia-treatment of annealed and oxidized carbon at high temperatures. They reported that the nitric acid treatment created high acid strength and high number of surface groups of carboxyl (pKa 4) and hydroxyl (pKa >12). The annealing in ammonia enhances the basic properties of the carbon and increases the presence carbonyl groups (Biniak et al., 1997). Similar studies were reported by Castilla et al., and Ramon et al. They studied the modification of a variety of activated carbon using wet oxidation with different oxidizing agent such as nitric acid (HNO_3), hydrogen peroxide (H_2O_2) and ammonium peroxydisulphate ($(NH_4)_2S_2O_8$). Castilla et al. determined that, the highest oxygen content was obtained by HNO_3 treatment, followed by H_2O_2 treatment and the lowest oxygen content treatment was in $(NH_4)_2 S_2O_8$. All oxidized samples exhibited oxygen surface groups with single C – O bond, lactone, carboxyl, quinone and carboxyl- carbonate structures (Castilla et al., 2000; Ramon et al., 1999).

The study on thermal stability of oxygenated functions in activated carbon was conducted by numerous researchers. Puente and colloquies oxidized activated carbons with various degrees of oxidation by treating it with concentrated nitric acid at various temperatures. The thermal gravimetric analysis (TGA) indicates the decomposition of carboxylic acid groups in form of CO_2 in the lower temperature range of 400 – 623 K. The decomposition of lactone groups takes place in the temperature range of 623 – 823 K and phenol or ether groups was the most stable functional groups that decomposed at the temperature above 823 K (Puente et al., 1997). It was also reported by Symanski et al. that the TPD analysis observed desorption of CO_2 from the carboxylic acid group at low temperature (453 -573 K) and, anhydrides and lactones at higher temperature (623 – 775 K). The carboxylic anhydrides give rise to desorption of both CO and CO_2 at temperature of 700 – 775 K, while phenol, ether and carbonyls produce only CO at temperature of 823 – 973 K (Symanski et al.,2002).

Several researchers have reported the effects of modification on the textural characteristic of activated carbon such as the surface area and pore volume. Castilla et al reported the wet oxidation of activated carbon with nitric acid (HNO_3), hydrogen peroxides (H_2O_2) and ammonium peroxydisulphate ($(NH_4)_2S_2O_8$). They observed that samples treated in $(NH_4)_2S_2O_8$ and HNO_3 show decrease in macropore volume compared to the original sample, while samples treatment in H_2O_2 show increases in macropore volume (Castilla et al.,2000). Pereria et al. studied the chemical treatment such as HNO_3, H_2O_2 and NH_3 and thermal treatment under H_2 and N_2 on activated carbon and reported the decrease in micropores volume after the treatments (Pereria et al,. 2003).

However, there are also a number of reports that suggest that surface area remained constant or showed an increase after wet oxidation. Julien et al., reported the increase in surface area of activated carbon to 1000 m^2/g by oxidation with nitric acid (Julien et al., 1998). Besides, it was reported by Ania et al., that oxidation of activated carbon by nitric acid will result in increase in micropores and mesopores (Ania et al., 2002). Also, it was reported that the increase in surface area of activated carbon treated with nitric acid and hydrogen peroxide can be attributed to pore widening, where conversion of micropores to mesopores occurs (Xue et al., 2008). Valdes et al. observed an increase in surface area in the early stage of activated carbon oxidation by ozone (O_3) and a reduction in the surface area as the time of exposure lengthens (Valdes et al., 2002).

2.2.2 Multiwalled Carbon Nanotubes

Since the discovery of multiwalled carbon nanotubes (MWCNTs) by Iijima in 1991, many studies have been conducted by researches on the functionalization of MWCNTs due to the requirement for various applications such as sensor, optical, catalyst and adsorbent materials (Yu et al., 2008). Various methods have been established to modify the MWCNTs, including covalent or non-covalent chemical routes, microwave method and ionic liquids method (Ma et al., 2006; Yu et al., 2008;).

