REMOVAL OF CHROMIUM (VI) FROM WATER USING TITANIA NANOCOMPOSITES

(ACTIVATED CARBON AND TITANIA NANOPARTICLES)

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

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Have been found satisfactory for the requirements of the degree of

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Supervisor: _____

Engr. Arsalan Khalid

Lecturer

IESE, SCEE, NUST

DEDICATED

TO

OUR LOVING PARENTS

AND FAMILIES

By virtue of whose prayers, we have been able to attain this position and whose hands are always raised for prayers, for our well-being.

ACKNOWLEDGEMENT

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Table of Contents

LIST OF ABBREVIATIONS

EDS   Energy Dispersive Spectroscopy

IESE   Institute of Environmental Sciences and Engineering

SEM   Scanning Electron Microscopy

TiO_2 Titanium Dioxide

UV   Ultra Violet

Vis   Visible

XRD   X - Ray Diffraction

DPC   Diphenylcarbazide

US EPA   United States Environmental Protection Agency

Cr   Chromium

NEQS   National Environmental Quality Standards

UNIDO   United Nations Industrial Development Organization

Abstract

Chromium, mainly Cr (VI), is removed from industrial effluents before their discharge into water bodies, because of its toxicity. It is removed by an array of techniques, including adsorption. The goal of this research was to remove Chromium from water using Titania Nanocomposites. Titania nanoparticles were synthesized using liquid impregnation method. The crystallite size of Titania nanoparticles was found to be 55 nm. Nanocomposites were synthesized using Activated Carbon and Titania nanoparticles. The Nanocomposites used consisted of 90% CAC & 10% TNP. These nanoparticles were characterized by using Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) techniques which revealed the surface morphology and elemental composition. Synthetic solution of Chromium was prepared and adsorption efficiency of TNP's, CAC and Nanocomposites were compared in UV light and dark conditions and also by varying dosage and contact time. The removal of Chromium was found to be more dominant under UV light conditions as compared to dark. As the contact time increased from 1h to 3 h, the percentage removal also increased. At 1 h, the removal by Nanocomposites was 80.5% which increased to 98.9% after 3 h. Similarly, as the dosage of Nanocomposites was increased from 250mg/l to 1250 mg/l, percentage removal increased but there wasn't much difference in percentage removal between 1000mg/l and 1250mg/l. It was established that 1000 mg/l gave the most percentage removal.

Introduction

Chromium is one of those elements that are abundantly present in the earth's layer. It is a naturally happening element that can be found in soil, rocks plants, animals, volcanic ash and gases. Chromium exists in different oxidation state though the most stable forms of chromium are trivalent (III) chromium and hexavalent (VI) chromium (Becquer *et al*., 2003). In nature Cr is primarily found as trivalent form. Hexavalent chromium in the environment almost fully originates from human activities (Schneider *et al*., 2012). Chromium is mainly used in chemical, metallurgical, tanning, textile, chrome plating and refractory industries. These industries are also the main sources of chromium pollution in our environment. (Sharma *et al*., 2012)**.**

1.1 Chromium Toxicity

A lot of research has been done on the toxic effects of chromium exposure. Chromium raises some serious concerns in its hexavalent oxidation state, as its toxicity, high solubility along with mobility in water results in making it 500 times more toxic than the trivalent chromium (Krishna *et al*., 2012). Hexavalent chromium is a known pulmonary carcinogen which is also responsible for causing other harmful health effects like respiratory, skin, carcinogenic, renal, hepatic and hematological problems while being genotoxic and mutagenic (Saha *et al*., 2011). Cr (VI) is carcinogenic to rats and mice after chronic oral exposure (Matthew et al., 2009).Exposure to Cr (VI) causes elevated stomach and lung cancer risk in the human body (Beaumont *et al*., 2008). In skin Cr (VI) penetration is most like to cause "chrome holes" with delayed healing (Erniza *et al*., 2014). In plants Cr accumulates and alters the germination process by effecting the growth and development of roots, stems and leaves (Shanker *et al*., 2005).

1.2 Chromium Waste Treatment Methods:

Cr can be removed from industrial wastewater by different methodologies some of these are chemical precipitation, ion exchange, electrochemical treatment, coagulation, flotation, coagulation, membrane filtration flocculation and adsorption (Barakat *et al*., 2011; Wang *et*

al., 2011). Adsorption is considered as one of the most fitting chromium removal method because it is cost effective, highly efficient, easy to operate (Djellabi *et al*., 2014) and 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) are available. The reason we chose activated carbon is because of its wide range of pore sizes, large surface area, ease of availability, and great capacity to absorb a wide range of pollutants. One of the most exceptional adsorbents for chromium is Titania nanoparticles because of its one of a kind feature like chemical and physical stability along with low cost, non-toxicity and resistance to corrosion (Hung *et al*., 2007). In one study titania demonstrated most noteworthy limit for Cr (VI) removal out of other photograph catalyst including zinc oxide and cadmium sulfide (Joshi et al., 2011). Titania likewise helps in the photo-catalytic reduction of Cr (VI) to Cr (III) (Malaviya *et al*., 2011).

1.3 Objectives:

The objectives of the research work are

1. Calibration Curve of chromium using UV-Visible spectrophotometry
2. Synthesis of titania nanocomposites
3. Removal of chromium using titania nanocomposites
4. To find a suitable isotherm model to fit the adsorption data obtained by experiments.

1.4 Significance of Work

Chromium can be adsorbed more effectively using a combination of activated carbon and titanium dioxide. So the objective of our research is chromium removal using Titania Nanocomposites.
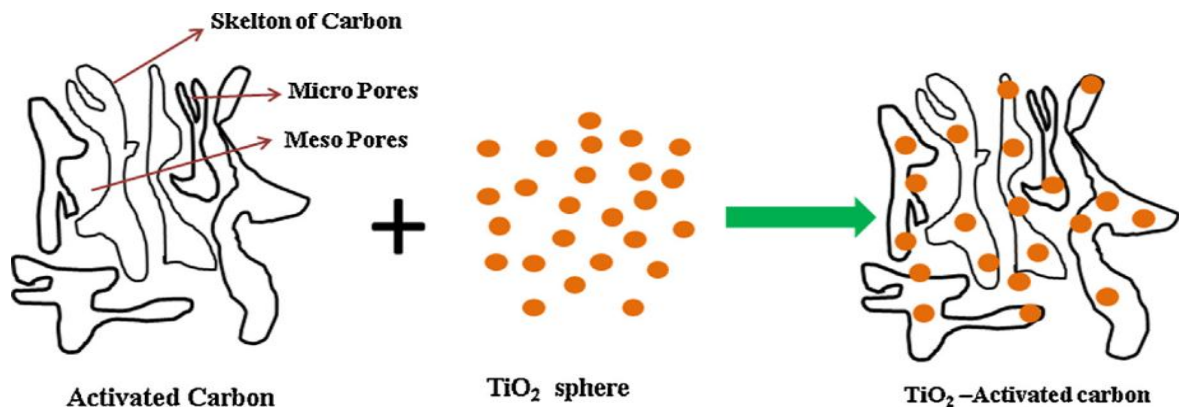
Figure.1 A diagrammatical representation of the structure of Nanocomposites

Literature Review

2.1 Background

One of the major concerns facing the world today is environmental pollution. Many countries along with Pakistan are faced with this problem due to ever growing population rate, consumption of natural and synthetic resources, industrialization and heavy dependency on fossil fuels. Every aspect of our life contributes to air pollution, water contamination or soil pollution one way or the other. Rapid industrialization is a major contributor to water pollution. The effluent released, contaminates fresh water bodies like rivers, lakes, and fresh underground water reservoirs. This renders the water unsuitable for domestic usage.

