ADDIS ABABA INSTITUTE OF TECHNOLOGY

SCHOOL OF GRADUATE STUDIES

ASSESSMENT OF CACTUS BIOSORPTION POTENTIAL IN THE REMOVAL OF HEXACHROMIUM IONS FROM SYNTHETIC AND TANNERY WASTE WATER

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(WATER SUPPLY AND ENVIRONMENTAL ENGINEERING STREAM)

By:

Getahun Mebrate

Advisor:

Dr. Ing.Geremew Sahilu Gebrie

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List of Abbreviations and Acronyms

APHA	American Public Health Association
ASTM	American society test material
AAS	Atomic Absorption Spectrophotometer
Cr (VI).	Hexavalent Chromium
Cr (III)	Trivalent Chromium
Cr	Chromium
FTIR	Fourier Transform Infrared Spectrometry
LIDI	Leather Industry Development Institute
rpm	revolution per minute
TDEV	Standard Deviation
OFI	Opuntia- Ficus Indicus
UV-Vis	Ultraviolet Visible
UNIDO	United Nations Industrial Development Organization
UNEP	United Nations Environment Programme
UNDP	United Nations Development Programme
UNICEF	United Nations Children’s Fund
WHO	World Health Organization

ABSTRACT

Chromium (VI) is environmentally mobile owing to its high solubility in water. Its pollution is largely attributed by discharge of inadequately treated effluents of chrome utilizing industries. Discharges of such effluents pose a potential threat to human health unless are treated properly before its disposal. Adsorption using activated carbon prepared from biomaterials is a new technology for the treatment of heavy metals rich industrial effluents. Opuntia Ficus Indicus (OFI) activated with H_3PO_4 (45%) was evaluated for Cr (VI) removal capability from both synthetic and tannery waste water. The present work was aimed at assessing the biosorbent capability of OFI in removal of Cr (VI) from synthetic aqueous solution and tannery waste water. OFI was activated with H_3PO4 (45%) and carbonized at 450^oC in muffle furnace for 1hr and its different physical properties such as bulk density and moisture content was determined. Besides; the sorbent characterized by FTIR spectroscopy test analysis before and after adsorption processes, suggested possible key contributions of hydroxyls and carboxyls in the sequestering of Cr(VI) on OFI. Maximum Cr(VI) removal efficiency of 99.5% was achieved by OFI under different study parameters. The percentage removal of Cr (VI) ions increased with increase of the amount of sorbent concentration for which the Optimum removal of Cr (VI) was observed at sorbent dose of 125 mg. The adsorption efficiency of Cr (VI) on OFI was increased at low pH values between 2 and 3, attending its optimum at pH of 2. Percentage removal was observed to increase, while decreasing the initial concentration of Cr (VI) to which 6mg/l was the minimum of adsorption system. Whereas; the removal was increased with increasing the agitating speed and its corresponding contact time, whereby; the optimal adsorption reached at 60 minutes at 150rpm agitating speed. Both Langmuir and Freundlich models and followed adsorption process with high regression correlation coefficient (R^2) values of 0.999 and 0.956 respectively. But, Langmuir isotherm with higher $R^2$was best fitted to the experimental values, with monolayer adsorption capacity of 4.587mg/l. Besides; the RL values were obtained in range of 0 < RL < 1 that confirmed the favorability of adsorption process. The optimized parameters were applied to the real waste water resulted in 88.7% of optimal adsorption removal efficiency. The reduction in percentage of removal might be due the matrix effect of the competing ions present the chrome liquor spent. Adsorbent used in present study was prepared at laboratory scale and observed to hold distinct position for its efficient removal of Cr (VI) both from synthetic aqueous solution and tannery waste water and could be an alternative promising plant based biosorbent in field.

Keywords: Adsorption, Sorbent, Opuntia- Ficus Indicus and Langmuir-Freundlich Isotherm Models.

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CHPTER ONE
INTRODUCTION

1.1 Background

Water is most important gift of nature next to air required for the survival of humankind and other forms of life (Osasona et al., 2013; Kumar and Majumde, 2014). However; the varying degrees in pollution of water bodies with bacteria and waste matter, at present has posed serious public health problem to human beings and animals (Alluri et al., 2007; Kalandar and Yadav, 2014). As for instance; in India alone over 70% of the existing water is polluted (Alluri et al., 2007; Kalandar and Yadav, 2014). Heavy metals are reported as priority pollutants with hazardous contamination level in waste water streams (Qaiser et al., 2007). Chromium (Cr), Cadmium (Cd), Copper (Cu), Mercury(Hg), Lead(Pb), Nickel(Ni) and Zinc(Zn) are identified among at least 20 frequently used heavy metals that intern classified as the most toxic contaminants emanated into the environment (Nomanbhay and Palanisamy,2005;Thilakar et al., 2012).Unlike organic wastes, heavy metals, are non-biodegradable and they can be accumulated in living tissues, causing various diseases and disorders(Tahiruddin and Ya'akub,2013).

Heavy metals reach into the receiving water bodies through two major sources; gynogenic and anthropogenic sources, the latter representing the predominate source (Wanee et al., 2012). Industrial effluents represent major sources of toxic heavy metal pollution contributing the deterioration of water quality (Thilakar et al., 2012). These Pollutants can also seep down and affect the groundwater deposits (Kumar and Majumde, 2014). Chromium is one of the different heavy metals in concern. Chromium and its compounds are toxic metals introduced into natural water from a variety of industrial wastes (Attia et al., 2010; Khedr et al.,2014). In Egypt, about 2000–5000 tons of chromium pollute the environment annually from several industries in the aqueous effluent compared to the recommended permissible discharge limits of 2mg/l (Khedr et al., 2014).

Chromium can exist in several oxidation numbers but only chromium (III) and chromium (VI) are stable enough to occur in the environment (Mandina et al., 2013). However, Cr(VI) is of particular concern as because of its high toxicity and its potential carcinogenic properties and acute exposure to Cr(VI) causes nausea, diarrhea, liver and kidney damage, dermatitis, internal hemorrhage and respiratory problems (Swathi et al.,2014).Furthermore; Cr(VI) also has higher mobility than Cr(III) in that, it has higher potential to contaminate groundwater (Tahiruddin and Ya'akub,2013).Considering its toxicity and carcinogenic nature, the maximum levels permitted for Cr(III) in wastewater is 5 mg/L and for Cr(VI), 0.1 mg/l (Wanee et al., 2012).

Discharge of wastes containing chromium occurs into environment, with its varied concentration between 5 and 220 mg/L which is much higher than the permissible limits for discharge to surface waters are 2 and 0.1mg/l as total chromium and Cr(VI) respectively (Wanee et al.,2012; Kumar and Majumde,2014). Therefore; the treatment of Cr (VI) from wastewater streams has become one of the most important ongoing environmental issues faced by all countries in today's world (Alluri et al., 2007). According to the world health organization guidelines, the maximum level of Cr (VI) in drinking water is 0.05 mg/l, subsequently; chromium containing water must be treated to attain the Cr (VI) to permissible limit (Kumar and Majumde, 2014).

In light of reducing discharged effluent level, the most common conventional methods of Cr (VI) ions removal from aqueous system are chemical precipitation, ion exchange, membrane processes, electro dialysis and adsorption (Swathi et al., 2014). A number of physicochemical techniques are being used world-wide to depollute water loaded with heavy metals (Liu et al., 2010). However, many of these processes are not widely practiced due to their disadvantages including incomplete metal removal, requirements for expensive equipment and monitoring systems, or generation of toxic sludge or other waste products that require disposal (Ahalya et al., 2005).

Moreover; Hexavalent chromium usually exists in wastewater as oxy anions such as chromate CrO_4^{-2} and dichromate Cr_2O_7-^{2} and does not precipitate easily using conventional precipitation methods. Ion exchange, reverse osmosis and electro dialysis are efficient for Cr (VI) ions removal but the cost is relatively high. The other chromium removal techniques such as; co-precipitation, membrane techniques and solvent extraction are challenged by the removal of lower concentrations of metals from solution (Wanee et al., 2012).

On the hand; Adsorption on the carbonaceous materials named; activated carbons are very effective owing to their highly developed porosity, internal surface area, and relatively high mechanical strength (Khedr et al., 2014). Adsorption technique using sorbent activated carbon remains the most economical and widely method used for the removal of toxic pollutants from wastewater so, is also for Cr(VI) removal(Mutongo et al.,2014).However; cost is an important parameter while, selecting sorbent materials, in which case, commercial activated carbons are cost prohibited due to the use of non-renewable and relatively high-cost starting materials; requires chelating materials to enhance the performance (Meena and Rajagopal,2003).

In view of the aforementioned facts, most of the conventional methods are neither effective nor economical, especially when used for the reduction of heavy metal ions to low concentrations. Thus, an effective, low cost and environmentally sound new alternative separation method are required to reduce heavy metal concentrations to acceptable levels (Alluri et al., 2007). In this regards; biological processes like bioaccumulation, biosorption have acquired due attention owing to number of advantages and engaged the scientists from all over the world to identify the potent biomass type. The term, bioremediation or biosorption is used to describe the passive non- metabolically mediated process of metal binding to living or dead biomass (Suryan and Ahluwalia,2012).

In recent years, several reports made on the need and use adsorption of Cr(VI) using different biomaterials such as; neem Leave(Pandhram and Nimbalkar,2013), Banana Peel (Kumar and Majumde,2014), Peach Kernel and Nut Shell (Modrogan et al., 2007), Alfa grass (Tazrouti and Amrani,2009) and oil palm shell (Nomanbhay and Palanisamy, 2005). Leaves of different plants are very resourceful natured chemical species attributed to high adsorption capacity, as these contain a variety of organic and inorganic compounds; cellulose, hemi cellulose, pectins and lignin present in the cell wall are the most important sorption sites (Qaiser et al., 2007). Plant leaves have chlorophyll, carotene, anthocyanin and tannin which contribute to metal biosorption. The important feature of these compounds is that they contain phosphate, hydroxyl, carboxylic, carbonyl, sulphate, amino and nitro groups which are important sites for metal sorption (Qaiser et al., 2007; Kumar and Majumde, 2014; Rahimizadeh and Liaghat, 2015). Utilization of raw plant materials is limited, owing to leaching of their organic components like, cellulose lignin into the solution for which chemical modification is required to improve the physical, chemical and biosorption capacity (Mandina et al., 2013).

The Fourier Transform Infrared (FTIR) spectra of the low cost and edible Opuntia Ficus-Indica cactus leave; characterized to contain the above presented significant multifunctional groups (Fox, 2011; Nharingo and Moy, 2015). And, thoroughly; surveyed literatures indicated that OFI as biosorbent, exhibits efficient primary coagulant (Buttice et al., 2010; Pichler et al., 2012; Nharingo and Moy, 2015).

The present study is therefore; aimed at investigating the bioadsorption potential of activated cactus; Opuntia Ficus-Indicus cactus leave powder in removing of Cr(VI) ions from synthetic and Tannery waste water. The study further focused to describe the effect and optimized values of important parameters. Besides; best fitted adsorption isotherm model is evaluated.

1:2 Problem Statement

Chromium (Cr) is toxic metals and causes severe environmental and public health problems when it gets into natural water from a variety of industrial wastes (Attia et al., 2010; Khedr et al., 2014). Cr is considered as one of the 14 most noxious heavy metals (Melaku, 2005). It occurs in different valence states, but Cr (III) and Cr(VI) are the most common forms of chromium in the environment. In comparison to Cr (III), the chromate anions of Cr(VI) are highly soluble and are 100-1000 times more toxic because of carcinogenic and mutagenic properties to micro organism, plants, animals and humans (Dhal et al.,2010; Wanees et al., 2012; Sarker et al., 2013; Desai et al., 2014). Hence, concerns regarding the presence of chromium in the environment focus on the potential adverse public health and environmental effects of Cr (VI) (Wanees et al., 2012).

Chromium predominantly; gain access to water sources through discharges of industrial waste water, than the natural path (Osasona et al., 2013).Tanneries are ranked as the highest chromium pollutants of all other industries (Sarker et al., 2013; Gebregiorgis, 2015).In India, alone about 2000-3000tons of elemental Cr annually escapes into the environment and chromium concentrations from these sources range between 2000 and 5000mg/l in the aqueous effluent, while the recommended permissible discharge limits is 2mg/l into surface water(Abebe,2010; Rameshraja and Suresh,2011; Khedr et al., 2014)**.** More, specifically; Cr(VI) concentration in industrial waste water ranges from 0.5 to 270 mg/l which is much higher when compared to tolerance limit of its discharge into inland water surface,0.1and in potable water and bathing 0.05mg/l (Desai et al., 2014). In Ethiopia, there is growing concern about water pollution due to discharge of tannery effluents without proper treatment (Woldemichael et al., 2011). The country releases about 200-300tons of Cr into the environment annually (Gebregiorgis, 2015). Indeed; more than 80% of industries in Addis Ababa city and its vicinity discharge their effluent into the environment without treatment (Woldemichael et al., 2011). For instances; Tinish Akaki River (TAR), is such a river that is reported to have higher total Cr concentration of 16 mg/l compared with the assumed maximum level in unpolluted natural waters, 0.001-0.01mg/l(Melaku, 2005).

In light of these facts; suitable removal of Cr (VI) metal from industrial waste water is critical (UNIDO, 2000; Wanees et al., 2012).The various physicochemical Cr(VI) removal techniques have disadvantages such as; incomplete metal removal, costly, discouraged for their prerequisite of excessive chemicals and production of sludge and secondary pollution issues(Mandina et al.,2013;Shoaib et al.,2013). Adsorption using commercial activated carbon (CAC) is an effective and frequently used method for the treatment of waste water rich in metals, like Cr. Nevertheless; CAC is cost prohibitive and limited in its use as adsorbent for heavy metals removal from industrial wastewater especially in developing countries (Osasona et al., 2013; Mulani et al., 2013). Hence, development of new alternative of low cost and ecological friendly removal methods is necessitated.

Accordingly; in recent years, removal of heavy metals by biosorption has been an emerging field of research that gained due attention for which, about 70 natural sorbents have been tested (Dhungana and Yadav, 2008/09).Thoroughly; surveyed literatures indicated, the low cost and edible cactus leaves; Opuntia Ficus-Indica (OFI), is efficient primary coagulant (Young, 2006; Iona, 2011; Pichler et al., 2012; Gandhi, 2013).

Therefore; these unique characteristics potential of leaves/pads of OFI could make it an ideal candidate for investigating its enhanced adsorbent capacity in removal of chromium. In this context, the present study aimed to assess the biosorption potential of OFI carbon activated with H_3PO_4 for Cr(VI) from synthetic and tannery wastewater. The study also further attempted to describe the influences and the optimized values of key parameters in the adsorption process and identify best fitted adsorption isotherm model.

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1:3 Objectives of the study

1:3:1 - General Objective

- Is to investigate the biosorption potential of activated Opuntia Ficus-Indicus (OFI) leave powder, as an alternative treatment option of Cr (VI) ions from synthetic aqueous solution and Tannery waste water.

1:3:2- Specific Objectives

- To assess the biosorption potential of activated OFI leaves powder in removing of Cr (VI) ions.
- To optimize the important parameters that affect adsorption process.
- To find out the adsorption model that best fit with experimental data.
- To forward valuable base line information for further studies based on the result findings.

CHAPTER TWO
LITRATURE REVIE

2.1 Chemistry of Chromium

Chromium (Cr) is a metallic element which is listed by the Environmental Protection Agency as one of 129 priority pollutants and is considered one of the 14 most noxious heavy metals. Chromium belongs to the transition group elements from group VIB and can therefore, occur in each of the oxidation states from -2 to +6 which are of unequal stability. Only the 0 (elemental), +2, +3 and +6 states are common. The divalent Cr form is unstable in most compounds as it is easily oxidized to the trivalent form by air or by H^+ (Melaku, 2005).

In natural and waste waters, chromium exists essentially in its trivalent and hexavalent form Cr(VI) may be present in aqueous solution as mono chromate, bichromate or hydrogen chromate, depending on the pH and the chromium concentration in solution (Swathi et al., 2014).

Chromium chemistry is very complicated. It would seem that ozone would oxidize the trivalent chromium to hexavalent chromium. Because of the reaction kinetics, hexavalent chromium does not easily reduce in neutral to basic aqueous solutions (Melaku, 2005).

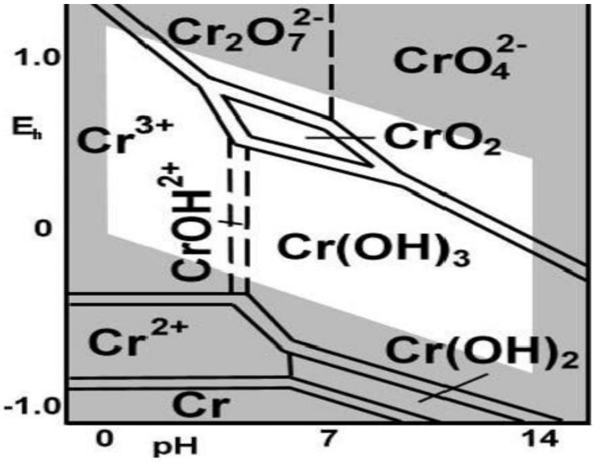

Figure 1: Eh-pH diagram of chromium (Melaku, 2005).

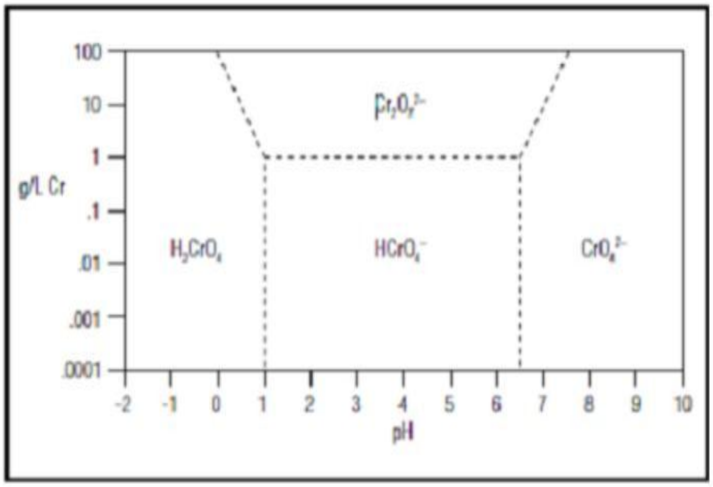

Figure 2: Relative distributions of Cr (VI) species in water as a function of pH and Cr (VI) concentration (Mohan et.al. 2006; Mulani et al., 2013).

2.2 Sources of Chromium Contaminations

The typical concentrations of Cr from natural source in river water is 1µg/L and surface soil and plants 60 µg/g and 0.2µg/g dry weight respectively. The total Cr concentration in unpolluted natural waters is 1-10µg/l In general, all naturally occurring chromium is found in the trivalent state and most surface water contain very low levels of chromium (1 to a few µg/l), except for waste waters coming from industries (Melaku,2005).

The various anthropogenic sources of chromium and its compounds are widely used in electroplating, leather tanning, cement, dyeing, metal processing, wood preservatives, paint and pigments, textile, steel fabrication and canning industries (Nomanbhay and Palanisamy, 2005).The effluent discharge from these sources, in particular; contains moderate to excessive amounts of hexavalent chromium compounds beyond the conventional statutory limit of 0.1mg/L. The leaching of sanitary landfills also leads to substantial amounts of chromium in ground water (Mutongo et al., 2014).

The wastewater of the tanning process is an important source adding Cr pollutant to the environment. Chromium ion concentration in the tanning wastewater varies from 1500−3000 ppm (parts per million); however, high exhaust chrome tanning methods lead to a wastewater containing 500−1000 ppm of chromium (Abebe, 2010).

