

**IMMOBILIZATION IN MORTAR OF CHROMIUM REMOVED FROM
WATER USING TITANIA NANOPARTICLES**



By

AHMED HUSNAIN

NUST201362303MSCEE65213F

A thesis submitted in partial fulfillment of the requirements for the degree
of

Master of Science

In

Environmental Science

Institute of Environmental Sciences and Engineering (IESE)

School of Civil and Environmental Engineering (SCEE)

National University of Sciences and Technology (NUST)

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It is certified that the contents and forms of the thesis entitled

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Submitted by

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Master of Science in Environmental Science

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DEDICATED TO.....

MY BELOVED PARENTS & RESPECTED TEACHERS

***WITHOUT THEIR SUPPORT ALL THIS WOULD NOT HAVE BEEN
POSSIBLE***

ACKNOWLEDGEMENTS

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 planning, executing and finally, presentation, of this study.

First and foremost, I would like to express my sincere gratitude to my thesis supervisor Prof. **Dr. Ishtiaq A. Qazi** (IESE) for his continuous support throughout my stay at IESE, for his patience, motivation, enthusiasm, and immense knowledge. His guidance helped me through my research and writing of this thesis. I could not have imagined having a better advisor and mentor for my MS studies.

Many thanks also go to **Dr. Muhammad Arshad** (IESE) for their guidance and support.

I am also very thankful to the **Dr. Wasim Khaliq** (NICE) for his unfailing moral support as my external advisor.

I am grateful to the staff of the Waste Water Lab, for the technical assistance. Last but not least, I would like to express my gratitude to all my friends, for their support during this arduous academic odyssey.

Ahmed Husnain

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LIST OF ABBREVIATIONS

EDS	Energy Dispersive Spectroscopy
FWHM	Full width of a diffraction line at half of maximum intensity
GPR	General Purpose Reagent
IESE	Institute of Environmental Sciences and Engineering
LI	Liquid Impregnation
SEM	Scanning Electron Microscopy
TiO ₂	Titanium Dioxide
UV	Ultra Violet
Vis	Visible
XRD	X - Ray Diffraction
λ	Wavelength
TCLP	Toxicity Characteristic Leaching Procedure
DPC	Diphenylcarbazine
US EPA	United States Environmental Protection Agency
WHO	World Health Organization
MCL	Maximum Concentration Level
Cr	Chromium
NEQS	National Environmental Quality Standards
UNIDO	United Nations Industrial Development Organization

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ABSTRACT

Because of the high toxicity of chromium, particularly as Cr (VI), it is removed from industrial effluents before their discharge into water bodies, by a variety of techniques, including adsorption. Ultimate disposal of the sludge or the adsorbate, however, is a serious problem. While titania, in nanoparticle form, serves as a very good adsorbent for chromium, as an additive, it also helps to increase the compressive strength of mortar and concrete. Combining these two properties of the material, titania nanoparticles were used to adsorb chromium and then added to mortar up to a concentration of 20% by weight. The compressive strength of the resulting mortar specimen that replaced 15% of cement with chromium laden titania showed an improved strength than that of the one without titania, thus confirming that this material had positive effect on the mortar strength. Leachate tests using the Toxicity Characteristics Leaching Procedure (TCLP) confirmed that the mortar sample chromium leachate was well within the permissible limits. The proposed technique thus offers a safe and viable method for the ultimate disposal of toxic metal wastes, in general, and those laden waste chromium, in particular.

INTRODUCTION

Chromium (Cr) is a naturally occurring element found in rocks, soil, animals, plants and volcanic ash and gases, is one of the most abundant elements in the Earth's crust. It exists in different oxidation states ranging from - IV to + VI inclusively. The most stable forms of chromium are trivalent (III) chromium and hexavalent (VI) chromium (Becquer *et al.*, 2003). In nature Cr is chiefly found in the trivalent form (Kotas *et al.*, 2000) while, hexavalent chromium is almost totally derived from anthropogenic activities in the environment (Schneider *et al.*, 2012). Whereas, the principle users of chromium are the metallurgical, chemical, and refractory industries (Dayan *et al.*, 2001). The major sources of chromium pollution include leather tanning and chrome plating processes (Sharma *et al.*, 2012).

1.1 Chromium Toxicity

Chromium in the hexavalent oxidation state, Cr (VI) is of grave concern because its toxicity, high solubility, and mobility in water (Santonen *et al.*, 2009; Rashid *et al.*, 2011) makes it 500 times more toxic than the Cr (III) (Krishna *et al.*, 2012). It has been recognized as a pulmonary carcinogenic along with causing other health effects such as respiratory, skin, carcinogenic, renal, hepatic and haematological problems while being genotoxic and mutagenic (Saha *et al.*, 2011). Cr (VI) was found to be carcinogenic to rats and mice after chronic oral exposure (Stout *et al.*, 2009). Cr (VI) penetration in skin will cause erosive ulceration "chrome holes" with deferred healing (Erniza *et al.*, 2014) and increased stomach and lung cancer risk in humans due to Cr (VI) exposure has also been reported (Beaumont *et al.*, 2008). Alteration in the germination process and effect on the growth of roots, stems and

leaves are the toxic effects of accumulated Cr on plant growth and development (Shanker *et al.*, 2005).

1.2 Chromium Waste Treatment Methods

Methodologies have been developed for removing chromium from industrial wastewater by chemical precipitation, ion exchange, electrochemical treatment, membrane filtration, flotation, coagulation, flocculation and adsorption (Barakat *et al.*, 2011; Wang *et al.*, 2011). Adsorption is considered to be one of the most suitable chromium removal methods due to its cost effectiveness, higher efficiency, ease of operation (Djellabi *et al.*, 2014) and the availability of a wide range of adsorbents like silica composites (Kumar *et al.*, 2007), activated carbon (Babu *et al.*, 2012), fly ash (Veni *et al.*, 2012), bone charcoal (Dahbi *et al.*, 2002) and microbes (Liu *et al.*, 2013).

Titania nanoparticles have also proven themselves to be excellent adsorbents for chromium due to their unique features like physical and chemical stability, low cost, non-toxicity and resistance to corrosion (Hung *et al.*, 2007). In one study titania showed highest capacity for Cr (VI) removal out of other photo-catalysts including zinc oxide and cadmium sulfide (Joshi *et al.*, 2011). Titania also helps in the photo-catalytic reduction of Cr (VI) to Cr (III) (Malaviya *et al.*, 2011).

Now, no matter, how chromium is removed from an effluent, the ultimate disposal of the concentrate, or sludge, with concentrated chromium still remains a major problem. In what follows, we propose a viable solution for safe and permanent disposal of such concentrated waste by incorporating it in cement mortar.

1.3 Applications of Titania Nanoparticles

While, environmental pollution remediation, self-cleaning and self-disinfection are the principal applications of titania based photo-catalytic building materials (Chen *et al.*, 2012), there is a potential for using chromium-tanned leather residue in civil engineering to obtain technical, economic and environmental benefits (Oliveria *et al.*, 2012). The application of titania for decreasing oxides of nitrogen and volatile organic compounds has received greater attention of the civil engineering community because of potential benefits in reducing environmental pollution (Cardenas *et al.*, 2012). White cement containing titania, possessing photo-catalytic properties allows maintaining the aesthetic characteristics of concrete over time, while eliminating dangerous pollutants from the urban environment. White cement also increases the mechanical strength of concrete (Cassar *et al.*, 2003).

On the other hand, several nanomaterials including titania can be used in cementitious matrices to improve their physicochemical behavior in cement, mortar and concrete (Chen *et al.*, 2012). Similarly, partial replacement of cement with nanophase titania particles improves the compressive strength of mortar and concrete (Nazari *et al.*, 2010). The addition of nano-titania powders in cement mortar significantly decreased the porosity and accelerated the hydration rate of such materials at early stages. Thus, compression strength of the mortar was increased, virtually at the early stage (Meng *et al.*, 2011).

1.4 Ultimate Disposal Problem

Removal and ultimate disposal of the heavy metals, from industrial waste water, in general, and chromium, in particular, is of critical importance. Ultimate safe disposal of the chromium wastes generated from steel and other alloy production, chrome plating, pigments

and leather tanning industries to safeguard human health and environment is an issue of grave concern (Wang *et al.*, 2000).

1.5 Proposed Solution

Since there have been reports in the literature where the chromium metal has been immobilized within solid matrices including geo-polymers and concrete for final disposal (Galiano *et al.*, 2011; Giergiczny *et al.*, 2008), this opens up the possibility of immobilizing chromium, in mortar and concrete, in such a manner that the probability of leaching is considerably reduced, leading to a safe and permanent solution for the disposal of hazardous waste containing chromium. A technique is introduced whereby Cr (VI), from aqueous solution is photo-catalytically reduced to Cr (III) and adsorbed on titania nanoparticles the latter being incorporated into mortar blocks with improved mechanical properties and showing little leaching of the toxic metal. On the basis of what has been discussed above, it was, therefore hypothesized that chromium adsorbed on titania nanoparticles can be effectively immobilized in mortar blocks.

1.6 Objectives

The objectives of this research work were:

1. Remove chromium from waste water using titania nanoparticles.
2. Incorporate chromium adsorbed on titania, into mortar blocks for chromium immobilization.
3. Test the effectiveness of chromium immobilization by chromium leachate test using Toxicity Characteristic Leaching Procedure (TCLP).

1.7 Significance of Work

Chromium sludge handling by immobilizing into mortar after adsorbing on titania nanoparticles offers a sustainable, safe and ultimate disposal option for the hazardous waste. The procedure is recommended for pavements, structural and non-structural works in the construction industry for ultimate safe disposal of toxic metals in general, and chromium in particular.

LITERATURE REVIEW

2.1 Background

Environmental pollution is a major concern for many countries including Pakistan with an increasing rate of population, fast consumption of natural and synthetic resources, deficient in energy and power requirements and increase in industrialization. Every aspect contributes towards the increase of pollution either air pollution, water contamination or soil pollution. Rapid industrialization is a major threat for causing water pollution as industrial waste water contaminates the rivers, lakes and fresh water underground for domestic usage.

Many industries like, leather, textile, paints and pigments, fertilizer and chemicals are responsible for polluting water with heavy metal ions. The combination of different toxic metals in our environment can cause extreme exposure which may be harmful to human health. Metal pollution comes from both natural sources including erosion of the drainage basin and human activities (Bertin, et al., 1995).

Heavy metal ions like, chromium, mercury, lead, phosphorous, copper, iron, and cadmium are toxic with a high solubility in water (Labanda et al., 2009). Removal of these heavy metal ions from industrial waste water is an area under focus by many scientist and researchers since the last few decades throughout the world to meet the local environmental standards. Industries need to treat the waste water before it mixes with major resources of water.

Many conventional routes have been adopted for the eviction of these toxic metal ions from waste water but the problem of ultimate safe sludge disposal option still needs much

attention. Of all the heavy metals, chromium is considered highly toxic as it is found in two different valence states and is a health hazardous (Krishna *et al.*, 2012).