Many industries like textile, leather, paints, fertilizers and chemicals are to blame for heavy metal pollution. Different toxic metal combinations in the environment can prove very harmful to human health. Metal pollution comes from both natural sources including erosion of the drainage basin and human activities (Bertin, et al., 1995).

Multiple uses of heavy metals in various industries like agriculture, medical and technological applications have led to widespread distribution of heavy metals in the environment. Arsenic, mercury, chromium, lead and cadmium have very high degree of toxicity (Clement G, et al., 2012).Researchers across the globe are focusing on removing heavy metals from industrial waste water to meet local environmental standards. Industries need to treat the waste water properly before it mixes with water resources.

Many procedures have been adopted for the removal of toxic heavy metal ions from waste water but their safe sludge disposal still requires 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.

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

Two primary forms of Chromium are Cr (III) and Cr (VI). They are both stable forms. Chromium is mainly used in metallurgy, electroplating, and pigments. Biological and toxicological properties of Chromium depend on its chemical form. Cr (VI) is very toxic and carcinogenic whereas Cr (III) is essential for mammals (Grabarczyk M*et al*., 2008).

Chromium is very harmful to human health because of its toxic effects. Complete removal of Cr from the environment is still a daunting task and researchers are trying to come with ways for its removal (Barakat *et al*., 2011). All chromium compounds are colored and the most important compounds are chromates and di-chromates of sodium and potassium (Wang *et al*., 2011).

2.3 Occurrence of Chromium

Chromium exists as the most abundant element in Earth's crust with a concentration of 100ppm (Emsley *et al*., 2001). Chromium trivalent Cr (III) and Chromium hexavalent Cr (VI) are the most stable forms of chromium. They are both very different in their physicochemical, chemical and biochemical properties. Cr (III) is a trace element and it is very important for living organisms to function properly (J. Kotaś *et al*., 2000). It is also less toxic and less mobile. Cr (VI) has toxic effects on the environment and human health. Hexavalent Chromium is mainly produced by human activities and barely occurs in nature naturally (USEPA, 1984). It exists naturally in a rare mineral Crocoites ($PbCrO_4$) (Hurlburt *et al*., 1971).

2.4 Sources of Chromium

Chromium does not exist freely in nature. The main Chromium mineral is Chromite ($FeCr_2O_4$). Cr (VI) comes generally comes from the effluent of tanning, Electroplating and painting industries. Chromium compounds are used as pigments and 90% of leather is tanned using chromium pigments. Chromium can spread in the environment if it is not properly disposed (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 occurs naturally and is found in animals, soil, animals, volcanic ash, plants and gases. Coal and oil 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

Some of the anthropogenic chromium comes from wood preservation, glass industry, dyes and pigments, production of steel and alloys, mining of chrome ore, leather tanning, electroplating, and metal cleaning (Ihsanullah *et al*., 2015). Globally, approximately 12 million tons of Chromite ore are mined annually (Belay etal., 2010). Chromium is usually in the form of chromium (III) oxide or Chromite, in refractory products. Chromite ore is used as foundry sand (Lytle *et al*., 1998).

2.4.3.1 Tanning Process a Major Chromium Pollution Source in Pakistan

Chromium pollution from tanneries is among the top ten of the toxic twenty World's worst pollution problems (Brown et al., 1997). In Pakistan, major chromium contribution in water bodies is from tanneries in Kasur. 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 compounds are used as pigments. Chromium gives Rubies their red color. Glass that has been treated with chromium gets an emerald color. Polished mirror finish can be given to steel using chromium. The refractory industry uses Chromite ores for forming brick sand molds, as it has a high melting point, and crystalline structure stability (Song Z. et al., 2000). Chromium helps in building muscles. Blood flow regulation, cholesterol levels moderation, lean, 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 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).

2.6 Chromium Toxicity

Chromium toxicity is mainly due to Cr (VI) because Cr (III) is not readily absorbed by the body through any route. Cr (VI) can be absorbed by the lung and gastrointestinal tract (Mohanty et al., 2005). Cr (VI) is 300 times more toxic than Cr (III) due to its mutagenic and carcinogenic nature (Ihsanullah *et al*., 2015). Toxicity of Cr increases as PH of precipitation decreases. Acid rain increases the harmful effects of heavy metals toxicity on aquatic life (Tasneem Abbasi et al., 2009).

Annual contribution of chromium resulting from human activities into water is expected to exceed the amount of chromium in the atmosphere (Pacyna et al., 1988;(Danadevi et al., 2003).

Workers in leather industries have higher concentration of toxic chromium in their bodies due to direct and indirect exposure (Vellingiri *et al*., 2010). Direct skin contact can result in rashes, ulcers and skin allergies dermal necrosis and dermal corrosion (Gad et al., 1989).

2.6.1 Environmental Effects of Chromium on Plants

High concentration of hexavalent chromium is very dangerous for flora and fauna (Alazemi e*t al.,* 1996). Symptoms of chromium toxicity in plants include but not limited to lower seed gestation, reduction of growth, decrease of yield, impairment of photosynthesis, nutrient and oxidative imbalances, and mutagenesis. Cr is toxic for agronomic plants at about 0.5 to 5.0 mg L−1 in nutrient solution and 5 to 100 mg g−1 in soil (L. R. Hossner, 1996).

2.6.2 Chromium Impacts on Human Health

Cr (VI) is 300 times more toxic than Cr (III) (Ihsanullah *et al*., 2015). Studies by Agency for Toxic Substances and Disease Registry (ATSDR) have shown that workers in direct contact with Cr (VI) have an increased risk of lung cancer. Chronic inhalation of Cr (VI) can lead to asthma, effects on respiratory tract, pneumonia, and bronchitis (Agency for Toxic Substances and Disease Registry (ATSDR)). Cr (VI) can also result in kidney, liver and gastric damages (US Department of Health and Human Services 1991; Golonka *et al*., 1995).

2.6.2.1 Respiratory Effects

Inhalation of Chromium from industries can result in pulmonary irritation. Some of the common respiratory effects include asthma, chronic bronchitis issues, chronic irritation, 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).

