

**Synthesis and Application of  $\text{Al}_2\text{O}_3/\text{TiO}_2/\text{CeO}_2/\text{CNTs}$  Composite for  
Removal of Heavy Metals from Aqueous Solution**



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**ISLAMABAD**

**2016**



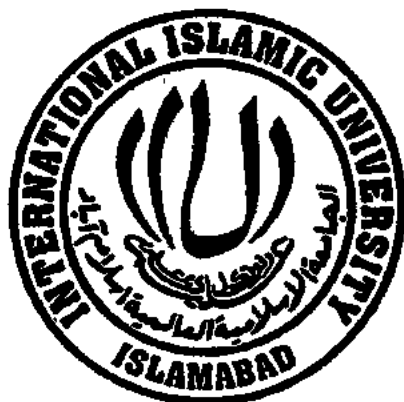
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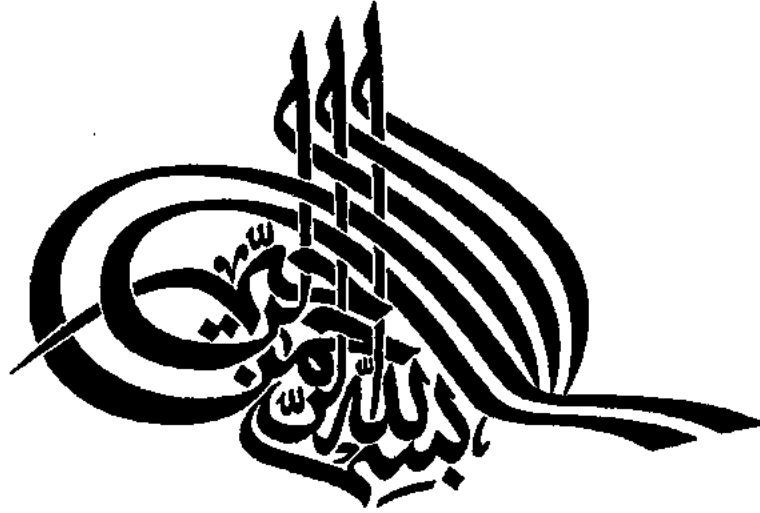
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*In the name of ALLAH, the Beneficent, the Merciful*  
*Read (Proclaim!!) In The Name of your Lord who created*  
*created man, out of a clot (of congealed blood) Read (Proclaim), and your*  
*lord is the Most Generous,*  
*Who taught by the pen,*  
*Taught man that which he knew not*

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Removal of Heavy Metals from Aqueous Solution**

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A thesis submitted in partial fulfillment of the requirement for

the degree of *MS* in discipline of Environmental Sciences

at faculty of Basic & Applied Sciences

International Islamic University,

Islamabad

**Supervisor**

**Dr. Maliha Asma**

## Final Approval

**Title of the Thesis: Synthesis and Application of  $\text{Al}_2\text{O}_3/\text{TiO}_2/\text{CeO}_2$  CNTs Composite for Removal of Heavy Metals from Aqueous Solution**

It is certificate that we have read the thesis submitted by Ms. Amina Anser 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.

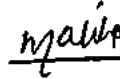
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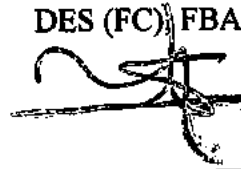
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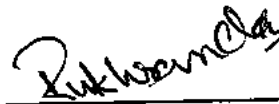
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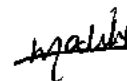


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## Forwarding Sheet

A thesis entitled "Synthesis and Application of  $\text{Al}_2\text{O}_3/\text{TiO}_2/\text{CeO}_2$  CNTs Composite for Removal of Heavy Metals from Aqueous Solution" by Amina Anser 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.



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**Dr. Maliha Asma**

## **DEDICATION**

*This thesis is dedicated to my Beloved Parents,  
Teachers & friends  
For their endless affection, support and encouragement*



## ACKNOWLEDGEMENTS

*All the praises, thanks and acknowledgement are for creator, the omnipresent, Almighty Allah. His mercifulness and kindness helped me to pass ups and downs of life. My special praise for Prophet Muhammad (ﷺ).*

*This dissertation would not have been possible without the guidance and the help of several individuals who in one way or another contributed and extended their valuable assistance in the preparation and completion of this study. First and foremost, my utmost gratitude to my supervisor, Dr. Maliha Asma whose sincerity and encouragement I will never forget. She helped me in each and every way, her hard work and determination really boost up my courage to achieve objectives of my research work. She has been my inspiration as I hurdle all the obstacles in the completion this research work and my MS journey.*

*Many thanks also go to Dr. Waqar Adil Syed (Chairperson of Physics department) who had kind concern and consideration regarding my research work. Especially in experimental work. My special gratitude to Sir Nouman Rafiq whose unselfish technical assistance regarding synthesis and characterization of Nanoparticles took me out of struggling situation many times.. My deepest good wishes to my brother Eram Ilyas for his sincere support, without his support and understanding this would have taken a much longer time to finish. It is all because of his corporation, that I was able to start my experimental work.*

*I would also like to pay special thanks to my Best friend Sidra Ehsan who gave me support by all means in all my hardships. Finally, my heartiest feeling for my lovely father Muhammad Anser, mother Riffat Sultana for their support and love. They made us available quality education and it is all because of them that I am able to complete my educational career. May Allah bless all the above and help them in both the worlds AAMEEN.*



*Amina Anser*

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## List of Abbreviation

CNTs	Carbon Nanotubes
MO	Metal oxides
CVD	Chemical Vapour Deposition
SWCNTs	Single Walled Carbon Nanotubes
DWCNTs	Double Walled Carbon Nanotubes
MWCNTs	Multi Walled Carbon Nanotubes
NPs	Nano Particles
SEM	Scanning Electron Microscopy
XRD	X-Ray Diffraction analysis
TEM	Transmission Electron microscopy
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
CNFs	Carbon Nanofibers
FAAS	Flame Atomic Adsorption Spectroscopy
Cr	Chromium

Pb	Lead
Cd	Cadmium
Cu	Copper
As	Arsenic
mgL <sup>-1</sup>	Milli Gram per liter
µgL <sup>-1</sup>	Micro Gram per liter
M	Molarity
DD	Double Distilled Water
TiO <sub>2</sub>	Titanium Dioxide Nano Particles
TiCl <sub>4</sub>	Titanium Tetrachloride
HCl	Hydrochloric Acid
NaOH	Sodium Hydroxide
(NH <sub>4</sub> ) <sub>2</sub> Ce(NO <sub>3</sub> ) <sub>6</sub>	Ceric Ammonium Nitrate
TNTs	Titanium Nano Tubes
CeO <sub>2</sub>	Cerium Oxide
Al <sub>2</sub> O <sub>3</sub>	Aluminum Oxide
EDTA	Ethylenediaminetetraacetic Acid

**CHAPTER 1**  
**INTRODUCTION**

## 1.1. Background:

It is appropriate to say that water is a vital environmental factor and have importance as an significant component of metabolic process within human body as well as universal solvent. For existence of life, fresh and clean water is essential (T. Pradeep 2009). However, supply of fresh water is running out and allowed contamination level is becoming more severe leading to great challenges to meet these specified standards

Waste water contamination with heavy metals has become a great concern worldwide, because polluted water is releasing in soil and aquatic environment which greatly impact human health and ecosystem. Heavy metals have got importance in treated and source water because of its properties which are, long term accumulation in soil and non-biodegradability. Heavy metal can cause damage to human health (Table 1), after exposure to heavy metals people can face cancer kidney damage, Gastrointestinal distress, allergy dermatitis, high blood pressure etc. (Leing pui Sze, 2009)

Some toxic heavy metals include Arsenic, Chromium, Cadmium, Lead, and Copper. Toxicity of heavy could result from drinking water contamination, ingestion via food chain. Industries are using huge amount of metals, resulted in increased concentration of metallic compound in fresh water sources (I. Sheet et al., 2014) (M. Karnib et al. 2014) Therefore, there is need to produce advanced technologies in area of water treatment and development of improving technologies in this field is fundamental.

**Table 1: National Drinking water standard ( PAK-EPA, 2008)**

<u>Inorganic Chemicals</u>	<u><sup>a</sup>MCL (mg/L)</u>	<u>WHO Guidelines (mg/L)</u>	<u>Potential Health Effects after Ingestion</u>
Arsenic (As)	≤0.05 (P)	0.01	Skin damage or problems with circulatory systems and may have increased risk of getting cancer
Cadmium (Cd)	0.01	0.003	Kidney Damage

Chromium (Cr)	≤0.05	0.05	Allergy Dermatitis
Copper (Cu)	2	2	Short-term exposure: Gastrointestinal distress, Long-term exposure: Liver or Kidney damage
Lead (Pb)	≤0.05	0.01	Infants and Children: Delay in physical or mental development Adults: Kidney problem, High blood pressure

### 1.2. How Heavy metal Contamination Occur?

The main sources of heavy metals are chemical manufacturing, fossil fuel, mining, battery manufacturing industries, tannery, many of which are metal compounds generating of plastics, such as polyvinyl chloride, the modern chemical industry based largely on catalysts, manufacturing of metallurgical involving the use of metal compounds, mainly as heat stabilizers. The effects of heavy metals such as chromium, cadmium, lead, copper and on human health have been examined expansively and have negative impacts on water resources. (Nordberg et al 2007)

The primary sources of metals in are industry and automobiles. A significant source of input of heavy metals is atmospheric deposition which can make a high level pollution of water bodies as well. Also, metals can be very toxic to aquatic life. In waste water mostly found metals, are chromium (Cr), lead (Pb), copper (Cu), mercury (Hg), cadmium (Cd), arsenic (As) and There are several methods to remove heavy metals from the contaminated waste water.

### 1.3. Vital Methods for Heavy Metal removal

Numerous methods have been applied over the years for the removal of metal ions in industrial effluents. Advance and Conventional methods like reverse osmosis, precipitation and coagulation, activated alumina, and ion exchange, are not able to practical because of these methods are unapproachable and expensive. More over conventional techniques are not



effective to an extent, that it produce industrial effluent that can fulfil all regulations of discharge water quality .

Adsorptive filtration is the most capable technology for removal of contaminants such as dissolved heavy metal, with an effective adsorbent. There is a widespread range of sorbents available as potential filtration media:, granulated activated carbon (GAC), fly ash (FA), granulated ferric hydroxide (GFH), alumina, iron oxide-coated sand (IOCS), natural zeolite (NZ), sand , bark etc. (Genç-Fuhrman, et al., 2007). Presently, mostly used metal adsorbent is iron-based bonding materials .These are commonly selected because they are cheap, easily produced and have low potential for addition of further impurity to the system (Deliyanni, et al., 2007). One most usually used adsorbents iron oxides is iron oxide-coated sand (IOCS).

Nanotechnology is best one, from most capable technologies, it based on nano devices and products, which are used for this water treatment purpose. Nanotechnology is molecular scale (1-100 nm) engineering of functional systems, which generate many modified products and alternative processes for purification of water. The basic advantage of using nanomaterial over other conventional materials, is availability of high surface area. High surface area provide enough space for physical interchanges and chemical reactions.(T. Pradeep 2009)

Carbon nanotubes (CNTs) with special chemical and physical properties have come under multidisciplinary study. They have been used as an adsorbent for gasses and hydrogen due to their hollow and highly porous structure, light mass density, large specific surface area and strong interaction between hydrogen and carbon molecules.(Figure 1,2).

