Exploring the removal efficiency of metal oxide/MWCNTs for heavy metals in soil

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Heavy metal

Soid

Bioremediation

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بسم الله الرحمن الرحيم

In the name of ALLAH, the Beneficent, the Merciful

Read (Proclaim!!) In The Name of your Lord who created

created man, out of a clot (of congealed blood) Read (Proclaim), and your lord is the Most Generous,

Who taught by the pen,

Taught man that which he knew not

Exploring the removal efficiency of metal oxide/MWCNTs for heavy metals in soil

Sidra Ehsan

198-FBAS/MSES/S14

A thesis submitted in partial fulfillment of the requirement for
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Supervisor

Dr. Maliha Asma

Final Approval

Title of the Thesis: Exploring the removal efficiency of metal oxide/MWCNTs for heavy metals in soil

It is certificate that we have read the thesis submitted by Ms. Sidra Ehsan and it is our judgment that this project is of sufficient standard to warrant its acceptance by the International Islamic University, Islamabad for the Master Degree in Environmental Sciences.

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Forwarding Sheet

A thesis entitled "Exploring the removal efficiency of metal oxide/MWCNTs for heavy metals in soil" by Sidra Ehsan in partial fulfillment of MS in Environmental Sciences has been completed under my guidance and supervision. I am satisfied with the quality of student's research work and allow her to thesis, for further processes per IIU rules and regulations.

Dr. Maliha Asma
Assistant Professor
Chairperson DES

Dr. Maliha Asma

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May ALLAH bless all the above and help them in both the worlds AAMEEN

Sidra

(Sidra Ehsan)

I would like to dedicated my thesis to my respectable Parents, who made my dreams successful.

And

My Dearest *Amina Anser*

List of Abbreviation

CNTs	Carbon Nanotubes
MO	Metal oxides
CVD	Chemical Vapour Depsition
SWNTs	Single Walled Carbon Nanotubes
DWNTs	Double Walled Carbon Nanotubes
MWNTs	Multi Walled Carbon Nanotubes
NPs	Nano Particles
SEM	Scanning Electron Microscopy
XRD	X-Ray Diffraction analysis
TEM	Transmission Electron microscopy
VSM	Vibrating sample magnetometry
BET	Brunauer Emmett Teller
EDX	Energy Dispersive X-Ray
EDS	Energy Dispersive X-Ray Spectroscopy
FTIR	Fourier Transform-Infrared Spectroscopy
IR	Infra Red
FESEM	Field Emission Scanning Electron Microscopy
PSD	Position Sensitive Device

CNFs	Carbo Nanofibers
FAAS	Flame Atomic Adsorption Spectroscopy
Zn	Zinc
Pb	Lead
Ni	Nickle
Cd	Cadmium
Cu	Copper
As	Arsenic
mg/ L^{-1}	Milli Gram
$\mu g/L^{-1}$	Micro Gram
L	Litter
M	Molarity
DD Water	Double Distilled Water
CuO	Copper Oxide nano Particles
ZnO	Zinc Oxide Nano Particles
F_e3O_4	Magnetic Iron Oxide Nano Partcles
TiO_2	Titanium Dioxide Nano Particles
$TiCl_4$	Titanium Tetrachloride
HCl	Hydrochloric Acid
NaOH	Sodium Hydroxide
CH_3COOH	Glacial Acetic Acid

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1-Introduction

1.1-Background

Soil is very important for a country because it plays very vital role in the economy of a country. The growth of agricultural and horticulture crops is the best function of soil. Soil is also essential for maintaining the natural and semi-natural vegetation, forests, and grasslands. Soil itself consist millions of nutrients which are important for living organisms.

But soil ecosystems are contaminated with heavy metals by human-induced activities (Naidu et al., 1996, Younas & Shahzad, 1998). A lethal concentration of heavy metals is not known in agricultural soils; however, land dumping of wastes as soil amendments for crop fabrication is liable for sequential accretion of heavy metals in soil (Nriagu & Pacyna, 1988, Shahzad and Younas, 1998).

Soils is infected in the environment with a number of heavy metals by expected (weathering and erosion of parent rock material or ore deposits) or imitation (wastewater irrigation, mining activities) sources. The existence of one toxin can increase or decrease the impacts of others. To date, bulk of studies have paying attention to the effects of a single metal on plant species (Cao.H.et.al,2009 and He. J.Y.et.al,2008). However, the mixture of heavy metals for the study of plant requires more concentration throughout the world.

The heavy metals such as Cu, Ni, Zn are necessary nutrients for soil but in safe limit, when crossed this safe limit caused deceases. Arsenic is very toxic in rare quantity. In the agricultural areas these metals in soil may also be ingested to human body through soil-crop system (Wei B. et.al 2010). Due to their contribution in earth crust Heavy metals are a part of the environment. On the other hand the emission of heavy metals resulting through anthropogenic activities in the form of fine particulates pollute the environment not only itself but also change the chemical composition of the aerosols present in the atmospheric environment. The anthropogenic activities like industries, building deteriorations, factories, foundries, combustions, traffic sources, smelters, mining activities, and constructions contribute to heavy metal pollution in air.(Abbasi M.N. et.al 2013)

The following table shows the safe limit of above heavy metals and their deceases.(Níquel,2005)

Name of metals	**Safe intake limit**	**Human health effects**
Nickle	< 1 mg/day	Chronic bronchitis, reduced lung function, and cancer of the lung and nasal sinus.
Arsenic	15 – 25 µg/day (adults)	Pigmentation changes, skin lesions and hard patches on the palms and soles of the feet, skin cancer, cancers of the bladder and lungs.
Lead	20 - 280 micro g/day (adults), 10 – 275 µg/day children	Anaemia, hypertension, renal impairment, immunotoxicity and toxicity to the reproductive organs.
Zinc	15 µg/day	Stomach cramps, skin irritations, vomiting, nausea and anaemia, respiratory disorders.

Table 1:Safe limit and health effects of heavy metals

1.2-Sources of heavy metal contamination

The following are the major sources of soil contamination with heavy metals.

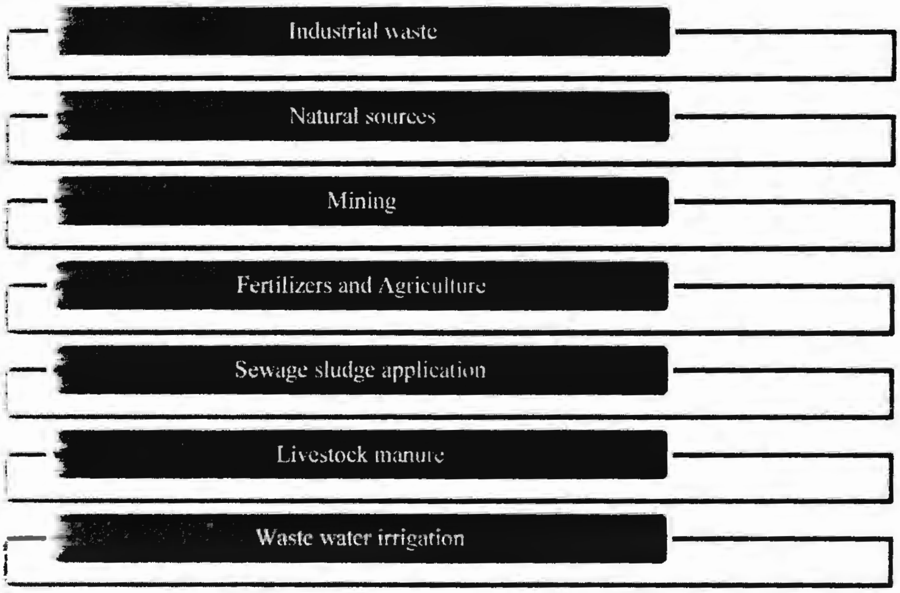

Figure 1:Flow chart of heavy metals sources

Most of industrial waste consist on harmfull heavy meals such as(Pb,Ni,Cu,Zn,Cd,Co,Mn,As etc) all these heavy metals dangerous in large amount. Therefore industrial areas polluted with all these heavy metals because all these heavy metals are present with high concentration in the soil of these areas.

The parent materials are the the primary sources of heavy metals in soils from which the soils were derivative, but on the total concentrations of parent materials and forms of metals in soils is personalized to unreliable degrees (Herawati et al., 2000). In areas pretentious lightly by human activities, heavy metals in the soils derivative mainly from pedogenetic parent materials, and metals accrual status was pretentious by numerous factors such as soil moisture and management patterns.

There are different sources of metal pollution in mining areas, including grinding, absorbed ores and tailings disposal (Wang et al., 2004; Adriano, 1986). The agricultural fields could pollute surrounding the mining areas from acid mine due to unsuitable treatment of these tailings and drainage.(Willians et al., 2009)

Heavy metals enter into arable soils through fertilizers courses for increasing their potential risk to environmental health. The phosphate fertilizers were generally the major source of trace metals along with all inorganic fertilizers, and much concentration had also been remunerated to the Cd concentration in phosphate fertilizers.(Lu et al. 1992)

While the stuffing of toxic metals in sewage sludge had also been patently compact, and the majority of them were below the national expulsion usual of pollutants for municipal wastewater treatment plants, due to the vast increase in the amount of wastewater treated, the sewage sludge formed increased rapidly.

