CHAPTER 3

METHODOLOGY

3.0 Methodology

In this study MWCNTs were purified and then functionalized using two different methods. The functionalized MWCNTs with the best properties were tested in the removal of mercury ion from aqueous solution. The sorption capacity of the mercury ion onto pristine and functionalized MWCNTs were investigated using two models, which are Langmuir and Freundlich Isotherms.

3.1 Materials

3.1.1 List of Chemicals

The chemicals and equipment used for the functionalization of MWCNTs and performance testing of functionalized MWCNTs are shown in Table 3.1 and Table 3.2, respectively.

Table 3.1: Chemicals used for functionalization of MWCNTs and performance testing of functionalized MWCNTs.

No.	Chemical Name	Brand	Purity (%)
1	Nitric Acid (HNO_3)	Merck	65
2	Sulfuric Acid (H_2SO_4)	Merck	95-97
3	Sulfuric Acid Fuming 65 % SO_3 (H_2SO_4 *SO_3)	Merck	-
4	Argon Gas	Mox	99
5	Sodium Hydroxide (NaOH)	Merck	-
6	Potassium Chloride (KCl)	R&M	99
7	Mercury (II) Nitrate Monohydrate ($Hg(NO_2)_3$	Merck	99
8	Mercury ICP Standard	Merck	99
9	Silicon Oil	Merck	-

Table 3.2: Equipment used for functionalization of MWCNTs and performance testing of functionalized MWCNTs.

No.	Equipment	Brand
1	Universal Temperature Programmed (UTP)	Custom made (Fritz Haber Institute, Germany)
2	Shaker Heating Bath	Grant, Fisher Scientific (OLS200)

3.1.2 Multiwalled Carbon Nanotubes (MWCNTs)

MWCNTs prepared by Catalytic Chemical Vapor Deposition (CCVD) process were supplied by Bayer MaterialScience AG, Germany. The MWCNTs have >95% purity and the diameter of tubes averages 13 – 16 nm with outer mean diameter about 13 nm, inner mean diameter about 4nm and length of > 1µm according to the supplier.

3.2 Purification of MWCNTs

The pristine MWCNTs were treated in concentrated nitric acid to remove metal catalysts, metal supports and amorphous carbon produced during the synthesis process. 10 g of prestine MWCNTs was refluxed in 500 mL nitric acid at 100 ^{o}C for 2 hours. After refluxing, the solution mixture was cooled at room temperature for 1 hour. This solution mixture was then diluted with deionised water (DI) and filtered through a Buchner funnel. The residue from the Buchner funnel was washed thoroughly with DI water and dried in an oven at 100 ^{o}C overnight. Then the purified MWCNTs were subjected to two different functionalization processes that are liquid and gas phase oxidation treatment.

3.3 Modification of MWCNTs

Functionalization process was carried out using two different methods. The first method was a gas phase treatment in a Universal Temperature Program (UTP) reactor (Figure 3.1 and Figure 3.2) by flowing SO_3 gas onto the MWCNTs while being heated to different temperatures (100, 200, 300 ^{o}C) for 2 hours, see Table 3.3. The gas phase reaction was carried out in a horizontal quartz tube reactor heated by a UTP reactor. A weighed sample of MWCNTs (approximately 3g) was placed in the horizontal quartz tube reactor fitted with gas inlet and the outlet was connected to trapping system. A multi-necked flask containing 20% SO_3 in concentrated H_2SO_4 fitted with gas inlet/outlet tubes was connected to the reactor tube. Argon stream was used to carry SO_3 vapor into the quartz tubes.

The second method is liquid phase treatment (Figure 3.3) which includes refluxing approximately 3g of MWCNTs in H_2SO_4 for 2 hours at different temperatures (100, 200, 300 ^{o}C) (F. After refluxing, the mixture was cooled to room temperature, diluted with DI water and filtered through a Buchner funnel filtration system. The product was washed thoroughly with DI water and dried in an oven at 100^{o}C overnight. The flow chart for liquid phase treatment is shown in Figure 3.4.