Carbon nanotubes (CNTs) modified with chemical treatment Like bases or acids , are relatively enhance adsorbents efficiency and are very effectual for removal of many trace heavy metals such as cadmium and copper(Janusz, 2007). Other variety of metal oxide nanoparticles have also confirmed for efficient removal of heavy metal from contaminated water like cerium oxide, aluminum oxide and titanium oxide

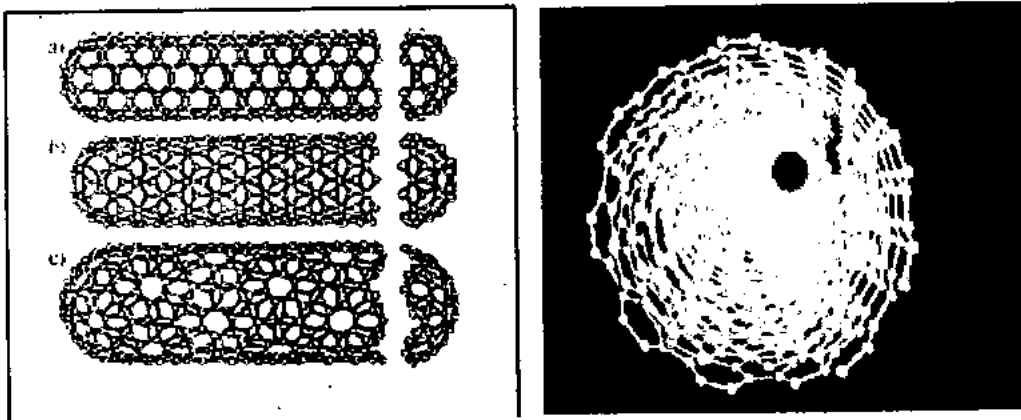


Figure 1: Single Walled Carbon Nanotubes (SWCNTs) Figure 1: Multi Walled Carbon Nanotubes (MWCNTs)

#### 1.4. The Present study

Keeping earlier work in mind, the main purpose of this research is to explore the possibilities of using selected series of nanostructured material for adsorption of Pb (II), Cr(VI) dissolved in single component system.

Main objectives of this proposed research are summarized in following points:

- 1- To oxidize prepared Carbon nano-tubes (CNTs) by oxidation treatment and then characterize the oxidized CNTs (o-CNTs).
- 2- To Synthesize and characterize nano-structure ceric ammonium nitrate/carbon nanotubes composite by FT-IR and SEM.
- 3- To synthesize Iron.doped  $\text{TiO}_2/\text{Al}_2\text{O}_3$  nano composite and characterized by FT-IR, UV-Vis spectroscopy, SEM
- 4- To Reveal the adsorption ability or removal efficiency of these composites for heavy metal ( $\text{Pb}^{2+}$ ,  $\text{Cr}^{6+}$ ) in water media

**CHAPTER 2**  
**LITERATURE REVIEW**

## 2.1. Heavy Metals

In the natural environment the distribution of heavy metals is mostly concerned with evaporation of oceans, rock decay, volcanic eruptions, forest fire and soil formation processes. The anthropogenic sources of contamination include waste dumping sites, power industry, transport, municipal waste management, transport and fertilizers. These sources disperse heavy metals and contaminate air, water and soil. (Szyczewski, P. et al., 2009)

Having greater than 4.5g/cm mass density, during chemical reaction they form cations by releasing electron. The immediate concerned metals are copper, cobalt, cadmium, lead, zinc, chromium, mercury and nickel according to WHO (2006) (Zaied, K, et al., 2008 ; Thippeswamy, B. et al., 2012). Due to high toxicity of cadmium, lead, Mercury, in most of countries these metals have referred as “priority pollutants” (Thippeswamy, B. et al., 2012). Some metals are essential for living organisms such as Co (vitamin B12), Fe (hemoglobin), Cu (respiratory pigments), Zn (enzymes) and Mn and Mo (enzyme) but very toxic at their higher concentrations. Na, Ca and K also play most important biological roles. Metals e.g. Se, Cr, Hg, As and Sc at their low concentration are very toxic and have no role in metabolic activity (Valavanidis, A., Vlachogianni, T., 2010). Although zinc, selenium, copper are trace heavy metals and are compulsory for maintenance of human body metabolism, but cause harmful effects on higher concentration levels. Heavy metals are prominent because of their bioconcentration, bioaccumulation and toxicity in living organisms, and are persistent in environments (Yoon, Y. et al., 2006). Some heavy metals accumulate in soil and due to their uptake in plants, transferred to food chain (Spiro, T.G., Stigliani, W.M, 2004; Malla, R. Y. et al 2007). Heavy metals via food chain cause poisonous effects on both plants and human health (Takahashi, C.K, et al., 2012; Dutton, J., Fisher, N.S, 2011)

It is necessary to remove them before they reach the receiving water body, due to their high toxicity. For application of appropriate treatment it is required to understand the nature of heavy metals in water and their impacts on environmental and human health. This section gives insight of the chemistry, environment and health impacts of lead, chromium, copper, arsenic and cadmium.

### 2.1.1. Lead

#### A- Chemistry of Lead

Lead is a main element of group 14 with atomic number 82 and symbol Pb (Latin: plumbum). It is a bluish-white metal, very soft, ductile, highly malleable, and poor conductor of electricity. From all stable elements, lead has the highest atomic number (West, et al., 1987). Lead can be found in nature as:  $PbS(s)$  (galena),  $PbCO_3(s)$  (cerussite), and  $PbSO_4(s)$  (anglesite). In natural water bodies concentration of lead may range from  $<1.0$  to  $890 \mu\text{g/l}$  (Faust and Aly, 1998). Physico-chemical speciation indicates little ionic lead presence in drinking water. Depending on the composition of water a significant portion of lead is bound to colloids, either organic macromolecules or hydrous iron oxides. A substantial fraction is non-ion-exchangeable (Moore and Ramamoorthy, 1984).

#### B- Environmental and health impacts

The sources of lead in water bodies are numerous. Important sources for lead are atmospheric deposition and building sites (Davis, et al., 2001). Adjacent to the sources of lead, ecosystems show widespread harmful effects like changes in community composition of plants and animals, losses in biodiversity and neurological effects in vertebrates (US EPA, 2009). For centuries people are aware of lead and its toxic properties. People are exposed to lead in different ways that can be found in food, air, and water. Once lead is absorbed by the body, the largest deposits are in the bones followed by the kidneys and liver. Even at low levels of lead young children and infants are particularly sensitive (Sarkar, 2002).

### 2.1.3 Chromium

#### A- Chemistry of Chromium

Chromium is a chemical element having atomic number 24 and the symbol Cr. It is a hard metal steel-gray and lustrous which takes high polish (West, et al., 1987). In water chromium (III) is mostly found as a cation that forms hydroxide precipitates and aqueous complexes. In surface waters, the ratio of chromium (III) to chromium (VI) varies widely, and relatively high

concentrations of Cr(VI) can be found locally. Chromium (VI) is relatively mobile in water due its more solubility than those of Cr(III) (WHO, 2003). Low solubility of Cr(III) limits the detection of amount of chromium in natural waters. Natural water bodies are usually contaminated with Cr from industrial effluents (Faust and Aly, 1998). In which form chromium is present, depends on the pH, the redox potential, the formation of chromium(III) complexes as insoluble chromium(III) salts, the kinetics of the redox reactions and the total chromium concentration. The toxicity mechanism is pH dependent. Chromium (VI) under anaerobic conditions reduced to chromium (III) compounds and stable under aerobic conditions.

Oxidizing environment can inverse the process (Lenntech, 2009). Chromium is used to manufacture stainless steel, to harden steel, and to form many alloys. It is used in plating to produce beautiful and hard surface, and to avoid corrosion. As a catalyst it is also widely used and as mordant in the textile industry and by the aircraft and other industries for anodizing aluminum. The refractory industry use chromium for forming bricks and shapes, as it has moderate thermal expansion, high melting point, stability of crystalline structure. Chromium is typically mined as chromate ore (West, et al., 1987).

### **B- Environmental and health impacts**

Highest chromium source in environment is tannery effluents. Currently 90% Tannery effluents Currently, 18 billion sq.ft of global leather production is processed by chrome tanning process (Sundar. V.J. et al., 2002). Mostly used chromium salt is chromium sulphate (Wionczyk, B. et al., 2006). Many other industrial activities like cement, dyeing, electroplating, leather tanning and metal cleaning also increase chromium into environment (Kisku, G.C, et al., 1999). On chemical forms of exposure of chromium health effects depend (Calder, 1988).

As Chromium (III) is a nutritionally essential element, poorly absorbed and non-toxic but if its concentration exceed the recommended values than it will cause toxic impacts to human health. On the other hand, chromium (VI) is very toxic to all living creatures and cause liver and kidney damage, respiratory disorders and internal hemorrhage. Skin ulceration and dermatitis are example of chronic and sub-chronic effects. At higher concentration of chromium it can result some health problems like tumor, weak immune system, birth defects, infertility, respiratory problems. In plants it affects seed germination, stunting, photosynthetic pigments, chlorosis and

ultimately cause death of plant (Altaf Masood, M.M, et al 2008). The Maximum Contaminant Level (MCL) for total chromium in drinking water is 0.1 mg/l (Faust and Aly, 1998).

## 2.2 Industries releasing Heavy Metals

Heavy metals are dangerous pollutant. Discharge of these contaminants into waterways come from different industrial processes like battery, metal finishing, leather, chemical manufacturing, tanning, electroplating, dyes, mining, pigment, paint industries, metallurgical work (Adclaja, O.A, et al.,20011 ; Acykel, U. et al.,2002 ; Ahalya, N. et al., 2003, Ahluwalia, S.S.,Goyal, D., 2007). Annual discharge of metals have reached to 783,000t for lead, 22,000t (metric to) for copper, 1,350,000t for cadmium (Singh, O.V, et al., 2003)

Industrial activities and vehicular exhaust increase more lead into atmosphere that input of natural processes. Concentration of lead was increased in atmosphere due to addition of lead into gasoline fuel (Valavanidis, A., Vlachogianni, T., 2010). Electroplating and processes of metal surface treatment produce large amount of metals e.g. vanadium, lead, cadmium, silver, titanium, zinc chromium, platinum (Chuah, T.G, et al., 2005; Ting H.C, 2009). Arsenic waste produce from wood processing industries during arsenate wood treatment. Inorganic pigments manufacturing produce large amount of chromium and cadmium sulfide compounds. During refining of petroleum some conversion catalyst formed which are contaminated with nickel, vanadium and chromium ( Rana, P. et al., 2004). Some major industries such as wood industry, refining, petroleum, paper and pulp and metal plating industry are releasing copper in their effluents (Barrell, D.C,et al., 1975).

Heavy metals like cadmium, chromium, nickel, mercury and other phenolic compounds are discharged from pharmaceutical industries (Ramola, B., Singh, A., 2013). Ni is released from waste water of silver refineries, zinc base casting, storage batteries and electroplating industries (Mishra, G.K, et al., 2005). Large quantities of Zinc goes to water bodies due to direct discharge of industrial effluents from paint, batteries, galvanization, smelting, pigment, fossil fuel combustion, polymer stabilizer, fertilizers and pesticides ( Holdren, C. et al., 1991).

## 2.3. Techniques for Heavy Metal removal from waste water

1. Chemical Precipitation
2. Sulfide Precipitation
3. Chemical Precipitation Combined with other Methods
4. Heavy Metal Chelating Precipitation
5. Chemical Precipitation Combined with other Methods
6. Heavy Metal Chelating Precipitation
7. Ion Exchange
8. Flotation
9. Electrochemical treatment
10. Coagulation and Flocculation
11. Adsorption

### 2.3.1 Adsorption

Adsorption is now known as an economic and effective method for metal contaminated wastewater treatment. The adsorption process offers flexibility in operation and design, in many cases will produce excellent treated effluent.

#### I- Activated Carbon Adsorbents

Activated carbon (AC) adsorbents are also used for treatment of heavy metal contaminants. Its usefulness is its mesopore and micropore volumes and the high surface area. Nowadays, the depleted commercial coal-based sources of activated carbon results in the increase in price. Additives of magnesium, surfactants, tannic acid, and activated carbon composite could be effective adsorbent. Converting carbonaceous materials into activated carbon for heavy metals removal has been reported (Dias, 2007).

#### II- Bioadsorbents

Biosorption of from aqueous solutions is a comparatively new process that has been proven a very promising process in the treatment of heavy metal contaminants. Its high effectiveness is major advantage of biosorption. By using inexpensive biosorbents I can reduce heavy metal



ions.. Bio-sorption processes are particularly suitable to treat dilute heavy metal wastewater. Typical biosorbents can be derived from three sources as follows:

- Non-living biomass such as bark,shrimp, lignin, crab shell, squid etc.
- Alga biomass.
- Microbial biomass, e.g. bacteria,yeast, fungi (Aman, 2008).