People's demand for meat, eggs and dairy raised tremendously over the ancient times , due to their living standard going up constantly. Heavy metals are existing in livestock fodders as additives for health and valuable reasons. Take As for example, it had been used as feed preservative for pig and poultry diseases control and augmentation enhancement (Li and Chen, 2005).

A common practice of irrigation and wastewater disposal of domestic and industrial effluents in pakistan is its application to nearby agricultural fields.(Lone *et al.*, 2000; Ensink *et al.*, 2004) after application of heavy metals contaminated water, metals get fixed to the soil components. Thus continuous use of wastewater for irrigation increase large quantities of metals to toxic level, and tend to persists there for an indefinite period to have long lasting effects in the soil environment (Kabata-Pendias and Pendias, 2002).

1.3- Remediation technologies for soil contaminated by heavy metals

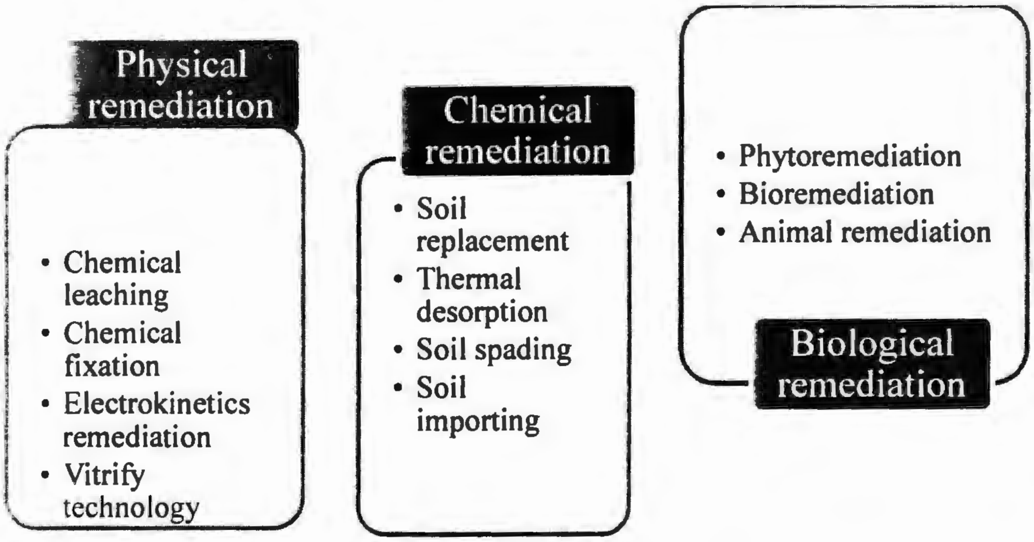

Figure 2:List of Remediation technologies

1.4-Objectives

The main objective of present study are as following:

- To synthesize and characterized iron oxide, Copper oxide, and zinc oxide nano particles.
- To synthesize and characterized iron oxide/MWCNTs composite.
- To find a highly efficient nanomaterial for the adsorption of heavy metal in soil.

2-Literature review

2.1-soil contamination issues

Industry is the moral fiber of a country for its improvement and with the emergent population, the need for establishing new industries is increasing. Industries on one side invent useful products but on the other side time generates waste products, causing various environmental problems. The waste products may be in the form of solid, liquid or gas which lead to the creation of hazards, pollution and losses of energy. The wastes containing different pollutants and heavy metals are discharged into water and soil and ultimately pose a serious peril to human and ecosystem. By-products of different industries like textile, metal, dying chemicals, fertilizers, pesticides, cement, petrochemical, energy and power, leather, sugar processing, construction, steel, engineering and food processing industries are the main contributors to the soil pollution. So the hurried industrialization is accompanied by both direct and indirect adverse effects on environment (Amin, N., 2013). Industrial improvement may result in the generation of industrial effluents. It has been studied that many industries discharge crude effluents into river and only 10% industries surveyed had primary treatment ranging from oxidation tanks, sedimentation tanks in developing countries. (Amin.N.et.al, 2009 and Ali.K.et.al,2008)

Because of the hurried industrialization, soil pollution by heavy metals is becoming a serious problem. Being an crucial sink for industrial wastes, almost all industrial wastes are dumped into soil. Heavy metals in wastes find specific adsorption sites in soil where they are retained relatively stronger either on inorganic or organic colloids(Zhang, C.S.et.al,2006 and Cui, Y.J.et.al,2004). Research has verified that long term use of sewage effluent for irrigation contaminates soil and crops to such an extent that it becomes toxic to plants and causes corrosion of soil. This contains extensive amount of potentially harmful substances including soluble salts like Fe2+, Cu2+, Zn2+, Mn2+, Ni2+ and Pb2+. Additions of these heavy metals are unwanted.

Pakistan is an agrarian county with high population growth. Soils are intensively cropped to meet the increasing demand for food production. However, soils of Pakistan are essentially low in productiveness to support monetary crop fabrication (Rashid, 1993, Jamal *et al.*, 2002). Due to high cost and shortage of chemical fertilizers, the land dumping of agricultural, municipal and industrial wastes is broadly adept as a main and monetary source of nutrients and natural matter for growing cereal crops by poor farmers in Pakistan (Rashid, 1993, Younas & Shahzad, 1998, Jamal *et al.*, 2002). The ravage creation in Pakistan has increased by 120% between 1980 and 1996 with a total of 16.2 TG generated in 1995 (Younas & Shahzad, 1998). The most reported heavy metals in waste amended farming soils are Cu, Pb and Zn (Nriagu & Pacyna, 1988, Younas & Shahzad, 1998, Jamal *et al.*, 2002).

Heavy metal contagion of soil due to tannery waste is a wide-reaching problem (D. Alvarez-Bernal,2006 and S. S. Gowd,2010). Many chemicals, such as NaCl, H_2SO_4, $Ca(OH)_2$, and $Cr_2(SO_4)_3$, are broadly used during leather dispensation. As a outcome, wastewater from leather industry is enriched with chromium and sodium. Extensive discharges of chromium enriched sewage from leather industries has resulted in chromium-contaminated soil and at fabrication sites, which are a cruel menace to human health (S. R. Tariq,2005 and L. Shakir,2011). Leather dispensation is an important industrial activity in Pakistan, where more than 600 tanneries are resolute in three major cities (Kasur, Karachi, and Sialkot). Waste release from leather industries pollutes the air, soil, and water, causing serious health problems. The most cruelly pretentious area is around Kasur, which has the highest number of tanneries in the country. These are discharging about nine million liter of highly grimy wastewater daily, however, required working health principles, safety from disclosure to destructive chemicals and defense at the work place are not measured. Currently, improved environmental pollution due to leather industry is badly disturbing local population health situation. Different diseases such as respiratory disorders, lung infection, diarrhea/dysentery, and typhoid are commonly reported in the local population of Kasur (S. R. Tariq,2005 and M. Syed, T. Saleem,2010).

A large number of small-scale leather industries located in Pakistan have no admittance to wastewater treatment amenities and thus expulsion their waste into open fields or ditches (R. Ullah,et.al 2009 and R. N. Malik,et.al 2010). Large areas of land in the surrounding area of Kasur have become unfeasible for agriculture due to infectivity with heavy metals (F. Bareen, S. A. Tahira, 2010 and F. Bareen, S. A. Tahira, 2011).

2.2.3-Lead

Lead is omnipresent in developed societies, and indication of the harmful affects of Pb on humans has been noted for centuries. Due to similar chemical properties, human body confuses Pb with calcium when ingested and incorporates it into the bone marrow, nerve tissue, brain, and kidneys. The body does not decay Pb into another, more easily tolerated material as it is an element. Lead poses a exclusive hazard to developing minds and learning capacities of infantile children. Children can be bare from eating Pb-based paint chips or playing in contaminated soil. Lead can damage the nervous system, kidneys, and reproductive system. (Yasir Faiz ,2009)

2.2.4-Copper

Copper occurs physically in elemental form and as a part of many minerals. Copper is an vital trace element that is broadly dispersed in the environment. basic Cu does not break down in the environment. Copper can be initiate in plants and animals, in many foods and beverages, including drinking water. Acute gasp exposure to Cu dust or fumes at concentrations of 0.075-0.12 mg m−3 may cause metal fume fever with symptoms such as cough, chills and muscle ache (US Air Force,1990). The suggested safe and tolerable dietary intake for Cu is 1.5-3.0 mg d-1 for adults, 0.7-2.5 mg d-1 for children and teenagers, and 0.4-0.7 mg d-1 for infants.(US Air Force,1990)

2.2.5-Cadmium

Cadmium is a moderately exceptional heavy metal, which occurs physically in amalgamation with other metals. The gasp exposure to Cd can occur from road dust. After gasp, the amalgamation of Cd compounds may fluctuate greatly depending upon the particle sizes and their solubility. Cadmium is a metal, which can cause rigorous toxicity in humans. Prolonged contact to Cd can distress a diversity of organs with the kidney being the principal target. (Yasir Faiz ,2009)

2.3-Methods for removal of heavy metals

2.3.1-Physical remediation

The physical remediation generally consist on:

- **Soil replacement method**

The soil replacement means using clean soil to substitute the infected soil with endeavor of dilute the contaminant absorption, increase the soil environmental capability, and thus remediate the soil (Qian SQ,et.al 2000 and Zhang YF,et.al 2004). Soil replacement is removing the infected soil and putting into new soil. This method is appropriate for infected soil with small area. Moreover, the replaced soil should be treated credibly, or else it will acquire the second pollution.