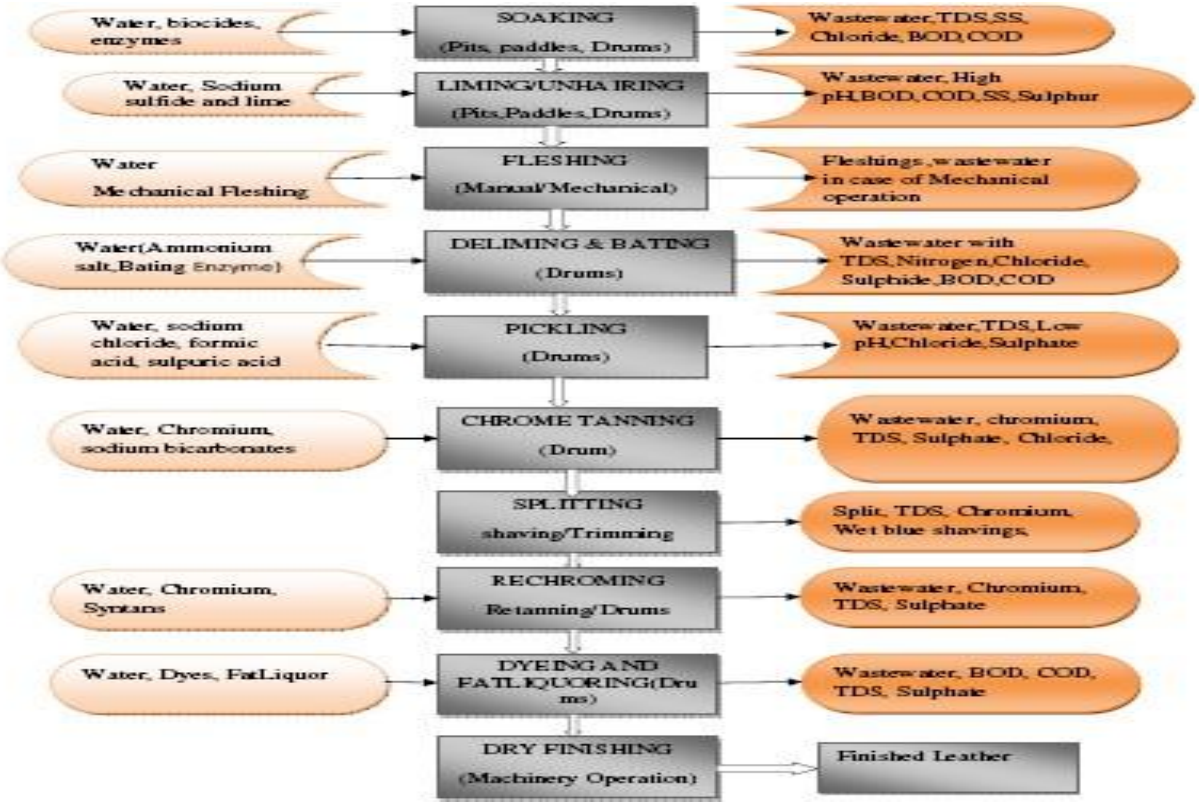

Figure 3: Inputs and outputs of tanning process adopted from (UNIDO, 2011).

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2.3 Chromium Accumulation and Toxicity

Heavy metal contamination of industrial effluents is one of the significant environmental problems due to their toxic nature and accumulation throughout the food chain as non-biodegradable pollutant (Swathi et al., 2014). Unlike organic wastes, heavy metals are non-biodegradable and they can be accumulated in living tissues, causing various diseases and disorders, therefore they must be removed before discharge. Widely used heavy metals such as Chromium (Cr), Cadmium (Cd), Copper (Cu), Mercury (Hg), Nickel (Ni), Lead (Pb) and Zinc (Zn) are recognized to be toxic in nature (Tahiruddin and Ya'akub, 2013).

The hexavalent form of the elemental chromium is considered to be a group “A” human carcinogen adhere to its mutagenic and carcinogenic properties, in that Cr(VI) compounds cause mutations and allied effects such as chromosomal aberrations both in prokaryotic and eukaryotic test systems (WHO, 2004; Ahalya, et al., 2005)).

Chromium (VI) also has higher mobility than chromium (III). Study carried out indicated that accumulation of chromium in four fresh water plant species, clams, crabs, and fishes showed that, all the four fresh water species and animals were found with high concentration of Chromium which is a denotation of its eminent assemblage potentiality (Sarker et al., 2013). Hexachromium moves readily through soils and aquatic environments and is a strong oxidizing agent capable of being absorbed through the skin (Nomanbhay and Palanisamy, 2005).

Therefore; the high risk of chromium (VI) is associated with its high reactivity and its potential carcinogenic properties. Acute exposure to Cr (VI) causes nausea, diarrhea, liver and kidney damage, dermatitis, internal hemorrhage, and respiratory problems. Ingestion may affect kidney and liver functions. Skin contact may result in systemic poisoning damage or even severe burns, and interference with the healing of cuts or scrapes. If not treated promptly, this may lead to ulceration and severe chronic allergic contact dermatitis. Eye exposure may cause permanent damage (Tahiruddin and Ya'akub, 2013; Mandina et al., 2013; Kalandar and Yadav et al., 2014).

2.4 Description of Tannery Production Process and Wastewater Generation

The wastewater from industries varies so greatly in both flow and pollution strength (Ahmed et al., 2012). Tannery effluent is one of the most polluting industrial wastes generating about 75,000 m^3/ day (Kalandar and Yadav, 2014). Nearly 80% of the tanneries in India are engaged in the chrome tanning processes. Most of them discharge untreated wastewater into the environment. In such aqueous waste, Cr(VI) is present as either dichromate ($Cr_2O_7^{2-}$) in acidic environments or as chromate (CrO_4^{2-}) in alkaline environments (Swathi et al., 2014).

From the total chromium used for tanning only 60% to 70% is utilized, while the rest 30 to 40% remains in the spent tanning liquor, which is normally sent to a wastewater treatment plant. But, the discharge limits for trivalent chromium vary broadly ranging from 1 to 5 mg/l in the case of direct discharge into water bodies and 1 to 20 mg/l in the case of discharge into the public sewer system. Therefore, the treatment plant used by the tanning industry needs to treat the influent by 200 fold to send to water bodies, which is not practical in most of the cases (Abebe, 2010).

In Ethiopia, The tanning industries are especially large contributors of chromium pollution. Two types of effluents are discharged during the tanning process: vegetable tanning, which does not contain chromium, and chrome tanning, which contains chromium (Gebregiorgis, 2015). Study reports from Sheba tannery Tigray, Ethiopia indicated that the levels of hexavalent chromium in the downstream river and spring water samples exceed the World Health Organization. The daily basis discharges from this tannery is 120, 0000liters of waste water into the environment (Gebrekidan et al., 2009).

Characteristics of wastewater generated from the tanning process industries are chromium , COD, BOD, sulfate, ammonia, chlorides, sulfates and other mineral salts, which end up as waste water and represent an immense pollution load, causing technical problems, sophisticated technologies and high costs (Sarker et al., 2013).

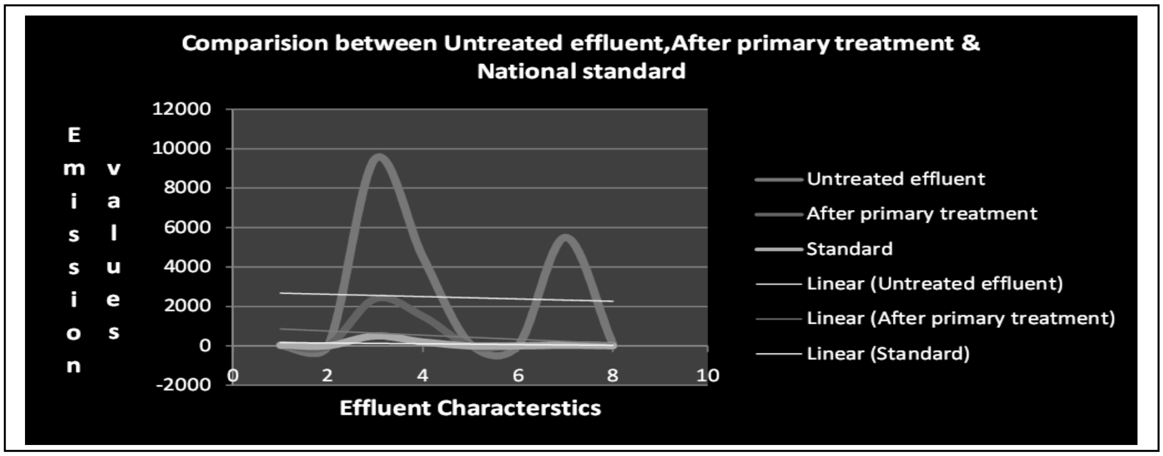


Figure 4: Description of emission values of the different tannery waste water characteristic in Ethiopia, adopted from (Z. Abebe; 2011).

2.5 Chromium from Tannery Effluent

Chromium is one of the most common heavy metals presents in sludge. Chromium and its compounds, widely used in various industrial and chemical processes, generate a large amount of toxic effluents containing hexavalent chromium with concentrations ranging from tens to hundreds of mg/l along with other forms of chromium. The main aqueous species of Cr (VI) in waste waters are CrO_4^{2-} (pH >6.5) and $Cr_2O_7^{2-}$ /$HCrO_4^{-}$ (pH < 6.5) (Dula et al., 2014).

According to the study undertaken in Tinishu Akaki River (TAR), the mean concentrations of Cr, Cu, Pb and Zn exceed the Canadian Council of Ministers of the Environment (CCME) interim fresh water guidelines for the protection of aquatic life by a factor of 56, 1.6, 3 and 2, respectively. These results have showed that the highest concentration of chromium in the TAR water is directly related to the discharge of solid and liquid wastes from the tanneries (Melaku, 2005).

2.6 Chromium Removal Technologies

Chromium concentration in industrial waste water ranges from 0.5 to 270 mg/l. The tolerance limit for chromium for discharge into inland surface waters is 0.1 mg/l and in potable water is 0.05 mg/l. In order to comply with this limit, it is essential that industries treat their effluents to reduce the chromium concentration in water and wastewater to acceptable levels before its transport and cycling into the natural environment (Desai et al., 2014). Appropriate technologies are applied to reduce the level of chromium in final effluents.

In these regards; various methods utilized to remove chromium that includes reduction followed by chemical precipitation, electrochemical precipitation, adsorption, ion exchange, reverse osmosis, solvent extraction, membrane separation and etc (Dhal et al., 2010). However; most of the physicochemical techniques have disadvantages such as incomplete metal removal, high reagent and energy requirements and generation of toxic sludge (Mandina et al., 2013; Khedr et al., 2014). Hexachromium in wastewater exists as oxyanions which does not easily precipitate using the common conventional precipitation techniques. Ion exchange, reverse osmosis and elctrodialysis are efficient for Cr(VI) ions removal but the cost is relatively high. Besides; co-precipitation, membrane techniques and solvent extraction are not effective by the removal of metals at their lower concentrations in aqueous solution (Wanees et al., 2012)

On the other hand; adsorption is by far most versatile and effective method for removing any contaminants like heavy metal (Gandhi et al., 2013; Desai et al., 2014). Adsorption by activated carbon prepared from biosorbent has proved to be an economical and effective alternative to conventional metal removal techniques particularly; in treating low concentrations of wastewater streams (Singh and Singh, 2012; Khedr et al., 2014) .

2.6.1. Chemical Precipitation

Chemical precipitation is the method, in which dissolved and suspended metal ions are transformed to the insoluble solid through a chemical reaction. Usually a precipitating agent accelerates the conversion from metal ions into insoluble solid. The commonly used precipitation agents are lime and magnesia (Mahmood et al., 2008).

The removal of Cr (VI) by chemical reduction from industrial waste water involves a two-step process: reduction of Cr(VI) under acidic conditions (usually pH 2 to 3) and the precipitation of Cr(III) as hydroxyl species. Besides; gaseous sulphur dioxide, sodium sulfite, sodium metabisulphite, ferrous sulphate, barium sulphite are the most commonly used reducing agents. This technique has been proven as an effective and most widely used to remediate heavy metals including chromium from wastewater because it is a simple, inexpensive, convenient, and safe method (Madhavi et al., 2013). .

However; this technique requires large amounts of chemicals, and excessive toxic sludge is produced. Sludge filtration and disposal increase the overall cost of the process. Sometimes metal precipitation is slow and aggregation of metal precipitates take place (Kurniawan et al., 2006).

2.6.2. Reduction

The removal of toxic Hexavalent chromium from aqueous solution by biosorption by different biomass types has been extensively reported. This removal is often associated with the simultaneous reduction of Cr (VI) to Cr (III). The biosorption mechanism is a two-step process: initiation of the uptake at discrete points by chemical bonding, then reduction of the metal ions (Tsezo et al., 2004).

2.6.3. Ion Exchange

Ion exchange is a suitable technique to remove heavy metal from the wastewater and this technique has also been applied as a remediation measure for Cr(VI) (Ranjana et al., 2012).Various ion exchange resins are commercially available which can effectively remove Cr(VI) below the standard limit of Cr(VI) (0.1 mg/l) in wastewater. This process reduces the amount of waste for disposal and the cost of operation is generally lower. However; the limitation of this method is that efficiency dependent on the pH of water (Rengaraj et al., 2003).

2.6.4. Adsorption

Adsorption offers significant advantages like low cost, availability, profitability, ease of operation and efficiency, in comparison with the conventional methods such as; membrane filtration and ion exchange) especially from economical and environmental points of view. The adsorption process is being widely used by various researchers for the removal of heavy metals from waste streams and adsorption using activated carbon as adsorbent has been frequently used (Madhavi et al., 2013).In recent years, the need for safe and economical methods for the elimination of heavy metals from contaminated waters has necessitated research interest towards the production of low cost alternatives to commercially available activated carbon (Khan et al., 2004).

Typical biosorbents can be obtained from various source of non-living biomass like; wool, olive cake, sawdust, pine needles, almond shells, cactus leaves, charcoal used tires, soot, hazelnut shell, coconut shell charcoal; banana peel, seaweed, dead fungal biomass, cyan bacterium, and green alga have been used for the removal of chromium from waste waters. These materials can be used as adsorbents with little processing and available locally in large quantities. The term charcoal generally refers to the carbonaceous residue of wood; cellulose, coconut shells or various industrial wastes left after heating organic matter in the absence of oxygen. This very fine, odorless, tasteless black powder is an adsorbent for many toxic metals, toxins, gases, drugs, fat, and fat-soluble substances without any specific action (Tahiruddin and Ya'akub, 2013).

Adsorption of hexavalent chromium from aqueous medium by rice husk activated carbon prepared by physical method studied with the extent to identify adsorption process as a function of PH, contact time, adsorbent dose, and initial adsorbed concentration. Optimum results obtained to be 150 minutes, 20 mg/l , 2 ,and 5g/l for time contact, initial concentration, PH, and adsorbent dose respectively. And, the adsorption of hexavalent chromium found to be 95.2%, at the optimal condition (Ahmed et al., 2012).

In adsorption, the solute present in dilute concentration in liquid or gas phase is removed by contacting with suitable solid adsorbent so that the transfer of the component first takes place on the surface of solid and then into the pore of the solid. Carbon adsorbent prepared from neem leaves studied at laboratory scale, observed to be very effective for removal of chromium from its aqueous solution. This study describes the various methods of investigation and the detailed experimental procedure to obtain adsorption equilibrium and the effect of various parameters on batch adsorption system. It is revealed that the maximum removal efficiency is observed up to 85% for biosorbent prepared from Neem Leaves (Pandhram and Nimbalkar, 2013).

The adsorption process, carried out through batch method investigated over a range of pH (2-7), agitation time (0-150mins) and adsorbent mass (1.0-3.0g per 50 mL of metal solution). The adsorption isotherms obtained using initial metal concentrations ranging from15 to100mg/L (Osasona et al., 2013).

2.7 Biosorption and its Mechanisms

2.7.1 Biosorption

The ability of biological materials to adsorb heavy metals found in waste water through non-metabolic mediated physicochemical pathways is termed biosorption. Simply it can be referred as the concentration or binding of heavy metals from wastewater stream by either dead, inactive or plant based biomass (Sulaiman, 2015).A number of non-living biomass sources of biosorbents for the adsorption of Cr(VI) such as; forestry waste, fruit peelings and leaves, fungi, dead bacterial, and diatom biomass has been reported in the literature (Mutongo et al.,2014).

Biosorption is relatively new technology and a new alternative to other methods of heavy metal ions removal from wastewater especially industrial wastewater, due to their numerous disadvantages like high cost, partial metal removal and generation of sludge. Thus, unlike to those prevalent/conventional treatment methods, the significant advantage of biosorption are low cost, high efficiency, no additional requirement of nutrient, ability to regenerate Biosorbents, minimization of chemical and biological sludge and possibility of metal recovery (Alluri et al.,2007; Rahimizadeh and Liaghat,2015).Moreover; biosorption is a good applicant for the removal of toxic metals even from large volume and lower concentration of aqueous solutions (Sulaiman,2015).

It is has been further reported that, apart the upper mentioned various advantages of biosorption over the conventional once, the biosorption by nonliving biomass as metal binding compounds has also gained popularity over the use of live biomass. This is mainly because living cells are subject to toxic effects of heavy metals, resulting in cell death. Living cells also require the addition of nutrients and hence increase the BOD and COD in the effluent. Dead cells on the other hand require little care and maintenance, are cheaper, and can be easily regenerated and reused. Metal recovery is also not possible with the use of biosorbent made from nonliving biomass (Mutongo et al., 2014).

2.7.2 Biosorption Mechanism

The understanding of biosorption mechanism is necessary to enable the technology to be developed (Tsezo et al.,2004). Biosorption process involves two phases: a solid phase (Biosorbent) and a liquid phase (Solvent, usually water) which actually contain dissolved species to be sorbed /solute (Alluri et al., 2007). The Key factors that controls and characterizes these mechanism are: type of biological ligand available for metal sequestering, status of the biomass, i.e. living /non-living, chemical, stereo chemical and coordination characteristics of the targeted metals and metal species and the characteristics of the metal solution such as pH and the presence of competing co-ions (Tsezo et al., 2004).

For adsorption to occur there must be forces that attract the sorbate to the solid surface in a solution. This mechanism or forces which attract the absorbate to the solution of the solid interface can either be physical or chemical. We can also say it is by donor-acceptor complexion mechanism where atoms of the surface functional group donate electrons to the absorbate molecules. The position of these functional groups determines the type of absorbate/adsorbent bond and therefore, decides whether the process is chemical or physical (Young, 2006; Rahimizadeh and Liaghat, 2015).

Physical adsorption (physiosorption) is a reversible method in which there is the attraction of molecules by mechanical forces when the molecules come in contact with the adsorbent The reversible process depends basically on the force of attraction between the sorbate and adsorbent. This type of adsorption is multilayer which means that each molecule layer forms on the top of previous with the number layers being proportional to the contaminate concentration (Rahimizadeh and Liaghat, 2015).

In comparison to physical adsorption, chemical adsorption is an irreversible process which is caused as a result of the reaction taking place between molecules of the adsorbed substance and the sorbate. It involves the formation of covalent or ionic bonds, consumes high energy and it can occur over wide range of temperature. “Due to its irreversibility, monolayer is expected to form chemisorptions while multilayer is encountered in physiosorption” (Sulaiman, 2015).

There are a various ways for a metal to be uptake by the complex structure of adsorbent which signify, that the mechanism of biosorption follows a complex process. Biosorption mechanism thus, can further be perceived by dividing into two subdivisions on the basis of dependence of cells’ metabolism, namely; metabolism dependent and non-metabolism dependant, while classified also into extracellular accumulation /precipitation, cell surface sorption/precipitation and intracellular accumulation adhere to the location of sorbent species (Alluri et al., 2007;Rahimizadeh and Liaghat,2015). These classifications are well summarized, in Fig.4.

In the physiochemical interaction between the heavy metal and the functional group of cell surface, there is a cell surface sorption based on physical adsorption, ion exchange and complexation, which is independent to the metabolism. Non-metabolism dependant biosorption is relatively quick and can be reversible (Rahimizadeh and Liaghat, 2015).

Biosorption of metals involves several mechanisms that differ qualitatively and quantitatively, according to the species used, the origin of the biomass, and its processing procedure. There are several chemical groups in biomass that can attract and sequester the metals: acetamido, amino, amido, sulfhydryl, sulfate, and carboxyl. (Raize et al., 2004; Rahimizadeh and Liaghat,2015). The binding characteristics of metallic cations during bio sorption can partially be explained by Pearson's concept of Hard and Soft Acid and Base theory (HSAB) (Tsezo et al., 2004).

