# "Equilibrium Modeling and Kinetic Studies on the Biosorption of Chromium (III) from Synthetic waste Water using *Cupressus torulosa* and *Taxus baccata*"

Thesis

**Submitted to the**


**G. B. Pant University of Agriculture & Technology**
**Pantnagar- 263145, Uttarakhand, India**

**By**

**Anil Verma**
**(M. Sc. Agricultural Chemicals)**

***IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF***

# Doctor of Philosophy
## (Agricultural Chemicals)

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*God keep me and guide me and go with me today"*

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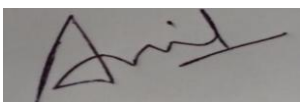


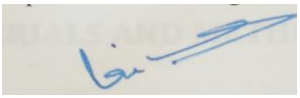
Pantnagar
August, 2017

**(Anil Verma)**
Author

# CERTIFICATE

This is to certify that the thesis entitled **"Equilibrium Modeling and Kinetic Studies on the Biosorption of Chromium (III) from Synthetic waste Water using *Cupressus torulosa* and *Taxus baccata*"** submitted in partial fulfillment of the requirements for the degree of **DOCTOR OF PHILOSOPHY** with major in **Agricultural Chemicals** & minor in **Environmental Science** of the college of Post Graduate Studies, G.B. Pant University of Agriculture & Technology Pantnagar, is a record of bonafide research carried out by **Mr. Anil Verma, ID. No. 39376,** under my supervision, and no part of the thesis has been submitted for other degree or diploma.

The assistance and help received during the course of this investigation have been acknowledged.



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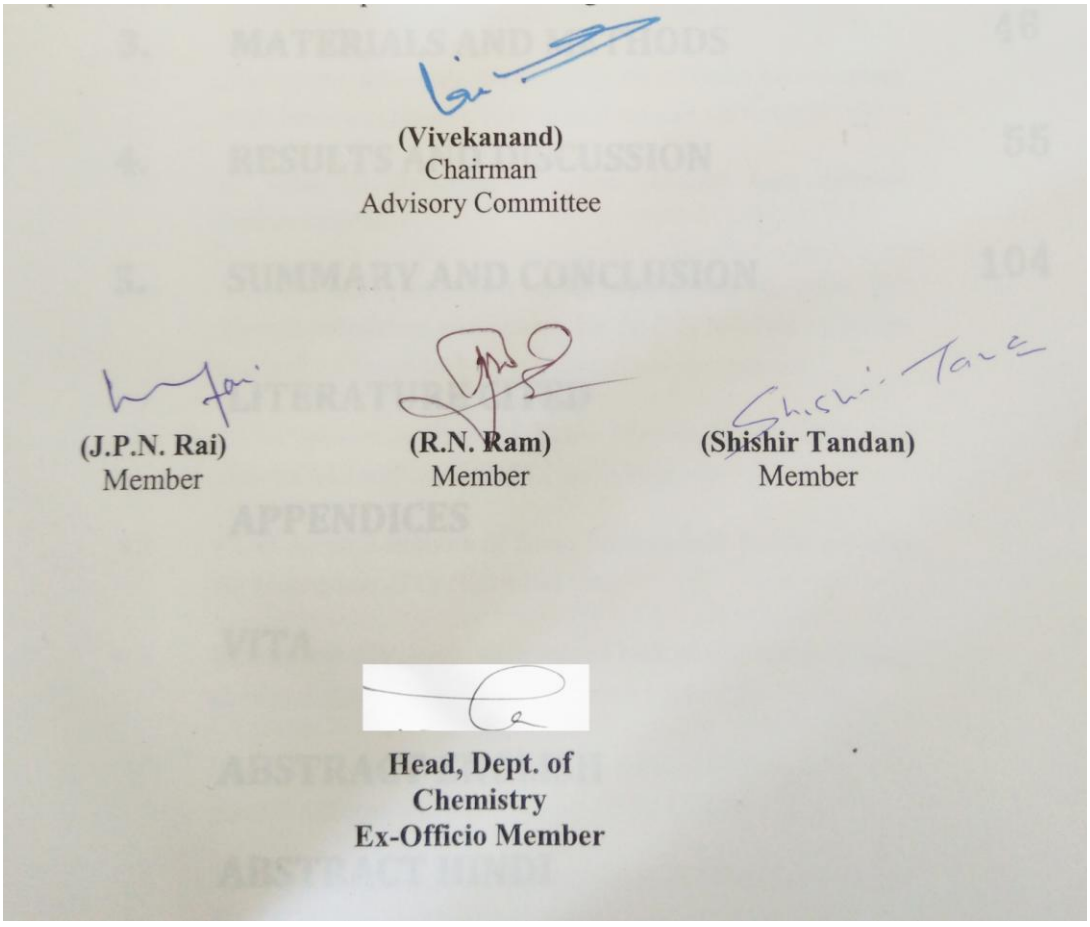
August, 2017

**(Viveka Nand)**
Chairman
Advisory Committee

# CERTIFICATE

We, the undersigned, member of the Advisory committee of **Mr. Anil Verma, ID. No. 39376,** a candidate for the degree of **DOCTOR OF PHILOSOPHY** with major in **Agricultural Chemicals** & minor in **Environmental Science** agree that the thesis entitled **"Equilibrium Modeling and Kinetic Studies on the Biosorption of Chromium (III) from Synthetic waste Water using *Cupressus torulosa* and *Taxus baccata*"** may be submitted in partial fulfillment of the requirements of the degree.



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**(J.P.N. Rai)**
Member

**(R.N. Ram)**
Member

**(Shishir Tandan)**
Member

**Head, Dept. of Chemistry**
**Ex-Officio Member**

# CONTENTS

# *Chapter 1* INTRODUCTION

The rapid growth in global population and urbanization has driven an exponential increase in industrial activities, which is convoyed by an increase in the amount of industrial wastes being release into the environment, hence the increase in heavy metals such as cadmium, mercury, lead, copper, zinc, nickel and chromium posting substantial risk to soil, water and human health. Heavy metal states to any element atomic weight between 63.5 to 200.6 and specific gravity greater than 5.0 **(Srivastava, N.K. and C.B. Majumder, 2008).** Heavy metals are known to pose grave health danger to human, terrestrial and aquatic lives if their concentration exceeds the maximum permitted limits. Concentration below these limits have prospective for long term contamination, because heavy metals are known to acquisitive within biological systems (**Malakootian *et al*., 2008**).

Heavy metals in the aquatic medium may create from wastewater of many industries, such as batteries, tanneries, electrical, electroplating, fertilizers, pesticides, mining, refining ores, etc. **(Banerjee *et al*., 2012; Manzoor *et al*., 2013**). Due to their dangerous effects, persistency and accumulation tendency, heavy metals can pose a risk to the human and environmental health **(Kumar *et al.*, 2012; Marin *et al*., 2010).** The contact to heavy metals can cause damage to many parts of human bodies, even at very low concentrations. Therefore, the removal of heavy metals from aqueous solutions is of dangerous importance **(Bharakat, 2011).**

In recent times, Heavy metals in general and Chromium in particular has received a great deal of consideration because of their toxicity. Though the most principal forms of chromium are Cr (VI) and Cr (III), Cr (VI) is more toxic **(Smith and Lec, 1972).** The anthropogenic sources include, burning of oil and coal, production of ferrochromium, chromate, chromium steels, fungicides, cement, pigments, catalysts, and oxidants. It is also increasingly used in metal plating, tanneries, and oil well drilling (**Abbasi and Soni, 1985 & 1998).** Revelation to Cr (VI) causes cancer in digestive tract and lungs **(Kaufaman, *et al.* 1970)** and may cause epigastric pain, nausea, vomiting, severe diarrhoea and haemorrhage **(Browning, 1969)**. It can cause serious disorders and disease when hoarded at high levels and it can be ultimately lethal. There is suggestive evidence that Cr (VI) causes

augmented risk of bone prostate cancer, lymphomas, Hodgkins, leukemia, stomach, genital, renal, and bladder cancer, dazzling the ability of Cr (VI) to penetrate all tissues in the body **(Max Costa, 1997**).The hexavalent form of chromium is considered to be a group "A" human carcinogen because of its mutagenic and carcinogenic properties **(Cieslak-Golonka, 1995).**

The hexavalent form of chromium is deliberated to be a group "A" human carcinogen because of its mutagenic and carcinogenic properties **(Cieslak, 1996)**. It leads to liver damage, pulmonary congestion, edema, and causes skin irritation, resulting in ulcer formation **(Raji and Amiridhan, 1998)**. Its concentration in industrial waste water ranges from 0.5 mg/L to 270,000 mg/L **(Patterson, 1985)**. The tolerance limit for the discharge of Cr (VI) into inland surface water is 0.1 mg/L and in potable water is 0.05 mg/L **(EPA, 1990**). Heavy metal removal from inorganic effluent can be attained by conventional treatment processes such as chemical precipitation, ion exchange, and electrochemical removal. These processes have important disadvantages which are, for instance, incomplete removal, high-energy requirements, and production of toxic sludge (Eccles, 1999). Recently, many approaches have been studied for the growth of cheaper and more effective technologies, both to decrease the amount of wastewater produced and to improve the quality of the preserved effluent. Adsorption has become one of the alternative treatments, in recent years, the search for low-cost adsorbents that have metal-binding dimensions has intensified **(Leung *et al.,* 2000**). The adsorbents may be of mineral, organic or biological origin, zeolites, industrial byproducts, agricultural wastes, biomass, and polymeric materials **(Kurniawan *et al.,* 2005)**. Membrane separation has been increasingly used recently for the treatment of inorganic effluent due to its suitable operation. There are different types of membrane filtration such as ultrafiltration (UF), Nanofiltration (NF) and reverse osmosis (RO) **(Kurniawan *et al.,* 2006)**. Electro treatments such as electrodialysis **(Pedersen, 2003)** has also contributed to environmental protection. Photocatalytic process is an advanced and promising technique for efficient destruction of pollutants in water **(Skubal *et al.,* 2002)**. Although many techniques can be employed for the treatment of inorganic effluent, the ideal treatment should be not only suitable, suitable and applicable to the local conditions.

Many technologies have been established for heavy metal decontamination. Traditional treatment processes include precipitation, ion exchange, membrane filtration, electroplating, adsorption **(Banerjee *et al.*, 2012).**These methods represent significant failings, such as high chemical and energy requirements, hazardous sludge formation, low productivity when heavy metals concentration below 100 mg/L, high cost at large scale **(Marin-Rangel *et al.*, 2012; Mishra *et al.*, 2012).** Likewise, high price and limited reusability are key problems, hindering the widespread application of activated carbon, a commonly used adsorbent in heavy metal treatment **(Turan and Mesci, 2011)** In that context, bio sorption has emerged as a promising method, with such advantages as (1) high efficiency even with low metal concentrations, (2) low cost, (3) no additional nutrients requirements, (4) easy operation, (5) possible metal recovery, and (6) without destructive effects on the environment **(Jiménez Cedillo *et al.*, 2013; Manzoor *et al.*, 2013; Mishra *et al.*, 2010).**

Gymnosperm is frugally important group of plant spread all over the globe, primarily in the temperate regions and higher elevation of tropics. The trees are used for landscaping, timber, building construction, resin, and for the manufacture of paper and board. They are also used in medicines, perfumes, varnishes, and essential oils **(Bhatnagar and Moitra, 2004).** The Gymnosperm are a group of seed-producing plants that comprise Conifers, Cycads, Ginkgo, and Gnetals. The term "Gymnosperm" comes from Greek words gymnosperms, meaning "naked seeds", after the unenclosed condition of their seeds (called ovules in their unfertilized state). **Tewari *et al.* (2010)** reported that a total 63 species fit in to 10 families, of these 47 species are exotic to the state. Origin-wise status of both bizarre and wild gymnosperms demonstrated that 26.98% species are of American source followed by the Indian subcontinent (19.04%), China (11.11%), japan (9.52%), Asia-temperate and Europe (7.93%), Africa (6.34%), Australia (4.76%), indo-china and the Mediterranean region (3.17%).

1. ***Cupressus torulosa* D.Don**

| | | |
|---|---|---|
| Kingdom | : | Plantae |
| Division | : | Pinophyta |

| | | |
|---|---|---|
| Class | : | Pinopsida |
| Order | : | pinales |
| Family | : | cupressaceae |
| Genus | : | *Cupressus* |
| Species | : | *C.torulosa Don* |
| English Name | : | Himalayan Cypreass |
| Common name | : | Surai Raisal |

General distribution and habitat : China in arid areas at 1500-2500 in India (Kashmir, Arunanchal Pradesh, Nepal, Tibet, Pakistan, Bhutan, W. Himalaya at 1800-3000 m limestone substrates, It is dimness intolerant species thriving in tropical and subtropical rainforest ,and desires calcareous substrates (**Fig. 1.1).**

**Morphological Description:** A large evergreen tree commonly 3.6 m in girth and 45 m in height, with a pyramidal crown with horizontal or loose branches .Bark is dense grey brown, peeling off in long thin strips. Leaves are scale – like triangular closely described, obtuse, dark green, often with a small dorsal furrow, flowers are monoecious, male catkins 5-6 mm long, often tinged purple, solitary at the tips of the branches lets, Cones globose, woody, male cone sub globuler, 5-6 mm long, female cones globose or elliptic grouped on very short stalks,10-20mm across, green or purple when young, later turning dark brown, compound of 6-8 (10 ) scales, with a small central depression and a small, triangular, scales are woody and 6-10 and seeds are compressed 6-8 on each scale, pale brownish.

**Uses**

The plants is burnt as incense .The essential oil of leaves is used in medicine to treatment inflammatory wounds, or as an antiseptic. It is a prime timber with straight grain and fine texture, resistant to termites and insects, wood – moderately hard, very durable ,used for general construction and utilized for aroma purpose, especially the root –wood , and an essential oil removed from these parts is used in cosmetics and used as antiseptics **(The plants Database).**

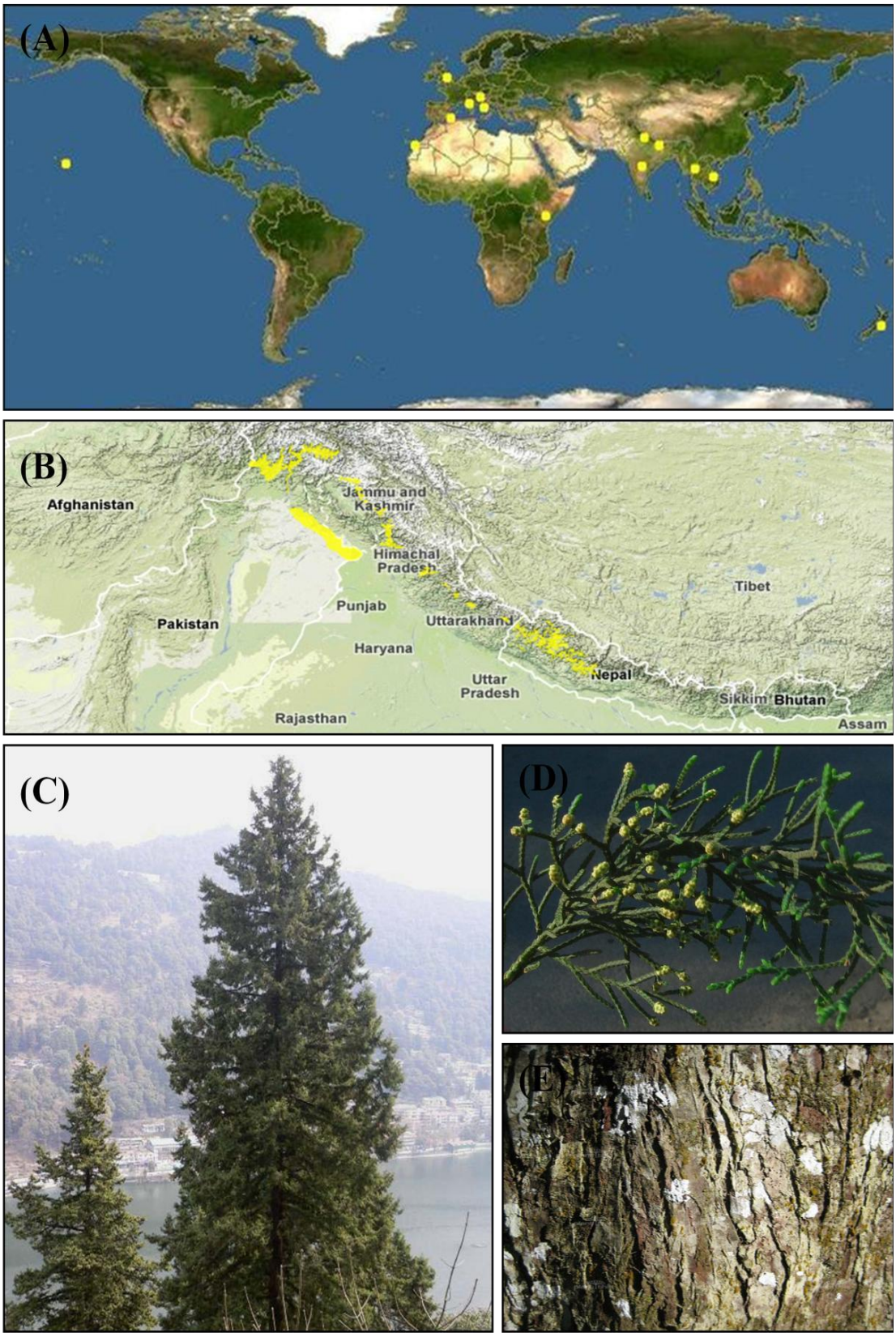



**Fig.1.1 (A) worldwide distribution, (B) distribution in india, (C) complete plant, (D) leaf and (E) bark of *Cupressus torulosa***