Commonly, MWCNTs is covalently functionalized by oxidation reaction which introduces the oxygen-containing functional groups leading to acidic surfaces of

MWCNTs. Kim and Sigmund reported the MWCNTs oxidized in a mixture of sulphuric acid and nitric acid had increased the concentration of carboxylic group from 4.0×10^{-4} g/mol to 1.1×10^{-3} g/mol (Kim & Sigmund, 2004). Xia et al., reported the use of nitric acid and oxygen plasma to synthesis the oxygen-containing functional groups. The nitric acid resulted in 60% higher surface oxygen concentration compared to the plasma treatment. Nitric acid mainly resulted in the formation of carboxylic (COOR) and phenolic (C – OR) groups, where as the plasma treatment led to higher carbonyl (C=O) groups (Xia et al., 2007). Daksyuk and co-workers also conducted a study on oxidation of multiwalled carbon nanotubes through acidic oxidative treatment. They treated the pristine material with concentrated HCl, hot nitric acid, piranha mixture (H_2SO_4/H_2O_2) and ammonium hydroxide/hydrogen peroxide mixture. It was found that the nitric acid treatment creates the highest acidic surface side oxygen-containing functional group such as carboxyl and hydroxyl on the carbon surfaces (Datsyuk et al., 2008).

Additionally, the study on modification of MWCNTs with nitric acid and DBD plasma in an oxygen atmosphere was reported by Naseh et al . They detected the formation of carboxyl, phenol, lactol, and lactone groups and confirmed the presence of these acidic functional groups by the decomposition of CO_2 and CO gases at temperature 250 ^{o}C and 750 ^{o}C. The nitric acid treatment generates more acidic functional groups as compared to DBD plasma treatment (Naseh et al, 2009).

Recently, Wepasnick and colleagues investigated the surface chemistry and structural properties of MWCNTs using different oxidative treatments. Six wet chemical oxidants such as HNO_3, $KMnO_4$, H_2SO_4/HNO_3, $(NH_4)_2S_2O_8$, H_2O_2 and O_3 were used in the study. The extent of surface oxidation was measured by XPS, showed the oxidative treatments with HNO_3, H_2SO_4/HNO_3 and $KMnO_4$ resulted in the highest level of oxidation (9.5–10.2 %). In contrast, oxidation with H_2O_2, $(NH_4)_2S_2O_8$, and O_3 generally resulted in lower level of oxidation (4.2– 5.1 %). They also studied the effect of varying the weight per weight percentage (w/w%) of HNO_3 on both the overall atomic oxygen concentration and the distribution of hydroxyl, carbonyl and carboxylic acid groups. They found that the atomic oxygen increases linearly with increasing w/w% HNO_3. The higher carboxylic group [O]COOH concentration are observed for MWCNTs treated with the most aggressive oxidant such as HNO_3 and $KMnO_4$, while the MWCNTs treated with H_2O_2, $(NH_4)_2S_2O_8$, and O_3 yielded higher concentration of carbonyl and hydroxyl functional groups (Wepasnick et al., 2011).

Meanwhile, Chen et al., investigated surface chemical modification of MWCNTs by wet-mechanochemical reaction using potassium hydroxide (KOH) in alcohol solvent at room temperature under mechanical milling. They detected the presence of hydroxyl group (O – H) on the functionalized carbon surface. The increase in negative zeta potential value after functionalization was due to the hydroxyl group attached onto the MWCNTs surface. The more negative zeta potential value indicates their high dispersibility in polar solvent. (Chen et al., 2008).

In general, non-covalent functionalization normally involves molecules with planar moieties that could adsorb onto the surface of carbon via $\pi - \pi$ interactions (Ma et al., 2006). The functionalization of MWCNTs with isocyanate groups was reported by Zhao and colleagues. They functionalized the MWCNTs surface via the amidation reaction between toluene 2,4-diidocyanate (MWCNT-NCO) and carboxylated carbon nanotubes (MWCNT-COOH). The existence of carboxyl groups in MWCNT-COOH at

1714 cm^{-1} peaks while the characteristic of asymmetric stretching isocyanate groups at 2264 cm^{-1} and peaks at 1223 cm^{-1} for stretching amide groups was obtained. (Zhao et al., 2004).