The binding of metal ions to biopolymers, in general is likely to be via two major mechanisms, the first of these being simple ion-exchange and the second through the formation of complexes (co-ordination compounds) which may be chelates. Because of the complexity of most biopolymers, it is very likely that more than one processes of binding take place in a system at the same time (Tsezo et al., 2004).

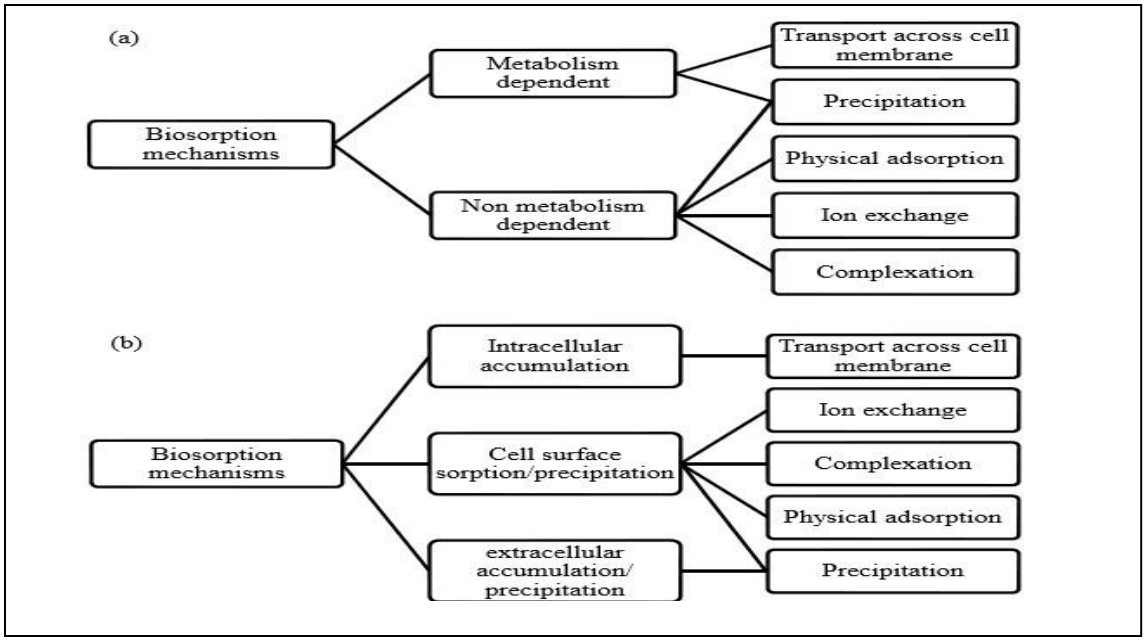


Figure 5: Showing biosorption mechanisms: a) classified according to the dependence on the cell's metabolism, b) classified according to the metal where removed the solution (Adapted from Rahimizadeh and Liaghat, 2015).

2.8 Driving force in Biosorption

The phenomena of heavy metals sorption takes place as a result of either solvent motivated force, which is related to the surface tension, or through sorbent motivated force that combines chemical, electrostatic and physical interactions between metals and sorbing surface (Volesky, 2003).

Generally, the biosorption is driven by a combination of both forces. There are four steps which occur in the process of metals biosorption by a porous bio sorbent.

Step 1- the metals is transported from the stock solution to the boundary film surrounding the bio sorbent.
Step 2- the metals is transported from the boundary film to surface of the biosorbent, through external diffusion.
Step 3- the metals are transported from the surface to the intra-particle active sites, through internal diffusion.
Step 4- finally in the fourth step uptake of metals at the active sites of the Biosorbent occurred, through various mechanisms including, physical sorption, and ion exchange chemical reaction. These steps are highlighted in figure 5.

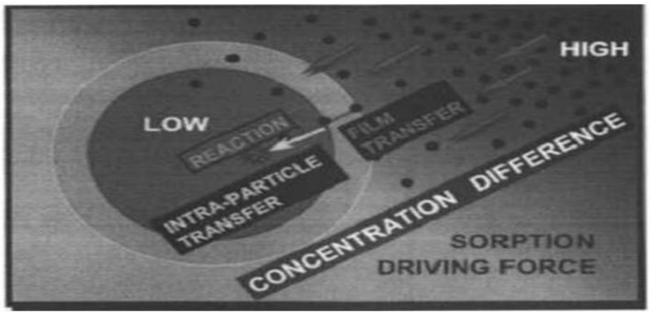


Figure 6: Driving Force for Biosorption (adopted (Volesky, 2003).

2.9 Adsorption Equilibrium

Analysis of the isotherm data is important in order to develop an equation that accurately, represents the results of batch experiment. Adsorption isotherms are describing the equilibrium relationships between the adsorbent and adsorb at combination. Several models have been used in the literature to describe the experimental data of adsorption isotherms. The Langmuir and Freundlich isotherm models are the most frequently employed models. These models help in calculating the adsorption capacity of materials (Dula et al., 2014).

The equilibrium biosorption processes usually described by fitting the experimental data with Isotherm models. The two well known equilibrium adsorption isotherms are Langmuir (Langmuir,1996) and the Freundlich (Freundlich,1906) adsorption isotherm models which commonly used as a single component adsorption (Rahimizadeh and Liaghat, 2015). In the present work these models were evaluated.

2.9.1 Adsorption isotherm models - Langmuir and Freundlich

$$q = qmax * b * Ce/1 + bCe$$

Where q is milligrams of metal accumulated per gram of the biosorbent material; Ceq is the metal residual concentration in solution; q_{max} is the maximum specific uptake corresponding to the site saturation and b is the ratio of adsorption and desorption rates.

The Langmuir isotherm is based on the assumptions that metal ions are chemically adsorbed at a fixed number of well-defined sites; each site can hold only one ion; all sites are energetically equivalent and; there is no interaction between the ions (Langmuir, 1918). The linearized Langmuir isotherm allows the calculation of adsorption capacities and the Langmuir constants and is equated by the following equation (Ahayla et al., 2005; Khedr et al., 2014).The linear form of Langmuir formula is defined as, follows:

$$Ce/qe = 1/(qmax * b) + Ce/qmax$$

Where, qe (mg/g) is the equilibrium concentration of hexavalent chromium in the adsorbed phase and C (mg/L) is the equilibrium concentration in the liquid phase. Langmuir constants, which are related to the adsorption capacity (q_{max}) and energy of adsorption (b), can be calculated from the slope of the linear plot of Ce /qe versus Ce; a straight line with slope $1/q_{max}$ and intercept of $1/q_{max} *b$ is obtained. The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless factor, RL which is given as;

$$RL = \frac{1}{(1 + bC_o)}$$

Where b is the Langmuir constant and Co is the initial concentration of Cr (VI). The RL value indicates the shape of isotherm as given (Dula et al., 2014).

Table -1: Showing RL values based on isotherm.

R Value	Type of Isotherm
RL > 1	Unfavorable
RL = 1	Linear
0 < RL < 1	Favorable
RL = 0	Irreversible

Freundlich Adsorption Isotherm is based on the assumption that the adsorbent heterogeneous surface composed of different classes of sites with adsorption on each sites following; the Langmuir Isotherm (Pandhram and Nimbalkar, 2013).

The Freundlich adsorption isotherm models will be use. The Freundlich isotherm (Freundlich, 1906) is expressed as:

$$N_e = K_f C_e^{1/n}$$

Where; N_e = x/m (amount of metal ions per unit mass of adsorbent) when the equilibrium concentration is C_e. To simplify the equation, it is linearized thus,

$$\log N_e = \log K_e + 1/n \log C_e$$

The Freundlich Isotherm Coefficients will be determined by plotting Log Ne against Log Ce. The Freundlich equation is an empirical equation based on adsorption on a heterogeneous surface. The constants indicate the adsorption capacity and the adsorption intensity (Olayinka et al., 2009).

Table -2: Best fit parameters for Langmuir and Freundlich isotherm models

Parameters	pH			
	3	4	5	6
Langmuir				
q_{max}(m.mol/g)	0.13	0.222	0.255	0.309
K_d(m.mol/l)	0.645	0.07	0.002	0.002
R^2	0.999	0.998	0.972	0.99
Freundlich				
K_f ([m.mol/g][l/m.mol])1/n)	0.08	0.22	0.287	0.344
n(-)	1.704	3.551	7.174	7.544
R^2	0.993	0.94	0.924	0.922

(Adapted from, (Chu et.al, 2002)).

2.10 Factors Affecting Adsorption Capacity of Biosorbent

2.10.1. Initial Adsorbate Concentration

The effect of initial metal concentration Cr (VI) on ATBP investigated at different chromium concentrated solutions showed that maximum removal takes place at lower ion concentration at optimum pH and adsorbent dose. Increasing Cr(VI) concentration decreased the percent removal at optimum pH 2.0.The increase in initial concentration of chromium results in the increased uptake capacity and decreased percent removal since at high initial concentrations, number of moles of chromium available to surface area is high (Kumar and Majumder, 2014).

2.10.2 Biosorbent Concentration

Biosorbent concentration is one of the factors affecting the sorption process. The biosorption efficiency found to increase when the biosorbent concentration is increased. The study revealed that the effect of the amount of adsorbent on the rate of uptake of Cr(VI) ions increases with an increase in the amount of adsorbent dose. The amount of adsorbent dose varies from 2gm/100ml to 10gm/100ml. The result obtained for neem leaves, the removal efficiency is maximum at dose of 8gm/100ml which is up to 85 %.(Pandhram and Nimbalkar, 2013).

2.10.3 PH

One of the most important parameter that affects biosorption process is pH. "At low pH, concentration of protons is high and the ion exchange sites become solidly protonated". Solution chemistry of the metals, metallic ions competition and functional groups activity are all influenced by pH (Sulaiman, 2015). Studies have shown that the pH solution has an important effect on the biosorption of metal and Adsorption of anionic species favored at pH lower than and vice versa for cationic species (Nomanbhay and Palanisamy, 2005).

The adsorption capacity of Cr (VI) from aqueous solution onto ATBP is strongly affected by the pH. Adsorption experiments were carried out over the pH range of 1–6; while other parameters were keep constant. The experimental results show that the adsorption was favorable at acidic condition, which is maintained by 0.1 N HCl and 0.1 N NaOH. Maximum Cr (VI) uptake was observed at pH 2 (Kumar and Majumder, 2014).

2.10.4 Contact time

Biosorption increases with increase of contact time from 0-120 minutes (Sulaiman, 2015)**.**The effect of contact time on heavy metal removal can be determined by phasing different time periods. The study conducted using cactus powder for removal of Pb and Cd has indicated that adsorption rate initially increased from 20% to 58 % for Pb ion, and 17% to 43% for Cd ion when the contact time increased from 30-120 min. After 120min, there is no significant change in heavy metal removal of both Pb and Cd ion. This is because, as the contact time increased there is formation of stable complexes between the Cd and Pb metal ions with the active site of the cactus powder. Hence, the heavy metal removal capability of cactus powder increased with the contact time (Derbe, 2015).

2.10.5 Temperature

Temperatures have a substantial influence on biosorption. Temperature influence has more effect in a situation where by metal uptake increases within a temperature range of about 20-30^{o}C, but decreases with an increase of temperature above a critical value. An increase of temperature might increase the metal ions kinetic energy which makes it easier for the metal ions to be attached to the Biosorbent surface. Different research have shown that the binding of metal ions to the surface of the Biosorbent at a low temperature is more rapidly, easily and reversible because of low requirement of energy (Sulaiman, 2015).

On the basis of the research study, the percentage removal of Pb by cactus powder has decreased from 65.05% to 29% as the temperature increased from 25^{o}C to 150 ^{o}C. In similar condition, the percentage removal of Cd by cactus powder also decreased from 43% to 31% as the temperature increased from 25 ^{0}C to150^{o}C. This decrement in percentage removal of both Pb and Cd ions with increase temperature is due to the weak binding interaction between the active site of cactus powder and (Pb, Cd) ions which support physicosorption process (Derbe, 2015).

2.10.6 Shaking Speed

Research conducted has shown an increase 30-40% in adsorption of Cr(VI) by Bengal gram husk while, agitating the samples for a duration of 120 rpm of biosorption. This is because agitation facilitates proper contact between the metal ions in solution and the biomass binding sites and there by promotes effective transfer of sorbet ions to the sorbent sites.

At 60 and 180 rpm, the adsorption rates monitored have found to be slightly lower than that at 120 rpm. These results indicate that the contact between solid and liquid is more effective at moderate agitation 120 rpm.

Maximum of 97.77 % Cr(VI) removal by activated carbon prepared from coconut shell has achieved at 200 rpm. The effect of chromium adsorption on low and high agitation speed has observed in an increase of adsorption from 66.66 % to 97.77 %, when increasing the agitation speed from 90 to 200 rpm. Due to agitation, proper contact has developed between metal ion in solution and the binding sites, promoting effective transfer of sorbate ions onto the adsorbent sites (Ahayla et al., 2005).

2.11 Preparation of Activated Carbon

Activated carbon is a crude form of graphite with a random or amorphous structure, which is highly porous, exhibiting a broad range of pore sizes, from visible cracks, crevices and slits of molecular dimensions. Active carbons have been prepared from coconut shells, wood char, lignin, petroleum coke, bone char, peat, sawdust, carbon black, rice hulls, sugar, peach pits, fish, fertilizer waste, waste rubber tire, etc. Activated carbons adsorptive properties are due to such factors as surface area, a micro-porous structure, and a high degree of surface reactivity (Rahimizadeh and Liaghat, 2015).

The starting material and the activation method used for activated carbon production determine surface functional groups. The carbon surface chemistry depends upon the activation conditions and temperatures employed. Activation also refines the pore structure. Mesopores, micropores and ultra micropores are formed yielding large surface areas up to $2000 m^2/g$ (Radovic et al., 2000).

2.11.1 Activation

During the activation process, the spaces between the elementary crystallites are cleared by removal of less organized loosely bound carbonaceous material. The resulting channels through the graphitic regions, the spaces between the elementary crystallites, together with fissures within and parallel to the graphite planes constitute the porous structure, with a large internal surface area. There are two types of activation; thermal /physical or chemical activation which impart a porous structure within a starting material of relatively low surface area (Mohan et al., 2006).

2.11.2 Physical Activation

Physical activation is a process in which the precursor is developed into activated carbons using gases. The precursor is usually subjected to carbonization followed by activation or using either. Carbonization is the first stage where the precursor is pyrolyzed in the temperature Range 600–900◦C, in an inert atmosphere (nitrogen, argon) resulting in the formation of char, which is normally non-porous. The activation is the process in which the material is exposed to oxidizing atmospheres (carbon dioxide, oxygen, or steam) usually in the temperature range 600–1200◦C, which results in the removal of the more disorganized carbon and the formation of a well-developed porous structure, leading to high surface area(Gupta et al.,2009).

2.11.3 Chemical Activation

This is the other method used for the preparation of activated carbons and involves impregnation with chemicals such as; H_3PO_4, KOH or NaOH, $ZnCl_2$ followed by heating under a gas usually (nitrogen) flow in the temperature range 450 to 900◦C. It is believed that carbonization and activation steps proceed simultaneously in chemical activation. Generally, chemical activation is preferred over physical activation owing to the lower temperature and shorter time needed for activating the material (Rodenas et al., 2007).

The basic differences between physical and chemical activation is the number of stages required for activation and the activation temperature. Chemical activation occurs in one step while physical activation employs two steps, carbonization and activation. Physical activation temperatures (800–1000^o C) are higher than those of chemical activation (200–800^{o}C).The product formed by either of the methods is known as activated carbon and generally has a very porous structure with a large surface area ranging from 500 to 2000 m^2/g (Mohan,2006).

2.12 Cactus Opuntia Ficus-Indicus

2.12.1 Cactus

Cactus is a xerophytic plant: survives in hot and dry environments by promoting efficient water use. The plant probably originated in Central Mexico (FAO, 2013). Opuntia Ficus Indicus (L.) Mill. commonly called prickly pear or nopal cactus belongs to the dicotyledonous angiosperm Cactaceae family, a family that includes about 1500 species of cactus (El-Mostafa et al., 2014).

The Opuntia species is known by different names in the various countries. It is called Nopal (Mexico), Beles (Eritrea and Ethiopia) and as prickly pear (Australia, South Africa and the United States). Prickly pear is slowly evolving into the name cactus pear, to reduce the negative connotation of the word ‘prickly’ (meaning ‘with spines’). OFI is the most widely cultivated species throughout the world, used as food source for both human and animals.

In Mexico, the tender stems (nopalitos) of Opuntia Ficus-Indica /OFI are mainly eaten as a vegetable. It is also used for livestock forage in Brazil, Chile, Mexico and elsewhere. In Ethiopia, It is considered ‘Bridge of life’ because the stems and fruit store large quantities of water and provide both feed for cattle in times of drought and food for livestock (FAO,2013)..

The OFI is a succulent plant which grows up to 3-5 meters, many times in a dense and tangled structure. It is recognized by its green thick long pads that look like sports rackets. They grow one linked to the next and can be considered as both leaves and stalks. The plant surface is covered by spines which help to conduct water, reduce water loss, and protect the succulent tissue from herbivores and other predators (Kebede, 2013).

Scientifically, the stems are known as cladodes and commonly referred to as ‘fleshy leaves’. The stems have the capacity to store considerable amounts of water, because they possess abundant parenchyma. This is a whitish tissue in which water is stored, enabling the plants to survive long periods of drought. And, most importantly, hydrocolloid present in the tissue, has high water binding capacity known as mucilage whereas, bright green tissue in the outer layer of the pad is composed of chlorenchyma (Iona, 2011; FAO, 2013).

The fruits and cladodes are widely used for food, but the flowers are considered as a vegetable and can be eaten as such. Cladodes are an important source of fiber, calcium and mucilage. Cladodes, when they are tender stems (10-15cm), they can be used as a vegetable (nopalitos) and, partially lignified at 2-3 years, they can be used for the production of flours and other products. When completely lignified they can be burned as fuel (FAO, 2013).

The fruit of OFI is sweet, juicy, yellow, orange, red or purple, full of pulp and with skin of variable thickness. The fresh fruit is normally eaten with its seeds. The flowers normally develop on the upper edge of the leaves, have variable color and includes; red, yellow and white. In most parts of the world the plants flower once a year (El-Mostafa et al., 2014).

Figure 7: Photograph /Pictographic view of Opuntia -Ficus-indica cactus.

2.12.2 Geographical Distribution

Opuntia ficus indica is a tropical and subtropical plant. It can grow in arid and semi-arid climates with a geographical distribution encompassing: Argentina, Greece, Turkey, Bolivia, Brazil, Eritrea, Ethiopia, Israel, Italy, Mexico, Morocco Peru, South Africa, Spain, Tunisia and the United States (Kebede, 2013; El-Mostafa et al., 2014).

2.12.3 Cactus Distribution in Ethiopia

Cactus introduced to Northern Ethiopia by missionaries in the mid-19th century. Since, then cactus has become one of the most common plants in Northern Ethiopia particularly in Tigray Region and its fruits are immensely popular. Even though there are little efforts made so far to estimate the distribution of cactus in Ethiopia, the plant is available in the Eastern part of the country stretching from North east to South east with some in the highlands of Showa. Cactus pear is well known in Ethiopia, where a total of around 355, 000 hectares of grow, including a cultivated area of 30, 000 hectares (Kebede, 2013; FAO, 2013).

2.12.4 Common Uses of Cactus

2.12.4.1 Nutritional Use

Cactus fruit contains substantial amounts of ascorbic acid, vitamin E, carotenoids, fibers, amino acids and antioxidant compounds. Several reports have documented the abundance of vitamins and minerals in cactus. In this respect, the fruit of Opuntia ficus indica is a valuable source of nutrients. Opuntia ficus indica flowers contains different flavonoids notably kaempferol and quercetin. Cactus peel and seeds can be used to prepare cactus oil, peel lipids being enriched in essential fatty acids and liposoluble antioxidants. The cactus cladodes contain vitamins, antioxidants and various flavonoids, particularly quercetin 3-methyl ether, a highly efficient radical scavenger (Young, 2006; El-Mostafa et al., 2014).