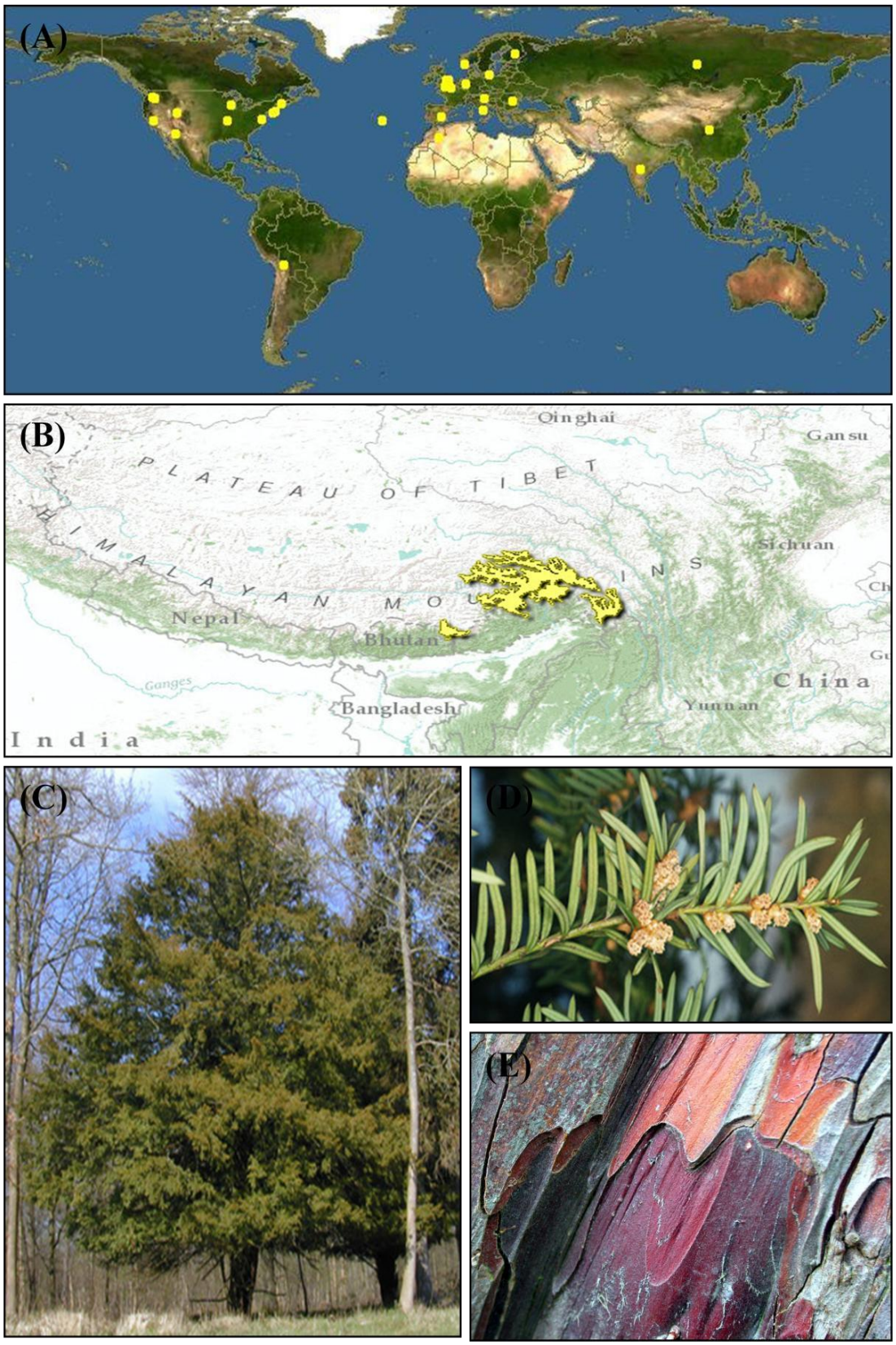



**Fig.1.2 (A) worldwide distribution, (B) distribution in india, (C) complete plant, (D) leaf and (E)bark of *Taxus baccata* plant**

**2. *Taxus Baccata* Linn**

Taxonomy:

| | | |
|---|---|---|
| Kingdom | : | Plantae |
| Division | : | Pinophyta |
| Class | : | Pinopsida |
| Order | : | Pinales |
| Family | : | Taxaceae |
| Genus | : | *Taxus* |
| Species | : | *T. baccata* |
| English name | : | Common yew |
| Common name | : | Thuner |

General distribution and habitat: Taxaceae Buccata Linnis a conifer native to Western, Central and Southern Europe, North West, Africa, Afganistan, India (eastern and Western Himalaya from Kashmir to Arunanchal Pradesh, Naga Hills, khasi hills Manipur, Myanmar, South West china, West Pakistan, Europe, including Britain. The plant prefers light (sandy), medium (loamy) and heavy (clay) soils, requires well exhausted soil and can grow in heavy clay soil. It requires dry or moist soil and can tolerate drought **(Fig 1.2).**

**Morphological Description:**

It is a small to medium - sized evergreen tree, growing 10-20 m (exceptionally up to 28 m) tall, with a trunk up to 2 m (exceptionally 4 m) diameter. the bark is reedy, reddish or scaly brown, coming off in small flakes aligned with the stem leaves are highly poisonous, flowers are dioecious, male flowers in tassels which are sub-globose and solitary in the leave axils ,stamens about ten, pollen sacs 5-4, globose ,arranged around the filament beneath the tip of the stamen female, female flowers solitary, axillary, each consisting of a few imbricate scales around in erect ovule surrounded at the base by a membranous cup shaped disk, seeds are 4-7 mm long surrounded by a adapted scale which develops into a soft, bright red berry –like structure called an aril.

**Uses**

The colourful wood (red heartwood, white sapwood) used to veneer furniture, to make lute bodies, bowls, tankards, combs, tool handles, pages, and various art objects. The red aril surrounding the seed can be bothered bark used as a tea substrates.

**Objectives**

1. The plant materials shall be collected from the low altitudinal areas of Uttarakhand hills.
2. The biomass was be obtained from the leaves and barks of *Cupressus torulosa* and *Taxus baccata*. Biomass have activated by chemical modifications for activation of different functional groups.
3. Identification of active sites of bioadsorbent and ligation by Infrared Spectroscopy (IR).
4. Preparation of Chromium waste water solution by using chromium sulphate.
5. Characterization of bioadsorption through SEM and concentration of residual metallic ion shall be determined by Atomic Absorption Spectroscopy (AAS).
6. Comparative adsorption potential studies will be carried out with respect to time, temperature, pH, concentration of chromium solution and amount of bio adsorbent through batch experiment.

The proposed investigation give an environmental friendly, low cost and high efficiency water purification technique for villages.

# *Chapter 2* REVIEW OF LITERATURE

Water is vital for survival. But today about 200 million people in India do not have admittance to safe drinking water due to water pollution. Water pollution raises a great concern now-a-days since water founds a basic necessity in life. The fast-paced development of industries such as metal mining operations, fertilizers and paper industries and pesticides have consciously discharged various types of pollutants into the environment (**Abas *et al.*, 2013).**

Water pollution due to the disposal of heavy metals continues to be a great matter concern. Consequently, the treatment of polluted industrialized wastewater remains a topic of global concern since wastewater collected from municipalities, communities and industries must ultimately be to getting waters or to the land **(Weber Jr *et al.*, 1991).** Heavy metals pollution occurs in much industrial wastewater such as that shaped by metal plating facilities, mining operations, battery manufacturing processes, the production of paints and pigments, and the ceramic and glass industries. This wastewater commonly includes Cd, Pb, Cu, Zn, Ni and Cr **(Argun and Dursun, S. 2008).** Whenever toxic heavy metals are free to the environment, accumulation of metal ions in human and animal bodies will enter through direct intake or food chains. Therefore, heavy metals should be stopped from reaching the natural environment **(Meena *et al.*, 2008)**. In order to eliminate toxic heavy metals from water systems, traditional methods have been used were chemical precipitation, coagulation, solvent extraction, ion exchange, and filtration, evaporation and membrane methods **(Panayotova, M. and Velikov, B. 2008).** Adsorption of heavy metals on traditional adsorbents such as activated carbon have been used on big scale in used as as an effective adsorbent, and the activated carbon produced by carbonizing organic materials is the most widely used adsorbent. However, the high cost of the activation process limits its uses in wastewater treatment function **(Amarasinghe and William 2007).**

Chromium is a common heavy metal pollutant with different species of varying valence states. In recent years of the cosmopolitan process of industrialization and urbanization, the industry of tannery and electroplating has discharged a large amount of hazardous chromium into water, air and soil **(Belay, 2010; Deveci and**

**Kar, 2013; Mohan *et al*., 2011; Montanes *et al*., 2014; Wang *et al*., 2014)**. Trivalent chromium [Cr (III)] ion and hexavalent chromium [Cr (VI)] ion are two common major species of chromium. Trace Cr (III) ion is essential for mammals, but detrimental when present in excess. Meanwhile, Cr (VI) ion with significantly higher solubility and mobility than Cr (III) is highly dangerous because of its toxic, carcinogenic, allergenic, and irritant effects, especially causing damage of liver, lung and kidney **(Dayan and Paine, 2001; Kimbrough *et al*., 1999; Mohan and Pittman, 2006; Saha *et al*., 2011).**

## 2.1 Heavy metals

Heavy metal states to any element atomic weight between 63.5 to 200.6 and specific gravity greater than 5.0 **(Srivastava, N.K. and C.B. Majumder, 2008).** Any metallic element that own relatively high density and is toxic or poisonous at low concentration **(Lenntech, 2004).** A general collective term which appropriate to the group of metals and metalloids with atomic density greater than 4g/cm$^{3,}$ or 5 times or more greater than water **(Hutton and Symon, 1986; Nriagu and Pacyna, 1988; Nriagu, 1989; Garbarino *et al*., 1995, Hawkes, 1997).** However, being a heavy metal has little to do with density but concerns chemical properties.

Heavy metals are non-biodegradable pollutants and they are very difficult to remove naturally from the Environment. Almost all heavy metal elements are highly toxic when their concentration exceeds their permissible limit in the ecosystem. High concentration of heavy metals may accumulate in the human body once they interrupt in human food chain and possibly in effect, cause severe health problems if the metals crosess the permitted concentration **(Babel and. Kurniawan, 2004).**

## 2.2 Carcinigenic/Toxic metals

Metals are an important class of human carcinogens. At least five transition metals arsenic, cadmium, chromium, beryllium and nickel, are accepted as human carcinogens in one form or another or in particular way to exposure (NTP, 2002). The mechanism responsible for metal carcinogenesis is subtle partly because of the complex nature of metals interactions in biological systems. This is probably due the result of similar binding preferences between carcinogenic metals and nutritionally essential metals **(Clarkson, 1986)**. Metals are not required bioactivation at least not in

the sense that an organic molecule undergoes enzymatic modification that produces a reactive chemical species **(Waalkes, 1995)**. Enzymatic alteration is normally not a mechanism accessible to detoxify metals. However, metals use other detoxification mechanisms such as long-term storage (e.g., cadmium) and biliary and/or urinary excretion. main organ sites for metals as carcinogens are concluded by **Waalkes** (**1995**). It should be noted that essential metals can be carcinogenic on the basis of oxidation state. For example, chromium (III) is essential and chromium (VI) is carcinogenic.

**Effects of heavy metals on aquatic organism's**

Aquatic organisms affected by heavy metals in the environment. The toxicity is mainly a function of the water chemistry and sediment composition from surface water system. **(Volesky, 2003)** shows how metal ions can become bioaccumulated in an aquatic ecosystem. The metals are mineralized by microorganisms, which in turn are taken up by plankton and further by the aquatic organisms. Finally, the metals now, several times biomagnified is taken up by man when he consumes fish from the contaminated water.

i.) Slightly elevated metal levels in natural waters may cause the following sub lethal effects in aquatic organisms: histological or morphological change in tissues.

ii.) Changes in physiology, such as conquest of growth and development, poor swimming performance, changes in circulation

iii.) Change in biochemistry, such as enzyme activity and blood chemistry

iv.) Change in behaviour; and

v.) Changes in reproduction **(Connell *et al*., 1984).**

Many organisms are able to control the metal concentrations in their tissues. Fish and crustacea can excrete essential metals, such as copper, zinc, and iron that are present in excess. Some can also excrete non-essential metals, such as mercury and cadmium, although this is usually met with less success **(Connell *et al*., 1984**). Research has shown that aquatic plants and bivalves are not able to successfully regulate metal uptake **(Connell *et al*., 1984).** Thus, bivalves tend to suffer from metal

accumulation in polluted environments. In estuarine systems, bivalves often serve as bio-monitor organisms in areas of suspected pollution. Shell fishing waters are closed if metal levels make shellfish unfit for human consumption. In comparison to freshwater fish and invertebrates, aquatic plants are equally or less sensitive to cadmium, copper, lead, mercury, nickel, and zinc. Thus, the water resource should be managed for the protection of fish and invertebrates, in order to ensure aquatic plant survivability **(USEPA, 1987)**. Metal uptake rates will vary according to the organism and the metal in question. Phytoplankton and zooplankton often assimilate available metals quickly because of their high surface area to volume ratio. The ability of fish and invertebrates to adsorb metals is largely dependent on the physical and chemical characteristics of the metal. With the exception of mercury, little metal bioaccumulation has been observed in aquatic organisms. Metals may enter the systems of aquatic organisms via three main pathways:

i.) Free metal ions that are absorbed through respiratory surface (e.g., gills) are readily diffused into the blood stream.

ii.) Free metal ions that are adsorbed onto body surfaces are passively diffused into the blood stream.

iii.) Metals that are sorbed onto food and particulates may be ingested, as well as free ions ingested with water **(Connell *et al*., 1984)**. For eg: Chromium is not known to accumulate in the bodies of fish, but high concentrations of chromium, due to the disposal of metal products in surface waters, can damage the gills of fish that swim near the point of disposal.

**Irrigation effects of heavy metals**

Irrigation water contaminated with sewage or industrial effluents may transport dissolved heavy metals to agricultural fields. Although most heavy metals do not pose a threat to humans through crop consumption, cadmium may be incorporated into plant tissue. Accumulation usually occurs in plant roots, but may also occur throughout the plant **(De Voogt *et al*., 1980**). Most irrigation systems are designed to allow for up to 30 percent of the water applied to not be absorbed and to leave the field as return flow. Return flow either joins the groundwater or runs off the field surface (tailwater). Sometimes tailwater are rerouted into streams because of

downstream water rights or a necessity to maintain streamflow. However, usually the tailwater is collected and stored until it can be reused or delivered to another field **(USEPA 1993a)**. Tailwater is often stored in small lakes or reservoirs, where heavy metals can accumulate as return flow is pumped in and out. These metals can adversely impact aquatic communities. An extreme example of this is the Kesterson Reservoir in the San Joaquin Valley, California, which received subsurface agricultural drainwater containing high levels of selenium and salts that had been leached from the soil during irrigation. Studies in the Kesterson Reservoir revealed elevated levels of selenium in water, sediments, terrestrial and aquatic vegetation, and aquatic insects. The elevated levels of selenium were cited as relating to the low reproductive success, high mortality, and developmental abnormalities in embryos and chicks of nesting aquatic birds **(Schuler *et al*., 1990)**.

## 2.3 Source of heavy metal contamination

Informed sources of heavy metals in the environment include geogenic, industrial, agricultural, pharmaceutical, domestic effluents, and atmospheric sources. Environmental pollution is very prominent in point source areas such as mining, foundries and smelters, and other metal-based industrial operations **(Fergusson 1990; Bradl; 2002; ZL *et al*., 2005).**

Although heavy metals are naturally occurring elements that are found all over the earth's crust, mainly environmental contamination and human exposure result from man-made activities such as mining and smelting operations, industrial production and use, and domestic and agricultural use of metals and metal-containing compounds **(Goyer 2001; Herawati *et al*., 2001; Shallari *et al*., 1998).** Environmental contamination can also occur through metal corrosion, atmospheric deposition, soil erosion of metal ions and leaching of heavy metals, sediment re-suspension and metal evaporation from water assets to soil and ground water **(Nriagu 1989)**. Natural phenomena such as weathering and volcanic eruptions have significantly contribute to heavy metal pollution Industrial sources include metal processing in refineries, coal burning in power plants, petroleum combustion, nuclear power stations and high tension lines, plastics, textiles, microelectronics, wood

preservation and paper processing plants **(Arruti *et al.*, 2010; Sträter *et al.*, 2010; Pacyna 1996).**

Wastewater from Industrial streams containing heavy metals are produced from various industries. Electroplating and metal surface treatment procedures generate significant quantities of wastewaters containing heavy metals (such as cadmium, zinc, lead, chromium, nickel, copper, vanadium, platinum, silver, and titanium). Other sources for the metal wastes include; the wood processing industry where a chromated copper-arsenate wood treatment produces arsenic containing wastes; inorganic pigment manufacturing producing pigments that contain chromium compounds and cadmium sulfide; petroleum refining which generates conversion catalysts contaminated with nickel, vanadium, and chromium; and photographic operations producing film with high concentrations of silver and ferrocyanide. All of these generators produce a large quantity of wastewaters, residues, and sludges that can be categorized as hazardous wastes requiring extensive waste treatment (**Sorme and Lagerkvist, 2002**). Therefore, there has been increasing concern about exposures, intakes and absorption of heavy metals by humans.

