# Synthesis of Carbon Nanotubes (CNTs) from Poultry Litter for Treatment of Heavy Metals


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# CERTIFICATE

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# DECLARATION

I hereby declare that this research work titled as **"Synthesis of Carbon Nanotubes (CNTs) from Poultry Litter for Treatment of Heavy Metals"** is the outcome of my own efforts and has not been published anywhere else before. The material quoted in the text has been properly referred and acknowledged.

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# DEDICATION

***Dedicated to my respected, loveable and humble parents who would always be a source of inspiration for me***

# ACKNOWLEDGEMENTS

**In the name of Allah, the Most Gracious and the Most Merciful**

Foremost, I would like to express my sincere gratitude to my supervisor **Prof. Dr. Muhammad Anwar. Baig (**IESE, SCEE, NUST) for his constant supervision, guidance and useful suggestion. Special thanks to my thesis committee members, **Dr. Yousuf Jamal** (Assistant Professor IESE, SCEE NUST), and **Dr. Iftikhar Hussain Gul** (Associate Professor SCME, NUST) for all their help and beneficial advice on this research work. I am also grateful to the lab staff of IESE, SCME, and USP-CASEN for being accommodative to all my queries and providing support and help during my research work. I would also like to thanks my friend **Mr. Muhammad Shabir** for their kindness, well wishes and constant prayer

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**Noor Haleem**

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# ABSTRACT

Poultry litter is one type of agricultural waste being generated in our country as a result of raising more than 146 million commercial and domestic poultry birds. This waste find its final disposal in the field as soil fertilizer or amendment. However, the uncontrolled use of poultry litter for this purpose can result in environmental impacts such as the emission of methane, a greenhouse gas. Various other options like thermochemical conversion of this waste can be a solution to this problem. Poultry litter can be a low-cost carbon sources for synthesis of Carbon Nanotubes (CNTs). In this study efforts have been mad to utilize the cheap and readily available carbon source for synthesis of CNTs in the presence of Ni/Mo/MgO as a catalyst through combustion technique. Molar ratios of Ni, Mo and MgO as catalytic precursors were optimized using response surface methodology (RSM) to obtain the maximum CNTs yield. The optimum mole ratio of catalyst (4:0.2:1) was found to yield more carbon product. Further, process parameters such as combustion temperature, time, and polymer & catalyst weight were also optimized by RSM using Box–Behnken three-level and four-factorial design. The best possible combination of process parameters noted were (combustion time of 12 min, at a temperature of 825$^{o}$C, and catalyst weight of 100 mg) in order to gain yield of CNTs (44.21%). Structure and morphology was confirmed through X-ray Diffractometer (X-RD) & Scanning Electron Microscopy (SEM). The environmental application of these carbon nanotubes was tested in lab with synthetic chromium solution. Different experimental conditions (pH, dosage of adsorbent and the contact time) that enhances the adsorption of Cr (VI) by carbon nanotubes were studied. UV-Visible spectrophotometer was used to measure the absorbance of Cr (VI) at 540 nm. It was found that 81.83% of Cr (VI) removal is achieved by using 8 mg of CNTs at pH 3 with 400 rpm, and 180 min of contact time. This makes CNTs from poultry waste as potential adsorbent for heavy metals.

# 1 CHAPTER INTRODUCTION

## 1.1 Poultry Industry

Poultry production is one of the vibrant segments of livestock sector in the world. In 2015 the global poultry production was 111 million metric tons and an increase in production is predictable by 24% (137.64 million metric tons in 2025). Poultry meat production will be leading more than half of the growth of all the supplementary meat produced by 2025. Asia is the top regional exporter of prepared chicken products, delivery more than 800,000 tons in 2014, while Europe is the main buyer, purchasing more than one million tons in that year (Dalolio et al., 2017).

Poultry meat and eggs are cheaper source of protein diet. In Pakistan poultry industry is making a wonderful influence in bridging the existing animal proteins source for the masses and as such is an efficient check upon the spiraling animal protein prices. We as a nation are already using less quantity of protein as compared to other nations. Around 29% of meat demand is done by poultry meat and thus it helps in normalizing mutton and beef demand. Poultry business, being a source of livelihood across the country attained second position in rural businesses and thus became backbone of rural economy. Contribution of poultry business in 2013-14 is 1.27% towards total GDP. Its influence in agriculture and cattle farming business worth was recorded as 6.2% and 10.7%respectively (Hussain et al., 2015).

### 1.1.1 Poultry Litter

Litter is waste material that consists of chicken urine and feces. Poultry manure along with wasted out chicken feed, chicken feathers and other materials over floor like wheat husk, saw dust or wood shavings contributed as poultry litter. This is basically organic manure consists of major elements required by plants (Nitrogen, Phosphorus and Potassium) along with trace elements like Zinc, Copper, Arsenic etc. Factors like diet, types of poultry feeds, feed components, storage of feed as well as litter storage techniques effects quality and composition of poultry litter (Ali et al., 2014).

### 1.1.2 Composition of poultry litter

Composition of organic matter of poultry litter is shown in Table 1.1. Microbial activity continuously converted the available forms of nitrogen through temperature change, as well as changes in moisture conditions, Oxygen and pH level. Organic matter concentration and composition is directly affected by litter production and its management in the farm. Burned litter reveled that ashes contain large amount of elements like P, Ca and K. Table 1.1 indicates additional details about poultry manure which serves as interesting fuel as compared to wood. Poultry litter has more concentration of Potasium oxide ($K_2O$) and Sodium oxide ($Na_2O$) as compared to wood. Wood has 0.4 while poultry litter ash contain 9.2 lb alkali/MBtu (Bock, B. R. 2002).

Table 1.1: Ultimate analysis of poultry litter

| Parameters | Percentage (%) |
|---|---|
| **Carbon** | 27.2 |
| Hydrogen | 3.7 |
| Oxygen (by difference) | 23.1 |
| Nitrogen | 2.8 |
| Sulfur | 0.3 |
| Chlorine | 0.7 |
| Ash | 15.7 |
| Moisture | 29.4 |
| Higher heating value (HHV) | 4,637Btu/lb |

(Lynch et al., 2013)

## 1.2 Carbon Nanotubes (CNTs)

Nanomaterials are progressively used for diverse modern technologies and among them are prominent CNTs. These are made of graphene sheets of hexagonal structure rolled up into a nanoscale tube. They varies in their lengths up to a million times as compared to their diameter which down up to is 0.4 nm (Mamalis et al., 2004). CNTs synthesis and its utilization have been studied across the world in the past couple of years with extraordinary attention. Now a day, CNTs and their use in different areas have been discussed widely in scientific circles. Due to exceptional structural and its physical, electrical and mechanical properties. CNTs have exceptional properties in terms of physical, electrical and mechanical aspects and thus encouraged for new technologies some years ago. Other factors that make it different from other materials are their density (nearly half the density of aluminum) crisp stiffness and big surface area (Zhu et al., 2018).

### 1.2.1 Types of carbon nanotubes

i. Single Wall Nanotubes

Structure of Single-walled carbon nanotubes (SWCNTs) is like hollow long cylinders, in a honeycomb like settings. They are one of the best nanomaterials with excellent thermal, mechanical, and electrical properties, used widely for academic and scientific research.

ii. Multiwall nanotubes

Multiwall nanotubes (MWNTs) consist of numerous rolled layers of graphene. MWCNTs are made up of pure carbon polymers which can be used by manipulating their chemistry. The solubility and diffusion of particles changes thus application in materials electronics, chemical processing and energy management becomes easy.

### 1.2.2 Catalyst for growth of CNTs

Transition metals reinforced on silica, mesoporous silica, calcium carbonate, zeolites or magnesium oxide is used as catalysts for the growth of CNTs. A large number of catalysts have been studied by improving and changing the structure and properties of CNTs to increase their yield. Various catalysts i.e Ni, Co, Mo and Fe have been used for growth of CNTs. Supported metal catalysts has been formed by using impregnation method. Keeping in view all parameters related to chemistry of metal is important while performing impregnation method for manufacturing of supported metal catalyst. It has been observed that homogenousity and stability of CNT-Ni is better than other CNTs grown with other catalysts (Palacio et al., 2014).

## 1.3 Synthesis of Carbon Nanotubes

The hydrocarbon sources used for the growth of CNTs include mainly ethylene, methane and acetylene. While the liquid hydrocarbons like benzene, xylene, cyclohexane and alcohol also been used as CNTs precursors. Carbon nanotubes can also be generated from solid waste like rice straw and propylene bottles (Saito et al., 2002). In this study we have used poultry litter as a source of hydrocarbon for synthesis of CNTs. Global synthesis attempts to produce CNTs in a high temperature environment. Methods for synthesis of CNTs such as Chemical Vapor Deposition (CVD),Arc Discharge, Laser Ablation and Combustion are used globally (Chrzanowska et al 2015).

## 1.4 Applications of Carbon Nanotubes

In order to take full advantage, CNTs have lots of varied application (Volder et al., 2013)

i. High electrical conductivity
ii. Very high tensile strength
iii. Highly flexible
iv. Very elastic
v. High thermal conductivity
vi. Low thermal expansion coefficient
vii. Good electron field emitters
viii. CNTs are good adsorbent for heavy metal removal from wastewater

## 1.5 Carbon Nanotubes as Adsorbent

Water pollution as a result of heavy metals disposal is at alarming rate worldwide. These toxic metals are mostly generated from activities like tannery, battery and chemical manufacturing, mining etc. Removal of toxic metals, especially chromium from earthly bodies is a matter of serious concern for scientists and authorities (Farabegoli et al., 2004).Removal of impurities (both organic and inorganic) through different technologies from water bodies has already established since years. Examples of such methods include ion exchange (Shaidan et al., 2012), Adsorption (Mittal et al., 2010b), chemical precipitation (Altas and Buyukgung,2008), photocatalytic degradation, membrane filtration (Juang and Shiau, 2000), and electrochemical methods(Gupta et al., 2007a).In situations like this, multiwall carbon nanotubes MWCNT have been also used as adsorbent (Dahbi et al., 2002). CNTs have large specific surface area as well as their reaction activity is higher as compared to other nanoparticles, making them better option for adsorption of heavy metals and organic pollutants (Ren et al., 2011).

### 1.6 Aim of the Study

The aim of this work was based on the hypothesis that poultry litter should be converted to valuable industrial product (CNTs) for the purpose of heavy metal removal from wastewater. The effects on adsorption were studied by changing different parameters like pH, contact time, and CNT's amount to note its efficiency

### 1.7 Objectives of the Study

Main objectives of the study are given as follow

1. Synthesis and characterization of carbon nanotubes (CNTs) from poultry litter.
2. To study its efficiency in removal of heavy metals Cr (vi) from wastewater

# 2 CHAPTER LITERATURE REVIEW

## 2.1 Status of Commercial Poultry

Commercial poultry is providing proteins to Pakistani people since its start in 1960. The promotional policies of the government was appreciated by industries in the beginning but certain issues like outbreaks of diseases, price hike etc remained a challenge for them. In Pakistan poultry sector is one of the vibrant segments of livestock division. According to 2016-17 statistics production of domestic poultry was 85.86 million nos. and commercial poultry was 60.6 million nos. (Iram, 2018).

## 2.2 Poultry Litter Production

Different materials like wood flakes, paper trimmings and rice rind have been used as bedding materials .With the extension of poultry industry, generation of poultry litter has increased extremely (Sistani et al., 2003). According to data, a single bird produces around 1.5 to 5.7 kg of waste in a 42 days cycle (a cycle for a complete flock production), which is quite fluctuating (Leytem et al., 2007). Poultry waste production is 3.72kg/bird. Usually poultry litter used for more than one flock of birds, depending upon number of birds and other factors. This helps in reduction of volume of generated bed (Dalolio et al., 2017). The amount of poultry litter generated in a unit/farm depends upon factors like waste (bedding material), feed taken by chickens, management and digestion rate of feed (Irfanet al.2017).

Table. 2.1. Production of poultry litter according to 2016-17 statistics

| **Poultry Sector** | **No of Birds** (Million) | **Average Litter** (Kg) | **Total Litter Production** (Ton) |
|---|---|---|---|
| **Domestic** | 85.86 | 3.72 | 319,399 |
| **Commercial** | 60.6 | 3.72 | 225,432 |

(Iram, 2018)

## 2.3 Options for the Use of Poultry Litter

The poultry growers facing a big concern worldwide for environmentally safe utilization or disposal of poultry litter (Chaudhry et al., 2013).Literature shows multiple uses of poultry litter i.e. fertilizer, soil amendment, biogas generation, as a adsorbent& other uses.

### 2.3.1 As organic fertilizer

People are using poultry litter as fertilizer for centuries since it has many important nutrients for plant growth. Macro nutrients especially Nitrogen, Phosphorus and Potassium as well as micro nutrients like Copper, Zinc etc are also present in poultry litter (Chen et al.2014). An average nutrient percentage content of N.P.K is 3:3:2. This implies that a ton of poultry litter contains nitrogen, phosphate ($P_2O_5$) and potash ($K_2O$) with a ratio of 60:60:40 pounds. Another factor is physicochemical properties of litter which comprises of parameters like material type from which waste is generated, number of flocks for which material is being used as well as the management practices involved during all process. Best material, to be used as bedding purpose should have properties like good adsorption capacity without being hardened, medium sized, remove moisture easily, less thermal conductivity, highly dense and cost effective (Ghaly et al. 2013).

### 2.3.2 As an effective soil amendment

Cultivation of a same crop for a very long time in same field causes deterioration of soil structure and also lowers soil quality. Soil quality can be improved by adding poultry manure and litter. Soil properties like bulk density, organic matter, aggregate stability and water holding capacity increases with addition of poultry manure. Poultry manure can also be used as a mulch over soil surface to keep it safe from dryness by preserving soil moisture, this in turn also increases soil nutrient capacity (Franzluebbers & Doraiswamy 2007).

### 2.3.3 As fuel

Poultry litter has few important features, working against it direct use as a fuel (Pandey et al., 2016).

i. It has high moisture content.
ii. It is less energy dense than coal, oil and natural gas.
iii. It isn't easy to gravity feed or auger.
iv. It is produced on individual farms and has to be picked up and trucked to a large-scale user like a power plant.

Above characteristic proves poultry litter as one of the best fuel for production of fuel gas (Palma et al., 2013). Poultry litter is gasified with use fluidized bed combustor and mixed with other wastes like turf and tailings from mineral and charcoal production for technical and environmental feasibility (Kantarli et al., 2016). Reactivity of the fuel can be checked by checking out volatility of the organic matter which is directly proportional to the amount of materials that is being volatilized at high temperatures (Torretta et al., 2013). Temperature directly effects with presence of fixed carbon content during thermochemical processes, such as pyrolysis (Burra et al., 2016).

### 2.3.4 As source for activated carbon

Activated carbon is a valuable product which can be obtained from poultry litter by burning the litter to at least 700$^{o}$C resulting in the formation of a lattice-like carbon particle structure. Activated carbon may be used for the adsorption of contaminants in wastewater. Nowadays adsorption of impurities in wastewater is being processed with bituminous coal and coconut shell in the form of activated carbon. In this case Poultry litter is allow-cost renewable resource that is produced in mass quantities in Pakistan making its use a feasible option (Lima and Marshall, 2004).