Nanotechnology is considered to be one of the most important future technologies. Development of new materials and their understanding at ever increasingly smaller scale is at the root of progress in the materials research. Removal of heavy metal ions by employing the nanoparticles is an area under focus due to unexpected results found at nano-scale dimensions as compared to bulk properties. In recent years, nano-crystalline materials have thus become a subject of great concern in research because of their different properties, both from the principal and application point of view (Lida *et al.*, 2007).

2.2 Introduction to Chromium

Trivalent chromium, Cr (III), and hexavalent chromium Cr (VI) are the two primary and stable forms of chromium (Wang *et al.*, 2011). Plants and animals required trivalent chromium in low doses and hexavalent Chromium is an environmental pollutant of grave concern. Chromium and its compounds are largely used in electroplating, alloy formation, pigment synthesis, glass and ceramic manufacturing and tanning of leather.

Exposure to heavy metals like chromium even in small concentrations is a threat for healthy environment therefore their complete removal is still a challenging task for current researchers (Barakat *et al.*, 2011). All chromium compounds are colored and the most essential chromium compounds are the chromates of sodium and potassium and their dichromates (Wang *et al.*, 2011).

2.3 Occurrence of Chromium

Chromium is one of the most abundant element in Earth's crust with an average concentration of 100 ppm (Emsley *et al.*, 2001). The most stable forms of chromium are trivalent chromium (III) and hexavalent chromium (VI). Trivalent chromium is less mobile, less toxic and is primarily found bound to organic matter in soil and aquatic environments (Becquer *et al.*, 2003). Hexavalent chromium is the second most stable state. However, it barely occurs naturally, but is produced from human activities (USEPA, 1984). Naturally, it exists in the rare mineral crocoite (PbCrO_4) (Hurlburt *et al.*, 1971).

2.4 Sources of Chromium

Chromium does not exist freely in nature. Chromite (FeOCr_2O_3) is the main chromium mineral. Chromium (VI) in industrial waters primarily emerges from tanning and painting. Compounds of chromium are used as pigments, and 90% of the leather is tanned by using pigmented chromium compounds. Chromium may be used as a catalyst, in wood impregnation, in audio and video production and in lasers. Chromium may be present in household waste from different synthetic materials. Chromium may spread to the environment through waste incineration, when protection is not sufficient (Sharma *et al.*, 2012).

2.4.1 Environmental Sources of Chromium

Environmental origins of chromium include:

- Airborne emanations from chemical plants and incineration facilities,
- Dust of cement,
- Polluted landfill,

- Chemical plants effluents,
- Asbestos lining erosion,
- Dust of road from catalytic converter erosion and asbestos brakes,

2.4.2 Natural Sources of Chromium

Chromium is a naturally occurring element which is found in rocks, soil, animals, plants and volcanic ash and gases. Oil and coal have traces of chromium (III). Chromium is primarily found in form of chromium (III) in nature (ATSDR, 2000).

2.4.3 Anthropogenic Sources of Chromium

Globally, approximately 12 million tons of chromite ore are mined annually (Belay *at al.*, 2010). Cr (III) complexes are used particularly in wool dyes (Santonen *at al.*, 2009). Chromium is usually in the form of chromium (III) oxide or chromite, in refractory products. Chromite ore is used as foundry sand (Lytle *at al.*, 1998).

2.4.3.1 Tanning Process a Major Chromium Pollution Source in Pakistan

According to Blacksmith Institute's The World's Worst Toxic Pollution Problems Report 2011, chromium pollution from tannery operation is among the top ten of the toxic twenty World's worst pollution problems (Brown *et al.*, 1997). In Pakistan tannery industries in Kasur are mostly responsible for Chromium discharged into water bodies. In District Kasur Pakistan, there are about 230 tanneries out of the total 650 in the country (Atiq *et al.*, 2004). According to United Nations Industrial Development Organization (UNIDO), at present the tanneries in Kasur discharge around 13,000 cubic meters per day of tannery wastewater. In Sialkot, Pakistan tannery wastewater is highly polluted in nature and is affecting the soil, and

indirectly, the ground water by leaching into the water table of the Sialkot region (Mahmmod *et al.*, 2010).

2.5 Chromium Applications

Chromium oxide (CrO_2) is used to fabricate magnetic tape. Chromium is used to give glass an emerald green color. Compounds of chromium are used in the textile industry as mordents (Kumar *at al.*, 2007). The refractory industry uses chromite ores for forming bricks and molds, as it has a high melting point, and crystalline structure stability (Song Z. *et al.*, 2000). Blood flow regulation, cholesterol levels moderation, lean muscle mass contribution, arterial health promotion, immune system boosting and protein synthesis stimulation are the main functions of chromium in trace element form in the body (Costa *et al.*, 2003).

2.5.1 Historical Uses of Chromium

In the mid-1800s, iron manufacturers discovered that chromium addition to steel produced a harder, more useful metal. As early as, 1820 the cotton and wool industries were using large amounts of compounds of chromium such as potassium dichromate in the dyeing processes. Red and green pigments developed from the compounds of chromium were also used for printing wallpaper. In 1849, a Frenchman obtained a copyright for a method that made gold stick to iron with an intermediate film of chromium. R. W. von Bunsen, inventor of the Bunsen burner, investigated chromium electroplating and fabricated small samples of electro-deposited chromium in 1854 from chromium chloride solutions (Saha *at al.*, 2011).

Jewelry fabrication was the first application of chrome plating. As the process of plating became cheaper and more common, plumbing fixtures and household devices were plated with chrome. The attractive lustrous surface and the resistance to corrosion made

plated devices aesthetically adorable. Soon, end users were demanding chrome plating on all their devices, and car manufacturers began making the chrome bumpers and molding which was the characteristic of 1950's auto designs (Kotas *et al.*, 2000). In the 19th century, potassium dichromate was used as an excellent mordant in textile dyeing and chrome began to be used in refractory bricks and foundry sands, for molding purpose (Dhabi *et al.*, 2002).

2.5.2 Modern Uses of Chromium

The metallurgical, chemical, and refractory industries are the primary users of chromium (Dayan *et al.*, 2001). Cr (III) oxide pigments are used in paints, plastics, concrete building products, artistic colors, ceramics, and glass. It is also used in the cosmetic and personal care products such as eye shadows and soaps (Barnhart *et al.*, 1997). The pigments of chromium oxide are used due to their color, firmness, and persistence. (Paine *et al.*, 2001).

Chromium (III) is an important dietary mineral in low doses. Its scarcity in the body has been linked with diabetes, infertility, and cardiovascular disease (EPA 1998; ATSDR 2000). Chromium (III) is considered to be a trace element important for the proper functioning of living organisms. It is noted to be liable for the control of glucose and lipid metabolism in mammals (Anderson *et al.*, 1989).

2.6 Chromium in Cement Manufacturing

Chromium in the cement can originate from:

- 1) Raw materials or fuel
- 2) Magnesia-chrome kiln refractory brick, if used
- 3) Wear metal from raw mill grinding process, if chromium alloys are used (Sinyog *et al.*, 2011).

2.7 Chromium Toxicity

Since Cr (III) is poorly absorbed by any route of the human body, chromium toxicity is mainly determinable to the Cr (VI) form. It can be absorbed by the lung and gastrointestinal tract (Mohanty *et al.*, 2005). Generally, Cr (VI) is considered 1,000 times more harmful than Cr (III) (Dayan and Paine 2001). The chromium toxicity notably increases as the pH of the precipitation decreases. Acid rain elevates the harmful effects of heavy metals toxicity on aquatic life (Tasneem Abbasi *et al.*, 2009).

The annual contribution of chromium due to human activities into water has been predicted to exceed the contribution of chromium into the atmosphere (Pacyna *et al.*, 1988; (Danadevi *et al.*, 2003). Hexavalent chromium, direct and indirect exposures causes genetic changes in leather tanning industry workers (Vellingiri *et al.*, 2010). Skin contact of hexavalent chromium compounds can cause skin allergies, dermal necrosis and dermal corrosion (Gad *et al.*, 1989).

2.7.1 Environmental Effects of Chromium

Hexavalent chromium compounds are lethal for both flora and fauna at high concentrations (Alazemi *at al.*, 1996). They are stable under aerobic conditions, but are reduced to trivalent chromium compounds in absence of oxygen. Chromium concentrations, between 500 and 6000 mg/L in soils, are not toxic for plants. Generally, under normal conditions plants consist of approximately 0.02-1 mg/L chromium in form of dry mass, although values may rise to 14 mg/L (Altaf *et al.*, 2008). The toxicity process of chromium is pH dependent (Lee *et al.*, 1989).

2.7.2 Chromium Impacts on Human Health

Generally, Chromium (VI) is more harmful than Chromium (III). The hexavalent form is 500 times more harmful than the trivalent form (Kowalski, 1994). There is a study in the Liaoning province in China which illustrates the increased stomach and lung cancer risks due to hexavalent chromium following ingestion of Cr VI in drinking water (Beaumont *et al.* 2009). According to the Occupational Safety and Health Administration (OSHA), occupational risk to chromium (VI) can result in asthma and may cause nasal epithelia and skin irritations (Federal Register, 2006).

Chromium (VI) is toxic to microorganism plants, animals and humans and includes lung cancer, as well as kidney, liver, and gastric damage (US Department of Health and Human Services 1991; Golonka *et al.*, 1995). Shortness of breath, coughing, wheezing, septum, bronchitis, decreased pulmonary function, pneumonia, and other respiratory disorders have been observed from chronic exposure of hexavalent chromium (Cr) (Mugica *et al.*, 2002). Cr (III) is an important nutrient for humans and its shortage may cause heart conditions, disruptions of metabolisms and diabetes (DuPont *et al.*, 2003). People who smoke tobacco are also more vulnerable to chromium (Belay *et al.*, 2010).

2.7.2.1 Respiratory Effects

The chromium dust can cause pulmonary irritant effects following inhalation. Some of the common respiratory effects include asthma, chronic bronchitis issues, chronic irritation, chronic pharyngitis, chronic rhinitis problems, congestion issues, hyperemia and ulceration of the nasal mucosa with potential septal perforation. Many problems of nasal mucosa injury have also been reported in workers vulnerable to Chromium (VI) in chrome plating and tannery industries (Nomanbhay *et al.*, 2005).

2.7.2.2 Skin Effects

Injurious effects of the chromium (VI) on skin include ulcerations, dermatitis, and allergic skin reactions. Further, it causes dryness, erythema, fissuring, papules, scaling, small vesicles, and swelling issues. Skin penetration can cause painless erosive ulceration "chrome holes" with delayed healing (Marchese *et al.*, 2008). These commonly appear on the fingers, knuckles, and forearms.

2.7.2.3 Renal Effects

Serious exposure to chromium (VI) can lead to acute tubular necrosis and acute renal failure. Injury to the brush border membrane is a feature of chromate nephropathy. Low-dose chronic chromium (VI) exposure typically can result in acute renal effects (Zhou *at al.*, 2008).