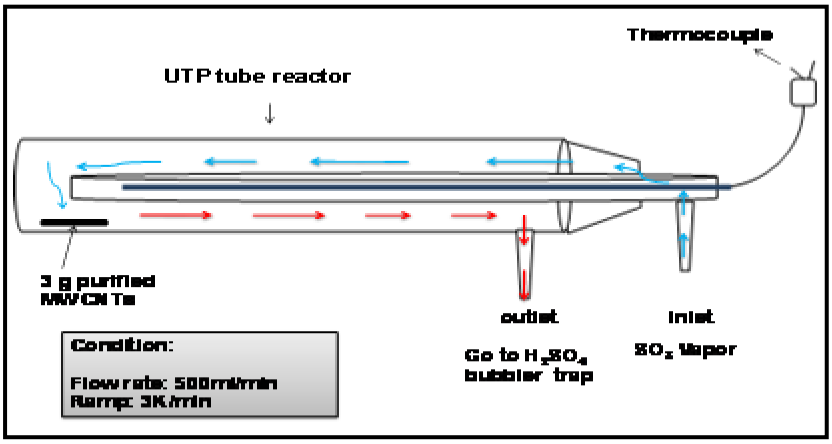


Figure 3.1: Schematic diagram of gas phase treatment using UTP reactor.

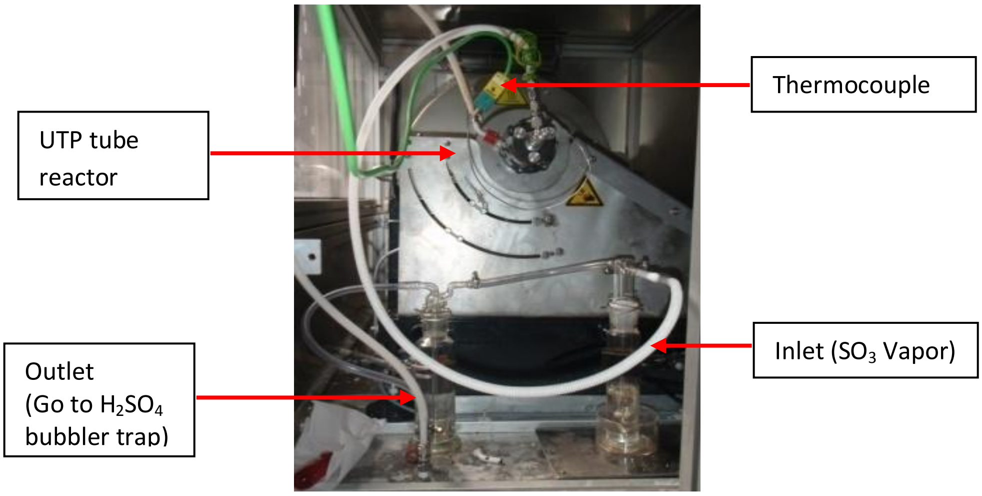


Figure 3.2: Gas phase treatment using UTP reactor.

Figure 3.3: The diagram of refluxing purified MWCNTs.