## 2.4 Structure of Carbon Nanotubes (CNTs)

CNTs is of cylindrical shape made up of graphitic sheets. Carbon can exist in different having diverse chemical and physical properties. The total six electrons of carbon atom occupying the 1s2, 2s2, and 2p2 orbital's (Saito et al., 2002).The graphitic sheets has carbon atoms whose structure determines and explains physical properties of CNTs (Treacy et al 2016). The types of SWCNTs can be divided in three forms i.e armchair, chiral, and zigzag depending upon wrapping to a cylinder way (Fig. 1B). CNT' structure is characterized by a pair of indices (*n*, *m*) that describe the chiral vector and have an effect on different properties of nanotubes. The number of unit vectors in the honeycomb crystal lattice of graphene along two directions is determined by the integer's *n* and *m*. As a common opinion, when $m = 0$, the nanotubes are named zigzag nanotubes; when $n =$ m, the nanotubes are named armchair nanotubes, and other state are called chiral (Luo et al., 2017).

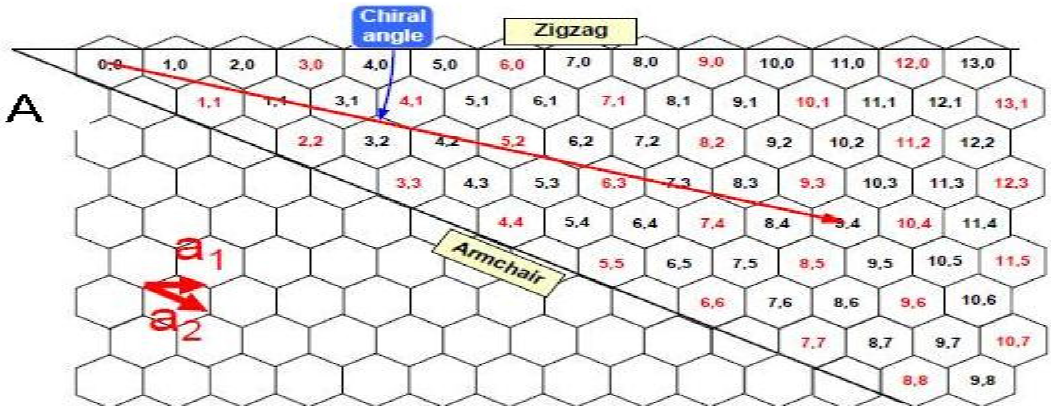



**Fig- 2.1-A**. 2-D honeycomb lattice of carbon shows the chiral vector and the unit vectors a1 and a2

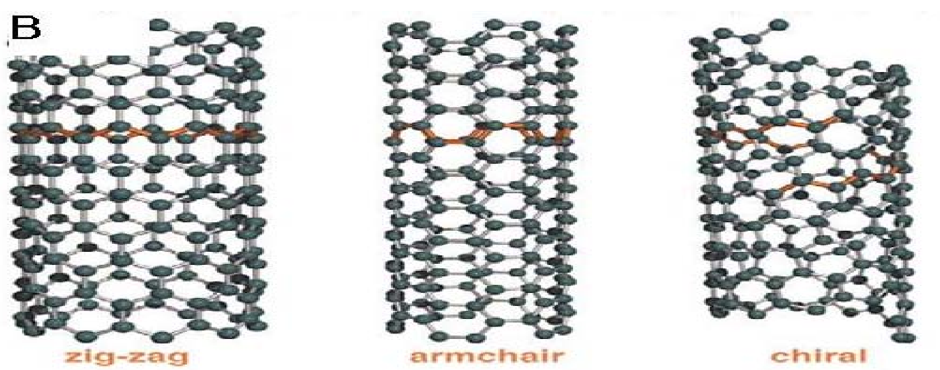



**Fig. 2.1-B**: showing structure of different nanotubes (a) armchair, (b) Zigzag, and (c) chiral nanotubes (Saito et al. 2002).

### 2.4.1 Multiwalled carbon nanotubes

Two structural models are used for MWCNTs: Russian Doll model and Parchment model. Russian doll model resembles a Russian doll means outer structure has an inner one and diameter of inner is lesser than outer structure. Parchment model, as the name reveals is one like a parchment of paper rolls around itself manifold times (Kumar et al., 2018)

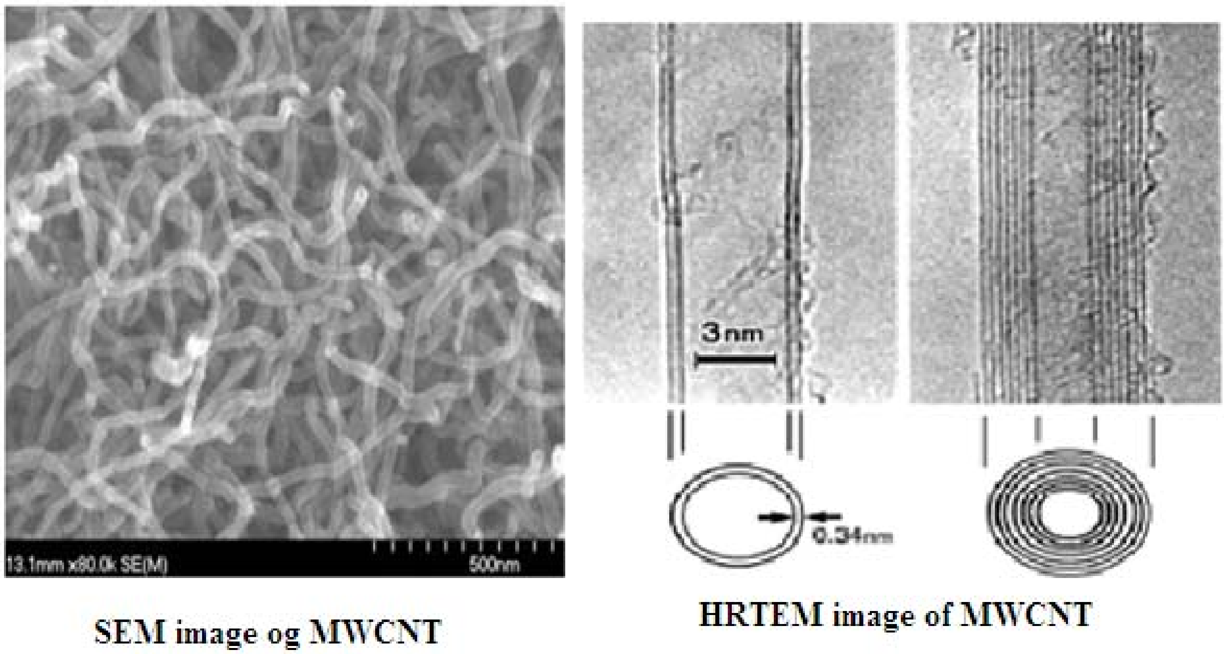



**Fig. 2.2** SEM & HRTM image of MWNTs (Mubarak et al., 2014)

### 2.4.2 Comparison between various types of CNTs

There are two main types of CNTs (a) single walled nanotubes (b) double walled nanotubes both have significant properties.

Table.2.2 Difference between SWNT & MWNT (Raunika et al 2017).

| S. No | SWNT | MWNT |
|---|---|---|
| 1. | It is a single layer of graphene | Multiple layers of graphene |
| 2. | Catalyst is required for synthesis | Can be produced without catalyst |
| 3. | It requires proper control over growth and atmospheric condition therefore, Bulk synthesis is difficult. | Synthesized in bulk easily |
| 4. | Having poor purity | Having high purity |
| 5. | During functionalization possibility of defects are greater. | Less chance of defect but once occurred it is difficult to improve |
| 6. | Characterization and evaluation is easy | It has very complex structure |

### 2.5 Synthesis Techniques

Many methods exist through which CNTs are produced, including but not limited to chemical vapor deposition (Koziol et al 2010), arc discharge(Arora et al., 2014)and laser ablation as given in fig. 2 (Chrzanowska et al 2015). These three techniques are the most common in research and industrial manufacturing environments.

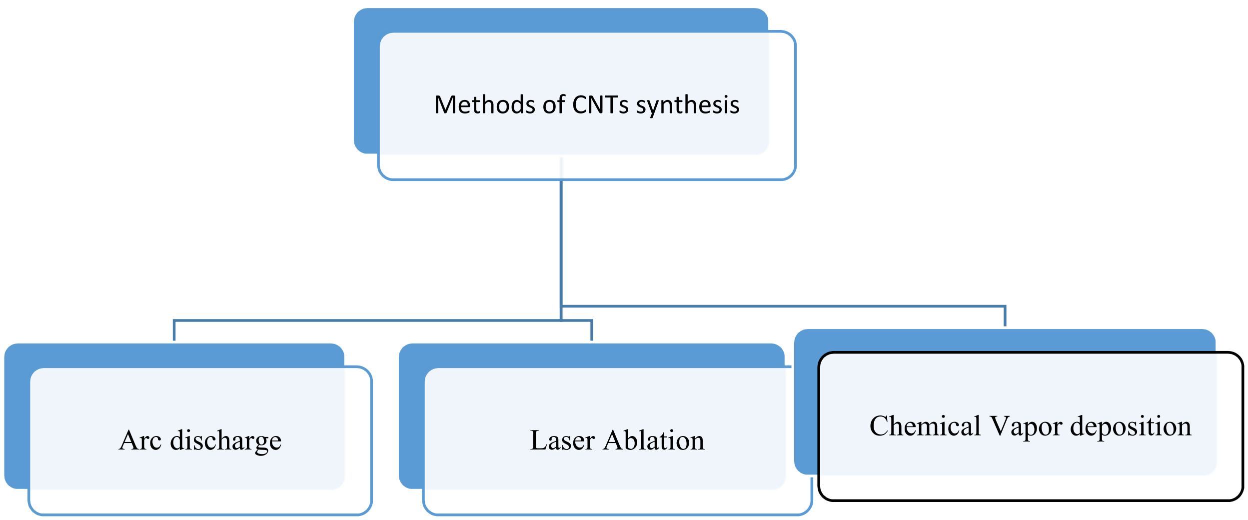



Fig. 2.3 Synthesis techniques for growth of CNTs (Chrzanowska et al 2015).

Uniform chilarity or definite shape of CNTs is a major challenge for industrialists and research scientists (Raunika et al 2017). Researchers have find out techniques to separate metal and semi conducting CNTs Recently, researchers are trusting on techniques that separate metal and semiconducting CNTs by using method of ultrasonic sonication. The product is then filtered to get clarity (Ago et al., 2004).

**Table -2.3** Comparative analysis of techniques for synthesis of CNTs

| Parameters | Thermal CVD | Laser Ablation | Arc Discharge |
|---|---|---|---|
| Mechanism of synthesis | Volatile liquid solid (VLS) | VLS | VLS |
| Process temperature | 600-1000°C | 3000 - 4000°C | |
| Source of carbon | Carbon Gasses or vapors | Solid Carbon | |
| Source of catalyst | Particle or thin film | Particles | |
| CNT surface | High temperature | Copper collector | Carbon rod |
| Diameter control. | Large distribution | Small distribution | |
| CNT relative failure | high | Low | |
| Nanostructure arrangement | Yes, vertical alignment possible | No, randomly arranged | |

(Scott et al., 2001)

### 2.5.1 Combustion method

Combustion method which is the cost effective method that provides high production rate of CNTs. Nanomaterials synthesis required energy which is provided in the form of heating. Setup for this process is simple and efficient (Randall et al., 2002). Fuel combustion is widely studies process for production of carbon nanotubes (CNTs). For example carbon nano-fibers, multi-walled carbon nanotubes (MWCNTs) and coiled carbon nanotubes have been successfully made through combustion method. Multi walled carbon nanotubes was produced from polypropylene in the presence of nickel as a catalyst recently (Bajad et al., 2015). It was also studied that how CNTs can be synthesized by using polymer/catalyst and polytetrafluoroethene by decomposing them under inert atmosphere (Tao et al., 2005).

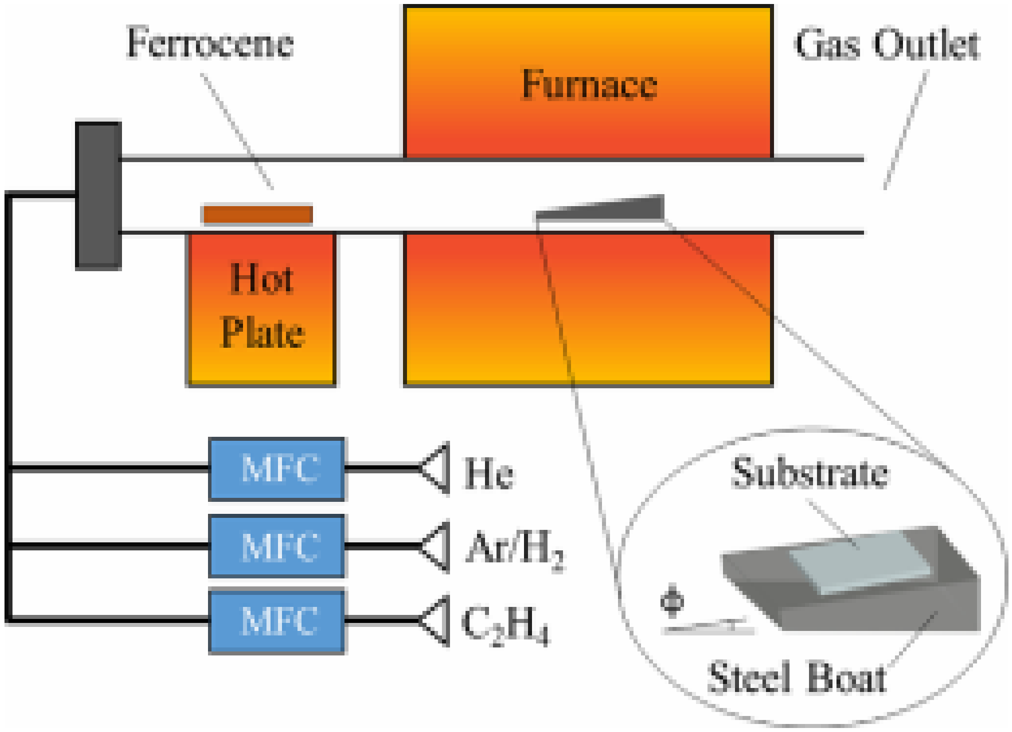



**Fig. 2.** Tube furnace set-up used for synthesis of CNTs (Randall et al., 2002)

### 2.5.2 Mechanism of CNTs growth

The catalyst particles in molten state absorb carbon in vapor form and form an alloy. When the particle becomes saturated with carbon, solid CNTs begins to extrude from the particles. The final location of the catalyst particles defines tip grown or root grown CNTs. As more and more carbon elements are incorporated into the catalyst particle, the concentration of carbon exceeds the solubility of the catalyst particle. At this point, the catalyst particle beings to extrude a solid formation in the form of CNTs as seen in fig. 2.5. Based on the final location of the catalyst particle, the nanotube is typically classified as either tip grown or root grown (Mubaraket al 2011).