2.6.2.2 Skin Effects

Dermal contact with Cr (VI) can lead to skin irritations, ulcers, and dermatitis. It can also cause swelling, fissures, papules. Skin penetration can result in painless erosive ulceration "chrome holes" with delayed healing (Marchese et al., 2008). These usually appear on the fingers, knuckles, and forearms.

2.6.2.3 Renal Effects

Severe contact with 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 can result in acute renal effects (Zhou at al., 2008).

2.6.2.4 Hepatic Effects

Chromium (VI) has been reported to cause severe liver effects in workers of chrome plating industries. Increase in Kupffer cells, liver cell damage, necrosis, lymphocytic and histiocytic infiltration were also reported (Wionczyk *et al*., 2006).

Materials and Methodology

3.1 Test Materials

All the materials that we have used in our experiments were standard scientific grade. Titanium Dioxide, Activated Carbon, Potassium Dichromate, DiPhenyl Carbazide, Acetone, Phosphoric Acid, and Ethanol were manufactured by Daejung chemical & metal Co. Ltd. Wherever the need arose, only distilled water was used.

3.1.1 Preparing the Stock and Standard Chromium solution:

In order to determine the concentration of chromium in the solutions, the standard Diphenylacarbazide (DPC) method was used. A standard solution of potassium dichromate of a Chromium concentration of 500 ppm was made by dissolving 1.414 g of oven dried potassium dichromate in 1000 ml of distilled water in a volumetric flask. The DPC solution was made by dissolving 250 mg of 1, 5 Diphenylacarbazide powder in 50 ml acetone. For all pH adjustments (2.0 ± 0.5) 2N Phosphoric acid was used. In the end standards, between 0 mg/l to 2 mg/l were made using the above mentioned solutions.

3.2 Test Instruments

During our experiments, we used the following instruments: a UV lamp (8W) with a wavelength of 365 nm, quartz cell (20849 Hach); UV/Vis spectrophotometer (Hach DR2400), pH meter, magnetic stirrer, Sonicator and Oven.

3.3 Test Procedures

3.3.1 Titania Nanoparticles Synthesis:

In order to synthesize the Titania Nanoparticles, we have used the liquid impregnation method (Khan et al., 2013; Younas et al., 2014). The details of this method have been described in figure.

(i)   **Mixing:** In the first step, 50 g of titanium dioxide was mixed with 300 ml of distilled water in a beaker and was set on continuous stirring for 24 h.

(ii)   **Settling:** The solution from step (i) was then allowed to rest for a further 24 h in order to allow settling of the solids.

(iii)   **Drying:** The solution was then kept in the oven for 24 h at 105ºC so as to remove all the water from the solution.

(iv)   **Calcination:** After drying, the remaining substance was crushed thoroughly using a mortar and pestle (for approximately 10-15 minutes). The crushed powder was then put into a china dish and placed inside a muffle furnace set at 550 ºC for 5 h.

3.3.2 Synthesis of Titania and Activated Carbon Nanocomposites

For the preparation of Nanocomposites, we have used the liquid impregnation method. The detailed procedure has been described as follows:

(i)   **Sonication:** In the first step of the process, 9 g of activated carbon and 1 g of Titania nanoparticles were mixed with 100ml ethanol in separate beakers and sonicated for 30 minutes respectively.

(ii)   **Mixing:** The mixture from both the beakers was then added to a single beaker and then stirred for 2 h using a magnetic stirrer.

(iii)   **Drying:** The stirred mixture was then placed in heating oven at 70ºC for 24 h to dry.

(iv)   **Calcination:** The material left after drying was then thoroughly crushed using mortar and pestle for 15 minutes. This was then placed in muffle furnace at 350ºC for 3 h.

3.3.3 Characterization of Nanoparticles

The surface properties of synthesized nanoparticles, activated carbon and composite were determined using Scanning Electron Microscopy JEOL, JSM 6490A, Japan. The elemental composition was further confirmed using Energy Dispersive X-Ray Spectroscopy (JEOL, JED 2300).

3.3.4 Spectrophotometric Determination of Chromium

In order to estimate the quantity of Chromium (VI) we have used a UV/Vis spectrophotometer which measured the absorbance at the wavelength of maximum absorbance which in this case was 540 nm. The device model used was Hach DR 2400.

3.3.4.1 The Working Principle of the Spectrophotometer

Spectrophotometry is a methodology that is used all around the world during the quantitative analysis of organic and inorganic compounds. The molecules are exposed to UV-light, which they absorb. Due to this, electrons become excited, and then move to higher energy orbitals. The spectrophotometer measures the light which is transmitted, known as transmittance. The absorbance is a result of measuring the difference between the light transmitted before and after the sample's exposure to UV light (Thomas and Burgess, 2007).

3.3.4.2 Beer-Lambert Law

The Beer-Lambert Law states that absorbance is directly proportional to the concentration of the sample.

$$A = \varepsilon.\ c.\ L$$

Where,

A = absorbance

ε = absorption coefficient, specific to sample solution

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

3.3.5 Chromium Adsorption and Photo Reduction: Batch Study

The setup for the batch study of photo reduction of Chromium (VI) and its adsorption on Titania Nanocomposites was done in light using UV lamps (8W) and in dark. The Chromium concentration for all experiments performed was 10 mg/L and the dosage of nanoparticles, activated carbon and Nanocomposites was kept 1 g/L. The flasks were kept in a chamber of UV lamps on a shaker. The speed of shaker was set at 200 rpm. The removal of Chromium was measured at pH 5.5-6. Samples were taken from the solution after every 60 minutes interval. The chromium adsorbed Titania was removed from the samples by filtration using 0.2μm filters. After filtration absorbance of each sample was measured to determine the concentration of remaining chromium using the DPC method described above. Following formula was used to calculate the percentage removal.

$$\% \text{ Removal } = \frac{C_o - C_t}{C_o} \times 100$$

Whereas:

C_o = Initial Cr concentration

C_t = Residual Cr concentration

Results and Discussion

4.1 Characterization of Nanoparticles and Nanocomposites

4.1.1 Scanning Electron Microscopy (SEM) Analysis

The surface properties (i.e., size and morphology of synthesized catalysts) were confirmed using SEM as shown in the figures below. Titania nanoparticles are spherical in shape (Figure 3) while in composite the TNPs are agglomerated in the porous structure of CAC (Figure 4). It shows that TNPs attach themselves to the most approachable pores of CAC, keeping the smaller pores unblocked and consequently increasing the efficiency by enhancing the surface area. It is expected that only weak interaction exists between TNPs and surface of CAC instead of a strong chemical bond.
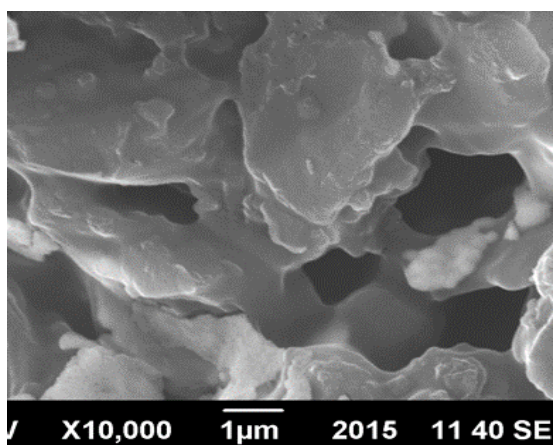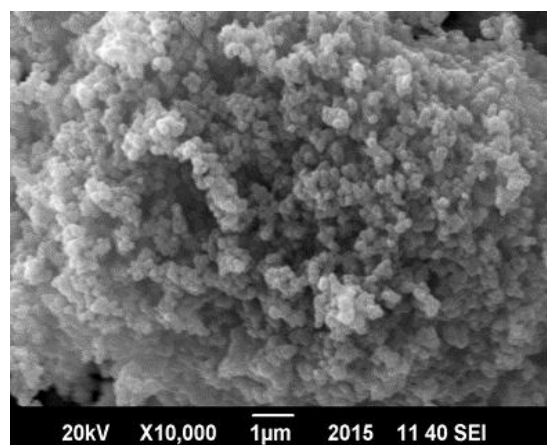

Figure 2 SEM Image of Activated Carbon

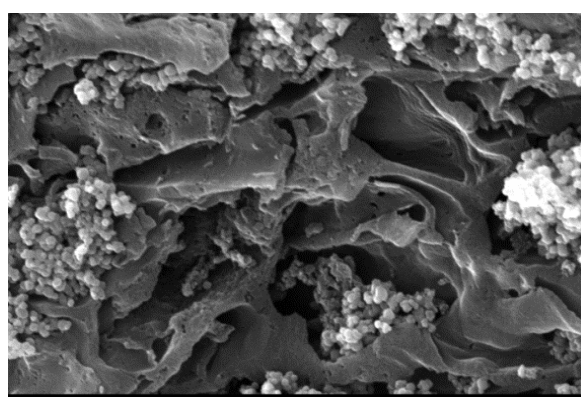**Figure 3 SEM Image of Titania Nanoparticles**

Figure 4 SEM Image of Titania and Carbon Nanocomposites

4.1.2 Energy Dispersive Spectroscopy (EDS) Analysis

The Energy Dispersive X-Ray Spectroscopy depicts the elemental composition of synthesized TNPs, CAC and TiO2/CAC. The EDS pattern of composite (10 wt% of TNPs in CAC) confirms the availability of CAC in composite (Fig. 7) for efficient removal of Cr. The Energy Dispersive X-Ray Spectroscopy depicts the elemental composition of Activated Carbon, synthesized Titania Nanoparticles, and TiO2/AC Nanocomposites. The Fig. 5 shows the EDS of TiO2 showing that there is 60% Titania and 40% Oxygen in it without any impurities. Fig. 6 shows the EDS of Activated Carbon in which there is 72% Activated Carbon and 28% Oxygen. And Fig. 7 is the EDS of Synthesized Nanocomposites; the EDS pattern of composite which is 90% Activated Carbon and 10% Titania confirms the availability of Activated Carbon and Titania in composite for efficient removal of Chromium.
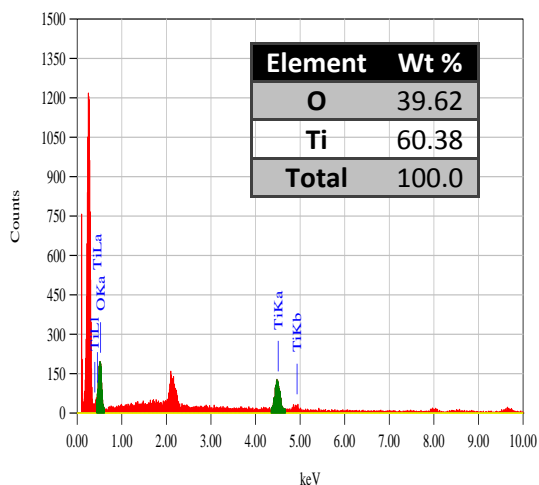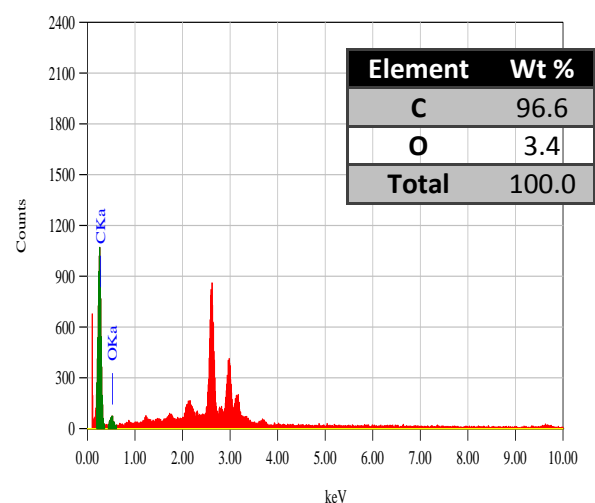

Element	Wt %
O	39.62
Ti	60.38
Total	100.0

Figure 5. EDS Spectra of Nanoparticles

Element	Wt %
C	96.6
O	3.4
Total	100.0

Figure 6. EDS Spectra of Activated Carbon

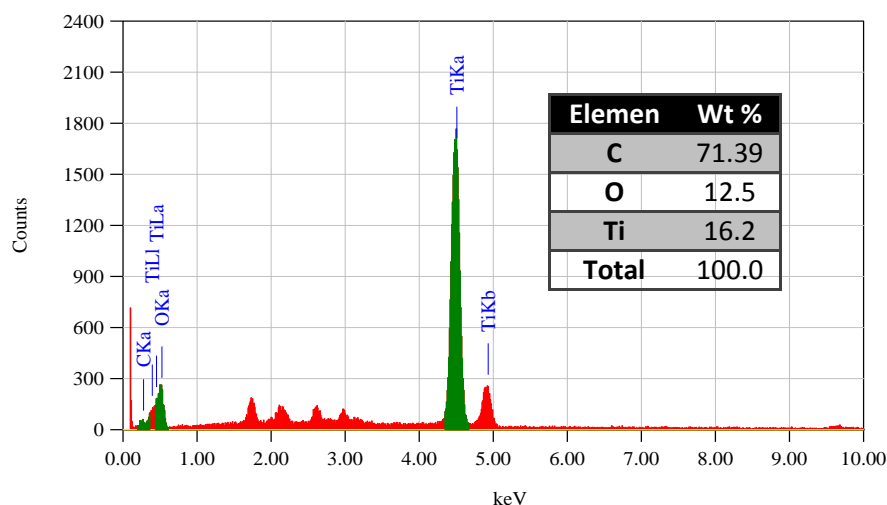| Elemen	Wt %
C	71.39
O	12.5
Ti	16.2
Total	100.0