### 2.3.2 Membrane Filtration

In recent years, a promising technique for removal of pollutant especially heavy metals the polymer- enhanced technique has been shown to in solution. The process comprises removal of 1 heavy metals such as Ni(II), Cu(II), and Cr(III) from industrial wastewater solutions. A considerable attention has given to membrane filtration for the removal of inorganic effluent, as it is capable of removing not only organic compounds and suspended solid, but also inorganic contaminants such as toxic heavy metals. Various types of membrane filtration depending on the particle size that can be used, such as nano filtration, reverse osmosis and ultra-filtration, can be used for heavy metal removal from contaminated waste water ( Barakat, 2008).

### 2.4. Nanotechnology for Water Treatment

Among the most innovative and progressive technologies, nanotechnology is one of them in the world. Nanotechnology is a range of technologies which performed on very small scale (nanometer) and as an enabling technology it has widespread applications in numerous industries. Unlike other technologies, which come directly from a particular scientific discipline, nanotechnology have a wide spectrum of science. Nanotechnology involves the application and production of biological, chemical, physical systems ranging from smaller scale to 100 nanometers, as well as the assimilation of the resulting nanostructures into many other larger systems. Nanotechnology's principal way which might help to lessen water problems is by solving the challenges (technical) that removing water pollutants including pesticides, bacteria, toxic metals, salts and viruses.

Several scientists' claims that for more effective, affordable, durable and efficient ways of achieving precise nanoparticles for water purification, nanotechnology is best, it would permit manufacturer to prepare less poisonous particles using classical methods. (Suvardhan, 2014).

Waste water treatment under nanotechnology successfully excludes the pollutants and to get purified water, helps in the recycling process. Nanotechnology leads to reduction in time, expenditure and labour to industry and resolves the various environmental problems. Based on their surface and physical properties nanomaterials (NMs) are mainly categorised into several groups. Nanomaterials include metallic nanoparticles (Au & Ag NPs), carbon nano-adsorbents (CNTs), mixed oxide nanoparticle (Fe-Ti NPs), metal nano-adsorbents (Al<sub>2</sub>O<sub>3</sub> NPs, ZnO NPs, TiO<sub>2</sub> NPs and CeO<sub>2</sub> NPs), polymer nano-adsorbents, nanoclays, nanofibers. Additionally, it also utilizes the existence of nanoscopic pores in zeolite filtration membranes, as well as nanocatalysts. Metal oxide \metallic nanoparticles such as palladium nanoparticles and Titanium oxide nanoparticles and are used as Nanosensors for the inorganic and organic analysis and for other pollutants in the water bodies.

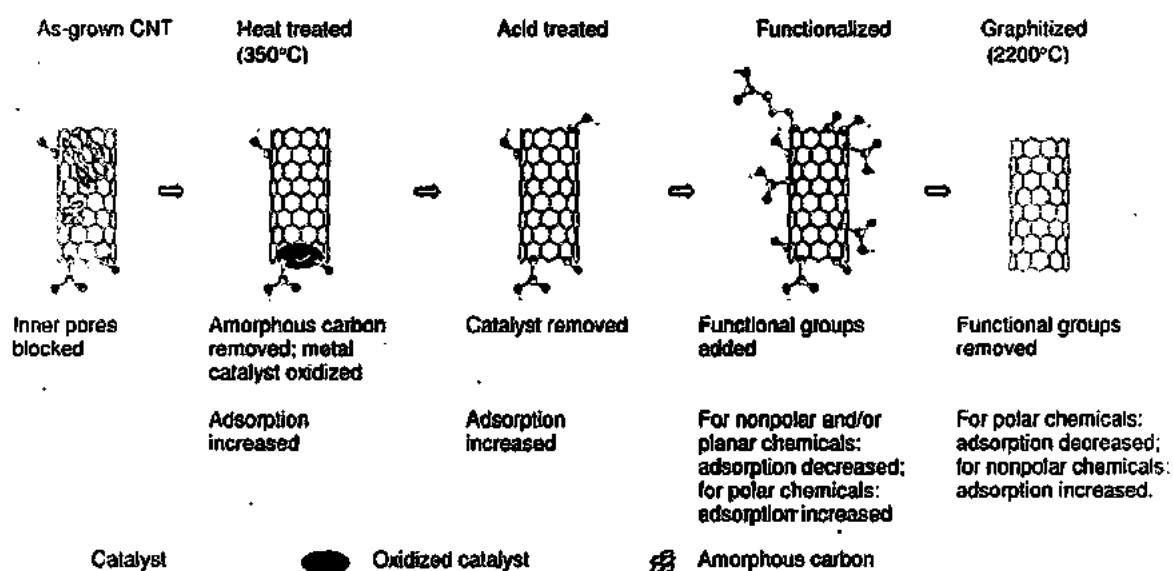
Carbon nanotubes are exceptional nanomaterials which can remove wide range of pollutants including inorganic, organic, turbidity, viruses and bacteria. Because of the smooth interior of the carbon nanotubes have a faster or equal flow rate as compared to contaminants' larger pores. Some nanofiber materials such as nanofibrous alumina remove negatively charged pollutants such as inorganic and organic colloids, bacteria, viruses at a faster rate than conventional sorbent filters. Carbon nanotubes are classified in different classes (SWCNTs, MWCNTs).

Multiwalled carbon nanotubes (MWCNTs) and singlewalled carbon nanotubes (SWCNTs) are different from by their number of layers, and many scientists are focusing due to its excellent properties, variety of potential applications and unique structure (Suvardhan, 2014). Hundreds of individual CNTs has entanglement due to attraction of Van der Waals force between them (Donaldson, 2006) (Yan, 2007) which, for adsorption of contaminant \ analytes provide large exterior surface area (Li YH, 2003) (Liu G, 2007). Carbon nanotubes (CNTs), a interesting new member in the carbon family, comprise of single walled CNTs and multi-walled CNTs have been the research focus due to their adsorption of analytes, unique dimensional structures, adsorption of analytes, excellent electronic properties and potential applications.

Moreover, there is the possibility of making CNTs composites at advanced level and nano scale electro devices, just because of its chemical and thermal stabilities. Its properties stimulated the applications as catalyst carriers. Structurally, CNTs are considered as ideal adsorption material due to layered and hollow structures and large surface areas (Alyuz, 2009).

Removal of contaminants relies on sorption behavior. CNTs with their controlled size distribution, high surface to volume ratio and have exceptional sorption ability and high efficient adsorption compared to powder activated carbon and other conventional granular which has fundamental limitations like surface active sites and the activation energy of sorption (Jiang, 2002).

Numerous studies found that the adsorption capacity of CNTs depends on both the nature and surface functional groups of the sorbate. For instance, the amounts of surface acidity (phenolic groups, lactonic and carboxylic group) increase the adsorption of polar compounds. On the other hand, the unfunctionalized CNTs surface is proved to have higher capacity adsorption for non-polar compounds such as polycyclic aromatic hydrocarbons. Some previous studies showed that carbon nanotubes (CNTs) and their composite with other metal oxide nanoparticles have used for wastewater treatment. (Table: 2.1,2.2) Carbon nanotubes has high adsorption capacity for adsorption of heavy metal



**Figure 3.1 : Functionalized CNTs and Adsorption efficiency of chemicals**

As a photo degradable TiO<sub>2</sub> NPs is used for organic pollutants. In fact, successful application of TiO<sub>2</sub> NPs have been used in environmental technology for the treatment of contaminated surface and ground water, for the removal of organic pollutant. Ceria NPs has diverse properties of strong size dependent and would show significant quantum size (Xu H, 2008). However, in the field of material science the synthesis of CeO<sub>2</sub> nanoparticles (Tok AIY, 2007) below 10 nm is a hard to achieve task for the scientist. Al<sub>2</sub>O<sub>3</sub> NPs have more reactivity, greater adsorption capacity, high surface area, hence; from literature review it has been working effectively for the determination and separation of toxic heavy metals of environmental importance (Manzoori, 2012).

For organic pollutants removal, TiO<sub>2</sub> nanoparticles is used as a photo degradable. For the treatment of contaminated waste water and ground water. In fact, TiO<sub>2</sub> nanoparticles have been successfully used in technology of environment for the removal of organic wastes. Ceria NPs has diverse properties of having show significant quantum size effect and strong size dependent (Xu H, 2008).

Some previous research work on aluminum oxide, cerium oxide and titanium oxide nanoparticles and their composites with some other metal oxides have studied for their applications on heavy metals adsorption. ( Table 2.3, 2.4 )

**Table 2.1: Previous studies on CNTs for Heavy metal Removal**

<u>Sorbent</u>	<u>Doping\</u>	<u>Charaterization</u>	<u>Removal of</u>	<u>References</u>
<u>Material</u>	<u>Modification</u>	<u>tools</u>	<u>Heavy Metals</u>	
CNTs	Activated Carbon (AC)	FE-SEM, EDS	Cr <sup>6+</sup>	Muataz Ali Atieh, 2011
MWCNTs	Amino modified	FT-IR, FE-SEM, TEM, TGA	Pb <sup>2+</sup>	Goran et.al, 2011
MWCNTs	---	---	Cu <sup>2+</sup> , Pb <sup>2+</sup> , Co <sup>2+</sup> , Zn <sup>2+</sup> , Mn <sup>2+</sup>	Anna Stafiej, et.al 2007.
MWCNTs	---	SEM, BET, RAMAN	Co <sup>2+</sup> , Cu <sup>2+</sup>	Krystyna et.al, 2010
MWCNTs	---	SEM, BET, FT-IR	Cu <sup>2+</sup>	Soheil et.al, 2015
Oxidized- CNTs	---	TEM, BET	Cd <sup>2+</sup>	Yan-Hui Et.al, 2003
CNTs	Activated Carbon (AC)	FE-SEM	Cr <sup>6+</sup>	Muataz Ali Atieh, 2011
CNTs	---	---	Pb <sup>2+</sup>	Yan-Hui et.al, 2005
MWCNTs	Different outer diameters and oxygen contents	---	Pb <sup>2+</sup>	Fei Yu et.al 2013
Oxidized- CNTs	---	---	Cd <sup>2+</sup> , Cu <sup>2+</sup> , Ni <sup>2+</sup> , Pb <sup>2+</sup> , Zn <sup>2+</sup>	Saksham Srivastava, 2013
MWCNTs	---	TEM	Cd <sup>2+</sup> , Cu <sup>2+</sup> , Pb <sup>2+</sup>	Yan-Hui, 2003

**Table 2.2: Previous studies on CNTs composites for water treatment**

<u>Nano-composite</u>	<u>Characterization Tools</u>	<u>Removal of Containants</u>	<u>References</u>
CeO <sub>2</sub> -CNTs	XRD, TEM, zeta potential analyzer	As(V)	Xianjia et.al 2005
Al <sub>2</sub> O <sub>3</sub> -CNTs	SEM, XRD	Fluoride adsorption	Yan-Hui et.al, 2001
TiO <sub>2</sub> -CNTs	TEM, FT-IR, XRD, UV-Vis Spectrophotometer, Raman,	Organic compounds	Wei Zhou et.al 2010
Al <sub>2</sub> O <sub>3</sub> -CNTs	SEM, TG, EDS, BET	Ni <sup>2+</sup>	Renata et.al 2007
Iron doped MWCNTs.	SEM-EDS, TEM, FT-IR, TGA, DSC	Bromate	Aasem et.al 2014
TiO <sub>2</sub> -CNTs	---	Organic pollutant	Qiming et.al, 2013
Iron oxide-CNTs	XRD. SEM	Pb <sup>2+</sup> Cu <sup>2+</sup>	Xianjiaet.al 2005
CeO <sub>2</sub> -ACNTs	SEM, TEM	Cr <sup>6+</sup>	Ze-Chao et.al 2006
MnO <sub>2</sub> -CNTs	XRD	Pb <sup>2+</sup>	Shu-Guang et.al 2007
CNTs-AC	FESEM	Cr <sup>6+</sup>	Muataz Ali 2011

Table 2.3: Previous studies on Al<sub>2</sub>O<sub>3</sub> nanoparticles for heavy metal removal