The two most common valences for chromium in aqueous solutions are $3^+$ and $6^+$ **(Dahbi *et al.*, 2002)**. Water soluble hexavalent chromium is extremely irritating and toxic to tissues of human body **(Peräniemis and Ahlgrén, 1995)**. When tanning wastewater is disposed without treatment, the infiltration of liquid wastes into ground water resources may cause major pollution problems because Cr (III) would be oxidized to Cr (VI), and hence create high risks to environment and people. On this basis, it was considered worthwhile and essential to monitor and control the chromium content in tanning wastewater. The toxicity, mobility and bioavailability of Cr, a versatile industrial metal and a contaminant, depends on its chemical form, *viz*: Cr (III) ion and Cr(VI) ion. It may enter humans through plants grown on contaminated soil or irrigated by contaminated water. The chemical form in which Cr (III) is transported by xylem sap was investigated **(Shikha and Satya, 2006)**. In tanning industry, the chromium concentration in terms of total chromium in the exhaust chromium liquor, with a volume of 4% to 6% of the total wastewater volume discharged from the tanning process, ranges from 1,500- 5,000 mg/L. The liquor is mixed with other effluent streams from tannery process causing dilution, and thus the

concentration of chromium becomes 100-300 mg/L. In maximum countries, pollution control authorities do not permit the presence of more than 2 mg/L of Cr (III) in treated effluent. Although international standards of wastewater effluents is not more than 0.05 mg/L Cr(VI) and 5.0 mg/L Cr(III) **(Reilly, 1991).**

**Chromium and its Toxicity in living organism**

**Environmental Occurrence, Industrial Production and Use**

Chromium (Cr) is a natural element present in the earth's outside, with oxidation states (or valence states) ranging from chromium (II) to chromium (VI) **(Jacobs and Testa, 2005).** Chromium compounds are stable in the trivalent [Cr(III)] form and occur in nature in this state in ores, such as ferrochromite. The hexavalent [Cr(VI)] form is the second-most stable state **(Patlolla *et al.*, 2009).** Elemental chromium [Cr(0)] does not occur obviously. Chromium enters into various environmental matrices (air, water, and soil) from a wide variety of natural and Man made with the largest release coming from industrial establishments. Industries with the largest contribution to chromium release include metal processing, tannery facilities, chromate production, stainless steel welding, and ferrochrome and chrome pigment production. The increase in the environmental concentrations of chromium has been linked to air and wastewater release of chromium, mainly from metallurgical, refractory, and chemical industries. Chromium freed in the environment from anthropogenic activity occurs mainly in the hexavalent form [Cr(VI)] **(ATSDR 1990).** Hexavalent chromium [Cr (VI)] is a toxic factory pollutant that is classified as human carcinogen by several regulatory and non-regulatory agencies **(ATSDR, IARC and USEPA 1990)**. The health hazard associated with exposure to chromium which may depend on oxidation state, ranging from the low toxicity of the metal form to the high toxicity of the hexavalent form. All Cr (VI)-containing compounds were once thought to be man-made, with only Cr (III) naturally ubiquitous in air, water, soil and biological materials. Recently, however, naturally occurring Cr (VI) has been found in ground and surface waters at values exceeding the World Health Organization limit for drinking water of 50 µg of Cr(VI) per liter **(Velma *et al.*, 2009).** Chromium is widely used in numerous industrial processes and as a result, is a contaminant of many environmental systems **(Cohen *et al.*, 1993)**. Commercially

chromium compounds are used in industrial welding, chrome plating, dyes and pigments, leather tanning and wood preservation. Chromium is also used as anticorrosive in cooking systems and boilers **(Norseth 1981, Wang *et al.*, 2006).**

**Potential for Human Exposure**

It is estimated that more than 300,000 workers are exposed annually to chromium and chromium-containing compounds in the workplace. In humans and animals, [Cr(III)] is an essential nutrient that plays a role in glucose, fat and protein metabolism by potentiating the action of insulin **(Goyer, 2001)**. However, occupational exposure has been a major concern because of the high risk of Cr-induced diseases in industrial workers occupationally exposed to Cr(VI) **(Guertin, 2005)**. Also, the general human population and some wildlife may also be at risk. It is estimated that 33 tons of total Cr are released annually into the environment **(ATSDR 2009)**. The U.S. Occupational Safety and Health Administration (OSHA) recently set a "safe" level of 5µg/$m^3$, for an 8-hr time-weighted average, even though this revised level still pose a carcinogenic risk **(OSHA, 2006)**. For the general human population, atmospheric levels range from 1 to 100 ng/$cm^3$ **(Singh *et al.*, 1999),** but may exceed this variety in areas that are close to Cr manufacturing.

Non-occupational exposure occurs via ingestion of chromium containing food and water whereas occupational exposure occurs via inhalation **(Langård 1983)**. Chromium concentrations range between 1 and 3000 mg/kg in soil, 5 to 800 µg/L in sea water, and 26 µg/L to 5.2 mg/L in rivers and lakes **(Jacobs and Testa, 2005)**. Chromium content in foods varies greatly and depends on the processing and preparation. In general, most fresh foods typically contain chromium levels ranging from <10 to 1,300 µg/kg. Present day workers in chromium-related industries can be exposed to chromium concentrations two orders of magnitude higher than the general population **(ATSDR, 2008)**. Even though the principal route of human exposure to chromium is through inhalation, and the lung is the primary target organ, substantial human exposure to chromium has also been reported from the skin (**Costa 1997 and Shelnutt, 2007)**. For example, the widespread incidence of dermatitis noticed among construction workers is attributed to their exposure to chromium present in cement. Occupational and environmental exposure to Cr (VI)-containing compounds is known

to cause multiorgan toxicity such as renal damage, allergy and asthma, and cancer of the respiratory tract in humans **(WHO/IPCS, 1988).**

Breathing high levels of chromium (VI) can cause irritation to the lining of the nose, and nose ulcers. The main health problems seen in animals following ingestion of chromium (VI) compounds are irritation and ulcers in the stomach and small intestine, anemia, sperm damage and male reproductive system damage. Chromium (III) compounds are less toxic and do not appear to cause these problems. Some individuals are extremely sensitive to chromium(VI) or chromium(III), allergic reactions consisting of severe redness and swelling of the skin have been noted. An increase in stomach tumors was observed in humans and animals exposed to chromium (VI) in drinking water. Accidental or intentional ingestion of extremely high doses of chromium (VI) compounds by humans has resulted in severe respiratory, cardiovascular, gastrointestinal, hematological, hepatic, renal, and neurological effects as part of the sequelae leading to death or in patients who survived because of medical treatment. Although the evidence of carcinogenicity of chromium in humans and terrestrial mammals seems strong, the mechanism by which it causes cancer is not completely understood **(Chen *et al.*, 2009).**

**Mechanisms of Toxicity and Carcinogenicity**

Major factors governing the toxicity of chromium compounds are oxidation state and solubility. Cr(VI) compounds, which are powerful oxidizing agents and thus tend to be irritating and corrosive, appear to be much more toxic systemically than Cr(III) compounds, given similar amount and solubility **(Connett and Wetterhahn, 1983, De Flora *et al.*, 1990**). Although the mechanisms of biological interaction are uncertain, the variation in toxicity may be related to the ease with which Cr(VI) can pass through cell membranes and its subsequent intracellular reduction to reactive intermediates. Since Cr(III) is poorly absorbed by any route, the toxicity of chromium is mainly attributable to the Cr(VI) form. It can be absorbed by the lung and gastrointestinal tract, and even to a certain extent by intact skin. The reduction of Cr(VI) is considered as being a detoxification process when it occurs at a distance from the target site for toxic or genotoxic effect while reduction of Cr(VI) may serve to activate chromium toxicity if it takes place in or near the cell nucleus of target

organs **(Dayan and Paine, 2001)**. If Cr(VI) is reduced to Cr(III) extracellularly, this form of the metal is not readily transported into cells and so toxicity is not observed. The balance that exists between extracellular Cr(VI) and intracellular Cr(III) is what ultimately dictates the amount and rate at which Cr(VI) can enter cells and impart its toxic effects **(Cohen *et al.*, 1993)**.

Cr(VI) enters many types of cells and under physiological conditions can be reduced by hydrogen peroxide ($H_2O_2$), glutathione (GSH) reductase, ascorbic acid, and GSH to produce reactive intermediates, including Cr(V), Cr(IV), thiylradicals, hydroxyl radicals, and ultimately, Cr(III). Any of these species could attack DNA, proteins, and membrane lipids, thereby disrupting cellular integrity and functions **(Mattia *et al.*, 2006, Brien *et al* 2003).**

Studies with animal models have also reported many harmful effects of Cr (VI) on mammals. Subcutaneous administration of Cr (VI) to rats caused severe progressive proteinuria, urea nitrogen and creatinine, as well as elevation in serum alanine aminotransferase activity and hepatic lipid peroxide formation **(Kim, 2003)**. Similar studies reported by Gumbleton and Nicholls found that Cr (VI) induced renal damage in rats when administered by single sub-cutaneous injections. Demonstrated that rats received Cr (VI) orally in water induced hepatic mitochondrial and microsomal lipid peroxidation, as well as enhanced excretion of urinary lipid metabolites including malondialdehyde (**Bagchi *et al*., 1995 Bagchi *et al*., 1997).**

Adverse health effects induced by Cr (VI) have also been reported in humans. Epidemiological investigations have reported respiratory cancers in workers occupationally exposed to Cr (VI)-containing compounds **(Costa 1997, Shelnutt *et al.*, 2007)**. DNA strand breaks in peripheral lymphocytes and lipid peroxidation products in urine observed in chromium-exposed workers also support the evidence of Cr (VI)-induced toxicity to humans **(Gambelunghe *et al.*, 1997; Goulart *et al.*, 2005**). Oxidative damage is considered to be the underlying cause of these genotoxic effects including chromosomal abnormalities **(Wise *et al.*, 2002; Wise *et al.*, 2005)** and DNA strand breaks **(Xie *et al.*, 2005).** Nevertheless, recent studies indicate a biological relevance of non-oxidative mechanisms in Cr(VI) carcinogenesis.

Carcinogenicity appears to be associated with the inhalation of the less soluble/insoluble Cr(VI) compounds. The toxicology of Cr(VI) does not reside with the elemental form. It varies greatly among a wide variety of very different Cr(VI) compounds **(Katz *et al.*,1993).** Epidemiological evidence strongly points to Cr(VI) as the agent in carcinogenesis. Solubility and other characteristics of chromium, such as size, crystal modification, surface charge, and the ability to be phagocytized might be important in determining cancer risk.

Studies in our laboratory have indicated that chromium (VI) is cytotoxic and able to induce DNA damaging effects such as chromosomal abnormalities **(Patlolla, 2008)**, DNA strand breaks, DNA fragmentation and oxidative stress in Sprague-Dawley rats and human liver carcinoma cells **(Patlolla *et al.*, 2009)**. Recently, our laboratory has also demonstrated that chromium (VI) induces biochemical, genotoxic and histopathologic effects in liver and kidney of goldfish, *Carassius auratus* **(Velma and Tchounwou, 2010)**.

Various hypotheses have been proposed to explain the carcinogenicity of chromium and its salts, however some inherent difficulties exist when discussing metal carcinogenesis. A metal cannot be classified as carcinogenic per se since its different compounds may have different potencies. Because of the multiple chemical exposure in industrial establishments, it is difficult from an epidemiological standpoint to relate the carcinogenic effect to a single compound. Thus, the carcinogenic risk must often be related to a process or to a group of metal compounds rather than to a single substance. Differences in carcinogenic potential are related not only to different chemical forms of the same metal but also to the particle size of the inhaled aerosol and to physical characteristics of the particle such as surface charge and crystal modification **(Norseth, 1986**).

**Conventional methods for the treatment of metals**

Owing to the toxic and adverse effects of heavy metals, most industries are advised to treat waste waters systematically so that the metal contents can be minimized in their wastes. Numerous treatments on the heavy metal removal from contaminated water have already been applied years ago which can be divided into biological, chemical and physical processes. However, in most treatments, physical

and chemical processes are more pronounced. The conventional method for heavy metal removal includes chemical precipitation, membrane filtration, ion exchange, reverse osmosis, electrodialysis, solvent extraction, evaporation, oxidation and activated carbon adsorption (**Yu *et al.*, 2000**) but most of these methods are only suitable for large scale treatments and incur high cost to be practiced. Generally, all these treatments lead to certain disadvantages such as incomplete removal of heavy metals, high-energy requirements and production of toxic sludge (**Eccles, 1999**). Numerous approaches have been studied for the development of more effective methods in removing metal pollution and the adsorption process is found to be more practicable over other techniques. Adsorption process is one of the easiest, safest and most effective method for heavy metal removal from industrial effluents (**Shah *et al.*, 2009**; **Rahmani *et al.*, 2009**).

**Chemical precipitation**

Precipitation of metals is achieved by the addition of coagulants such as alum, lime, iron salts and other organic polymers. The large amount of sludge containing toxic compounds produced during the process is the main disadvantage.

**Hydroxide precipitation:** Chemical precipitation of heavy metals as their hydroxides using lime or sodium hydroxide is widely used. Lime is generally favoured for precipitation purposes due to the low cost of precipitant, ease of pH control in the range of 8.0 –10.0 and the excess of lime also serves as an adsorbent for the removal of metal ions. The efficiency of the process depends on a number of factors, which include the ease of hydrolysis of the metal ion, nature of the oxidation state, pH, presence of complex forming ions, standing time, degree of agitation and settling and filtering and characteristics of the precipitate. The limitations of this method include difference between metals in the optimum pH for hydroxide formation may lead to the problems in the treatment of effluents containing combined metal ions. Variability in metal hydroxide solubility at a fixed pH is another drawback.

**Carbonate precipitation:** Carbonate precipitation of metals using calcium or sodium carbonate is very limited. **Patterson *et al.* (1997)** reported improved results using carbonate precipitate for Cd (II) and Pb (II) from electroplating effluents. When the

pH was brought to 7.5, residual concentration of Pb (II) and Cd (II) were 0.60 and 0.25 mg/L respectively.

**Sulphide precipitation**: Since most of the heavy metals form stable sulphides, excellent metal removal can be obtained by sulphide precipitation. Treatment with sulphides is most advantageous when used as a polishing step after conventional hydroxide precipitation or when very high metal removals are required.

**Chemical reduction**

Reduction of hexavalent chromium can also be accomplished with electro-chemical units. The electrochemical chromium reduction process uses consumable iron electrodes and an electric current to generate ferrous ions that react with hexavalent chromium to give trivalent chromium as follows **(USEPA, 1979).**

$3Fe^{2+} + CrO_4^{2-} + 4H_2O \; 3Fe^{3+} + Cr^{3+} + 8OH^-$……(1)

Another application of reduction process is the use of sodium borohydride, which has been considered effective for the removal of mercury, cadmium, lead, silver and gold.

**Xanthate process**

Insoluble starch xanthate (ISX) is made from commercial cross linked starch by reacting it with sodium hydroxide and carbon disulphide. To give the product stability and to improve the sludge settling rate, magnesium sulphate is also added. ISX works like an ion exchanger, removing the heavy metals from the wastewater and replacing them with sodium and magnesium. Average capacity is 1.1-1.5 meq of metal ion per gram of ISX **(Anon, 1978).** ISX is most commonly used by adding to it the wastewater as slurry for continuous flow operations or in the solid form for batch treatments. It should be added to the effluent at pH $\geq$ 3. Then the pH should be allowed to rise above 7 for optimum metal removal **(Wing, 1978**). Residual metal ion level below 50 µg/L has been reported **(Hanway *et al*., 1978; Wing *et al*., 1978).** The effectiveness of soluble starch xanthate (SSX) for removal of Cd (II), Cr (VI) and Cu (II) and insoluble starch xanthate (ISX) for Cr (VI) and Cu (II) have been evaluated under different aqueous phase conditions. Insoluble starch xanthate had better binding capacity for metals. The binding capacity of SSX and ISX respectively for different

metal ions follows the sequence of Cr (VI)> Cu (II)> Cd(II) and Cr (VI)> Cu (II) **(Tare *et al*., 1988).**

**Solvent extraction**

Liquid-liquid extraction (also frequently referred as solvent extraction) of metals from solutions on a large scale has experienced a phenomenal growth in recent years due to the introduction of selective complexing agents. In addition to hydrometallurgical applications, solvent extraction has gained widespread usage for waste reprocessing and effluent treatment. Solvent extraction involves an organic and an aqueous phase. The aqueous solution containing the metal or metals of interest is mixed with the appropriate organic solvent and the metal passes into the organic phase. In order to recover the extracted metal, the organic solvent is contacted with an aqueous solution whose composition is such that the metal is stripped from the organic phase and is reextracted into the stripping solution. The concentration of the metal in the strip liquor may be increased, often 110 to 100 times over that of the original feed solution. Once the metal of interest has been removed, the organic solvent is recycled either directly or after a fraction of it has been treated to remove the impurities.

**Membrane Filtration**

Membrane filtration has received considerable attention for the treatment of inorganic effluent, since it is capable of removing not only suspended solid and organic compounds, but also inorganic contaminants such as heavy metals. Depending on the size of the particle that can be retained, various types of membrane filtration such as ultra filtration, nano filtration and reverse osmosis can be employed for heavy metal removal from wastewater. Unique specialties enable UF to allow the passage of water and low-molecular weight solutes, while retaining the macromolecules, which have a size larger than the pore size of the membrane (**Vigneswaran *et al*., 2004**). The main disadvantage of this process is the generation of sludge (**Wingenfelder *et al*., 2005**).

**Evaporators**

In the electroplating industry, evaporators are used chiefly to concentrate and recover valuable plating chemicals. Recovery is accomplished by boiling sufficient

water from the collected rinse stream to allow the concentrate to be returned to the plating bath. Many of the evaporators in use also permit the recovery of the condensed steam for recycle as rinse water. Four types of evaporators are used throughout the elctroplating industry **(USEPA, 1979a).**

(i) Rising film evaporators;

(ii) Flash evaporators using waste heat;

(iii) Submerged tube evaporators;

(iv) Atmospheric evaporators. Both capital and operational costs for evaporative recovery systems are high. Chemical and water reuse values must offset these costs for evaporative recovery to become economically feasible.

**Cementation**

Cementation is the displacement of a metal from solution by a metal higher in the electromotive series. It offers an attractive possibility for treating any wastewater containing reducible metallic ions. In practice, a considerable spread in the electromotive force between metals is necessary to ensure adequate cementation capability. Due to its low cost and ready availability, scrap iron is the metal used often. Cementation is especially suitable for small wastewater flow because a long contact time is required. Some common examples of cementation in wastewater treatment include the precipitation of copper from printed etching solutions and the reduction of Cr (VI) in chromium plating and chromate-inhibited cooling water discharges **(Case, 1974)**. Removal and recovery of lead ion by cementation on iron sphere packed bed has been reported **(Angelidis *et al.*, 1988, 1989)**. Lead was replaced by a less toxic metal in a harmless and reusable form.

**Ion exchange**

Ion exchange resins are available selectively for certain metal ions. The cations are exchanged for $H^+$ or $Na^+$. The cation exchange resins are mostly synthetic polymers containing an active ion group such as $SO_3H$. The natural materials such as zeolites can be used as ion exchange media **(Van der Heen, 1977).** The modified zeolites like zeocarb and chalcarb have greater affinity for metals like Ni and Pb (**Groffman *et al.*, 1992)**. The limitations on the use of ion exchange for inorganic

effluent treatment are primarily high cost and the requirements for appropriate pretreatment systems. Ion exchange is capable of providing metal ion concentrations to parts per million levels. However, in the presence of large quantities of competing mono-and divalent ions such as Na and Ca, ion exchange is almost totally ineffective.

**Electrodeposition**

Some metals found in waste solution can be recovered by electrodeposition using insoluble anodes. For example, spent solutions resulting from sulphuric acid cleaning of Cu may be saturated with copper sulphate in the presence of residual acid. These are ideal for electro-winning where the high quality cathode copper can be electrolytically deposited while free sulphuric acid is regenerated.