Figure 7. EDS Spectra of Nanocomposites

4.2 Hexavalent Chromium Determination

Diphenylcarbazide (DPC) standard method APHA 3500-CR was used to determine Cr (VI) in synthetic waste water using UV/Vis spectrophotometer. For this reason, UV/Vis spectrum of a dye Diphenylcarbazide (DPC) was recorded for determining Cr (VI) in waste water to validate the wavelength of maximum absorbance of 540 nm, which is in compliance with the standard method as shown in Fig. 8.
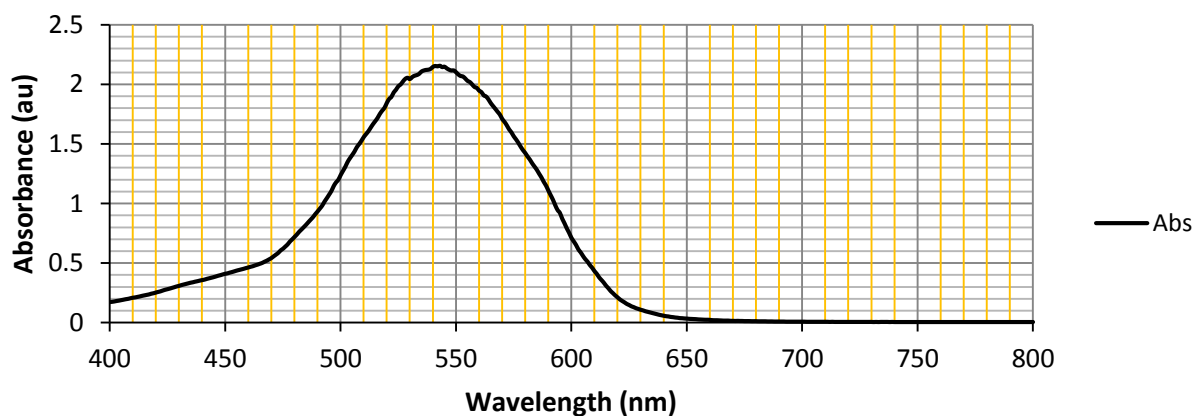
Figure 8. Absorbance Spectrum showing the Wavelength of Maximum Absorbance

A calibration curve was developed at λmax 540 nm using serial dilutions starting from 0.1 mg/L to 1 mg/L of solution as shown in Fig. 9
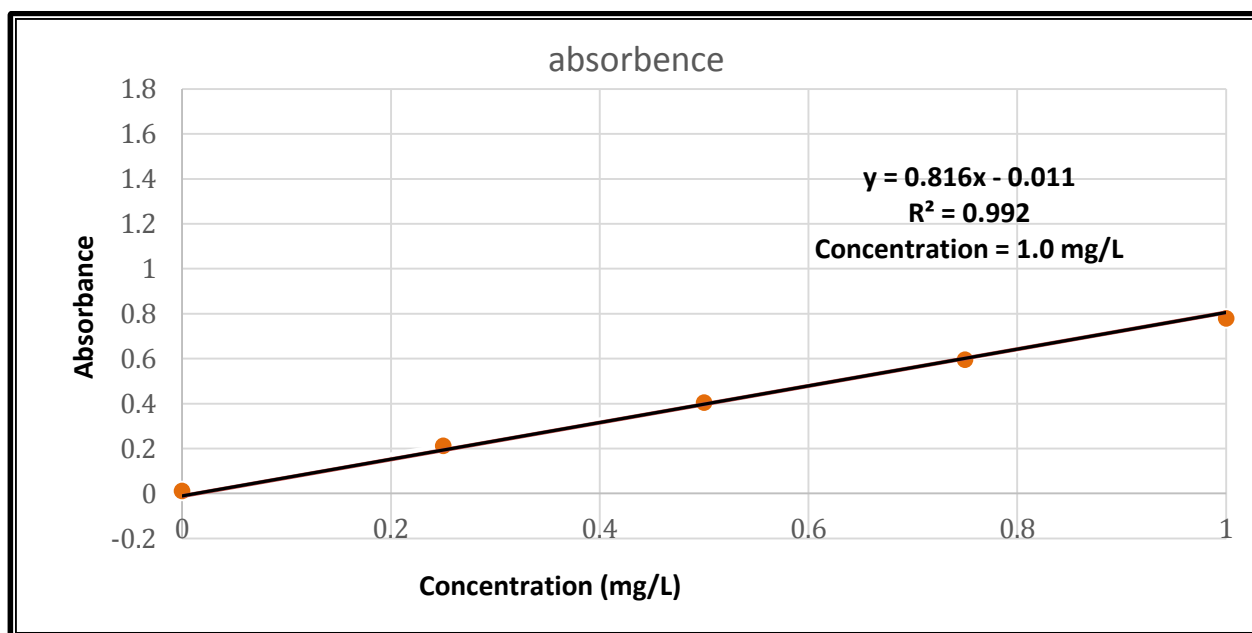
Figure 9. Calibration Curve for Hexavalent Chromium Determination

4.3 Chromium Removal under Dark and Light Conditions

4.3.1. Chromium Removal in Dark

The removal of chromium was studied for all three adsorbents over a period of 3 h. At the end of the experiment, 52% removal of chromium was achieved by Activated Carbon, whereas the Nanoparticles and Nanocomposites achieved 58 % and 66 % removal respectively. A comparison between Activated Carbon, Nanoparticles and Nanocomposites (Fig. 10) shows that the composites have achieved the highest chromium removal under dark conditions. Activated Carbon shows less chromium removal than Nanoparticles as Titania Nanoparticles are better adsorbent then the Activated Carbon. The Nanocomposites show the highest removal of chromium as they have largest surface area because they have both Activated Carbon and Nanoparticles adsorbing together hence higher removal of Chromium from water and removing about 65% of chromium under the dark conditions i.e. no UV-light was provided during removal time period of 3 h.
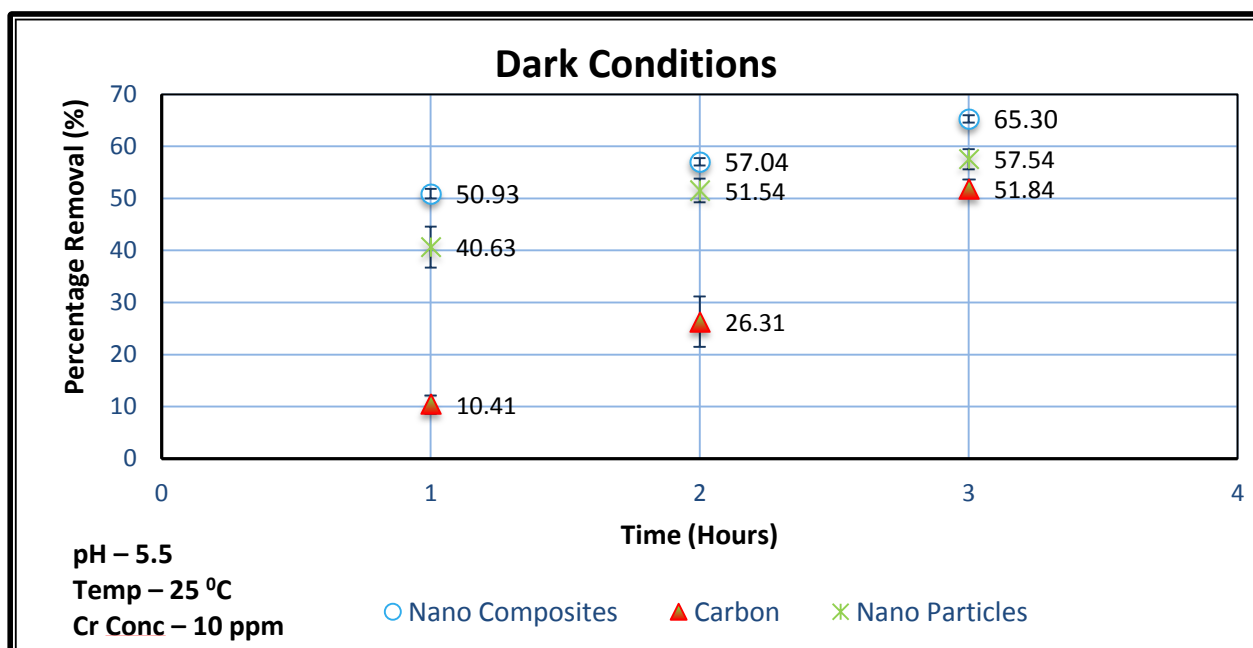