- **Soil spading**

Soil spading is deeply digging the infected soil, making the contaminant multiply into the deep sites and achieving the endeavor of diluting and physically degrading.

- **Soil importing**

soil importing is adding lots of clean soil into the contaminated soil, covering it at the surface or mixing to make the contaminant concentration decreasing.

- **Thermal desorption**

The thermal desorption is on the basis of pollutant's instability and heat the infected soil using steam, microwave, infrared radiation to make the contaminant (e.g. Hg, As) volatile. The volatile heavy metals are then collected using the vacuum negative pressure or carrier gas and achieve the aim of removing the heavy metals(Li J,et.al 2010). According to the temperatures, the traditional thermal desorption can be classified into high temperature desorption (320~560°C) and low temperature desorption (90~320°C). This technology has advantages of simple process, devices with mobility and the remediated soil being reused.

2.3.2-Chemical remediation

- **Chemical leaching**

Chemical leaching is washing the infected soil using fresh water, reagents, and others fluids or gas (Tampouris S,et.al 2001 and Ou-Yang X,et.al 2010) that can percolate the pollutant from the soil. Trough the following methods used for soil transferred from soil to liquid phase:

- Ions exchange
- Precipitation
- Adsorption
- Chelation

- **Chemical fixation**

Chemical fixation is adding reagents or materials into the infected soil and using them with heavy metals to form insoluble or hardly movable, low toxic matters, thus decreasing the migration of heavy metals to water, plant and other environmental media and achieving the remediation of soil (Zhou DM,et,al 2004). The soil conditioning materials used include clays, metallic oxides, biomaterials, etc.

- **Electrokinetic remediation**

Electrokinetic remediation is a new remediation technology (Luo QS,et.al 2004), which is generally applying energy at the two sides of soil and then forming electric field gradient. The contaminant was conceded to two poles treatment room via electromigration, electroosmotic flow or electrophoresis and then treated further (Acar YB,1993 and Swartzbaugh JT,et.al 1990). It is appropriate for low permeable soil, and has recompense of easily install and operate, low cost (Virkutyte J,et.al 2002 and Xu Q,et.al 2006) and not destroy the original nature environment (Alshawabkeh AN,et.al 2000 and Zhang XH,et.al 2001), so can achieve the environmental remediation and protect the original ecotope.(Luo QS,et.al 2004)

- **Vitrify technology**

Vitrify technology is heating the soil at temperature of 1400~2000°C, in which process the organic matters volatilize or decompose. The steam produced and pyrolysis product was collected by off-gas treatment system. The melt after cooling forms rock shape vitreous, sieges the heavy metals and make it lose migration. It was reported that the strength of the vitreous is high 10 times than concrete.

2.3.3-Bioremediation

- **Phytoextraction**

Phytoextraction is adsorbing the heavy metals using forbearing and accumulating plants, and then transferring, storing at the overground parts.

- **Phytoremediation**

The phytoremediation is the use of living green plants to fix or adsorb pollutants, and cleaning the pollutants or making their risk decrease or disappearance.

- **Phytostabilization**

Phytostabilization is fixing heavy metals by plants through the adsorption, precipitation and reduction of root, and thus reducing their migration and bioavailability and preventing them migrating into the groundwater and food chain. (Wang HF,et.al 2009)

- **Phytovolatilization**

Phytovolatilization is transferring the heavy metals into volatile state.

- **Biological remediation**

The microorganisms can not degrade and destroy the heavy metals, but can affect the migration and transformation through changing their physical and chemical characterizations. The remediation mechanisms include:

- Extracellular complexation,
- Precipitation
- Oxidation-reduction reaction
- Intracellular accumulation
- Microbial leaching

- **Animal remediation**

Animal remediation is according to the characterization of some lower animals adsorbing heavy metals, degrading, migrating the heavy metals and thus removing and inhibiting their toxity.

2.4-Present research field

The aim of present study is to remediation of contaminated soil. The advance technique which is used for this purpose is nanotechnology. Nanotechnology is a field of functional science, focused on the design, synthesis, characterization and application of materials and devices on the nanoscale. The sub-classification of this technology is:

- Chemistry
- Biology
- Colloidal science
- Physics

and other scientific fields and involves the study of phenomena and exploitation of materials in the nanoscale (G.A. Mansoori,et.al,2005 and Washington D.C.et.al,2001). The nano materials which are used mostly in nano technology are CNTs,nano fiber, nano cell, metal oxides nano particles, nano membrane, nano wires, nano crystals etc.

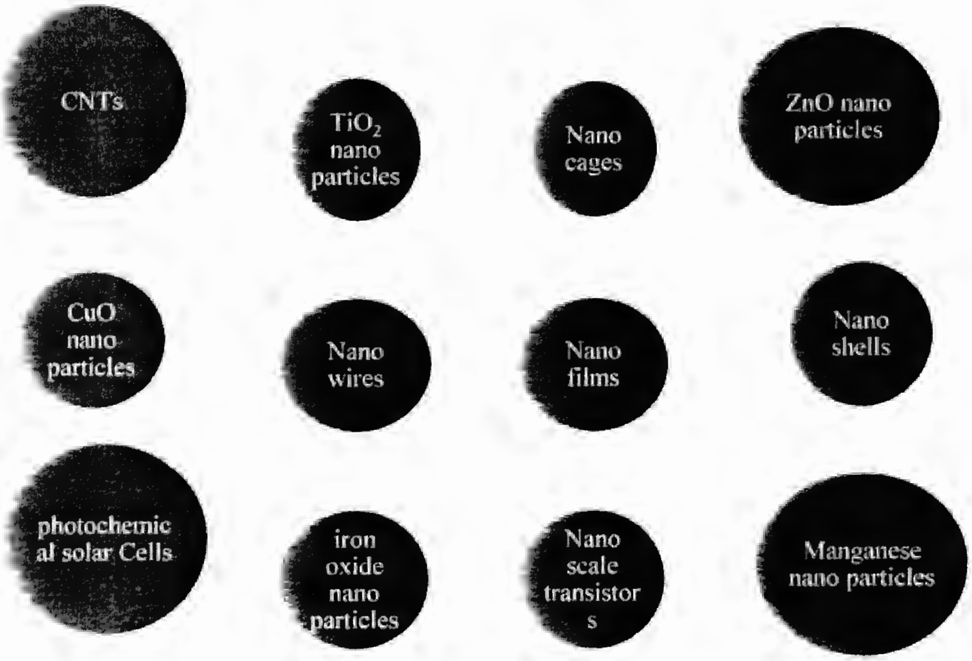

Figure 3: List of Nano material

2.4.1-Advantages of Nnao material

The advantages of these nano material are:

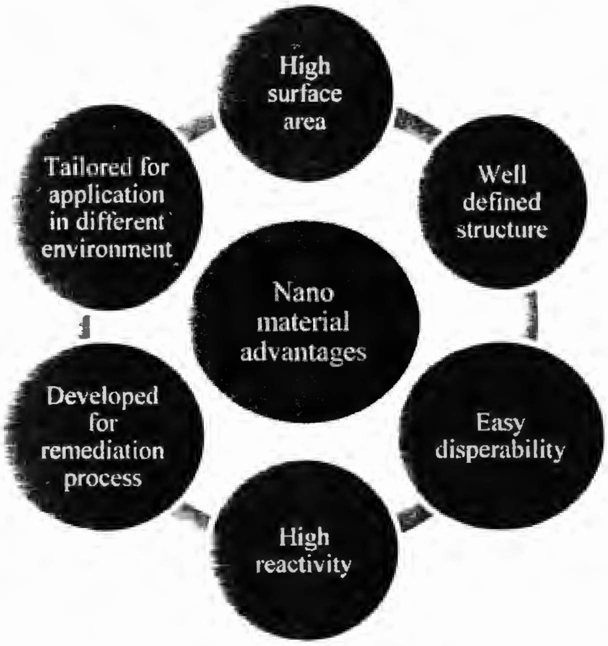

Figure 4:Flow chart of Nano material Advantages

2.4.2-Synthesis Strategy

The structure of carbon nanotubes/metal oxide (CNT/MO) composites is both of basic and scientific interest because the composite combines the exceptional properties of CNTs and metal oxide nanoparticles, and adding up show some new strange properties caused by the interface between them (Eder, D. , 2010); Chu, et al., 2010). Thus, a new class of nanocomposites can be made with strange properties meeting a wide range of applications in different disciplines. For example, alumina is one of the most widely used ceramic materials because of its high hardness, good oxidation resistance and chemical stability. However, its applications are limited because of its low fracture stiffness. CNTs have been widely used to reinforce and increase the fracture toughness of alumina owing to their unique one dimensional structure with robust mechanical and thermal properties.(Chan, et al., 2005)

Various approaches are used to synthesize CNT/MOs composites. This includes hot pressing of composite powder, pressureless sintering technique, direct in-situ growth, in situ CVD synthesis route, high-intensity ultrasonic radiation method, assembling presynthesized metal oxide nanoparticels as building blocks on CNTs, spontaneous formation of metal oxide nanoparticels on CNTs, thermal decomposition of metal oxides precursor directly onto the surface of carbon nanotube, hydrothermal crystallization, sol–gel followed by spark plasma sintering process, surfactant wrapping sol–gel method, chemical precipitation and controlled heteroaggregation method (Liu et al., 2009; Zhang et al., 2010; Keshri et al., 2010; Datye et al., 2010; Zhen et al., 2007; Flahaut et al., 2000; Lupo et al., 2004; Gupta et al., 2011; Zhang et al., 2006; Gao et al., 2008; Chan et al., 2005; Yang et al., 2009; Estili and Kawasaki, 2008).