2.7.2.4 Hepatic Effects

The reported hepatic effects due to chromium (VI) exposure include derangement of the liver cells, necrosis, lymphocytic and histolytic infiltration, and elevation in Kupffer cells (Wionczyk *et al.*, 2006).

2.7.3 Chromium impacts on Plants and Animals

Harmful effects of Chromium on plant growth and development include alterations in the germination process, growth of roots, stems and leaves. It also causes injurious effects on plant physiological processes such as photosynthesis, water relations and mineral nutrition (Shanker *et al.*, 2005). Animals exposure to chromium (VI) in drinking water causes tumors in the alimentary tract, with linear and supralinear responses in the mouse small intestine (Zhitkovich *et al.*, 2011). Hexavalent chromium is carcinogenic to rats and mice after chronic

oral exposure (Matthew *et al.*, 2009). As pH of water decreases, chromium toxicity to the earthworm increases (Sivakumar *et al.*, 2005).

2.8 Chromium Guideline and Standards

According to Revised National Environmental Quality Standards for Municipal and Liquid Industrial Effluents 2010, the maximum permissible limit for total Chromium is 1 milligram per liter (Shakir *et al.*, 2013). The National Standard for drinking water 2008, maximum permissible limit for chromium is < 0.05 milligrams per liter. The WHO standard for the acceptable amount of chromium in drinking water is 0.05 mg/l. The USEPA maximum concentration level (MCL) for total Cr in drinking water is 0.1 mg/l (USEPA, 1999).

According to the D list of USEPA hazardous waste code D007, the maximum concentration of chromium contaminant for toxicity characteristic is 5 mg/l. In 2014 California's maximum contaminant level (MCL) for hexavalent chromium is 0.01 mg/L. A guideline of 0.05 mg/L is approved for domestic and livestock water according to Canadian water quality standards for Chromium (Pawlisz *et al.*, 1997). The chromium level in Kasur, Pakistan tanneries was found to be 21-42 folds higher as compared with the above recommended standards (United Nations Industrial Development Organization, 2002).

2.9 Heavy Metal Chromium Removal Methods

Toxic metal pollution has become one of the most severe environmental issues nowadays. The treatment of toxic heavy metals is of grave concern due to their endurance in the environment. Major techniques used for the removal of toxic metals from waste water are as under;

- Chemical precipitation

- Hydroxide Precipitation
- Sulphide Precipitation
- Heavy metal Chelating Precipitation

- Ion exchange
- Electrochemical Treatment
 - Electrocoagulation (EC)
 - Electro flotation (EF)
 - Electro deposition (ED)

- Membrane Filtration
 - Ultra Filtration (UF)
 - Reverse Osmosis (RO)
 - Nano-Filtration (NF)
 - Electro dialysis (ED)

- Flotation
 - Dissolved Air Precipitation (DAF)
 - Ion Flotation
 - Precipitation Flotation

- Coagulation Flocculation
- Adsorption
 - **Titania as Adsorbent**

- Carbon Nanotubes Adsorbents
- Activated Carbon (AC) Adsorbents
- Low Cost Adsorbents
- Agricultural Wastes
- Industrial Byproducts
- Natural Substances
- Bio-sorbents
- Algae, Bacteria, Fungi
- Egg shells, Banana Peels, Potato peels
- Zeolite Clay etc.

All the heavy metal waste water treatment methods can be used to remove heavy metals but they have their own fundamental advantages and disadvantages. Traditionally, Chemical Precipitation method was used for its simplicity, but it is ineffective when metal ion concentration is low. It is not cost effective and can generate large amount of sludge which cannot be treated easily. Ion exchange has been generally used for heavy metal removal from waste water. It is costly, especially when treating a large amount of waste water containing toxic metals in low concentration, so they cannot be applied at large scale.

Electrochemical heavy metal waste water treatment methods are fast and well-controlled that need fewer chemicals, provide good reduction yields and generate less sludge. However, this technology involves high initial capital investment and the expensive supply of electricity, which restricts its development (Hunsom *et al.*, 2005). Membrane filtration technique can remove toxic metal ions with high efficiency, but its high cost, process complexity and membranes fouling have limited its use in toxic metal removal technologies (Owlad *et al.*, 2009).

Flotation offers many advantages over the more conventional techniques, such as high metal selectivity, high removal efficiency, high overflow rates, low detention periods, low operating cost and generation of more concentrated sludge (Rubio *et al.*, 2002). But high initial capital cost, maintenance and operation costs are its limitations. Coagulation flocculation is another method for heavy metals removal but this method involves chemical consumption and increased sludge volume generation (Aber *et al.*, 2010).

Although all of the above methods can be used for the treatment of toxic heavy metal waste water, it is pertinent to mention that the selection of the most appropriate treatment method depends on the initial metal concentration, the component of the wastewater, capital investment and operational cost, reliability and environmental impact (Kurniawan *et al.*, 2006). These processes have important limitations, which include incomplete removal, high-energy requirements, and generation of toxic sludge. Hence, we need to move towards a method which is time and cost effective.

Adsorption is an accepted method for heavy metal removal at low concentration from waste water containing toxic metals (Barkat *et al.*, 2011). But, the high cost of Activated Carbon (AC) limits its use in adsorption (Babu *et al.*, 2012). Many of low-cost adsorbents including titania have also been developed and tested to remove toxic metal ions. However, efficiency of adsorption depends on the type of adsorbent. Bio-sorption is a relatively new technique that has proven very efficient for the removal of toxic metals from wastewater (Wang *et al.*, 2011).

Cost effectiveness order

A comparison of adsorption method was carried out with other water treatment technologies are given below:

Adsorption > Evaporation > Aerobic > Anaerobic > Ion exchange > Electro dialysis > Micro- and Ultra-filtration > Reverse osmosis > Precipitation > Distillation > Oxidation > Solvent extraction

2.9.1 Chromium Removal by Adsorption on Titania

Recently, several approaches have been reported for the development of cost effective and more efficient technologies for the removal of toxic metals from waste water. Nanotechnology is one of these due to Photo catalytic activity as well as time saving, low contact time and cost effectiveness characteristic. Nanoparticles have also proven themselves as excellent adsorbents due to their unique features like small size, catalytic potential, high reactivity, large surface area, ease of separation, and large number of active sites for interaction with different contaminants (Sheenam Thatai *et al.*, 2014).

The most frequently used nanoparticles for the metal ion removal are the aluminum and iron oxides, zerovalent iron nanoparticles and titania nanoparticles (Imran Ali, 2012). These nanoparticles have been applied for the removal of inorganic pollutants like cadmium, copper, chromium, lead, and mercury metal ions from waste water (Pacheco *et al.*, 2001; Jian-Wei Fan *et al.*, 2011). In one study, the photo-catalytic degradation of chromium (VI) from wastewater inspected by using nanomaterial's like TiO₂, ZnO, and CdS. Titania showed highest capacity for chromium (VI) removal out of these photo-catalysts (K. M. Joshi *et al.*, 2011).

2.10 Titania Polymorphs

Titania exists in three polymorphs i.e anatase, brookite and rutile. It has been seen that photocatalytic degradation involves only anatase and rutile phase (Augugliaro et al., 1988). Almost all studies have used Anatase and Rutile phase of TiO_2 in photocatalytic degradation processes. Of the two, the Anatase phase is the preferred polymorph having highest photocatalytic degradation activity (Beydoun *et al.*, 1999; Carp *et al.*, 2004). Crystal structure of polymorphs of TiO_2 , Rutile, Anatase, Brookite are shown in Fig.2.1

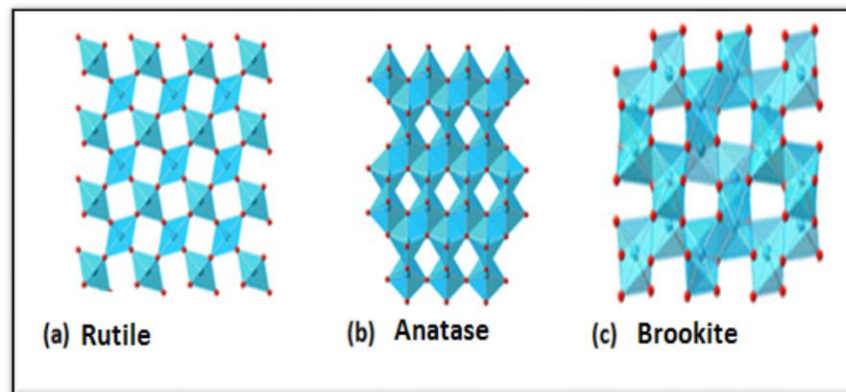


Figure 2.1: Crystal Structures of Polymorphs of TiO_2

Table 2.1: Required Wavelengths for activation of Polymorphs of TiO_2

Polymorph	Band Gap Value	λ Photo-excitation (nm)
Rutile	3.2 eV	Upto 385
Anatase	3.02 eV	Upto 385
Brookite	2.96 eV	Upto 375

2.11 Photocatalytic Reduction of Cr (VI) into Cr (III) by Titania

Several research studies were reported for the photo-catalytic reduction of Cr (VI), which is more mobile and highly toxic, than Cr (III), which is immobile and less harmful (Jiang *et al.*, 2006). In one study, thin films of titania immobilized on glass plates and synthesized by sol-gel method was reported. Chromium (VI) was successfully removed by the photo-activity of the synthesized TiO₂ thin films (Kajitvichyanukula *et al.*, 2005). The toxic chromium (VI) in industrial wastewaters can be eliminated by a reduction from chromium (VI) to chromium (III) using precipitation treatment (Owlad *et al.*, 2009). The reduction of Cr (VI) to Cr (III) is carried out by a photo-catalytic process. Thus, Photo-catalytic reduction chromium (VI) over TiO₂ catalysts is observed in both the absence and presence of organic and inorganic compounds (Papadama *et al.*, 2007).

In another research work, the photo-catalytic reduction of chromium (VI) to chromium (III) using TiO₂-immobilized onto glass slides under natural sunlight using commercial TiO₂ Degussa P25 was applied as a photo-catalyst in this work (Wang *et al.*, 2008). A novel photo-catalyst, titanium dioxide (TiO₂) doped with neodymium (Nd), was synthesized by the sol-gel method and applied for the photo-catalytic reduction of chromium (VI) under UV illumination. The results determined that the presence of Neodymium (III) in TiO₂ catalysts substantially increases the photo-catalytic reaction of chromium (VI) reduction (Rengaraj *et al.*, 2007).

2.12 Titania as Cement Additive

The photo catalytic activity of Titanium dioxide (TiO₂) in construction materials and coatings are being used for smog abatement, biocidal properties super hydrophobic/phylic and self-cleaning ability. The application of TiO₂ for decreasing Nitrogen Oxides (NO_x) and Volatile Organic Compounds (VOC's) has received attention of the civil engineering community because of potential benefits while decreasing pollution (Maggos *et al.*, 2007).