2.12.4.2 Medical Use

In traditional medicine, Opuntia ficus indica has been used for the treatment of burns, wounds, and edema. Meanwhile, these benefits have progressively received a scientific basis to treat different diseases. Therapeutic potential has been suggested for metabolic syndrome (including diabetes type-2 and obesity), non-alcoholic fatty liver disease (NAFLD), rheumatism, cancers, and virological and bacterial infections. Interestingly, cactus preparations might exert preventive and therapeutic effects against alcoholism and alcohol addiction (El-Mostafa et al., 2014).

Cladodes of Opuntia ficus-indica extracts may lower cholesterol level and convey antiulcer and anti-inflammatory mechanisms, and the water extract remarkably improves wound healing (FAO, 2013).

2.12.4.3 Other Uses

- **Ecological Preservation and Environmental use:** Cactus has the potential of not only decreasing the carbon dioxide (CO_2) levels in the atmosphere through the gas exchange pattern, but also assists in the control of soil erosion by providing cover and controlling of wind and enhancing afforestation. The cultivation of cactus helps in maintaining soil fertility through their geo-biogene and microelement cycling activities (Isaac, 2016).

- **Detergent use:** Nopalitos" or young pads juice uses as shampoo (FAO, 2013**).**

- **Food Preservative use**: the mucilage from prickly pear cactus act as preservative in extending the shelf life of strawberries (Isaac, 2016).

- **Sediment and Bacterial Removal Potential in Water Treatment:** OFI mucilage extract has increased particulate settling rates by 330% compared with aluminum sulfate, at dosage concentrations of 3 mg/L(Pichler et al.,2012). OFI mucilage concentrations lower than 5 ppm, for high bacteria concentration tests (>108 cells/ml) has reported to have a remarkable removal rates between 97-98% (Buttice et al, 2010).

2.12.5 Chemical Compositions

Cactus Opuntia ficus-indica formed of complex carbohydrates that have the ability to store and retain water, allowing these plants to survive in extremely arid environments (Buttice et al., 2013). Carbohydrates varied from 42.94 to 60.77%. Carbohydrates found to increase with age of prickly pears indicating that they are the main component of the plant. Research studies on OFI cladodes and mucilage chemical composition has shown the existences of carbohydrates; arabinose, D-galactose, L-rhamnose, D-xylose and galacturonic acid (Nharingo and Moy, 2015). Fgure:7 and 8, well describes the complex carbohydrate formation of OFI.

Nopal mucilage is a neutral mixture of approximately, 55 high-molecular weight sugar residues composed basically of arabinose (67.3%), galactose (6.3%), rhamnose (5.4%) and xylose (20.4%) (Pichler et al.,2012). It contains several ionic species (Iona, 2011). Phosphorus, 0.1-0.5%, potassium (3.02%) and calcium 0.18-0.66% in dry matter are among the major constitutes of Opuntia species (Isaac, 2016).

In addition of the carbohydrates, OFI materials have ash varied from 17.65% to 24.30%, fat (1.42%-2.38%), fibre (11-22.33%), protein (5.85-8.99%). The surface functional groups of above mentioned compounds /carbohydrate and non-carbohydrate contribute to the pollutant adsorption ability evident in OFI (Nharingo and Moy, 2015).

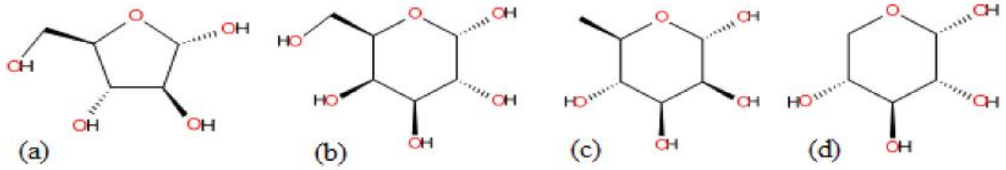


Figure 8: The Sugars present in OFI mucilage (Adapted from Iona, (2011).

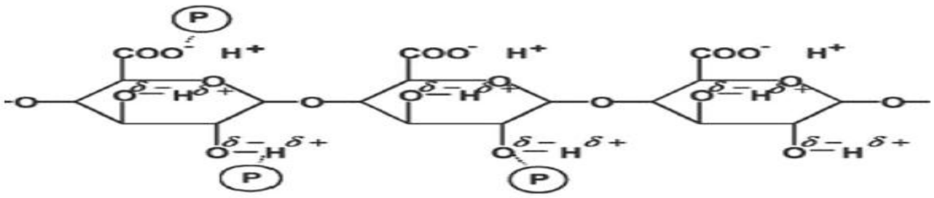


Figure 9: Adsorption bridging mechanism involving, polygalacturonic acid; where P is a cationic or anionic pollutants (Nharingo and Moy, 2015).

2.12.6 Cactus as a Suitable Natural Biosorbent

Opuntia species and cactus latiferi mucilage have used by Chilean and Venezuelan indigenous peoples for centuries for removal of pathogens and turbidity of surface water. The use of green chemistry shows, Opuntia ficus Indica cladode powder and mucilage is a resource for achieving clean water, as the use of natural eco-friendly agents in the treatment of drinking water (Pichler et al., 2012; Buttice et al, 2013; Nharingo and Moy, 2015).

This is rapidly gaining interest due to OFI inherently renewable character and low toxicity. In recent development, Opuntia ficus-indica has received much research attention for wastewater decontamination through adsorption processes (Nharingo and Moy, 2015).The mucilage is extracted from the pads of the cactus. Cactus mucilage is a thick, gummy substance swells but does not dissolve in water. Natural gums have unique surface activity characteristics which make them ideal candidates for enhancing dispersion properties, creating emulsifications and for reducing the surface tension of high polarity liquids (Pichler et al., 2012).

Cactus Opuntia ficus-indica cladodes can be prepared either being fresh or as dry powdered material have been used for the treatment of wastewaters through biosorption processes (Nharingo and Moy,2015).The presence of complex carbohydrates, proteins, crude oil/fats and fibers in OFI cladodes and their mucilage make the plant a good candidate in surface chemistry where the functional groups on these materials provide surface active groups and complex molecules that partake in sorption processes in wastewater treatment. It also contains several ionic species. In fact, its composition gives the OFI the capacity to interact with metals, cations and biological substances (Pichler et al., 2012).

The existence of alkali and alkali earth metal ions in the cladodes promote the ion-exchange mechanism between the bulk wastewater and the adsorbent. The FTIR confirmed that complex materials of OFI surfaces to be multifunctional comprising of phosphates, phenolic, hydroxyl, carboxylates, carbonyl, amides, amines and alkyl groups which among others at varied absorption wave numbers, give rise to efficient biosorption of heavy metals from wastewaters.

The open literature revealed that OFI based Biosorbents has found to offer ideal surfaces that promote efficient adsorption of various pollutants from wastewaters..The exploitation of this cheap, abundant, renewable, simple and nontoxic natural resource must be encouraged to develop clean point-of-use water in developing countries (Nharingo and Moy, 2015).

Table -3: Comparisons of adsorbents for Cr(VI) ion removal.

S.No	**Adsorbent**	**Heavy metal removal efficiency in % [Cr(VI)]**
1	Rice husk carbon	> 99
2	Rice husk (water and HCl	79
3	Phosphate-treated rice husk	_
4	Dyestuff-treated rice hulls	39.7
5	Dyestuff-treated rice	39.1
6	Tartaric acid modified rice	_
7	Rice hull biomass	98.93
8	Rice husk carbon	_

9	Raw rice husk	66
10	Cactus leaves	90-100

Adopted **:[**(Khan et al., 2004; Suryan and Ahluwalia, 2012)]

CHAPTER THREE
METHODOLOGY

3.1 Study Design and Period

Batch experimental study was performed to investigate the biosorption potential of activated carbon powder prepared from Opuntia Ficus-Indicus pad in removing of Cr (VI) ions from synthetic waste water and tannery waste water under variable working parameters. The study was conducted in Addis Ababa University; Chemistry Science Laboratory; Food Science and Leather Industry Development Institute /LIDI-Research Development Laboratory Centers from January to December, 2018.

3.2 Study Variables

3.2.1. Dependent Variables

☐ Cr (VI) Biosorption efficiency

3.2.2. Independent Variables

☐ Biosorbent dose
☐ Initial Cr (VI) concentration
☐ Contact time
☐ Stirring speed
☐ PH
☐ Temperature

3.3 Data Quality Control

All batch experiment were performed by analytical reagent grades chemicals of checked shelf life, high purity water were used for preparing any solution and experimental blanks were run in parallel for testing each study parameter. The test experiments carried out in replicates and results average was reported. Operating errors of the instruments were avoided by managing the calibration of equipments regularly.

Utmost care and due attention was taken to bring about accurate preparation, preservation and analyzing of all the samples. Besides; Deionized water was also used for rinsing of the glassware, sample bottles and syringes; following pre- soaking in 2N HNO_3 solution for 1hr which all were then, dried up in an oven. Besides; sterilized rubber gloves were used to avoid contact of waste water to skin.

3.4 Experimental Set Up

Opuntia Ficus-Indica cactus pad collected from bank Bishoftu Lake situated in Bishoftu town was processed in activation unit. And the activated carbon was mixed with Cr (VI) ion in biosorption unit, after which the filtrate containing Cr (VI) ions was measured in UV-Vis spectrophotometer and respective readings were taken at a wave length of 540 nm.

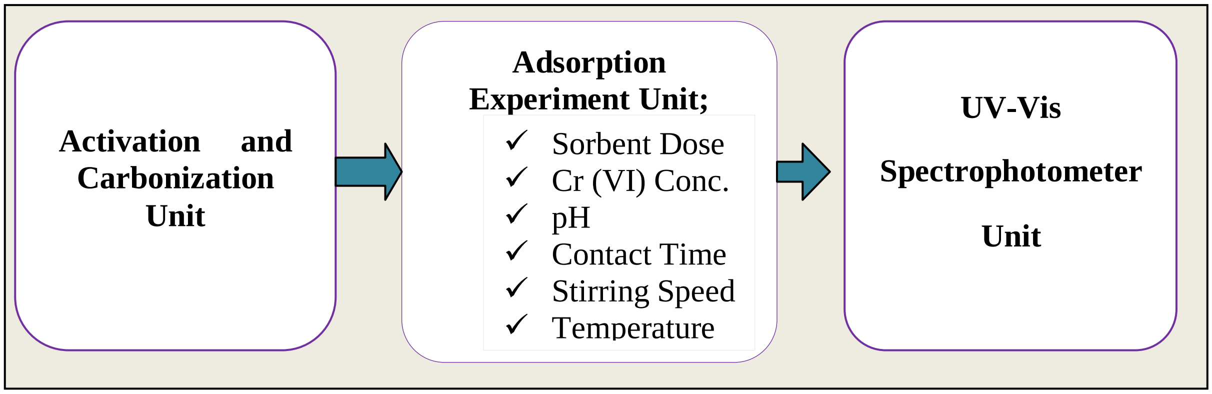


Figure 10: Experimental setup of the study.

3.5 Preparation of Biosorbent

3.5.1 Collection and Drying

Young fresh healthy pads of *O. Ficus-Indicus /OFI* were collected from the banks of Bishoftu Lake situated in Bishoftu town. The spines of pad was removed and washed with a tap water to remove the leachable impurities. The pad was cut into strips of 1 cm width/ dissections, then the tip egged and their thick epidermis were peeled off and chopped to be sundried easily for two weeks after which, it was dried at 105^{0}c in electric oven for 24hrs, to get rid of moisture and other volatile impurities.

3.5.2. Impregnation

The dried OFI was impregnated by mixing thoroughly with 45 %(w/w) H3PO4 in ratio of 2:1 to OFI and left soaked overnight. Activating agent, H_3PO_4 was selected since it was used widely in the preparation of activated carbons and offers some advantages such as non polluting character and ease of elimination by extraction with water and yields higher surface area than ZnCl2. Medium impregnation ratio was selected due to the fact that higher impregnation ratio leads to excessive reaction between H_3PO_4 and carbon which may hinder the pore formation.

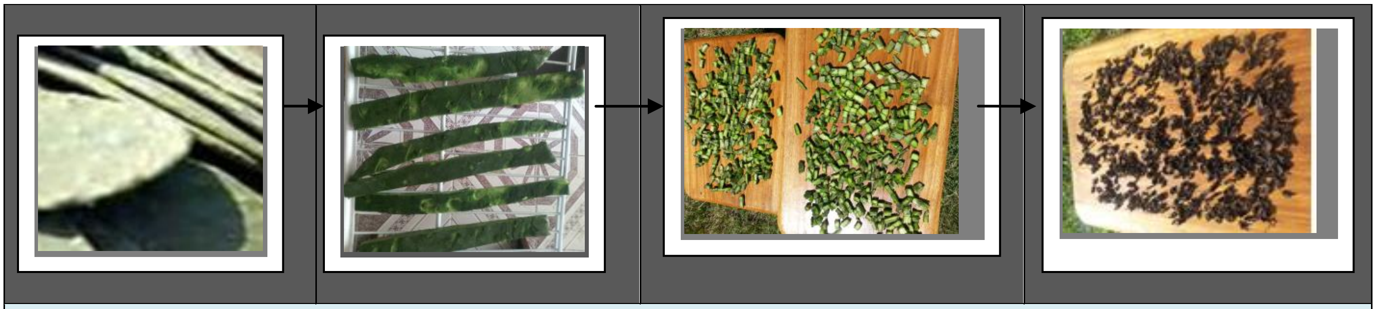
3.5.3. Carbonization

The impregnated OFI was then carbonized by heating for 60 minutes at 450^{0}c in adjustable electrical furnace. The carbonized product was then; cooled at room temperature in a desiccator and sealed by aluminum foil to prevent formation of tar arrived due to contact with atmospheric oxygen. The above temperature and contact time were selected because samples, carbonized at

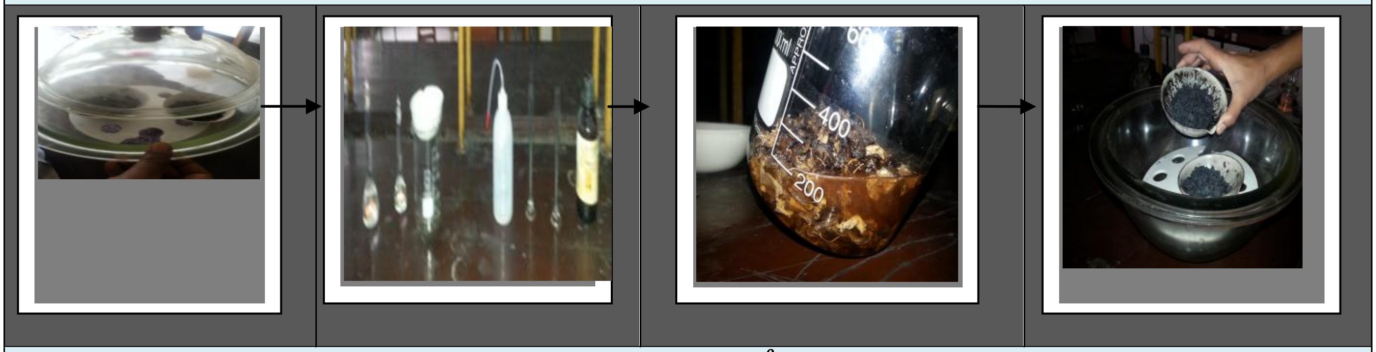
450°c for 1 hr showed better structured pores on the surface morphology of the sample than samples carbonized at 500°c for 1 hr which resulted knocking and breaking of the porous formation due to excessive heat. The carbon then was grinded and sieved to pass through in stainless steel of mesh size 0.425mm. Mesh size was selected in such a way to obtain quite fine and uniform carbon powder.

4.5.4. Drying

Removal of the activator, phosphoric acid from the carbonization products was performed through washing by distilled water, then after the powder was dried at 110^0C for 24hrs. Finally, the activated cactus powder was kept in tightly closed plastic bottles and was labeled to be ready for the subsequent use of FTIR analysis and adsorption experimentation.



Six of the Spine removed, young fresh OFI pads were washed, peeled and dissected to facilitate sun drying



Sun dried OFI and hot air dried in an oven for 24hrs at 105^0c, cooled in the disscator, soaked with 45% of H_3PO_4over night /impriganted / and carbonized at 450^0c for 1hr, in the furnace and was cooled in disscator.

Cooled carbonized OFI material was grinded, sieved with stainless sieve of 0.425mm size and was kept / reserved in water tight plastic bottle to be used for the subsequent FTIR test analysis and batch experiment.

Figure 11: Preparation of *O. ficus-indica /OFI.*

3.6 Characterization of Activated Cactus

Physical characterization such as moisture content and bulk density were performed, so as to control the quality of activated biosorbent.

3.6.1. Moisture Content

The moisture content of activated Biosorbent was determined from the loss in mass of wet sample after drying in an oven at 110 °c for 60 minutes. About one gram of activated Biosorbent prepared from cactus was taken in a previously weighed crucible. The crucible then was placed in an electric hot air oven maintained at about 110°C. After one hour the crucible was taken out, cooled in desiccators and weighed again. The loss in weight of the Biosorbent reported on percentage basis as moisture content in the sample and finally, was calculated using the following equation (ASTM D 2974-87).

$$\text{Moisture content (\%)} = \frac{(W_1 + W_2) - W_3 * 100}{W_2}$$

Where, w1 = weight of crucible, W_2 = weight of activated carbon and W_3 = weight of residue after drying at 110^0C

3.6.2. Bulk Density

Determination of bulk density was carried out by volume which was filled by dried biosorbent. Accordingly; about 1g of activated cactus was filled in 50ml measuring cylinder and the amount of activated carbon taken by the cylinder was calculated.
Bulk density = M/V, where; M = gram of activated cactus placed in the cylinder; V= volume of the cylinder taken up by the activated cactus powder.

3.7 FTIR (Fourier Transform Infrared Spectrometry)

Infrared spectrum represents fingerprint of sample with absorption peaks which correspond to the vibrations frequency between the bonds of the atoms from which the material is made. Because each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. Thus, infrared spectroscopy can result in identification of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present. FTIR analysis of OFI was carried out in order to identify the surface functional groups that contributed significantly to enhance biosorption efficiency of the activated OFI powder.

3.8 Determination of Cr (VI) using Colorimetric Method

3.8.1 Cleaning of Glassware's

Glassware's was soaked in warm, mild detergent solution to remove any residual grease or chemicals. After the initial cleaning the glassware was soaked in 2N HNO_3 for 1hr then rinsed thoroughly with distilled water and dried in the oven (APHA, 1998).

3.8.2 Removal of Reducing Agents from the Extraction Reagent (2%NaOH).

Two ml of 0.1% KMnO4 solution was added using a 5ml pipette to the flask containing 2% NaOH solution and mixed thoroughly. Then the solution was waited for a few second and drop wise addition of 0.1% KMnO4 was continued until a faint pink color was attained which indicates that an excess of KMnO4 was added, thus neutralizing the reducing agent present in the extraction reagent. Then the flask was capped and ready for use (APHA, 1998).

3.8.3 Removal of Reducing Agent from 6H_2SO_4

A volume of 0.75ml KMnO4 (0.1%) was added using a 5ml pipette to the flask containing 6N H_2SO_4 and mixed thoroughly. Then the solution was waited for a few second and drop wise addition of KMnO4 was continued until a faint pink color was attained which indicates that an excess of KMnO4 was added, thus neutralizing the reducing agent present in the extraction reagent. Then the flask was capped and ready for use (APHA, 1998).

3.8.4 Preparation of Stock Solution

A stock solution of Cr(VI)(1000mg/l) was prepared by dissolving 2.83g analytical reagent grade potassium dichromate ($K_2Cr_2O_7$) in 1000ml distilled water (APHA, 1998).

Figure 12: Potassium Dichromate Solution.