The chemical modification of MWCNTs is important due to the strong van der Waals interaction between carbon atoms that has contributed to solubility problems in the various applications. Many studies have been carried out to solve the solubility problem of MWCNTs. The non-covalent amidation reaction between toluene 2,4-diidocyanate (MWCNT-NCO) and carboxylated carbon nanotubes (MWCNT-COOH) showed the MWCNTs-COOH was hydrophilic and well dispersed in water (Zhao et al., 2004). Kim and Sigmund reported the colloidal stability of aqueous oxidized MWCNTs dispersion was enhanced through elongated oxidation (Kim & Sigmund, 2004). Besides, Jeong and co-workers non-covalently functionalized MWCNTs with sodium lignosulfonate (SLS) at various SLS/MWCNTs ratio. They reported that the functionalization method proposed in the study could disperse MWCNTs well with a very small amount of SLS, and its stability in water was quite good as verified by zeta potential measurement and UV-Vis spectroscopy (Jeong et al., 2010). Naseh et al. found that the nitric acid treatment shows better dispersibility behaviour of MWCNTs in comparison with DBD plasma treatment. The BET analysis indicate that both acid and DBD plasma treatment increase specific surface area of the MWCNTs (Naseh et al., 2009).

Zhao et al., reported the MWCNT-COOH was thermally stable than MWCNT-NCO with the onset temperature at 460 ^{o}C and 239 ^{o}C, respectively (Zhao et al., 2004). Besides, Xie et al., detected the release of carbon dioxide (CO_2) using TPD analysis at

350 ^{o}C and 450 ^{o}C indicating the decomposition of carboxylic (COOR) groups and the carbonyl (C=O) groups were more stable decomposing above 600 ^{o}C . They also reported the evolution of CO at temperatures above 600 ^{o}C indicating the decomposition of phenol, carbonyl, quinine and ether groups (Xia et al., 2007).

2.2.3 Singlewalled Carbon Nanotubes

The functionalization of SWCNTs also has attracted many researchers to study its properties since it was discovered by Iijima and colleagues in 1993 (Iijima et al., 1993). The chemical modification and solubilisation of SWCNTs represent an emerging area in the research on nanotubes based materials. Several research groups have reported successful covalent and non-covalent functionalization reaction for SWCNTs. Hu and co-workers reported the purification treatment of single-walled carbon nanotubes (SWCNTs) by refluxing in nitric acid. They studied the effect of refluxing time and concentration of nitric acid on the SWCNTs. The 3M of HNO_3 at 12 hours and 7M of HNO_3 at 6 hours treatment was found to be the most efficient (Hu et al., 2003). The study on physical and chemical properties of functionalized SWCNTs with anchored phenol structures was reported by Bae et al. .The SWCNTs had been functionalized by introducing azomethine ylide containing anchored phenol structures. The functionalized SWCNTs showed the formation of phenolic and azomethine ylides groups with the presence of –CNC starching and –CN stretching of tertiary amine groups (Bae et al., 2007).

Numerous studies have been conducted on the modification of carbon nanotubes with the aim to introduce oxygen and sulfur containing functional groups besides increasing the dispersibility in aqueous environment. Nakamura and co-workers reported the chemical modification of SWCNTs with sulphur containing functionalities. The increase in defect intensity of sulfonated SWCNTs compared to raw SWCNTs have been showing by the presence of scattering defect on the sidewalls of SWCNTs due to the occurance of covalent functionalization. They confirmed the presence of sulphur-containing methylene group, $–S(CH_2)_4SH$ on the surface of sulfonated SWCNTs (Nakamura et al.,2006). Yu and colloquies treated SWCNTs with sulfuric acid (H_2SO_4) at 300 ^oC to synthesize sulfonated SWCNTs (s-SWCNTs) for solid acid catalyst. The functionalization of SWCNTs by concentrated H_2SO_4 at elevated temperature results in the sulfonation for SWCNTs. Covalent $–SO_2OH$ groups were created on the surface of SWCNTs. This functional group tunes the SWCNTs into a hydrophilic surface with high acidity. This allows the SWCNTs to be uniformly dispersed in water and organic solvent (Yu et al., 2008). Bae et al., also reported the high zeta potential value of –16.31 mV for functionalized SWCNTs that indicates its higher dispersing ability in solvent compared to raw SWCNTs. (Bae et al., 2007).

2.3 Removal of divalent ions using functionalized carbon based materials

2.3.1 Activated Carbon for Divalent Ions Removal

Activated carbon is one of the most important adsorbent used to capture a variety of species such as organic substances and metal ions. Activated carbon are usually non selective and their surfaces suffers from lack of enough reactive group. In order to improve the capability of this material as adsorbent, many researchers have developed methods of modification to change the surface chemistry and textural characteristic of activated carbon to suite the targeted metals ion.