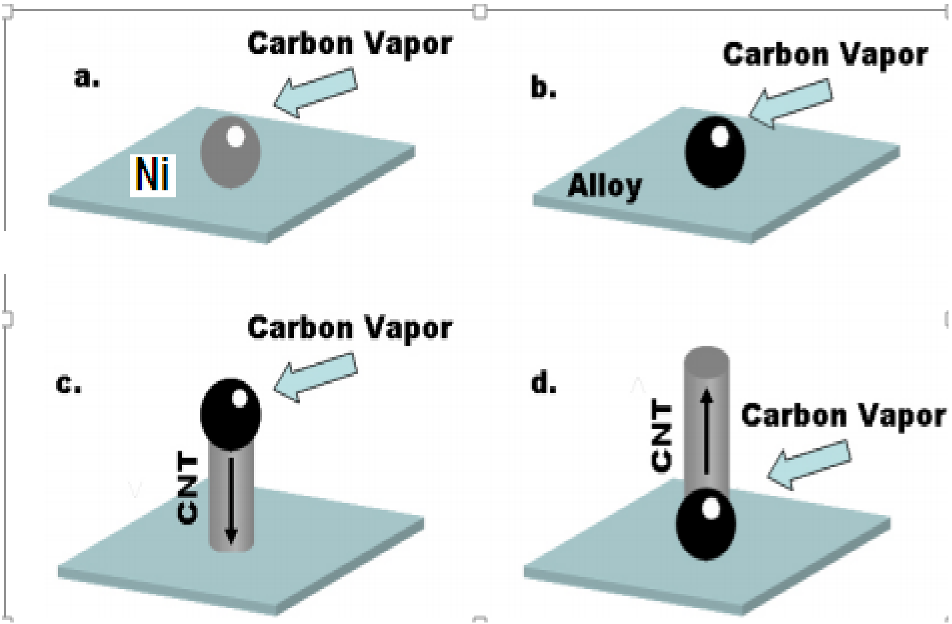



**Fig. 2.5.**Various stages of vapor-liquid-solid (VLS) growth mechanism (a)Carbon adsorb on surface of catalyst (b) Formation of alloy (c) catalyst particle becomes saturated with carbon (d) solid CNTs begins to extrude from the particles (Mubaraket al 2011).

## 2.6 Process Optimization Using RSM

Optimization of useful process conditions through Response Surface Methodology (RSM) method is an important method used extensively because of fewer experimental data presence. This is most studied method for optimized experimental conditions. Most important factor is that it doesn't consume extra chemicals for each step. Further it doesn't need intensive labor and is less time consuming (Ahan, S &Ozturk 2014). Statistical techniques are used for designing of program and checking validity of quadratic model for making up of results. Optimization of experimental conditions are achieved through application of quadratic polynomial and linear functions. Literature review is used in RSM as a base for knowledge of researcher for analysis of independent variables. An experimental matrix is selected to perform according to selected experimental designs. Results are then treated with mathematical-statistical functions, preferably a polynomial function. Optimal values for each variable is then studied for checking out suitability of model. RSM is basically a mathematical model which integrates data used for analysis plus all of the studied parameters also varies at the same time. Thus, RSM is unique since it needs lesser number of experiments as compared to conservative methods (Bezerra et al., 2008).

### 2.6.1 Effect of catalyst on growth of CNTs

Transition metal catalysts are needed for growth of CNTs. Catalysts such as Fe, Co, Ni and their alloys with Mo are often used for CNTs synthesis. CNTs can be grown with use of metal catalysts like Fe and Co-Mo to get a high yield in various forms like films and nanoparticles. Literature is used to optimize the yield of CNTs by following the recipe present in literature, adjusting it locally. Absence of metal catalysts produce amorphous carbon or diamond. According to observation, catalyst in the form of particles works better as compared to smooth films (Mizuno et al., 2005).

Diameter of nanotubes and catalyst particle size was correlated in several studies. Following are the major steps involved in preparation of catalyst

a. Dissolve proper ratio of catalyst precursors
b. Constant stirring
c. Heating at desired temperature
d. Cooling at room temperature
e. Drying in oven
f. Calcination in Electrical tube furnace

Metals with low melting point show better results when used as catalyst in liquid solid mechanism to absorb gaseous species. Carbon absorption capacity of metal catalysts such as nickel, molybdenum and iron is higher for CNTs preparation. Solution of metal catalyst can be used for introduction in chamber (Bajad et al., 2015). CNTs properties and modules can be improved as well as their yield by use of different catalysts. Catalysts like silica, magnesium-supported catalysts, like Fe, Ni, Co and Mo have been reported during synthesis of CNTs (Palacioet al., 2014).The proper mechanism of CNTs growth on catalyst surface is discussed in section 2.5.2.

### 2.6.2 Effect of temperature on growth of CNTs

Growth temperatures varies on a large scale and produce changes in tube-diameter, crystalline structure of tube and percentage of carbon in per unit area using XRD &SEM. Overall, an important transition temperature system (800–840ºC) in CNTs synthesis process has been investigated. The growth rate of nanotubes and tube diameter increases within this temperature ranges (Hofmann et al., 2003).It is reported that CNTs which have low crystalline and temperature independent structure live within their specific range, above or below these transitional temperatures. Synthesizing parameters greatly affects the qualities of CNTs as well as size, quantity and structure. However, relatively high temperatures are still needed to produce tubes of high quality (Englander et al., 2003).

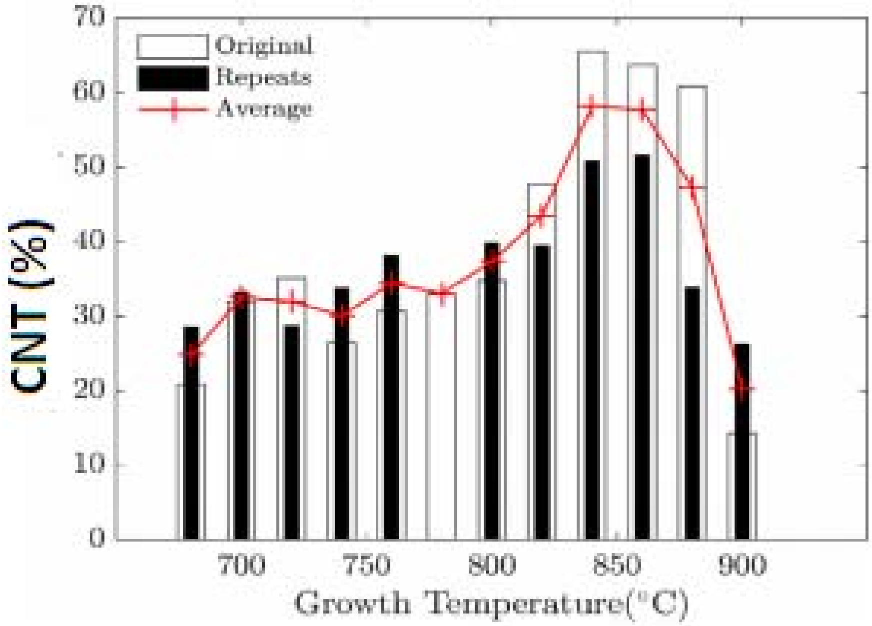



Fig. 2.6. Effect of temperature on CNTs production (Hofmann et al., 2003).

## 2.7 Purification of CNTs

Residues of metal catalyst and amorphous carbon can be removed by different treatments i.e chemical and thermal. Concentrated hydrochloric acid is used for ultrasonication process of CNTs for catalyst particles removal. Duration of this process is around 20 minutes. Next step is dilution of mixture with distilled water and then filtration. Deionized water is used for rinsing of filter to remove residue (solid carbon) so that pH become neutral. CNTs is then oxidized in a tube furnace at a temperature of 400˚C for 2 h to remove amorphous carbon (Bajad et al., 2015).

## 2.8 Functionalization of CNTs

Functionalization process is carried out using chemical treatment which includes refluxing in HNO3 for 4 hr. Functionalization process have greater chances to creates defects on the opening of the ends and sidewalls of CNTs. Functionalization of CNTs through chemical and dry oxidation process have been investigated. CNTs have been modified with nitric acid ($HNO_3$) chemically. On heating pure CNTs under helium atmosphere causes removal of acidic functional groups. It is known that the amount and types of oxygen-containing functional groups depends on the process parameter (Naseh et al., 2009).

## 2.9 Carbon Nanotubes for Wastewater Treatment

Freshwater is getting shorter day by day because of multiple reasons. This shortage is expected to increase in coming years. A number of water cleaning techniques are being introduced. Treatment with CNTs is one such method which is getting popular because of factors like large surface area, good chemical reactivity, high aspect ratio, less chemical mass, less environmental impact and large surface area (Lining et al., 2017). CNTs are gaining commercial interest as well as in terms of research and development worldwide for treatment of water to reduce impacts on flora and fauna, both terrestrial and aquatic. CNTs technologies for water purification includes adsorption, desalination, disinfection, hybrid catalysis and monitoring of all three classes of water pollutants (organic, inorganic and biological).CNTs exhibit encouraging adsorption, catalytic and electrochemical properties. For wastewater treatment technologies, research articles are mostly focusing on removal of oil and grease, removal of heavy metal ions and emerging pollutants (Volder et al., 2013).

### 2.9.1 Adsorption of Cr (vi)

Toxic heavy metals and organic pollutants adsorbed on CNTs because of large surface area and high reaction activity (Anjum et al., 2016).There is also difficulties In dealing CNTs like small particle size, difficulty In separation and low dispersion ability CNTs also faces difficulties (Adeleye et al., 2016). Medicine industry, cell biology, analytical chemistry, environmental technology are some fields which are getting benefitted from CNTs application (Amin et al., 2014). Very less information regarding collaboration between Cr (vi) and MWCNTs has been stated while adsorption capacity of CNTs regarding organic pollutants removal has been researched widely (Ferroudj et al., 2013).

### 2.9.2 Effect of adsorbent dosage on Cr (vi) adsorption

The adsorption of Cr(VI) with different adsorbent dosages in dichromate solution has been studied. It is clear from Fig. 2.7 that the efficiency (E) of adsorption increases as the dosage of MWCNTs improved. These results agree with the recent work. Dosage and equilibrium adsorption capacity is inversely proportional to each other. When former increases later decreases (Kosa et al. (2012).

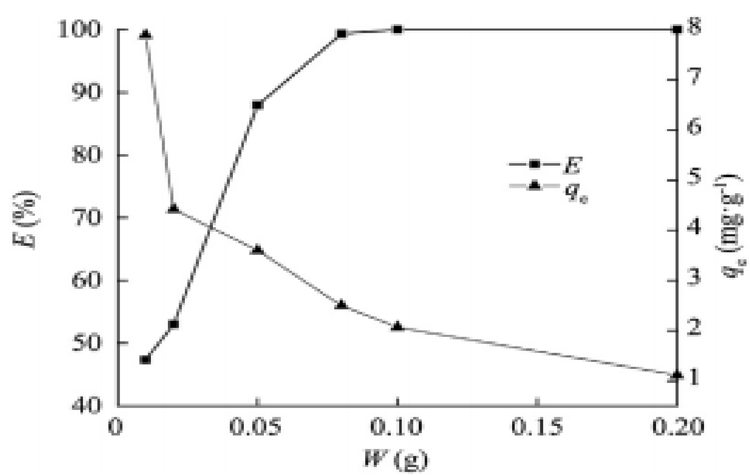



Fig. 2.7Effect of adsorbent dosage on Cr (VI) adsorption using MWCNTs (Kosa et al. (2012).

### 2.9.3 Effect of pH on adsorption of Cr (vi)

The adsorption process of Cr (vi) is controlled by different parameters and pH value is significant among them. Different pH values has been teste, keeping other experimental conditions constant, to check the adsorption behavior of Cr (vi). Researchers studied the effect of pH value on Cr (vi) adsorption behavior. Studies revealed that Cr (vi) adsorption by MWCNTs is greatly affected by pH values. The pH value has reverse effect on adsorption capacity of MWCNTs i.e it decreases with increase in pH from 3.0 to 9.0 (Huang et al., 2015)

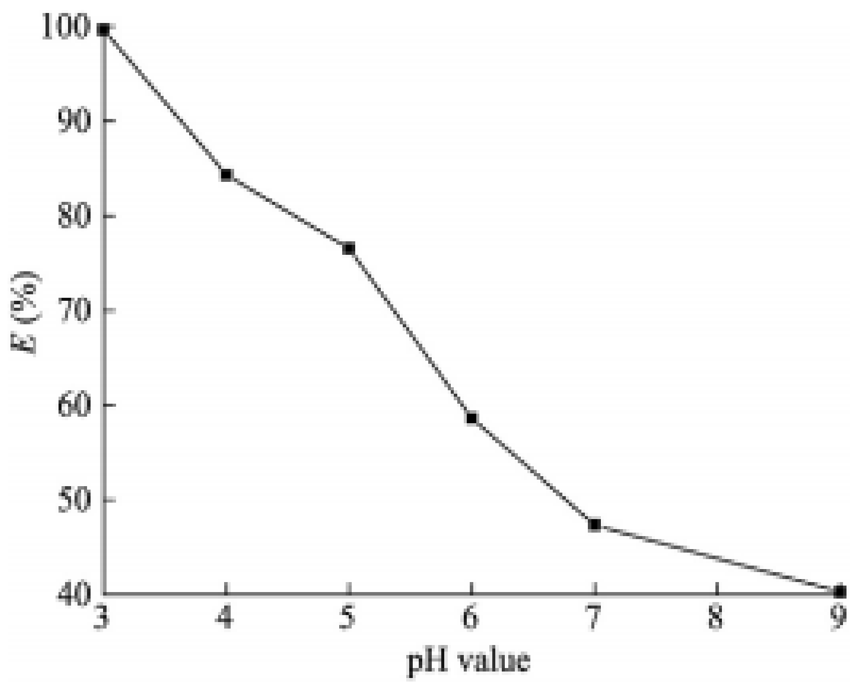



Fig. 2.8.Effects of pH value on adsorption of Cr (VI) by MWCNTs (Huang et al., 2015)

# 3 CHAPTER MATERIALS AND METHODS

## 3.1 Selection of Materials

### 3.1.1 Poultry waste

Commercial poultry house in Islamabad, Pakistan was reached for collection of poultry litter. Litter was fresh since bird flock was just removed from the farm. Litter was then transported to the Institute of Environmental Science and Engineering (IESE). Bedding material was constituted of saw dust and no medicine was given to the birds during growth phase. The initial poultry litter sample of3kg was kept in closed bags.

### 3.1.2 Catalyst precursors

For the synthesis of catalyst following chemicals of analytical grade were purchased from Sigma Aldrich.

a. Nickel Nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$)
b. Ammonium Molybdate tetrahyderate$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$)
c. Magnesium nitrate hexa-hydrate ($Mg(NO_3)_2$. $6H_2O$)
d. Citric acid
e. Hydrochloric Acid (HCl)
f. Sodium Hydroxide (NaOH)
g. Ethanol

These chemicals were used for the preparation of catalyst through liquid impregnation method, which was further used for carbon nanotubes (CNTs) synthesis. In all the experimental run distilled water were used.

## 3.2 Analysis of Poultry Waste

### 3.2.1 Physical analysis

Sample was heated in oven at 105˚C for 8 h to remove the moisture content (w /w %). Following formula was applied to calculate the moisture content percentage

$$M = \frac{W2 - W1}{W2} \times 100 \qquad (1)$$

### 3.2.2 Elemental analysis

Ultimate analysis which is the quantitative analysis of different elements present in the poultry litter sample, such as carbon, hydrogen, sulfur, oxygen and nitrogen. Energy dispersive spectroscopy (EDS) was used for elemental analysis.

Table.3.1. EDS of Poultry litter through Scanning Electron Microscope

| Element | Weight% |
|---|---|
| C | 54.30 |
| N | 7.52 |
| O | 30.12 |
| Mg | 0.48 |
| Al | 0.94 |
| Si | 2.82 |
| S | 0.67 |
| Cl | 0.32 |
| K | 1.62 |
| Ca | 1.20 |
| Totals | 100.00 |

### 3.3 Optimization of CNTs Synthesis Using Software

Response Surface Methodology (RSM) was used in order to maximize the yield of CNTs by optimization of processes parameters. In contrast to conventional methods and the interaction among process variables were determined by statistical technique. A 2-level half factorial design with three central points was preferred for the optimization of CNTs production. The optimized parameters were as follow

a. Reaction Time
b. Reaction Temperature
c. Catalyst concentration

Thirteen number of experimental run for synthesis of CNTs sample are determined by the statistical software. The response for each run based on the yield was further statistically analyzed to find out the optimum reaction conditions (Bezerra et al., 2008).