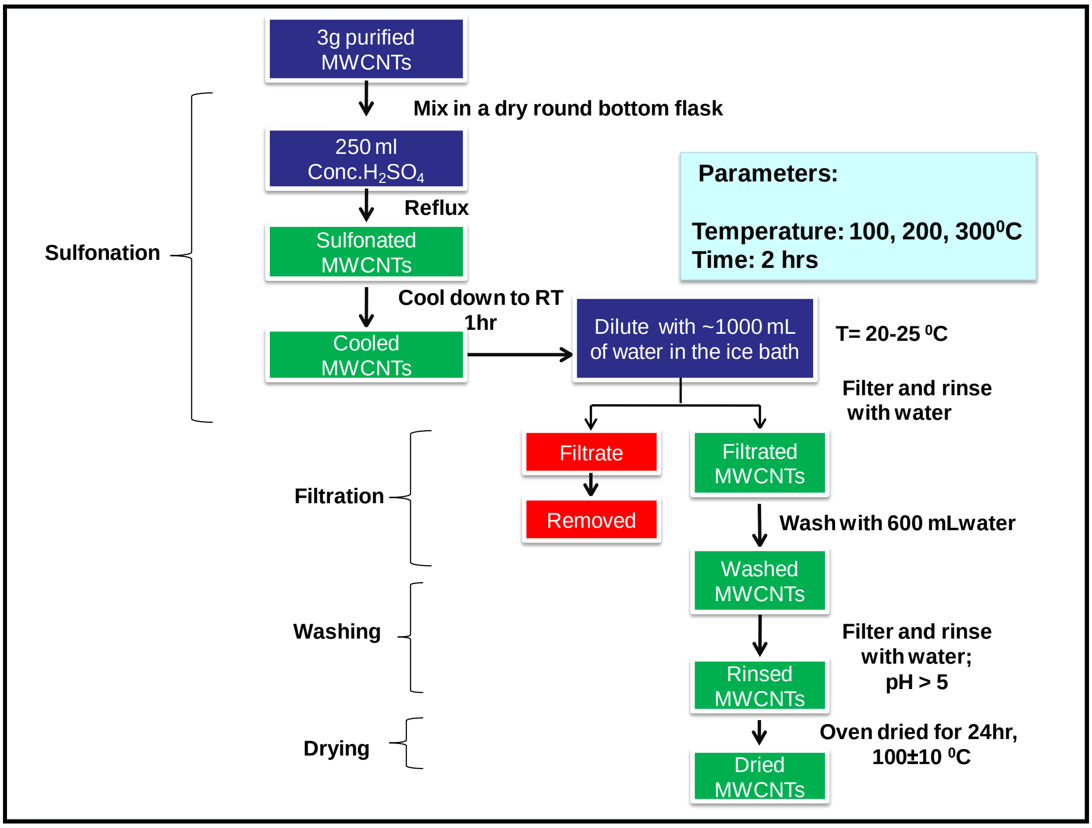


Figure 3.4: The flow chart of liquid phase treatment.

Table 3.3: Parameters for functionalization process.

Samples	**Parameters**		**Treatment**		
	Temperatures (^oC)	Time (h)	Purification	Gas Phase	Liquid Phase
B6	100	2	Pretreatment in conc.HNO_3	Gas sulfonation [SO_3/H_2SO_4]	
B7	200				
B8	300				
B9	100				Refluxing in conc.H_2SO_4
B10	200				
B11	300				

3.4 Characterization of The Modified MWCNTs

3.4.1 Surface Acidic Determination

The amounts of acidic sites in functionalized MWCNTs were determined by direct titration with 0.01 M of NaOH solution. A weighed amount of treated MWCNTs (0.1 g) was transferred into 100 mL Erlenmeyer flask. 50 mL of the 10^{-3} M KCl (conducting salt) solution was added into the flask. The flask was shaken at 400 rpm for 24 hrs under vigorous magnetic stirring to ensure equilibrium was reached. KCl solution acted as electrolyte so that the acidic site in functionalized MWCNTs will be dissociated in the solution. The solution was then directly titrated with 0.01 M NaOH solution. The titration was carried out using a Mettler DL25 Autotitrator. This equipment is equipped with titrator DL25, automatic burette (20 mL), and stirrer. It was connected to a computer, which controlled the equilibrium condition and titrant delivery. The dynamic dosing of the titrant in increments of 0.1 mL to the suspension samples and the pH of the solution was measured every 10 second. Using acid-base titration, the number of surface acidic functional groups was determined using the assumption that base neutralizes acidic functional groups. Direct titration with sodium hydroxide (NaOH) having pKa value of 15.74 is a simple technique to quantify the acidic groups present on treated CNT samples.

Titration was done for the purpose of determining the concentrations of the acid solution by measuring the volume of strong base solution consumed for titration. In this analysis, NaOH solution was added into the samples until the equivalent point was reached. At this point, enough NaOH has been added to react with all acid present in the samples.