3.8.5 Preparation of Standard Curve for Hexavalent Chromium

One ml of the chromium stock standard solution was added into 100 ml volumetric flask and diluted to the mark with distilled water. Then the flask was stoppered and inverted several times to mix the solution thoroughly and 25 ml of the extraction solution, previously treated with dilute KMnO4 solution was added to each of 7 series of 100 ml volumetric flasks. 0, 0.5, 1.0, 2.0, 4.0, 6.0ml of the chromium working standard solution and 7.8 ml of 6N H_2SO_4 was added to each flask and shaked well to remove the carbon dioxide gas, the flasks was not capped while shaking.

Then 2 ml diphenyl carbazide solution was added to each flask, and diluted to the mark with distilled water. After that the flasks was capped and mixed thoroughly by inverting the flasks several times. Then the mixture was standing for at least 15 minutes for full color development but not more than 1 hour. The absorbance of each standard was read in 1cm curette at 540 nm after setting the instrument to zero with the reagent blank. Finally; absorbance Vs.mg Cr^{+6} /50ml was plotted using linear graph paper (APHA, 1998).

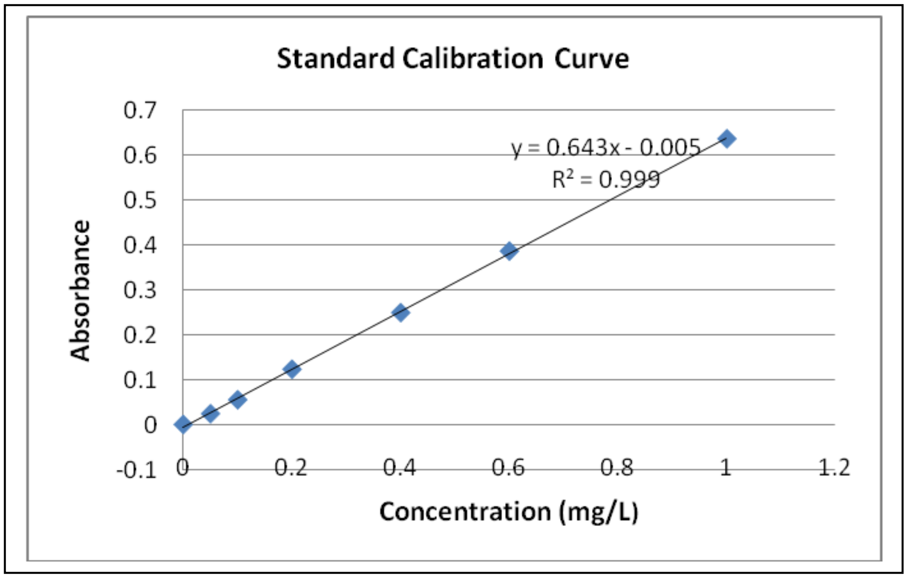


Figure 13: Standard Instrument Calibration Curve of Hexavalent Chromium.

3.8.6 Preparation of Synthetic Hexavalent Chromium Solution

Different volume of the stock solutions were diluted with water to obtain desired experimental solutions of 50ml Cr(VI) having various initial concentration and temperature ranging from (2-10 mg/l) and (25-35◦c) respectively. Various pH, O. Ficus Indicus dose, contact time, stirring speed ranging from (1-7),(0.075-2.5g),(30,60,90,120,150min), and (50rpm,100rpm,150rpm, 200rpm) respectively.

3.9 Batch Adsorption Experiment

The adsorption experiment test by batch process carried out in which a 50 ml of required Cr (VI) solution was added in the 100 mL conical flask. The pH of the adsorbate solution was calibrated by buffer solution (pH =7 and 9) and adjusted to the desired value by adding 0.1M H_2SO_4 and NaOH solution and measured by a micro-processor pH meter model 210 as shown in (fig.13).

Figure 14: PH Adjustment using Hanna PH 210 Micro Processor PH Meter

Measured concentration of the desired Cr(VI) ion prepared from the stock solution was place in 100ml of volumetric flask to make 50ml of solution. Then, the required amount of O. ficus-indica activated carbon on analytical digital balance model E42S-Bwasmeasured and mixed in the flask with the adsorbate.

Figure 15: Digital Balance of model E42S-B**.**

The mixture of the adsorbent and sorbate was placed in multi functional orbital shaker of model PSU-20i for mixing the solution properly for known minutes by setting the instrument at desired shaking speed. The mixing of adsorbate and adsorbent in shaker is shown in (fig.15).

Figure 16: Mixture of Adsorbent and Adsorbate in orbital shaker.

The samples of mixture were filtered using Whatmann No. 41 filter paper into 100 ml volumetric flask. Then, previously prepared 25 ml extraction solution (2% NaOH) and 7.8ml H_2SO_4 was added to the flask.

Figure 17: Whatmann N0.41 filter paper.

Finally; filtrate of the sample were analyzed calorimetrically in acidic media using 1,5 diphenyl carbazide solution to identify the Cr(VI) concentration at a wave length of 540 nm using Evolution 300 Uv-vis spectrophotometer (APHA,1998). The residual Cr (VI) concentration was measured using UV-Vis spectrophotometer as shown in (fig.17). Similar procedures were performed for all adsorption experiment of batch tests.

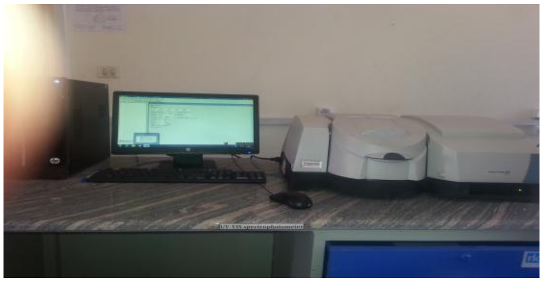


Figure 18: Evolution 300 UV- Vis Spectrophotometer.

3.10 Data analysis and Presentation

3.10.1 Analysis of Adsorption Data

The percent sorption of Cr(VI) and the amount of Cr(VI) adsorbed by O. ficus-indica carbon (q) were calculated by the following equations:

$$R = C_o - C_e/C_o * 100\,, \qquad q = V * (C_O - C_e)/M$$

Where R=% removal efficiency Co=initial Cr (VI) concentration (mg/l), Ce=final Cr(VI) concentration(mg/l).q=Adsorption capacity (mg/g), V=volume of the solution (L), m = mass (g) of the adsorbent.

3.10.2 Analysis of Adsorption Isotherm Data

Analysis of the isotherm data is important in order to develop an equation which accurately represents the results and which could be used for design purposes. Langmuir and Freundlich equations were used for describing the adsorption equilibrium for Cr(VI) removal. Thus, out of the several possible isotherms, the Langmuir isotherm with an equation of the following.

$$C_e/q = 1/q_{Max} * b + C_{eq}/q_{Max}$$

,was used. The constants b and q_{max} were calculated from the slope and intercept of the graph for each parameter and Freundlich isotherm models was tested by using an equation:

$$\log q_e = \log K_f + 1/n \log C_e.$$

Where K_f and n were calculated from the slope and intercepted of the linear plots of the graph. The data was analyzed in excel sheet and the one which better fits or having large R^2 value was then be selected as a general equation for extrapolation and generalization of the results. Finally the results were presented using excel sheet.

3.11 Application to Tannery Waste water

Biosorption adoptability technique for removal of hexachromium on adsorbent under study was further extended with some real tanning effluent. Accordingly; sample was collected from Batu Leather Tannery Industry from untreated chrome liquor, Addis Ababa. The pH and the respective chromium concentration were measured ahead of the application and respectively were found to be and 3.78 and 2358mg/l. The adsorbent removal potential was subsequently; studied by varying the contact time at different optimum adsorption conditions of the study parameters values that were obtained from synthetic waste water results and as per the experimental procedure described below.

3.12 Experimental Procedures for Digestion and Oxidation of Real Waste Water

The sample digestion and extraction procedures were employed for determination of dissolved (free) Cr (VI) or total chromium as Cr (VI) values. Subsequently; the chrome waste of 100ml was transferred to a beaker and 5ml HNO_3 (conc.) was added with a few boiling chips. The sample was allowed to a slow boiling and evaporated in a hood to the lowest possible volume of 20ml before precipitation to occur. HNO_3 (conc.) of 5ml was again added to the final volume of 20 ml digested sample to until a clear solution and complete digestion observed, which then, was cooled and filtered through 100ml volumetric flask using Whatmann filter paper.

Oxidization of Cr (III), as a subsequent step was performed by taking a portion of digested filtrate sample into 125 ml conical flask and several drops of methyl orange indicator was added. NH4OH (conc.) then was added until solution just turned to yellow. It then followed 1+1 H_2SO_4 drop wise addition until it became acidic and the volume was adjusted to 40ml while boiling chips was continually added and subjected to heat for boiling. Accordingly; 2ml drops KMnO4 solution was added, then the solution was faded then an excess of two drops of KMnO4 solution was again added and that resulted a dark red color. After boiling the solution for 5 minutes, a 1ml sodium azid solution was added and boiled gently for a minute. Similarly; 1ml sodium azid solution was added again and continued boiling for 1 minute until color was faded completely and then allowed to cool. The resulting solution was finally, subjected to atomic absorption spectroscopy test for total chromium concentration as Cr (VI) ions reading.

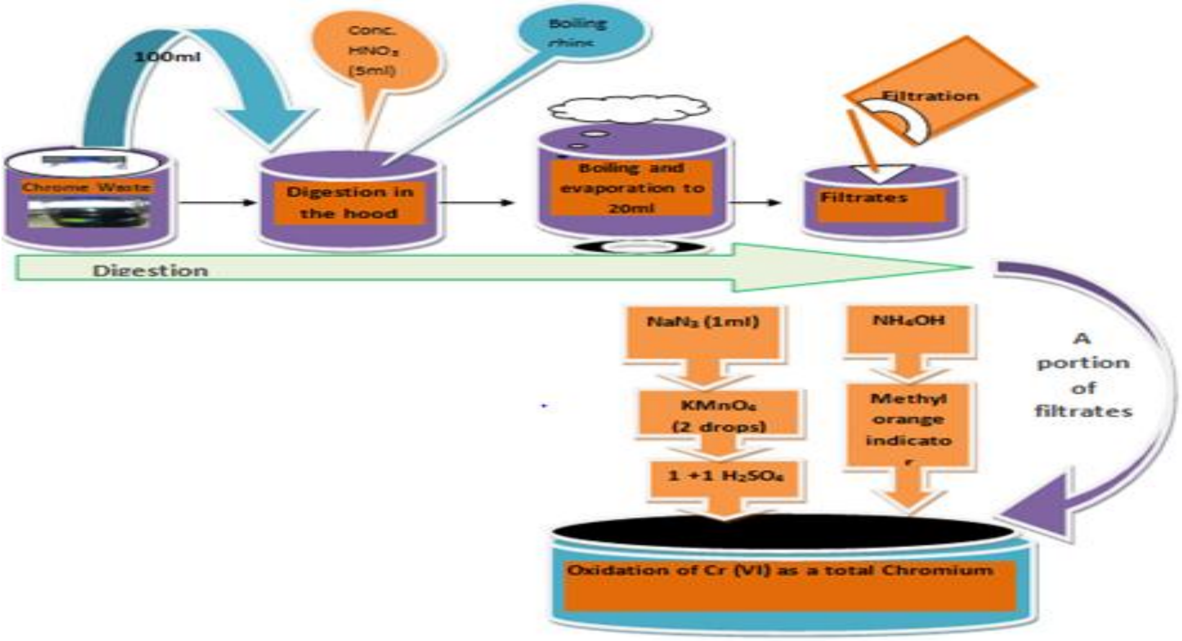


Figure 19: Flow chart of experimental procedures for digestion and oxidation of wastewater sample.

CHAPTER FOUR
RESULT

4.1 Physical Characteristics of Activated O. Ficus-Indicus (OFI):

Table -4: The Proximate Analysis of Activated O. Ficus-Indicus carbon powder

S.No	Physical characteristics	Unit	Value
1	Moisture content	%	1.685
2	Bulk density	g/ml	0.676
3	Particle Size	mm	0.425

The proximate analysis of activated OFI carbon powder of diameter 0.425mm was found out to with 1.7% and 0.676 g/ml of moisture content and bulk density respectively (table-4).

4.2 Fourier Transform Infrared Spectrophotometer (FTIR) Test:

Samples of activated OFI carbon powder before and after the adsorption process were measured on spectrum 65 FT-IR (PerkinElmer) in the range 4000-400 cm-1 using KBr pellets. Accordingly; the FT-IR tests of both respective samples displayed in the fig-17 and fig-18 below demonstrated a number of absorption peaks.

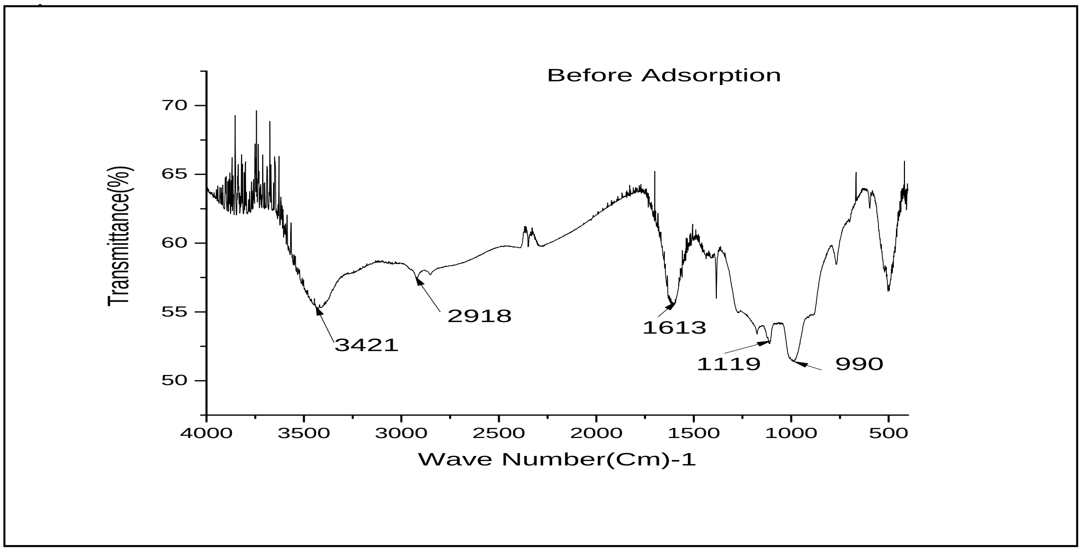


Figure 20: FTIR Spectrum of OFI using KBr Disc before adsorption process.

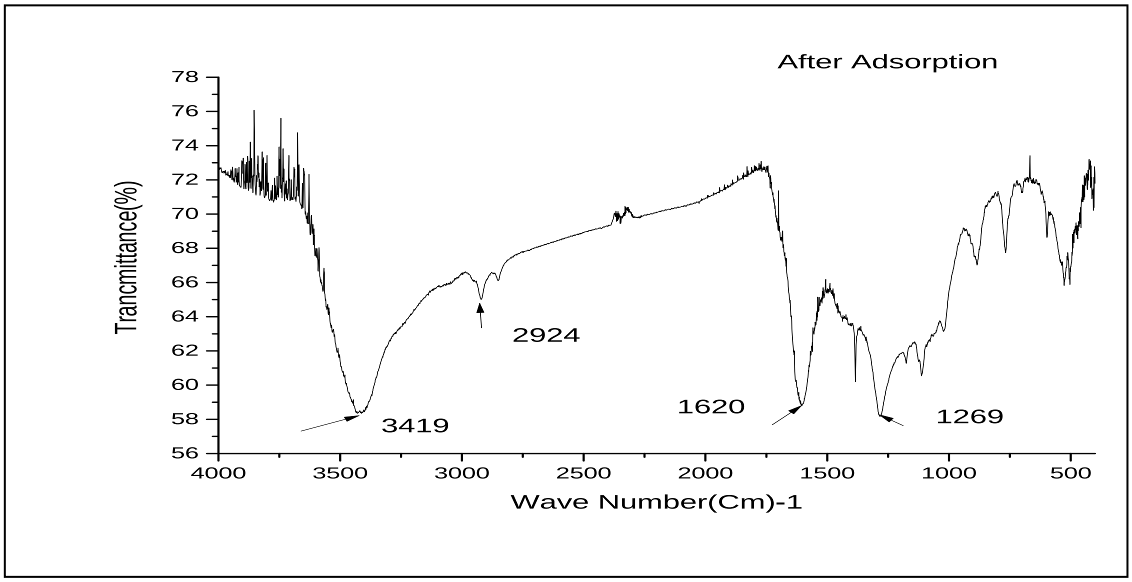


Figure 21: FTIR Spectrum of OFI using KBr Disc after adsorption process.

Table -5: Frequencies and respective functional groups present on the surface of activated OFI.

IR-Spectrum of Activated OFI Carbon before and After Adsorption					
IR-Peak	Frequency (cm-1) before adsorption	Frequency (cm^{-1}) after adsorption	Difference	Bond	Functional groups
1	3,421	3,419	-3	-OH Stretching, Hydrogen bonded	Hydroxyl
2	2,918	2,924	6	C-H Stretching	Aliphatic
3	1,613	1,620	7	C-O Stretching	Carboxyl
4	1,119	1,269	150	C-O bending	Carboxyl

It can be seen from (table -5), H_3PO_4 activated OFI carbon revealed the broad absorption peak at 3421 and 3419cm-1of H-bound hydroxyl (carbohydrate) before and after adsorption respectively. The respective changes in the intensity of 2918 to 2924 cm^{-1} and 1613 to1620 cm^{-1} indicated the presence of free C-H stretching aliphatic hydrocarbons and C-O stretching vibrations of carboxyls. And, the bands at 1119 to 1269 cm^{-1} correspond to fingerprint of C-O bending carboxyls.

4.3 Batch Adsorption Experiment Results

4.3.1. The Effect of Biosorbent Dose

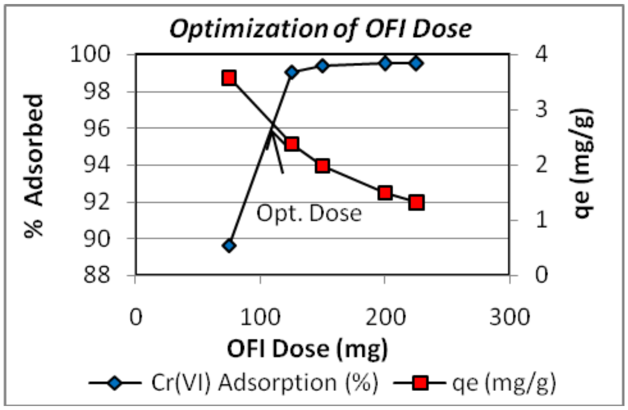


Figure 22: Illustrated, effect of adsorbent dose Vs removal % and capacity under initial Cr (VI) concentration; 6mg/l, pH; 2, contact time; 60minutes and shaking speed; 200rpm at temperature of 25^{o}C.

The Fig-22, above showed the percentage Cr (VI) metal adsorbed was increased from 89.63%, 99.07, 99.42, 99.51 to 99.52% with respective increase in the mass of the adsorbent doses from 0.075g, 0.125g, 0.15g, 0.2g to 0.25g. Whereas; Cr(VI) adsorbed per unit OFI dose was decreased from 3.59mg/g to 2.38, 1.99, 1.49 and 1.327mg/g, under constant initial concentration;60mg/l, pH;2, contact time; 60minutes and agitation speed;20 rpm at temperature of 25^{0} C in 50ml solution.

It is also evident from figure that maximum optimum removal of 99.07 % was taking place at adsorbent dose of 0.125g for which the sharp break in the curve of sorbent doses was reaching the optimal dose at 0.125g, showing the trade-off between removal % and capacity of OFI dose. Sorbent dose in excess of this value has a limited effect on the removal of additional Cr (IV) ion from adsorption system or little to increase adsorptive capacity of sorbent material under the study.