El-Sheihk conducted a study on the effect of oxidizing activated carbon (AC) with various oxidizing agents such as nitric acid, hydrogen peroxide, ammonium persulfate on preconcentration of metal ion (Cr^{3+}, Mn^{2+}, Pb^{2+}, Cu^{2+}, Cd^{2+} and Zn^{2+}). He noted that nitric acid oxidation produced maximum number of oxygen-contianing groups of 2.164 $mmolg^{-1}$, for ammonium persulfate treatment was 2.151 $mmolg^{-1}$ and for hydrogen peroxide treatment was 2.151 $mmolg^{-1}$. Nitric acid, hydrogen peroxide and ammonium persulfate treatment decrease the surface area and pore volume of the activated carbon from 303 m^2g^{-1} to 240 m^2g^{-1} , 265 m^2g^{-1} and 205 m^2g^{-1}, respectively. He found that, the highest recoveries and sorption capacity for all metals ions were achieved when using nitric acid-oxidized AC (AC-NA) as preconcentration adsorbent at pH 9. It is noted that, the recovery for Mn^{2+},Cd^{2+}, Cr^{3+}, Cu^{2+}, Zn^{2+} and Pb^{2+} were 85, 100, 60, 102 ,85 and 80 %, respectively. Comparing the performance using AC-NA as preconcentration adsorbent between non-oxidized and oxidized MWCNTs indicates that the AC-NA is close to oxidized MWCNTs, but the performance of AC-NA is much better than non-oxidized MWCNTs (El-Sheihk, 2008).

A similar study was conducted by Jaramillo et al., the oxidation of cherry stones based activated carbon with several oxidizing agent such as air, air-ozone mixture, nitric acid and hydrogen peroxide for removal of Cu^{2+} ion. Oxidation treatments with nitric acid and ozone led to fixation of high amount of acidic surface oxygen complexes. All oxidative treatment performed on cherry stones activated carbon led to decrease of the BET surface area and the micropores volume while the external surface area and the volume of large pores (meso- and macropores) were increased. These effects can be most likely due to the pore widening (micropore destruction) or micropore blockage by the formation of surface oxygen complexes (Jaramillo et.al., 2009). Recently, the removal of heavy metals such as lead (Pb^{2+}), cadmium (Cd^{2+}) and copper (Cu^{2+}) from aqueous solutions using activated carbon produce from cotton stalks was reported (El Zayat & Smith, 2010).

The metal ion sorption equilibrium studies on the activated carbon were categorized such as their sorption capacities, mechanism, and the process parameter such as effect of pH, adsorbent dosage and contact time. Abdel-Shafy and co-workers studied the removal of Ni^{2+} and Hg^{2+} ion onto powder and granular activated carbon (PAC and GAC). They found that the adsobility of Hg^{2+} is much higher than that of Ni^{2+} with respect to both PAC and GAC (Abdel-Shafy et al., 1998). Uzun and Guzel reported, the sorption capacities of metals ion (Mn^{2+}, Fe^{2+}, Ni^{2+} and Cu^{2+}) adsorbed onto raw activated carbon follow roughly the order of $Mn^{2+} < Fe^{2+} < Ni^{2+} < Cu^{2+}$. The result showed that Mn^{2+} ion was the lease adsorbed and Cu^{2+} was the most adsorbed. This is due to the hardness order of acidities of heavy metals ion. For example, Mn^{2+} (hard acid) react more with OH^- (hard base) as Mn^{2+} was the most hydrolysed heavy metal ion as compared to others. The hydrolysed part of Mn^{2+} react with OH^- in short time and Mn(OH) was formed. Therefore less or no Mn^{2+} ion in the aqueous medium was absorbed by negative group on the activated carbon (Uzun & Guzel, 2000). Besides, the uptake capacity of the three heavy metals appears to be greatest for Pb^{2+}, followed by Cu^{2+} than Cd^{2+} (El Zayat & Smith, 2010). In contrast, Schneider et al., reported only the adsorption of Cr^{2+} on activated carbon. They found the highest percentage of Cr^{2+} adsorbed of 75.3 to 83.4 % at optimum pH ranging 4.0 to 4.5 (Schneider et al., 2007). Yahaya and co-workers reported the adsorption capacity of Cu^{2+} onto rice husk activated carbon increased with the attained maximum value at 45 minutes was 75.81 mg/g (Yahaya et at. 2011).