Figure 10. Cr Removal in Dark Condition

4.3.2 Chromium Removal in UV light

According to Fig. 11, the maximum percentage removal after 3 h in the presence of UV light was 98.9 %, 90.3 % and 56.9 % by Nanocomposites, Nanoparticles and Activated Carbon, respectively. Due to the presence of UV light Titania Nanoparticles convert Cr (VI) to Cr(III) by photo catalytic reduction. There is no effect of UV on AC, the % removal is mainly because of adsorption. In case of AC-TiO2, highest % removal was achieved as AC provides adsorption sites while TiO2 nanoparticles under UV light effect helps to degrade Cr. Therefore, nanocomposite performed best in all three adsorbents with only 10% chromium addition.

Figure 11. Cr removal in Light Condition
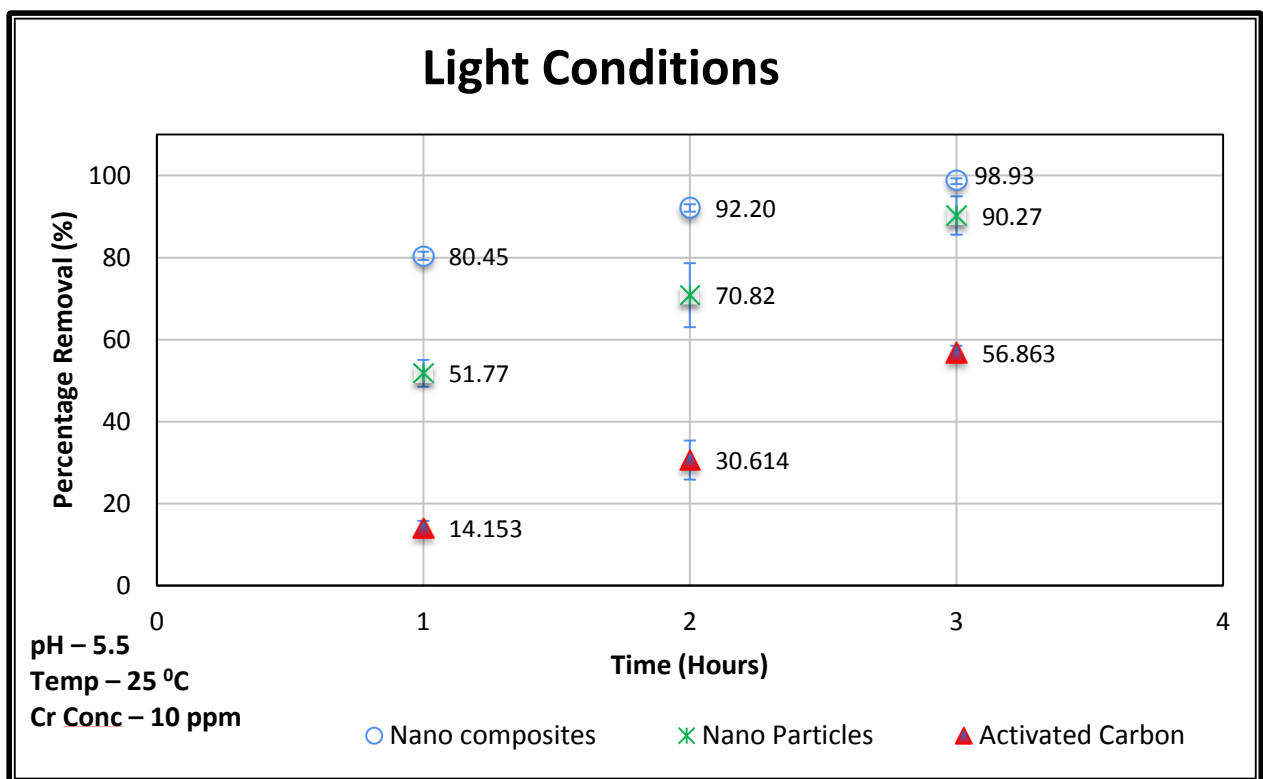
4.3.3 Effect of Composite Dosage

The percentage removal increased with the increase in composite dosage as shown in Fig. 12. This occurred until an optimal dosage of 1 g/L was reached after which the removal was more or less the same. Starting from 250 mg/L with an increment of 250 mg/L, the dosage was increased up to 1250mg/L showing increase removal with increased dosage until the