4.3.2. The Effect of Initial Cr (VI) Concentration

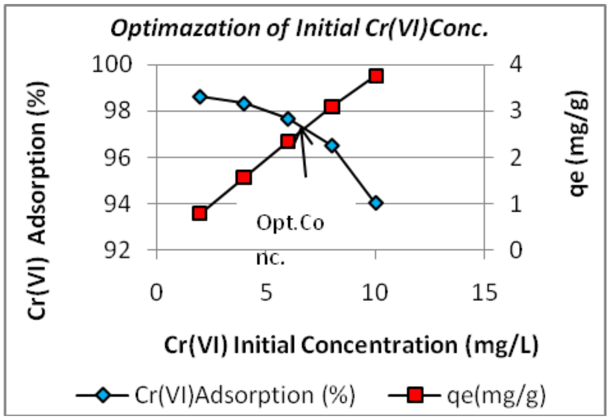


Figure 23: Describes, the effect of initial Cr (VI) ion concentration against adsorption removal % and capacity studied under adsorbent dose; 0.125g, pH;2,contact time; 60minutes, agitation speed; 200rpm at a temperature of 25^{0}C.

Hexachromium adsorption is notably influenced by the initial concentration of Cr(VI) in aqueous solutions. In the present study, the adsorption experiments was performed to study the effect of initial Cr(VI) concentration by varying it from 2mg/l, 4mg/l, 6mg/l, 8mg/l and 10mg in 50ml solution in which, 98.61%, 98.32%, 97.66%,96.49%, and 94.02% adsorption removal was observed to be decreased respectively. Contrarily; the adsorption capacity was found to increase from 0.79mg/g to 1.57, 2.34, 3.09 and 3.76.mg/g, while maintaining other parameters constant.

The study results showed that with increase in Cr (VI) concentration from 2 to 10 mg/l, the percentage removal decreases from 98.6% to 94.02 %. The decrease in removal efficiency from 98.6 to 97.66 %was observed when the initial Cr (VI) concentration was increased from 2 to 6 mg/l. An optimized initial concentration was observed at 6mg/l with 97.67% Cr (VI) metal uptake efficiency.

However; further decrease in initial concentration below 6mg/l didn't show significant effect. The maximum removal efficiency of 98.6% was obtained at lower initial Cr (VI) ion concentration of 2mg/l and the maximum adsorption density was observed at higher Cr(VI) concentration of 10mg/l.

4.3.3 The Effect of pH

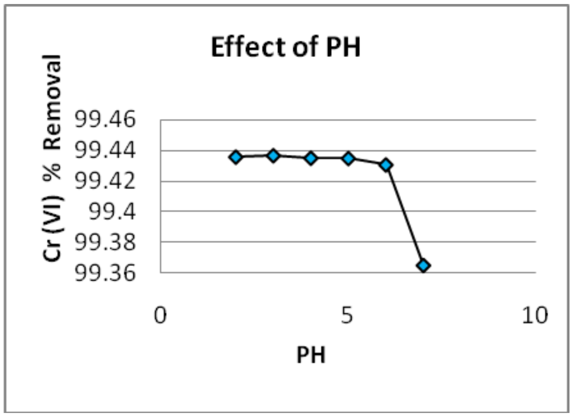


Figure 24: The effect of pH; under initial Cr(VI) ion concentration;6mg/l, adsorbent dose;0.125g, contact time;60 minutes and Shaking speed;200rpm at temperature of 25^0C.

It is well known that the pH of a system is an important parameter in the adsorption of Cr (VI). In the present work, effect of pH on the adsorption of Cr(VI) using OFI activated carbon as an adsorbent was tested in the initial pH range of 2-7.The relation between the initial pH of the solution and percentage removal of Cr (VI).

Removal efficiency showed slight increase from 99.43 to 99.44% with increasing initial pH from 2 to 3 and again it, appeared to slightly decrease above pH from 3 to 7. In which case, about, 99.4% adsorption efficiency was observed between pH ranges 2-6 and thereafter, above 6 started to slightly exert further decline in removal efficiency. Maximum % removal of test result was obtained between the pH values 2 to 3.

4.3.4 The Effect of Contact Time

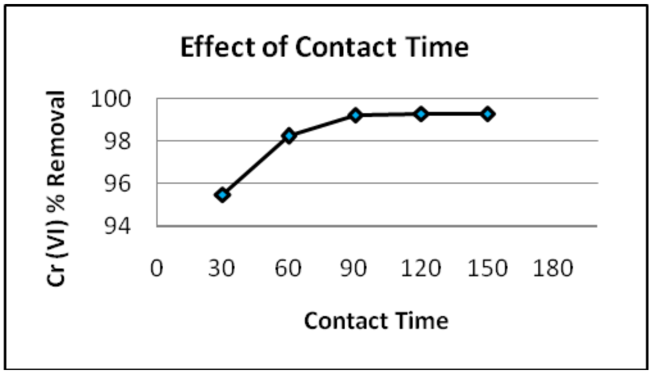


Figure 25: The effect of contact time under adsorbent dose; 0.125g, Initial Cr(VI) concentration;6mg/l, pH;3 and Shaking speed; 200rpm at temperature 25^0C.

Adsorption experiment was conducted to observe the effect contact time on removal efficiency of activated O. Ficus -Indicus. The removal efficiency of OFI at contact time interval of 30, 60, 90, 120 and 150 minutes was carried out and found to be 95.48%, 98.22%, 98.22%, 99.28%, and 99.3% respectively. As it is well described in Fig-24, the percentage removal increased from 95.48 to 99.3% from 30 to 150 minutes of contact time.

The rate of Cr (VI) binding with adsorbent was greater in the initial stages of 30 minutes, then gradually decreased and remained almost constant after an optimum period was reached at 60 minutes. In that, in contact times between 30 to 60 minutes, the amount of Cr (VI) removed from the solution was increased from 95.48% to 98.2%. Hence, the maximum optimized removal efficiency was attended at 60 minutes of agitation time, above which no significant effect in increasing of Cr (VI) removal.

4.3.5 The Effect of Shaking Speed

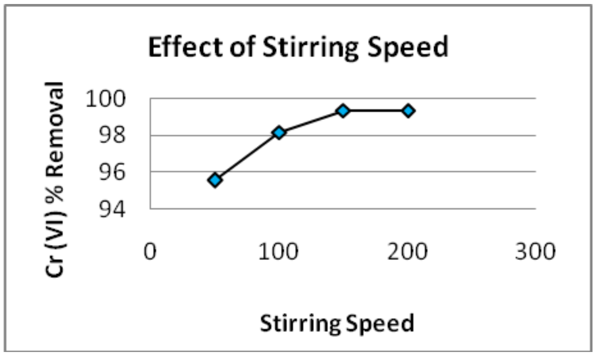


Figure 26: The effect of shaking speed at adsorbent dose; 0.125g,pH;3,initial Cr (VI) concentration; 6mg/l, and contact time; 60 minutes at room temperature of 25^0C.

The effect of the shaking speed of the sorbent/sorbate system in Cr (VI) adsorption was studied at 50,100, 150 and 200 rpm for 60 minutes of contact time, 0.125 g of activated OFI carbon in 50 ml of the solution containing 6mg/l of Cr (VI) at pH 3 at temperature 25^0C. As it is well described above, in the figure-25, the percent adsorption increased from 95.55%, 98.15%, and 99.35% to 99.36% with respective increase of shaking speed from 50 to 200 rpm.

A maximum of 99.36 % removal was achieved at 200 rpm, whereas; maximum optimized adsorption of 99.36 % was occurred at about 150 rpm above which, no significant effect on the adsorption of Cr (VI).

4.3.6 Effect of Temperature

Temperature in the interval of 25^{o} C, 30^{o}C, and 35^{o}C was considered to draw out the effect of adsorption efficiency of Cr (VI) ion on O.Ficus Indicus. Following to the result to the assigned first value temperature in the interval; 25^{o}C showed, adsorption efficiency of about 99.5% in its triplicates test trials. Thus, the higher adsorption percentage of Cr (VI), obtained at a lower assigned interval of temperature value that possibly ascribe for the reason why variation in temperature values had no further effect on the adsorbent, O.Ficus Indicus as it already reached a maximum percentage removal about 99.5% of Cr (VI) ion from the solution at 25^{o}C.

4.4 Adsorption Isotherm Analysis

4.4.1 Langmuir Isotherm

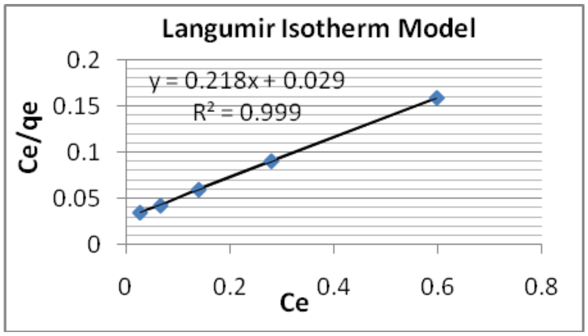


Figure 27: Langmuir Isotherm plot for the adsorption of Cr (VI),under optimum Adsorbent dose;0.125g,pH;2,Contact time; 60 minutes and Shaking speed;200rpm at a temperature of 25^{0}C.

Figure-27, above described a straight line plot of Ce/qe against Ce with the slope of 1/qmax and intercept 1/qmax*b. The Langmuir constants qmax and b were calculated from the regression equation and obtained 4.587mg/g and 7.5 respectively, while the correlation coefficient (r^{2}) value was 0.999.

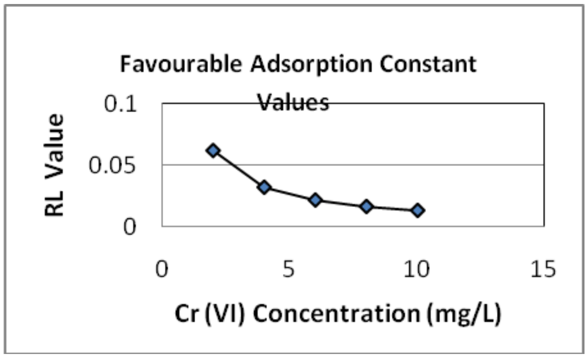


Figure 28: Langmuir isotherm model, separation factor (RL) values against varying initial concentrations under study.

The values of RL, dimensionless separation factor, one of the characteristics of Langmuir isotherm, define by **RL = 1/(1 + b*Co).** The calculated value of RL, ranges between 0.01313 and 0.0624 for Langmuir model followed the condition 0< RL<1.

4.4.2 Freundlich Model

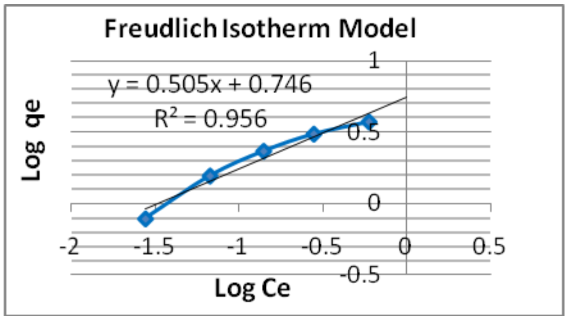


Figure 29: Freundlich Isotherm plot for the adsorption of Cr(VI), under optimum conditions of adsorbent dose; 0.125g, pH;2,Contact time; 60minutes, Shaking speed; 200rpm at a temperature of 25^0C.

A plot of log qe and Log Ce showed in fig-29 yields a straight line for adsorption data that followed the Freundlich theory. The values of Freundlich parameter constants 1/n and Kf determined from the slope and intercept of the plot found out to be 0.505 and 5.52 with correlation coefficient (r^2) value of 0.956 confirmed the applicability of the model.

4.5 Application to Tannery Waste Water

The Biosorbent, O. Ficus-Indicus was tested to check its Cr (VI) removal applicability with respect to the actual tannery industry wastewater. Percentage adsorption of chromium on activated OFI carbon increased with time tested under previously, optimized study parameters; adjusted pH: 2.0; adsorbent dose: 0.125g, agitation speed: 150 rpm at room temperature in 100ml aqueous solution. Accordingly; the optimum adsorption removal was reached 88.7% at contact time of 90 minutes at which further increase from this value didn't have significant effect on the percentage removal, unlike to that observed in aqueous solution at 60minutes.

However; the rate of adsorption of chromium on O. Ficus- Indicus carbon was almost similar with the results obtained from batch experiment in aqueous solution both at initial as well as later stages of optimum adsorption contact time. The selected sorbent understudy, altogether manifested remarkable removal capability of Cr (VI) metal and can be proposed as an alternative Cr (VI) removal of from tannery industry wastewater.

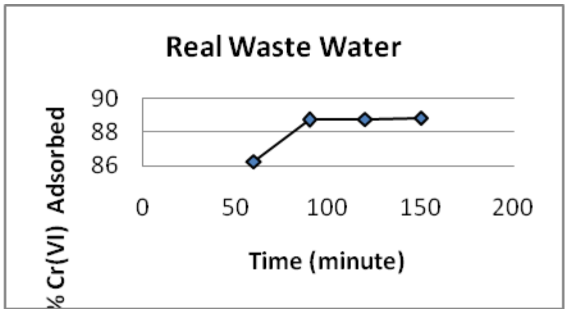


Figure 30: Effect of contact time on Cr (VI) ions adsorption from Batu Tannery waste water under optimum conditions; pH: 2.0; adsorbent dose:0.125g, agitation speed: 150 rpm at room temperature.

CHAPTER FIVE
DISCUSSION

5.1 Physical Characteristics of Activated carbon of OFI

The higher (99.5%) uptake of Cr (VI) by H_3PO_4 (45%) treated O. Ficus-Indicus/OFI carbon from aqueous solution can be ascribed due to the proximate characteristic values of the adsorbent under study, which are about 1.7 % and 0.676 g/ml moisture content and bulk density respectively. Study result is reported a maximum adsorption of Cr (VI) (94%) on H_3PO_4 (45%) activated rice husk with moisture content (13.82%) and bulk density (0.68g/ml) (Singh, S.R and Singh, A.P., 2012).

Though, both adsorbents have similarities with respect to the bulk density and activating agent, the low percentage moisture content of activated O. Ficus- Indicus carbon contrasted with that of rice husk could contribute to the better adsorption removal of Cr (VI) metallic ion. This can be elucidated as higher moisture content increases, the internal pores spaces which are filled with some water and interferes in pore structure development as a result prevents the diffusion of Cr (VI) ion on to the adsorbent site (Veena et al., 2012).

The adsorption efficiency of Cr (VI) ion 99.5% onto H_3PO_4 treated OFI is better than that of 93.28% H_2SO_4 acid treated rice husk. This might be explained with the type of activating agents used in activation processes of the raw biomaterials which possibly result in different removal efficiencies. This is well supported with study finding of literature reports that H_3PO_4 acid treated raw material has a better yield than H_2SO_4 acid treated raw material adhere to considerable increases in the pore structure and production of high porosity: the formation of new pores; hence higher surface area and more binding sites (Mohan et al., 2006; Hoong, 2013).

The lower the bulk density value indicates that the highly branched and porous with more void space. The American water work association has set a lower limit at 0.25gm/l for practical use of activated adsorbent. Therefore; the bulk density obtained from O. Ficus- Indicus carbon powder under study satisfies the condition (Veena et al., 2013).

5.2 FTIR (Fourier Transform Infrared)

IR technique is an essential tool to identify surface functional groups that significantly involved for enhanced adsorption efficiency by activated carbon O.Ficus Indicus (Mandina, et al., 2913). Accordingly FTIR spectra of OFI before and after Cr (VI) adsorption process were recorded in the range of 4,000- 400 cm^{-1}. The spectroscopic characteristics spectra of H_3PO_4 treated OFI carbon revealed the broad band at 3421 and 3419 cm^{-1} of H-bound hydroxyl (carbohydrate) before and after adsorption respectively. Dropping in wave number in Cr (VI) laden O. Ficus Indicus after sorption process (3,419cm^{-1}) in comparison to before adsorption (3,421cm^{-1}) signify, the role of H-bound hydroxyl stretching of hydroxylates in Cr (VI) ion uptake.

Consequently; hydrogen bonded ^{-}OH stretching in finger print region of O.Ficus Indicus before adsorption (3421 cm^{-1}) likely supports the electrostatic bindings of negatively charged chromate ions. In that, a notable hydroxyl band shifting to a low wave number (3,419cm^{-1}) confirms its possible involvement in adsorption processes.

Changes in the intensity of 2918 to 2924cm^{-1}and 1613 to1620 cm^{-1} in OFI carbon spectra indicated that free C-H stretching and carboxyl C-O stretching vibrations probably get interacted with Cr (VI) ion. The vibration shift of the functional group like, C-O bending vibrations of polysaccharides of 1,119 cm^{-1} to higher modes of 1,269 cm^{-1} bending frequencies indicates their contribution in Cr (VI) binding onto OFI.

The findings are well supported with literatures reported that O.Ficus Indicus FTIR confirmed to contain complex materials having multifunctional surface groups that comprise: phosphates, phenolic, hydroxyl, carboxylates, carbonyl, amides, amines and alkyl groups at varied absorption wave numbers (Pichler et al.,2012; Nharingo and Moy, 2015)

5.3 The Effect of Biosorbent Dose

Study on the effect of adsorbent amount for Cr (VI) removal is important to get the trade-off between the adsorbent capacity and percentage removal of Cr (VI) resulting in optimum Opuntia Ficus indica amount (Shirzad et al., 2011). The percentage adsorption removal of Cr (VI) ions increased from 89.63 to 99.5 % with increased in Opuntia Ficus indicus concentration and equilibrium was reached to optimum dose at 0.125g (99.07%) at constant initial Cr (VI) concentration of 6mg/L and pH of 2 and contact time of 60 minutes.

Related literature studies reported, about 65 and 58.3% optimum adsorption removal of Cr(VI) metal ion were achieved at 3g dose of unmodified plant bark powder prepared from Pongamia Glab and Mangifera indica, studied at the same Cr(VI) concentration (6mg/L), pH(2) and contact time (60min) (Kalandar and Hiranmai Yadav,2014). Besides; an optimum percentage of 81.9% Cr (VI) removal was succeeded at an adsorbent dose of 0.3g conducted with H_2SO_4 acid activated cajanuscajan (L) milp carbon with similar adsorption study conditions with the present work (Thamilarasu et al., 2011).

The highest removal efficiency of H_3PO_4 activated OFI as compared with other aforementioned adsorbents (untreated) could be due to its higher surface reactivity. This is well supported with different literatures, reported that activated carbon exhibits significant increase in the pore structure and production of high porosity: the formation of new pores, hence higher surface area and more binding sites than unmodified once (Mohan et al., 2006;Veena et al., 2012;Hoong, 2013).

The improved optimum adsorption efficiency of Cr (VI) ion 99.07% onto OFI than that compared with 81.9% H_2SO_4 acid treated cajanuscajan (L) milp might be explained with differences activating agents used in activation processes which possibly result in different removal efficiencies. This is well supported with literature reports that H_3PO_4 acid treated raw material has a better yield than H_2SO_4 with respect to the development of well structured pores and production of high porosity (Hoong, 2013).

Above all, the enhanced adsorption performance of O. Ficus indicus may be explained due to the fact that, H_3PO_4 impregnation introduces more acidic functional groups such as; hydroxyl which is among those various surface functional groups of OFI that have been identified by FTIR analysis of the present study (See table-5, fig 20 and 21), whereby they probably provide more adsorption sites for Cr (VI) ion. This is in consistency with literature FTIR test study reports of O.Ficus-Indicus for which it is confirmed to contain; phenolic, hydroxyl, carboxylates, carbonyl, amides, amines and alkyl groups (Pichler et al.,2012; Nharingo and Moy, 2015).

The increase in Cr (VI) removal with increase adsorbent amount is due to the increase in surface area and adsorption sites available for adsorption, thus makes easier penetration of Cr (VI) to the adsorption sites. The present study result findings shows nearly similar adsorption percentage removal of Cr (VI) with different adsorption studies observed on acid Treated Banana Peel (99.53%) and crude tamarind (99.09%); (See comparison, table-6) (Kumar and Majumder, 2014; Sudhanva et al., 2014).

However, the amount of metal uptake per unit gram decreases rapidly from 3.59 to 1.327 mg/g as the mass of adsorbent dose added increases from 0.075 to 0.25g.The drop in adsorption capacity is basically due to the sites remaining unsaturated during the adsorption process. The respective optimum values of Cr (VI) adsorption capacity of O.Ficus Indicus is found to be 3.378 mg/g occurred at activated OFI carbon dose of 0.125g. The present study result is agreement with different literature reports; (See comparison, table-7) (Nasim et al., 2004; M Tahiruddin and M. Ya'akub, 2013; Osasona et al., 2013).