**Ultra filtration**

Ultrafiltration (UF) is a membrane technique working at low transmembrane pressures for the removal of dissolved and colloidal material. Since the pore sizes of UF membranes are larger than dissolved metal ions in the form of hydrated ions or as low molecular weight complexes, these ions would pass easily through UF membranes. To obtain high removal efficiency of metal ions, the micellar enhanced ultrafiltration (MEUF) and polymer enhanced ultrafiltration (PEUF) was proposed (**Fenglian Fu and Qi Wang, 2011**). Ultra filtration technologies can be used in a variety of ways in wastewater treatment and water reuse systems. Ultra filtration can reduce the amount of treatment chemicals, has smaller space requirements, and reduce labor requirements. On the contrary this method uses more electricity, may need pre-treatment, and requires replacement of membranes (**W.W. Eckenfelder, 2000**).

**Reverse Osmosis**

The reverse osmosis (RO) process uses a semi-permeable membrane, allowing the fluid that is being purified to pass through it, while rejecting the contaminants. RO is one of the techniques able to remove a wide range of dissolved species from water. It accounts for more than 20% of the world's desalination capacity (**Shahalam *et al*., 2002**). RO is an increasingly popular wastewater treatment option in chemical and environmental engineering. $Cu^{2+}$ and $Ni^{2+}$ ions were successfully removed by the RO process and the rejection efficiency of the two ions increased up to 99.5% by using

$Na_2EDTA$ (**Mohsen-Nia *et al.*, 2007**; **Dialynas and Diamadopoulos, 2009**). The major drawback of RO is the high power consumption due to the pumping pressures, and the restoration of the membranes and it is expensive as well.

**Electrodialysis**

In this process, the ionic components (heavy metals) are separated through the use of semi-permeable ion selective membranes. Application of an electrical potential between the two electrodes causes a migration of cations and anions towards respective electrodes. Because of the alternate spacing of cation and anion permeable membranes, cells of concentrated and dilute salts are formed. The disadvantage is the formation of metal hydroxides, which clog the membrane.

**Complexing agents**

The electrokinetic experiments, using ethylenediamine tetraacetic acid (EDTA) as a complexing agent for the removal of three different heavy metals, chromium(VI), nickel(II), and cadmium(II) over a wide range of pH conditions (2-10), showed low heavy metal removal efficiency **(Reddy *et al.*, 2004)**.

**Coagulation and flocculation**

Coagulation–flocculation can be employed to treat wastewater laden with heavy metals. Principally, the coagulation process destabilizes colloidal particles by adding a coagulant and results in sedimentation (**Shammas, 2004**). To increase the particle size, coagulation is followed by the flocculation of the unstable particles into bulky floccules (**Semerjian and Ayoub, 2003; Ayoub *et al.*, 2001; El Samrani *et al.*, 2008**) investigated the removal of heavy metal by coagulation of combined sewer overflow with two commercial coagulants, a ferric chloride solution and a polyaluminium chloride (PAC). They found excellent heavy metal elimination was achieved within a narrow range of coagulant around optimum coagulant concentrations. The general approach for this technique includes pH adjustment and involves the addition of ferric/alum salts as the coagulant to overcome the repulsive forces between particles (**Licskó, 1997**). In spite of its advantages, coagulation–flocculation has limitations such as high operational cost due to chemical

consumption. The increased volume of sludge generated from coagulation–flocculation may hinder its adoption as a global strategy for wastewater treatment.

**Flotation**

Flotation has nowadays found extensive use in wastewater treatment. It has been employed to separate heavy metal from a liquid phase using bubble attachment, originated in mineral processing. The attached particles are separated from the suspension of heavy metal by the bubble rise.

Flotation can be classified as:

(i) dispersed-air flotation, (ii) dissolved-air flotation (DAF), (iii) Vacuum air flotation, (iv) Electro-flotation and (v) Biological flotation.

Among the various types of flotation, DAF is the most commonly used for the treatment of metal-contaminated wastewater (**Zabel, 1984**). Adsorptive bubble separation employs foaming to separate the metal impurities. Ion flotation has been shown a promising method for the removal of heavy metal ions from wastewaters. **Yuan *et al*. (2008)** investigated the potential of ion flotation to remove cadmium, lead and copper from dilute aqueous solution with a plant-derived biosurfactant tea saponin. The maximum removal of $Pb^{2+}$, $Cu^{2+}$ and $Cd^{2+}$ can reach 89.95%, 81.13% and 71.17%, respectively.

Although flotation is only a kind of physical separation process, heavy metal removal by this method has the potential for industrial application (**Jokela and Keskitalo, 1999**). Low cost materials such as zeolite have been found to be effective collectors with removal efficiency of higher than 95% for an initial metal concentration ranging from 60 to 500 mg/L. Flotation can be employed to treat inorganic effluent with a metal concentration of less than 50 mg/L or higher than 150 mg/L. Other advantages such as a better removal of small particles, shorter hydraulic retention times and low cost make flotation one of the most promising alternatives for the treatment of metal-contaminated wastewater (**Matis *et al*., 2003**).

**Phytoremediation**

Phytoremediation is a multi-faceted approach towards Cr remediation. Plants contain the Cr by converting it to the less mobile Cr(III) (phytostabilization) and

simultaneously reduce its toxicity. In addition, phytoremediation can be a removal technology, if Cr is sequestered in plant tissue and the plants are harvested (phytoextraction and rhizofiltration). For simplicity, all three mechanisms of phytoremediation are classified primarily as toxicity reduction methods and are discussed here. All three techniques are currently in the lab-scale or pilot-scale of development **(USEPA, 1997).** Phytoaccumulation one of the most common forms of Cr(VI) phytoremediation, consists of the uptake of the Cr from the soil to the plant roots and ultimately into the above ground parts of the plants. Some plants can accumulate very large amounts of a specific metal, such as Cr. The plant, *Leptospermum scoparium* was found to contain soluble Cr in the leaf tissue as the trioxalatochromium(III) ion $(Cr(C_2O_4)_3)^{3-}$. The function of the chromium-organic acid complex was to reduce the toxicity of the Cr.

**Granular Activated Carbon**

Granular Activated Carbon (GAC) is a well-established technology for removing organics from water supplies and has been demonstrated to remove heavy metals as well, including Cr. GAC has an extremely high internal surface area, on the order of 1000 m2/g. Cr(III) adsorbs only weakly to GAC and passes through the carbon. Cr(VI) is removed by two different mechanisms:electrostatic adsorption to GAC surfaces and reduction to Cr(III). Adsorption of Cr(VI) is a strong function of pH, owing to electrostatic surface interactions. Quantitative results vary with the type of GAC, because different types of GAC have different point of zero net charge (pznc) values **(Corpapcioglu and Huang, 1987)**. The adsorption capacity of Calgon filtrasorb 400 GAC was shown to peak between pH 5 to 6 (Huang and Wu, 1977). Although $CrO_4^{2-}$, $HCrO^{4-}$, and $Cr_2O_7^{2-}$ are all adsorbed, $HCrO^{4-}$ is the most easily adsorbed species. Coconut-fibre pith-based GAC (pznc = 7.5) achieved optimal removal at pH 2 **(Manju and Anirudhan, 1997)**. Grinding GAC particles did not change Cr(VI) adsorption owing to the relatively small change in GAC internal surface area **(Huang and Wu, 1977).**

**Adsorption**

Since activated carbon also possesses an affinity for heavy metals, considerable attention has been focussed on the use of carbon for the adsorption of

hexavalent chromium, complexed cyanides and metals present in various other forms from wastewaters. **(Watonabe and Ogawa ,1929)** first presented the use of activated carbon for the adsorption of heavy metals. The mechanism of removal of hexavalent and trivalent chromium from synthetic solutions and electroplating effluents has been extensively studied by a number of researchers. According to some investigators, the removal of Cr (VI) occurs through several steps of interfacial reactions **(Huang and Bowers, 1979).**

(i) The direct adsorption of $Cr^{6+}$ onto carbon surface.

(ii) The reduction of $Cr^{6+}$ species to $Cr^{3+}$ by carbon on the surface.

(iii) The adsorption of the $Cr^{3+}$ species produced, which occurs to a much lesser extent than the adsorption of the $Cr^{6+}$ species.

Adsorption of Cr (III) and Cr (VI) on activated carbon from aqueous solutions has been studied **(Toledo, 1994)**. Granular activated carbon columns have been used to treat wastewaters containing lead and cadmium **(Reed and Arunachalam, 1994, Reed *et al*., 1994)**. Granular activated carbon was used for the removal of Pb (II) from aqueous solutions **(Cheng *et al*., 1993)**. The adsorption process was inhibited by the presence of humic acid, iron (III), aluminum (III) and calcium (II).

Adsorption is now recognized as an effective and economic method for treatment of wastewater laden with heavy metals. Basically, adsorption is a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid, and becomes bound by physical and/or chemical interactions (**Kurniawan and Babel, 2003**). The effectiveness of the adsorption process is mainly influenced by the nature of solution in which the contaminants are dispersed, the molecular size and the polarity of the contaminant and also the type of adsorbent used.

Various low-cost adsorbents, derived from agricultural waste, industrial by-product, natural material, or modified biopolymers, have been recently developed and applied for the removal of heavy metals from metal-contaminated wastewater. In general, there are three main steps involved in pollutant sorption onto solid sorbent: (i) the transport of the pollutant from the bulk solution to the sorbent surface; (ii) adsorption on the surface; and (iii) transport within the sorbent. Technical

applicability and cost-effectiveness are the key factors that play major roles in the selection of the most suitable adsorbent to treat inorganic effluent. The advantages of the adsorption process in removing or minimizing the heavy metals even at low concentration enhance the application of adsorption as one practical treatment process (**Barakat, 2011**). In addition, because adsorption is sometimes reversible, adsorbents can be regenerated by suitable desorption process.

The presence of heavy metals in the environment is of major concern because of their toxicity, bioaccumulating tendency, and threat to human life and the environment. Conventional methods for the removal of heavy metals from waste waters are often cost prohibitive. These constraints have caused the search for alternative technologies for metal sequestering to cost-effective environmentally acceptable levels. The removal of heavy metals from our environment especially wastewater is now shifting from the use of conventional adsorbents to the use of biosorbents **(Igwe and Abia, 2006; Oboh and Aluyor, 2008).**

Hence the disadvantages like incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste products that require careful disposal has made it imperative for a cost-effective treatment method that is capable of removing heavy metals from aqueous effluents **(Ahalya *et al*., 2003)**. Considerable attention has been focused in recent years upon the field of biosorption for the removal of metal ions from aqueous effluents. Compared to other technologies, the advantages of biosorption are the high purity of the treated waste water and the cheap raw material **(Sag and Kutsal, 2001)**.

**Disadvantages of conventional methods for treatment of waste water containing heavy metals**

Metals are a class of pollutants, often toxic and dangerous, widely present in industrial and household wastewaters. Electroplating and metal finishing operations, electronic circuit production, steel and aluminum processes to name but a few industries, produce large quantities of wastewater containing metals. Although metal precipitation using a cheap alkali such as lime (calcium hydroxide) has been the most favoured option, other separation technologies are now beginning to find favour. Precipitation, by adjusting the pH value is not selective and any iron (ferric ion)

present in the liquid effluent will be precipitated initially followed by other metals. Consequently precipitation produces large quantities of solid sludge for disposal, for example precipitation as hydroxides of 100 mg/l of copper (II), cadmium (II) or mercury (II) produces as much as 10-, 9- and 5 fold mg/l of sludges respectively. The metal hydroxide sludge resulting from treatment of electroplating wastewater has been classified as a hazardous waste. The performance characteristics of heavy metal waste water treatment technologies are identified. The versatility, simplicity and other technology characteristics will contribute to the overall process costs, both capital and operational. At present many of these technologies such as ion exchange represent significant capital investments by industry.

Conventional treatment methods to reduce or minimize the amount, concentration and dangers of chromium include coagulation, chemical precipitation, ion-exchange, membrane separation, electrolysis and electrodialysis. Despite their high efficiency and utility, these techniques also have some disadvantages that limit the application, such as considerable toxic waste production, high cost, and huge energy consumption **(Mohan and Pittman, 2006)**. Adsorption is a promising process because of its operational simplicity and economic efficiency. The use of low-cost and effective absorbents is crucial in adsorption **(Wang *et al*., 2013)**. Biochar derived from biomass via oxygen-limited pyrolysis is an alternative to activated carbon (AC), which is the most commonly used absorbent.

Biological methods such as biosorption/ bioaccumulation for the removal of heavy metal ions may provide an attractive alternative to physico-chemical methods **(Kapoor and Viraraghavan, 1995**).

**Biosorption**

Biosorption can be defined as the removal of metal or metalloid species, compounds and particulates from solution by biological material **(Gadd, 1993)**. Biosorption may be simply defined as the removal of substances from solution by biological material. Such substances can be organic or inorganic, and in soluble or insoluble forms (**Ahemad and Malik, 2011**).

Biosorption may be simply defined as the removal of substances from solution by biotic material. Such substances can be organic and inorganic, and in gaseous,

soluble or insoluble forms. Biosorption is a physico-chemical process and includes such mechanisms as absorption, adsorption, ion exchange, surface complexation and precipitation. Biosorption is a property of both living and dead organisms (and their components) and has been heralded as a promising biotechnology for pollutant removal from solution, and/or pollutant recovery, for a number of years, because of its efficiency, simplicity, analogous operation to conventional ion exchange technology, and availability of biomass. Most biosorption studies have carried out on microbial systems, chiefly bacteria, microalgae and fungi, and with toxic metals and radionuclides, including actinides like uranium and thorium. However, practically all biological material has an affinity for metal species and a considerable amount of other research exists with macro-algae (seaweeds) as well as plant and animal biomass, waste organic sludges, and many other wastes or derived bio-products. While most biosorption research concerns metals and related substances, including radionuclides, the term is now applied to particulates and all manner of organic substances as well **(Gadd and Michael, 2009)**.

The biosorption process involves a solid phase (sorbent or biosorbent; biological material) and a liquid phase (solvent, normally water) containing a dissolved species to be sorbed (sorbate, metal ions). Due to higher affinity of the sorbent for the sorbate species, the latter is attracted and bound there by different mechanisms. The process continues till equilibrium is established between the amount of solid-bound sorbate species and its portion remaining in the solution. The degree of sorbent affinity for the sorbate determines its distribution between the solid and liquid phases **(Ahalya *et al*., 2003)**.

Biosorption is emerging as a potential alternative to the existing conventional technologies for the removal and/or recovery of metal ions from aqueous solutions. The major advantages of biosorption over conventional treatment methods include: low cost, high efficiency, minimization of chemical or biological sludge, regeneration of biosorbents and possibility of metal recovery. Cellulosic agricultural waste materials are an abundant source for significant metal biosorption. The functional groups present in agricultural waste biomass viz. acetamido, alcoholic, carbonyl, phenolic, amido, amino, sulphydryl groups etc. have affinity for heavy metal ions to form metal complexes or chelates. The mechanism of biosorption process includes

chemisorption, complexation, adsorption on surface, diffusion through pores and ion exchange etc **(Sud *et al*., 2008)**.

The biosorption process involves a solid phase (sorbent or biosorbent; adsorbent; biological material) and a liquid phase (solvent, normally water) containing a dissolved species to be sorbed (adsorbate, metal). Due to the higher affinity of the adsorbent for the adsorbate species, the latter is attracted and bound there by different mechanisms. The process continues till equilibrium is established between the amount of solid-bound adsorbate species and its portion remaining in the solution. The degree of adsorbent affinity for the adsorbate determines its distribution between the solid and liquid phases. There are many types of adsorbents; Earth's forests and plants, ocean and freshwater plankton, algae and fish, all living creatures, that including animals are all "biomass/ adsorbents". The renewable character of biomass that grows, fuelled directly or indirectly by sunshine, makes it an inexhaustible pool of chemicals of all kinds. Biosorption has advantages compared with conventional techniques **(Volesky, 1999)**. Some of these are listed below:

- Cheap: the cost of the biosorbent is low since they often are made from abundant or waste material.
- Metal selective: the metalsorbing performance of different types of biomass can be more or less selective on different metals. This depends on various factors such as type of biomass, mixture in the solution, type of biomass preparation and physicochemical treatment.
- Regenerative: biosorbents can be reused, after the metal is recycled.
- No sludge generation: no secondary problems with sludge occur with biosorption, as is the case with many other techniques, for example, precipitation.
- Metal recovery possible: In case of metals, it can be recovered after being sorbed from the solution.
- Competitive performance: biosorption is capable of a performance comparable to the most similar technique, ion exchange treatment. Ion exchange is, as mentioned above, rather costly, making the low cost of biosorption a major factor. Biosorbents intended for bioremediation environmental applications are

waste biomass of crops, algae, fungi, bacteria, etc., which are the naturally abundant. Numerous chemical groups have been suggested to contribute to biosorption.

Biosorption by microorganisms have various disadvantages, and hence many low cost adsorbents (industrial/agricultural waste products/byproducts) are increasingly used as biosorbents. This chapter also provides review of the low cost adsorbents used for removal of heavy metals **(Ahalya *et al*., 2004).**

Numerous technologies have been developed for heavy metal decontamination Traditional treatment processes include precipitation, ion exchange, membrane filtration, electroplating, adsorption **(Banerjee *et al*., 2012)**. These methods represent significant demerits, such as high chemical and energy requirements, hazardous sludge formation, low efficiency when heavy metals concentration below 100 mg/L, high cost at large scale **(Marin-Rangel *et al*., 2012; Mishra *et al*., 2012)**. Likewise, high price and limited reusability are key problems, hindering the widespread application of activated carbon, a commonly used adsorbent in heavy metal treatment **(Turan and Mesci, 2011**). In that context, biosorption has emerged as a promising method, with such advantages as

(1) High efficiency even with low metal cencentrations,

(2) Low cost,

(3) No additional nutrients requirements,

(4) Easy operation,

(5) Potential metal recover.