3.4.2 Elemental and Structural Characterization

Thermogravimetric Mass Spectrometer (TG-MS) was used to study the thermal stability of the oxygen and sulfur containing functional groups anchored on MWCNTs. The analysis was carried out with a Netzsch STA 449 equipped with a mass spectrometer detector (Pfeiffer Omnistar, Avi applied vacuum GmbH). The thermal gravimetric analyzer (TGA) experiments were performed in purified Argon (99% purity) at a temperature range from 30 to 1000 ^{o}C using a ramp rate of 5 ^{o}C.min^{-1}.

The surface functional group of sulfonated MWCNTs was determined using a Fourier Transforms Infrared Spectroscopy (FT-IR). The IR spectra of the functionalized samples were recorded using a Perkim Elmer Spectrum 100 series. The machine is equipped with Universal ATR sampler accessories. The scanning range of the experiment was 600 – 2500 cm^{-1} and during the test, the number of scanning with the air as background was kept the same.

The structure of the functionalized MWCNTs was determined using Powder X-ray Diffraction (PXRD) method. The XRD were measured with a Bruker D8 diffractometer (EVA software version 2002) equipped with a focusing primary Ge monochromator and a scintillation detector (SD), using Cu Kα (1.5405 nm) radiation.

The Raman spectrograph used in this study was HORIBA Jobin Yvon spectrometer and the light source used was 632.8 nm with 10x objective. Raman spectroscopy has proved to be an exceedingly powerful tool useful in the study of the vibrational properties and electronic structures of CNTs. Raman spectroscopy has been successfully applied for studying the order of carbon atoms. The large van der Waals interactions between the CNTs lead to an agglomeration of the tubes in the form of bundles or ropes. This problem can be solved by functionalizing the MWCNTs by attaching appropriate chemical moieties to the sidewall of the tubes. Functionalization causes a local change in the hybridization from sp^2 to sp^3 of the sidewalls carbon atoms, and Raman spectroscopy can be used to determine this change.

3.4.3 Texture and Porosity Determination

Textural properties such as surface area, porosity and pore size distribution of MWCNTs was measured by N_2 adsorption-desorption isotherm using Quantachrome Autosorb- 6B KR sorptometer. Measurements were performed on 40mg samples. The total surface area was calculated using the Brunauer, Emmett and Teller (BET) equation. The surface area and porosity of the functionalized samples are important parameters for various applications, for example as trapping material. As such, it is necessary to specify the nature of the pore structure since this may control the transport and exchange of adsorbate and adsorbent of a trapping process.

The DFT provides a method to determine both microporosity and mesoporosity of materials. In fact, there are six physical adsorption isotherm types recommended by International Union of Pure and Applied Chemistry (IUPAC) (Kaalfaoui et al., 2003). The most common are types I (Langmuir type isotherm for microporous solid), II (for nonporous solid where only multilayer adsorption can take place), III (porous solid materials with mixed micro and mesoporosity), IV (for mesoporous solid in which capillary condensation takes place at higher pressures of adsorbate in addition to multilayer adsorption at lower pressure), V (is uncommon, is related to the type III isotherm), and VI (represents multilayer adsorption on a uniform non-porous surface) (Schneider, 1995).

3.4.4 Morphology

The graphitic character of the carbon sample was investigated by high resolution transmission electros microscopy (HRTEM). The investigation was conducted in a Zeiss 4BRA 200FE at an accelerating voltage of 200kV. The sample specimens were prepared by suspension of the modified MWCNTs powder in ethanol. Drops of the suspension were deposited on carbon-enhanced C grids and dried in air.

The microstructure and the structural defects of MWCNTs were investigated using Scanning Electron Microscopy (SEM) and Raman Spectroscopy, respectively. The SEM images were taken using FEI Quanta 200F FESEM at accelerating voltage of 20kV. It was equipped with Energy Dispersive X-ray (EDX) with INCA energy of 400kV.