White cement is a key ingredient in architectural and decorative concrete due to its high mechanical strength. White cement containing titania, possessing photo-catalytic properties which allow maintaining the aesthetic characteristics of concrete over time and contributing to eliminate dangerous pollutants from the urban environment (Luigi Cassar *et al.*, 2003). Titanium Nanoparticles are used to increase the compressive strength of concrete blocks (Moiz *et al.*, 2013).

The progress in research significantly motivates the practical applications of titania nanoparticles, including the field of photocatalytic construction and building material. Titania modified building materials are the most popular because titania has been conventionally used as a white pigment. The major applications of titania based photo-catalytic building materials include environmental pollution remediation, self-cleaning and self-disinfecting. The advantage of using sun light and rainwater as driving force has promoted a new domain for environmental friendly building materials (Chen *et al.*, 2009). Nano-particles have also found useful applications in the field of medicine (Yang Xia *et al.*, 2008).

2.13 Disposal Options for Chromium

Generally, there are three options feasible for handling chromium waste disposal:

- Temporary containment and recovery
- Dilution
- Encapsulation

The danger linked with the temporary containment of hazardous chromium wastes, in drums and any other incompatible manner that would result in serious environmental issues of lung cancer, skin irritations and cause damage to aquatic life in case of leakage into water bodies, this limits the temporary containment disposal option for hazardous chromium waste (Leist *et al.*, 2008). After chromium recovery sustainable sludge handling is an issue of grave

concern. Incorporation of such sludge into cement provides a safe disposal option. Further, dilution and dispersion does not provide any original technical solution to handle chromium contamination, but just a legal solution. Chronic exposure to low concentrations of chromium causes severe health issues, including increases risks of skin and lung cancers (Marchese *et al.*, 2008).

These limitations have led to interest in methods for long term or “ultimate” safe disposal of hazardous wastes containing chromium. Therefore, recently, the most interesting option for dealing with chromium wastes is encapsulating and incorporation of the contaminated material, usually through solidification/stabilization methods and to dispose of the treated contaminated wastes in secure landfills. This technique also engages fixing or immobilizing the toxic elements by physical and or chemical means (Chen *et al.*, 2009)

2.13.1 Chromium Encapsulation

Solidification/stabilization (S/S) technique, also known as encapsulation, fixation or immobilization, is applied to transform possibly hazardous liquid and solid wastes into less hazardous or nonhazardous solids before dumping in a landfill site, thus avoiding the waste from entering into the environment and to reduce the leaching rate. (Leist *et al.*, 2000). Solidification of toxic metals in mortars and concretes using Ordinary Portland Cement (OPC) is an efficient way of immobilization or incorporation (Giergiczny *et al.*, 2008). Cement is the most suitable binder recently available for the immobilization of toxic metals including chromium. Cement-based stabilization/solidification technique is an effective option for the handling of heavy metal-bearing waste to promote handling leading to ultimate disposal and decreases the release of toxic contaminants into the environment (Chen *et al.*, 2009).

There have been reports in the literature where partial replacement of cement with nanophase titania particles improves the compressive strength of concrete (Nazari *et al.*,

2010). A report on immobilization of nanoparticles in cement-based concrete reported the properties of cement mortars combined with nanoparticles to promote their mechanical potentials (Hui Li *et al.*, 2003). In another study, titania nanoparticle blended concrete had extremely higher compression strength as compare to the concrete without titania nanoparticles. Several nanomaterials, other than titania, can also be applied in cement matrices to promote the physicochemical property of cement, mortar and concrete (Chen *et al.*, 2012).

The addition of nano-titania powders in cement mortar primarily reduced the porosity and increased the hydration rate of the cement materials at early stages, thus, compression strength of the mortar was increased, particularly at the early stage (Meng *et al.*, 2012). The basic reason for the enhancement of strength is the alteration of the orientation index for the nucleation function. Similarly, white cement containing titania increases the mechanical strength of concrete (Cassar *et al.*, 2003). If Titania nanoparticles, that have good photocatalytic properties, were added into concrete, the gaseous contaminants could be decomposed and the concrete performance could be accelerated and optimized at the same time which encourages titania immobilization in concrete (Wu *et al.*, 2006).

A method of incorporating toxic waste materials including heavy metals such as arsenic, mercury, nickel and chromium contaminants, as well as radioactive materials is reported in one study which involves adding the hazardous waste material to a settable composition, forming slurry and to allow the slurry to set to incorporate the waste material. (Rechichi *et al.*, 2002). In another research study, composition for treating heavy metals in solid waste and sludge is reported in which composition includes a reducing agent such as ferrous sulfate or sodium sulfite and a fixative agent containing solid calcium oxide or solid magnesium oxide. (Falk *et al.*, 1989).

A composition and method for encapsulation of aqueous toxic waste material in cement based materials like in grout is introduced by the addition of an ionic aluminum compound to the waste material mixture and dry-solid cement-based materials (Tallent *et al.*, 1989). The direct encapsulation of chromium sometimes, accelerates the initial and final setting time of cement and hinders the process of cement hydration (Wang *et al.*, 2000). In another study it was illustrated that photocatalytic mortars can be used in new and old buildings, because the nano-additives like titania do not compromise the mortar hardened state properties (Luca *et al.*, 2013).

MATERIALS AND METHODS

3.1 Test Materials

Materials used in this research were of scientific standard. Titania (GPR, BDH Chemicals Ltd. Poole England), Potassium dichromate, Diphenylcarbazide (DPC), Acetone, Sulphuric acid, Glacial Acetic acid, Sodium Hydroxide and Nitric acid (Analytical grade), were obtained from Sigma Aldrich. Cement and sand were purchased from the local market. Distilled water was used throughout the experiments.

3.1.1 Mortar Specimens Mix Proportions

For the mortar specimen used in this research, a water to cement ratio (w/c) of 0.5 was selected. Ordinary Portland cement was used with sand to cement ratio (s/c) of 1. The volume of mortar specimen used was 125 cm³ and cement mortar density of 2162 kg/m³ was selected in this research work. Dry mass of mortar specimen calculated was 270.25 g containing 135.12 g of cement and same amount of sand. Total number of mortar specimens cast were 15 with 3 samples each for 0%, 5%, 10%, 15% and 20% cement replacement with chromium laden titania as shown in Table 3.1.

3.1.2 Preparation of Chromium Stock and Standard solution

The chromium concentration in watery solutions was determined using Diphenylcarbazide (DPC) standard method (APHA 3500-CR). Potassium dichromate stock solution of 500 ppm was processed by dissolving 141.4 mg of dried potassium dichromate in 100 ml distilled water in a volumetric flask. DPC solution was processed by dissolving 250

mg of 1,5 diphenylcarbazine powder in 50 mL acetone. To adjust the pH of the solution to pH 2, 0.2 N sulphuric acid was used. Then Standards ranging from 0 mg.L⁻¹ to 1 mg.L⁻¹ were prepared from the chromium stock and DPC solutions.

Table 3.1: Mortar mix design proportions

% TiO ₂ + Cr	TiO ₂ + Cr (g) + Cement (g)	Sand (g)	Water (g)
		S/C = 1	W/C = 0.5
0%	0 g TiO ₂ + Cr + 135.12 g Cement	135.12 g	67.56 g
5 %	6.75 g TiO ₂ + Cr + 128.37 g Cement	128.37 g	64.18 g
10%	13.51 g TiO ₂ + Cr + 121.61 g Cement	121.61 g	60.80 g
15%	20.26 g TiO ₂ + Cr + 114.86 g Cement	114.86 g	57.43 g
20%	27.02 g TiO ₂ + Cr + 108.1 g Cement	108.1 g	54.05 g
Total sample × 1	67.54 g TiO ₂ + Cr + 608.06 g Cement	608.06 g	304.02 g
Total sample × 3	202.62 g TiO ₂ + Cr + 1824.18 g Cement	1824.18 g	912.06 g

3.2 Test Instruments

For the experimental work, a UV Lamp (6W), Scanning Electron Microscope (JEOL JSM-6460); Energy-dispersive spectroscopy (EDS, JEOL JSM-6460); X-ray diffraction (XRD, JEOL JDX-II); Centrifuge (D3752O Sigma); quartz cell (20849 Hach); UV/Vis spectrophotometer (HACH DR 2400) and pH meter (CyberScan 500 Eutech), were used.

3.3 Test Procedures

3.3.1 Synthesis of Titania Nanoparticles

Liquid Impregnation method (Khan *et al.*, 2013; Younas *et al.*, 2014) was used for the synthesis of pure titania nanoparticles as described below Fig.3.1.

(i) Mixing

Slurry of TiO₂ nanoparticles was prepared in water by mixing 50 g of TiO₂ in a beaker and continuous stirring for 24 hours.

(ii) Settling

This solution was allowed to settle, for 24 hours so that proper settling of the solids could take place.

(iii) Drying

After decanting the supernatant, the solid material was placed in oven for 12 hours at 105⁰C so that water could evaporate.

(iv) Calcination

After drying, the material was crushed properly using a pestle and mortar and placed in china dishes. The china dishes were placed in a muffle furnace for 6 hours at 550⁰C to obtain the pure TiO₂ nanoparticles (Sahoo *et al.*, 2005).

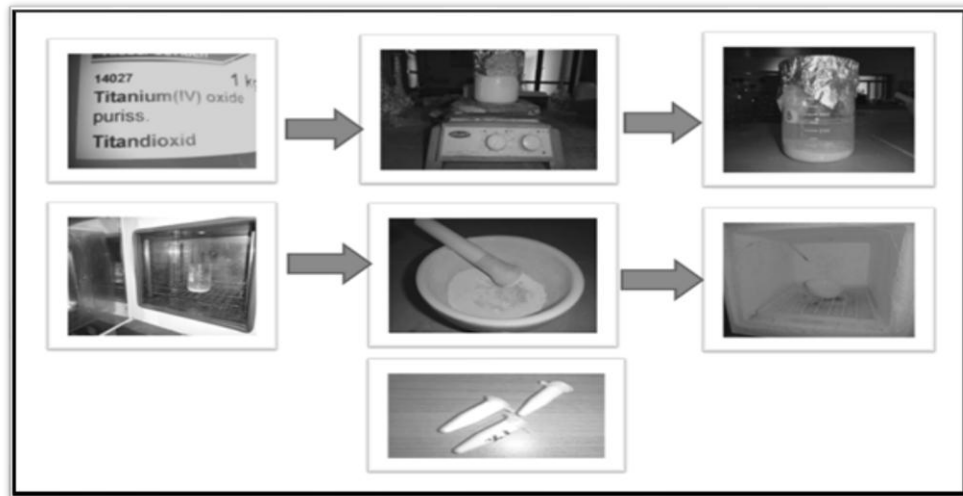


Figure 3.1: Steps Involved for the synthesis of Titania Nanoparticles

3.3.2 Characterization of Nanoparticles

3.3.2.1 Scanning Electron Microscopy (SEM)

Scanning Electron Microscope (SEM) is a powerful technique which uses a focused beam of electrons to obtain largely magnified picture. The high-resolution, three-dimensional images produced by SEM provide information like;

- Topography
- Morphology
- Chemistry
- Crystallography

The topography and morphology of the titania, was carried out using scanning electron microscope (JEOL JSM-6460) at 10,000x magnifications. Scanning Electron Microscopy was used for the direct estimation of particle size and examination of sample powders. It is the type of electron microscope that uses focused beam of electrons to scan a sample for image

production. It has the resolution of less than 1 nm. X-rays informed us about the elemental and chemical composition of the sample as shown in Fig. 3.2 (Goldstein *et al.*, 1981).