Some studies have made comparisons between biosorbents based on the removal percentages. However, this could lead to misleading conclusions as removal efficiency does not always reflect exactly the adsorption capability of biosorbents. For example, **Aman *et al*. (2008)** reported that one gram of potato peel charcoal could remove 99.8% of the copper from the solution of 150 mg/L (100 ml) at pH 6.0 with a shaking time of 20 min. However, this biosorbent hold a relatively low maximum adsorption capacity (0.3877 mg/g). Similar observation was reported in a research conducted by **Saka *et al*. (2012).** It was found that Palmyra palm fruit seed showed

higher Pb(II) removal percentage (100%) than onion skins (93%). Nevertheless, the adsorption capacity for Pb(II) of Palmyra palm fruit seed (24.6 mg/g) was found far lower than that of onion skins (200 mg/g). For that reason, in searching for a 'good biosorbent, comparison should be made based on the maximum adsorption capacity (qmax) rather than on percentage removal (%) of heavy metals. the adsorption capacities of AWBs vary significantly. The influential factors include types of crop residues, elements of heavy metals, pretreatments of AWBs and especially operating conditions. AWBs tended to prefer some heavy metals to others. **Kelly-Vargas *et al.* (2012)** reported that lemon peel and orange peel demonstrated the adsorption capacities for Cu and Pb 48% and 15% higher than banana peel, respectively. In contrast, the Cd uptake by banana was higher than that of lemon peel and orange peel 82% and 57%, respectively. A study, conducted by (**Mosa *et al.*, 2011)** released that the removal efficiency of heavy metals decreased in the order cotton stalks > maize stalks > rice straw. They credited the highest removal percentage by cotton stalks to its highest concentration of cellulose, hemicellulose, and lignin as compared to other crop-residues. (**Osman *et al.* 2010)** reported that rice hull showed the highest efficiency in confiscating zinc, cadmium and iron among biosorbents investigated. For example, the removal efficiencies by rice hull, sawdust, sugarcane bagasse and wheat straw were 98.15%, 96.90%, 93.00% and 91.19%, respectively. They suggested that the higher adsorption capacity of rice hull than other sorbents for removal of heavy metals was mainly due to the presence of silanol (SiOH) groups in structure of rice hull and higher surface area of rice hull. Most AWBs even without any chemical pretreatments showed better adsorption capacities for heavy metals as compared with conventional adsorbents. For instance, the Cu uptake capabilities of cortex banana, orange, lemon waste, garden grass, palm oil fruit shell, etc. in the raw form (ranging from 27.68 to 70.40 mg/g) were similar to or even higher than that of ion exchange resins (26.73 mg/g). Some other kinds of original AWBs, such as tamarind seed, watermelon shell or rose petal waste exhibited the adsorption capacity for Cu (II) ions 210%, 315% and 364% higher than that of above ion exchange resins. This can be attributed to the abundant availability of binding sites on the AWBs, which increase the retention of heavy metals onto AWBs surface **(Jiménez-Cedillo *et al.*, 2013; Marin-Rangel *et al.*, 2012).** Predominantly, cashew nut shell modified with $H_2SO_4$ exhibited an extremely high adsorption capacity (406.6 mg/g) for Cu (II) ions. The

remarkable enhancement in adsorption capacity for Cu(II) using $H_2SO_4$ is probably due to elimination of competing cations and the increase in surface area as well as the porosity on the biosorbent surface **(Boota *et al.*, 2009; Lasheen *et al.*, 2012; Osman *et al.*, 2010).** Some AWBs showed very high affinity toward heavy metals in the natural form. For example, the adsorption capacity for Cr (VI) ions of the raw coir pith was relatively high (165 mg/ g). However, coir pith grafted with acrylic acid even exhibited much better Cr (VI) uptake capability (196 mg/g) **(Suksabye and Thiravetyan, 2012).** Obviously, chemical pretreatments can vastly enhance adsorption capacities of ABWs. Similar observations can be reported for the remaining heavy metals such as As, Cd, Cr, Pb and Zn. The experimental conditions in the literature were very diverse. Therefore, it would be challenging to identify the best AWBs for this purpose **(Sahmoune *et al.*, 2011). Saka *et al*. (2012**) claimed that AWBs with loading capacities P 90 mg/g should be considered as good biosorbents. Based on this criteria, this present review introduces the promising AWBs including prawn shell activated carbon **(Arulkumar *et al.*, 2012);** watermelon shell/rind **(Banerjee *et al*., 2012; Liu *et al.*, 2012);** rose petals waste **(Bhatti *et al*., 2011; Manzoor *et al.*, 2013)**; orange peel **(Feng *et al.*, 2011; Liang *et al*., 2009)**; durian shell waste Cedrus deodara sawdust **(Mishra *et al.*, 2012);** onion skins **(Saka *et al*., 2011 );** cashew nut shell **(Senthil Kumar *et al.*, 2012);** coir pith **(Suksabye and Thiravetyan, 2012**) **(Kurniawan *et al.*, 2011 ).**

A number of materials have been used as adsorbents for Cr (VI) like powdered activated carbon **(Aggarwal *et al*., 1999)**, saw dust **(Hamadi *et al.*, 2001)**, soya cake **(Daneshvar *et al.*, 2002)**, fly ash **(Meng, 2003)**, and rice husk based activated carbon **(Guo *et al.*, 2003)**,chemically modified plant wastes **(Wan Ngah *et al*., 2008**) etc. Recently natural materials are used as adsorbent and are eco friendly in nature **(Khattri and Singh, 2009)** Water hyacinth (*Eichhornia crassipes*) is a floating mycrophyte whose appetite for nutrients and explosive growth rate has been put to use in cleaning up municipal and agriculture waste water **(Gupta *et al*., 2001)**. The living plants are to be highly effective in removing $Cd^{2+}$, $Cu^{2+}$, and Ni $^{2+}$, Zn $^{2+}$, $Pb^{2+}$ and Cr. Some studies have reported the use of biomaterials derived from non living dried water hyacinth roots for the removal of toxic metals **(Shaban *et al.*, 2005).** In the present study, Cr (VI) adsorption capacity of water hyacinth was conducted in

relation to various parameters such as pH, contact time, amount of adsorbent, concentration of adsorbent and temperature.

Adsorption is very popular due to its efficiency and low cost. An adsorbent must be eco-friendly, cost-effective, industrially viable and efficient for a wide range of concentration of different heavy metals. The recent studies have focused on the search of a low-cost and efficient adsorbent. In recent years, a wide variety of materials have been studied as low-cost adsorbents for the removal of heavy metals from water, such as fly ash, phosphate rock, kaolinite-based clays, sawdust, loess soil, green algae husk of wheat and rice, red loess, epicarp of *Ricinus communis* and *Acacia nilotica* leaf **(Nascimento *et al.*, 2009; Saxena and Souza, 2006; Hizal and Apak, 2006*).*** Activated carbon adsorption has proved to be the least expensive treatment option, particularly in treating low concentrations of wastewater streams and in meeting stringent treatment levels. Activated carbon is an extremely versatile material with a high surface area and porous texture. There are two methods of preparing activated carbons: physical and chemical activation. But chemical activation is better than physical activation due to relatively high yield in this process and is also more economical in comparison to physical activation. In a chemical activation, an activating agent is used for the impregnation of a raw material. Several activating agents such as $AlCl_3$, KOH, $ZnCl_2$, NaOH, $CaCl_2$, $H_3PO_4$, etc., are used in chemical activation processes, but $H_3PO_4$, is the most widely used impregnation agent due to some environmental and economical concerns. Other activating agents create some disadvantages such as corrosion and inefficient chemical recovery,and the carbons obtained using these agents cannot be used in pharmaceutical and food industries as they may contaminate**(Wang *et al.*, 2009; Sciban *et al.*, 2007; Gupta 2001; Aydin *et al.*, 2008; Shengtao *et al*., 2011; Thilagavathy and Santhi, 2014).**

Among various biosorbents, chitin is the second most copious natural biopolymers after cellulose. However, more important than chitin is chitosan, which has a molecular structure similar to cellulose. Presently, chitosan is enticing an increasing amount of research interest, as it is an effective scavenger for heavy metals. Chitosan is produced by alkaline *N*-deacetylation of chitin, which is widely found in the exoskeleton of shellfish and crustaceans. It was estimated that chitosan could be produced from fish and crustaceans at a market price of US$ 15.43/kg. The

growing need for new sources of low-cost adsorbent, the increased problems of waste disposal, the increasing cost of synthetic resins undoubtedly make chitosan one of the most attractive materials for wastewater treatment.

Rice husk carbon can be used as potential adsorbent since it is widely available in India as rice is the major staple food. It is burnt as a less efficient fuel causing air pollution mainly during harvesting season. Therefore it is useful to use it as adsorbent rather than wasting it and creating problems of its disposal. The present work describes the batch adsorption characteristics of Cr (VI) on rice husk carbon and activated alumina. The effects of different operating parameters were investigated on the synthetic sample of Cr(VI).

Tamarind (*Tamarindus indica*) is a common tree in tropical countries. It is found mainly for its sour fruits pulp. Tamarind seed, a by product of the tamarind pulp industry, is an underutilized or useless material **(Bhattacharya *et al.*, 1997)**. Adsorbent is made from tamarind seeds and studies are carried out for chromium (VI) removal. Tamarind seeds are activated by giving heat treatment with the use of concentrated sulfuric acid (98% w/w). Batch experiments are carried out for kinetic studies on the removal of chromium (VI) ion from aqueous solution using the activated tamarind seeds adsorbent. The effect of various parameters such as contact time, adsorbent dosage, initial chromium (VI) concentration and pH has been studied (**Suresh and Babu).**

The capability of some living microorganisms to accumulate metallic elements have been found at first from toxicological point of view **(Volesky, 1990a,b,c).** However, further researches have revealed that inactive/dead microbial biomass can passively bind metal ions via various physicochemical mechanisms. Therefore researches on biosorption have become an active field for the eliminate of metal ions or organic compounds. Biosorbent behavior for metallic ions is a function of the chemical make-up of the microbial cells of which it consists **(Volesky and Holan, 1995)**. Mechanisms responsible for biosorption, although understood to a limited extent, may be one or combination of ion exchange, complexation, coordination, adsorption, electrostatic interaction, chelation and microprecipitation **(Veglio and Beolchini, 1997; Vijayaraghavan and Yun, 2008; Wang and Chen, 2006)**. A large quantity of materials has been investigated as biosorbents for the removal of metals or

organics extensively. The tested biosorbents can be basically classified into the following categories: bacteria (e.g. *Bacillus subtillis*), fungi (e.g. *Rhizopus arrhizus*), yeast (e.g., *Saccharomyces cerevisiae*), algae, industrial wastes (e.g., *S. cerevisiae* waste biomass from fermentation and food industry), agricultural wastes (e.g. corn core) and other polysaccharide materials, etc. **(Vijayaraghavan and Yun, 2008)**. The role of some groups of microorganisms has been well reviewed, such as bacteria, fungal, yeast, algae, etc. These tested biomasses have been reported to bind a variety of heavy metals to different extents **(Gupta *et al*., 2000)**. Some potential biomaterials with high metal binding capacity have been identified in part. Some types of biosorbents binding and collecting the majority of heavy metals with no specific priority, while others can even be specific for certain types of metals **(Volesky and Holan, 1995)**. The biosorbent materials among more easily available include three groups: algae, fungi, and bacteria, the former two may giving broader choices. Waste materials or by-product biomass from largescale fermentation processes are the source of new family of biosorbents more conveniently. In particular, some waste mycelia are available in large quantities for the removal of heavy metals **(Kapoor and Viraraghavan, 1995; Wang and Chen, 2006)**. Seaweeds from the oceans produced in copious quantities are another inexpensive resource of biomass. Marine algae, especially brown algae such Sargasso seaweed was investigated for metal removal **(Davis *et al*., 2003c)**. Abundant natural materials, particularly cellulosic nature, have been suggested as potential biosorbents for the removal of heavy metals. For economical reasons, other low-cost biosorbents are of interest recently, such as agricultural wastes **(Bailey *et al*., 1999)**. The first major challenge for the biosorption field was select the promising types of biomass from an extremely large pool of readily available and inexpensive biomaterials **(Kratochvil and Volesky, 1998)**. Although many biological materials can bind heavy metals, only those with sufficiently high metal-binding capacity and selectivity for heavy metals are suitable for use in a large-scale biosorption process. A large number of biomass types have been explored for their metal binding capability under various conditions. **Volesky and Holan (1995)** have presented an exhaustive list of microbes and their metal-binding capacities. The published work on testing and evaluating the performance of biosorbents offered a good basis for looking for new and potentially feasible metal biosorbents. Another challenge is that the application of biosorption is facing up with

great difficulty **(Tsezos, 2001)**. Great efforts have to be made to improve biosorption process, including immobilization of biomaterials, improvement of regeneration and re-use, optimization of biosorption process etc.

**Gymnosperm as bioadsorbent**

Gymnosperms are economically significant group of plant range globally, primarily in the temperate regions and at higher elevations of tropics. Gymnosperms plants are mainly used as ornamentals, effective windbreaks, garden plants and commercial lumber. Some types of biosorbents such as seaweeds, molds, yeasts, bacteria, fungus, crab shells or plant wastes are examples of biomass tested for metal biosorption with very encouraging results **(Vieira and Volesky, 2000)**. But there has less reports of the use of Gymnosperms plant materials for the removal of copper metal ions. As the reviews revealed that lignin, carbohydrates, polysaccharides and starch materials are responsible for binding of metals **(Aliabadi *et al.*, 2006)**. In view of this fact it is thought worthwhile to study the biosorptive removal of selected heavy metal ions from synthetic waste water by biomass of gymnosperm plants. *Cunninghamia lanceolata* has high cellulose and lignin contents, while the contents of polypentaglucose and other chemical constituents were low **(Wang *et al.*, 2001)**. *Abies bornmulleriana* (Mattf.) have cellulose contents **(Istek *et al.*, 2005)**. Analyses of wood from 120-150 yr old trees of *Taxus baccata* grown near Szczecinek, Poland, showed that cellulose, pentosan, lignin and mineral contents were similar to published results from elsewhere, whereas the contents of substances soluble in aqueous and organic solvents were considerably higher **(Surminski and Dziurzynski, 1978)**.

**(Min *et al.* 2004)** reported on the use of juniper fiber for removing Cd from aqueous solution. The juniper fiber consisted of a mixture of wood and bark. They observed that base treatment of the juniper fiber increased Cd adsorption capacity and that adsorption of Cd was greater for bark compared to wood. However, there was no answer as to why bark performed better than wood. These researchers focused on improving the sorption capacity by base hydrolysis of surface carboxylate functional groups (RCOOR). *Juniper* bark and wood used for removals of Cd, Zn, Pb and Hg metal ions in neutral or acidic solutions **(Shin *et al.*, 2007).** Spruce, coconut coir, sugarcane bagasse, kenaf bast, kenaf core, and cotton were tested for their ability to

remove copper, nickel and zinc ions from aqueous solutions as a function of their lignin content. All of the fibres having lignin did remove heavy metal ions representing that lignin does play a role in metal ion sorption **(Lee and Rowell, 2004)**.

The almond tree (*Terminalia catappa* L.) has been known for its usefulness in the medical world. The gainful use of this medicinal tree which produces edible fruits will also bring about practical exploitation that would encourage local farmers. In addition, the anticipated use of the biomass from this tree as a biosorbent for trace metals in water and waste effluents will solve environmental problems. The principal aim of the present work is to assess the potential use of the biomass of Terminalia catappa L. as a novel biosorbent for the sorption of valuable and toxic metal ions from aqueous media. The purpose of this paper is to report the effect of initial metal ion concentration and thermodynamics on the sorption of $Al^{3+}$ and $Cr^{6+}$ ions from aqueous effluents by *Terminalia catappa* L. biomass.

Green Coconut Shell economically, which should have best efficiency towards the removal of heavy metals from industrial effluent. The effect of various parameters that affect adsorption viz. Contact time, initial concentration, particle size, temperature, pH, and adsorbent dose were performed in batch experiment. To know the heavy These materials can absorb a wide variety of substances i.e. they are able to attract molecules to their internal surface. Therefore, it is called an adsorbent. The volume of pores of the activated carbon is generally greater than 0.2ml/g. The internal surface area is generally greater than 400ml/g. The adsorbent prepared from green coconut shell is still an excellent adsorbent for many toxic materials present in the various types of waste water. Adsorbent should be uniform in size and contain less ash and high volatile matter. This ability to arrest the different pollutant molecules is mainly attributed to its higher specific surface area **(Kumar and Meikap, 2014).**

The ability of sawdust (treated and untreated) waste of *Cedrus deodara* wood utilized to remove Cd(II) ions **(Memon *et al.*, 2007),** thallium(I) ions **(Memon *et al.*, 2008)** and Zn (II) ion **(Mishra *et al.*, 2011)** from aqueous solution was determined. Sorption was found to be rapid (approximately 97% within 8 min). Biosorption of arsenic from natural and model waters by native or chemically modified (with urea or

ferric oxyhydroxides) plant biomass prepared from sawdust of *Picea abies* was studied **(Uríkk *et al.*, 2009).** The feasibility of using cypress cone chips from *Cupressus sempervirens* as a low-cost biosorbent for the removal of two representative basic dyes, methylene blue (MB) and rhodamine B (RhB), from aqueous solutions was investigated in batch and continuous **(Fernandez *et al.*, 2010)** while the chromium biosorption onto *Cupressus lusitanica* Mill bark from aqueous Cr(VI) or Cr(III) solutions and proposes a mechanism of adsorption **(Netzahuatl *et al.*, 2012)** were studied.

**Horsfall *et al.* (2003)** investigated the ability of cassava (*Manihot esculenta* Cranz) waste biomass (untreated and acid treated) to remove heavy metals (Cu(II) and Zn(II) ) from single-ion solution and wastewater. The uptake capacities of the two metal ions tested on the untreated and acid treated cassava waste biomass were 71.3 and 85.2 mg/g for Cu (II), and 43.4 and 58.1 mg/g for Zn (II) in single-ion solution. For wastewater, the uptake capacities of untreated and acid treated biomass was found to be 40.1 and 59.7 mg/g for Cu (II), and 38.6 and 38.7 mg/g for Zn (II), respectively. Metal ion uptake capacities in wastewater were lower than in single-ion solution probably due to competition of metal ions of different sizes on available binding sites. Uptake capacities of these metal ions on the biomass surface increased with acid treatment. Equilibrium sorption studies showed that the extent of metal uptake was enhanced by chemically modifying the cassava waste biomass by thiolation. Cassava left-over can be used repeatedly for removal of heavy metals in single-ion solution and in wastewater effluents.

Agricultural waste is one of the amusing sources of low-cost adsorbents besides industrial by-product and natural material. Due to its abundant availability agricultural waste such as rice husk, wheat bran, peanut husk, and sawdust offer little economic value and, moreover, create serious disposal problems **(Igwe and Abia, 2007)**. Activated carbons derived from peanut husk and rice husk have been successfully employed for the removal of heavy metals from aqueous solutions **(Ricordel *et al.*, 2001).** The use of peanut hull carbon for the adsorption of Cu(II) from wastewater was studied by **(Periasamy and Namasivayam, 1996)** their comparative study of commercial granular activated carbon (GAC) showed that the adsorption capacity of PHC was 18 times larger than that of GAC.