3.5 Adsorption Isotherm Studies

3.5.1 Preparation of Mercury Stock Solution

The mercury (II) stock solution of 1000 mgL^{-1} was prepared by adding 0.855g of $Hg(NO_3)_2$ salt into 500 mL volumetric flask. This stock solution was diluted as required to obtain the series of mercury (II) standard solution. The calculations involved is shown showed below:

Molecular weight (MW) $Hg(NO_3)$ salt => 342.62 $g.mol^{-1}$

Molecular weight Hg^{2+} ion => 200.59 $g.mol^{-1}$

Thus,

$$1000ppm\ Hg^{2+} \Rightarrow \frac{342.62\ g.mol^{-1}}{200.59\ g.mol^{-1}}$$

=> 1.71 g $Hg(NO_3)$ salt in 1000 ml DI water

Or

1.71 g => 1000 ml

x g => in 500 ml

x g => 500/1000 X 1.71 g

x g => 0.855 g in 500 ml DI water

3.5.2 Preparation of Mercury Aqueous Solution Series

In preparation of Mercury aqueous solution, a 1000 $mg.L^{-1}$ stock solution of Hg^{2+} ion was prepared. The stock solution was diluted to the required initial concentration as shown in Table 3.4. The pH of the solution series was adjusted by using 0.01 M of HNO_3 or 1.0 M and 0.01 M of NaOH.

An example of mathematical calculations for the series of mercury standard solutions is shown below:

Standard : 50 mg.L^{-1}

$$M_1V_1=M_2V_2$$

$$V_1= \frac{M_2V_2}{M_1}$$

$$V_1= \frac{(50)(100)}{1000}$$

$$V_1= 5 \text{ mL}$$

Table 3.4: Series of mercury aqueous solution.

Stock Solution (mg.L^{-1})	1000								
Series of std solution(mg.L^{-1})	20	50	100	200	300	400	500	600	At pH 6, 25^{o}C, 6 hours
Volume stock solution required (mL)	2	5	10	20	30	40	50	60	
Dilute to Volume (mL)		100							
Volume required for test (mL)		100							

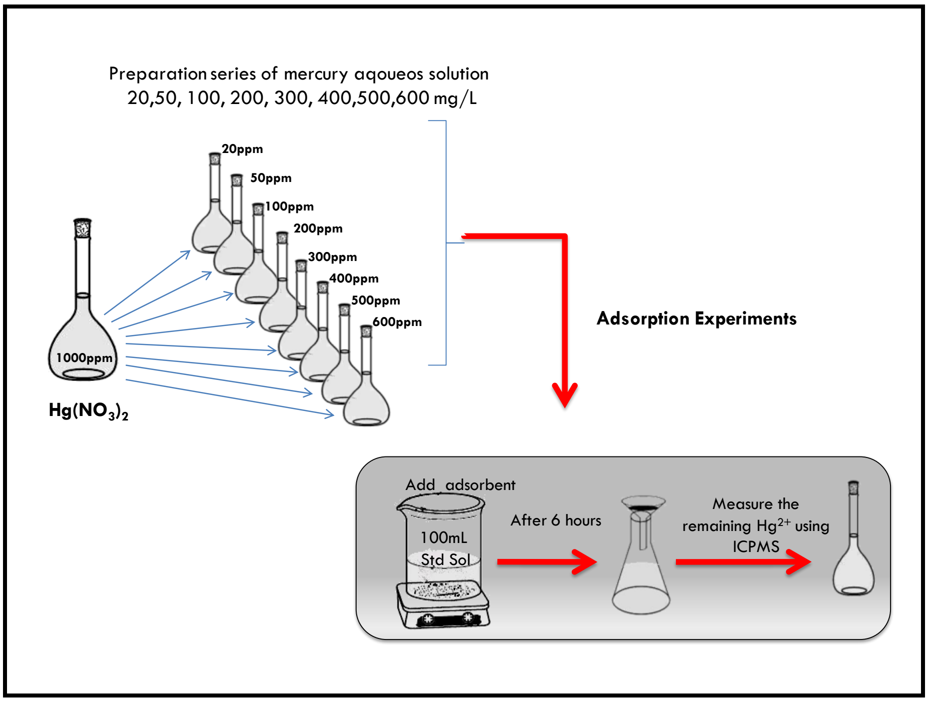


Figure 3.5: Diagram of adsorption experiment.