2.4.3-Functionalization of CNTs

Activation or functionalization of CNTs by oxidation treatment introduces chemical functional groups. It can be performed using oxidizing agents such as nitric acid, sulfuric acid, a mixture of sulfuric acid and nitric acid, potassium permanganate, sulfuric acid in presence of potassium permanganate, hydrogen peroxide in presence of nitric acid, hydrogen peroxide, ozone, an oxygen-based atmosphere by an inductively coupled plasma or microwave energy and water (Cuentas-Gallegos et al., 2006; Wang et al., 2009; Smith et al., 2009; Lu et al., 2008; Otvos et al., 2006; Aviles et al., 2009; Haydar et al., 2000; Peng et al., 2011; Ionescu et al., 2006; Hojati-Talemi & Simon, 2009). Treatment with different oxidizing agents might introduce different functional groups on the CNTs surface including alcoholic, carboxylic, aldehydic, ketonic, and esteric oxygenated functional groups, see Fig.1. Hydroxyl groups (b) on the edge of nanotube could be of phenolic character. Oxygen could be substituted for edge carbon atoms in xanthene- or ether-type (d). Carboxyl groups (a) might give carboxylic anhydrides (e) if they are close together. Also, carbonyl groups might condense to lactone groups (f) or form lactols (g) if they are in close to hydroxyl groups or carboxyl groups. The existence of carbonyl groups could be isolated (c) or arranged in quinone-like structure (h). The groups (a, b, e f, and g) have weak acidic character. The acidity of o-CNTs can be determined by acid-base titration method or Boehm titration (Boehm, 1994).

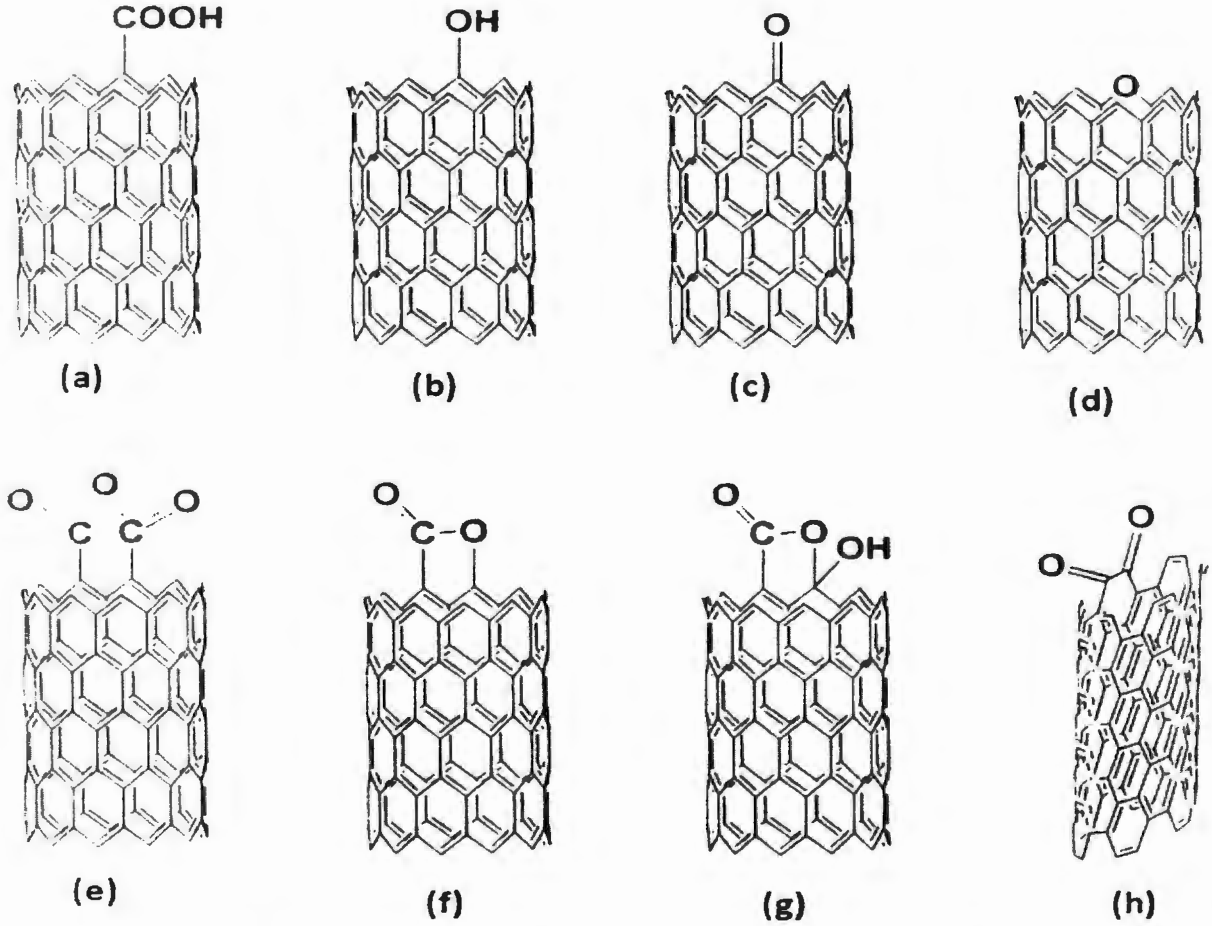

Figure 5: **Possible structures of oxygen-containing groups on the carbon nanotube surface**

2.4.4-Structure and Types of Carbon Nanotubes

To understand the crystal structure of CNTs, it is necessary to understand their atomic structure. CNTs are also classified to single-walled (SWNT), double-walled (DWNT), and multiwalled CNTs (MWNT) as presented in Fig. 2.3. The structure of SWNT can be conceptualized by wrapping a one-atom-thick layer of graphene into a seamless cylinder (Majumder et al. 2011c). MWNT consists of two or more numbers of rolled-up concentric layers of graphene. DWNT is considered as a special type of MWNT wherein only two concentrically rolled up graphene sheets are present. There are two models to describe the structures of MWNT.

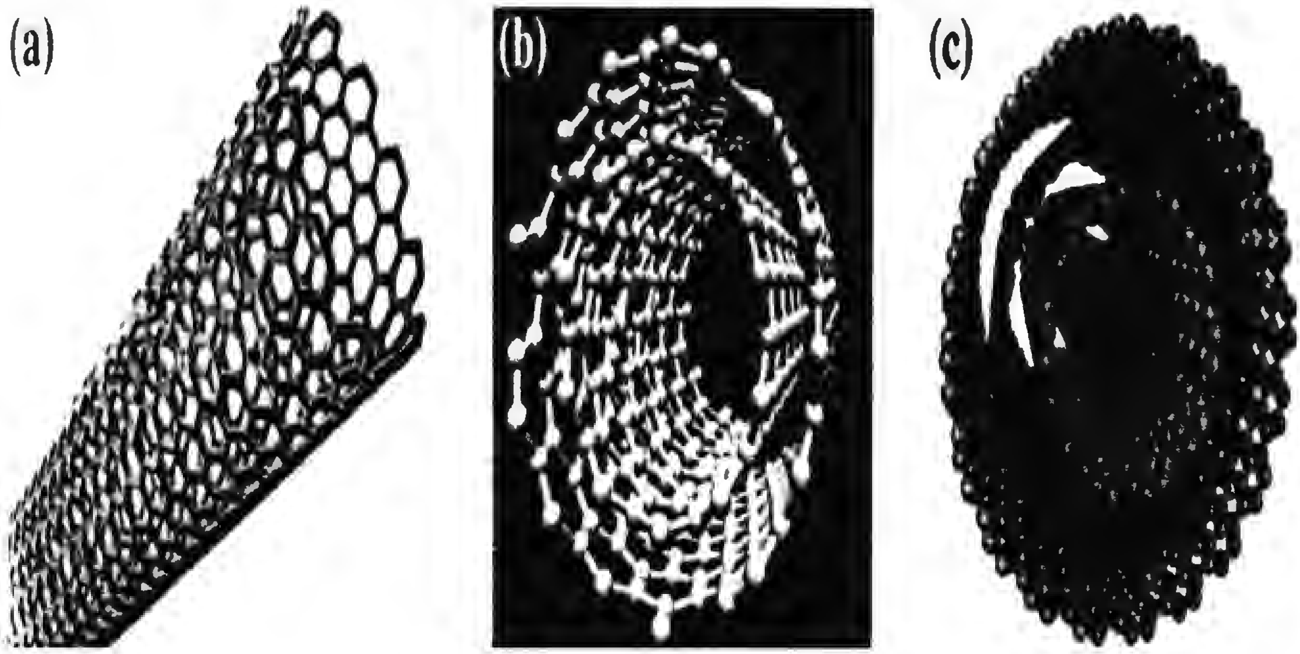

Figure 6:Structure of CNTs

2.5-Precious research work

The following table are some about previous research work of Fe_3O_4 NPs/ZnO NPs/CuO NPs/TiO_2 NPs/CNTs.