## 3.4 Research Plan

Figure 3.1 shows research plan followed in the study

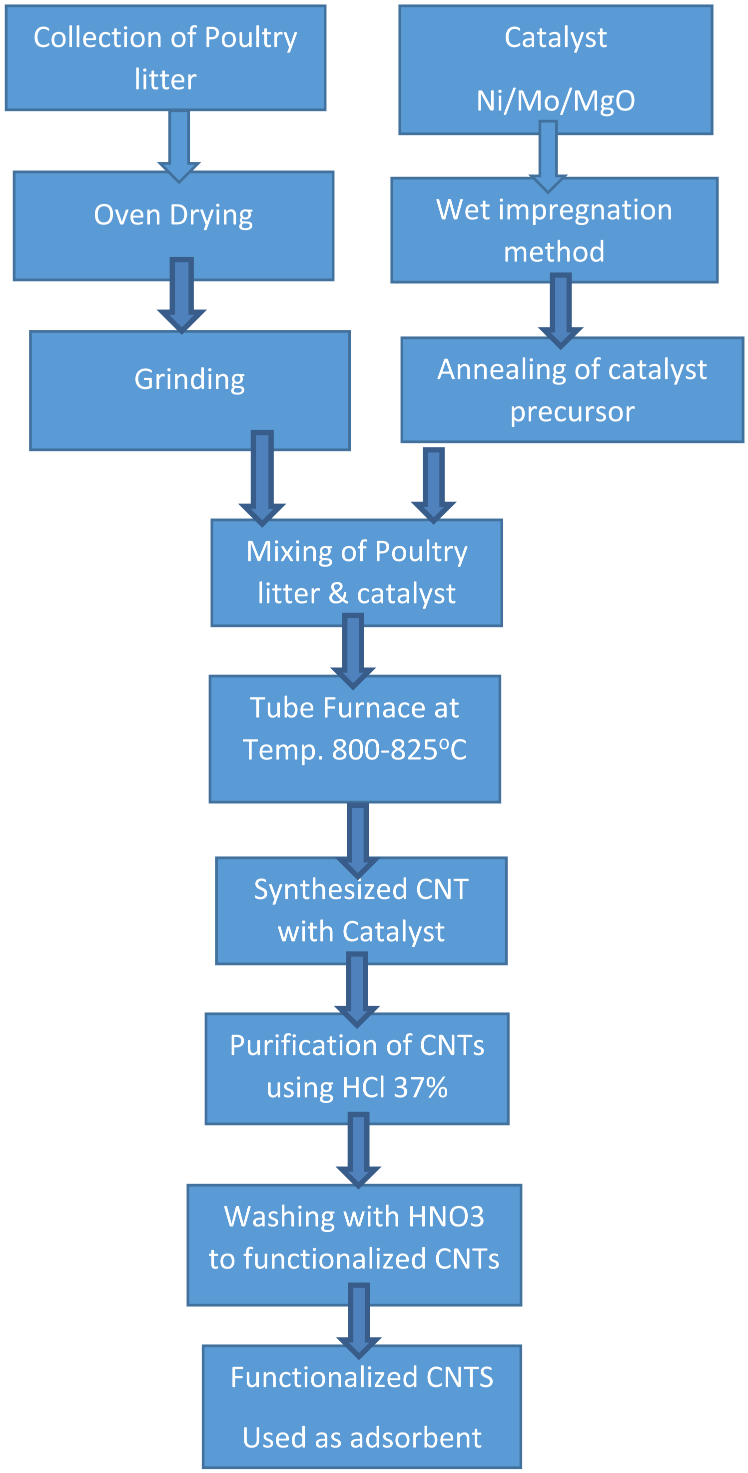



**Fig 3.1**.Flow chart showing the sequence of experimental set up for the study

## 3.5 Catalyst Preparation for CNTs Growth

For the preparation of Ni/Mo/MgO catalyst nanoparticles of Ni/Mo/MgO were used as precursor. Solution of 116.28g of $Ni(NO_3)_2{\cdot}6H_2O$, 24.71g of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ and25.64g of $Mg(NO_3)_26H2O$ were taken in 200ml distilled water and stirred for 1hr on a magnetic hot plate. Mixture was heated to 90°C up to 1hr after addition of two gram of anhydrous citric acid. The resultant mixture was left on a hot plate for evaporation. Viscous slurry was found which was oven dried at 120°C for 12 hr. Material was grinded in fine powder form and calcination was done in furnace of tube like structure (as shown in fig. 3.2)at 700 ◦C for 2 h (10° rise/min) (Palacioet al., 2014).

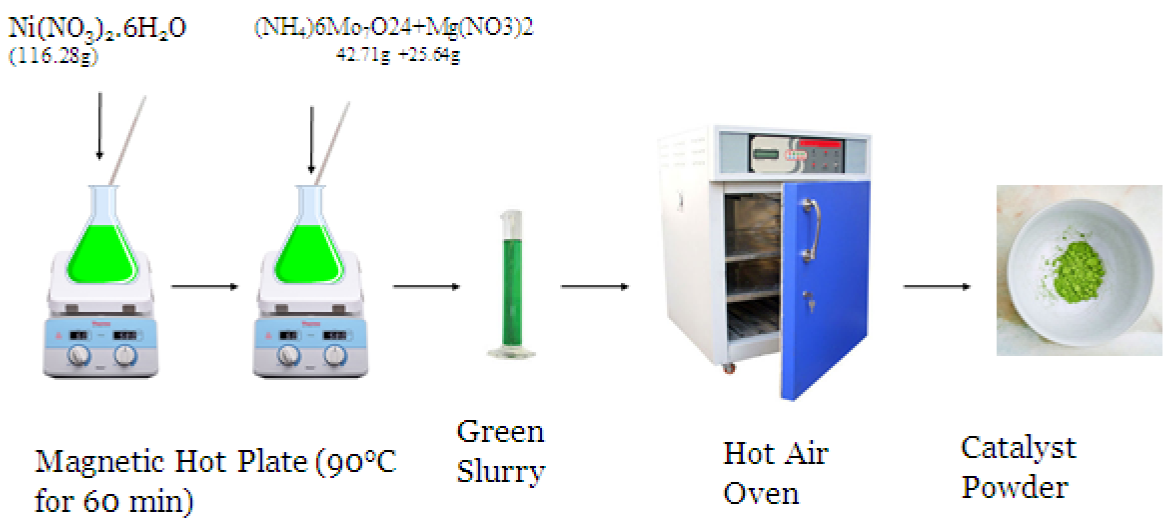



**Fig. 3.2** Different steps for synthesis of Ni/Mo/Mgo catalyst (Xiaosi et al., 2010).

### 3.6 Synthesis of CNTs

Raw material used for synthesis of CNTs was poultry litter. Litter was dried in oven at 120ºC for 3 hrs and grinded. 4g of litter was mixed manually with 2-8mg of catalyst as shown in table 3.1. The mixture was The mixture was reserved in an enclosed porcelain boat (volume 80 ml) and then electrically heated in tube furnace at 700-950ºC in continuous flow of helium gas to provide inert atmosphere (as shown in fig. 3.3).Porcelain boats were removed after 12 minutes from tube furnace. During the decomposition of organic compounds, carbon molecules are deposited on the nickel catalysts placed on magnesium oxide as supporting material. The reactions are carried out at temperatures mentioned above. These temperatures are selected referring to the literature. Syntheses are carried out within the range of 750–850ºC (Zirui et al., 2017).

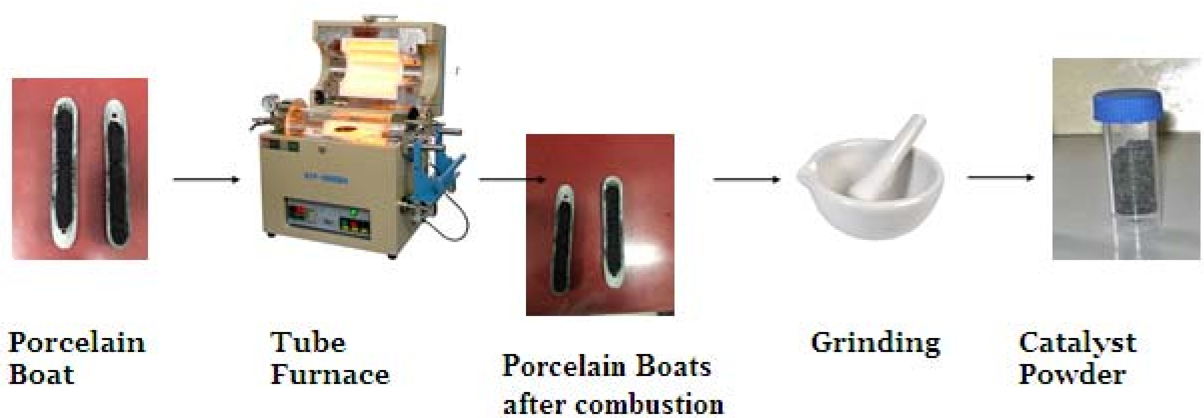



**Fig. 3.3** different steps for synthesis of CNTs using tube furnace

### 3.7 Purification of CNTs

Impurities like Residual catalyst and amorphous carbon are necessary to remove from CNTs. This requires chemical and thermal treatment. Catalyst particles were removed by ultrasonication process in which 37% concentrated hydrochloric acid was used and stirrer for 2 hr on magnetic hot plate. Resultant mixture was filtered by vacuum after dilution with de ionized water. Distilled water used to neutralize pH of solid carbon product. Oxidation of CNTs done in a tube furnace at temperature of 400˚C for a duration of 2 hr, following the method explained by (Vivekchand et al., 2004). The important steps are shown in fig. 3.4.

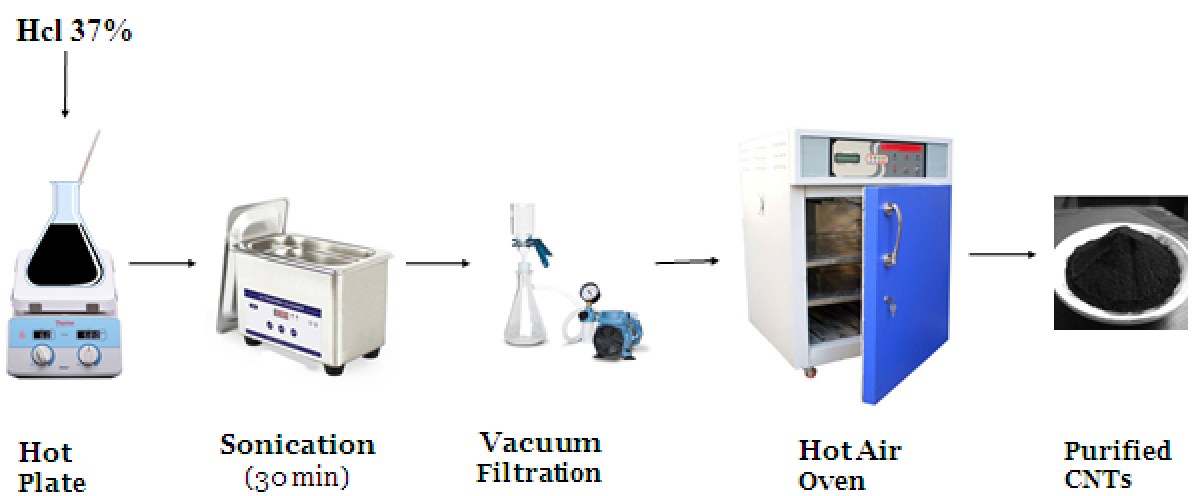



**Fig. 3.4** Different steps for purification of CNTs using HCl (37%)

### 3.8 Functionalization of CNT

A solution of 200 ml of 6.0 M $HNO_3$ (70 %) was prepared and 0.7g MWCNT was spread in this solution by dispersion method. Ultrasound bath was used for 20 min to maintain dispersion process. Magnetic stirring of dispersion was done for 12 hr period under nitric acid reflux under different temperatures range (50, 70, 90 & 110ºC. The dispersion was cooled down at room temperature after removing it from hot plate after 12 hrs of treatment. Centrifugation of dispersion was done at 4000 rpm for 10 min. This process separated supernatant from the mixture by sedimenting solid residues. The supernatant was filtered under vacuum by using 0.2 um acetate membrane filter. Distilled water was used to wash solid residue to remove extra nitric acid from sample. This washing process continued until pH of filtrate became neutral. Finally, MWCNTs were dried for further analysis (Naseh et al., 2009).

### 3.9 Determination of Yield of CNTs

Following equation (Eq-2) was used to calculate yield of CNTs

$$\text{yield} = \frac{m1-m2}{m1} \times 100 \qquad (2)$$

Where, $m_1$= weight of the as prepared product and $m_2$= weight of the catalyst

### 3.10 Adsorption Procedure

The Cr (vi) stock solution of 1000 mg $L^-1$ was prepared by dissolving 0.2829 g potassium dichromate ($K2Cr_2O_7$) in 100 mL distilled water. Several solutions with different concentrations of Cr (VI) were prepared by dilution of the stock solution with distilled water. Adsorption studies were carried out by mixing 2, 4, 6 & 8 mg of MWCNTs with 50 mL Cr (VI) solutions of 100ppm in 100 mL volumetric flask. The solutions were agitated at 500 rpm over different contact time (30, 60, 90, 120, 150, 180 & 210 min). The pH values of Cr(VI) solutions were adjusted to 2.0–70 by using 1.0MHCl and 1.0M NaOH solutions.