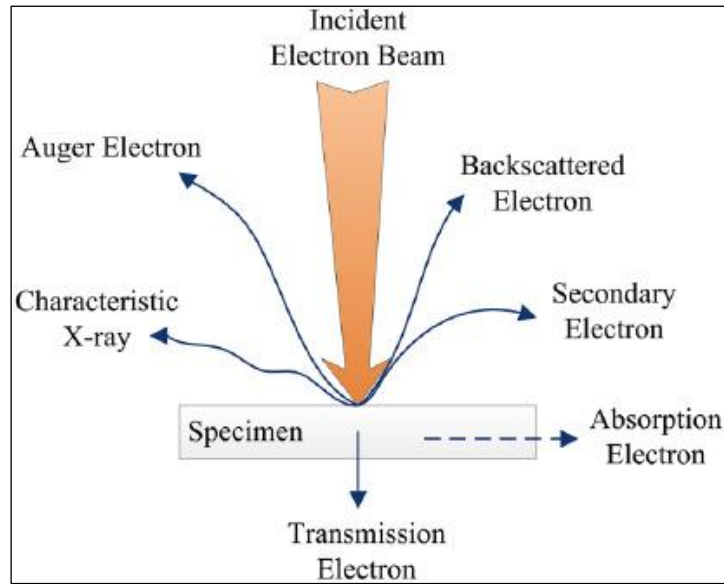


Figure 3.2: SEM working Principle

3.3.2.2 Energy Dispersive Spectroscopy (EDS)

Energy-dispersive spectroscopy (EDS, JEOL JSM 6490A) was used to identify the elements present in the nanoparticles. The principle of EDS is shown in Fig. 3.3 which involves the electron beam which falls on the sample atom. Due to the excitation in the inner shell of atom, every element produces x-rays. This moves the outer shell electrons to move towards inner shell to cover the gap. This difference in outer and inner shell is released in the form of x-rays. These x-rays form the specific peaks for each element which is detected by EDS as each element has a different atomic structure with different peaks on x-ray atomic spectrum. Thus from the controlled beam of electron it can also tell us about elemental composition of a selected area. The percentage composition of specific element can be determined by the number of counts on the graph (Goldstein *et al.*, 2003).

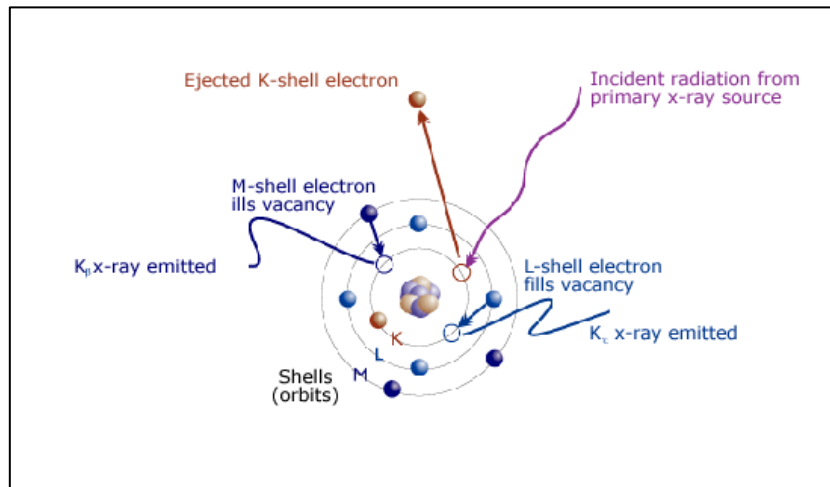


Figure 3.3: EDS working Principle

3.3.2.3 X-Ray Diffraction (XRD)

X-ray Diffraction (XRD, JEOL JDX-II) was used to find out the crystalline phase and size of nanoparticles. Average crystalline size of nanoparticles was determined by using the Scherer formula (Younas *et al.*, 2014). Principle mechanism of XRD is shown in Fig. 3.4 in which the x-rays fall on the specimen atoms and diffracted into many directions.

$$L = K\lambda / \beta \cos \theta$$

Where, L = Average particle size,

$K = 0.891$; $\lambda = 0.1542$,

β = full width of a diffraction line at one half of maximum intensity (FWHM) radian,

θ = the diffraction angle of crystal phase.

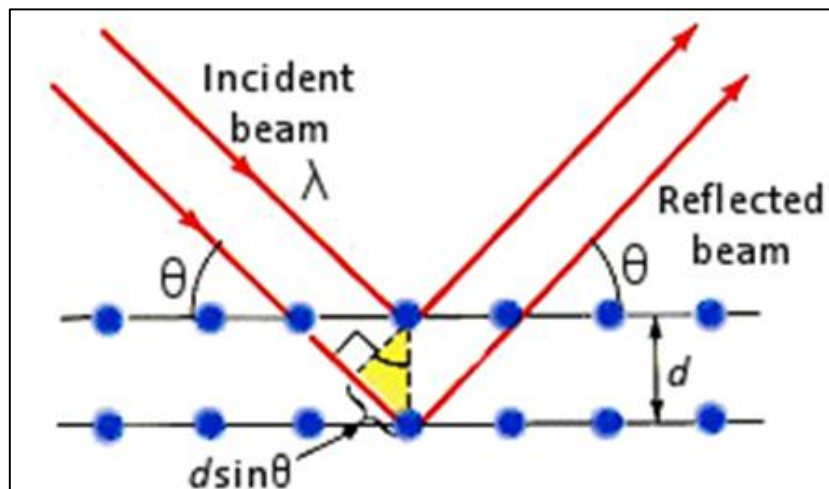


Figure 3.4: XRD working Principle

3.3.4 Spectrophotometric Determination of Chromium

UV/Vis Spectrophotometer was used for the quantitative estimation of Cr (VI) by measuring absorbance at the wavelength of maximum absorbance of 540 nm using the HACH DR 2400 instrument as shown in Fig. 3.5.

3.3.4.1 Working Principle of Spectrophotometer

Spectrophotometry technique is widely used for the quantitative analysis of organic and inorganic compounds. The molecules after exposure to UV-light absorb it. Due to absorption of light, electrons become excited and move to high energy orbitals. The instrument basically measures transmitted light which is commonly known as transmittance. The absorbance is recorded by taking the difference of light transmitted before and after the sample solution is being exposed to light (Thomas and Burgess, 2007).

3.3.4.2 Beer-Lambert law

According to Beer-Lambert law, absorbance is directly equivalent to the concentration of the sample and path length of the cell in which sample is taken.

$$A = \epsilon \cdot c \cdot L$$

Where,

A = absorbance

ϵ = absorption coefficient, specific to sample solution

c = concentration of sample solution and L = path length of cell



Figure 3.5: UV/VIS Spectrophotometer for quantitative determination of Cr (VI)

3.3.5 Chromium Adsorption and Photo Reduction: Batch Study

The batch study setup was used for photo reduction of Cr (VI) and adsorption onto titania nanoparticles under UV light (6 W) and in the dark as shown in Fig. 3.6. The used concentration of synthetic chromium solution was 50 mg.L^{-1} and titania dosage was 5 g.L^{-1} . UV light (6 W) was dipped in 1000 ml cylinder and cylinder being covered with foil of aluminum to avoid stray light. The solution was mixed on a magnetic stirrer at 200 rpm at room temperature for 180 minutes with UV illumination. Maximum and minimum Cr (VI) removal was investigated at pH 2. After removal chromium adsorbed titania was detached from solution by centrifugation at 4500 rpm for duration of 10 minutes using centrifuge instrument (D3752O Sigma) (Ilyas *et al.*, 2011). After centrifugation absorbance of each sample chromium content of the liquid was determined by the DPC method as described above.



(a) UV light batch study setup (b) Dark batch study setup

Figure 3.6: UV light & Dark Batch study setup for photo-reduction and adsorption of Cr (VI)

3.3.6 Preparation of Mortar Specimens for Chromium immobilization

Anatase titania nanoparticles were used in preparation of five types of mortar specimens including 0%, 5%, 10%, 15% and 20% cement replaced with Chromium adsorbed on Titania. These specimens were then compared with conventional mortar specimen (0%) and also with each other for compressive strength analysis. ASTM C39/C39M (Rukzon *et al.*, 2012), standard test method was used to investigate compression strength of mortar specimens using compression machine as shown in Fig. 3.7. Cube molds as per BIS: 10086-1982 (Thomas *et al.*, 2013), of size $50 \times 50 \times 50$ mm were used for casting of mortar specimens to immobilize chromium adsorbed on titania nanoparticles. Initially, weighing and mixing of cement, sand and chromium adsorbed titania nanoparticles in mortar mixer was done according to EN 196 standard method for cement testing. Mixture was then cast in mortar molds for 24 hours. After 24 hours demolding and labeling of mortar molds was done and finally curing of these mortar molds in water tank was performed, for compressive strength analysis, after 28 days.



Figure 3.7: Compression machine used for compressive strength analysis of mortar specimen

3.3.7 Chromium Leachate Study

The Toxicity Characteristic Leaching Procedure (TCLP) USEPA method No. 1311 was used to evaluate metal leach-ability. TCLP is constructed to inspect the mobility of both organic and inorganic contaminants present in liquid, solid, and multiphase wastes (Sinyoung *et al.*, 2012). The Leachate test was operated to inspect the concentration of chromium in the leachate, which can cause various hazardous environmental concerns. Extraction fluids were prepared by dissolving respective amounts of glacial acetic acid and NaOH in distilled water. To confirm the correct preparation of extraction fluids pH of both fluids was measured.