It thus, evident from result discussion that adsorption percentage removal and adsorption capacity of Cr (VI) ion on O.Ficus Indicus is highly a function of the amount adsorbent used. This is supported with literature reports (Liu et al., 2010; Mandeep and Majumder, 2014).

5.4 The Effect of Initial Cr (VI) Concentration

The adsorption experiment study conducted reveals that with increases of Cr (VI) concentration from 2 to 10mg/L decreases the percentage removal from 98.6% to 94.02%. The maximum optimum Cr (VI) ion adsorption percentage of about 98.6% was observed at lower initial concentration of 2mg/L, studied at constant optimum adsorbent dosage of 0.125g and pH 2.

The same lower optimum initial Cr(VI) ion concentration of 2mg/L at which 87.5, 90 and 75% maximum removal efficiencies were attended by each of the respective H_3SO_4 treated plant bark powder adsorbents prepared from different plants; Pongamia glabra, Tesphesia populnea and Mangifera indica (Kalandar and Hiranmai Yadav,2014).

In similar observation, an optimum initial concentration of 2mg/L was also obtained by H_3SO_4 treated cajanus cajan(L)milp seed shell and Ricinus Communis seed shell at low concentration a maximum of 83.2 and 89.5% Cr(VI) removals were obtained respectively(Thamilarasu et al., 2011 and 12). The improved adsorption removal observed by O.Ficus Indicus probably due to the nature of surface chemistry, the type of activating agent and the methods employed during activation processes (Mohan et al., 2006; Nharingo and Moy, 2015).

The decrease in percentage removal with increase of initial concentration can be due to the availability of limited number of unoccupied active sites on OFI surface per Cr (VI) ion at higher concentrations, which would have become saturated. The increase in adsorption capacity from 0.789 to 3.76 mg/g with increase in Cr (VI) concentration may be, a higher initial concentration enhances the number of collisions between Cr (VI) ions and adsorbent that results in an increase in adsorption rate and utilization concentration (Hasan, 2005; Talokar, 2011; Mohamed, 2012; Mutongo et al., 2014).

O.Ficus Indicus as an biosorbent demonstrates complete remove of Cr (VI) ions from solution, when the initial concentration is taken as low and a notable adsorption amount when initial Cr (VI) ion concentration get increased. The present study is in consistence with those reported in literature for adsorption of Cr (VI) ions on chemical activated Oxytenanthera abyssinica and Powder Activated Carbon (PAC) that are observed an increase in the Cr(VI)ion percentage adsorption when the initial concentration is taken as low for which 98.71 and 99% removal are attended respectively ((Talokar, 2011; Dula et al., 2014).Therefore; the adsorption of Cr (VI) ion onto O.Ficus Indicus has a strongly influenced by the initial concentration of Cr (VI) in aqueous solutions.

5.5 The Effect of pH

The pH of a system is a single important parameter that control the adsorption of Cr (VI) (Tazrouti and Amrani, 2009; Thilagavathy and Thirumalisamy, 2013). Sorption experiment was carried out to optimize the pH for maximum removal efficiency of Cr (VI) at six different pH levels by varying the pH values from 2 to 7 that was not influenced by the metal precipitation under optimized Cr (VI) ion concentration 6mg/L, adsorbent dose of 0.125g/50ml and contact time of 60min.

The experimental result revealed that the adsorption percentage removal increased as the pH was deceased and attended 99.24% at lower pH values from 2 to 3, hence optimum pH for maximum removal of Cr (VI) occurs at pH 2. When the pH increases above 3 the percentage removal observed to follow slight declining trend till the pH value reaches 6.This result, resembles most with adsorption of Cr(VI) on activated carbon materials (Olayinka et al., 2009; Tazrouti and Amrani, 2009; Mandina, et al.,2013).

The result finding of the present work shows similar optimum pH value and trend of pH influence but different removal efficiency, while comparing with H_2SO_4 modified activated Carbon Ricinus Communis seed shell, activated carbon Cajanus Cajan (L) Milsp seed shell, Tesphesia populnea and Mangifera indica that respectively; observed with Cr(VI)removal of 88.6, 80.3, 71.6 and 58.3%, under same study conditions; Cr(VI) concentration (6mg/L) and contact time (60min) **(**Thamilarasu et al., 2011 and 2012; Kalandar and Hiranmai, 2014). The different in removal efficiency might be due to surface reactivity that provided increased availability of active binding sites by surface oxidization of OFI by H_3PO_4 acid, as it was well discussed elsewhere. This is agrees with study observation reports; H_3PO_4 treated ends with a better yield than H_3SO_4 in the formation of more active sites (Hoong, 2013).

The favorable effect of low pH for maximum removal efficiency can be possibly explained on the basis of the assumptions of excess hydrogen ion (H^+) concentration in the solution at low pH values. In that, at low pH values, the surface of the adsorbent is highly protonated, thereby making the negatively charged surface of OFI to be saturated with positive charges enhancing the diffusion of Cr (VI) oxyanions and their subsequent adsorption by the electrostatic force of attraction. This agrees with the reports of the literatures (Tazrouti and Amrani, 2009; Liu et al., 2010; Mandina et al., 2013).

Furthermore; the oxidative treatment of OFI carbon with H_3PO_4, introduces more oxygenated acidic surface at a lower pH values (Nomanbhay and Palanisamy, 2005). Accordingly; marked presence of various oxygenated acidic surface functional groups on OFI identified by FT-IR test result; among which is hydrogen bound hydroxyl groups increase the availability of active binding sites at low pH conditions, and hence increase the adsorption of oxyanions Cr (VI) due to protonation at low pH values. It has been also suggested that formation of more acidic surface oxides on carbon surface enhances its hydrophilic character of the adsorbent (Mohan et al., 2006). This improves the hydrodynamic flow under which condition the interactions between negatively charged Cr(VI) anions and H^+ protonated OFI carbon surface could possibly made that favors in rapid and easy uptake of Cr (VI) ion through electrostatic attraction at low pH values. This is supported with literature report (Nomanbhay and Palanisamy, 2005).

It is also postulated that at lower pH values (<3) Cr (VI) metal ion can be reduced to Cr (III) in the presence of activated carbon (Liu et al.,2010; Thilagavathy and Thirumalisamy, 2013). Consequently; Cr (VI) sorbed is reduced to Cr (III) in the presence of negatively charged functional groups on surface of acid treated O.Ficus-Indicus carbon. Cr (VI) sorption and reduction to Cr (III) occur as Cr (VI) starts to act as an oxidant and hence, oxidize the surface that results in proportional released of the non toxic Cr (III) from OFI surface by reaction mechanism described below. Similar bioreduction process observations were made with different study reports (Mohan et al., 2006; Kumar and Majumder, 2014).

$$\boxed{\mathbf{HCrO_4^{-} + O.\ Ficus\ Indicus + H^{+} \longrightarrow Cr^{3+} + H_2O + O.\ Ficus\ Indicus\ (\mathit{Oxidized})}}$$

This observation agrees with literature as reported sorption coupled with reduction occurs on acid treated surface maize bran (Hasan et al., 2007; Kumar and Majumde, 2014). Reduction of Cr (VI) into Cr (III) is also clear from the aqueous chemistry of Cr (VI) at low pH value blow (Olayinka et al., 2009).

$$\boxed{\mathbf{HCrO_4^{-} + 7H^{+} + 3e^{-} \longrightarrow Cr^{3+} + H_2O}}$$

Here, anionic $HCrO4^{-}$ is dominantly sorbed as Cr (VI) metal ion on to OFI than the other species. This can be well explained as $HCrO4^{-}$ is dominating Cr (VI) species at concentration of below 1g/l under acid pH solution; see fig.-2 (Mohan et.al.,2006; Mulani et al., 2013). Furthermore; at pH of 2-3, $HCrO4^{-}$, exists predominately as Cr (VI) species and preferentially adsorbed over the other species on OFI due to its smaller ionic size and low adsorption energy, whereas; as the pH increases, this shifts to $Cr_2O_7^{2-}$ and CrO_4^{2-} (Mohan, 2006; Tazrouti and Amrani, 2009; Liu et al., 2010).

In view all above discussions, the dominate adsorption mechanism are anionic sorption and sorption coupled with reduction. Besides; electrostatic attraction and /or surface complexation provide the binding phenomenon between the opposite charges. The reduced adsorption efficiency at higher pH can be attributed due to increased negative charge density on surface OFI creating repulsive electrostatic with anionic Cr(VI) this is in conformity with many literature reports (Mandina et al., 2013; Osasona et al., 2013).

5.6. The Effect of Contact Time

Adsorption experiment was conducted to investigate the effect Cr (VI) adsorption on the OFI as a function of contact time with the range from 30-150 minutes, keeping other optimum parameters constant. The results, shows increasing of percentage removal of Cr (VI) from 95.5 to 99.3%, while increasing the contact time, from 30 to 150 minutes respectively. This agrees with various studies (Veena et al., 2012; Osasona et al., 2013).

Furthermore, a sharp increase of Cr (VI) adsorption efficiency was observed from 30 to 60 minutes, and thereafter begins to decline slowly till was reached the equilibrium time. Thus, the maximum percentage of adsorption was 99.3%. Whereas, the optimal maximum was 98.3%, attended at 60 minutes of contact time and further increase in the contact time has a negligible effect on the removal of Cr (VI). Similar result observations have been reported in different literature studies (Samadi et al., 2009; Veena et al., 2012; Osasona et al., 2013; Kumar and Majumder, 2014).

On the other hands; the result finding of the present study requires far lesser time to reach maximum Cr (VI) adsorption than rise husk carbon, for which 150minutes is required (Ahmed et al., 2012).This is essential result output as equilibrium time is one of the important parameters for an economical wastewater treatment system. In that; the various functional groups confirmed to exist on the surface OFI carbon by FTIR; significantly improved the binding capacity and rapid proceeding of the adsorption processes (Nomanbhay and Palanisamy, 2004).

However; the rate of adsorption is very rapid during initial time of 30 minutes and decreases through the later stages of Cr (VI) adsorption. This is because of the availability of large vacant binding sites for initial stage of adsorption compared to later stages, which encounter resistance to occupy the limited remaining binding sites due to repulsive forces between Cr (VI) on the solid and in the solution. The resulted presented shows solidarities with different literatures reports (Osasona et al., 2013; Kumar and Majumder, 2014).

5.7. The Effect of Stirring Speed

The effect of stirring speed was studied varying from 50-200 rpm, keeping the other previously optimized parameters constant. The removal efficiency of Cr (VI) found to increase from 95.6 to 99.4% with along with increasing of the speed values in the range between 50-200rpm. The result also indicates that a shaking rate in the range 100-200 rpm is sufficient to assure that all the surface binding sites are made readily available for Cr (VI) uptake. Then, the effect of external film diffusion on adsorption rate can be assumed not significant. Hence; a maximum of

99.36 % removal was reached at 200 rpm. Besides; it was shown that, further increase from the optimum removal of 99.35% observed at 150rpm, has no significant effect on the adsorption of Cr (VI). This result finings in conformity with Cr (VI) removal study conducted from industrial wastewater using chitosan coated oil palm shell charcoal ((Nomanbhay and Palanisamy, 2004).

The observed increasing of percentage removal associated increasing of stirring speed, is due to enhanced spreading of the sorbent particles towards the binding sites for which the diffusion of Cr ions towards the surface of the adsorbents is significantly facilitated. On the other hand; low agitating speed the sorbent occupies the bottom space flask, hindering immediate contact Cr (VI) ion with the active binding sites (Veena et al., 2012).

5.8 The effect of Temperature

Temperature in the interval of 25^{o} C, 30^{o}C, and 35^{o}C was considered to observe the effect of removal efficiency of Cr (VI) ion on O.Ficus Indicus. Accordingly; adsorption efficiency of about 99.5% was obtained at 25^{o}C which was the first value in proposed temperature interval. In this regards, the result indicates that further increase in excess of this temperature value could have little or negligible effect on additional removal of Cr (VI) ion, hence variation in temperature values had no effect in the adsorption system under the study. The result is consistency with the different research literatures; reported the temperature influence has more effect in situation where by metal uptake increases within a temperature range of about $20\text{-}30^{0}$C, in that the effect decreases with an increase of temperature above a critical value (Sulaiman, 2015).

The study result is also further agrees with the research study finding; the temperature in the range of $20\text{-}35^{o}$C does not seem to have an effect on the adsorption efficiency (Rahimizadeh and Liaghat, 2015). The other possible reason for the maximum percentage adsorption at lower temperature value could be due to fast binding energy requirement between the Cr (VI) ions and the adsorbent under the study. This agrees with literatures, reported the adsorption of metal ions to the surface of the Biosorbent at a low temperature is more rapidly, easily and reversible because of low requirement of energy (Sulaiman, 2015).

Further rising in temperature does have an effect on adsorption removal of Cr (VI) for monolayer dominated sorption process (Dula et al., 2014). Besides; it can be more explained with study result observed that the percentage removal of Pb by cactus powder has decreased from 65.05% to 29% as the temperature increased from 25^{o}C to 50^{o}C. Similarly; the percentage removal of Cd by cactus powder also decreased from 43% to 31% as the temperature increased from 25^{o}C to150^{o}C (Derbe, 2015).

Table -6: Comparison of adsorption % Cr (VI) ion onto O. Ficus Indicus and other different sorbents found in the literatures.

Name of Sorbent	**(%) Removal of Cr(VI)**	**Adsorbent Dose**	**Reference**
Alfa Grass(Stipa Tenacissima)	92.36	3.8/L	Tazirouti and Amarani, 2009
Neem Leaves	85	8gm/L	Pandhram and Nimbalkar, 2013
Potato peels,	96	4g/L	Mutongo et al., 2014
Trapa natans husk	99	1.5g/L	Liu et al., 2010
Trapa natans husk	94.6	1.5g/L	Liu et al., 2010
Activated Carbon	73	4/L	Wanees et al., 2012
Husk of Bengal gram (Cicer arientinum*)*	99.9	1g/L	Ahalya, N. et al.,2005
Olive stones	87	0.25/ L	Attia et al., 2010
Acid Treated Banana Peel(ATBP	99.53	0.2g/L	Kumar and Majumder,2014
Modified orange *(citrus cinensis)* peel	41.4	4g/L	Mandina et al., 2013
Coconut husk	96	0.2g/L	Olayinka et al., 2009
Teak tree bark	81.9	1g/L	
Crude tamarind	99.09	4.6g/ L	Sudhanva et al., 2014
Bamboo(Oxytenanthera abyssinica)	98.28	0.25g/25ml	Dula et al., 2014
Activated Coconut Shell	97.77	0.5g/L	Veena et al., 2012
Palm Tree Branches	55.1	1g/L	Khedr et al., 2014
Plants Bark Powder	98.6	0.015g/L	(Kalandar and Hiranmai Yadav, 2014)
Rice husk carbon	> 95	0.8g/L	Nasim et al., 2004
Raw rice husk	66	70g/L	Nasim et al., 2004
Activated bagasse carbon	99.97	0.8 g/l	Nasim et al., 2004
Raw bagasse (Untreated)	93.5	0.8 g/L	Nasim et al., 2004
Coconut tree saw dust carbon	98.84	0.8 g/L	Nasim et al., 2004
Cow Hooves	89.5	1g/50ml	Osasona et al., 2013
Opuntia Ficus Indicus (OFI)	99.52	0.125g/50 ml	Present Study

5.10. Adsorption Isotherm Study

The adsorption isotherm is a functional Expression for the variation of adsorption with concentration of adsorbent in bulk solution at constant Temperature. Langmuir and Freundlich Isotherm equilibrium models are analyzed to investigate best fitting adsorption isotherm.

5.10.1 Langmuir Isotherm

The Langmuir constants qmax and b which are measure adsorption capacity and adsorption energy and are obtained to 4.587 mg/L and 7.5 L/mg respectively from the slop and intercept of the linear plot of Ce/qe versus Ce. Higher maximum adsorption capacity (qmax) obtained by activated OFI while comparing with Coconut tree sawdust, 3.6mg/g and banana peel, 3.28 (Saroj et al., 2006; Khan A. and Murthy U., 2013). Rice straw, sugarcane bagasse and saw dust respectively have 3.15, 0.63 and 0.122 mg/g of qmax values (Memon et.al. 2009). Pine leaves 0.198 mg/g and Sawdust activated carbon,3.46mg/g (Liu et al., 2010; Mutongo et al., 2014). Besides; Cow Hooves, Chryseomonas Luteola, Modfied Saw Dust and Waste Tea saw respectively; have 3.57,3,1.7and1.55mg/g of qmax values (Osasona et al., 2013).

The regression correlation coefficient (r^2=0.999) is obtained, indicating good agreement between the experimental data and isotherm parameters that confirms monolayer adsorption of Cr (VI) onto the homogenous surface of OFI sorbent. The dimensionless separation factor, RL, is one of the essential feature of Langmuir Isotherm model that describes the affinity between adsorbent and adsorbate, unfavorable (RL>1), linear (RL=1), favorable (0<RL<1) or irreversible (RL=0). The RL value of Langmuir isotherm lies in the ranges between 0.0131 and 0.0624. Hence, Langmuir isotherm model follows the condition 0< RL<1 and implies the favorability of Cr (VI) removal adsorption process by activated OFI carbon under study.

5.10.2 Freundlich Isotherm

The applicability of the Freundlich isotherm is analyzed based on adsorption on heterogeneous surface using the same equilibrium data of Cr (VI) adsorption on OFI sorbent. Accordingly; Freundlich constants, K_f (L/mg) and 1/n are obtained by plotting the graph between log qe versus log Ce. The respective values of K_f and n are 5.57 and 1.980. Higher K_f values when comparing with potato peelings, 0.2985 and Bengal gram husk, 2.815mg/g, Activated sugar beet bagasse, 1.108 (Ahalya et al., 2005; Samadi et al., 2013;Mutongo et al., 2014).Value of 1/n ranges between 0 and 1, for which the value of n lies between 1 and 10 that indicates the beneficial adsorption, suggesting relatively strong adsorption of Cr(VI) ions onto the surface of OFI carbon (Samadi et al.,2009; Osasona et al., 2013; Mutongo et al., 2014).

Adsorption Isotherms with n>1,are reflecting high affinity between adsorbent and adsorbate which is an indicative of chemisorptions (Khedr et al., 2014; Mutongo et al., 2014). The regression correlation coefficient (r^2=0.956) obtained from Freundlich isotherm model is lower than that of Langmuir isotherm model. Hence, Langmuir isotherm gives a better fit. And q_{max} predicted from Langmuir isotherm and experimental Isotherm data are 4.54 and 3.76 mg/l respectively with the deviation of Langmuir model from the experimental result about 17.2 %. This is in consistence with most of related studies reported that Langmuir model was suitable for describing the adsorption isotherm of Cr (VI) on adsorbents (Shoaib et al., 2013; Mutongo et al., 2014; Khedr et al., 2014).See, table-7 that compares Langmuir adsorption capacity of OFI with various other sorbents.