<u>Sorbent Material</u>	<u>Doping/Modification material</u>	<u>Characterization tools</u>	<u>Removal of HeavyMetal</u>	<u>References</u>
Al <sub>2</sub> O <sub>3</sub> Nanopowder	---	XRD, SEM	Fe (III)	Mohamed and Mahmoud, 2015
Gamma-Al <sub>2</sub> O <sub>3</sub>	---	FT-IR, SEM, TEM, XRD, BET	Cd <sup>2+</sup> , Ni <sup>2+</sup> , Pb <sup>2+</sup> , Cr	A. Shokati et al 2015
Al <sub>2</sub> O <sub>3</sub> , Fe <sub>2</sub> O <sub>3</sub> Nanoparticles	---	---	Pb, Ni, Zn, Cd	Karen and Heather, 2009
Al <sub>2</sub> O <sub>3</sub> /Fe <sub>2</sub> O <sub>3</sub> composite	---	XRD, SEM, TEM, EDX, BET	Cadmium Ions	Mona Mahmoud et al 2013
Al <sub>2</sub> O <sub>3</sub> Nanoparticles	Natural and Chemical modifiers	FT-IR, SEM, XRD	Cd <sup>2+</sup> , Cu <sup>2+</sup> , Ni <sup>2+</sup>	Shahriar Mahdavi et al 2015
Nano-alumina	2,4-dinitrophenylhydrazine	SEM, FT-IR, BET	Pb <sup>2+</sup> , Cd <sup>2+</sup> , Cr <sup>3+</sup> , Co <sup>2+</sup> , Ni <sup>2+</sup> , Mn <sup>2+</sup>	Abbas Afkhami, et al 2010
Al <sub>2</sub> O <sub>3</sub> Nanoparticles	---	---	Cd <sup>2+</sup> , Zn <sup>2+</sup>	M. Hashem Stietiya and Jim J. 2014
Gamma Al <sub>2</sub> O <sub>3</sub>	---	XRD, FT-IR, SEM	Pb <sup>2+</sup> , Cd <sup>2+</sup> , Zn <sup>2+</sup>	Yvan J.O. and Maria, 2012

**Table 2.4: Previous studies on Titanium dioxide nanoparticles and composites for water treatment**

<u>Sorbent Material</u>	<u>Characterization Tools</u>	<u>Removal Of Heavy Metals</u>	<u>References</u>
TiO <sub>2</sub> / Montmorillonite- Kaolinite	SEM, XRD, PSD	Pb <sup>2+</sup> , Cu <sup>2+</sup> , Cd <sup>2+</sup> , Zn <sup>2+</sup>	Andelka et.al 2015
TiO <sub>2</sub> Nanoparticles	-----	Pb, Cd, Cu, Zn, Ni	Engates et.al 2011
Nano Structured Titanium (Iv) Oxide	-----	Cu <sup>2+</sup> , Cd <sup>2+</sup>	Sushanta and Uday, 2011
TiO <sub>2</sub> Film	-----	Reduction of Cr(VI)	Quanping Wu et.al 2013
TiO <sub>2</sub> Nanowire	TEM, SEM, XRD	Pb <sup>2+</sup> , Cu <sup>2+</sup> , Fe <sup>3+</sup> , Cd <sup>2+</sup> , Zn <sup>2+</sup>	Ahmed and Farag, 2014
TiO <sub>2</sub> , MgO, Al <sub>2</sub> O <sub>3</sub> Nanoparticles	SEM-EDX, TEM, XRD, BET	Cd <sup>2+</sup> , Cu <sup>2+</sup> , Ni <sup>2+</sup> , Pb <sup>2+</sup>	Shahriar et.al 2013



**CHAPTER 3**

**MATERIALS & METHODS**

### 3.1. Reagents and Materials

Carbon nanotubes (CNTs) with average diameter 20-40nm and the length was 2 $\mu$ m, were purchased from sigma Aldrich. The detail of remaining reagents and materials is described in table 3.1.

No.	The Material	Purity	Supplier
1	Carbon nanotubes ( CNTs)	95% (20-40nm)	Sigma Aldrich
3	Aluminum Chloride (AlCl <sub>3</sub> )	97% ( Analytical)	Daejung Korea
4	Titanium Oxide TiO <sub>2</sub>	96%	Daejung Korea
5	Fe <sub>2</sub> O <sub>3</sub>	98%	Sigma Aldrich
4	Ceric Ammonium nitrate (NH <sub>4</sub> ) <sub>2</sub> Ce(NO <sub>3</sub> ) <sub>6</sub>	98%	Merck
7	Lead Nitrate	97%	Sigma Aldrich
9	Potassium Dichromate (K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> )	99.5%	Daejung Korea
10	Ethanol	99.8% ( Analar)	BDH
11	Ammonia solution	25-30% GR	Daejung Korea
12	Hydrochloric acid	65-69%	Sigma Aldrich
13	Nitric acid	64-66%	Sigma Aldrich
14	Sodium hydroxide	99.0-100%	Merck
15	EDTA dibasic	99.01-101.0%	Sigma Aldrich

Table 3.1: Raw material their purity and suppliers

## PHASE I (Synthesis)

### 1- Preparation of Ceric Ammonium Nitrate\ MCNTs composite

#### A- Oxidation of MCNTs

For oxidation of Multi walled nanotubes (MWCNTs) 500 mL nitric acid (5 M) 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. (Muataz Ali et al. 2010). 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 7 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. (Fig 3.1)

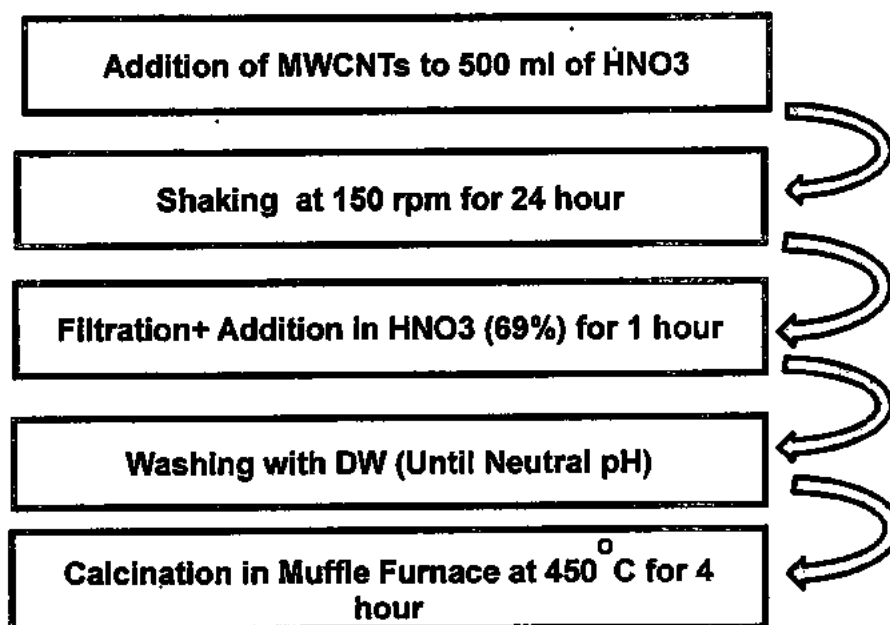


Fig 3.1: Flow sheet diagram for Oxidation Of MWCNTs

### B-Ceric Ammonium Nitrate\ MCNTs composite

For preparation of ceric ammonium nitrate\MWCNTs composite 3.0 gram  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$  was added into ethanol solution ( 40mL). This mixture remained under stirring at room temperature for 30 min, a yellow solution was obtained in result. 0.6 g of carbon nano tubes was added into yellow solution under continuous stirring for 5 h. The as- obtained solution was evaporated at  $60^\circ\text{C}$  and followed by oven drying at  $120^\circ\text{C}$  for 24 h.(Jie Shu et al. 2015) (Fig 3.2).

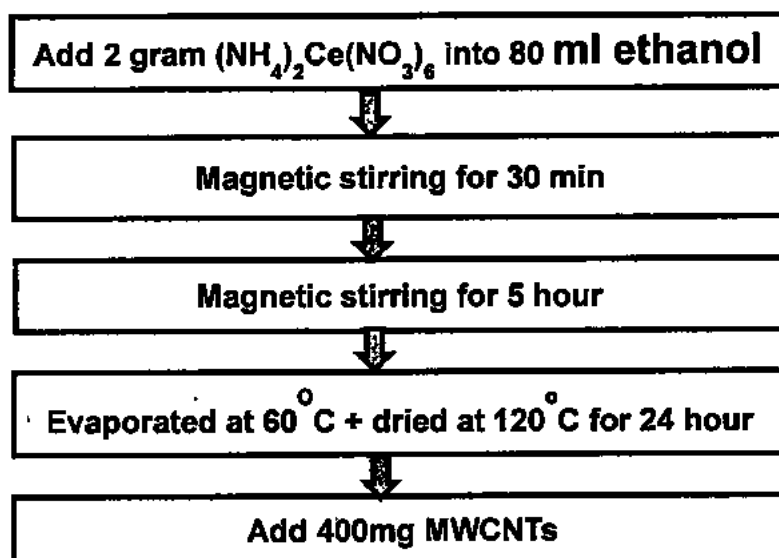


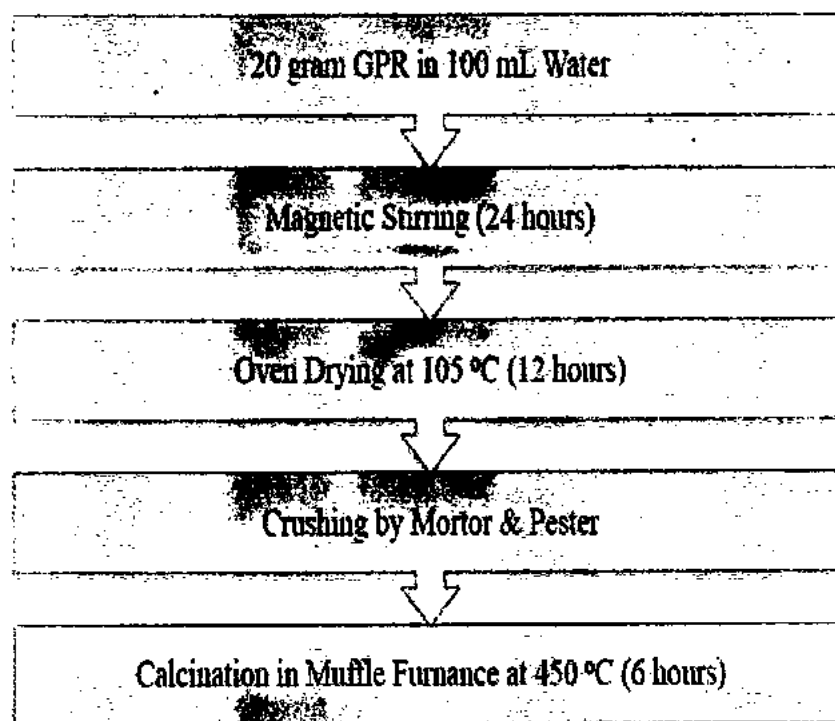
Fig 3.2: Flow sheet diagram for Ceric Ammonium Nitrate\ MCNTs composite

## 2. Synthesis of Iron doped $\text{TiO}_2\text{-Al}_2\text{O}_3$ Nano-composite

### A- Preparation of precursor material for $\text{TiO}_2\text{-Al}_2\text{O}_3$ Nano-composite

Titania Nanoparticles were used as a precursor for the formation of composite. In order to prepare precursor, titanium oxide was mixed in distilled water and stirred for 24 hours on

magnetic plate. Then the resulted slurry was placed in oven for 12 hours at 105 °C for drying. After drying and crushing, the dried slurry was placed in muffle furnace for 6 hours at 450 °C.