Lignocellulosic solid wastes such as sawdust and pine leaves can be utilized as effective adsorbents for removal of Cr(VI) from wastewater **(Aliabadi *et al.*, 2006)**. The ability of Calabrian pine bark wastes (*Pinus brutia* Ten) for the removal of Fe (II) from aqueous solution at different concentrations and temperatures at a fixed pH was investigated **(Bilal, 2004)**. The modified pine bark is as operative as granular activated carbon in removing hydrophobic pesticides (Removal for chlorpyrifos was 88% to 96%; for chlorothalonil, 84% to 92%; and for dichlobenil, 39% to 90%) from water and may be used as a less expensive alternative sorption medium for removal of pesticides from storm water runoff **(Tshabalala, 2003).**

**Characterization of the Biosorbent and Biosorption Mechanism**

Characterization of bacterial biomass and the biosorption mechanisms can be elucidated using different methods, including potentiometric titrations **(Texier *et al.*, 2000; Yee and Fein, 2001; Phoenix *et al.*, 2002)**, Fourier transform infrared spectroscopy **(Beveridge and Murray, 1980; Jiang *et al.*, 2004; Vannela and Verma, 2006)**, X-ray diffraction **(Carito *et al.*, 1967; Lopez *et al.*, 2000; Kelly *et al.*, 2002; Kazy *et al.*, 2006)**, Scanning electron microscopy **(Tunali *et al.*, 2006a*;* Lu *et al.*, 2006; Vijayaraghavan *et al.*, 2007)**, Transmission electron microscopy **(Mullen *et al.*, 1989; Kazy *et al.*, 2006; Vannela and Verma, 2006)** and energy dispersive X-ray microanalysis **(Small *et al.*, 1999; Kazy *et al.*, 2006)**.

The XRD analysis was done using "Panalytical High Resolution XRD-I, PW 3040/60" to know the crystalline structure of green coconut shell powder prior and after activation. From both tables, it can be concluded that there is a little change in crystalline structure of the sample before and after activation, which may be due to the reason that treatment was done at temperature around 350˚C and the pore structure changed due to change in the textural properties of samples.

The surface arrangement of green coconut shell by SEM at 1.00KX magnification was analyzed. The micrograph and composition of treated and untreated green coconut shell powder were analyzed by SEM and EDS analyzer. It was found that the pores of the untreated green coconut shell were closed prior activation. The activated green coconut shell had a porous structure showing large number of pores and larger size of pores indicating a large surface area shows that the

material is irregular and porous. This surface typical would substantiate high adsorption through mass transport inside the sorbent. EDS analysis, and it shows the presence of C, O, Si, P, Cl, K as natural species and the presence of these elements could have an effect on adsorption mechanism show significant difference between the surface before and after activation and the reason attributed was that a high percent of voids are being occupied by the volatile matters.

SEM images that the external surfaces of both samples were rough and contained abundant porous structures of different size and shapes. The pore walls of the carbon further contained narrow pores which are responsible for high surface area and high adsorption capacity. The micrographs showed that, during carbonization of the *Acacia Nilotica* leaf impregnated with $H_3PO_4$, the volatile matter develops high pressure, which bursts the cellular structure of the particle and creates cavities on the surfaces of the carbon samples, and also causes the evaporation of $H_3PO_4$ during carbonization, leaving the space open that was previously occupied by $H_3PO_4$. During impregnation, the molecules of the chemical impregnating agent diffused into the texture of the cellulosic material. On carbonization at the required temperature, the chemical permeating substrate evaporated and made the remaining carbon texture porous. The major elements present in both samples were carbon, hydrogen, and oxygen with a small fraction of nitrogen (**Thilagavathy1, T. Santhi 2012**).

The biomass generated from the dried leaves of *Terminalia Catappa*, *Dalbergia latifolia* and *Ficus benghalensis* was used for evaluating the biosorption characteristics of Pb and Cu ions in aqueous solutions. From the leaf structure from XRF, Ion exchange may be could be one of the options for studying the mechanism of adsorption of these cations on these leaves **(Nagpal and Hassan, 2010)**. It has been reported that the biosorption of Zn (II) ion onto surface of *Cedrus Deodara* Sawdust (CDS). Electron Micrograph (SEM) revealed the existence of functional groups like carboxyl, hydroxyl, amine, amide and methyl coupled within the presence of tremendous number of mesopores resulting in enhanced external surface area meant for metal ion adsorption **(Mishra *et al*., 2011)**.

Sorption of copper and nickel on grape stalks released an equivalent amount of alkaline and alkaline earth metals ($K^+$, $Mg^{2+}$, $Ca^{2+}$) and protons, pointing that ionic exchange is predominantly responsible for metal ion uptake. Fourier transform

infrared (FTIR) spectrometry analysis indicated that lignin C-O bond might be involved in metal uptake **(Villaescusa *et al.*, 2004)**.

**Factors affecting the biosorption and its Equilibrium & Kinetic studies**

With the increase contact time the uptake of adsorbate increased for all the metals studied and it remained stagnant after an equilibrium time. The equilibrium time may be varied with the kind of husk under consideration and it increased with the increase in initial metal concentration. Chromium adsorption by turdal husk was free of time and attained equilibrium within 5 minutes of contact. The equilibrium time was independent of the adsorbate amount as seen by chromium adsorption by bengal gram husk, tur dal husk and tamarind husk. The adsorbate concentration influenced the equilibrium time of the metal uptake by rest of the adsorbents. At any contact time, increase in initial adsorbate concentration decreased the percent adsorption and increased the amount of adsorbate uptake (q) per unit weight of the adsorbent. It was observed that for the low initial concentrations, the % uptake of the adsorbate was high. Even though the percent uptake of the adsorbate was lesser at high initial concentrations, the actual amount of the metals adsorbed (q) increased with increase in the initial adsorbate concentration in the solution. The uptake (q) vs time curves were single, smooth and continuous leading to saturation, suggesting the possible monolayer coverage of the adsorbate on the surface of the adsorbent. Several authors have reported similar results for the adsorption of metals **(Kanchana and Namasivayam, 1994; Namasivayam *et al.*, 1993; Singh *et al.*, 1992)** Equilibrium time change with the metals due to the difference in initial metal concentration and empathy of the adsorbent for the particular metal ion. In all the experiments conducted, 100 ppm solutions took longer to attain equilibrium due to the presence of proportionally high amount of metal ions.

**Mameri *et al.* (1999)** reported that the available adsorption sites on the biosorbent are the limiting factor for metal uptake. The equilibrium time required by the adsorbents used in the present study is less, compared to others reported in literature. This is significant as equilibrium time is one of the important considerations for economical water and wastewater applications. In process application, this rapid (or instantaneous) biosorption phenomenon is advantageous

since the shorter contact time113 effectively allows for a smaller size of the contact equipment, which in turn directly affects both the capacity and operation cost of the process

**Effect of pH on the adsorption of metal ions**

**Chromium:** The percent removal of Cr (VI) increased with decrease in pH for the different concentrations of Cr (VI) which is typical of oxyanion adsorption on metal hydroxides. Similar optimum pH conditions were seen for all the four adsorbents. Chromium (VI) removal increased from 8.3% at pH 4 to 99.8 at an initial pH of 1.5 for tamarind husk; more than 99% of 10 mg/L of Cr (VI) was removed at pH 2 by bengal gram husk, tur dal husk and coffee husk. The percentage of Cr (VI) adsorbed at optimum pH decreased with increase in the concentration of initial Cr (VI) ions. The amount of chromium adsorbed decreased with increase in pH. But the amount adsorbed increased with increase in initial chromium concentration. Chromium exhibits different types of pH dependent equilibria in aqueous solutions **(Rollinson, 1973)**.

The only species that can exist in solution, above pH 8.0 is $CrO_4^{2-}$ As the pH is shifted, the equilibrium will also shift; in the pH range 2-6, $HCrO_4$, and $Cr_2O_7^{2-}$, ions are in equilibrium. At still lower pH (pH <2.0) values, $Cr_3O^{10-}$ and $Cr_4O_{13}^{2-}$ species are formed. Thus the formation of more polymerized chromium oxide species occurs with the decrease in solution pH. In highly acidic media, the adsorbent surfaces are highly protonated and favour the uptake of Cr (VI) in the anionic form $HCrO^{4-}$. The removal of Cr (VI) by carbonaceous materials such as saw dust, sugar beet, sugar beet pulp, sugarcane bagasse and maize cob at an optimum pH 2.0 has been reported by **Sharma and Forster (1994)**

This section compacts with the prerequisites and technique applied during various experiments which were carried out during the research period.

The biosorption experiments were completed in the Post Graduate Research laboratory, Department of Chemistry, College of Basic Sciences and Humanities, G.B. Pant University of Agriculture & Technology, Pantnagar. Infrared Spectroscopy analysis of the plant materials were carried out in Banaras Hindu University, Banaras, Scanning Electron Microscopy imaging of the plant materials were carried out in Advanced Instrument Research Facility, JNU,NEW DELHI, **Advanced Instrumentation Research Facility, JNU, New Delhi, India**

## 3.1 Experimental Materials

### 3.1.1 Collection of Plant material

Biosorbent material was collected and erstwhile to it biosorption studies were executed. The samples of plant material were collected few months earlier the experiment from Uttarakhand hills. The plants were identified by Dr. D .S. Rawat, Associate professor and taxonomist, Department of Biological Sscience, C.B.S.H. The collection details is given in the table 3.1

**Table 3.1 Collection details of Gymnosperm plant species**

| S.No. | Plant name | Family | Place of collection |
|---|---|---|---|
| 1. | *Cupressus torulosa* D. Don. | Cupressaceae | Kumaun (Pithoragarh) |
| **2.** | *Taxux baccata* L. | Taxaceae | Kumaun (Munsyari) |

### 3.1.2 Chemicals

The solvents and chemicals used throughout the sequence of this investigation were of Laboratory and Analytical grade, supplied by E. Merck (India), Hi Media (India), B.D.H (India) and S.D. Fine chemicals (India). The solvents were distilled prior to use.

### 3.1.3 Glassware's

All the glassware's used were of corning grade manufactured by Borosil, India Ltd., Reviera, India and Agassi, India.

### 3.1.4 Equipment's

The following equipment's were used during the course of investigation:

1. Hot plate (Gamson Pvt. Ltd., India)
2. Electronic weighing machine (Petit balance) (K.Roy & Company, India)
3. Water distillation assembly (Infusil India Pvt. Ltd., Bangalore (Model no. AQDO-25-DB)
4. Grinder (Willy mill)
5. Sieve (1.5 mm sieve size)
6. Incubator Shaker (Bench- Top Model SI45)
7. Atomic Absorption Spectrophotometer- Model no ECIL-Hyderabad, AS-4141
8. Infrared Spectrophotometer- PerkinElmer Spectrum Version 10.03.05
9. Scanning electron microscope Ziess Evo40

## 3.2 Biosorption Experiments

### 3.2.1. Preparation of Bioadsorbent materials

The leaves and barks of two species of gymnosperm plants; *Cupressus torulosa* and *Taxus baccata* were used as bioadsorbent in the present study, collected from high area of kumaun hills of Uttarakhand state. The leaves and barks of all plants were collected from the twig, putted in to clean plastic bags and washed carefully in running tap water and then in deionized water to remove dirt and other particulate matter. The washed leave and barks were air dried for 2-3 month. Dry leaves and barks grounded in to grinder having 2.5 mm sieve size the grounded material was sieved with the help of a sieve of pore size 2.5 mm. now the material were stored in to air tight boxes for further use in experiments.

## 3.2 Preparation of Stock solution of Chromium Sulfate

For the preparation of 100 ppm of chromium solution, 0.469 g of chromium sulphate hexahydrate ($Cr_2(SO_4)_3.6H_2O$) was dissolved into 1000 mL of triple distilled water. This solution was used as stock solution for preparation of diluted concentration of 1 ppm and 2 ppm of chromium solution by using 1 mL and 2 ml respectively, dissolved In 100 ml of triple distilled water.

## 3.3 Preparation of Buffer solutions

Preparation of standard acidic, neutral and basic buffer solutions was carried out using buffer capsules of pH 4.2±0.05, 7.0±0.05 and 9.0±0.05 at 27ºC in 100 mL of triple distilled water respectively, which contains potassium dihydrogen orthophosphate and di-sodium hydrogen orthophosphate.

## 3.4 Assessment of Biosorption potential of leaves and barks of Gymnosperm plants on Chromium metal ion removal from synthetic solution at various parameters.

### Experiment I: Effect of initial metal concentration

To evaluate the effect of initial chromium metal ion concentration on the adsorption behavior of chromium metal ion, a set of four conical flasks were taken and 50 mL of synthetic solution of different concentrations (1 ppm and 2 ppm) with different pH, was added in all flasks. To the flasks 1 and 2g amount of biomass of *Cupressus torulosa* leaves and bark was added. The solutions were shaken well in an incubator shaker at 250 rpm at room temperature (25±5ºC) and at hot temperature (40±5ºC) for different time period. The slurry, after equilibrium, was filtered through Whatman No. 1 filter paper. The clear filtrate was analyzed for metal concentration using AAS.

The same procedure was repeated using the Leaves and bark of *Taxus baccata*.

### Experiment II: Effect of pH

To a set of conical flasks containing 1 and 2g biomass (bark) of *Cupressus torulosa* and 50 mL of synthetic solution (1 and 2 ppm of Cr) was added in all flasks. The pH of effluent in different flasks was varied from acidic to basic (4.2, 7.0 and 9.0). The solution of different pH were shaken well in an incubator shaker at 250 rpm

at room temperature (25±5ºC) and at hot temperature (40±5ºC) for different time period. The slurry, after equilibrium, was filtered through Whatman No.1 filter paper. The clear filtrate was analyzed for metal concentration using AAS

The same procedure was repeated using Leaves and bark of *Taxus baccata.*

**Experiment III: Effect of incubation period**

To a set of conical flasks, 50 mL of synthetic solution (1 and 2ppm) with different pH and 1 and 2g of biomass of *Cupressus torulosa* was added. The solution was shaken well in an incubator shaker at 250 rpm at room temperature (25±5ºC) and at hot temperature (40±5ºC) for different time period. The flasks were incubated for different time period of 30, 60, 90 and 120 min. The slurry, after equilibrium, was filtered through Whatman No.1 filter paper. The clear filtrate was analyzed for metal concentration using AAS.

The same procedure repeated using Leaves and bark of *Taxus baccata.*

**Experiment IV: Effect of biomass (Leaves and barks) amount**

To evaluate the effect of biomass amount on the adsorption behavior of chromium metal ion, a set of conical flasks were taken and 50 mL of synthetic solution of 1 and 2 ppm with different pH and different amount of biomass of 1 and 2g of *Cupressus torulosa* leaves and bark was added. The solution was shaken well in an incubator shaker at 250 rpm at room temperature (25±5ºC) and at hot temperature (40±5ºC) for different time period. The slurry, after equilibrium, was filtered through Whatman No.1 filter paper. The clear filtrate was analyzed for metal concentration using AAS.

The same procedure repeated using leaves and bark of *Taxus baccata*

### 3.5 Analysis of Chromium (III) metal ions

Analysis of Cr (III) was carried out from digested sample using atomic absorption spectrophotometer (AAS).

#### 3.5.1 Digestion

Digestion of sample was done using nitric acid-hydrochloric acid digestion according to **USEPA method**.

- Transfer 50ml representative aliquot of well mixed sample into a beaker and add 2 mL of concentrated nitric acid.
- Place the beaker on a hot plate and evaporate to near dryness, making certain the sample does not boil.
- Cool the beaker and add another 2 mL of the conc. nitric acid.
- Cover the beaker with a watch glass and return it to the hot plate. Increase the temperature of the hot plate so that a mild reflux occurs. Add additional acid, if necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change color or presence with continued refluxing).
- Again, evaporate to near dryness (do not bake) and cool the beaker. If any residue or precipitous results from the evaporation, add hydrochloric acid (5 mL per 100 mL of final volume).
- Warm the beaker and quantitatively transfer the sample to a volumetric flask and dilute to volume with deionized water.

### 3.5.2 Residual Metal Ion Analysis

After the filtration of the solution, the residual metal ion content in the filtrate was measured by using an Atomic absorption Spectrophotometer.

**Calculation of removal % of metal ions:**

Removal percentage was expressed as a percentage of complexed metal compared to initial metal ion concentration:

$$\text{Removal (\%)} = (C_i - C_{eq}) / C_i \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where $C_i$ and $C_{eq}$ are the initial and final concentrations of metal ion respectively.

### 3.5.3 Metal uptake by biomass

Specific metal uptake was calculated as follows:

The adsorption capacity:

$$Q_e = (C_i - C_e)\ V/m \quad \ldots\ldots\ldots\ldots\ldots\ldots..(2)$$

Where V is the volume (L) of metal solution and m is the weight of biomass in gram.$C_i$ and $C_e$ are the initial concentration and concentration at equilibrium of metal ion respectively. V is the volume (L) of metal solution and m is the weight of biomass in gram.

### 3.6 Adsorption isotherms

The biosorption isotherm indicate how the molecules distribute between the liquid phase and the solid phase when the biosorption process reaches the equilibrium state i.e. the presentation of the amount of solute absorbed per unit of adsorbent. To understand the effect of various factors on adsorption, different adsorption isotherms are available. The shape of an isotherm can usually forecast to know whether the adsorption is favourable or unfavourable. In our study Langmuir, Freundlich and Tempkin equations were used to evaluate the experimental data and described as:

#### 3.6.1 Langmuir Adsorption Isotherm

The Langmuir adsorption isotherm consider the supposition that there is a finite no. of binding sited which are homogeneously distributed over the adsorbent surface of the cells, having the same affinity for adsorption of a single molecular layer and there is no interaction between adsorbed molecules **(Langmuir, 1916).** The Langmuir equation was used to describe the observed sorption of chromium ions and is as shown by the following equation.

$$C_e / Q_e = 1/b\, Q_{max} + C_e / Q_{max} \qquad \ldots\ldots\ldots(3)$$

where, $Q_{max}$ (mg/g) is the measure of maximum metal ion per unit mass of sorbent to form a complete monolayer on the surface bound at high $C_{eq}$, and b (L/mg) is a constant related to the empathy of the biomass surface biding sites when the surface is fully covered with the metal ions and assist in the contrast of adsorption performance, particularly in the case where the sorbent didn't reach its full saturation.