3.5.3 Equilibrium Adsorption Experiment

The equilibrium study was performed using 250 mL conical flask with addition of 0.3g of modified CNTs and 100 mL of Hg^{2+} solution of increased initial concentrations (C_o) from 20 to 600 mg.L^{-1} (Figure 3.5). The conical flasks were covered and then were placed inside the shaker heating bath. The shaker was operated at 25 ^{o}C and 180 rpm for 6h. The pH of the solution was maintained at 6.0 with the exception of pH effect study. The pH was adjusted using 0.01 M HNO_3, 1 M NaOH and 0.01 M NaOH. At the end of agitation, the suspensions were filtered and the filtrate was analyzed for the remaining Hg^{2+} concentration by Inductive Coupled Plasma Mass Spectroscopy (ICPMS).

3.5.4 ICPMS Measurement

All samples after adsorption process were tested using Agilent 7500 Series simultaneously inductively coupled plasma mass spectrometer (ICP-MS) and equipped with radial torch and nitrogen purge (Figure 3.6). Samples were decomposed to neutral elements in high temperature argon plasma and analyzed based on their mass to charge ratios. An ICPMS can be thought of as four main process, including sample introduction and aerosol generation, ionization by an argon plasma source, mass discrimination, and detection systems. Instrument detection limits are at or below the single par per trillion (ppt) metals ions.

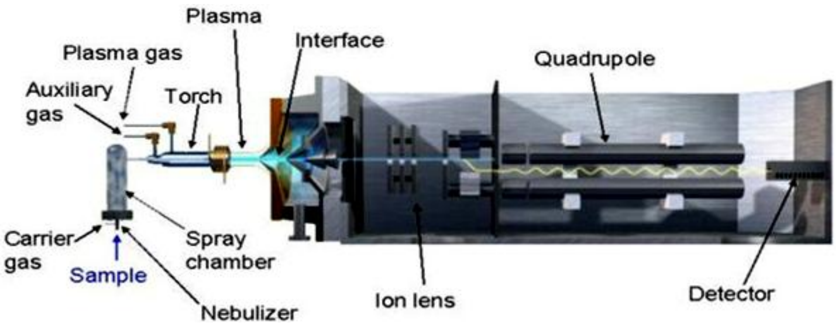
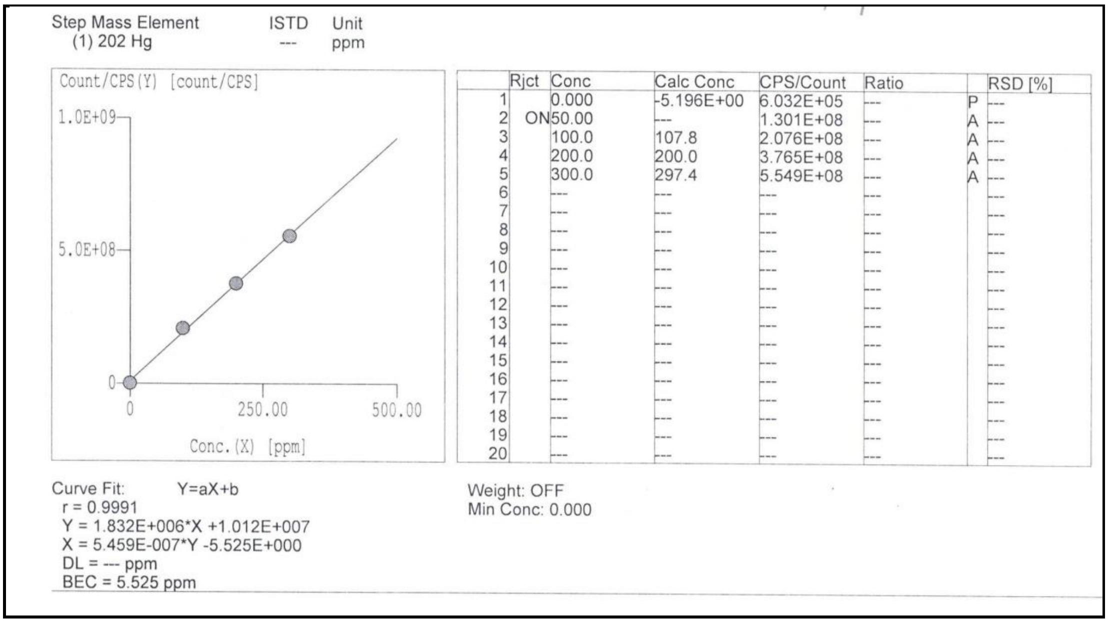


Figure 3.6: Schematic diagram of ICPMS instruments.