**Table. 3.2** Experimental set up for Cr (vi) adsorption from wastewater

| **pH** | **Maintained at six pH levels (2, 3, 4, 5, 6 & 7)** | | | | | | |
|---|---|---|---|---|---|---|---|
| **Dose (mg)**<br><br>Applied at each pH level | 2 ,4 ,6 ,8 | 2 ,4 ,6 ,8 | 2 ,4 ,6 ,8 | 2 ,4 ,6 ,8 | 2 ,4 ,6 ,8 | 2 ,4 ,6 ,8 | 2 ,4 ,6 ,8 |
| **Contact Time** (min) | 30 | 60 | 90 | 120 | 150 | 180 | 210 |

Effect of Adsorbent dosage was determined and pH value of 3 and the initial Cr (VI) were used. An acetate membrane filter of 0.2 um thickness was used to separate aqueous phase. UV-Visible spectrophotometer was used to find out the concentration of Cr (VI) in the filtrate solution Following equation (Eq-3) was used to find out the adsorption efficiency (E).

$$E = \frac{Co-Ce}{Co} \times 100 \_\_\_\_\_\_\_\_\_\_\_\_\_\_ (3)$$

Where

Co is the initial concentrations and

Ce is the initial equilibrium of Cr (vi)

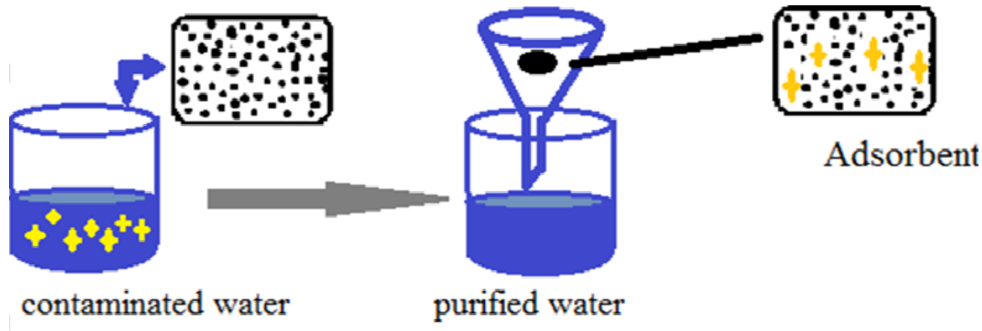



Fig. 3.5 Steps showing purification process of contaminated water through adsorption

### 3.10.1 Solution preparation

The Cr (vi) stock solution of 1000 mg $L^{-1}$ was prepared by dissolving 0.2829 g potassium dichromate ($K_2Cr_2O_7$) in 100 mL distilled water. The aqueous solutions with different concentrations of Cr (vi) were prepared by dilution of the stock solution with ultrapure water. Adsorption studies were carried out by mixing 2, 4, 6 & 8 mg of CNTs with 50 mL Cr (vi) solutions of 100ppm in 100 mL volumetric flask. The solution was agitated at 500 rpm over different time 30, 60, 90, 120, 150, 180 & 210 min. The pH values of Cr (vi) solutions were adjusted to 2.0–70 by using 1 mol $L^{-1}$ HCl and 1 mol $L^{-1}$ NaOH

### 3.10.2 Standard method for detection of Cr (vi)

Standard method (3500 Cr) was used for detection of Cr concentration through UV Spectrophotometer at 540 nm. Following chemicals were used for sample preparation

i. 0.2 ml of prepared sample (synthetic Cr (vi) solution)
ii. 50% Sulphuric Acid (0.5 ml)
iii. 50% Phosphoric acid (0.5 ml) and
iv. 1,5-diphhenylcarbazide solution (2 ml) in 10 ml of distilled water

v. Volume of solution adjusted to 50ml

vi. Shake well before placing the sample in UV-Visible spectrophotometer

$Cr^{6+} + 3\ DPCI + 8H^{+} \leftrightarrow 2Cr\ (DPCO)^{3+} + DPCO + 7H_2O$

$Cr^{6+} + DPCO + 3e^{-} \leftrightarrow Cr\ (DPCO)^{3+}$

Where

DPCO = Diphenylcarbazone

DPCL = Diphenylcarbazide

$Cr\ (DPCO)^{3+}$ is a red violet complex detected at 540 nm

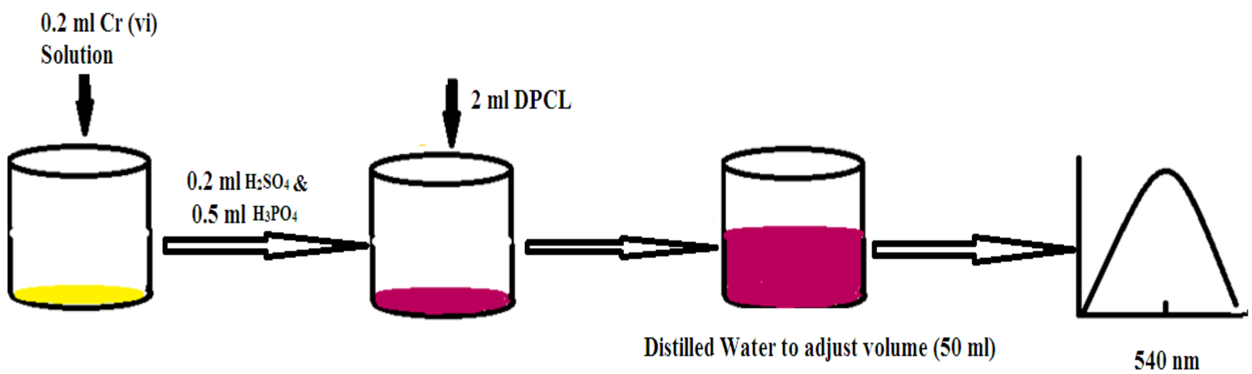



Fig. 3.6 sample preparation according to Standard method (3500 Cr)for UV-visible Spectrophotometer

# 4 CHAPTER RESULTS AND DISCUSSION

## 4.1 Initial Analysis of Poultry Litter

### 4.1.1 Moisture content

moisture content (w /w%) of the raw material was determined as the weight loss of about 97g of sample after drying in oven at 105◦C for 8 h. Total moisture content of raw material was found 69.825%.

Table. 4.1. Moisture content of poultry litter

| Sr.No | Weight of Poultry Litter before drying (W2) (gm) | Weight of Poultry Litter before drying (W1) (gm) | Moisture content (%) |
|---|---|---|---|
| 1. | 200 | 89.64 | 55.18 |
| 2. | 200 | 42.28 | 78.86 |
| 3. | 200 | 103.7 | 48.5 |

$$M = \frac{W2 - W1}{W2} \times 100 \text{\_\_\_\_\_\_\_\_\_\_\_\_} (4)$$

Average of the above dry weight =78.54. Putting this valve in eq.3

$$M = \frac{200 - 78.54}{200} \times 100 = 60.73\%$$

### 4.1.2 Elemental analysis

Spectroscopic method was used to determine elemental concentrations in poultry waste. Analysis of the composition of poultry litter is shown in table 4.1. Analysis shown that concentrations of N, P, CI, Ca, Na, Cu and Zn was more in poultry litter as compared to poultry litter. Manure sample has more moisture content as compared to poultry litter sample because of not mixing with bedding material.

Table. 4.2 Elemental Analysis of Poultry manure and poultry litter

| **Poultry litter (%)** | | **Poultry Manure (%)** | |
|---|---|---|---|
| C | 65.17 | Organic-N | 22.0 |
| N | 1.55 | Total-N | 34.0 |
| O | 18.77 | Ca | 7.6 |
| Na | 0.70 | Mg | 5.7 |
| Mg | 0.50 | S | 4.8 |
| Si | 0.04 | Zn | 0.35 |
| S | 0.08 | Cu | 0.058 |
| Cl | 0.72 | Mn | 0.44 |
| K | 1.71 | Na | 3.3 |
| Ca | 0.98 | | |
| Total | 100 | | |

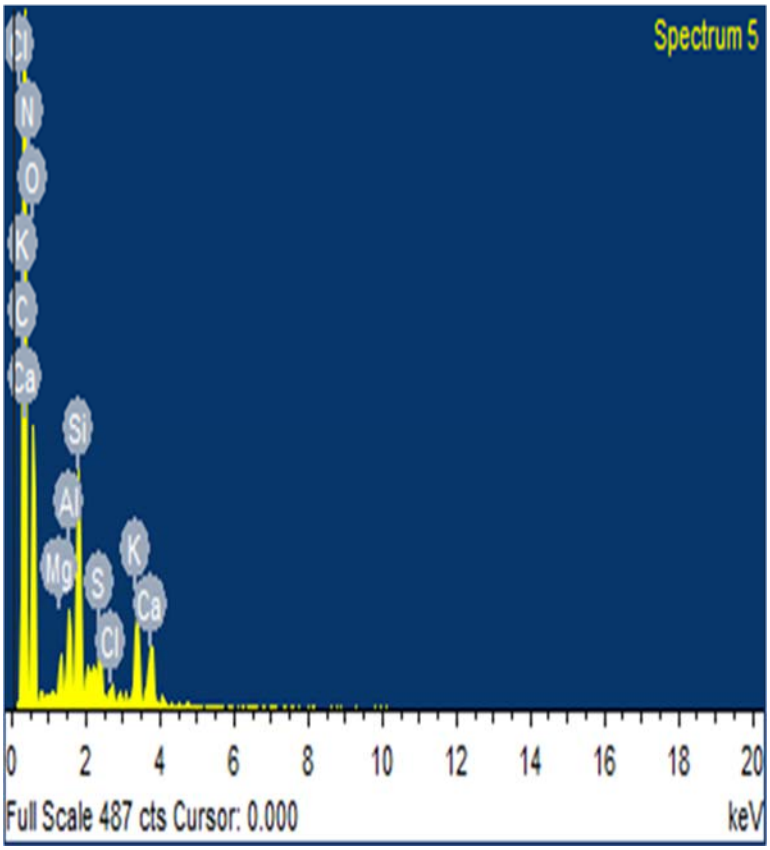



Fig. 4.1 EDS of Poultry litter through SEM

## 4.2 Optimization of Mole Ratio of Catalyst

Multiple linear regression was used to explain the association between one continuous dependent variable (Carbon yield %) and three independent variables (concentration of Ni, Mo, & MgO). To study the importance of independent variables and determining the dependent variable, this statistical analysis was applied. After one unit increase in the dependent variables the change in dependent variable was observed. To estimate the goodness of fit of the model multiple coefficient (R-square) was also applied. Table 4.2 shows the results of regression analysis which indicate that independent variables explain the dependent variables. The independent variables have highly influence on the yield of carbon as shown in table 4.2. Various features of model like R-square and F-value were investigated in order to find out the adequacy of model. All the independent variables included in the model were accountable for explaining 44.2% of the yield of carbon as indicated from the value of R-square (0.499). It has been observed that when R-square is greater than 0.4 the model will be considered to be the best. The F-value and P-value of the model which was 19.17535 & ($p < 0.05$) are very important to show the good fitness of the model (Memon et al., 2016).

To synthesize CNTs and to verify the effect of catalyst on the yield of carbon, various concentrations of Ni, Mo and MgO were studied. To study the effect of Ni/Mo mole ratio on the carbon yield response surface methodology (RSM) of one factor design process was adopted. For optimization of process parameter 15 experimental runs were carried out. Table 4.2 shows the effect of each independent variable on actual carbon yield of all 15 runs. The effects of each variable (Ni/Mo/MgO mole ratio) on the dependent variable (carbon yield) were subjected to regression analysis.

Table. 4.3 -Optimization of Ni/Mo/MgO catalyst

| **Sr.No** | **A: Nickel mol** | **B:Molybdenum mol** | **C:Magnesium mol** | **Carbon yield %** |
|---|---|---|---|---|
| 1. | 2 | 0.60 | 2.00 | 21.075 |
| 2. | | 0.40 | 3.00 | 22.24 |
| 3. | | 0.40 | 1.00 | 23.54 |
| 4. | | 0.20 | 2.00 | 24.84 |
| 5. | 4 | 0.60 | 1.00 | 37.7 |
| 6. | | 0.60 | 3.00 | 37.81 |
| 7. | | 0.40 | 2.00 | 39.25 |
| 8. | | 0.40 | 2.00 | 40.01 |
| 9. | | 0.20 | 3.00 | 40.2 |
| 10. | | 0.40 | 2.00 | 40.85 |
| 11. | | 0.20 | 1.00 | 44.12 |
| 12. | 6 | 0.60 | 2.00 | 25.85 |
| 13. | | 0.40 | 1.00 | 30.42 |
| 14. | | 0.40 | 3.00 | 38.21 |
| 15. | | 0.20 | 2.00 | 39.52 |

Table 4.3 shows the response of carbon yield as a function of Ni/Mo mole ratio as a result of analysis of variance (ANOVA). It was observed that the suitable model to study the response of carbon yield was the cubic model. From F-value, P-value and correlation coefficient (R2) of the model the adequacy of the model was confirmed. When the null hypothesis is essentially true the probability of achieving the experimental results was shown by P-value. Smaller the value of P indicates that the coefficient is very important. Degree of freedom represents the DF value. In this model F-value of 19.32 and $P < 0.0023$ propose that the model was significant. 97.20% of R2 value indicates the fitness of the cubic model (Bezerra et al., 2008).

**Table. 4.4** Analysis of variation of catalyst precursors [Partial sum of squares ]

| **Source** | **Sum of Squares** | **DF** | **Mean Square** | **F Value** | **P-value Prob> F** |
|---|---|---|---|---|---|
| Model | 879.22 | 9 | 97.69 | 19.32 | 0.0023 |
| A-Nickel | 223.71 | 1 | 223.71 | 44.24 | 0.0012 |
| B-Molybdinum | 86.10 | 1 | 86.10 | 17.03 | 0.0091 |
| C-Magnesium | 0.90 | 1 | 0.90 | 0.18 | 0.2010 |
| AB | 24.53 | 1 | 24.53 | 4.85 | 0.0789 |
| AC | 20.66 | 1 | 20.66 | 4.09 | 0.0992 |
| BC | 4.06 | 1 | 4.06 | 0.80 | 0.0113 |
| $A^2$ | 512.83 | 1 | 512.83 | 101.42 | 0.0002 |
| $B^2$ | 0.68 | 1 | 0.68 | 0.14 | 0.7282 |
| $C^2$ | 0.46 | 1 | 0.46 | 0.090 | 0.7763 |
| Residual | 25.28 | 5 | 5.06 | | |
| Lack of Fit | 24.00 | 3 | 8.00 | 12.49 | 0.0750 |
| Pure Error. | 0.28 | 2 | 0.64 | | |
| Cor Total. | 904.50 | 14 | | | |

Table. 4.5. ANOVA (Quadratic Model ) for Response Surface Reduced

| **Sr. No** | **Paramerters** | **Values** |
|---|---|---|
| 1. | Std. Dev. | 2.25 |
| 2. | Mean | 33.71 |
| 3. | R-Squared | 0.9720 |
| 4. | R-Squared. | 0.9217 |
| 5. | C.V (%) | 6.67 |
| 6. | Pred R-Squared. | 0.5723 |

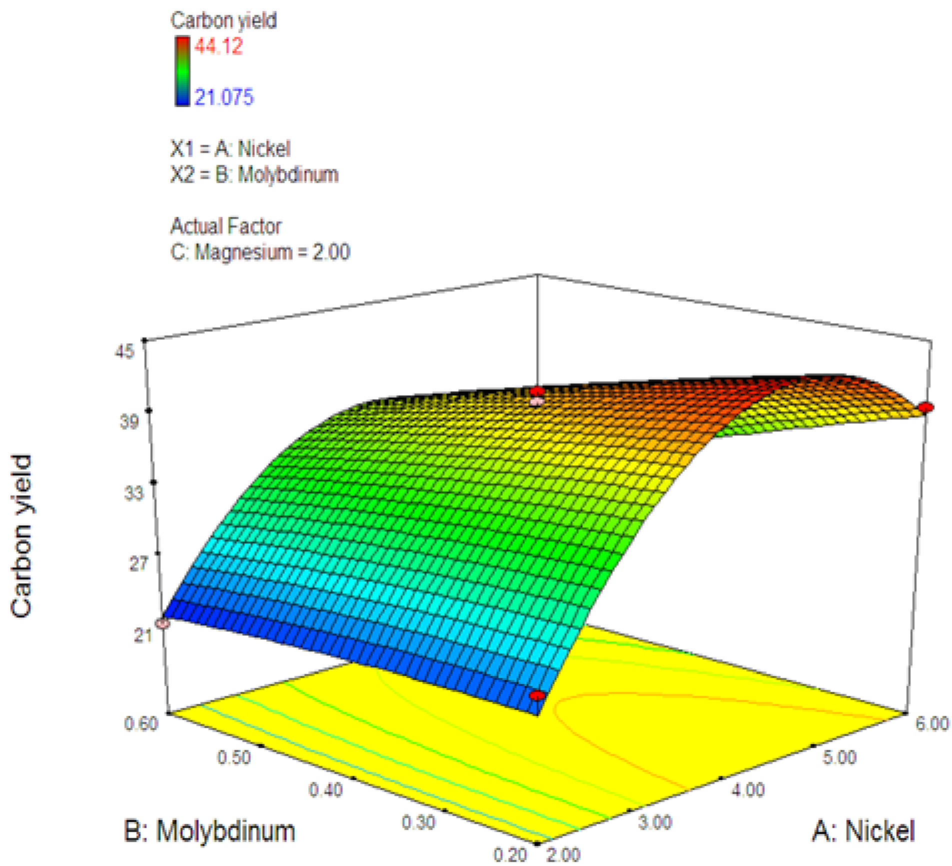



Fig. 4.2 Three-dimensional response plot showing catalytic activity of Ni, Mo and MgO over the carbon yield.