#### 3.6.2 Freundlich Adsorption Isotherm

Freundlich model is an empirical model used to describe the adsorption in heterogeneous surface **(Freundlich, 1906)** to explain the adsorption of chromium ions on to adsorbent. Freundlich model presumed that the adsorption energy of metal

binding to a site on the adsorbent depend on whether or not the adjacent sites are already occupied. The Freundlich isotherm is shown by the following equation:

$$\log Q_e = 1/n \log C_e + \log K_f \quad \text{.....(4)}$$

where **$K_f$** and **n** are Freundlich constants, characteristics of the system. $K_f$ (mg/g) and n (L/mg) is the maximum adsorption capacity of the sorbent and **n** is the indication of how favourable the adsorption process if value 1/n is below one it shows a normal adsorption. On the other hand, 1/n being above one indicates cooperative adsorption **(Mohan and Karthikeyan 1997).**

### 3.6.3 Tempkin Adsorption Isotherm

This isotherm contains into account the adsorbent-adsorbate interactions and suggested that because of these interfaces the heat of adsorption of all the molecules in the layer would decrease linearly with coverage. The model is given by the following equation **(Tempkin and Pyzhev, 1940):**

$$B = RT/b$$

$$Q_e = B \ln A + B \ln C_e \quad \text{.....(5)}$$

AT=Tempkin isotherm equilibrium binding constant (L/g),bT = Tempkin isotherm constant, R= universal gas constant (8.314J/mol/K), T= Temperature at 298K.,B = Constant related to heat of sorption(J/mol).

### 3.6.4 Separation factor

A dimensionless constant, separation factor ($R_L$) can be used to predict whether a sorption system is favorable or not in batch adsorption process. $R_L$ values between 0 and 1 represent the favourable isotherm. It will be calculated from Langmuir isotherm based equation **(Riaz *et al* 2009).**

$$R_L = 1/ (1+b* Co) \quad \text{.....(6)}$$

Where b (L/mg) is a constant associated to the affinity of the biomass surface binding sites. Calculated from Langmuir equation and Co is the initial Cr (III) concentration. The parameter, $R_L$ indicate the shape of isotherm and the nature of the sorption process as given below:

$R_L > 1$ = unfavourable isotherm

$R_L$ = 1= linear isotherm

$R_L$ =0= irreversible isotherm

0< $R_L$ < 1= favourable

### 3.7 Biosorption Kinetics

The prediction of the biosorption rate gives important information for designing batch biosorption systems. The sorption kinetics is significant in the treatment of wastewater, as it provides valuable insights into the reaction pathways and mechanisms of sorption reactions.

Several kinetic models have been applied to fit the biosorption data of different metal ions onto various biosorbents. These models include the pseudo-first order, pseudo-second order, etc.

#### 3.7.1 Pseudo-first-order kinetic model (Lagergren model):

This model accepts that metal ion binds only to one sorption site on the sorbent surface **(Lagergren 1998)**. In Lagergren model, the rate of occupation of biosorption sites is proportional to the number of unoccupied sites (**Ghaedi *et al*., 2013**).

The model is represented by:

$$\text{Ln } (Q_e - Q_t) = \ln Q_e - K_1.t \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots .(7)$$

where $K_1$ ($min^{-1}$) is the pseudo first order adsorption rate coefficient which is also known as Lagergren rate constant, Qe and Qt are the values of amount adsorbed per unit mass (mg/g) at equilibrium and at any time t. in most of the cases, the first order equation of Lagergren does not fit well for the full range of contact time and is generally applicable over the initial 20-30 min of the sorption process **(Abdel-Ghani, 2009 ).**

#### 3.7.2 Second order kinetic model

It assumes that the rate limiting step is utmost likely to involve chemical interactions leading to binding of the ions to the surface by bonding as strong as

covalent bonding. The pseudo-second-order equation (**Ho and McKay, 1998)** based on equilibrium biosorption is expressed as:

$$dQ_t / dt = K_2 (Q_e - Q_t) \quad \ldots\ldots\ldots\ldots\ldots\ldots (8)$$

After integration and applying boundary conditions, t = 0 to t = t and Q = 0 to Q = $Q_e$; the integrated form of this equation becomes:

$$t/Q = 1/ K_2 Q_e^2 + t /Q_e; \quad \ldots\ldots\ldots\ldots\ldots\ldots..(9)$$

Where $K_2$ (g/mg min.) is the rate constant of second-order adsorption. The product $K_2Q_e^2$ actually represents the initial biosorption rate.

### 3.7.3 Elovich equation

The Elovich equation was originally developed to describe the kinetics of heterogeneous chemisorption of gases on solid surface. It seems to describe a number of reaction mechanism, comprising bulk and surface diffusion and activation and deactivation of catalytic surfaces. The Elovich or ronginsky-zeldovich equation is generally expressed as follow **(Low, 1960):**

$$\mathbf{dQ_t / dt = \alpha_{exp} (-\beta Q_1)} \quad \mathbf{\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (10)}$$

To simplify the Elovich equation, **(Chien and Clayton 1980)** assumed $\alpha.\beta >>> 1$, and on applying boundary condition t=0 to t=t and $Q=Q_{eq}$ ; the integrated form of equation 11 Becomes **(Sparks, 1986)**:

$$\mathbf{Q_t = \beta \ln (\alpha\beta) + \beta \ln t} \quad \mathbf{\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(11)}$$

Where $Q_t$, is the amount of metal sorbed (mg/g) at any given time t while, αis the initial metal sorption rate (m mol/g.min) and β is the desorption constant (g/m mol).

## 4.1 Biosorption Experiment

It is always desirable that a system should work at its maximum efficiency. This can be achieved by optimizing the conditions which may affect the efficiency of a system. In present study leaves and bark of *Cupressus torulosa* and *Taxus baccata,*were used as biosorbents for the removal of chromium metal ions from the chromium sulphate solutions. Investigation have been incorporated along with discussion under two different sections. In the first section the physicochemical properties like pH, temperature, time and concentration of the samples were studied along with the AAS (Atomic Absorption Spectroscopy) analysis and were supported by Langmuir, Freundlich and Tempkin models. Second section deals with the comparative FTIR and SEM studies.

Furthermore the effects of these parameters on adsorption potential of two gymnosperm plants are discussed below:

### 4.1.1 Biosorption potential of *Taxus baccata*

The data pertaining to effects of reaction time, pH, concentration of Cr (III) ions, adsorbent dose and temperature on the sorption of Cr (III) by leaves and barks of *Taxus baccata* plant from aqueous solution of chromium sulphate.

#### 4.1.1.1 Effect of contact time

The effect of contact time was observed at initial metal concentration (1 mg/L), acidic pH (4.2), biomass amount (1g) and cold (25±5˚C) to hot (40±5˚C) temperature conditions. Leaves and bark showed maximum absorption at 120 min when measured at the interval of 30min, visualized in **Table 4.1.** It can be visualized by **Fig**. **4.1** that the maximum removal by *Taxus baccata* leaves was 89.40 and 93.60% at cold and hot temperature conditions while bark showed 90.33 and 93.23% removal at cold and hot temperature conditions respectively at 120 min. As the contact timings increased, percentage removal also increased in significant way. At 30 min leaves and barks showed minimum removal as 70.60, 78.93, 67.66 and 81.83 % removal at cold and hot temperature. The **Fig**.**4.1** also represented that the removal

percentage and removal capacity per 1.0g of adsorbent biomass. The data showed that at 120 min leaves and bark of *T.baccata* adsorbed 45.16, 46.83, 44.70 and 46.61 mg of copper ions at cold and hot temperature conditions respectively. It was the maximum removal capacity for leaves and bark biomass at 120 min while at 30 min these showed minimum 33.61, 39.46, 35.30 and 40.91 mg of copper ions removal capacity per 1.0g of biosorbents. There was an increasing trend of copper adsorption by leaves and bark at different temperature conditions with increase in contact timings but after 120 min, adsorption of copper decreased which could be due to the unavailability and saturation of metal binding sites present in *Taxus baccata* biomass.

#### 4.1.1.2 Effect of pH

To study the effect of pH on biosorption, experiment was conducted at three different pH (4.2, 7.0 and 9.0) with initial metal ion concentration of 1 mg/L, contact time of 120 min, biomass dosage of 1g and temperature at 25±5˚C and 40±5˚C. **Table 4.2** represented the biosorption data of Cr (III) removal by *Taxus baccata* leaves and barks biomass at varying pH. Maximum removal of Cr (III) by leaves biomass was observed at acidic pH (4.2) followed by removal at neutral pH (9.0) and basic pH (7.0) at cold temperature respectively. While, maximum removal of Cr (III) by leaves biomass was observed at neutral pH (9.0) followed by acidic pH (4.2) and basic pH (7.0) at hot temperature respectively. At cold and hot temperature, the removal of Cr (III) by bark biomass at different pH follows the order as: neutral pH (9.0)> acidic pH (4.2)> basic pH (7.0). **Fig**. **4.2** showed that leaves undergo maximum removal of Cr (III) at acidic pH (97.76%) followed by removal at neutral pH (91.13%) and removal at basic pH (89.10%) at cold temperature. But at hot temperature, leaves showed maximum removal of Cr (III) at neutral pH (95.90%), slightly higher than acidic pH (95.63%) and lowest at basic pH (86.53%). At cold (91.66%) and hot temperature (95.40%) bark showed maximum percentage removal of Cr (III) at neutral pH. In terms of adsorption capacity, maximum removal of Cr (III) by leaves at cold and hot temperature was 48.88 and 49.31mg at acidic pH respectively and bark absorbed 45.83mg in cold and 47.70mg in hot temperature from neutral solution of chromium sulphate When the pH increases, the concentration of $H^+$ ions decreases and negatively charged biomass surface can interact with the positively charged metal ions.

**Table 4.1: Biosorption efficiency of leaves and bark of *Taxus baccata* plant at different temperature and time interval for Cr(III)**

| Plants / Time | TBL-C | | TBL-H | | TBB-C | | TBB-H | |
|---|---|---|---|---|---|---|---|---|
| | Qe (mg/g) | % Removal | Qe (mg/g) | % Removal | Qe (mg/g) | % Removal | Qe (mg/g) | % Removal |
| **30 min** | 33.61±0.34 | 70.60±0.24 | 39.46±0.13 | 78.93±0.26 | 35.30±0.12 | 67.66±0.36 | 40.91±0.14 | 81.83±0.28 |
| **60 min** | 39.58±0.14 | 79.30±0.56 | 43.55±0.29 | 87.00±0.58 | 39.65±0.18 | 79.16±0.28 | 42.68±0.23 | 85.33±0.47 |
| **90 min** | 43.18±0.04 | 88.80±0.21 | 46.11±0.10 | 92.23±0.20 | 44.40±0.10 | 86.36±0.09 | 45.63±0.26 | 91.23±0.52 |
| **120 min** | 45.16±0.47 | 89.40±0.16 | 46.83±0.06 | 93.66±0.12 | 44.70±0.08 | 90.33±0.94 | 46.61±0.48 | 93.23±0.96 |

**Table 4.2: Biosorption efficiency of leaves and bark of *Taxus baccata* plant at different temperature and pH for Cr (III)**

| Plants / pH | TBL-C | | TBL-H | | TBB-C | | TBB-H | |
|---|---|---|---|---|---|---|---|---|
| | Qe (mg/g) | % Removal | Qe (mg/g) | % Removal | Qe (mg/g) | % Removal | Qe (mg/g) | % Removal |
| **Acidic (4.2)** | 48.88±0.06 | 97.76±0.11 | 49.31±0.08 | 95.63±0.15 | 44.70±0.08 | 89.4±0.09 | 46.61±0.0.48 | 93.23±0.87 |
| **Neutral (7.0)** | 45.56±0.12 | 91.13±0.25 | 47.95±0.09 | 95.90±0.17 | 45.83±0.13 | 91.66±0.24 | 47.70±0.10 | 95.40±0.08 |
| **Basic (9.0)** | 44.50±0.10 | 89.10±0.20 | 43.26±0.02 | 86.53±0.06 | 44.55±0.08 | 89.10±0.09 | 42.60±0.04 | 85.20±0.04 |

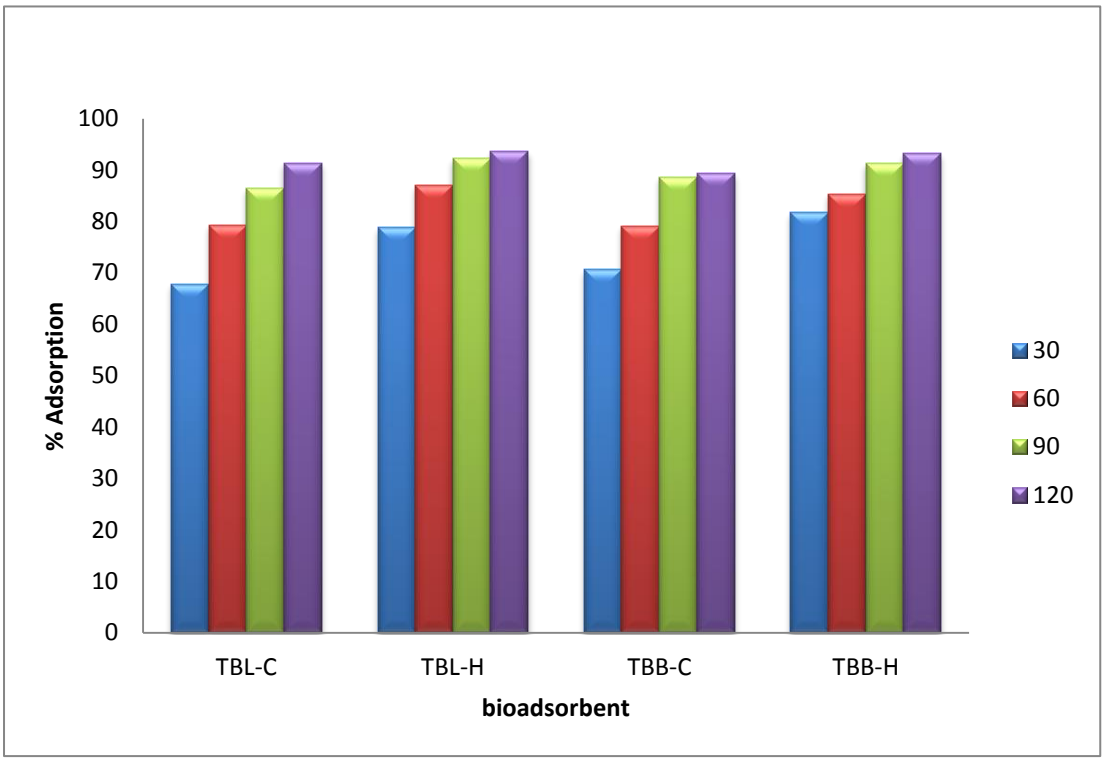



**Fig 4.1: Effect of contact time on biosorption of Cr (III) by leaves and barks of *Taxus baccata* at different temperatures (25±5˚C and 40±5˚C) (pH=4.2, initial metal conc. =1ppm and biomass = 1g)**

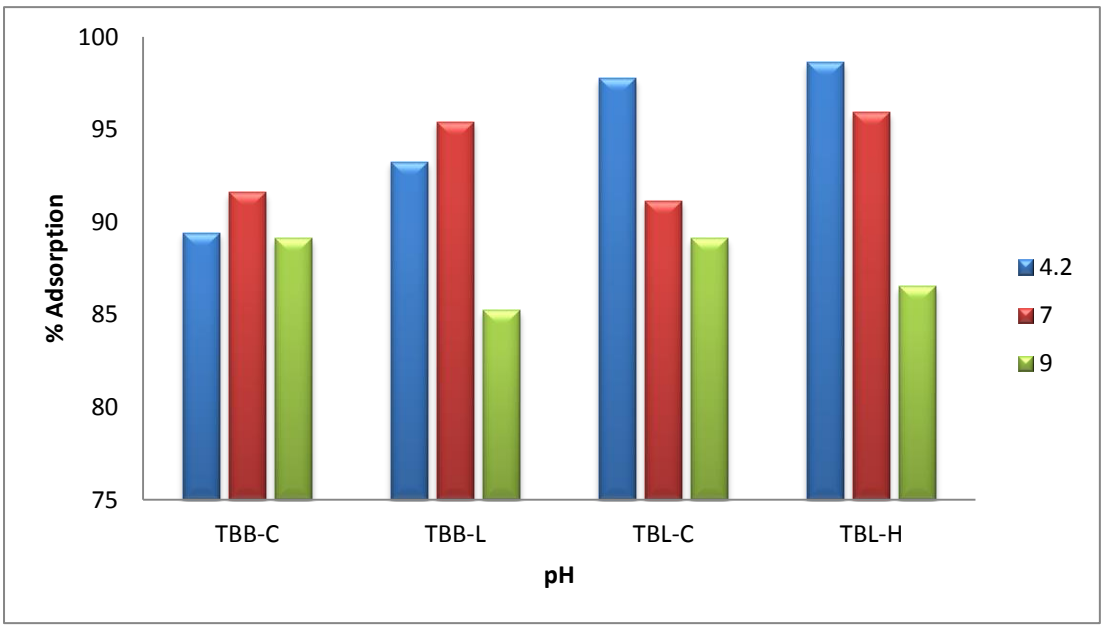



**Fig. 4.2: Effect of pH on biosorption of Cr (III) by leaves and barks of *Taxus baccata* at different temperatures (25±5˚C and 40±5˚C) (contact time= 120min, initial metal conc. = 1ppm and biomass = 1g)**

**Table 4.3: Biosorption efficiency of leave and bark of *Taxus baccata* plant at different temperature and Cr (III) metal ion concentration**

| Plants / Time | TBL-C | | TBL-H | | TBB-C | | TBB-H | |
|---|---|---|---|---|---|---|---|---|
| | Qe (mg/g) | % Removal | Qe (mg/g) | % Removal | Qe (mg/g) | % Removal | Qe (mg/g) | % Removal |
| **1.0 ppm** | 45.16±0.47 | 89.40±0.16 | 46.83±0.06 | 93.66±0.12 | 44.70±0.08 | 90.33±0.94 | 46.61±0.48 | 93.23±0.96 |
| **2.0 ppm** | 46.65±0.03 | 93.31±0.07 | 46.29±0.05 | 92.50±0.01 | 46.72±0.06 | 93.4 ±0.13 | 45.82±0.23 | 91.65±0.0 |

**Table 4.4: Biosorption efficiency of leave and bark of *Taxus baccata* plant at different temperature and biomass amount for Cr (III)**

| Plants amount | TBL-C | | TBL-H | | TBB-C | | TBB-H | |
|---|---|---|---|---|---|---|---|---|
| | Qe (mg/g) | % Removal | Qe (mg/g) | % Removal | Qe (mg/g) | % Removal | Qe (mg/g) | % Removal |
| **1 g** | 45.16±0.47 | 89.40±0.16 | 46.83±0.06 | 93.66±0.12 | 44.70±0.08 | 90.33±0.94 | 46.61±0.48 | 93.23±0.96 |
| **2 g** | 45.23±0.29 | 90.46±0.58 | 47.06±0.07 | 94.13±0.15 | 48.16±0.25 | 96.33 ±0.50 | 48.68±0.05 | 97.36±0.11 |

#### 4.1.1.3 Effect of initial metal ion concentrations

The data presented in **Table 4.3** shows sorption of Cr (III) by leaves and barks of *Taxus baccata* at two metal concentrations (1.0 and 2.0 ppm) with a contact time of 120 min biomass amount of 1g, acidic pH (4.2) and different temperatures (25±5˚C and 40±5˚C). Persual of **Table 4.3 and Fig. 4.3** evident that there was different trend observed for Cr(III) removal by leaves and bark at different temperature. At cold and hot temperature leaves and bark removed maximum 89.40, 93.66, 90.33 and 93.23% of chromium ions respectively from 1ppm of chromium ion solution. At cold and hot temperature leaves and bark removed maximum 93.31, 92.50, 93.4 and 91.65% of chromium ions from 2ppm chromium ion solution. Among the leaves and barks, leaves at hot temperature showed maximum removal efficiency at 1ppm while, bark at cold temperature showed maximum removal efficiency at 2ppm metal concentrations. Adsorption capacity follows the same trend in percentage removal of Cr (III) ions as in case of leaves at hot temperature at 1ppm (46.83mg) and bark at cold temperature at 2 ppm (46.72mg). At cold temperature the removal percentage of Cr (III) increases with increase of concentration which may be due to may be due to availability of binding sites in biosorbent material while decreasing trend may be due to fulfilling of functional groups sites at biosorbent surface.