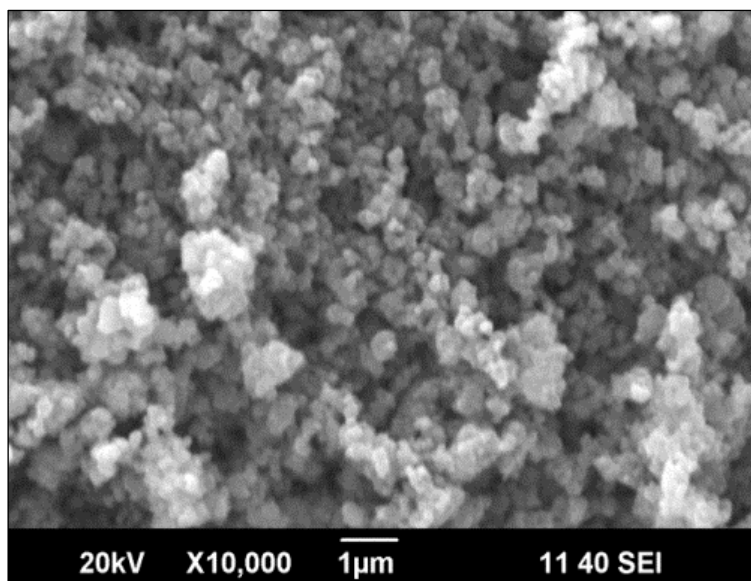
TCLP extracts are to be synthesized for investigation and analyzed as soon as possible to determine leachate concentration (Swarnalatha *et al.*, 2018). Calibration curve of extraction fluid was developed by using the Diphenylcarbazide (DPC) standard method as described above. Broken fragments of mortar specimens after compressive strength test were crushed and sieved through 9.5mm (0.375 inch) standard sieve and then mixed into the extraction fluid. The liquid to solid ratio used was 20:1. The sample was agitated in a TCLP rotatory agitator at 30 rpm for 18 hours and the liquid phase was detached from the solid phase by filtration through a 0.6–0.8 μm fiber filter. The filtrate was acidified to pH less than 2 by the addition of 1N nitric acid and Cr (VI) metal leachate concentration was determined by using UV/Vis spectrophotometer (HACH DR 2400).

RESULTS AND DISCUSSION

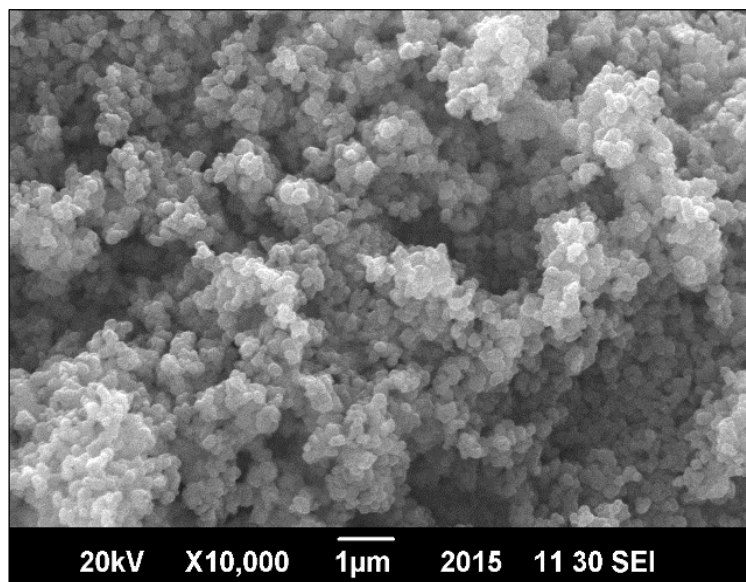
4.1 Characterization of Nanoparticles

4.1.1 Scanning Electron Microscopy (SEM) Analysis

The Scanning Electron Microscopy images show surface morphology of titania nanoparticles before and after chromium removal from synthetic waste water. The average particle size of the titania nanoparticles illustrated in Fig. 4.1 at 10,000 x magnification, before chromium removal was found to be 72 nm and after removal was found to be 97 nm. This indicates that the removed chromium has been adsorbed on titania nanoparticles. SEM images confirm the presence of porous, heterogeneous structure of high roughness and complexity which indicates the high surface area for adsorption of chromium.



(a) Before chromium removal



(b) After chromium removal

Figure 4.1: SEM images of Titania nanoparticles before and after Cr (VI) removal

4.1.2 Energy Dispersive Spectroscopy (EDS) Analysis

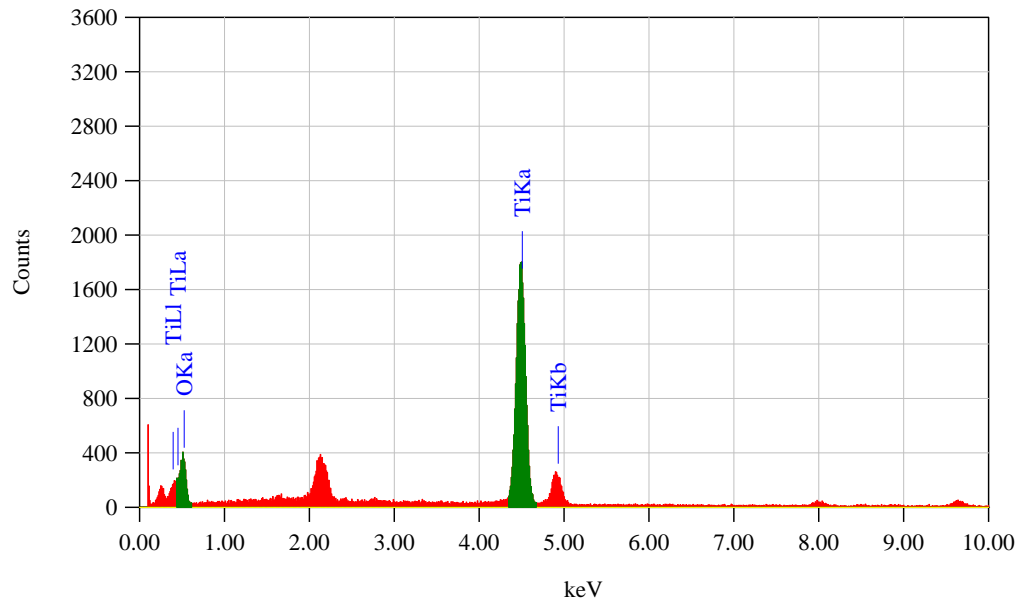
EDS examines elemental composition of pure titania nanoparticles. Relative elemental mass composition of nanoparticles before and after chromium removal is shown in Table 4.1. The results confirm that pure titania nanoparticles contain only titania and oxygen while no alien element or impurity is introduced in the synthesis process.

The Energy Dispersive Spectroscopy (EDS) images are illustrated in the Fig. 4.2 which identifies the elements present in the nanoparticles before and after chromium removal. It was found that pure titania nanoparticles before chromium removal, contain only titanium and oxygen with elemental composition of 51.6% and 48.4% respectively endorsing the successful fabrication of the desired nano-material whereas, after chromium removal the chromium adsorbed on the titania nanoparticles and this shows presence of chromium with

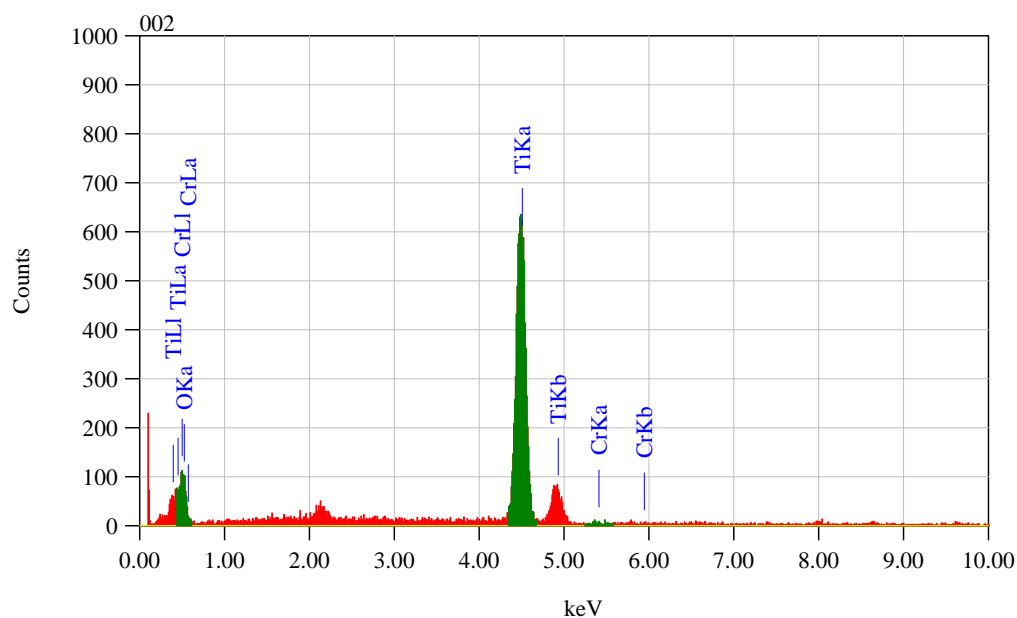
elemental composition of 1.15% along with titanium 54.07% and oxygen 44.78% respectively.

Table 4.1: EDS results of Titania nanoparticles before and after chromium removal

Titania Nanoparticles	Relative Elemental Mass Ratios		
	Ti%	O%	Cr%
Before Cr Removal	51.60%	48.40%	0%
After Cr Adsorption	54.07%	44.78%	1.15%



(a) Before chromium removal



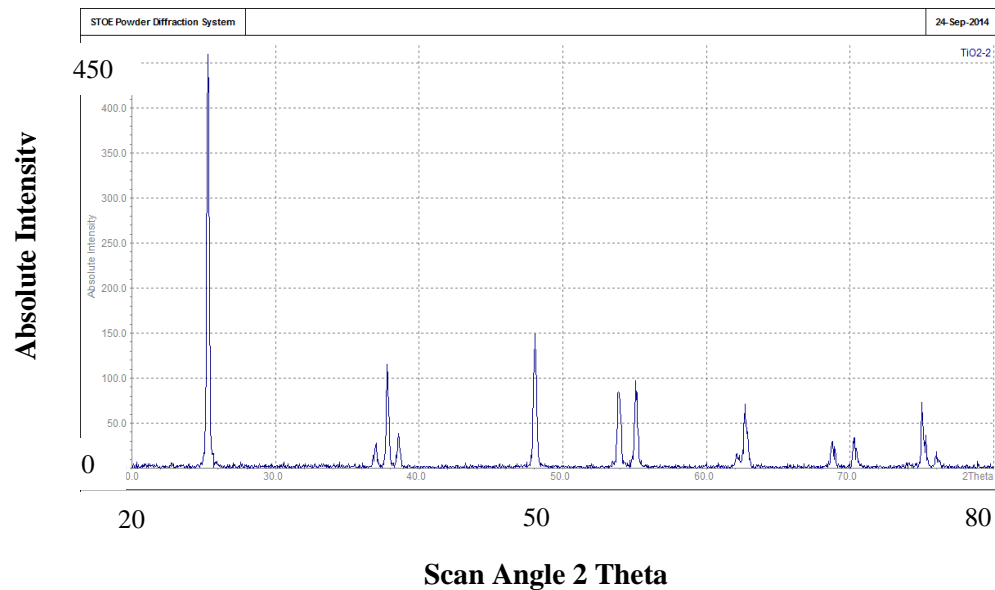
(b) After chromium removal

Figure 4.2: EDS spectrum of Titania nanoparticles before and after chromium removal