## 4.3 Optimization of Process Parameters

The preliminary detection of levels for the process parameters is necessary to carry out optimization was carried out using trial experiments. For generation of linear response the highest and lowest value of each parameter was set. In order to optimize the processes parameters full factorial design method and several runs were required. In this study, we have performed various initial trial runs based on the summary of results reported by (Bajad et al. 2015). In all experimental run it was observed (see table 4.5) that less than 12 min of combustion time leads to partial combustion of poultry waste while greater than 20 min leads to rapid oxidation of CNTs respectively. CNTs growth was not seen at less than 700°C and rapid combustion of raw material and oxidation of CNTs was observed at above 900°C. The highest and lowest values for weight of poultry waste and catalyst are selected based on the volume of porcelain boat used in our experiments.

Based on model fitting test and regression analysis an appropriate model was selected to sort out all possible interactions of selected factors with response function.

$$Y = ao \sum_{i=1}^{4} \text{aixi} + \sum_{i=1}^{4} \text{aiix2i} + \sum_{i=1}^{4} \text{aijxixj} \_\_\_\_\_\_\_\_ (5)$$

Where,

Y = Response

$a_0$ = Constant coefficient

$a_i$, $a_{ii}$ and $a_{ij}$ = are the coefficients predicted by regression for linear, quadratic and cross product effects of $X_1$, $X_2$, and $X_3$ respectively.

In this study the variables $X_1$, $X_2$ & $X_3$ are assign for reaction temperature [A], reaction time [B], catalyst weight [C] and reaction time [D] respectively (Ahan, S &Ozturk 2014).

**Table-4.6.** Optimization of process parameters for CNTs growth

| Run | A: Temperature ($^oC$) | B: Time (min) | C: Catalyst weight (mg) | D: Carbon yield (%) |
|---|---|---|---|---|
| **1.** | 700 | 12.50 | 80.00 | 13.24 |
| **2.** | | 12.50 | 120.00 | 13.85 |
| **3.** | | 5.00 | 100.00 | 14.12 |
| **4.** | | 20.00 | 100.00 | 15.51 |
| **5.** | 825 | 20.00 | 80.00 | 30.37 |
| **6.** | | 5.00 | 80.00 | 30.86 |
| **7.** | | 20.00 | 120.00 | 31.02 |
| **8.** | | 5.00 | 120.00 | 32.1 |
| **9.** | | 12.50 | 100.00 | 44.04 |
| **10.** | | 12.50 | 100.00 | 44.38 |
| **11.** | | 12.50 | 100.00 | 44.41 |
| **12.** | 950 | 20.00 | 100.00 | 16.7 |
| **13.** | | 12.50 | 80.00 | 16.72 |
| **14.** | | 12.50 | 120.00 | 17.12 |
| **15.** | | 5.00 | 100.00 | 18.32 |

To optimize the response when it is influenced by different parameters response surface methodology (RSM) was used. One of the best design methods for response surface methodology is Box–Behnken design that was used in the present study. The RSM three levels and three variable experimental designs of Box–Behnken were adopted and 15 experimental runs were carried out in order to study the effect of different variable on the carbon yield. Reaction temperature (700–950°C), poultry litter weight (2–4g), catalyst weight (80–120 mg) and reaction time (5–20 min) were chosen for the optimization in terms of maximum yield of carbon product. The optimized values for synthesis of catalyst (Ni/Mo/MgO) with moles of Ni, Mo and MgO for growth of CNTs were 4: 0.2:1 used.

### 4.3.1 Statistical analysis and modelling

To find out the effects of various processes parameter as independent variables on the carbon yield (dependent variable) as shown in results in Table 4.5 were subjected to regression analysis and the Eq. 4 in terms of actual factor was obtained.

$$\text{Carbon Yield (Y)} = A + B + C - (A \times B) - (A \times C) - (B \times C) - A^2 - B^2 - C^2 \ldots\ldots\ldots\ldots(6)$$

Where,

**A**: Temperature

**B**: Time

**C**: Catalyst weight

The correlation coefficient, R2 of 98.79% was indicated that the fitness of second order polynomial to guess response in terms of CNTs yield and the predicted values was in close range with experimental readings. The positive coefficient of the factors indicated the increase in levels of the variables increases the carbon yield. The obtained results as shown in fig 4.6 from ANOVA were helpful to find the effect of independent variable on CNTs yield. Combustion method which is carried out in electrically heated tube furnace was used CNTs growth. The F-value 87.30 of the model and $P<0.0001$ indicated that the model was significant. The lack of fit was significant by observing the lack of fit F-value 139.93. The predicted values were found in the range with experimental readings (Bezerra et al., 2008).

**Table**-4.7. Study of variance table [Partial sum of squares] for growth of CNTs

| **Source** | **Sum of Squares** | **DF** | **Mean Square** | **F Value** | **p-value Prob> F** |
|---|---|---|---|---|---|
| Model | 1975.25 | 9 | 219.47 | 1722.93 | < 0.0001 |
| A-Temperature | 18.42 | 1 | 18.42 | 144.62 | < 0.0001 |
| B-Time | 0.40 | 1 | 0.40 | 3.18 | 0.1347 |
| C-Catalyst weight | 1.05 | 1 | 1.05 | 8.25 | 0.0349 |
| AB | 2.27 | 1 | 2.27 | 17.78 | 0.0084 |
| AC | 0.011 | 1 | 0.011 | 0.087 | 0.7804 |
| BC | 0.087 | 1 | 0.087 | 0.68 | 0.4461 |
| $A^2$ | 1784.57 | 1 | 1784.57 | 14009.47 | < 0.0001 |
| $B^2$ | 138.73 | 1 | 138.73 | 1089.05 | < 0.0001 |
| $C^2$ | 184.02 | 1 | 184.02 | 1444.59 | < 0.0001 |
| Residual | 0.64 | 5 | 0.13 | | |
| Lack of Fit | 0.55 | 3 | 0.18 | 4.36 | 0.1922 |
| Pure Error | 0.084 | 2 | 0.042 | | |
| Cor Total | 1975.89 | 14 | | | |

Table. 4.8 ANOVA for Response Surface Reduced Quadratic Model

| Sr. No | Parameters | Value |
|---|---|---|
| 1. | Std. Dev. | 0.36 |
| 2. | R-Squared | 0.9997 |
| 3. | Mean | 25.52 |
| 4. | Adj R-Squared | 0.9991 |
| 5. | C.V. % | 1.40 |
| 6. | Pred R-Squared | 0.9954 |
| 7. | Adeq Precision | 106.298 |

Both positive and negative significant effects on the carbon yield were shown due to interaction of variables. The positive significant effect on the carbon yield was observed higher for reaction temperature (A), reaction time (B) and catalyst weight (C). The effect of polymer weight (B) and time (D) on the CNTs yield depends on the level of temperature used. Higher level of process variables causes a decrease in CNTs yield. A negative coefficient for the square terms (A2, B2, C2 and D2) was implied for these purposes. The selected model was appropriate for prediction of the carbon yield within the considered range of variables (Ahan, S & Ozturk 2014).

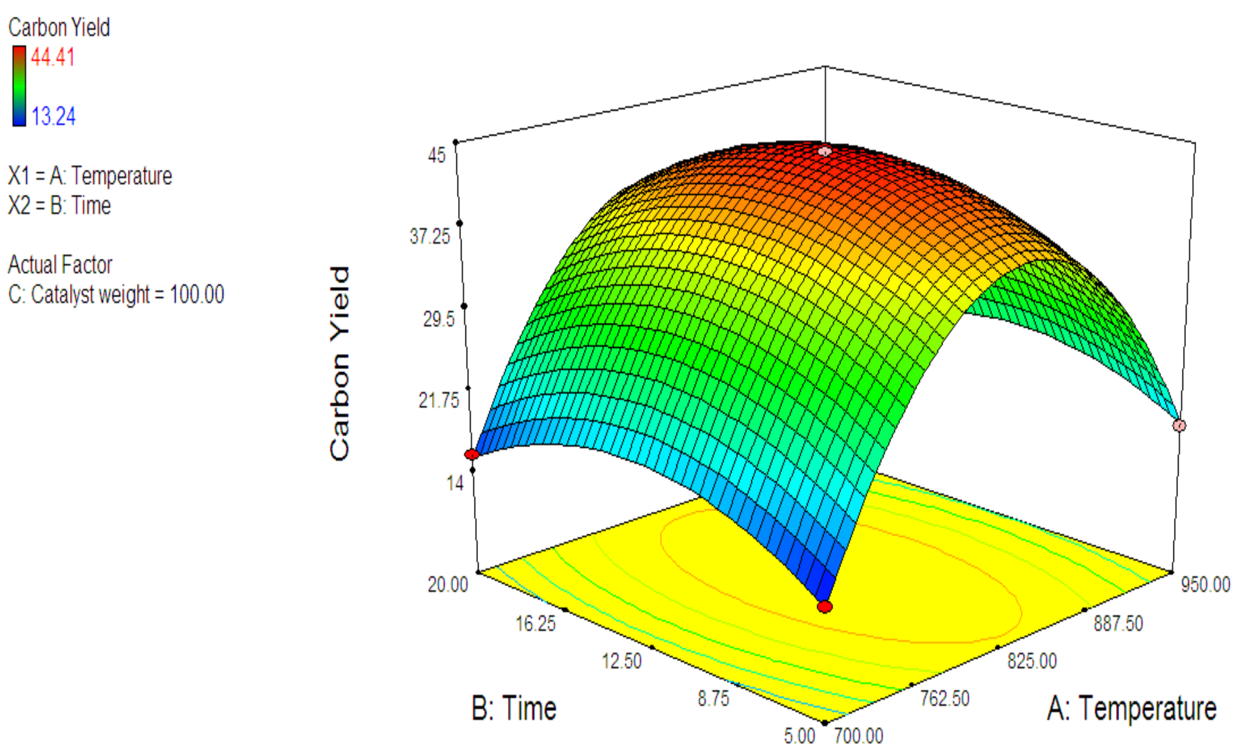



Fig. 4.2 Effect of combustion temperature and time on the yield of carbon

### 4.3.2 Effect of temperature on growth of CNTs

To investigate the effect of temperature on the carbon yield a three-dimensional response surface curve (fig 4.3) was used. Curves were obtained to assess the effect of independent variables and their interactive effect on the carbon yield. The carbon yield was found maximum with the catalyst load of 100mg at around 800-900˚C. however, at high temperature from 850 to 900˚C, vapors of hydrocarbon passes out of the crucible quickly which causes a reduction in the hydrocarbon source for CNT growth.

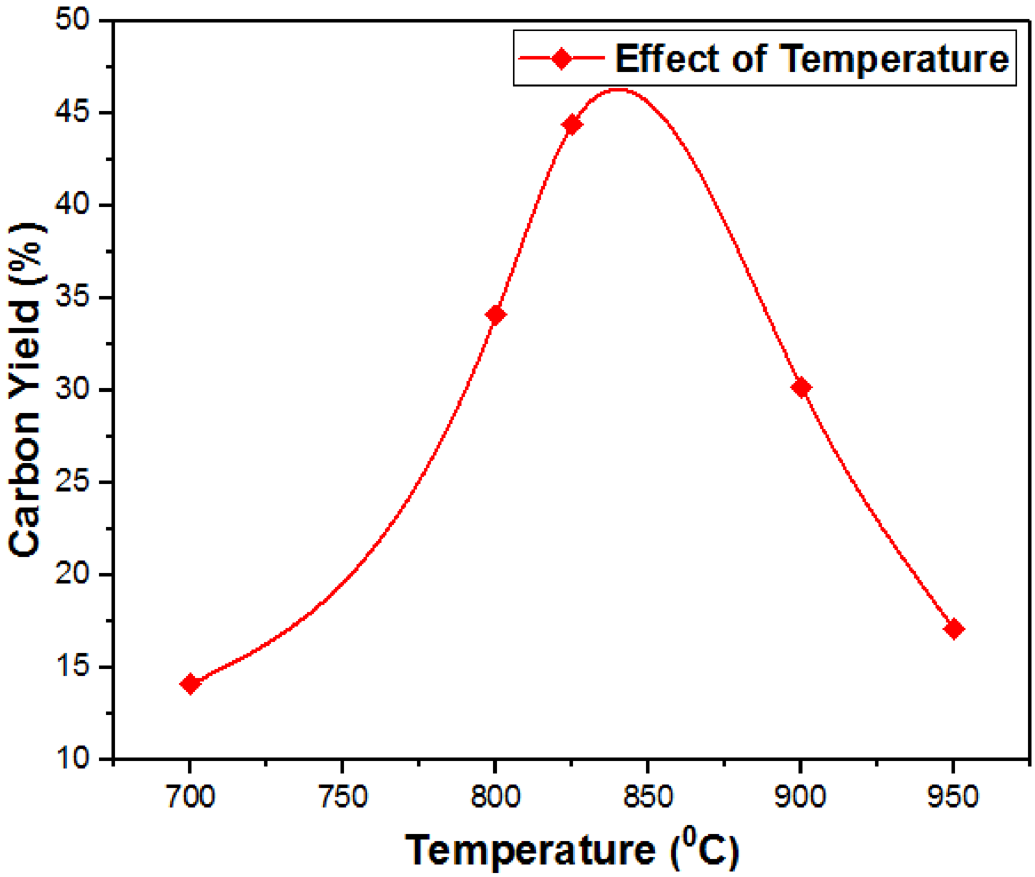



**Fig**.4.3 Effect of optimized temperature on carbon yield

### 4.3.3 Effect of reaction time on CNTs growth

The effect of reaction time on the CNTs yield is shown in fig 4.4. In all experiment the poultry waste weight (4g) was kept constant. It was observed that CNTs yield were continuously decreased as the reaction time with in the tube furnace was increased. It was also observed that only for 10-12 min the hydrocarbon vapors remain in contact with catalyst particles and then the carbon rich vapors start passing out from the porcelain boat. When the samples were exposed to higher temperature for longer time it resulted the oxidation of hydrocarbons which was the major cause reduction in CNTs yield (Arena et al., 2003).