Iron Oxide Nano Particles

Sr.no	Nano material	Characterisation technologies	Applications	Refrences
1.	CNTs/Fe_2O_3 NPs	SEM,XRD	Pb(II) and Cu(II	Xianjia, et.al 2004
2.	Double scalled CNTs/Fe_2O_3 NPs	SEM,TEM, XRD,BET	Cd(II)	Hadj,et.al 2013
3.	Fe3O4 NPs	SEM,TEM,FTIR,BET	Pb(II),Cu(II),Zn (II),Mn(II)	Liliana, et.al 2013

4.	MWCNTs/Fe_2O_3	SEM,XRD,VSM	Ni(II),Sr(II)	Changlun,et.al 2009
5.	Fe_2O_3 NPs	SEM,TEM	Cu(II),Cd(II),Ni(II)	Shahlaa, et.al 2015
6.	Fe_2O_3 NPs	SEM,EDX	Al(III),As(III), Cd(II),Cd(II), Cu(II),Ni(II).	K.A,et.al 2012
7.	Fe_2O_3 NPs	TEM	As(V),Cu(II)	Sai.et.al 2013
8.	Fe_2O_3 NPs	-----	Cu(II),Pb(II),Cr(VI),As(V),Hg(II),Ni(II)	Piao,et.al 2012
9.	Fe_2O_3 NPs/ Carrier oils	SEM,TEM, XRD,FT-IR	Cu(II),Cr(II),Ni(II)	K.L,et.al 2013
10.	Fe_2O_3 NPs	SEM,EDX,XRD,VSM	Zn(II),Ni(II),Cu(II)	Naim,et.al 2013
11.	Fe_2O_3 NPs	-----	Pb(II)	Zuolian, et.al 2012
12.	Fe_2O_3 NPs	BET,CCRD	Cr(VI)	Nirmala, et.al 2014
13.	Fe_2O_3 NPs/ Talc	SEM,XRD,TEM,BET,EDX	Cu(II),Ni(II),Pb(II)	Katayoon et.al 2014
14.	Fe_2O_3 NPs/ Alumina	SEM,FTIR,IR-spectroscopic,XRD	Cd(II)	Mona,et.al 2013

Table 2: Iron Oxide Nano Particles

Zinc Oxide Naon Particles

Sr.no	Nano material	Characterisation technologies	Applications	Refrences
1.	ZnO NPs/ Urea formaldehyde	SEM,FTIR,IR-spectroscopic,XRD	Cu(II)	Neeta,et.al 2015
2.	ZnO hollow microspheres/nanosheets	FESEM,XRD,TEM	Cd(II),Ni(II)	Xianbiao et.al 2013
3.	ZnO NPs/ Guar Gum	SEM,TEM,FTIR	Cr(VI)	Tabrez et.al 2013
4.	Indium ZnO NPs	SEM,TEM,XRD	Cr(VI),Cd(II),Ni(II)	Imed ghiloufi
5.	CuO,ZnO and Fe3O4 NPs	SEM,TEM,XRD,EDX	Cd(II),Cu(II),Ni(II),Pb(II)	Shahriar et.al 2012

Table 3:Zinc Oxide Nano Particles

Copper Oxide Nano Particles

Sr.no	Nano material	Characterisation technologies	Applications	Refrences
1.	CuO nano structure	XRD,BET,TEM	Pb(II)	A.A.Farg et.al 2013

Table 4: CuO Nano Particles

Titanium Oxide Nano Particles

Sr.no	Nano material	Characterisation technologies	Applications	Refrences
1.	TiO_2/Montmorillonite–kaolinite	SEM,XRD,PSD	Pb(II),Cu(II),Cd(II),Zn(II)	Anđelka et.al 2015
2.	TiO_2 NPs	-----	Pb(II),Cd(II),Cu(II),Zn(II),Ni(II)	Engates et.al 2011
3.	Nano structured Titanium(IV) oxide	-----	Cu(II),Cd(II)	Sushanta et.al 2011

4.	TiO_2film	-----	Cr(VI)	Quanpinget .al 2013
5.	TiO_2Nanowire	TEM,SEM,XRD	Pb(II),Cu(II), Fe(II),Cd(II), Zn(II)	Ahmed et.al 2014
6.	TiO^2,MgO,$Al2O^3$Na NPs	SEM,EDX,TEM,XRD, BET	Cd(II),Cu(II) ,Ni(II),Pb(II)	Shahriar et.al 2013

Table 5: Titanium Oxide Nano Particles

Carbon Nano Tubes

Sr. no	Nano Material	Characterisation Technologies	Applications	Refrences
1.	MWCNTs	SEM,TEM,FT-IR	Cu(II)	Yu,et.al 2014
2.	MWCNTs	IR-spectra,TEM	Cu(II)	Iman,et.al 2014
3.	CNTs	SEM,TEM,FTIR,Raman spectra	Zn(II)	Chungsyig et.al 2006
4.	Functionalized CNFs/Carboxylic Function Group	SEM,TEM,FTIR	Zn(II)	Muataz et.al 2011
5.	CNTs/Nanocages	-----	Cd(II),Cu(II) ,Ni(II),Pb(II), Zn(II)	Saksham et.al 2013
6.	MWCNTs	-----	Cu(II),Cd(II) ,Pb(II)	Yan,et.al 2003
7.	MWCNTs	SEM,TEM,GTIR,BET	Cu(II)	Soheil et.al 2015
8.	CNTs/activated	FESEM,EDS	Cr(VI)	Muataz Ali

	carbon			et.al 2011
9.	CNTs	SEM,BET	Pb(II),Ni(II), Cd(II),Zn(II)	Ashish et.al 2014
10.	CNTs	SEM,TEM	Pb(II),Cu(II), Cd(II),Zn(II), Co(II)	Maryam et.al 2011
11.	CNTs	-----	Pb(II)	Yan-Hui et.al 2005
12.	Carbon and Iron Based Particles	Differential pulse voltammetry	Pb(II),Cu(II), Cd(II)	Dana,et.al 2014

Table 6: Carbon Nano Tubes

Multiwall CNTs (MWNT) are the main subject in the development of the technology of ordered CNT arrays on various substrates. Ideal geometry of MWNT was obtained and optimized with respect to potential energy minima. Interlayer distance in MWNT is close to interplane graphite distance 3.4 Å and varies in the ±0.2 Å domain. Then two-atomic molecules can not penetrate into the MWNT wall and adsorption takes place at the external surface of MWNT. Dependence of adsorption energy on number of MWNT layers is weak. CNT functionalization by grafting of molecular fragments is based on the ability of their peripheral atoms to create chemical bonds with CNT carbon atoms which transform their hybridization state from sp2 to sp3 . It is necessary to mark that aromatic type of bonds in CNT during that process transforms to alternating single and double bonds at the essential part of CNT.

3-Materials and Methods

3.1-Reagents and Materials

No.	The Material	Purity	The Supplier
1	Carbon Nanotubes (CNTs)	99.0%	Daejung Korea
2	Zinc Acetate Dihydrated	98.0%	Sigma Aldrich
3	Copper Acetate	99%	Merck
4	Lead Nitrate	97%	Merck
5	Ethanol	99.8% (Analar)	BDH
6	Ammonia solution	25-30% GR	Daejung Korea
7	Hydrochloric acid	65-69%	Daejung Korea
8	Nitric acid	64-66%	Sigma Aldrich
9	Acetic Acid	100%	Sigma Aldrich
10	Sodium hydroxide	99.0-100%	Merck
11	Feric Chloride hexahydrated	98%	Daejung Korea
12	Ferrous sulphate	98%	Daejung Korea

Table 7: Reagents and Materials

PHASE I (Synthesis)

3.2-Methdology

3.2.1-Oxidation of MCNTs

For the oxidation of MWCNTs 500 mL nitric acid solution of 3M concentration was prepared. As received MWCNTs (2g) was added into 3M nitric acid solution under stirring at 300 rpm for 24 h. After that MCNTs remain dipped into concentrated nitric acid for 1 h. The reaction mixture was washed with distilled water and filtered through filter paper. Washing of MWCNTs was repeated until pH reached near 6 and followed by drying on hotplate at 150 °C overnight. These oxidized MCNTs was placed in preheated muffle furnace at 450 °C for 4 h.

3.2.2-Synthesis of zinc oxide Nano particles

Zinc oxide Nano particles were prepared by co-precipitation method. For this preparation 2.19g Zinc acetate dihydrated was dissolved in 500ml distilled water under enthusiastic stirring. After this aqueous 2.0M NaOH was added drop wise to reach pH 12. Then placed in a magnetic stirrer for 2hr. When reaction was completed, the white precipitate formed which was washed systematically with distilled water and ethanol for the removal of impurities. Then precipitate was dried on hot plate for 2hr at 200°C. Whole alteration of $Zn(OH)_2$ into ZnO Nano particles took place after drying.