Besides the sorption capacities, solution pH and contact time study, the adsorbent dosage is an important parameter because it determines the capacity of an adsorbent for a given initial concentration of the adsorbate. As reported by Yahaya et al., the amount of Cu^{2+} ion absorbed increased from 19.98 mgg^{-1} to 84.02 mgg^{-1} for rice husk activated carbon as the adsorbent dosage was increased from 3.0 g/L to 0.5g/L. The decrease in the unit adsorption with increase in the dosage of adsorbent was due to adsorption sites remaining unsaturated during the adsorption process (Yahaya et at. 2011).

2.3.2 MWCNTs for Divalent Ions Removal

MWCNTs have attracted considerable researchers interest as new adsorbent for metal ions due to their large specific surface area. MWCNTs were used for removal of metals ions such as lead, copper, cadmium, silver and nickel (Atieh et al., 2010; Kandah & Meunier, 2007; Li et al., 2002; Lu et al., 2006; Li et al., 2003). The chemical modification of MWCNTs such as oxidation is known to generate not only more hydrophilic surface structure but also more oxygen containing functional groups and increase the ion exchange capacity (Atieh et al., 2010). Kandah and Meunier reported the removal of nickel ion (Ni^{2+}) by raw and oxidized MWCNTs. They studied the effect of adsorption time, solution pH and initial nickel ions concentration on the adsorption uptake of Ni^{2+} for both raw and oxidized MWCNTs at room temperature (Kandah & Meunier, 2007). The surface functionalization of MWCNTs by amino acid based materials (ethylenediamine) was reported by Vukoric et al. They tested the adsorption characteristic of Cd^{2+} ion onto raw-MWCNT, oxidized MWCNT (o-MWCNTs) and ethylenediamine –functionalized MWCNTs (e-MWCNTs). They studied the influences of solution pH, contact time, initial metal ion concentration and temperature on all three materials (Vukoric et al., 2010). Atieh and co-workers studied the effect of carboxylic functional group functionalized on MWCNTs (COOH-MWCNTs) surface on the removal of lead (Pb^{2+}) from water. The independent variables including solution pH, MWCNTs dosage, contact time and agitation speed were carried out to determine the influence of these parameter on the adsorption capacity of the Pb^{2+} from water (Atieh et al., 2010).

In addition, the study on the relative roles of oxygen-containing functional groups and graphenic carbon on MWCNTs in the removal of zinc (Zn^{2+}) and cadmium (Cd^{2+}) ion from aqueous solution have been reported (Cho et al., 2010). This research evaluated how changes in oxygen concentration and distribution of oxygen-containing functional groups influenced the sorption of aqueous zinc and cadmium on MWCNTs. They also studied the sorption behaviour of Zn^{2+} and Cd^{2+} ions on two different types of adsorbents such as granular activated carbon (GAC) and natural char (NCI) with varying surface oxygen content (Cho et al., 2010).

Besides, the functionalization of MWCNTs by using polymer for remediation of heavy metals contamination in the aquatic environment was investigated by Mamba et al. (2010). They reported the result obtained from testing the pristine MWCNTs, oxidized MWCNTs and MWCNTs-cyclodextrins (MWCNT-CD) polymers for the removal of lead (Pb^{2+}) and cobalt (Co^{2+}) from synthetic water solution (Mamba et al., 2010).

The supported carbon nanotubes nanocomposite are increasingly attracting interest as adsorbent material for the removal of heavy metals from wastewater. Chen et al. studied the adsorption behaviour of MWCNTs iron oxide magnetic composites for removal of Ni(II) and Sr (II) ion from aqueous solution. The comparison study of the adsorption behaviour of the Ni(II) and Sr(II) on the iron oxide, MWCNT, and MWCNT-iron oxide was investigated (Chen et al., 2009). Besides, Zhao et al. also reported similar work which used titanium dioxide supported on MWCNTs (TiO_2/MWCNTs) nanocomposites as the adsorbent for the removal of Pb(II) ion from aqueous solution (Zhao et al., 2010). In addition, Gupta and co-workers also reported the use of MWCNTs-iron oxide magnetic composites as adsorbent. They studied the behaviour of Cr(III) ion removal from aqueous solution and the comparison adsorption capacity of this metals on MWCNTs-nano iron oxide, raw MWCNTs and activated carbon (Gupta et al., 2011).