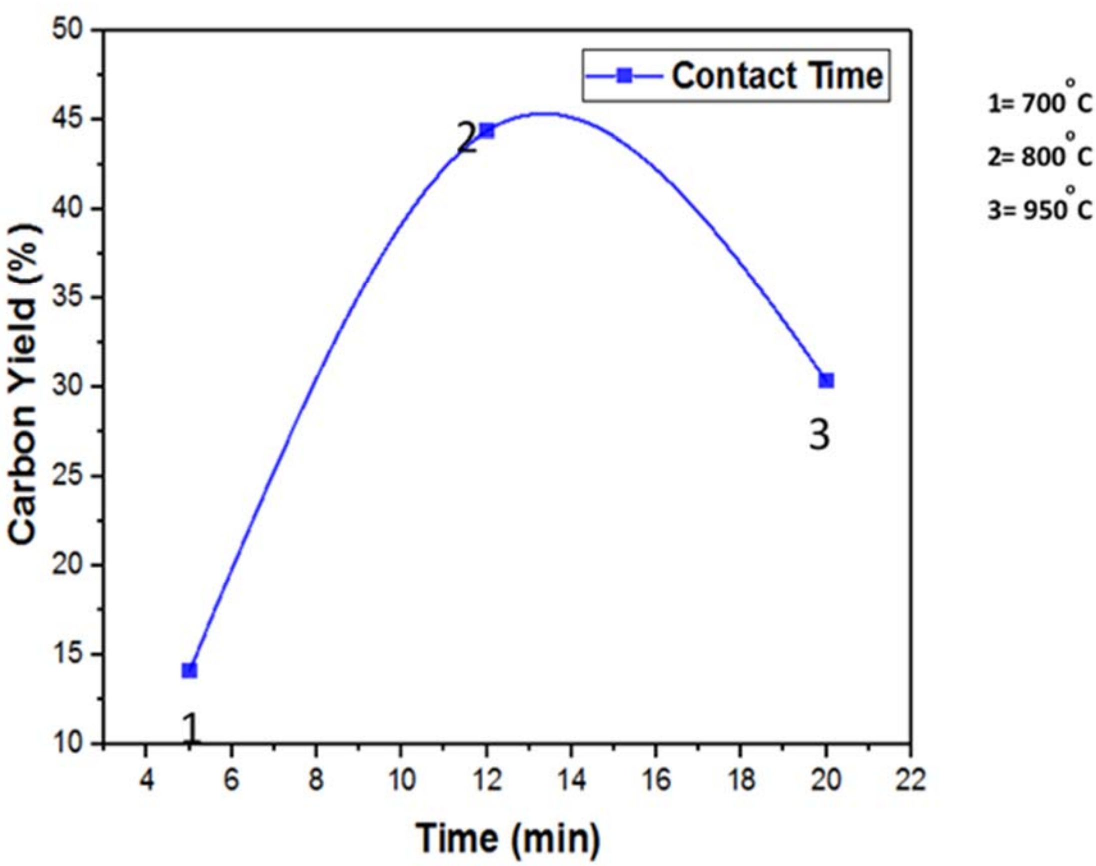



**Fig**.4.4 Effect of optimized contact time on carbon yield

## 4.4 Characterization of Catalyst

### 4.4.1 X-ray Diffraction (XRD)

Catalyst prepared from optimized ratio of precursor was analyzed by X-ray diffraction to ensure the crystalline structure of catalyst. In order to obtain X-Ray diffraction patterns of catalyst X-Ray diffractometer (Theta/Theta STOE Jeol Germany) was used. Samples were prepared by pressing the powders between two glass slides into a flattened sheet. Radiation source CuK was used for taking X-ray patterns and 40 kV and 40 mA was supplied to X-ray generator. The patterns were recorded at 2θ from 20˚ to 70˚. The XRD pattern of Ni/Mo/MgO (4: 0.2 :1) catalyst are shown in the Fig. 4.5. In these patterns the intense peaks at 37.30◦ and 43.28◦ corresponds to Mg and MoNi respectively. It was confirmed that Ni and Mo particles are well supported over MgO matrix and sintering was not observed due to presence of sharp peaks (Rodrigo et al., 2008).

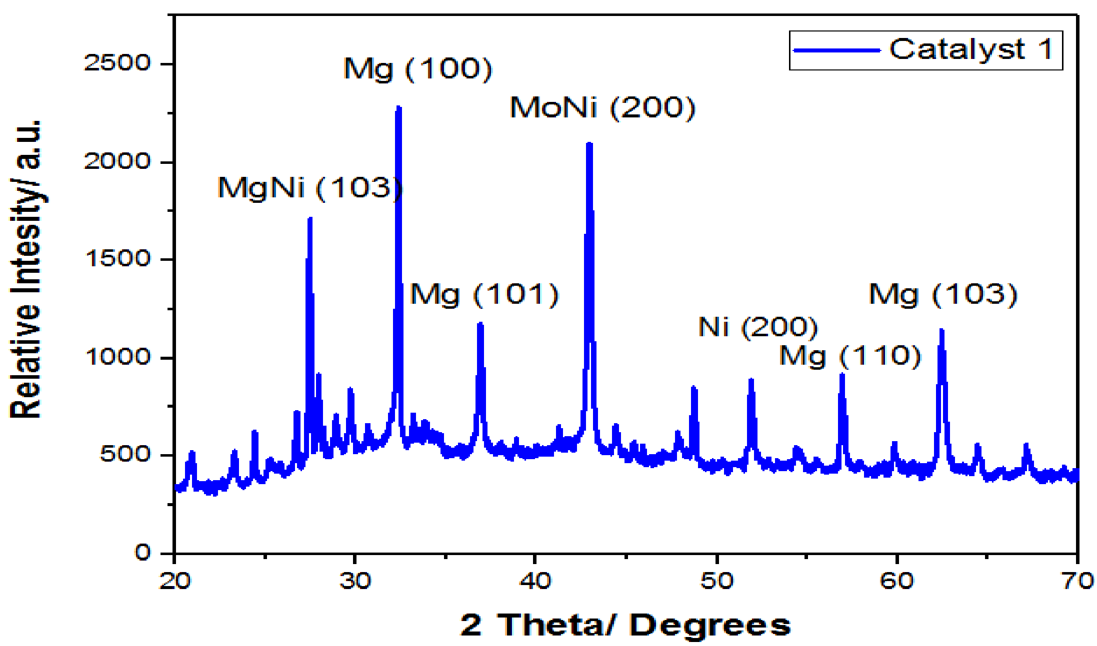



**Fig.**4.5 XRD of optimized molar ratio of Ni/Mo/Mg (4:0.2:1) catalyst

### 4.4.2 Morphological analysis of catalyst

SEM (Jeol JSM6490A, Japan Analytical scanning electron microscope) was used to examine the surface morphologies of various samples. The morphology of Ni/Mo/MgO catalyst at ×100,000/- magnification are shown in the Fig. 4.7.at this magnification the particle size is 18 nm. Uniform catalyst layer with well distribution of Ni, Mo and MgO (4:0.2:1) particles was observed from catalyst morphology. The metal particles were appeared in individual crystal as well as in segregated form. Due to dark and spherical shape of both Ni & Mo It was difficult to differentiate the Ni and Mo particles as shown in fig.4.7. Ni and Mo particles are well incorporated in the Mg matrix as shown from microstructure of the Ni/Mo/MgO. Various Mg–Mo and Ni–Mo phases for Ni/Mo/MgO catalyst was shown from XRD report therefore these results are in agreement with XRD.

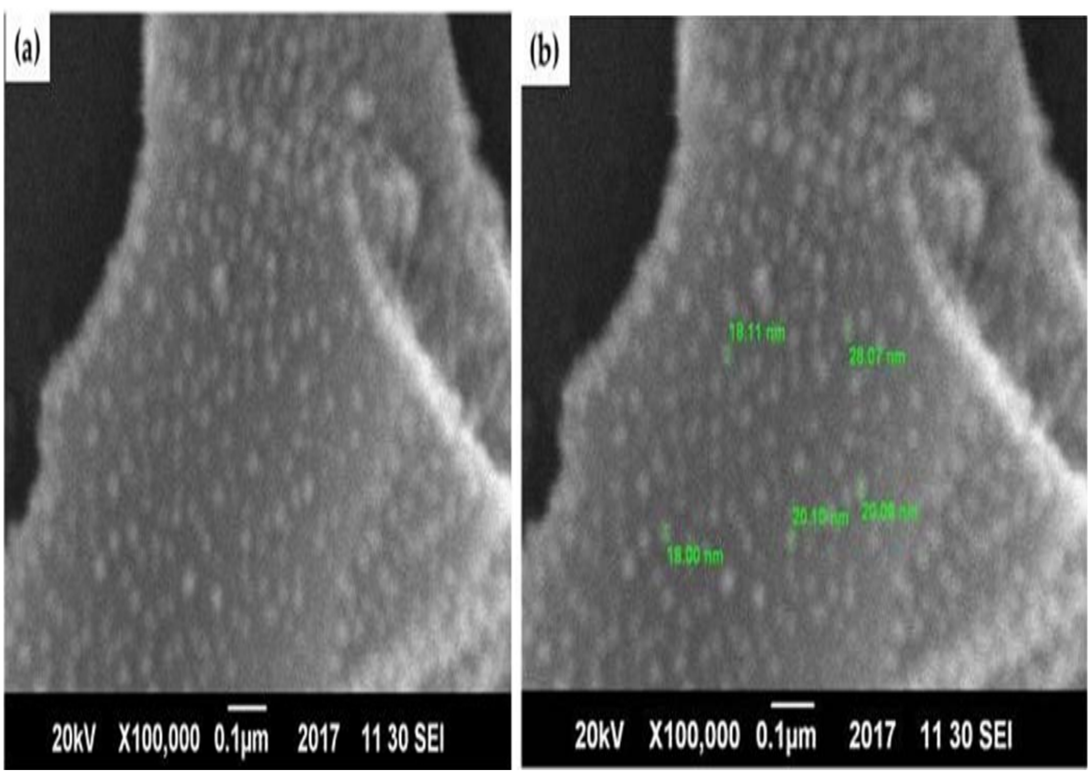



Fig.4.7 SEM of catalyst with ratio of Ni4 Mo0.1MgO1

## 4.5 Characterization of CNTs

XRD and SEM techniques was used to study the highest and lowest effects over the CNTs yield with different mole ratio of Ni/Mo/MgO catalysts (explained in section 4.3) and growth characteristic of CNTs.

### 4.5.1 X-ray Diffraction (XRD)

The XRD patterns of synthesized CNTs over 0.1g of Ni/Mo/MgO catalyst at 825°C, combustion time of 12 min and 4g of poultry litter is shown in fig. 4.8. It was observed that the well-resolved graphite (0 0 2) peak at 2θ = 26.62◦ for CNTs obtained using Ni/Mo/MgO (4:0.2:1) catalyst which indicates the growth of CNTs. During synthesis of CNTs the diffusion of carbon into Mo and Ni nanoparticles occurs and Mo get converted to Mo carbide phase (MoC and $Mo_2C$) (Bajad et al., 2015). Carbon nannotate bundles are formed due to precipitation of carbon atom takes place on Ni–Mo crystal plane. Precipitation of carbon atom on surface of catalyst takes place when more carbon atoms diffuse on Ni and Mo nanoparticles. The XRD pattern for the purified CNT as shown in fig. 4.8 shows sharp peak (0 0 2 peak) with high intensity which indicates the absence of amorphous carbon (Stamatina et al., 2007). Peak at 2θ = 44.60◦ is due to the presence of Ni particles in the CNT product. The intensity of this peak was decreases after purification of CNTs. In purification step the partial removals of the catalyst particles through acid treatment was confirmed (Dasa et al., 2015).

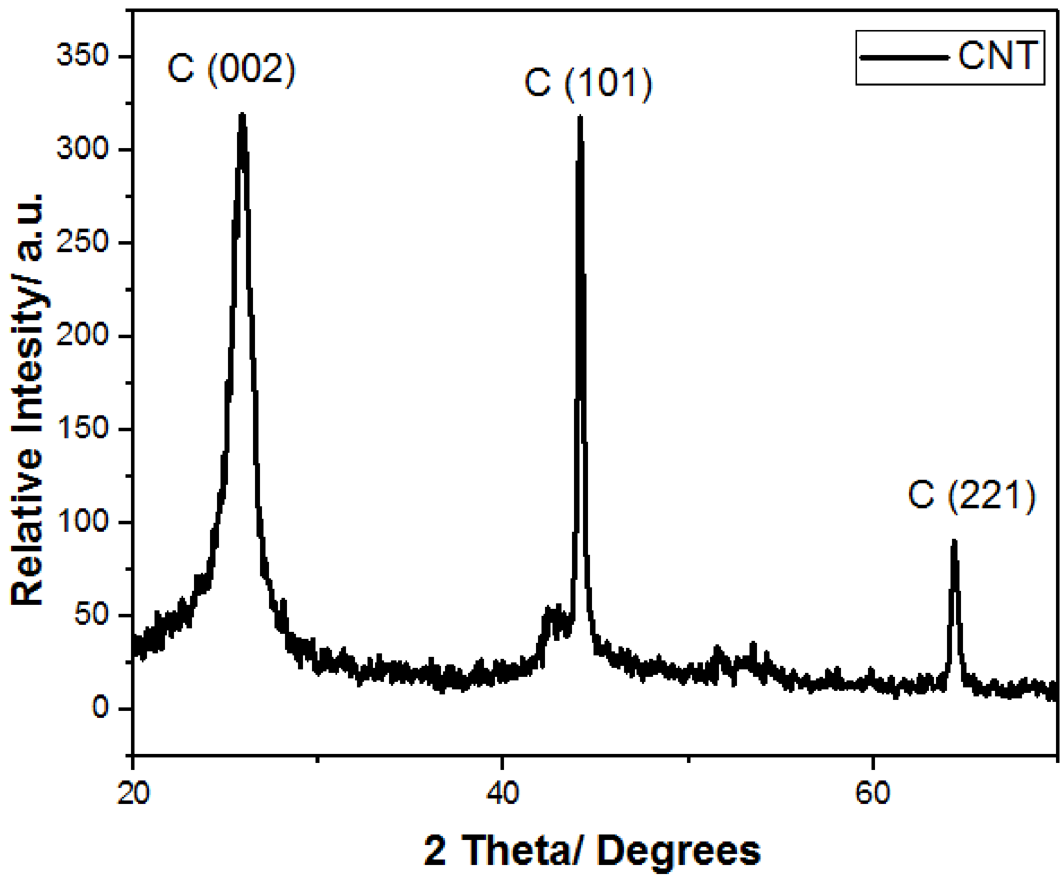
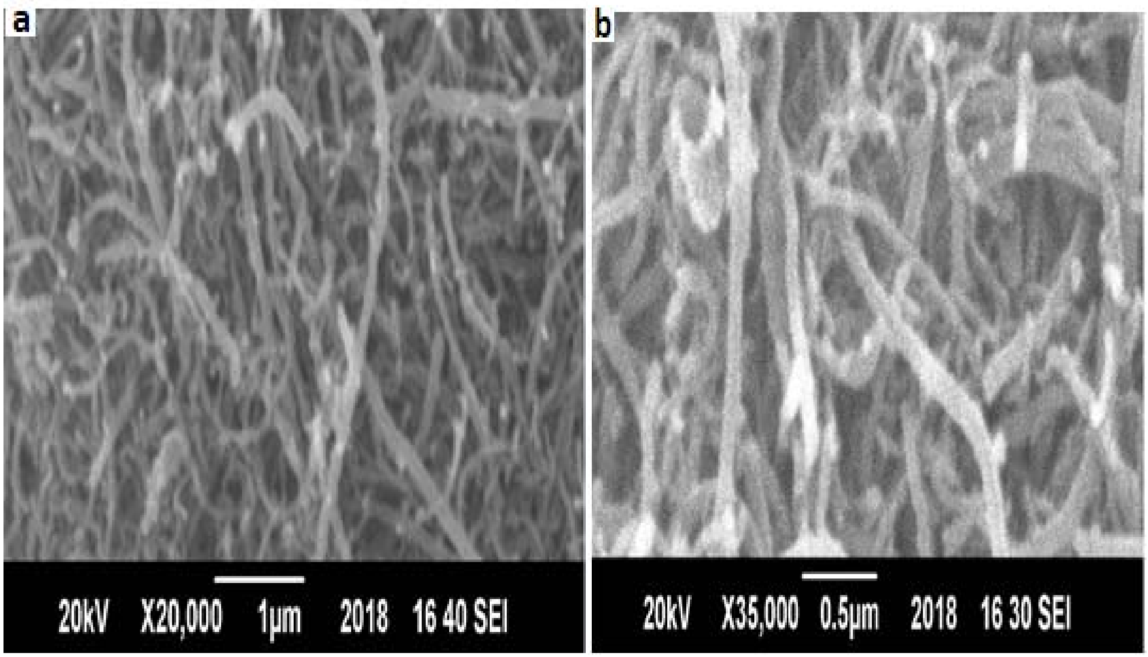



**Fig.**4.8 XRD of Synthesized CNTs

### 4.5.2 Morphological Analysis of CNTs

Scanning Electron Microscope (SEM) with high resolution is an influential instrument for imaging of fine structures of materials and nanoparticles fabricated through nanotechnology. SEM (Jeol JSM-6490A, Japan Analytical scanning electron microscope) was used to study surface morphologies of the samples. Samples were coated with a thin layer of conducting material (gold) and were imaged at ×20,000, ×35,000 & 75,000 magnifications. The accelerating voltage was 10–15 kV. A focused high energy beam of electron interacted with the surface of sample and generated secondary electron, back scattered electron and characteristic X-rays signals. These signals were perceived by the detector and images were displayed on the cathode ray tube screen. Scanning electron micrographs of the synthesized CNTs over Ni/Mo/Mg (4:0.2:1) catalyst is shown in fig 4.9. it was very difficult to determine the % removal of impurity from the SEM image of purified CNT as it look like to that of unpurified CNTs. CNTs follows the tip growth mechanism when, the catalyst appears on the tip of CNTs. Longer CNTs were produced when the catalyst at the tip of CNTs provides maximum exposure for hydrocarbon (Safarova et al., 2007). The size of synthesized CNTs at × 75,000 magnifications was 26nm as shown in fig.4.9.