**Fig 3.3:** Flow sheet diagram for Preparation of precursor material for  $\text{TiO}_2\text{-Al}_2\text{O}_3$  Nano-composite

### 3.2.3. Synthesis of iron modified Titanium oxide composite

For this purpose, 3 gram prepared Titania Nanoparticles were mixed with 64 mg  $\text{Fe}_2\text{O}_3$  in to 200 ml of 10 Molar NaOH solution with 1 and 2 hour of sonication and stirring respectively. The resulted mixture was placed in a Teflon lined steel autoclave, maintained at a temperature of 135 °C for 24 hours with constant stirring at 300 rpm. Then the resulted solution was allowed to cool to room temperature. The solution as washed with 0.1 M HCl and distilled water numerous

times, until neutral pH reached. The sample was dried for 24 hours at 105 °C. At the end sample was annealed in muffle furnace at 500 °C for 1 hour. (Figure:3.4)

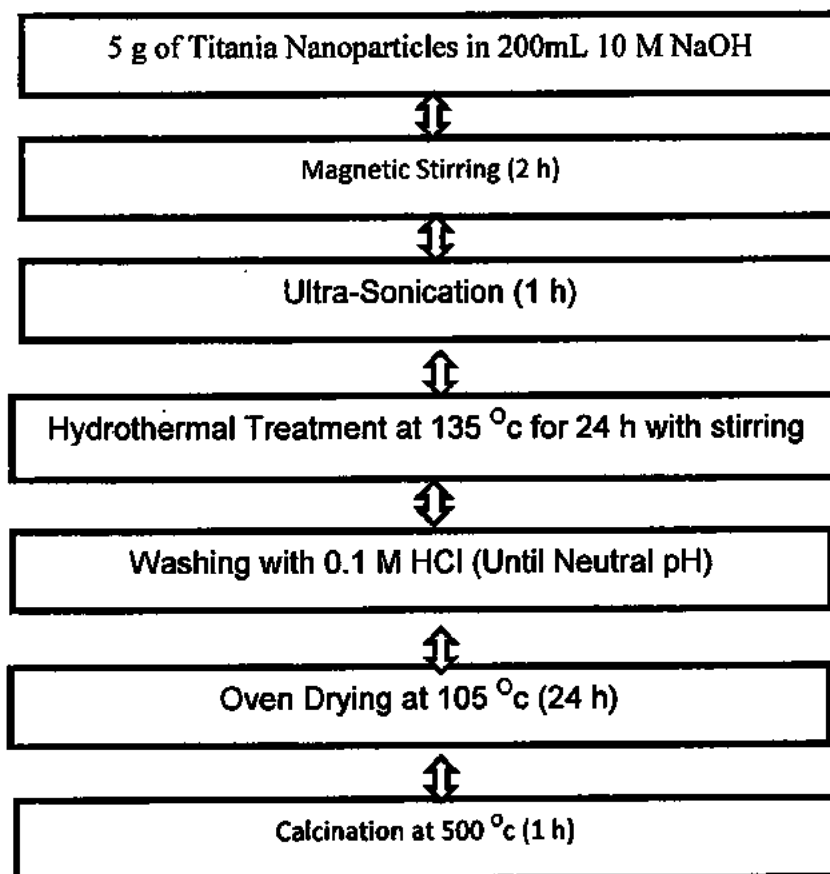


Fig 3.4: Flow sheet diagram for synthesis of iron modified Titanium oxide composite

### B- Synthesis of $Al_2O_3$ Nanoparticles

Alumina nanoparticles were prepared by sol-gel method (F. Kamil et al. 2015) with some modification 6.67 g Aluminum Trichloride was dissolved in 500 mL ethanol of 0.1 M concentration. 140 mL of Ammonia solution was added drop wise in stirred ethanolic Aluminum

Trichloride solution leading to gel formation. This gel remained under maturation for 30 h. After filtration in vacuum system, it was dried at 100 °C for 24 h. Collected material was introduced into preheated muffle furnace at 1000 °C for 2 h. (Figure 3.5)

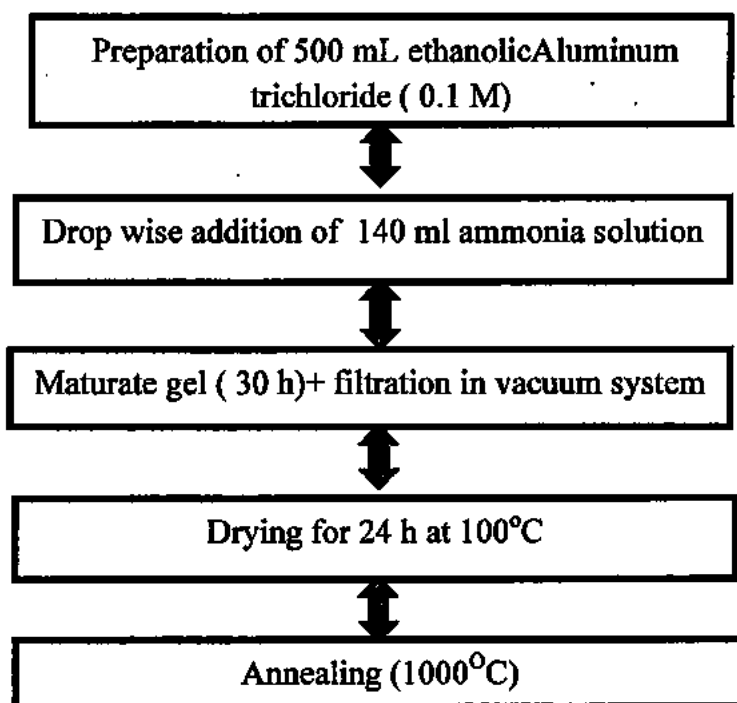


Fig 3.5: Flow sheet diagram for synthesis of Synthesis of  $Al_2O_3$  Nanoparticles

### 3.3.Characterization of Ce/CNTs and Iron Doped $TiO_2/Al_2O_3$ composite

Ceric ammonium nitrate\CNTs and Iron Doped  $TiO_2/Al_2O_3$  composite were characterized by Scanning Electron Microscopy (SEM): a more powerful tool for characterization, Fourier Transform Infrared Spectroscopy ( FT-IR): a nanoscale characterization tool, it was used to measure bonds in a material and UV-Vis spectroscopy: use to measure maximum absorption band of material.

### PHASE III (Application)

### A- Adsorption procedure for removal of Cr<sup>6+</sup> by ceric ammonium nitrate/CNTs

Adsorption experiments of Cr(VI) by magnetic MWCNTs were carried out in the batch mode. An amount of 0.1 g adsorbent was added to a 150 mL conical flask filled with 100 mL of chromate solution with a concentration of 2 mg/l. The solution was agitated at 500 rpm over different time periods. The aqueous phase was separated with centrifugation. The amount of Cr(VI) in the solution was measured with a spectrophotometer. The adsorption efficiency  $E$  is calculated using Eq. (1):

$$\text{Removal } E(\%) = \{(C_0 - C_e) / C_0\} * 100 \dots \dots \dots \text{ Eq. (1)}$$

Where  $C_0$  and  $C_e$  are the initial and equilibrium concentrations of Cr(VI) (mg/L), respectively. The adsorbed amount of Cr(VI) under equilibrium conditions,  $q_e$ , is calculated using Eq. (2):

$$q_e = \{(C_0 - C_e) * V\} / W \dots \dots \dots \text{ Eq. (2)}$$

Where  $V$  is the solution volume (L), and  $W$  is the adsorbent dosage (g).

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

#### Kinetic Modeling:

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:

$$1/q_e = 1/K_2q_e^2 + t/q_e \dots \dots \dots \text{ Eq. (3)}$$



Where:  $q_e$  and  $q_t$  are metal ions adsorbed at equilibrium and at time  $t$ , respectively, while  $K_2$  is the constant of second-order adsorption in  $\text{min}^{-1}$ .

### B- Adsorption procedure for Iron doped $\text{Al}_2\text{O}_3\text{-TiO}_2$ composite for lead (Pb) adsorption

The adsorption experiments were carried out with lead solutions at different initial  $\text{Pb}^{2+}$  concentrations (3.4 mg/l  $\text{Pb}^{2+}$ , 8.5 mg/l  $\text{Pb}^{2+}$ , 17 mg/l  $\text{Pb}^{2+}$ , 95 mg/l  $\text{Pb}^{2+}$ ) at pH 7 and at room temperature (Table 5). The composite suspension was made by using 320 mg/l, 340 mg/l and 560mg/l in de-ionized water. The pH of each composite suspension was adjusted at 7 using sodium hydroxide 0.1 M NaOH and 0.1 M HCl. Then 25 ml of lead solution was poured in a bottle and afterwards, 25 ml of each composite suspension was added drop by drop to the bottle. Finally, the suspension was continuously stirred at 150 rpm at room temperature. The samples obtained at different times were centrifuged.

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

$$\text{Removal } E(\%) = \{(C_0 - C_e) / C_0\} * 100 \dots \dots \dots \text{Eq. (1)}$$

Where  $C_0$  and  $C_e$  are the initial and equilibrium concentrations of Cr(VI) (mg/L), respectively.

The adsorbed amount of Cr(VI) under equilibrium conditions,  $q_e$ , is calculated using Eq. (2):

$$q_e = \{(C_0 - C_e) * V\} / W \dots \dots \dots \text{Eq. (2)}$$

Where  $V$  is the solution volume (L), and  $W$  is the adsorbent dosage (g).

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

**CHAPTER 4**

**RESULT & DISCUSSION**

### 1- UV-Vis analysis of TiO<sub>2</sub> nanoparticles

Room-temperature optical absorbance spectra of TiO<sub>2</sub> nanoparticles sample thermally decomposed at 400 and 500 °C for 5hr are shown in Fig. 1,2. The absorption spectra of all TiO<sub>2</sub> samples exhibit strong absorption at 340 nm and 360 nm. The characteristic spectrum of TiO<sub>2</sub> ranges from 220 to 370 nm, which is its fundamental absorption of Ti–O bond (Muneer M. Ba-Abbad, et al 2012), and as expected, Fe<sub>2</sub>O<sub>3</sub> shows the characteristic spectrum at 460 nm. Its fundamental absorption of Fe–O bond to UV light ranging from 220nm to 550 nm (Muneer M. Ba-Abbad, et al 2012).

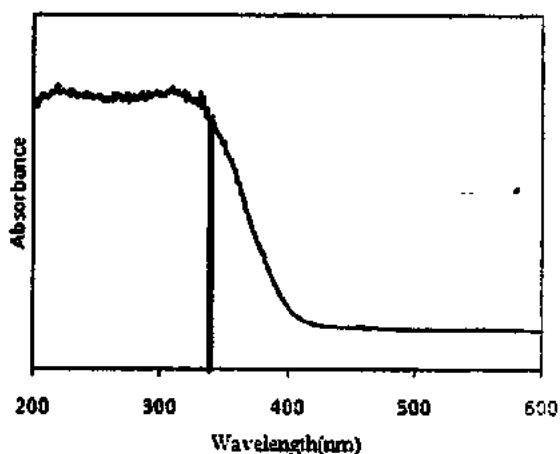


Fig1: UV-Vis Spectra of TiO<sub>2</sub> calcined at 400 °C

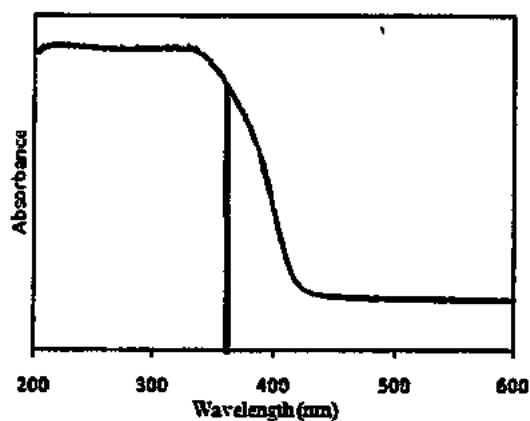


Fig2: UV-Vis Spectra of TiO<sub>2</sub> calcined at 500 °C

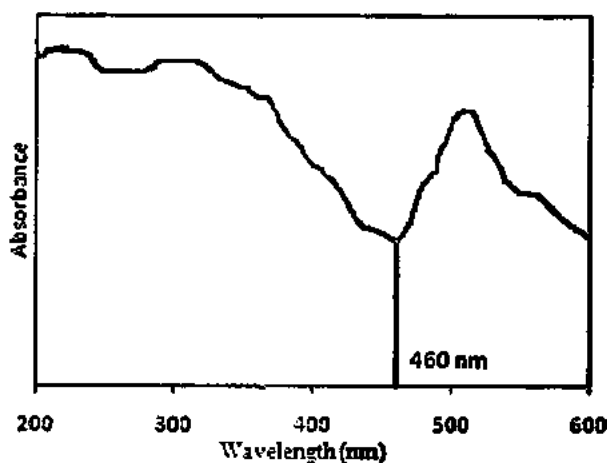


Fig 3:UV-Vis Spectra of iron oxide

## 2- UV-Vis analysis of Iron doped $\text{TiO}_2/\text{Al}_2\text{O}_3$ composite

From the spectrum of Iron doped  $\text{TiO}_2/\text{Al}_2\text{O}_3$  composite, it can be seen that there were a range 200-400 nm of absorption bands with maximum wavelength of 235, 340nm in ultraviolet region. The band from 220 to 330nm was assigned to the characteristic absorption of  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  and iron oxide in the UV light region. (Zhiyue Han et al, 2010). It is clearly seen that peaks in  $\text{TiO}_2/\text{Al}_2\text{O}_3$  composite are much sharper which are proving it good adsorbent material.