3.2.3-Synthesis of copper oxide Nano particles

CuO NPs were prepared by aqueous precipitation method. In this method 24g(0.2 M) copper (II) acetate and 2ml glacial acetic acid (CH_3COOH) was dissolved in 600ml distilled water added into a round-bottomed flask and heated under magnetic stirring till boiling. When solution was boiled, then 30 mL of 6 M NaOH solution poured into the flask. After this process the colour of the solution turned from blue to black instantaneously, and a black suspension formed concurrently. Then solution was boiled under magnetic stirring for 2 h. after this mixture was cooled at room temperature and centrifuged for 1hr. Then, a wet CuO precipitate was obtained. The precipitates were filtered and washed with distilled water and ethanol for numerous times. The resulting product was dried on hot plate at 80°C for 1h to attain the dry powder of CuO NPs.

3.2.4-Synthesis of CNTs/Fe_3O_4 Nano particles composite

The magnetic composite was prepared by using 1g oxidized MWCNTs in a 150ml solution of 2.98g $FeCl_3 \cdot 6H_2O$ and 1.53g $FeSO_4 \cdot 6H_2O$ at 70^0C under N_2 condition. NaOH solution (30 ml, 0.5 mol L^{-1})was added drop by drop to precipitate iron oxides. When NaOH solution was added, the pH of mixture adjusted to 11 and stirred under magnetic stirrer for 1h. The mixture was ripened at 70^0C for 4h and then washed 3 times with DD water. The obtained material was dried in an oven at 100^0C for 3h.

3.2.9-Preparation of soil sample

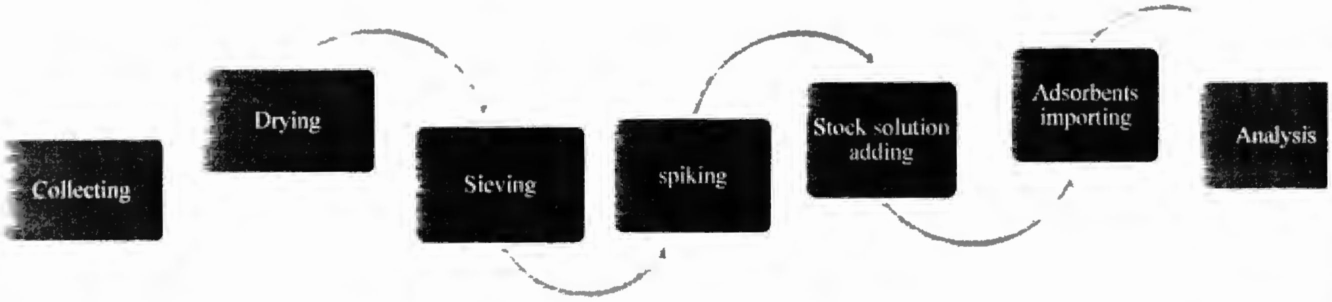

Figure 7:Process of soil sample preparation

- **Sample collection**

The soil sample was collected from local areas. The soil was collected by tapping the filters onto a clean polythene sheet and using a plastic brush to remove the other waste. Sample was stored in clean labeled polyethylene bags and brought to the lab for initial treatment.

- **Sample preparation**

The sample was dried on hot plate at 100^0C for 4 h. When sample was dried completely then it was sieved by using stainless steel sieve obtaining particle size of less than 125 µm. The elemental concentrations of the sample was determined on dry weight basis the moisture contents of the sample. 2–3 g soil was weighed and placed in a labeled glass vial. The vial was placed on hot plate at 200 ^{0}C for 24 h. The vial was removed and reweighed after it had attained room temperature in a desiccator. The difference in the weights provided the moisture content of the samples which was found to range from 0.81 to 0.99%.

- **Soil spiking**

The 500 mg soil was spiked with 0.5 mg/l for Cr(II) and 1mg/l for Pb(II) heavy metal. The spiking time period was 1 week. (Ritu Singh, Virendra Misra, Rana Pratap Singh 2011)

3.3-Characterization of CNTs, ZnO Nano particles, Fe_3O_4, CuO Nanoparticles

3.3.1-Scanning Electron Microscopy (SEM)

The SEM is broadly used to identify phases based on qualitative chemical analysis and crystalline structure. Precise measurement of very small features and objects down to 50 nm in size is also consummate using the SEM. The samples which are used for SEM must be solid and must fit into microscope chamber. The morphology of CNTs, ZnO Nano particles, Fe_3O_4 Nano particles, CuO Nanoparticles was measured by SEM.

3.3.2-Fourier Transform-Infrared Spectroscopy (FTIR)

The adsorption behavior of CNTs, ZnO Nano particles, Fe_3O_4 Nano particles, CuO Nanoparticles was determined by Fourier Transform-Infrared Spectroscopy (FTIR).It is an analytical technique used to identify organic and inorganic materials. This technique measures the absorption of infrared radiation by the sample material versus wavelength. Molecular components and structures are identify by infrared absorption bands.

3.3.3-UV-Vis Spectroscopy

The absorption and wavenumber of CNTs, ZnO Nano particles, Fe_3O_4 Nano particles, CuO Nanoparticles was determined UV-Vis Spectroscopy. The absorption or reflectance in the visible range directly affects the perceived color of the chemicals involved. In this region of the electromagnetic spectrum, molecules undergo electronic transitions. This technique is complementary to fluorescence spectroscopy, in that fluorescence deals with transitions from the excited state to the ground state, while absorption measures transitions from the ground state to the excited state.

3.4-Experimentation

- **Batch adsorption experiments for Iron oxide Nano particles/CNTs composite**

Batch adsorption experiments were performed by using 5mg spiked soil and 30 mg, 40 mg, 50 mg, 60 mg, 70 mg composite was added in 15ml Falcon tubes for each heavy metal ions. The pH of all solutions were maintained at 7. The solution was shaked for 24 h, the metal concentration in the aqueous solutions was determined by atomic absorption spectrophotometer. To study the effects of pH on metal ions adsorption.The initial pH values were adjusted from 3.0 to 9.0 using various NaOH. They were centrifuged at 1000 rpm for 1 hr and then filtered through 0.45 µm membrane filters.

The adsorption efficiency E is calculated using Eq. (1):

$$\textbf{Removal}\ \backslash\textbf{E(\%)} = \{(C_o - C_e) / C_o\} * 100 \ldots\ldots\ldots\ldots\ldots\ldots \quad \text{Eq. (1)}$$

Where C0 and Ce are the initial and equilibrium concentrations of Cr(VI) (mg/L), respectively. The adsorbed amount of Cr(VI) under equilibrium conditions, qe, is calculated using Eq. (2):

$$\mathbf{q_e} = \{(C_o - C_e) * M\} / W \ldots\ldots\ldots\ldots\ldots\ldots\ldots \ldots.. \quad \text{Eq. (2)}$$

Where M is the mass of soil (Kg), and W is the adsorbent dosage (g).
Effect of contact time, shaking speed and sorbent dosage on percentage removal of heavey metals was also studied.

- **Batch adsorption experiments for Nanoparticles (CuO, Fe_3O_4, and ZnO)**

Kinetic and adsorption capacity experiments were conducted in a series of 15 ml Falcon tubes 5mg spiked soil and 20 mg, 30 mg, 40 mg, 50 mg, 60 mg, 70 mg, 80 mg, 100 mg, 120 mg composite was added in 15ml Falcon tubes for each heavy metal ions. The pH of all solutions were maintained at 7. The solution was shaken (100 rpm) at 25^0C. Solid/liquid phases were then separated by centrifugation (1000 rpm) for 1 hr. and then samples were filtered through 0.22 µm filter membrane. The heavy metals concentration was measured by AAS. . The adsorption efficiency E is calculated using Eq. (1):

$$\textbf{Removal}\ \backslash\textbf{E(\%)} = \{(C_o - C_e) / C_o\} * 100 \ldots\ldots\ldots\ldots\ldots\ldots \quad \text{Eq. (1)}$$

Where C0 and Ce are the initial and equilibrium concentrations of Cr(VI) (mg/L), respectively. The adsorbed amount of Cr(VI) under equilibrium conditions, qe, is calculated using Eq. (2):

$$q_e = \{(C_o - C_e) * M\} /W \text{.......................... Eq. (2)}$$

Where M is the mass of soil (Kg), and W is the adsorbent dosage (g).

Effect of contact time, shaking speed and sorbent dosage on percentage removal of heavey metals was also studied.

Kinetic Modeling Study

The kinetics were investigated by using the information obtained from the effect of dosage (dry-weight basis) at 25°C at three different time intervals up to 120 minutes. The pseudo first-order kinetic equation was not applicable because is small comparing to of pseudo-second-order equation. In recent years, the pseudo-second-order rate expression has been widely applied to the adsorption of pollutants from aqueous solutions (Y.-S. Ho, 2006) Therefore, the pseudo-second-order equation was used in this study.

The pseudo-second-order kinetic model can be expressed as:

$$1\backslash q_t = 1/ K_2 q_{e2} + t/ q_e \text{ .... Eq. (3)}$$

Where: qe and qt are metal ions adsorbed at equilibrium and at time t, respectively, while K2 is the constant of second-order adsorption in min^{-1}.