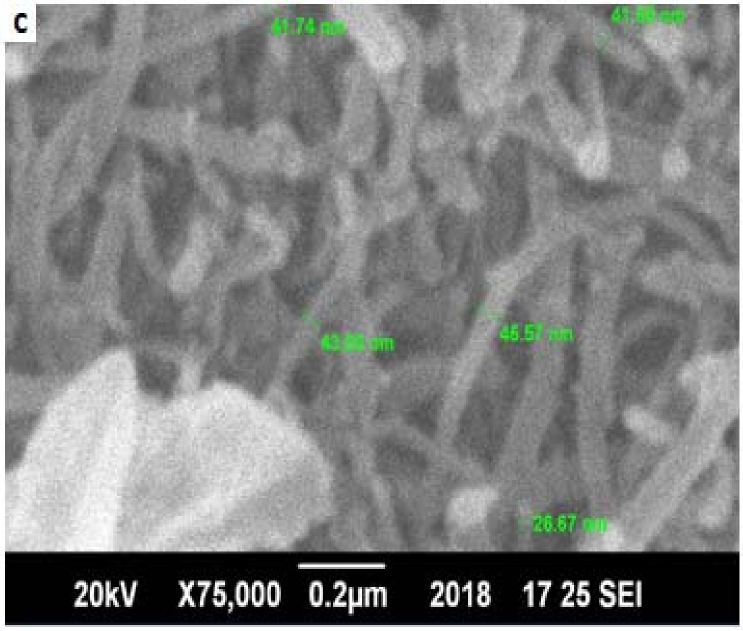



Fig. 4.9. Scanning electron micrographs of synthesized CNTs (a) × 20,000 magnification (b) ×35,000 magnification (c) × 75,000 magnification

## 4.6 Adsorption of Cr (vi)

Synthesized CNTs was used to remove chromium. 81.83% of Cr (VI) removal was achieved by using MWCNT at pH 3, 400 rpm, and 2.8 hrs for a dosage of 2-8mg of CNTs. While 78.8% removal of Cr (vi) from wastewater by using MWCNTs have been reported (Burakov et al., 2018). The outcomes of these studies confirmed that CNTs are an excellent adsorbent for the removal of heavy metal from aqueous solutions.

### 4.6.1 Effect of pH

For controlling the Cr (VI) adsorption process pH was observed one of the key parameter in this study. Maximum removal efficiency of Cr (vi) was found higher at low pH as shown in fig 4.10. The optimum pH was observed at pH 3.0 and remaining experiments were done at this pH. As pH increases, the surface of CNTs becomes more negatively charged. This causes repulsion between

Cr (vi) and CNTs therefore, the removal efficiency decreases with increase in pH (Jiang et al., 2013). Different results were obtained with varying the pH values and it was confirmed that removal of Cr (vi) by MWCNTs was highly dependent on the pH value of the solution. It was observed that as the pH values increasing from 2.0 to 7.0 the adsorption capacity decrease. This observable fact is explained here due to presence of different forms of Cr (vi) in the aqueous phase. The dominant forms of Cr (vi) were $Cr_2O_7^{-2}$ and $HCrO_4^{-2}$ ions in the pH range of 2 - 7. The surface of MWCNTs became positively charged at low pH values due to protonation and Cr (vi) adsorption was enhanced due to electrostatic forces between the MWCNTs and the negatively charged $Cr_2O_7^{-2}$ and $HCrO_4^{-2}$ ions (Li and Bowman, 2001). While $CrO_4^{-2}$ ions prevailed in the solution at higher pH values. It was also observed that with increase of the pH value the protonation decreases and the adsorption efficiency was decreased (Padmavathy et al., 2016).

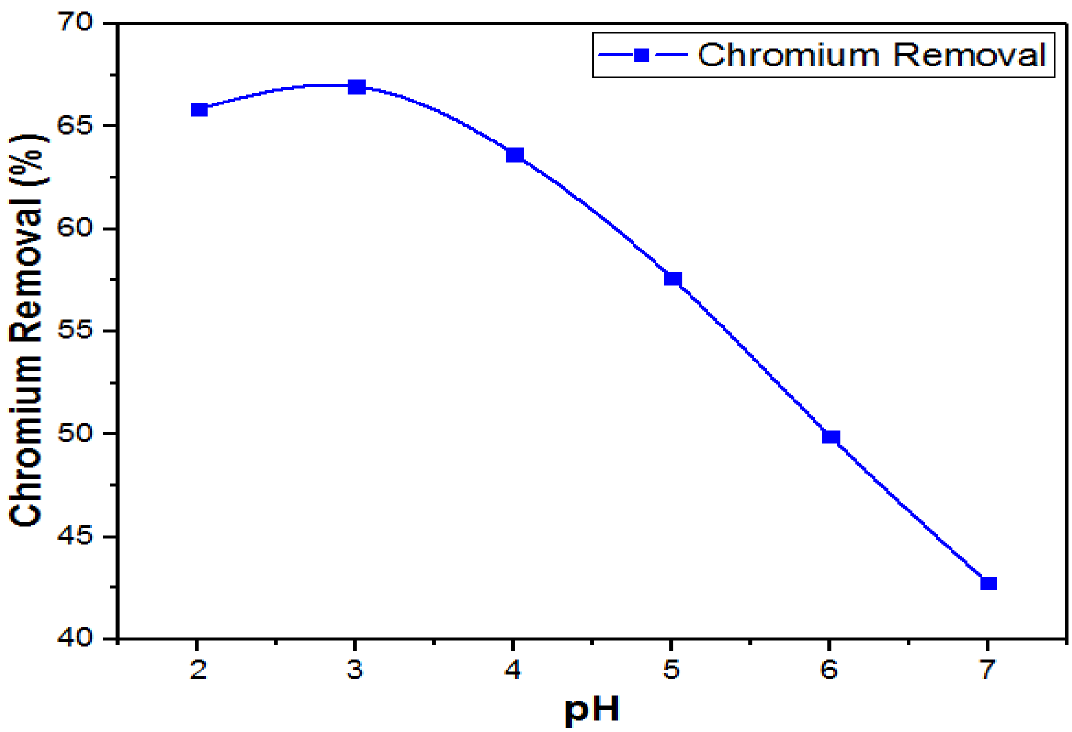



**Fig. 4.10** effect of pH on removal of Cr (vi)

### 4.6.2 Effect of adsorbent dosage on chromium removal

As the adsorbent dosage increases from 2 to 8 mg keeping all the other parameters constant, removal efficiency of Cr (vi) was observed in increasing mode. The number of active sites is higher at lower adsorbent concentration. It was also observed that aggregation of particles take place with higher concentration of adsorbent dosage and due to which the efficiency of Cr (vi) removal was decreased (Li et al., 2007).

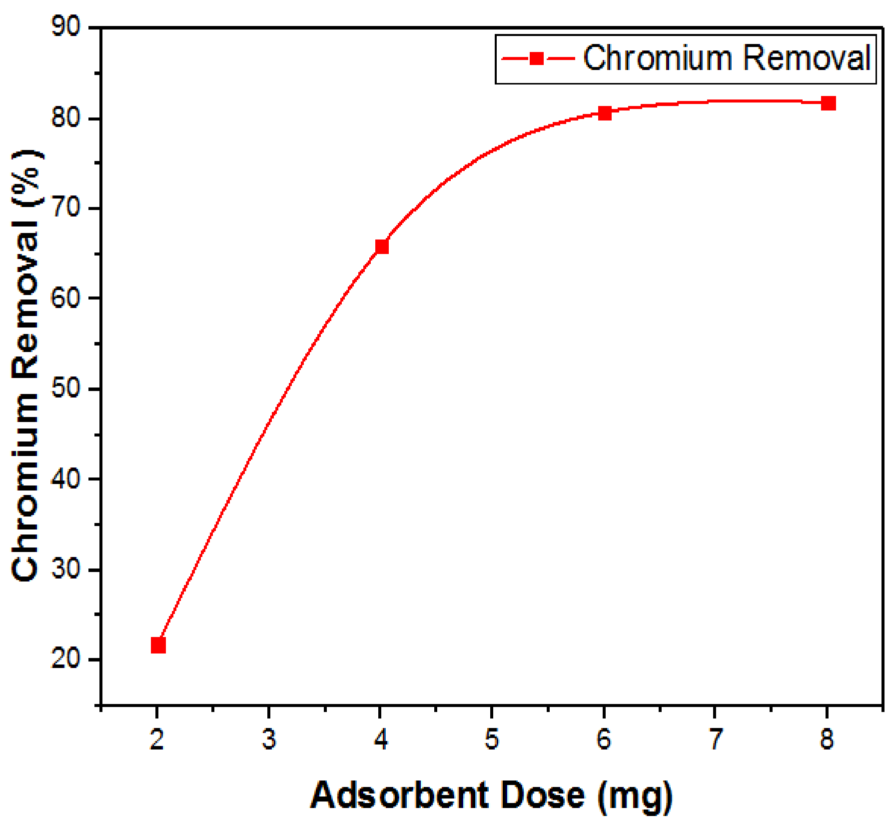



Fig.4.11 Effect of Adsorbent Dosage on removal of Cr (VI) from waste water

### 4.6.3 Effect of contact time

Removal efficiency of Cr (vi) was increased to 81% as time of adsorption is changed from 30 to 200 minutes and afterwards no observable change was occur. The surface coverage of the adsorbent was high as time progresses and furthers no adsorption take place. Fig 4.12 shows the effect of contact time on adsorption process.

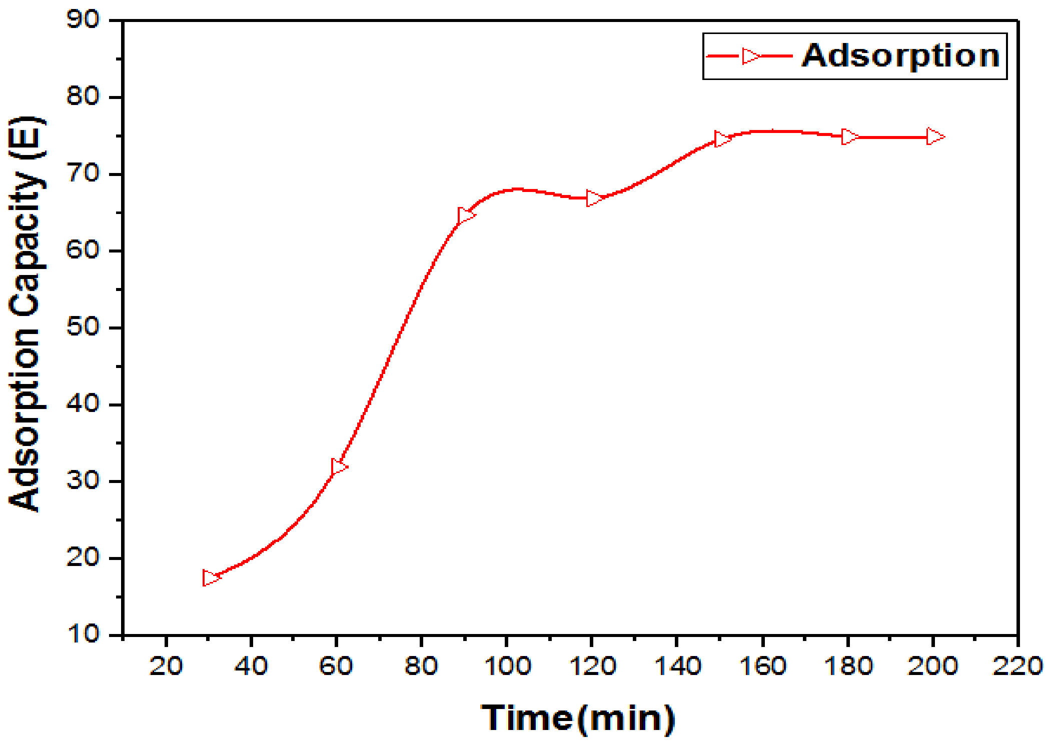



Fig.4.12. Effect of contact time on adsorption of Cr (VI)

# 5 CHAPTER CONCLUSIONS AND RECOMMENDATIONS

## 5.1 Conclusions

**Following are the conclusions drawn from the research done**

1. Poultry waste as a hydrocarbon source was combusted in presence of Ni/Mo/MgO catalyst in electrically heated tube furnace for growth of CNTs. High yield of CNTs was obtained using optimized molar ratio of catalytic precursors.
2. Response Surface Methodology (RSM) was adopted in order to optimize Ni/Mo/MgO mole ratio. 44.1% of CNTs were yielded at optimized molar ratio of Ni/Mo/MgO (4:0.2:1) catalyst at 825◦C, 4g poultry litter weight, 100 mg catalyst weight with 12 min of combustion time.
3. The synthesized CNTs were used in wastewater treatment for removal of Cr (vi) because MWCNTs exhibited excellent adsorption properties. Adsorption efficiency by MWCNTs was increased with high adsorbent dosage, but the equilibrium adsorption capacity decreased considerably.
4. As the pH value was increased the adsorption capacity was found to decrease. Adsorption of Cr(vi) from synthetic wastewater by synthesized MWCNTs was 81%

## 5.2 Recommendations

1. Despite the high surface area CNTs can be used as adsorbent material for other heavy metals i.e $Pb^{+}$ , $Cd^{+}$, $Ni^{+}$ & $Hg^{+}$.
2. Synthesis of CNT/SiC composite are also recommended for enhancing the strength of adhesive.
3. Synthesis of CMC/PVA/CNT composite membrane can be prepared for desalination and industrial wastewater treatment.

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