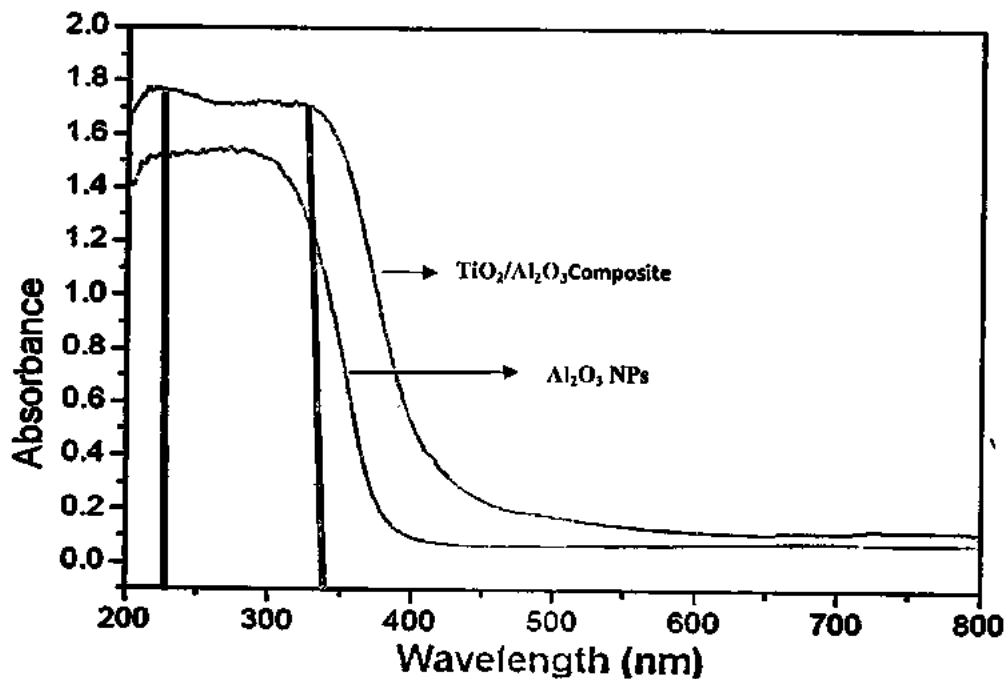


Fig 4 :UV-Vis Spectra of  $\text{TiO}_2/\text{Al}_2\text{O}_3$  Composite and  $\text{Al}_2\text{O}_3$  NPs

### 1- FT-IR spectra of TiO<sub>2</sub> nano-particles and Fe<sub>2</sub>O<sub>3</sub> particles

Fig 5 shows IR spectrum of TiO<sub>2</sub> nano-particles and Fe<sub>2</sub>O<sub>3</sub> particles. It can be seen that the FT-IR spectrum exhibits the characteristic absorption band of Ti–O–Ti at about 450–650 cm<sup>-1</sup>. From literature peaks comes at 460–700 cm<sup>-1</sup> for TiO<sub>2</sub> (J.C. Xu, et al 2005) It can be found the characteristic absorption band of Fe–O–Fe at about 470 and 560 cm<sup>-1</sup> in the FT-IR spectrum of the Fe<sub>2</sub>O<sub>3</sub> particles, which correspond to Fe–O stretching vibration and bending vibration.

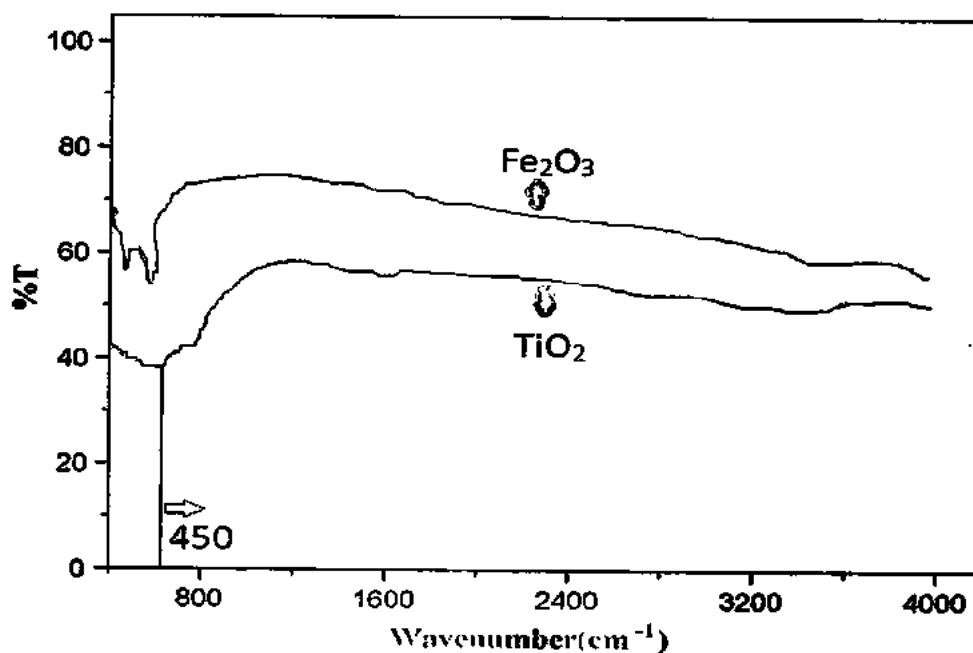


Fig 4: FT-IR spectra of TiO<sub>2</sub> nano-particles and Fe<sub>2</sub>O<sub>3</sub> particles

## 2- FT-IR spectra of Iron doped $\text{TiO}_2/\text{Al}_2\text{O}_3$ composite

FTIR spectra of  $\text{TiO}_2\text{-Al}_2\text{O}_3$  nano-composite are shown in Fig.3. The FTIR spectra of  $\text{TiO}_2\text{-Al}_2\text{O}_3$  nano-composite show pronounced bands at  $3600\text{ cm}^{-1}$  due to the hydroxyl group of the oxides. Hydroxyl group and surface-absorbed water show band  $3650$  and  $1650\text{ cm}^{-1}$ .(UmitOzlem and Fatima 2013).The IR band around  $3000\text{ cm}^{-1}$  shows the C-H stretching. The IR band of  $\text{TiO}_2\text{-Al}_2\text{O}_3$  nano-composite around  $700$  and  $800\text{ cm}^{-1}$  indicates the Ti-O-Ti and Al-O-Al bonds of composite (Ahmed MA et al 2011). In spectra of composite peaks of all components are sharper, which is confirming it as strong adsorbent.

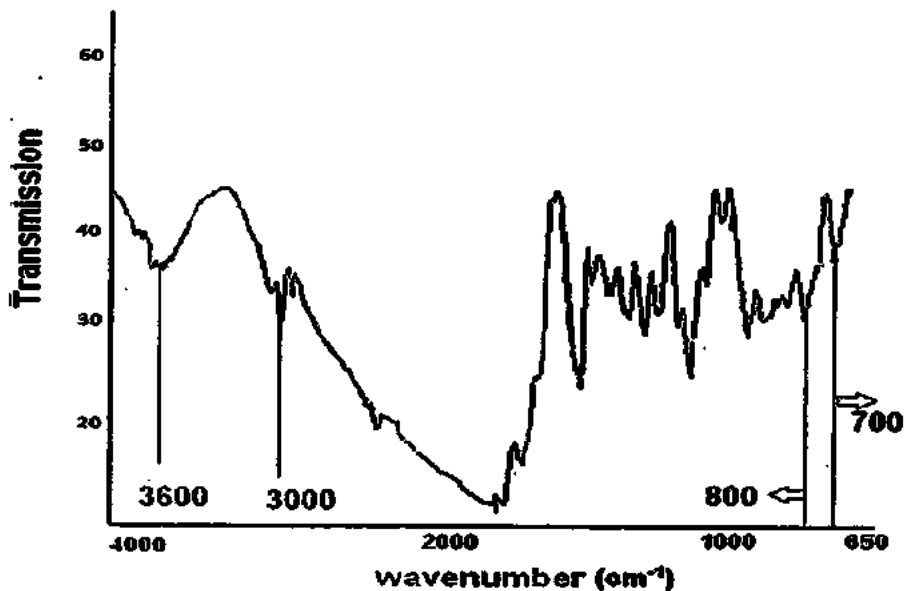
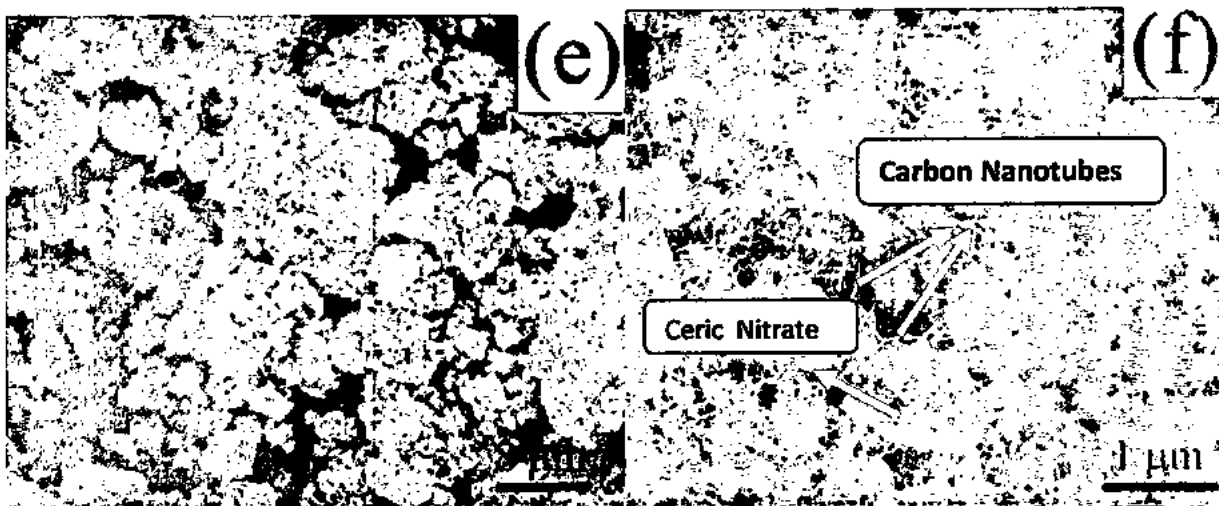


Fig 5: FT-IR spectra of Iron doped  $\text{TiO}_2/\text{Al}_2\text{O}_3$  composite

### 1- SEM characterization of Ceric Ammonium Nitrate\ MWCNTs composite

It can be seen from SEM images the morphology of Ceric Ammonium Nitrate\ MWCNTs composite and that many small particles can be obtained due to the CNT embedded in big  $(NH_4)_2Ce(NO_3)_6 \cdot 4H_2O$  particle. (Jie Shu et al, 2015) CNT attached on the surface of each small particle creates a CNT layer serving as a physical barrier to prevent the further aggregation of small particles. Thus providing larger surface area for adsorption of chromium in water media. (Fig 6)