Similar to activated carbon studies, many researchers reported the metal ion sorption equilibrium studies that categorized sorption capacities, mechanism, and process parameters such as effect of pH, adsorbent dosage and contact time. Kandah and Meunier reported the adsorption capacity for Ni^{2+} ions from aqueous solution increased significantly onto the surface of oxidized MWCNTs compared to that on raw MWCNTs. From the investigation, the optimum condition for removal of nickel ion from water by oxidized MWCNTs occurred at pH 6, 20 minutes and 200 mg.L^{-1} nickel ion concentration. According to Langmuir model the maximum nickel ion adsorption uptake (q_{max}) onto raw and oxidized MWCNTs were determined as 18.083 and 49.261 mg/g, respectively (Kandah & Meunier, 2007). Vukoric et al., reported the adsorption properties of raw-MWCNTs for Cd^{2+} ion were greatly improved by oxidation as well as by ethylenediamine-functionalized MWCNTs. The maximum sorption capacity (q_{max}) of Cd^{2+} ion was observed for raw-MWCNT, oxidized MWCNTs (o-MWCNTs) and ethylenediamine-MWCNTs (e-MWCNTs) of 3.19, 24.15 and 25.70 $mg.g^{-1}$ at 45^oC, respectively. The e-MWCNTs had the best adsorption capacity for Cd^{2+} removal with the optimum condition was at pH range of 8 to 9, contact time of 30 minutes and temperature of 45 ^oC (Vukoric et al., 2010). Atieh et al., reported that 100% of Pb^{2+} was removed by using COOH-MWCNTs at pH 7, 150 rpm, 10 mg of adsorbent and 2 hours. The maximum sorption capacity (q_{max}) of lead onto COOH-MWCNTs was 6.6 $mg.g^{-1}$ (Atieh et al., 2010).

Cho and colleagues reported that the maximum sorption capacities obtained for oxidized MWCNTs were found to be slightly higher than those of granular activated carbon (GAC). On the other hand, the maximum sorption capacities for a natural char pine (NCI) were much higher than those oxidized MWCNTs, consistent with the much higher oxygen content of the charcoal materials. Results confirmed that surface oxygen enhances the sorption of both Zn^{2+} and Cd^{2+} from aqueous solution (Cho et al., 2010). Mamba et al. found that the maximum sorption capacity (q_{max}) for pristine MWCNT was determined to be 8.73 and 10.92 $mg.g^{-1}$ for Pb^{2+} and Co^{2+}, respectively. The maximum sorption capacity (q_{max}) for MWCNTs-cyclodextrins (MWCNT-CD) polymer was calculated to be 28.86 and 21.44 mg/g for Pb^{2+} and Co^{2+}, respectively. The oxidized MWCNTs showed superior adsorption capacity for the two metals compared to the other two adsorbents used. The oxidized MWCNTs were found to have a maximum sorption capacity (q_{max}) of 54.38 and 49.94 mgg^{-1} for Pb^{2+} and Co^{2+}, respectively (Mamba et al., 2010). Chen et al., found that the adsorption capacity of the MWCNT-iron oxide is much higher than MWCNT and iron oxides for both Ni(II) and Sr(II) ion (Chen et al., 2009).

Zhao et al., reported the adsorption percentage of TiO_2/MWCNTs and MWCNTs increase as the pH increases from pH 2 to 7, and the adsorption percentage of TiO_2/MWCNT was higher than MWCNTs. The equilibrium contact time of Pb(II) ion was reached at 60 minutes for both TiO_2/MWCNT and MWCNTs. The maximum adsorption capacity of TiO_2/MWCNTs was much higher than MWCNTs that was determined to be 137.0 and 33.0 mgg^{-1} respectively (Zhao et al., 2010). The MWCNTs-nano iron oxide showed greater adsorption ability, approximately 90% after 60 minutes contact time as compared to MWCNTs and activated carbon. The maximum sorption capacity was reached at pH 5 – 6. The adsorption capability of MWCNTs-nano iron oxide was higher than that raw MWCNTs and activated carbon (Gupta et al., 2011).