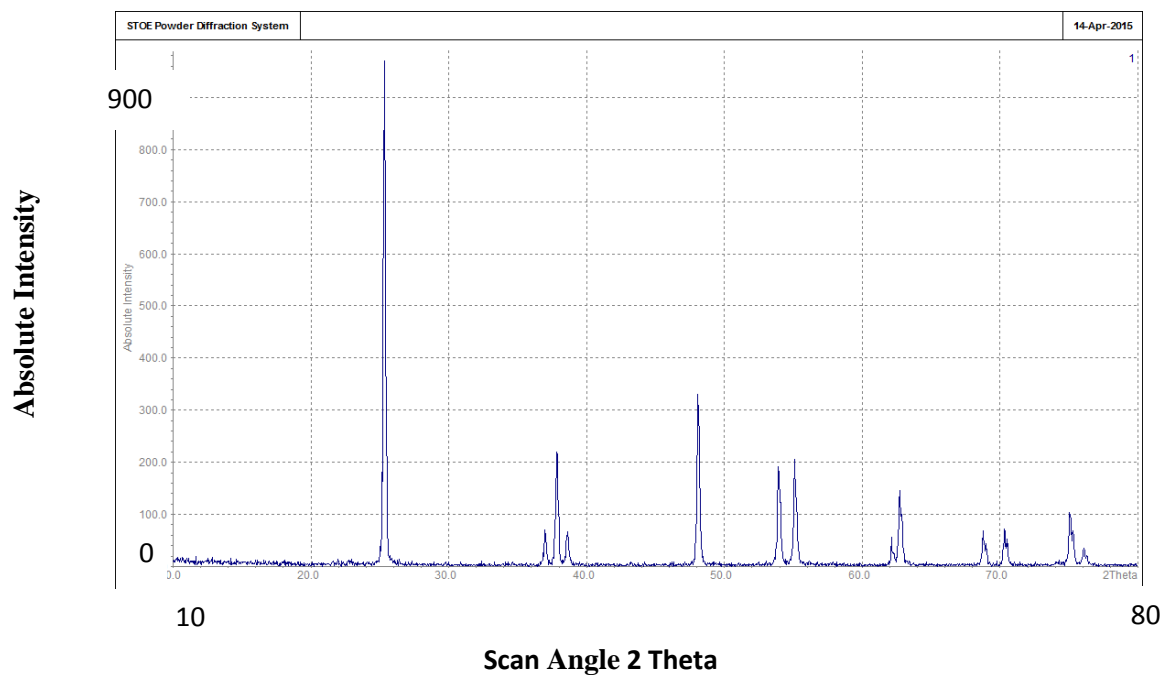
4.1.3 X-Ray Diffraction (XRD) Analysis

XRD results are illustrated in the Fig. 4.3. Structural analysis of the chromium adsorbed on titania nanoparticles was performed by X-ray diffraction (XRD) in the range of 2-theta ranging 20° - 80° at room temperature.

The crystalline size of particles confirmed to be in the nano range that is less than 100 nm. Peaks of XRD results reveal that pure titania nanoparticles have the desired anatase crystalline structure. Crystalline phase before chromium removal was found to be 89% while after chromium removal it was found to be 94%.



(a) Before chromium removal



(b) After chromium removal

Figure 4.3: XRD images of Titania nanoparticles before and after chromium removal

XRD image of pure titania nanoparticles shows two high peaks at 25.3° and 48° and it also shows peaks at regular intervals at angles 37.8° , 53.8° , 68.7° and 78.6° along with higher peaks mentioned above, revealing its anatase crystalline phase (Reyes *et al.*, 2008). The main reason behind this high crystalline nature is calcination of nanoparticles at 550°C for 6 hours.

4.2 Hexavalent Chromium Determination

Diphenylcarbazide (DPC) standard method APHA 3500-CR was followed to determine Cr (VI) in synthetic waste water using UV/Vis spectrophotometer. For this purpose, UV/Vis spectrum of a dye Diphenylcarbazide (DPC) was recorded for determining Cr (VI) in waste water to confirm the wavelength of maximum absorbance of 540 nm, which is in conformity with the standard method as shown in Fig. 4.4.

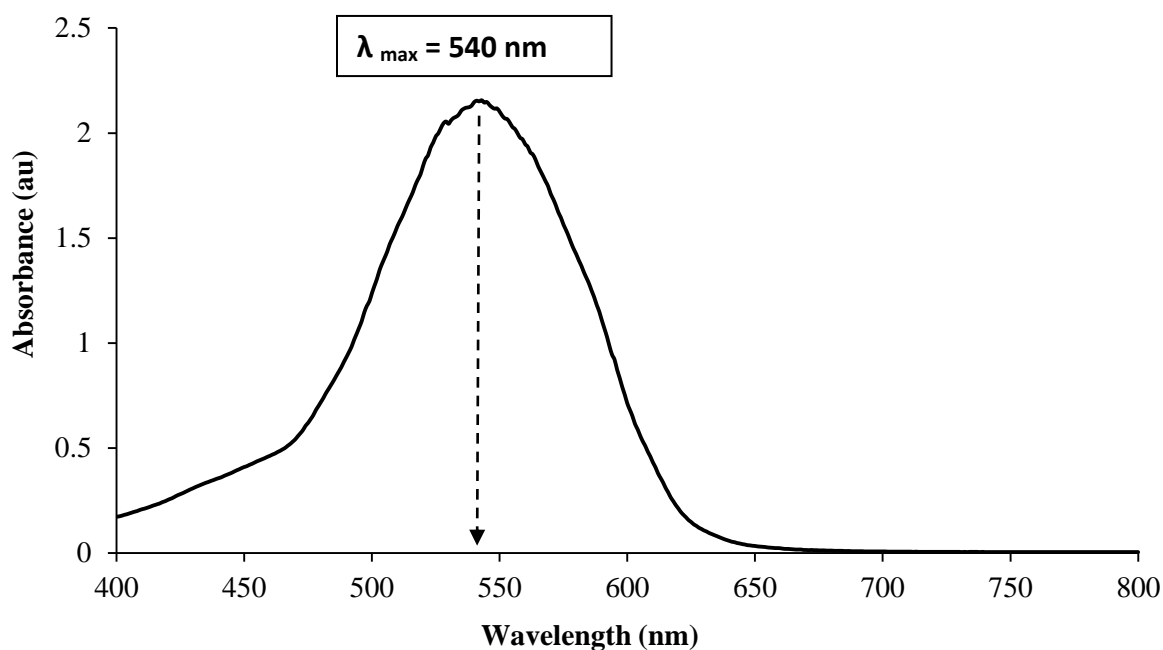


Figure 4.4: UV/Vis Absorbance Spectra of DPC dye to determine Cr (VI)

A calibration curve was developed at λ_{max} 540 nm using serial dilutions ranging from 0.1 mg.L^{-1} to 1 mg.L^{-1} of 500 mg.L^{-1} chromium stock solution as illustrated in Fig. 4.5.

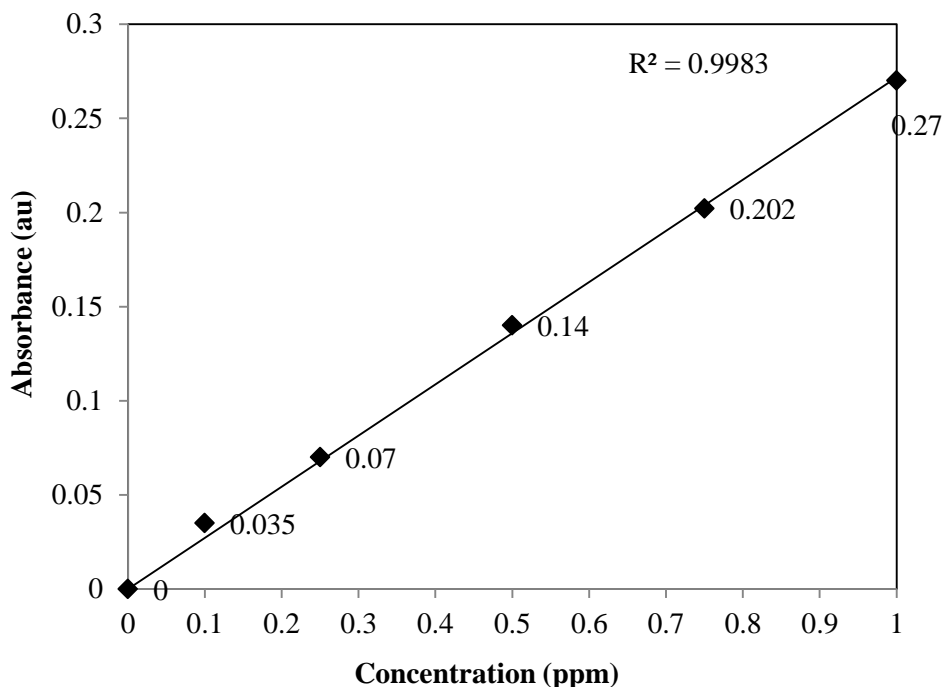


Figure 4.5: Calibration curve for determination of Cr (VI)

4.3 Adsorption and Photo Reduction Batch Study

Adsorption and photo reduction of hexavalent chromium from wastewater was done by using titania nanoparticles under UV light and in the dark. Maximum Cr (VI) removal estimated under UV light after 180 minutes (3 hrs.) at pH 2, was 95.1% as illustrated in Fig. 4.6. Maximum removal of hexavalent chromium observed in the dark after 180 minutes (3 hrs.) at pH 2, was 52.3% as shown in Fig. 4.7.