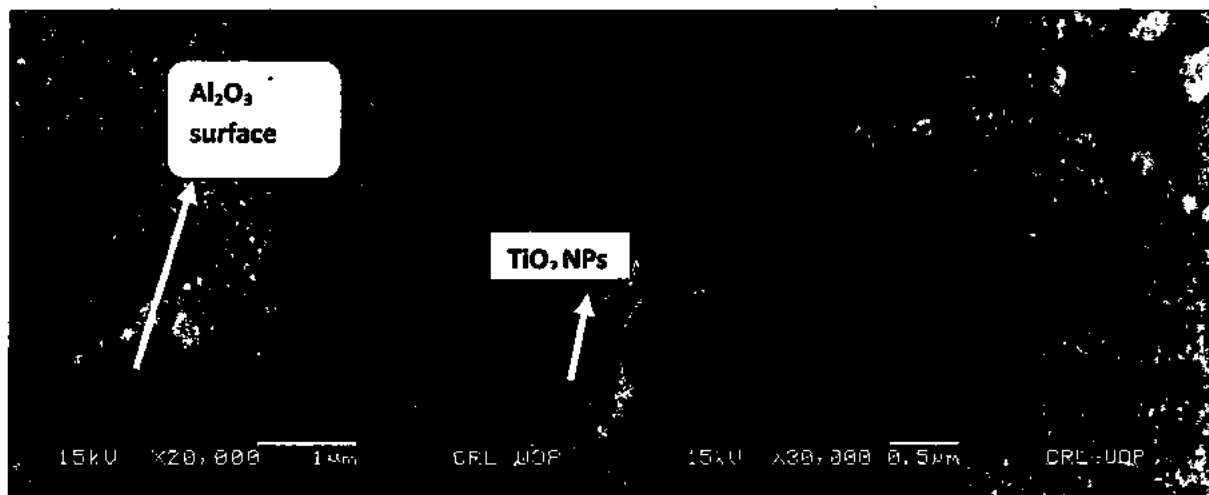
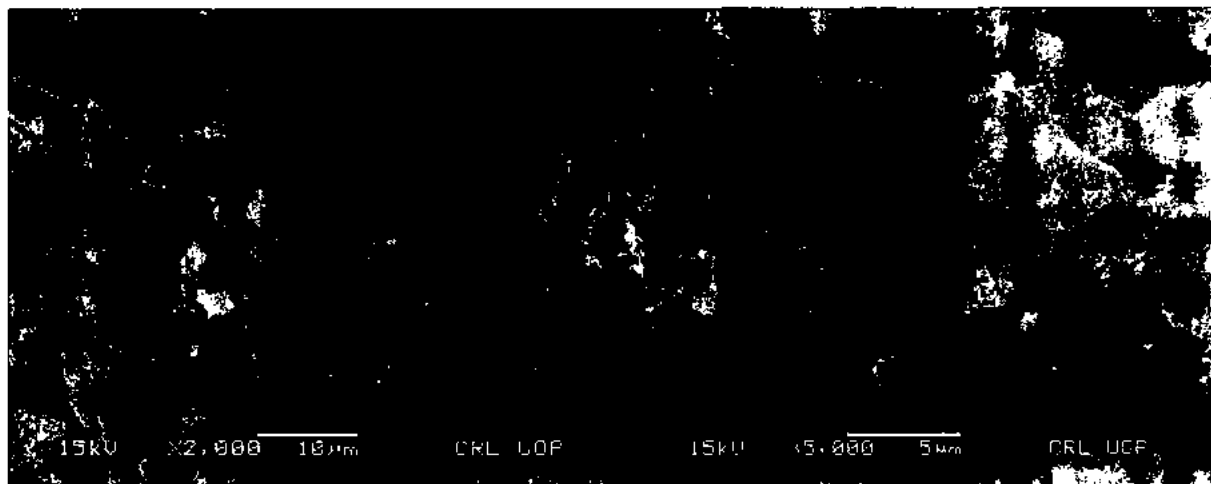


**Fig 6:** SEM images of Ceric Ammonium Nitrate\ MWCNTs composite

### 2- SEM characterization of Iron doped $TiO_2/Al_2O_3$

Fig.7 showing SEM images from high to low resolutions (10 μm, 5 μm, 0.5 μm, 0.2 μm). Images are displaying morphology of Iron doped  $TiO_2/Al_2O_3$ , and it is illustrated that high resolution have low particle size. The particles size was calculated by "J image software" which was 60 nm. It can be seen iron doped  $TiO_2$  were coated in the form of grain on the surface of  $Al_2O_3$  (L.-M. Wang et al 2008)

**Fig 7:** SEM images of Iron doped  $TiO_2/Al_2O_3$





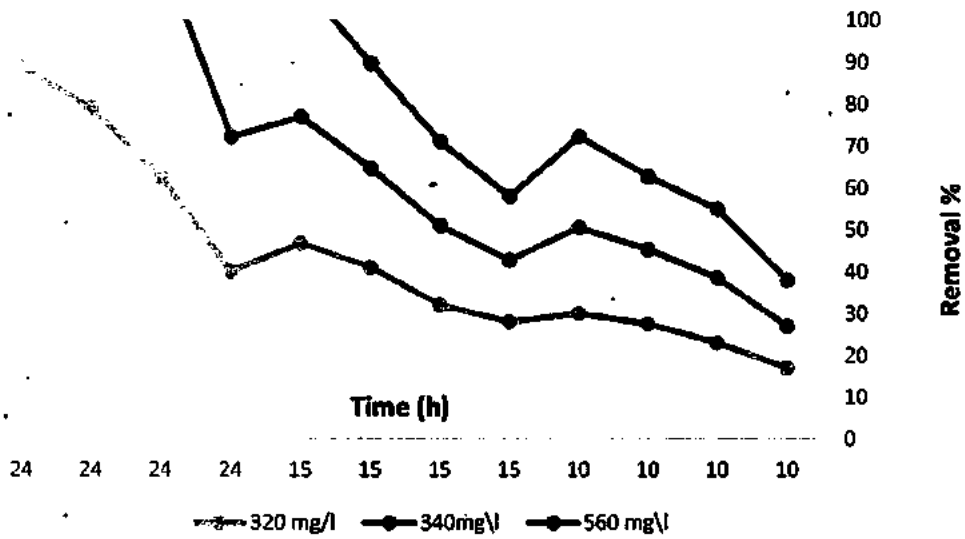
## Adsorption kinetics

### A-Iron doped $\text{TiO}_2/\text{Al}_2\text{O}_3$ nano-composite:

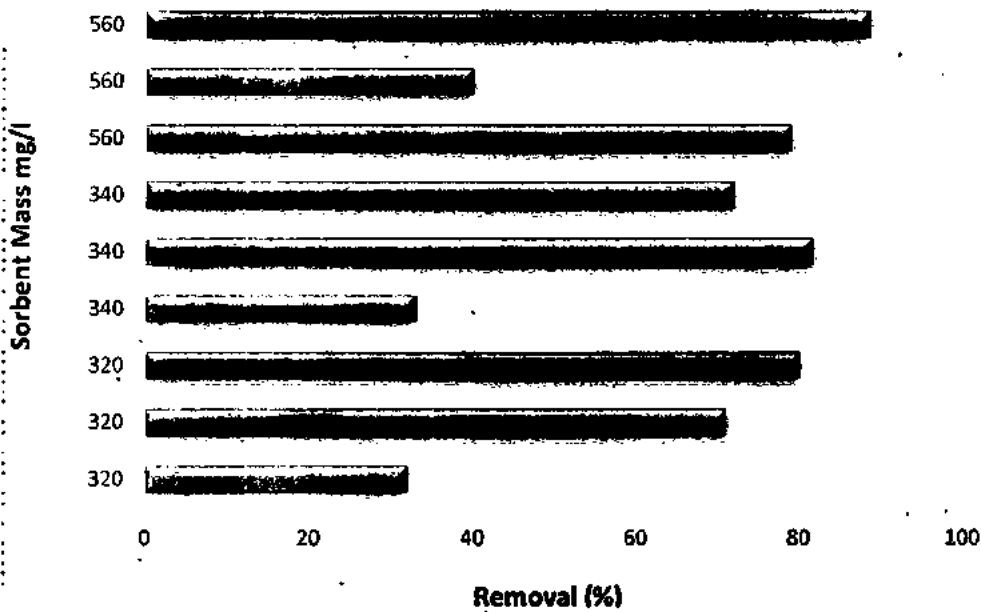
The adsorption evolution obtained for Iron doped  $\text{TiO}_2/\text{Al}_2\text{O}_3$  nano-composite is shown in Fig. 1. After around 10 h and 15 h the three batches reached equilibrium and were stable with time. The percentages of removal after 24 h of adsorption for 3.4 mg/l  $\text{Pb}^{2+}$  of initial concentration were: 88%, 81.6% and 80%. (Table 5) Experiments at different initial  $\text{Pb}^{2+}$  concentration were performed to evaluate the adsorption capacities of the  $\text{TiO}_2/\text{Al}_2\text{O}_3$  composite studied.

**Table 5:** Adsorption capacity (mg  $\text{Pb}^{2+}$ /g) after 24 h of reaction, Removal (%) and equilibrium  $\text{Pb}^{2+}$  concentration (mg/l) of  $\text{TiO}_2/\text{Al}_2\text{O}_3$  composite

$\text{Pb}^{2+}$ initial conc. (mg/l)	Composite Concentration (mg/l)	$\text{Pb}^{2+}$ equilibrium conc. (mg/l)	$q_e$ (mg pb/g adsorbent)	$\text{Pb}^{2+}$ removal (%)
3.4	320	0.68	8.5	80
8.5	320	2.47	18.84	71
17	320	7.99	28.16	53
95	320	64.6	95	32
3.4	560	0.39	5.37	88.5
8.5	560	1.78	12	79
17	560	6.37	19	62.5
95	560	57	67.8	40
3.4	340	0.62	8.17	81.6
8.5	340	2.38	18	72
17	340	7.9	26.8	53.5
95	340	63.6	92.64	33



**Fig 1:** Pb<sup>2+</sup> adsorption at pH=7 and room temperature. Initial composite concentration was 320mg/l, 340 mg/l and 560 mg/l and initial Pb concentration was 3.4 mg/l, 8.5 mg/l, 17 mg/l, 95 mg/l



**Fig 3:** Sorbent mass (Iron doped TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>) and Pb<sup>2+</sup> Removal efficiency

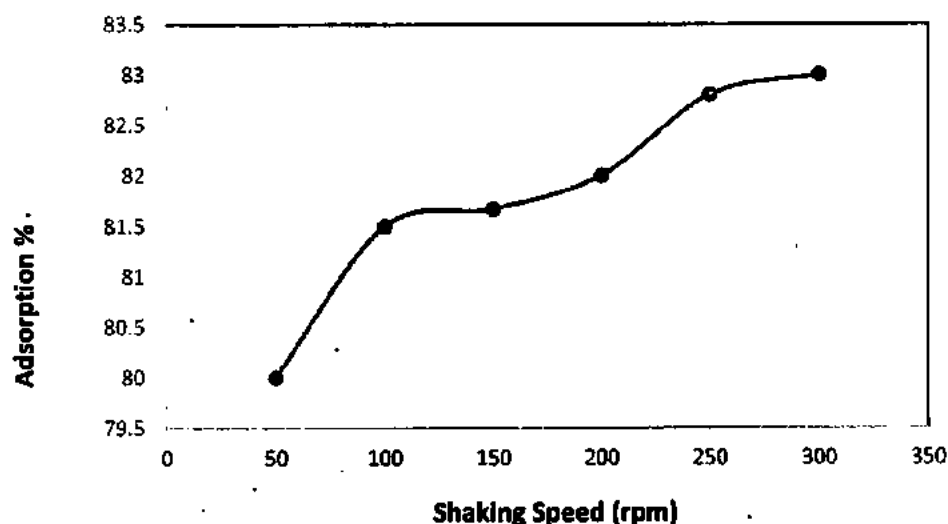


Fig 4: Effect of shaking speed on Adsorption of  $Pb^{2+}$  in water

The sorption equilibrium capacity ( $q_e$ ) of the adsorbed  $Pb^{2+}$  was calculated according to the following equation:

$$q_e = \frac{(C_0 - C_e) * V}{W}$$

Where:  $C_0$  and  $C_e$  represent the initial and equilibrium metal ion concentration (mg/l), respectively;  $V$  is the volume of the metal ion solution (mL), and  $m$  is the amount of adsorbent (mg) (Table 5).