maximum removal is achieved at the 1000 mg/L or 1g/L which is the optimum dosage for removal of Cr(VI) in the presence of UV-light. Increasing the percentage of adsorption with adsorbent dose may be due to the increase in adsorbent surface area and availability of more adsorption sites (Namasivayam et al, 1998 and Garg et al, 2007). The rate of adsorption, however, decreased with increase in adsorbent dose after the optimal value. This is may be due to overlapping of adsorption sites as a result of overcrowding of adsorbent particles (Garg et al, 2007).
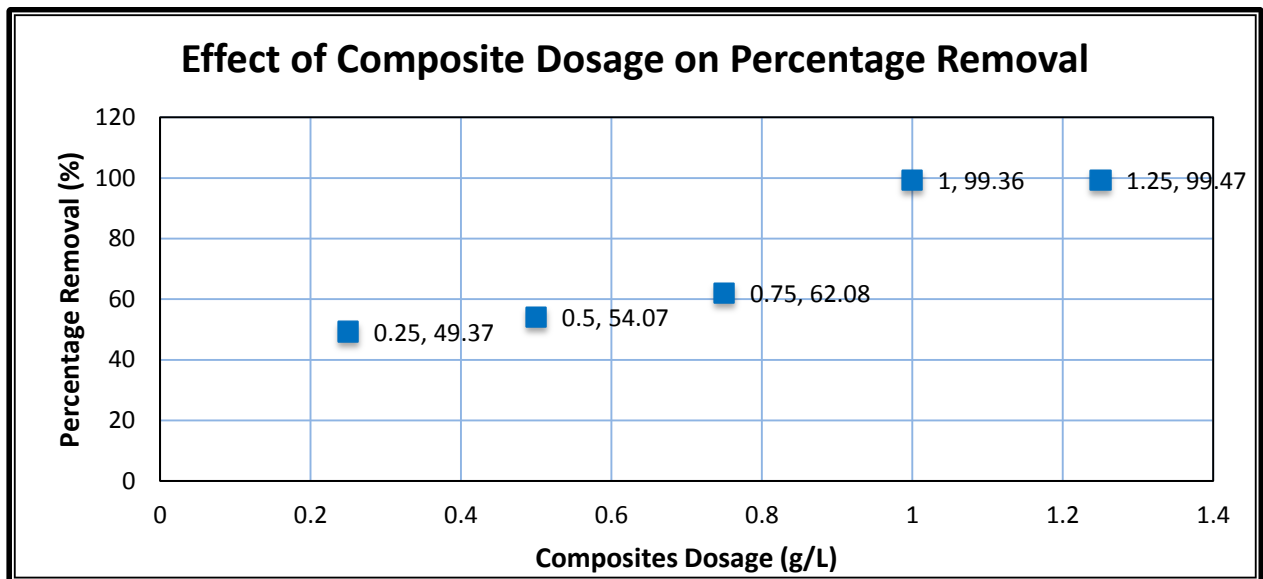

Figure 12 Effect of Dosage

4.4 Isotherm Models

Isotherm Models are used to predict the amount of solute that the composites can adsorb onto their surface. There are many well developed Isotherm Models, out of which the most popular and well-established are:

- Langmuir Isotherm Model

- Freundlich Isotherm Model

- Temkin Isotherm Model

4.4.1 Langmuir Isotherm

The Langmuir Isotherm Model is one of the most common isotherm models. This model helps to study the relationship between the variation of adsorption and the equilibrium concentration. This model also explains the adsorbent's characteristics at isothermal conditions. The following assumptions are made in order to follow the Langmuir Isotherm Model:

1. The adsorbing sites are located on a flat plane that has no corrugations
2. Only mono-layer coverage occurs.
3. No interactions occur between the adsorbate molecules and adjacent sites.

In order to apply the model on the available the data, the following variables were calculated:

*   The Maximum Adsorption Capacity (Q_m)
*   Adsorption Intensity (K_I)
*   Mass of Material Adsorbed per Mass of Adsorbent (Q_e)

The calculations and their results can be seen in Table 1:

Initial Concentration (C_0) mg/L	Equilibrium Concentration (C_e) mg/L	Change in Concentration (C_0-C_e)	Mass of adsorbent (g)	Mass Adsorbed $Q_e=(C_0-C_e)*V/M$ mg/g	C_e/Q_e
10	9.681	0.319	0.25	1.276	7.587
10	8.783	1.217	0.5	2.434	3.608
10	7.251	2.749	0.75	3.665	1.978
10	0.123	9.877	1.000	9.877	0.012
10	0.102	9.898	1.25	7.918	0.013

The equation for this model is:

$$Ce/qe = 1/Qm\ b\ Ce +1/Q_m$$

A graph was plotted between Ce/Qe and Ce as can be seen in Fig. 13. The parameters calculated from this graph are illustrated on the graph.

Langumuir Model

$y = 0.573x - 0.337$
$R^2 = 0.738$
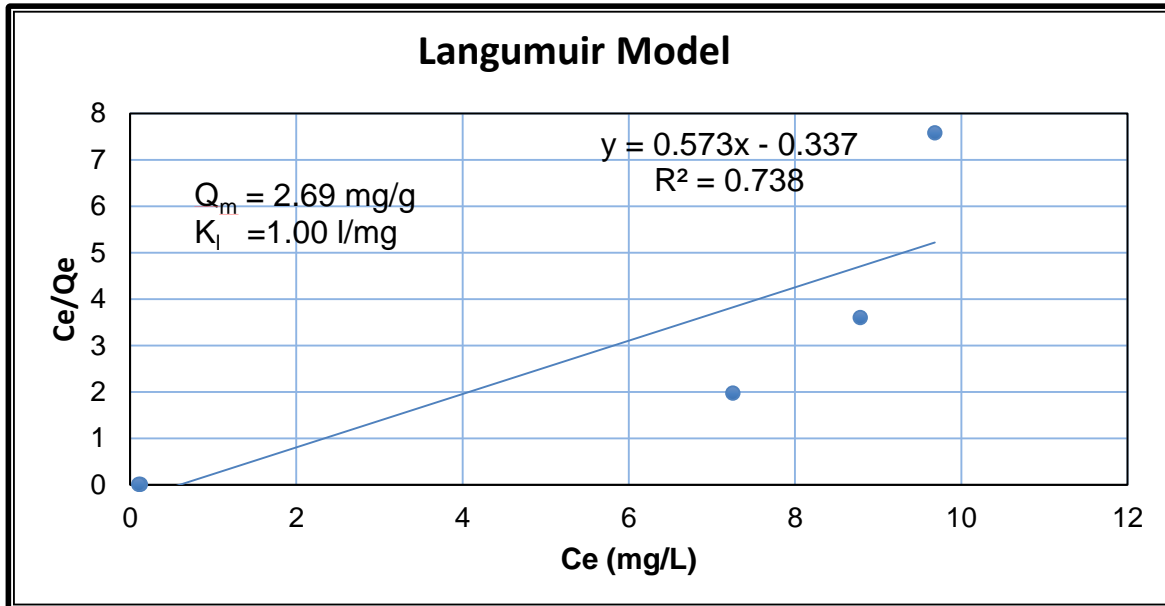
$Q_m = 2.69$ mg/g
$K_l = 1.00$ l/mg

Figure 13

4.4.2 Freundlich Isotherm

The Freundlich Isotherm Model is a curve that tells us the relationship between the concentration of a solute present on the surface of an adsorbent and the concentration of the solute with which it is in contact. An empirical equation is used for this representation and is called the Freundlich Adsorption Isotherm. The equation used is:

$$Q_e = k_f\ Ce^{\ 1/n}$$

Or more simply,

$$Ln\ q_e = ln\ k_f + 1/n\ ln\ Ce$$

For this equation the following parameters are calculated:

- K_f - amount of adsorbed material on the adsorbent surface
- n – Adsorption Intensity

The calculated parameters are as shown in Table 2:

Initial Concentration (C₀) mg/L	Equilibrium Concentration (Cₑ) mg/L	Change in Concentration (C₀-Cₑ)	Mass of adsorbent (g)	Mass Adsorbed $Q_e=(C_0-C_e)*V/M$ mg/g	Log Qe	Log Ce
10	9.681	0.319	0.25	1.276	0.106	0.986
10	8.783	1.217	0.5	2.434	0.386	0.944
10	7.251	2.749	0.75	3.665	0.564	0.860
10	0.123	9.877	1.000	9.877	0.995	-0.910

A graph was plotted between Log Qe and Log Ce and the required parameters were calculates as shown in Fig. 14.
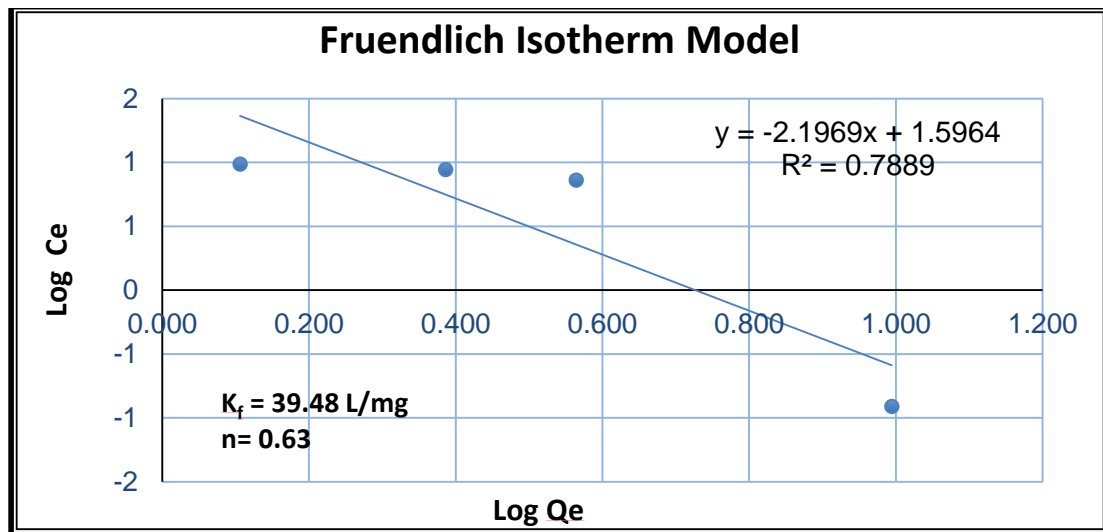

Figure 14

4.4.3 Temkin Isotherm:

The Temkin Model is also another well developed and well-tested adsorption model. The model is represented by the following equation:

$$Q_e = B \ln C_e + B \ln A$$

$$b = RT/B$$

Where A and B are Temkin Isotherm Constant (L/g) and heat of sorption (J/mol) respectively. R is the gas constant (J/mol. K), b is the Temkin isotherm constant linked to the heat of sorption as shown in the equation above. T is the absolute temperature measured in Kelvin.

The calculations for this model and their results can be seen in Table 3.

Initial Concentration (C_0) mg/L	Equilibrium Concentration (C_e) mg/L	Change in Concentration (C_0-C_e)	Mass of adsorbent (g)	Mass Adsorbed $Q_e=(C_0-C_e)*V/M$ mg/g	Ln Ce
10	9.681	0.319	0.25	1.276	2.270
10	8.783	1.217	0.5	2.434	2.173
10	7.251	2.749	0.75	3.665	1.981
10	0.123	9.877	1.000	9.877	1.780

A graph was plotted between Q_e and Ln C_e as shown in Fig. 15:

Temkin Isotherm Model

B= 0.053

A= e^43.03

y = -0.053x + 2.281
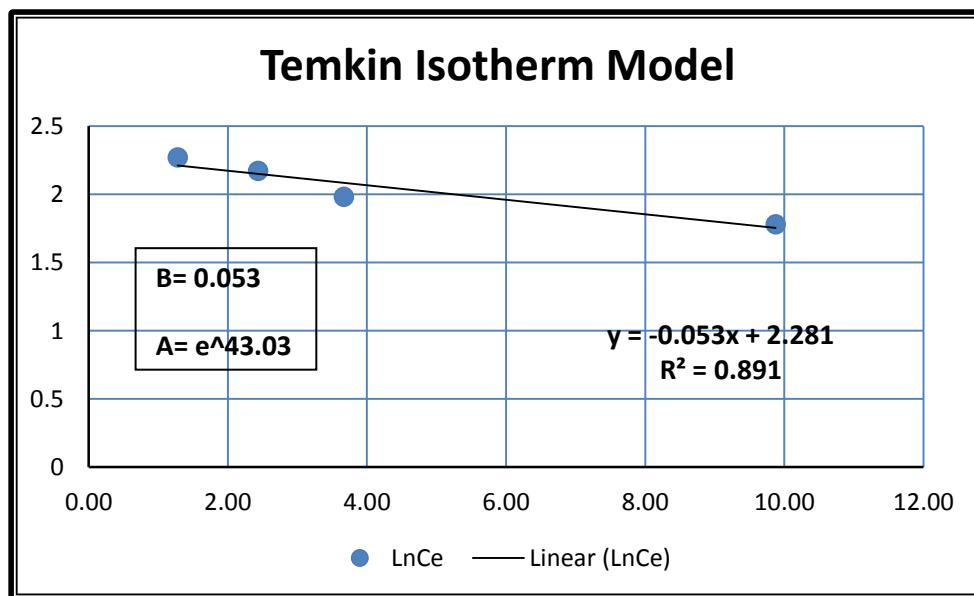R² = 0.891

● LnCe ——— Linear (LnCe)

Figure 15

Conclusion: The results show us that in comparison, the Temkin Isotherm Model has the best accordance with our results. The calculated parameters of each model have been enlisted in Table 4.

Table 4 Parameters of Isotherm Models

Langmuir		Freundlich		Temkin	
Q_m	2.69 mg/g	K_f	39.48 L/mg	A	e^43.03
K_l	1.00 l/mg	n	0.63	B	0.053
R^2	0.738	R^2	0.7889	R^2	0.891

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

From our research discussed above, we can conclude the following:

1. The Nanocomposites made of AC and TiO_2 Nanoparticles were successfully synthesized and used for the removal of Chromium from water.
2. SEM and EDS showed that TiO_2 Nanoparticles were attached onto the surface of Activated Carbon thereby increasing the Nanocomposites efficiency
3. The Removal of Chromium was further optimized with the help of UV light.
4. An increased Nanocomposite dosage leads to an increased Chromium removal until the optimal dosage of 1g/L.
5. Freundlich, Langmuir and Temkin Isotherm Models were applied to fit the adsorption data. After regression analysis, it can be seen that Temkin model is a better fit for our results (with aR^2 value of 0.89) as compared to Langmuir's and Freundlich's R^2 values of 0.74 and 0.79 respectively.

5.2 Recommendations

1. These Nanocomposites can be used for the removal of other heavy metals such as Arsenic, Cadmium and Lead etc
2. These Nanocomposites can be used to develop a continuous system.

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