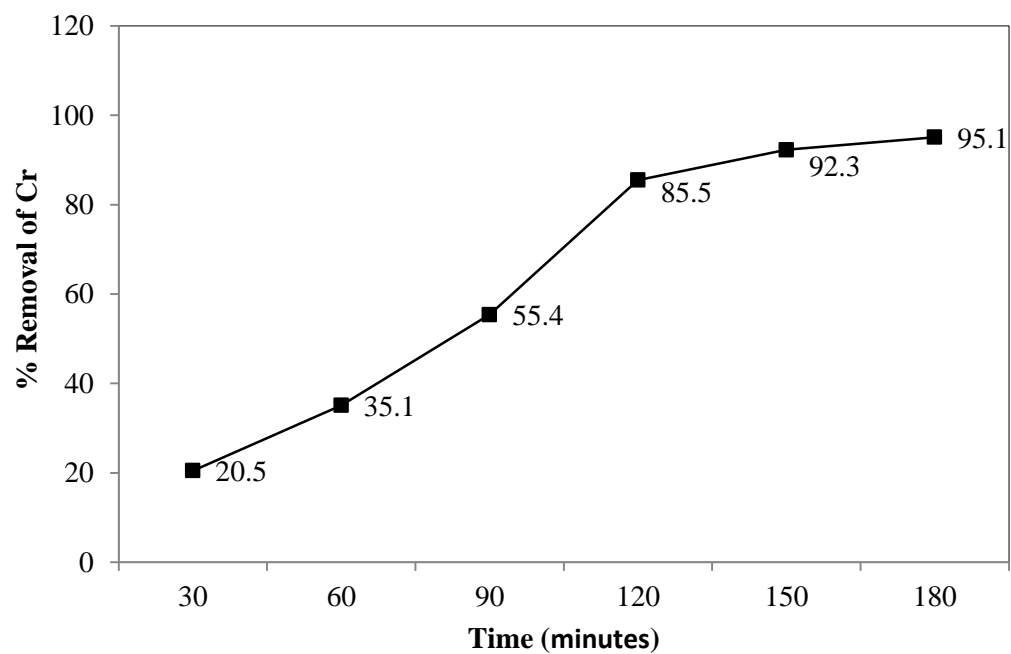


Figure 4.6: Removal of Cr (VI) by Titania under UV light

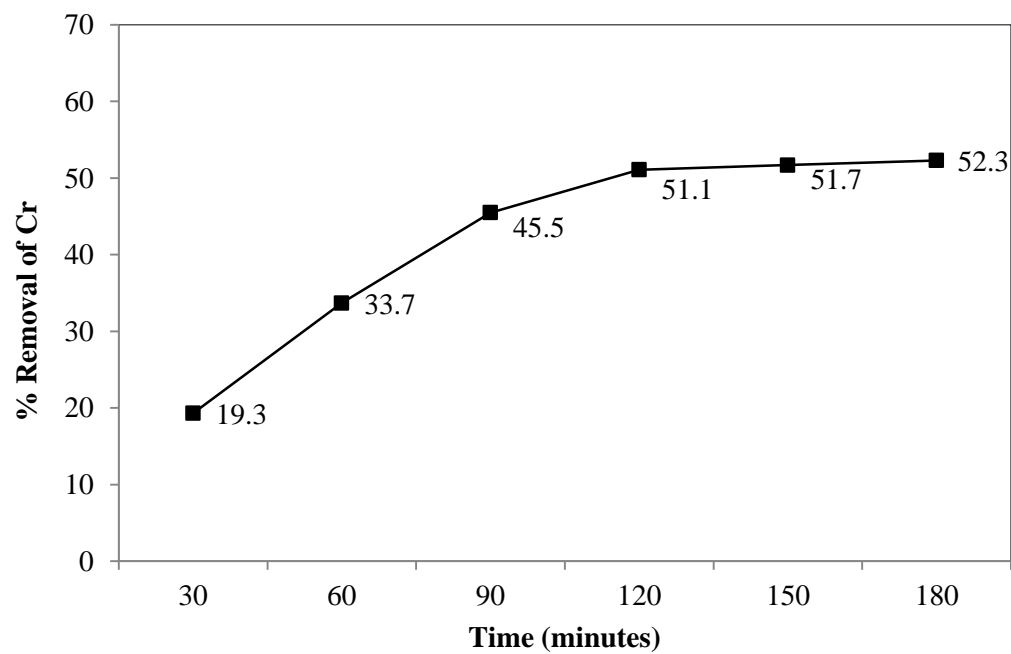


Figure 4.7: Removal Cr (VI) by Titania in the dark

4.4 Immobilization Study

Anatase titania nanoparticles were used in preparation of five types of mortar specimens for chromium immobilization including 0%, 5%, 10%, 15% and 20% cement substituted with chromium adsorbed titania nano-particles. The compressive strength of mortar specimens cured for 28 days are illustrated in Fig. 4.8. The specimens containing chromium adsorbed titania depicted more strength than conventional mortar specimen without titania.

There have been reports in the literature where partial replacement of cement with nanophase titania particles improves the compressive strength of concrete (Nazari *et al.*, 2010). In one study, titania nanoparticles blend concrete had significantly higher compression strength as compared to the concrete without titania nanoparticles. Several nanomaterials other than titania can also be used in cementitious matrices to improve their physicochemical behavior of cement, mortar and concrete (Chen *et al.*, 2012). The addition of nano-titania powders in cement mortar significantly decreased the porosity and accelerated the hydration rate of the cement materials at early stages, thus, compression strength of the mortar was increased, essentially at the early stage (Meng *et al.*, 2012).

Similarly, white cement containing titania increases the mechanical strength of concrete (Cassar *et al.*, 2003). The direct immobilization of chromium increases the initial and final setting times of cement and hinders the cementitious process of hydration. Thus, increasing the chromium content in the cement decreases the compressive strength of the solidified cement (Wang *et al.*, 2000).

From the results, it could be noted that the compression strength rises till 15% replacement of chromium adsorbed titania. The mortar specimen containing 15% chromium

adsorbed titania showed maximum compressive strength of 22.05 MPa as compared to 15 MPa for the control specimen with 0% chromium adsorbed titania. Overall, as the amount of Nano-particles in cement mortar mix increases, strength of mortar specimen increases. The strength decreases at 20% cement replacement with chromium adsorbed titania because increase of titania and chromium percentage as chromium imposes negative impact on the mechanical properties of the cement.

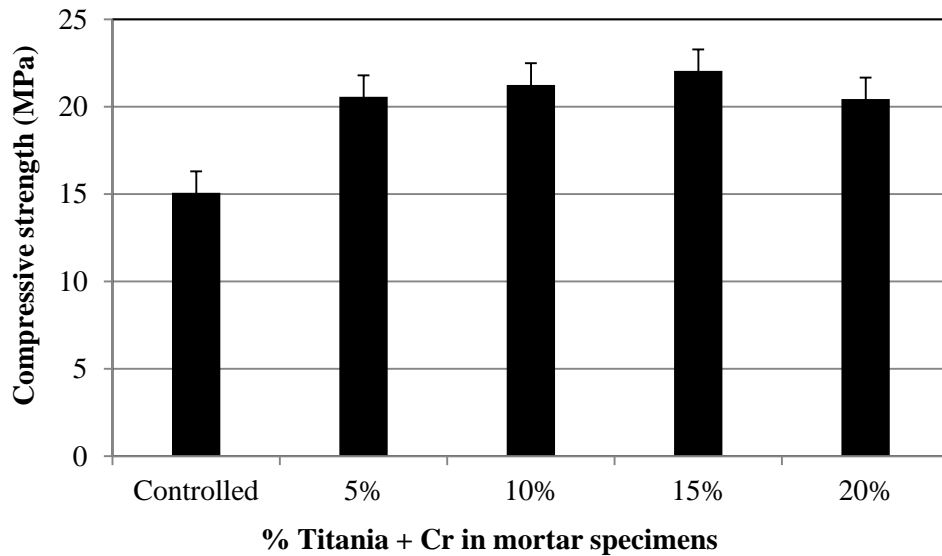


Figure 4.8: Compressive strength analysis of mortar specimens after 28 days

4.5 Leachate Study

The Leachate test was performed using TCLP technique to determine the chromium concentration in the leachate (Sun *et al.*, 2006). The concentration of chromium was 0.75 mg.L⁻¹ in the leachate after 18 hours of TCLP test for the mortar specimen having the highest compression strength of 22.05 MPa. The acceptable concentration of chromium leachate is less than 5 mg.L⁻¹, according to the U.S. EPA. It was noticeable that chromium leachate concentration from the extraction fluid after filtration was 0.75 mg.L⁻¹, which is well within

the allowable limit (Sinyoung *et al.*, 2011). Calibration curve of Extraction Fluid to determine of Cr (VI) leachate concentration is shown in Fig. 4.9.

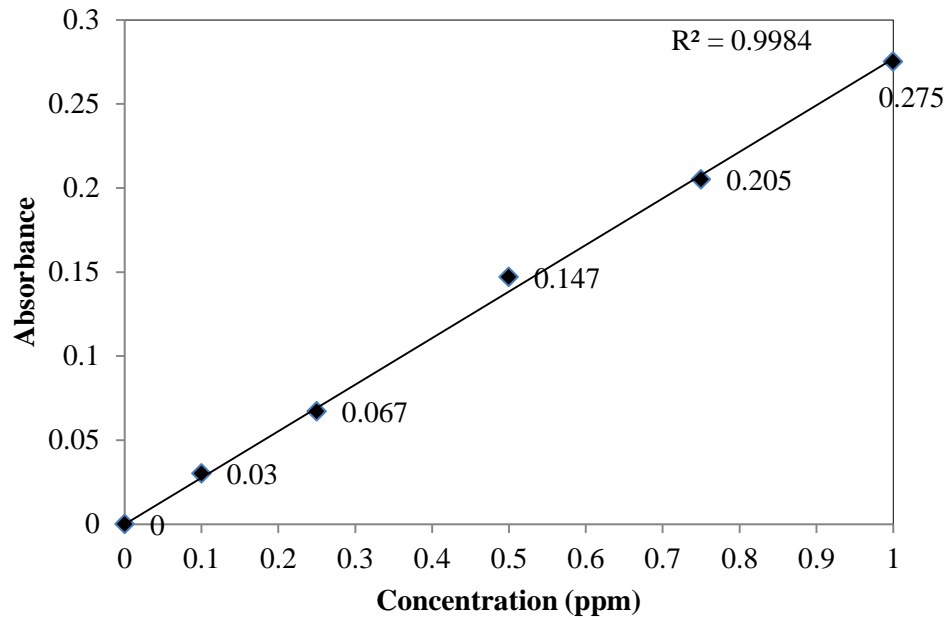


Figure 4.9: Calibration curve of Extraction Fluid to determine Cr (VI) leachate concentration

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

From the research work described above, it is concluded that:

1. The titania nanoparticles in UV light presence serve as excellent adsorbent material after photocatalytic reduction of Cr (VI) to Cr (III).
2. The adsorbed chromium can be effectively immobilized in mortar with a specimen containing 15% titania powder without adversely effecting it's strength.
3. Leachate of chromium from such mortar material is insignificant, 0.75 mg.L^{-1} which is lower than the allowable value of 5 mg.L^{-1} according to US EPA, thus suggesting complete immobilization of chromium into mortar.
4. The proposed scheme of photo-catalytically reducing and adsorbed chromium onto titania nanoparticles and then incorporating these into mortar can, therefore, be used for safe and efficient disposal of toxic heavy metals, in general, and for chromium in particular

5.2 Recommendations

Following are some of the suggestions for carrying forward the work reported in this thesis:

1. This research work is suggested for pavements, structural and non-structural works in the construction industry.
2. To investigate ultimate safe disposal of other heavy metals like arsenic and lead of hazardous environmental concern by immobilizing into mortar and concrete.
3. Similar Investigation should also be made for concrete to immobilize the hazardous waste.
4. Effect of addition of fly ash along with titania as additive in cement on chromium leaching may also be investigated.

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