Table- 7: **Comparison of monolayer maximum sorption capacity of Cr (VI) ion onto OFI and other different sorbents found in the literatures.**

Sorbent	**Sorption Capacity (mg/g)**	**Reference**
Soya Cake / tested at pH=<1	0.00028	Mohan et al., 2006
Soya Cake / tested at pH=1	0.28	Olayinka et al., 2009
Bagasse	0.001	Mohan et al., 2006
Carboxymethylcellulose (CMC)	5.1	Mohan et al., 2006
Agave lechuguilla biomass	3.3	Mohan et al., 2006
Ground nut shell (GS)	5.9	Mohan et al., 2006
Powder Activated Carbon (PAC)	0.03	Mohan et al., 2006
Carbonaceous adsorbent from sawdust (SPC)	2.2	Mohan et al., 2006
Maple sawdust	5.1	Mohan et al., 2006
Granular activated carbon (GAC)	0.988	Liu et al., 2010
Raw Rise bran	0.07	Liu et al.,2010
Sawdust activated carbon	3.46	Liu et al.,2010
Fe-modified Trapanatan	11.83	Liu et al., 2010
Sunflower Stem	4.9	Liu et al.,2010
Rice husks	0.6	Nasim et al., 2004
Rice husk carbon	8.9	Nasim et al., 2004
Alfa Grass(Stipa Tenacissima)	51.81	Tazirouti and Amarani, 2009
Fly ash impregnated with aluminum	1.8	Mohan et al., 2006
Fly ash Impregnated Iron	1.7	Mohan et al., 2006;Madhavi et al., 2012
Fly ash	1.4	Madhavi et al., 2012
Fly ash-wollastonite	2.9	Mohan et al., 2006
Chryseomonas Luteola	3	Osasona et al., 2013
Modfied Saw Dust	1.7	Osasona et al., 2013
Waste Tea	1.55	Osasona et al., 2013
Cow Hooves	3.57	Osasona et al., 2013
Modified oak saw dust	1.7	Osasona et al., 2013
Wallnut shell	1.33	Osasona et al., 2013
Activated tamarind seeds	0.08	Olayinka et al., 2009
Psidium guajava leaves powder	4.762	Mutongo et al., 2014
Pine Cone and Oak Cups	4.5	Mutongo et al., 2014
Powder of Mosambi fruit peel	7.51	Mutongo et al., 2014
Pine leaves	0.198	Mutongo et al., 2014
Brawn Sea Weed	0.629	Mutongo et al., 2014
Potato peels power	2.732	Khanam and Murthy, 2013
Opuntia Ficus Indicus (OFI)	4.585	Present Study

CHAPTER SIX
CONCLUSION AND RECOMMADATION

6.1.Conclusion

The present work shows that OFI activated with H_3PO_4 is sufficient enough to remove Cr (VI) from both synthetic and tannery waste water. The adsorption was found to be strongly dependent on pH, OFI dose, initial concentration, contact time and stirring speed under room temperature. Adsorption of Cr (VI) was highly pH dependent and the study results showed that the removal efficiency increased with deceasing the adsorbate and pH; and increasing the adsorbent dose, contact time and Stirring speed. About 99.5 % of maximum adsorption of Cr (VI) ions removal performance by OFI was accomplished within optimum 60 minutes, at pH of 2 and shaking speed, 150 rpm at room temperature. Besides; adsorption percentage removal of Cr (VI) with O.Ficus Indicus found out to be 88.7% while, applied to real tannery waste water.

FTIR spectroscopy revealed key roles of hydroxyl and carboxyl functional groups in binding of Cr (VI) on the surface of OFI carbon. The experimental equilibrium data fitted well to both Langmuir and Freundlich isotherm models with correlation coefficient values greater than 0.9. But; Langmuir isotherm with higher regression correlation coefficient was found to better describe the adsorption data with monolayer maximum adsorption capacity of 4.587mg/g on OFI. The Langmuir RL value satisfied the condition $0< RL<1$ and confirmed the favorability of adsorption process. Similarly; Freundlich isotherms adsorption constant value 1/n obtained to be 0.505 in the range of 0 and 1and reflected favorable adsorption. Besides; the isotherm adsorption constant, n =1.98 (greater than > unity) and is an indicative chemisorptions.

The higher Cr (VI) % adsorption and capacity on O.Ficus Indicus obtained, signifies efficient removal performance. The O.Ficus Indicus, in this regards; is possibly proposed for effective removal of Cr (VI) metal at industrial scales that consume chromium most as a major starting material. The adsorbent under this study can thus be recommended as best alternative to more costly adsorbents and can replace the expensive commercial activated carbon.

6.2. Recommendation

- Desorption study of chromium loaded OFI is required for respective recycling and recovering of the biosorbent and chromium metal, hence safe disposal is ensured.
- Removal efficiency of hexachromium on OFI needs to be further investigated by continuous method of filling the biosorbent in successive column.
- Studies on the adsorptive potential of OFI with other essential ions /trace elements need to be evaluated.
- Studies need to be carried out to determine the adsorption potential of Cr (VI) onto OFI with raw biomass and its combusted products like ash and charcoal, without activation.
- The matrix effect of competing anions found in the respective industrial waste water need to be studied.

CHAPTER SEVEN
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Annexes

Annex -1: Calculation of Moisture Content

Moisture content = $\frac{(W1+W2)-W3}{W1}$ * 100

Where, W_1 weight of dish = 65.474g

W_2 = weight of sample = 1.00357g

W_3 = weight of residue after drying at 110°C (W_1+W_2) = 65.45709g moisture content = (65.474+1.00357) - 65.45709*100= 1.685% =1.00357g

Annex-2: Calculation for the preparation of 6N H_2SO_4 from 98% stock standard solution of H_2SO_4

$$Morality = \frac{10*\%\ of\ stock\ \ H2SO4*Density}{M.wt}$$

$$Morality\ of\ 98\%\ \mathbf{H2SO4} = 10*\%*dessity/M.wt = \frac{10*98*\frac{1.84g}{l}}{98} = 18.385M$$

Morality =1/2 Normality implies that 6/2=3M

C1 =18.385M, C2=3M, V_1=1000ml, thus V_1 was calculated,

$C_1V_1=C_2V_2$

18.385 *V1 = 3M*100, V_1= 3000/18.385= 16.32ml (16.32ml of concentrated H_2SO_4 to 100ml water).

Annex-3: Calculation for the preparation of 2N HNO_3 from 69% stock standard solution of HNO_3

$$Morality\ of\ 69\%\ HNO3 = 10*\%*dessity/M.wt = \frac{10*69*\frac{1.415g}{l}}{63.01} = 15.49M$$

Given:

C_1=15.495M, C_2=2M (required concentration)

V_1=? V_2=500m1(required volume) , in this case normality =Morality since HNO_3 has one hydrogen ion

$C_1V_1=C_2V_2$

$15.495M*V_1=2M*500ml$

Therefore, 64.52ml was taken from the stock, added to 500ml volumetric flask and diluted to the mark

Annex -4: Calculation for the preparation of 2% NaOH

20g of NaOH pellet was dissolved by distilled water in 100ml conical flask

Annex-5: Calculation for the preparation 0.1% KMnO4

0.1g of KMNO4 was dissolved in 100ml conical flask and dilute to the mark

Annex-6: calculation for the preparation of 45 %(w/w) H_3PO_4

45g of H_3PO_4 in 100ml of water since the density of water is1g/ml

Density of H3PO4 = 1.692g/ml

1ml=1.692g, 45g=?

,45g =26.6ml

- Therefore, take 26.6ml of H_3PO_4 from the stock and dilute to 100ml with distilled water to the mark.

Annex -7: Calculation of potassium Dichromate Requirement to prepare 1000mg/L of Cr (VI) stock solution

Calculate how much $K_2Cr_2O_7$ is required to get concentration of Cr (VI) stock solution of 1000mg/L (1g/1)

Potassium dichromate ($K_2Cr_2O_7$) has molecular weight = 2*39 +2*52+7*16 =78 + 104 +112 =

= 294g/mol

104 Cr (VI) is available in =294g of $K_2Cr_20_7$

1g Cr (VI) is available in = (294/104)*1 = 2.8269g of $K_2Cr_2O_7$

Annex-8: Calculation of Cr (VI) Standard Solution

Concentration of Stock Cr (VI) Solution = 1000mg/L preparation of concentration of Standard Chromium Cr (VI) solution

Cr (VI) C_l =1000mg/l mass of stock solution =mass of diluted solution

V_1 = lml $C_lV_l = C_2V_2$, V_2=100ml, C2= C_lV_l/V_2 =1000mg/1*1m1/100mg/1 C_2 =10mg/l

Preparation of different initial Cr (VI) standard solution from Cr (VI) standard working solution

Volume of extraction solution =25ml initial concentration of Cr (VI) standard working solution

C_1= 10mg/l Initial volume of Cr (VI) solution V_l=(0ml,0.5ml,1ml,2ml,4ml,10ml) required diluted solution volume of Cr (VI) V_2 =100ml

Required diluted concentration of Cr (VI) C_2=?

$C_1V_1=C_2V_2$

$C_2=C_1V_1 / V_2C_2$

= (10mg/1*0ml) 100ml=0mg/l

The same procedure was followed to calculate required diluted concentration of Cr (VI) C_2 for 0.5m, lml, 2ml, 4ml,10ml and their respective concentrations are 0.05mg/l, 0.1mg/l,0.2mg/l,0.4mg/l ,1mg/l Volume of distilled water = Total volume – (initial Volume of Cr (VI) +volume of extraction solution =100 – (0ml+25ml) = 75ml

Table -1: Standard hexavalent chromium working solution

Working standard chromium solution (ml)	*Concentration of chromium in mg/l*	*Absorbance*
0	0	0
0.5	0.05	0.024
1	0.1	0.055
2	0.2	0.123
4	0.4	0.249
6	0.6	0.386
10	1	0.636

Annex-9: Dilution of Cr (VI) stock solutions from 1000mg/L to the required working concentrations

Initial concentration of stock of Cr(VI), C_l =1000mg/L; Initial volume of stock solution of [Cr(VI)] =?

How to then, find our reduction dilute concentration of Cr (VI), C_2 = (2mg/l, 4mg/l, 6mg/l, 8mg/l, and 10mg/l)
Reduction dilute solution volume of Cr [(VI), V_2 = 50ml] can vary to required volume. According to the mass balance equation; we know Mass of stock solution = mass of diluted solution
$C_1V_1=C_2V_2$, $V_1 = C_2V_2/C_1V_1$=2mg/*50ml/1000mg/l = 0.1ml

Required demonized water =total volume no solution – initial volume of Cr (VI) 50ml - 0.1ml =49.9ml

The same procedure is followed to calculate for other required Cr (VI) concentration and their respective initial volume and required deionized water are: 0.1ml, 0.2ml, 0.33ml, 0.4ml, 0.5ml and 49.8ml, 49.67ml, 49.6ml, 49.5ml.

This initial volume was taken from Cr (VI) stock solution using 5ml pipette and added to 5ml pipette and added to 50ml volumetric flask and the remaining portion was filled up by deionizer water.

Table-2 Calculations of removal efficiency and biosorption capacity at various adsorbent Doses

Dose(mg)	Co(mg/l)	Ce(mg/l)	Ce*DF	Volume (Liter)	R (%)	qe(mg/g
75	6	0.31104	0.62208398	0.05	89.6319	3.58528
125	6	0.02805	0.0561076	0.05	99.0649	2.37756
150	6	0.0175	0.03499222	0.05	99.4168	1.98834
200	6	0.01459	0.02917574	0.05	99.5137	1.49271
225	6	0.01454	0.02908243	0.05	99.5153	1.32687

$$*R\ (\%) = (Co - Ce) * 100/Co = R(\%) = (6 - 0.622) * 100/6 = \boldsymbol{89.6\%}$$

$$*qe\left(\frac{mg}{l}\right) = (Co - Ce)V/M = (6 - 0.622)mg/l * 0.05l/0.075g = 5.378 * 0.6667 = \boldsymbol{3.585mg/g}$$

Where Co = initial Cr (VI) concentration before Biosorption

Ce= equilibrium concentration of Cr (VI) left in the solution after Biosorption

M= mass of Activated *O. Ficus Indicus* /OFI

V= total volume of solution

R= removal efficiency of activated *O. Ficus Indicus* /OFI

qe= Biosorption capacity of Activated *O. Ficus Indicus*

- ✓ The same procedure was followed to calculate R and qe for 0.075, 125 mg,150 mg, 200 mg, and 250 mg of *O. Ficus Indicus, as an sorbent.*

Table-3: Calculations of removal efficiency and adsorption capacity at various initial Cr (VI) Concentration

Co(mg/l)	Amount (g)	Ce(mg/l)	Ce*DF	Volume (Liter)	R (%)	qe(mg/g
2	0.125	0.013865	0.027729	0.05	98.61353	0.788908
4	0.125	0.033634	0.067267	0.05	98.31831	1.573093
6	0.125	0.070256	0.140512	0.05	97.65813	2.343795
8	0.125	0.140093	0.280187	0.05	96.49767	3.087925
10	0.125	0.29916	0.59832	0.05	94.0168	3.760672

$* R\ (\%) = (Co - Ce) * 100/Co$ =

$R(\%) = (2 - 0.0277)mg/l * 100/2mg/l$ = 1.9723 *100/2mg/l =***0.98615 *100***

$* qe\left(\frac{mg}{l}\right) = (Co - Ce)V/M$ =

$(2 - 0.0277) * 0.05l/0.075g = 1.9723mg/l * 0.4l/g$ =***0.7889mg/g***

- ✓ The same procedure was followed to calculate R and qe for initial Cr(VI) concentrations of 4,6,8 and 10

Table -4: Calculations of Removal Efficiency and biosorption capacity at various pH

PH	Co(mg/l)	Amount (g)	Ce(mg/l)	Volume (Littre)	R (%)	qe(mg/g)
2	6	0.125	0.033863	0.05	99.43561	2.386455
3	6	0.125	0.033806	0.05	99.43657	2.386478
4	6	0.125	0.033906	0.05	99.4349	2.386438
5	6	0.125	0.033918	0.05	99.4347	2.386433
6	6	0.125	0.03417	0.05	99.4305	2.386332
7	6	0.125	0.038129	0.05	99.36452	2.384749

- ✓ The same procedure was followed to calculate R and qe for various pH range

Table -5: Calculations of Removal Efficiency and Biosorption capacity at different Contact Time

Contact Time (minute)	Co (mg/l	Amount (g)	Ce(mg/l)	Volume (Liter)	R (%)	qe(mg/g)
30	6	0.125	0.1356563	0.05	95.47812	2.291475
60	6	0.125	0.05353717	0.05	98.21543	2.35717
90	6	0.125	0.02355955	0.05	99.21468	2.381152
120	6	0.125	0.02154457	0.05	99.28185	2.382764
150	6	0.125	0.02099988	0.05	99.3	2.3832

- ✓ The same procedure was followed to calculate R and qe for initial Cr(VI) for a various contact time.

Table -6: Calculations of Removal Efficiency and biosorption capacity at different Stirring Speed

Stirring Speed	Co (mg/l	Amount (g)	Ce(mg/l)	Volume (Liter)	R (%)	qe(mg/g)
50	6	0.125	0.13354	0.05	95.5486	2.29317
100	6	0.125	0.05545	0.05	98.1515	2.35564
150	6	0.125	0.01949	0.05	99.3503	2.38441
200	6	0.125	0.01914	0.05	99.362	2.38469

- ✓ The same procedure was followed to calculate R and qe for initial Cr(VI) for a various agitating speed.

Annex-10: Calculation of Langmuir and Freundlich sorption isotherm parameters for Cr(VI)adsorption on to O. Ficus Indicus .

Table-7: Langmuir Isotherm Parameters

Co (mg/l)	***Parameters***						
	Ce (mg/l)	qe (mg/g)	Ce/qe (mg/l)	b	qmax (mg/g)	R^2	RL
2	0.02773	0.78891	0.03515	7.5	4.585	0.999	0.06237
4	0.06727	1.57309	0.04276				0.03219
6	0.14051	2.3438	0.05995				0.02169
8	0.28019	3.08793	0.09074				0.01636
10	0.59832	3.76067	0.1591				0.01313

$$Ce/qe = {}^{1}/_{(b * qmax)} + Ce/qmax$$

Y= 0.218x+0.029

Ce/qe =Y, 1/ qmax= 0.218 (slop), and the intercept= 0.029

, l/qmax = 0.218 qmax =1/0.218= ***4.587***

,l/b qmax (the slop) =0.029,implies, 1/b=4.587*0.029 = 0.13303,b= ***7.517***

$$RL = \ 1/1 + Co * b$$

, where Co=2, 4, 6,8,10

, when, Co is 2mg/l

= 1(1+(7.517*2)) =1/(1+15.034))= 1/ 16.034 = 0.062367

, and when, Co is 10mg/l

=1/(1+(7.517*10) =1/1+75.17 =1/76.17 = 0.013129

✓ Thus, RL values ranges between ***0.0131 to 0.0624***

Table-8 : Freundlich Isotherm Parameters

Co (mg/l)	***Parameters***						
	Ce (mg/l)	qe (mg/g)	Log Ce (mg/l)	Log qe (mg/g)	1/n	Kf	R^2
2	0.027729393	0.78891	-1.557065792	0.035149073	0.505	5.572	0.956
4	0.067267496	1.57309	-1.172107941	0.042761296			
6	0.140512286	2.3438	-0.852286585	0.059950756			
8	0.280186625	3.08793	-0.552552019	0.090736204			
10	0.598320373	3.76067	-0.22306648	0.15909933			

$$\mathbf{Log\ qe = Log\ Kf + 1/nLogCe}$$

Y= 0.505x+ 0.746

Log qe=Y, 1/n =0.505 Log Ce = x, Log Kf= 0.746

1/n=***0.505***,n=***1.980***

Log Kf= 0,746, implies; Kf= ***5.57***

Annex-11: FT-IR data Test result

11.1 Before Adsorption

```
PE IR       SUBTECH     SPECTRUM    ASCII       PEDS        4.00
   -1
Before(Getahun).asc
17/10/13
10:14:44.00
17/10/13
10:15:18.00
Administrator
Sample 002 By Administrator Date Friday, October 13 2017
400.000000
#HDR
-1
-1
#GR
cm-1
%T
1.0
0.0
4000.000000
-1.000000
3601
8
69.641744
51.370344
#DATA
4000.000000    63.881213
3999.000000    63.877609
3998.000000    63.845692
3997.000000    63.808483
3996.000000    63.806300
3995.000000    63.847730
3994.000000    64.024437
3993.000000    63.825945
3986.000000    63.634787


            ’’’’

           ’’’’’

406.000000     63.908025
405.000000     63.593230
404.000000     64.319072
403.000000     63.967025
402.000000     63.937673
401.000000     63.851650
400.000000    63.803051
```

11.2. After Adsorption:

```
     PE IR SUBTECH SPECTRUM ASCII PEDS  4.00
   -1
After(Getahun).asc
17/10/13
10:08:28.00
17/10/13
10:08:45.00
Administrator
Sample 001 By Administrator Date Friday, October 13 2017
400.000000
#HDR
-1
-1
#GR
cm-1
%T
1.0
0.0
4000.000000
-1.000000
3601
8
76.073546
58.174741
#DATA
4000.000000    72.737122
3999.000000    72.669196
3998.000000    72.630335
3997.000000    72.665281
3996.000000    72.605282
3995.000000    72.654408
3994.000000    72.710410
3993.000000    72.660917
3992.000000    72.638024
3991.000000    72.651937
3990.000000    72.705885
3989.000000    72.676521
      ,,,,,,

      ,,,,,,,

     ,,,,,,,,

406.000000     70.604315
405.000000     72.156246
404.000000     70.381187
403.000000     72.453949
402.000000     72.772656
401.000000     72.397898
400.000000     71.794183
```

Annex-12: Required Reagents and Equipments

12. 1. REAGENT CHEMICALS

1- Stock chromium solution -Analytical grade potassium dichromate ($K_2Cr_2O_7$) ,(2.83g $K_2Cr_2O_7$)dissolved in 1000 ml distilled water) .
2- Standard chromium solution (stock chromium solution diluted to 0 mg/l, 0.05 mg/l, 0.1mg/l ,0.2mg/l 0.6 and 1mg/l)
3- Potassium permanganate solution- Dissolve 0.1 g KMnO4 in 100 mL distilled water
4- Diphenyl carbazide solution: Dissolved 250 mg 1,5-dipHenylcarbazide(1,5-dipHenylcarbohydrazide) in 50 mL acetone.
5- 2 N NaOH
6- Nitric acid, HNO_3, conc.
7- Sulfuric acid, 6N H2SO4, conc. ,
8- Sulfuric acid, H2SO4, 0.2N:
9- Distilled water -reagent water
10- Phosphoric acid, H_3PO_4, conc. (45%)
11- Methyl orange indicator solution
12- Ammonium hydroxide, NH4OH, conc.
13- Sodium azide solution: Dissolve 0.5 g NaN3 in 100 mL water.

12.2. EQUIPMENTS

1- UV-Vis spectrophotometers of model Varian Cary 300
2- Funnels –plastic funnels
3- Volumetric and conical flask (50-250 ml)
4- Glass Pipette
5- Plastic Filler
6- Adsorption cell (1-cm)
7- PH meter –Orion, model SA 720
8- Analytical balance
9- Filter paper – Whatmann