4.1.2- FTIR analysis of CuO Nano particles

Figure 5. FTIR spectra exhibit only three vibrations: occurring at approximately 480 cm^{-1}, 530 cm^{-1}, and 580 cm^{-1} for the sample, which can be attributed to the vibrations of CuO, confirming the formation of highly pure CuO nanoparticles. The peaks of FTIR spectra indicates that the CuO Nano particles are pure. (Arunachalam Dinesh Karthik and Kannappan Geetha 2013)

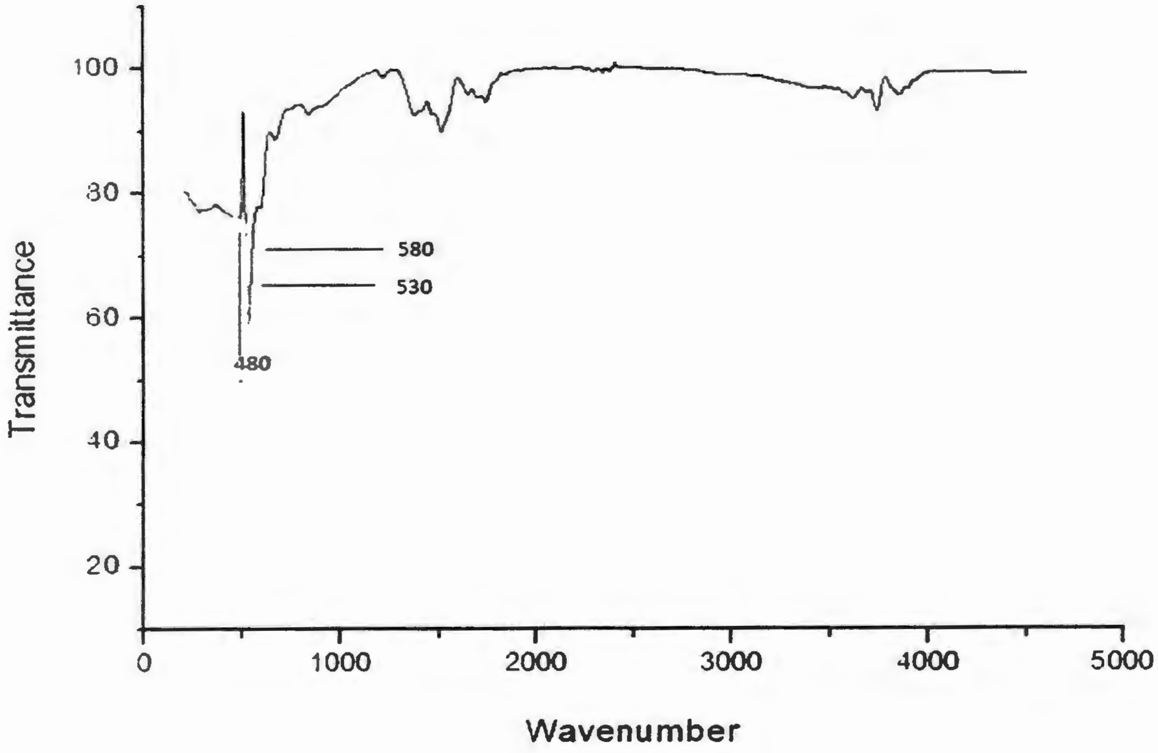

Figure 9: FTIR analysis(CuO)

4.2- UV-Vis Spectroscopy Analysis

4.2.1-UV-Vis Spectroscopy Analysis (ZnO)

The UV–Vis spectrum of Fe_3O_4 nanoparticles is shown in Fig. The Fe_3O_4 nanoparticles showed its absorption maxima at 235 nm. Which showed that the Fe_3O_4 nanoparticles are highly pure. (Akash Sharma ,Purnima Swaroop Khare 2015).

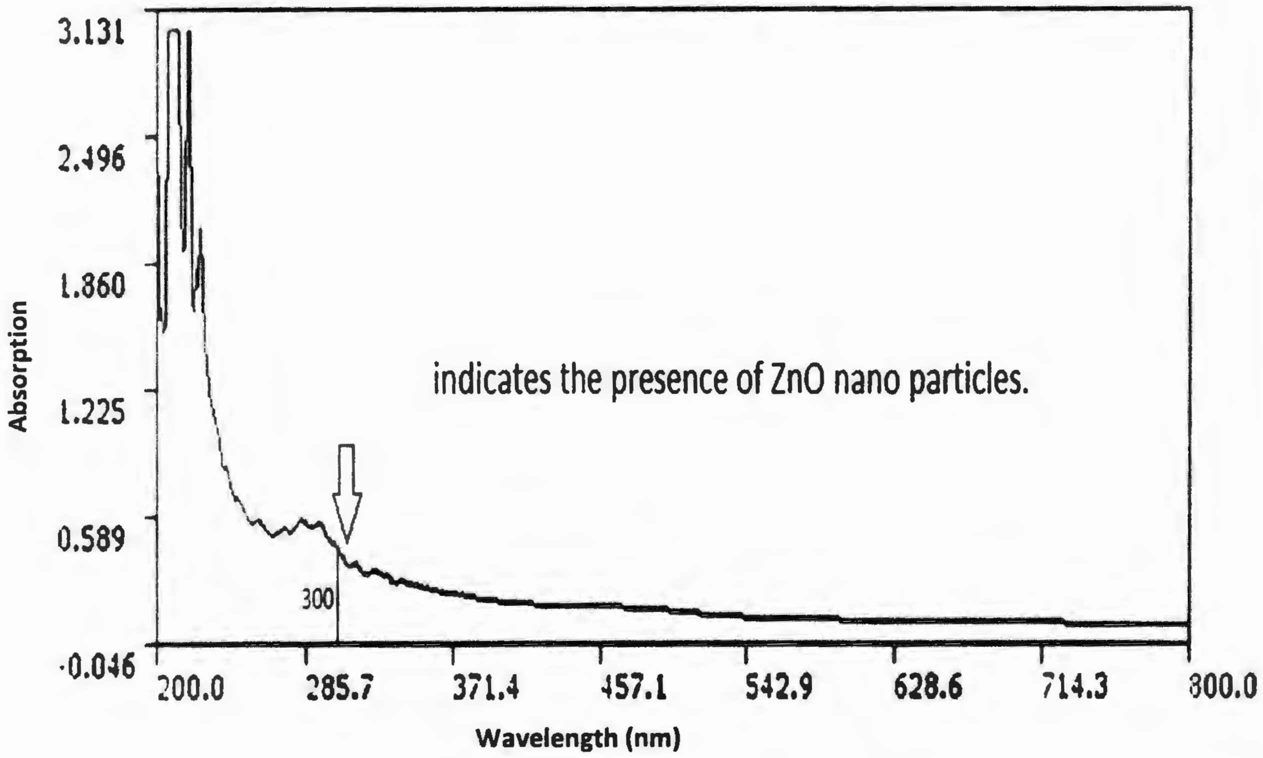

Figure 10: UV-Vis Spectroscopy Analysis (ZnO)

4.2.2-UV-Vis Spectroscopy Analysis of CuO

UV-VIS absorption spectrum of as synthesized colloidal solution of NPs in the 50mM concentration of anionic surfactant SDS is shown in figure 1. The absorption spectrum reveals four peaks at ~ 300, 380, 650 and 800 nm. The peak at 300 nm corresponds to inter band transition from deep level electrons of valance band of Cu2O while that of peak around 380 nm is due to the band edge transition of Cu2O. The peaks at 650 and 800 nm are attributed due to presence of CuO on the surface of synthesized material. (Henam Sylvia Devi and Thiyam David Singh 2014)