Recently, the adsorption of lead (Pb^{2+}) on O_2-Plasma oxidized MWCNTs (po-MWCNTs) in water was reported by Yu and co-workers. The adsorption capacity of MWCNTs for Pb^{2+} was greatly enhanced after plasma oxidation. They reported the amount of Pb^{2+} adsorbed onto po-MWCNTs increased with the time of plasma oxidation treatment. The MWCNTs oxidized for 30 minutes have the best adsorbability. The adsorption kinetic study showed the po-MWCNTs have higher adsorption capacity and faster adsorption efficiency towards Pb^{2+} compared with raw-MWCNTS. The equilibrium was reached within 90 minutes for raw-MWCNTs compared to only 40 minutes for po-MWCNTs. The maximum adsorption capacity (q_m) of Pb^{2+} increases with temperature for both raw-MWCNTs and po-MWCNTS. The q_m of Pb^{2+} for po-MWCNTs is much higher than for raw-MWCNT (Yu et al., 2011).

2.3.3 SWCNTs for Divalent Ions Removal

Studies on the adsorption of heavy metals with SWCNTs are still very limited in the literature. Lu and Chiu studied the adsorption characteristic of Zn^{2+} from water using purified SWCNTs, MWCNTs and powdered activated carbon (PAC). They studied the effect of contact time and solution pH on the adsorption of Zn^{2+} onto this three different adsorbent materials (Lu & Chiu, 2006). Moradi et al., studied on the interaction of some heavy metals including Pb(II), Cd(II) and Cu(II) ions from aqueous solution with raw SWCNTs. Carboxylate groups functionlized SWCNTs (SWCNT-COOH) was investigated by Moradi and co-workers (Moradi et al., 2011).

Several researchers was reported on the adsorption capacities, mechanism and process parameters such as solution pH, adsorbent dosage and contact time of some metals onto SWCNTs. The maximum sorption capacities of Zn^{2+} on purified SWCNTs, purified MWCNTs and PAC are 43.66, 32.68 and 13.04 $mg.g^{-1}$, respectively. As reported, the adsorption capacities of Zn^{2+} onto purified SWCNTs are higher than those onto purified MWCNTs followed by PAC (Lu & Chiu, 2006). The maximum sorption capacity (q_m) for Pb(II), Cu(II) and Cd(II) ions onto SWCNT-COOH were obtained as 96.02, 77.00 and 55.89 $mg.g^{-1}$, respectively. They reported that the SWCNT-COOH surface adsorb all tested metals more effectively than a raw SWCNT surface (Moradi et al., 2011).

Lu and Chiu reported the adsorption of Zn^{2+} increases with the increase of pH range of 1 to 8 and reaches a maximum in the pH range of 8 to 11 (Lu & Chiu, 2006). As reported by Moradi et al., the optimum solution pH for heavy metals (including Pb^{2+}, Cd^{2+} and Cu^{2+}) was reached for both SWCNT and SWCNT-OOH at pH 5 (Moradi et al., 2011). The contact times to reach equilibrium for Zn^{2+} ion was 60 minutes for purified SWCNT and MWCNTs and 120 minutes for PAC (Lu & Chiu, 2006). Besides, the SWCNT-COOH has short equilibrium time as compared to SWCNT for all examined metals (Pb^{2+}, Cd^{2+}, Cu^{2+}) as obtained by Moradi et al. The equilibrium contact time for all metals for SWCNT-COOH occurs at 120 minutes (Moradi et al., 2011).