3.5.4.1 Standard Calibration

The mercury standard calibration curve was obtained by preparing series of mercury standard concentration of 0, 50, 100, 200 and 300 mg/L. Then, these mercury standards were measured using ICPMS and the plot of count per second (CPS) versus concentration (ppb) of standard solution was obtained. The concentration of mercury element was determined by comparing the counts measured for mercury isotope to an external calibration curve that was generated for mercury element. This plot gave a straight line with the correlation coefficient of 0.9990. This means that the standard and sample elemental concentrations give an instrumental response that is described by the equation for a straight line. Example calibration curve of mercury standard solution for ICPMS measurement is shown in Figure 3.7



Step Mass Element	ISTD	Unit
(1) 202 Hg	---	ppm

	Rjct	Conc	Calc Conc	CPS/Count	Ratio		RSD [%]
1		0.000	-5.196E+00	6.032E+05	---	P	---
2	ON	50.00	---	1.301E+08	---	A	---
3		100.0	107.8	2.076E+08	---	A	---
4		200.0	200.0	3.765E+08	---	A	---
5		300.0	297.4	5.549E+08	---	A	---
6		---	---	---	---		---
7		---	---	---	---		---
8		---	---	---	---		---
9		---	---	---	---		---
10		---	---	---	---		---
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16		---	---	---	---		---
17		---	---	---	---		---
18		---	---	---	---		---
19		---	---	---	---		---
20		---	---	---	---		---

Curve Fit: Y=aX+b
r = 0.9991
Y = 1.832E+006*X +1.012E+007
X = 5.459E-007*Y -5.525E+000
DL = --- ppm
BEC = 5.525 ppm

Weight: OFF
Min Conc: 0.000

Figure 3.7: Standard calibration for ICPMS.

3.5.5 Analysis of Data

The Hg^{2+} concentration in aqueous solution were measured before and after adsorption (C_o and C_e respectively). Dry weight of adsorbent (W) and the volume of aqueous solution (V in liter), the amount of equilibrium adsorption of Hg^{2+} (Q_e) are calculated using Eq. (1);

$$Q_e = \frac{(C_o - C_e)\, V}{W} \qquad (1)$$

Where Q_e is the amount of Hg^{2+} adsorbed by modified CNTs (mg/mg^{-1}); C_o is the initial Hg^{2+} concentration (mg/L) ; C_e is the final Hg^{2+} concentration after certain period of time or the equilibrium concentration (mg/L); V is the initial volume (L) and W is the modified CNTs dosage (g).

3.5.5.1 Langmuir Isotherm

The theoretical Langmuir isotherm is often used to describe sorption of solute from a liquid solution as:

$$Q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \qquad (2)$$

The constant q_m and K_a are the characteristic of the Langmuir equation and can be determine from the linearised form as in Eq. (3) represented by:

$$\frac{C_e}{Q_e} = \frac{1}{q_m K_a} + \frac{C_e}{q_m} \qquad (3)$$

Where C_e is the equilibrium Hg^{2+} ion concentration (mg/L), Q_e is the amount of Hg^{2+} absorbed at equilibrium(mg/g) and q_m is Q_e for complete monolayer (mg/g) and K_a is sorption constant equilibrium constant (L/mg).