The sorption equilibrium capacity ( $q_e$ ) obtained for 95 mg/l initial concentration of  $Pb^{2+}$  were: 95 mg  $Pb^{2+}$ /g composite, 92.64 mg  $Pb^{2+}$ /g composite and 67.8 mg  $Pb^{2+}$ /g composite (Table 5). Nano-composite removed lead ions from water above 80% and 70 % in 3.4mg/l and 8.7 mg/l initial concentration of  $Pb^{2+}$  respectively.

The effect of sorbent mass on percentage of lead removal is significant. With increasing mass of Iron doped  $TiO_2/Al_2O_3$  composite the removal of lead was also increased (Fig 3). With high Contact time and shaking speed the adsorbent has increased the amount of lead (Pb) (Fig 1, 2).

In literature  $TiO_2$ ,  $Fe_2O_3$  and  $Al_2O_3$  nanoparticles was used separately, at 3.4 mg/l concentration of lead, these NPs removed it 100 % ( Sonia Recillas et al, 2011). In this study there composite showed removal efficiency upto 81%.

### **B- Ammonium ceric nitrate/ CNTs composite**

#### **Effect of adsorbent dosage on Cr(VI) adsorption:**

The effect of adsorbent dosage on Cr(VI) adsorption was investigated with adsorbent dosages of ammonium ceric nitrate/ CNTs composite and modified CNTs (M-CNTs) with 0.01, 0.02, 0.05, 0.08, 0.1, and 0.2 g in 100 mL of chromate solution with a concentration of 2 mg/L. It can be seen in Fig. 7 that adsorption rate was slow with modified carbon nanotubes and the adsorption efficiency (E) increased from 10.35% to 80% when the dosage of composite increased from 0.01 to 0.1 g. This finding agrees with the recent work by Kosa et al. (2012). When the adsorbent dosage increased, the equilibrium adsorption capacity ( $q_e$ ) decreased considerably. Consequently, 0.08 g of magnetic MWCNTs in 100 mL of solution with a concentration of 2 mg/L was considered optimal for the Cr(VI) adsorption.

#### **Effect of Contact Time:**

The adsorption behavior of Cr by ammonium ceric nitrate/ CNTs composite in relation to the effect of contact time was carried out by varying the time from 10 minutes to 2 hours at a Cr concentration of 2 mg/L, a dose of adsorbent of 10 mg/L, and optimum pH of 7. The results presented in Figure 5 show that the adsorption rate was increasing for ammonium ceric nitrate/ CNTs composite after two hours and removal was 80 percent of Cr. It is indicating that by using this composite the reaction is fast and the adsorption sites are well exposed as compared to M-CNTs, which has low capacity for adsorption.

#### **Effect of Agitation Speed:**

The effect of agitation speed on adsorption capacity of chromium has been studied by varying the speed of agitation from 50 to 150 rpm as shown in Figure 6. It has been observed that the percentage of chromium removal increased slightly with increasing agitation speed. Agitation facilitates proper contact between the metal ions in solution and the composite binding sites. At 50 rpm and 100 rpm, the adsorption rates monitored were found to be slightly lower than that at 150 rpm. These results indicate that the contact between solids and liquid is more effective at 150 rpm.

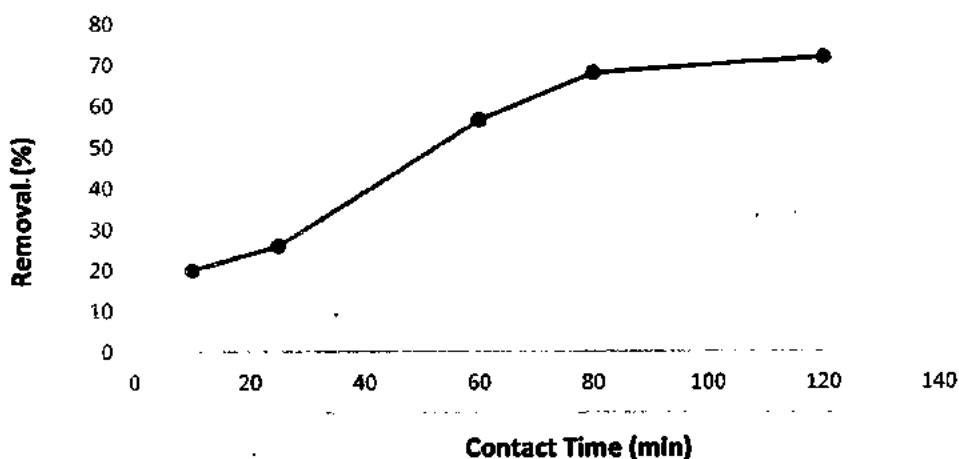


Fig 5: The effect time of contact time on percentage removal of chromium at 150 rpm at pH 7

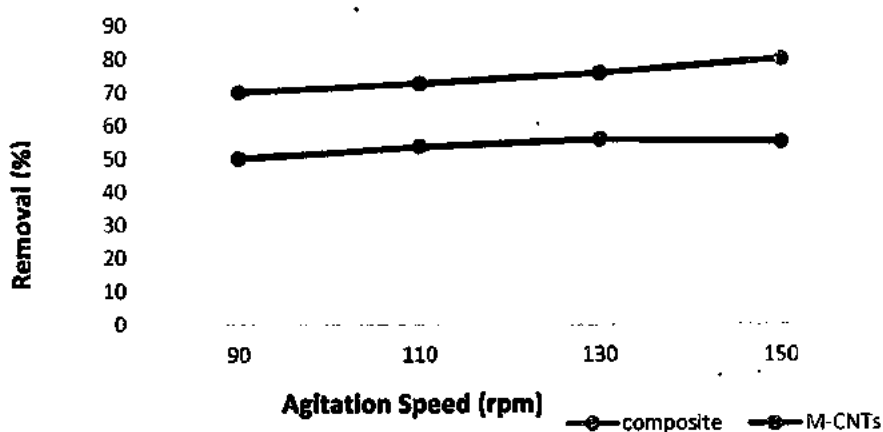


Fig 6: The effect time of agitation speed on percentage removal of chromium at pH 7

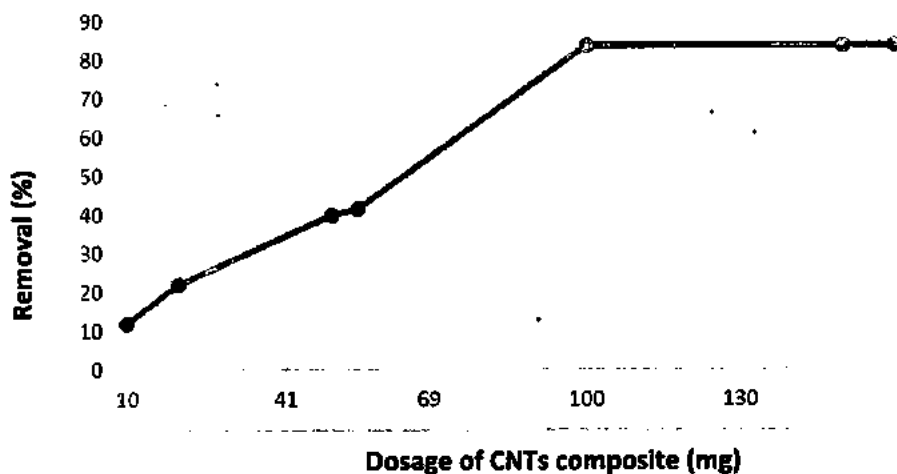


Fig 7: The effect time of Ammonium ceric nitrate/CNTs composite on percentage removal of chromium at pH 7

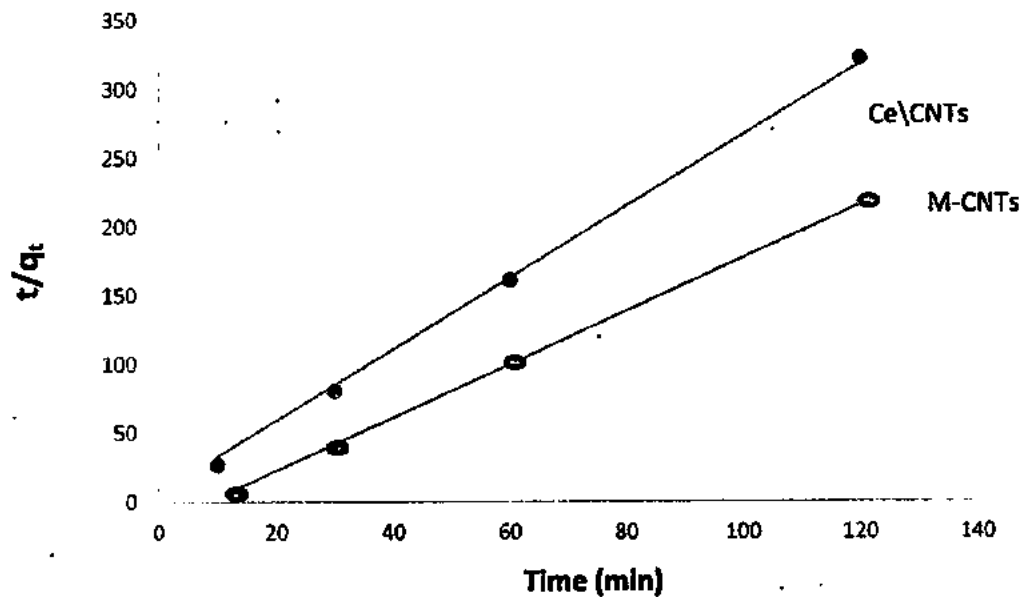


Figure 8: Pseudo-second-order kinetics of Cr (VI) using M-CNTs and Ce/CNTs

#### Kinetics Adsorption of Chromium (VI):

Modeling of kinetic data is fundamental for the industrial application of adsorption since it gives information for comparison among different materials under different operational conditions for designing and optimizing operational conditions for pollutant removal from wastewater systems (A. Nassereldeen et al, 2009)

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:

$$1/q_t = 1/K_2q_e^2 + t/q_e \dots\dots\dots \text{Eq. (3)}$$

The pseudo-second-order rate constants ( $k_2$ ) and the amount of  $Pb^{2+}$  adsorbed at equilibrium ( $q_e$ ) were calculated experimentally by plotting  $(t/q_t)$  versus  $t$  according to Eq. (3), where  $q_e$  is the amount of  $Pb^{2+}$  adsorbed (mg/g NPs) at equilibrium, while  $q_t$  is the amount of the adsorption (mg/g) at any time  $t$ .

The kinetics adsorption model has been done for chromium (III) at pH 7 to avoid forming chromium complexation that leads to precipitation. The parameters of modeling are shown in following table.

By plotting of versus time (Figure 8) yields very good straight lines. The second order-rate constant obtained from this figure are 0.097 for Ce/CNTs and 0.055 ( $g \cdot mg^{-1} \cdot min^{-1}$ ) for M-CNTs. The second order rate constant indicates that time to achieve equilibrium concentration of Cr (III) is less by using Ce\CNTs compare with M-CNTs. The equilibrium adsorption capacity, obtained from the graph also implies that Ce/CNTs have higher adsorption capacity (mg/g) as compared to M-CNTs (mg/g). This phenomenon is very similar to Zhuo-nan Huang et al. 2015. Differences in adsorption capacities were observed in literature: magnetic CNTs composite for Cr,  $q_e = 1.680$  mg/g (Zhuo-nan Huang et al. 2015) and for modified MCNTs  $q_e = 0.5$  (Muataz Ali et al, 2010). In the case of Ce\CNTs larger adsorption capacity has obtained.

**Table 2 Pseudo-second- order model for chromium by Ce/CNTs**

$C_0$ (mg/l)	$q_e$ (mg/g)	$K_2(g \cdot mg^{-1} \cdot min^{-1})$	$R^2$
2.00 (Ce/CNTs)	1.729	0.097	0.9997
2.00 (M-CNTs)	0.789	0.055	0.9996

# **Chapter 5**

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