2.4 Removal of mercury ion using carbon based materials.

2.4.1 Activated Carbon for Mercury Ion Removal

Khalkhali and Omidrary reported the adsorption of mercuric ion from aqueous solution using activated carbon. The adsorption of mercuric ion by impregnated activated carbon (AC) with different chemicals such as permanganate ($KMnO_4$), dichromate ($K_2Cr_2O_7$), EDTA and dithizone, methylene blue, and Na_2S were investigated. The AC impregnated with methylene blue and dithizone that have sulphur atom in their structure leads to improvement in adsorption of mercuric ions (Khalkhali & Omidvari, 2005). Zhu and colloquies modified activated carbon (AC) by combined treatment of nitric acid and thionyl chloride, followed by the reaction with ethylenediamine, to introduce N^-, S^-, and Cl^- containing functional groups for enhancing mercury removal from the aqueous solution. Characterization indicated that additions of the organic-inorganic ligands onto AC surface by nitric acid, thionyl chloride and ethylenediamine treatment were effective. Potentiometric titration showed that the modification introduced more negative surface charges favoring cation sorption (Zhu et al., 2009). The study on the adsorption of mercury (II) from liquid solutions using modified activated carbons has also been reported. Two sulphurization treatments by impregnation with sulphuric acid (AC-H_2SO_4) and with carbon disulphide (AC-CS) have been carried out to improve the adsorption capacity for mercury entrapment. The impregnation treatment with carbon disulphite exhibited the highest sulphur content on the activated carbon surface than with sulphuric acid (Silva et al., 2010).

Khalkhali and Omidvari found that adsorption of mercuric ion with AC impregnated with EDTA (11.6 $mg.g^{-1}$) was lower than AC impregnated with methylene blue (24.8 $mg.g^{-1}$) and dithizone (22.5 $mg.g^{-1}$). This can be due to the high solubility and stability of Hg-$EDTA^{2-}$ complex in water. The AC treatment by chemical oxidant such as $KMnO_4$ exhibited the highest adsorption of mercury ion of 25 mg/g. Among the chemicals investigated, Na_2S and EDTA showed poor adsorption by AC. This can be due to their high solubility in water (Khalkhali & Omidvari, 2005). The sorption isotherm were best described by the Freundlich model, and enhanced Hg sorption by modified activated carbon (MAC) was primarily accomplished by the coordination of ligand atoms (O, N and S) with Hg ions through the mechanisms of surface complexation, reduction and ion exchange (Zhu et al., 2009).

Kinetic and isotherms studies demonstrated that the Hg sorption by modified activated carbon (MAC) was faster (30 min) and higher (200%) than by AC, suggesting a high affinity of MAC for Hg ions. (Zhu et al., 2009). The sorption by modified activated carbon (MAC) occurred in a wider pH range (4 -10 vs 5-7), and low ionic strength appeared to enhanced Hg sorption. (Zhu et al., 2009). Silva and co-workers reported the highest adsorption of mercury corresponds to the AC-H_2SO_4 adsorbent at solution pH 3 and the lowest one on the AC solid. (Silva et al., 2010).

2.4.2 MWCNTs for Mercury Ion Removal

A number of studies have reported the use of carbon nanotubes sorbents for adsorption of Hg (II) from the aqueous solution. For example, the removal of Hg(II) ions from contaminated water using MWCNTs was investigated by Tawabini et al. The study showed that the Hg uptake by MWCNTs increased to 100% with an increase in pH from pH 4 to 8. The results also showed that higher dosage of MWCNTs, showed higher removal of Hg^{2+} (Tawabini et al. 2010). El. Sheikh and co-workers have recently reported the study on the use of oxidized and non-oxidized MWCNTs of difference geometrical dimensions for Hg (II) adsorption and preconcentration in water sample. Surface oxidation of L-MWCNT-4060 (nitric acid oxidized MWCNTs of external diameter 40 – 60 nm and length 5- 15µm) by nitric acid produced an efficient adsorbent for Hg (II) extraction from natural waters (El-Sheikh et al., 2011). The removal percentage of mercury increases to a maximum by increasing the pH of initial solution and then it decrease. The optimum pH for mercury removal by MWCNTs was near the neutral pH of 6.5 to 7.5 (Shahbad et al., 2010).

Tawabini and co-workers reported that MWCNTs slurry was very efficient in removing as high as 1.0 mg/L of Hg^{2+} from aqueous solutions via the adsorption mechanism. The experimental results also showed that mercury adsorption by MWCNTs follow a pseudo second-order reaction with a rate (k) of 0.018 and it is well described by the Langmuir isotherm model with maximum adsorptive capacity, q_m of 13.16 (Tawabini et al. 2010). They were found that, the adsorption of mercury onto MWCNTs increases with increase in temperature. The q_m was $93.45 mg.g^{-1}$ at 310K (Shahbad et al., 2010). This material exhibited the highest enrichment efficiency for a preconcentration of 100 $\mu g.L^{-1}$ Hg (II) at pH 7 (El-Sheikh et al., 2011).