The favourable equilibrium adsorption region obtained from Langmuir isotherm can be expressed by;

$$R_L = \frac{1}{1 + K_a C_o} \qquad (4)$$

where C_o is the initial metal ion concentration (mg/L) and Ka is the Langmuir constat (L/mg). Hall et al., reported using mathematical calculation that the parameter R_L indicates the type of the isotherm as follows (Hall et al., 1996);

R_L value	**Type of Isotherms**
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

3.5.5.2 Freundlich Isotherm

The Freundlich isotherm is the earliest known relationship describing the sorption equation and is expressed by the following equation:

$$Q_e = K_F\, C_e^{\,1/n} \qquad (5)$$

and the equation may be linearised by taking logarithms

$$\log(Q_e) = \frac{1}{n}\log(C_e) + \log(K_F) \qquad (6)$$

where K_F and 1/n are empirical constants dependent on several environment factor.

3.6 Scope of Study

Work programme of the study is shown in Figure 3.8. This research studies was generally divided into four phases which are Phase I, II, III and IV. Phase I is the functionalization of MWCNTs using gas and liquid phase treatment. Phase II and III involving the characterization and performance testing of functionalized MWCNTs. Phase IV is the data evaluation of the potential materials

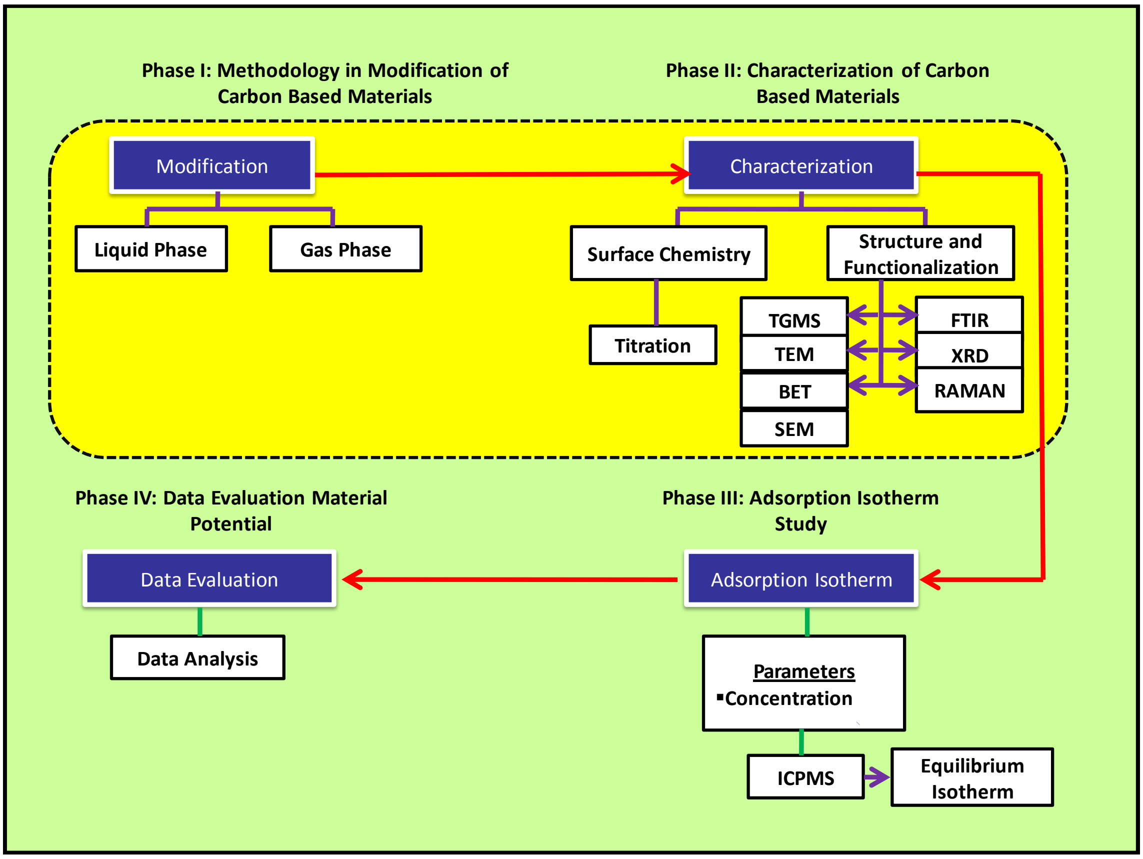

Figure 3.8: Flow chart of work program