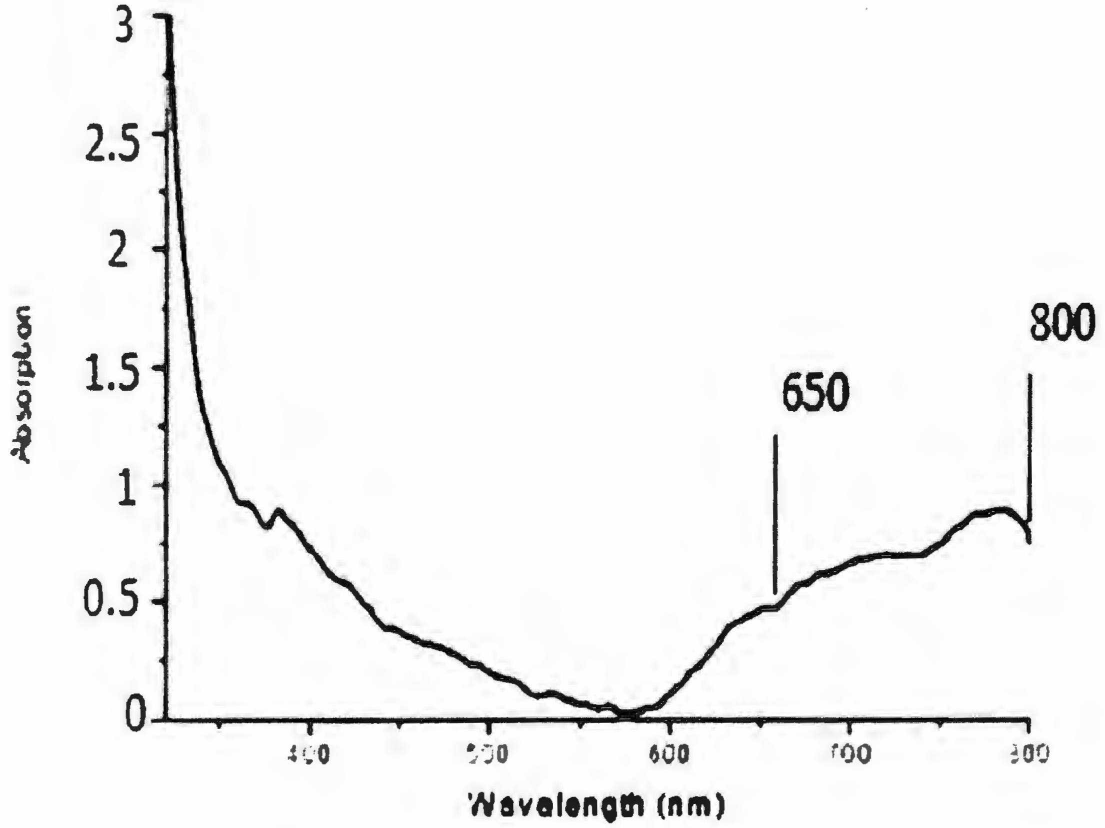

Figure 11: UV-Vis Spectroscopy Analysis (CuO)

4.3- SEM Analysis

4.3.1-SEM analysis of Fe_3O_4/MWCNTs

SEM image of the composites was shown in Fig. 2. It depicts an entangled network of carbon nanotubes with clusters of iron oxides attached to them. SEM studies on many flakes reveal the homogenous distribution of iron oxides agglomerates in the flakes, which indicates the formation of carbon nanotubes-iron oxides composites. (Changlun Chen et.al 2009)

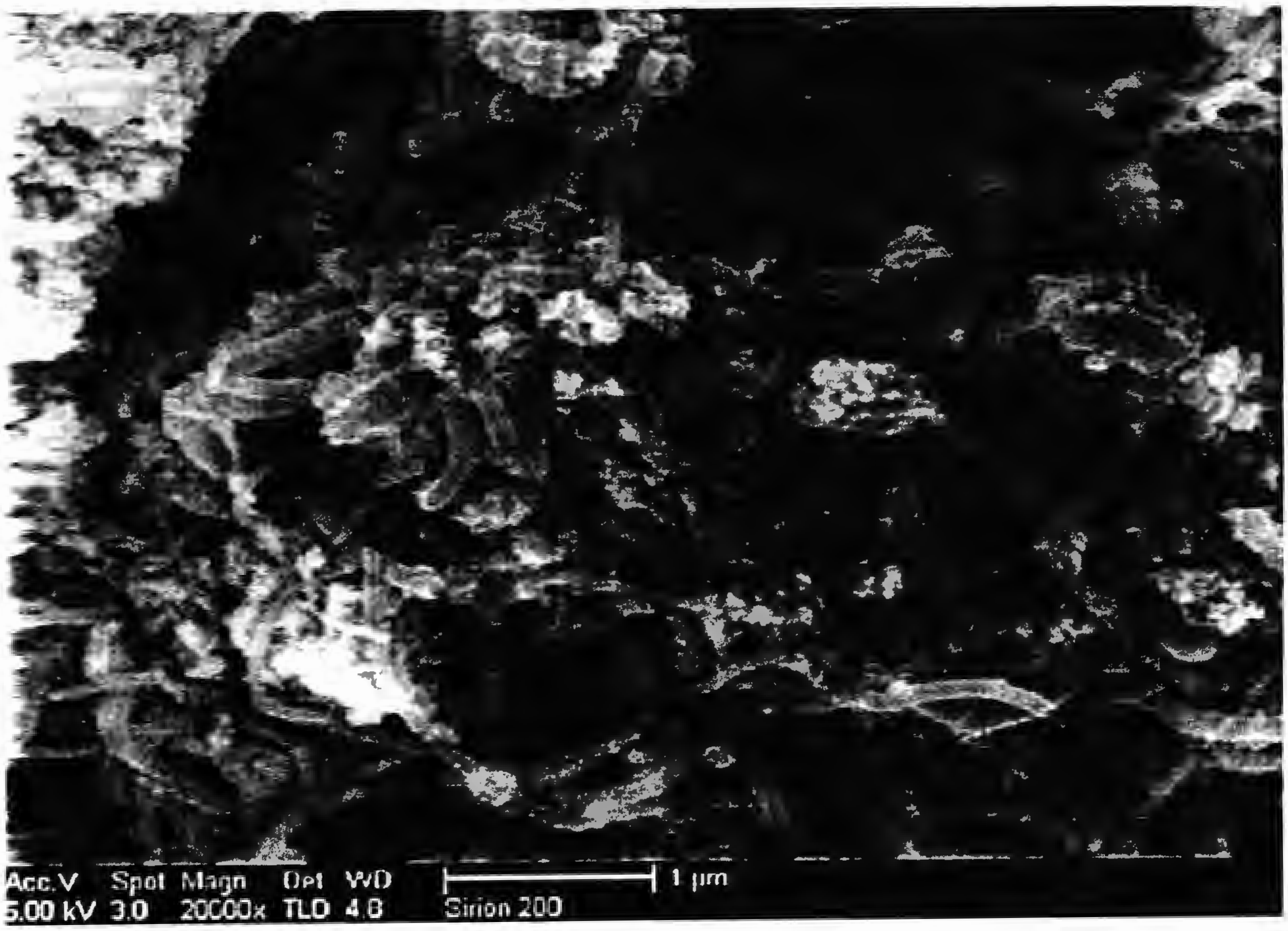

Figure 12: SEM Analysis (Fe_3O_4/MWCNTs)

By plotting of versus time (Figure 18) yields very good straight lines. The second order-rate constant obtained from this figure are 0.035 for Fe_3O_4/CNTs, 0.012 for CuO and 0.004(g.mg^{-1}.min^{-1}) for ZnO . The second order rate constant indicates that time to achieve equilibrium concentration of Cr (VI)& Pb(II) is less by using Fe_3O_4/CNTs compare with CuO and ZnO. The equilibrium adsorption capacity, obtained from the graph also implies that Fe_3O_4/CNTs have higher adsorption capacity (mg/g) as compared to CuO & ZnO (mg/g). (Zhuo-nan Huang et al. 2015).

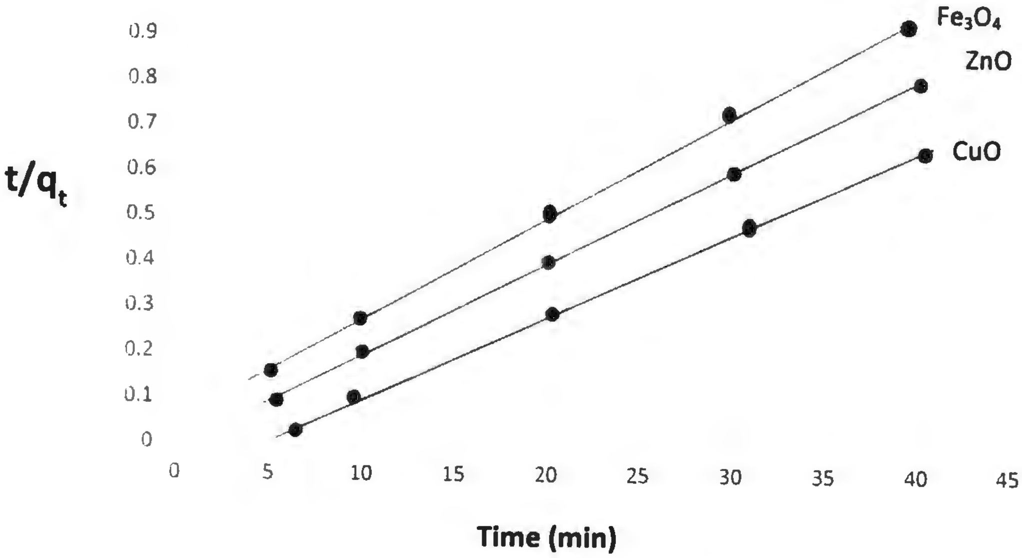

Figure 18: Pseudo-second-order kinetics using Fe_3O_4/CNTs, ZnO & CuO

Conclusions

- ZnO, CuO and Fe3O4/CNTs Nano composite were prepared by co-precipitation method and all were characterized by SEM, FTIR & UV-spectroscopy. SEM ananlysis showed the minimum particle size(0.1µm-1µm).

- The results of AAS showed the removal efficiency of Pb(II) & Cr(VI) with the %age of 60%, 70% 80%.

- The Fe3O4/CNTs Nano composite showed high removal efficiency of Cr(VI)&Pb(II) with 80% removal.

- The characterization of pb^{2+} and Cr^{6+} uptake showed that, these metal ions binding is dependent on amount of dosage, contact time and agitation speed. Percentage increase with increase in these parameters.

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