#### 4.1.1.4 Effect of biosorbent amount

To analyze the effect of biosorbent amount on biosorption of chromium ions, an experiment was conducted at two biomass amounts of leaves and barks of *Taxus baccata* (1.0 and 2.0g), initial metal ion concentration (1 ppm), contact time (120 min), pH (4.2) and different temperature conditions (25±5˚C and 40±5˚C).

**Table 4.4 and Fig. 4.4** describes the adsorption capacity and biosorption of Cr (II) by leaves and bark biomass at varying biomass amounts. 2.0 g leaves and bark biomass of *T. baccata* showed maximum removal of Cr (III) at cold and hot temperature respectively. At cold temperature leaves (90.46%) and bark (96.33%) showed maximum percentage removal of chromium metal ions while at hot temperature leaves (94.13%) and bark (97.36%) showed maximum percentage removal of chromium metal ions. At cold temperature leaves and bark absorbed 45.23 and 48.16mg of chromium while at hot temperature leaves and bark absorbed 47.06

and 48.68mg of chromium respectively. Results found that, with increase in biomass amount, sorption of metal ions increased.

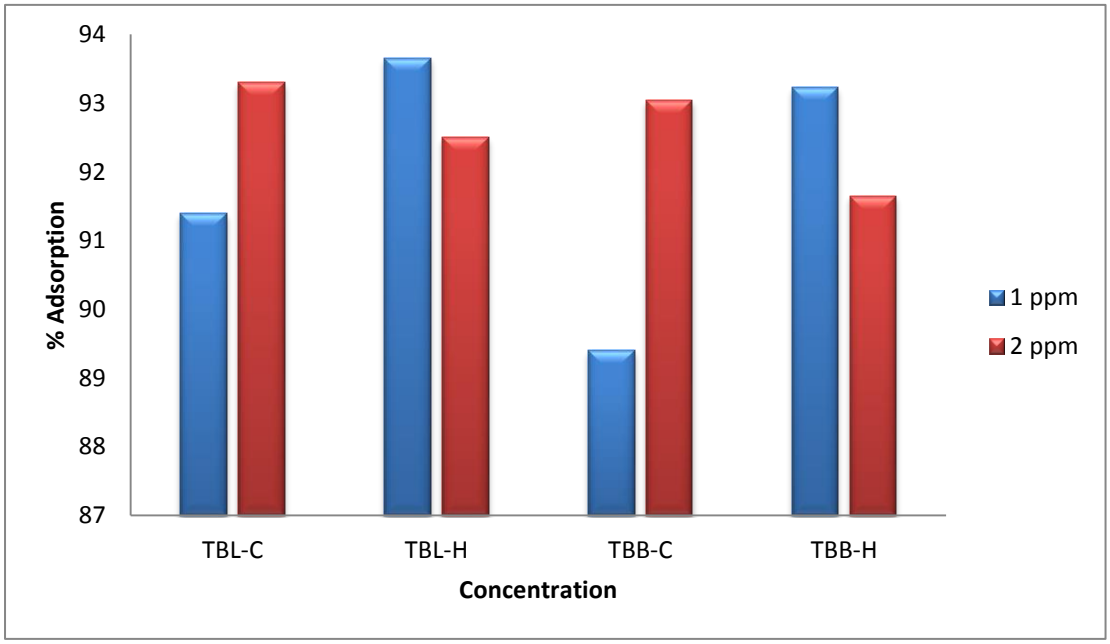



**Fig. 4.3: Effect of initial metal concentarations on biosorption of Cr (III) by leavesand barks of *Taxus baccata* at different temperatures (25±5˚Cand 40±5˚C) (contact time= 120min, pH = 4.2 and biomass = 1g)**

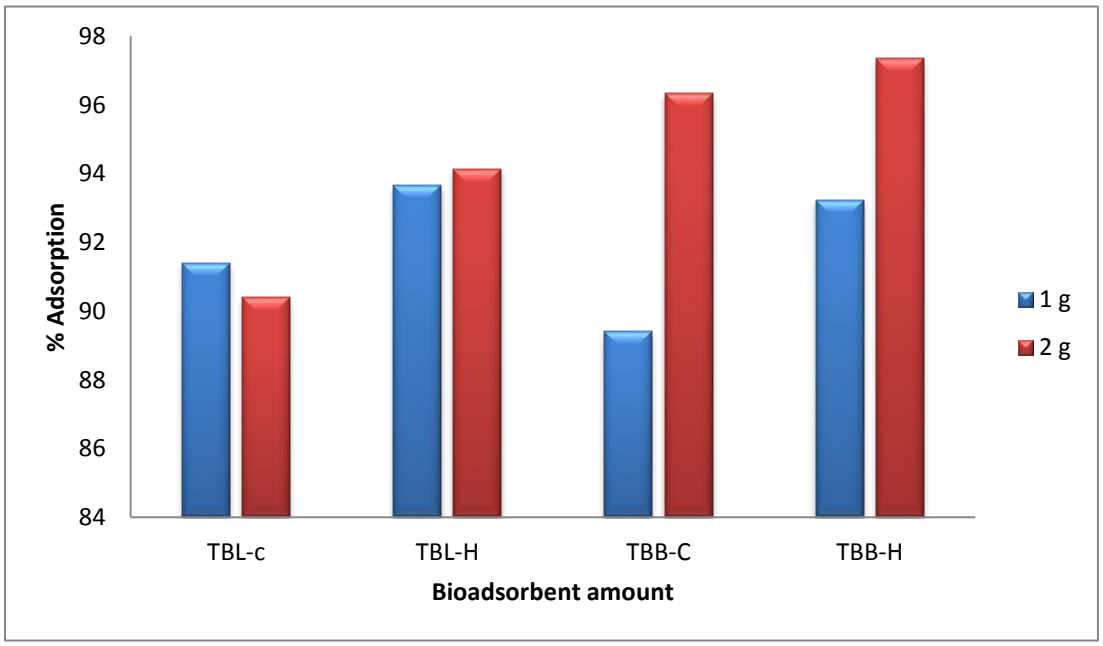


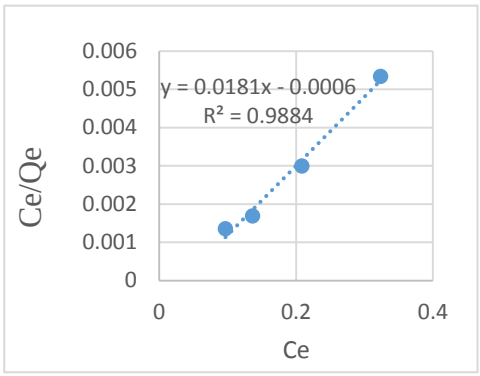

**Fig. 4.4: Effect of biomass amounts on biosorption of Cr (III) by leaves and barks of *Taxus baccata* at different temperatures (25±5˚C and 40±5˚C) (contact time= 120min, initial metal conc. = 1ppm and pH = 4.2**

### 4.1.2 Adsorption isotherms for Cr (III) removal by biomass of *Taxus baccata* plant

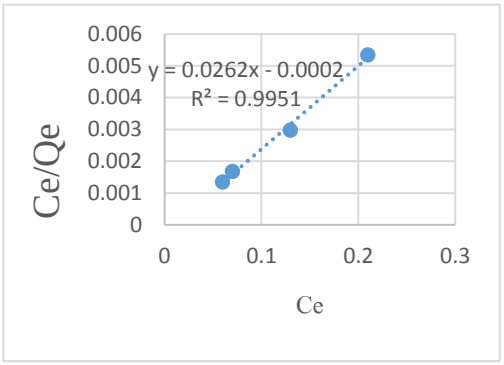
The Langmuir, Freundlich and Temkin models for leaves and bark of *Taxus baccata* were represented by **Fig. 4.5** and **Fig. 4.6** respectively. For leaves of *Taxus baccata* plant at cold temperature the $R^2$ values were 0.988, 0.952 and 0.968 while at hot temperature these were 0.995, 0.969 and 0.976 and for bark of *Taxus baccata* plant at cold temperature the $R^2$ values were 0.996, 0.978 and 0.986 while at hot temperature these were 0.999, 0.904 and 0.987 of Langmuir, Freundlich and Tempkin models respectively **(Table 4.5).** Langmuir isotherm model found to be most suitable at hot and cold temperature for leaves and bark shows monolayer type of adsorption chromium ions.

**Table 4.5: $R^2$ value for chromium adsorption obtained from different isotherm models**

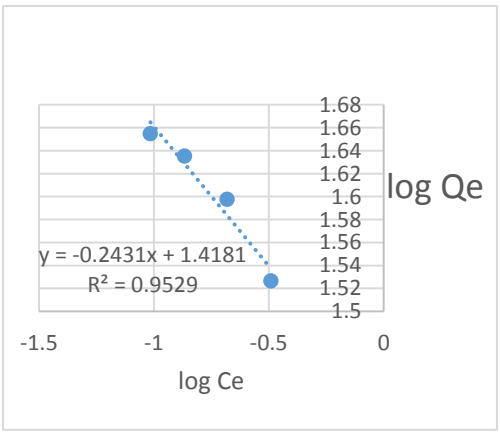
| Sample | Langmuir | Freundlich | Tempkin |
|---|---|---|---|
| **TBL-C** | 0.988 | 0.952 | 0.968 |
| **TBL-H** | 0.995 | 0.969 | 0.976 |
| **TBB-C** | 0.996 | 0.978 | 0.986 |
| **TBB-H** | 0.999 | 0.904 | 0.987 |



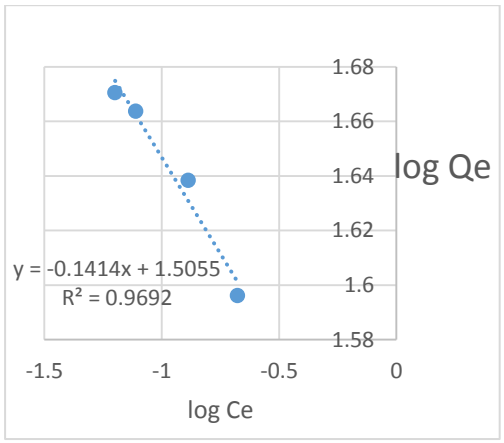

A



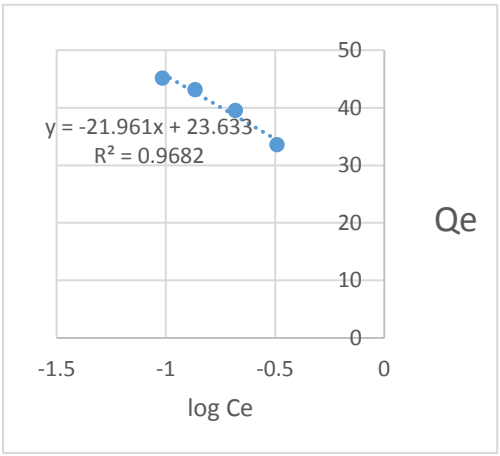

B



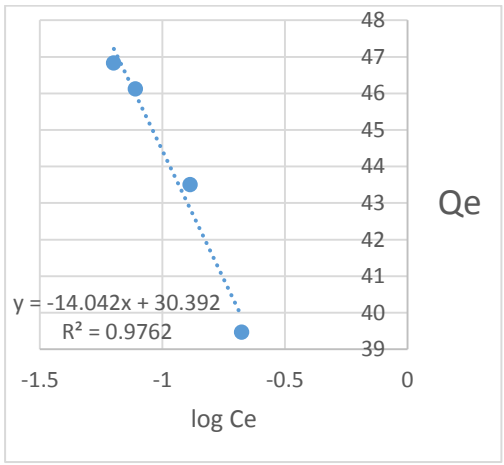

C




D

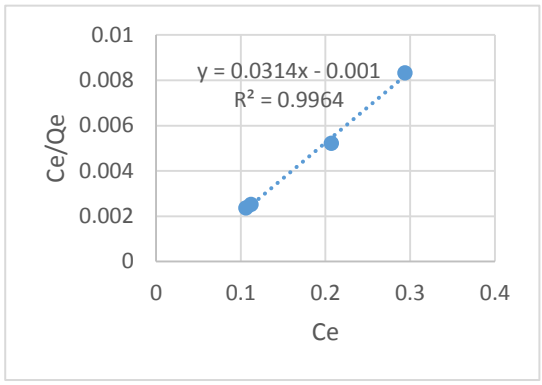



E

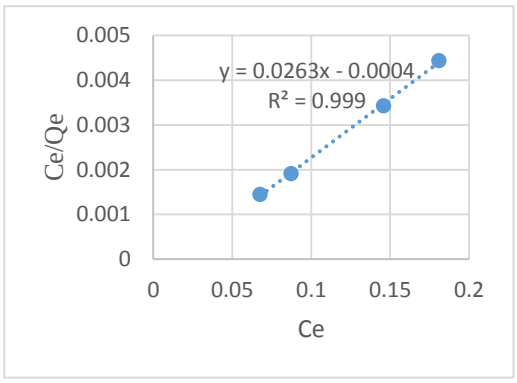



F

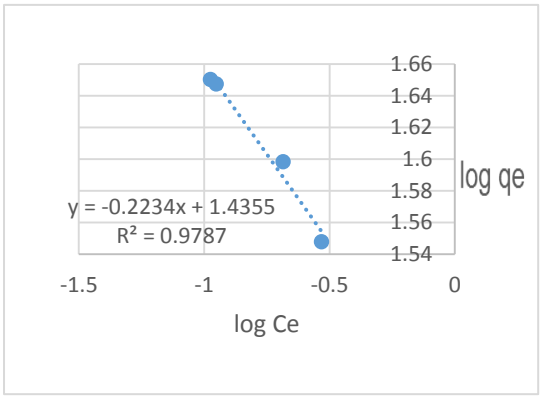
**Fig 4.5: Langmuir (A, B) Freundlich (C, D) and Tempkin (E, F) adsorption isotherms for biosorption of Cr (III) on leaves of *T. baccata* at 25±5˚C and 40±5˚C.**



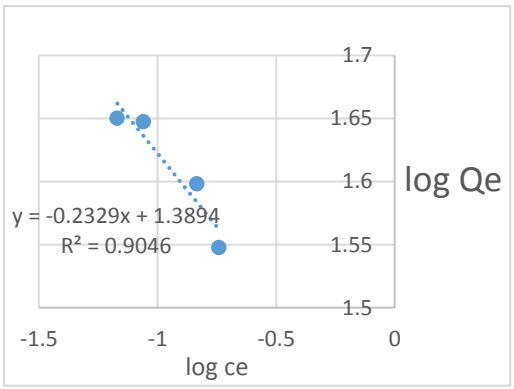

A



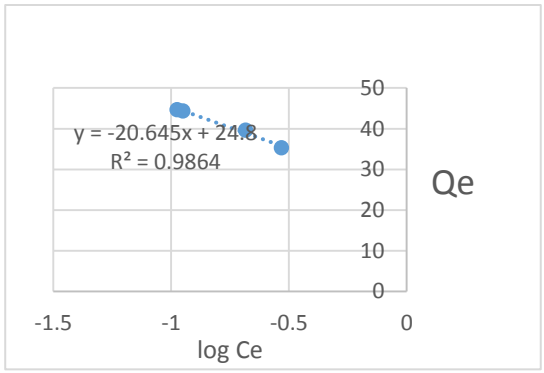

B



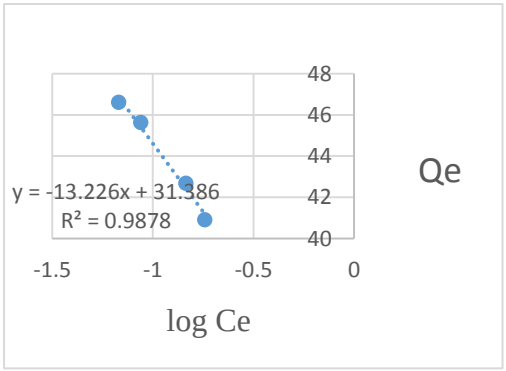

C




D




E




F

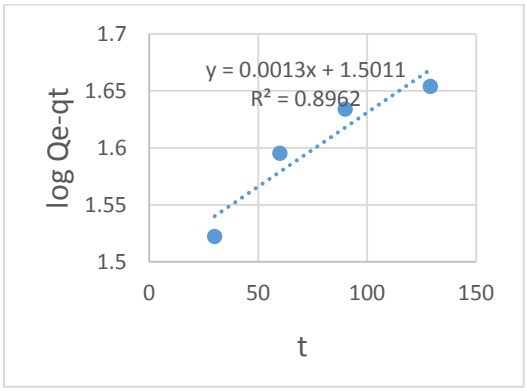
**Fig. 4.6: Langmuir (A, B) Freundlich (C, D) and Tempkin (E, F) adsorption isotherms for biosorption of Cr (III) on bark of *T. baccata* at 25±5˚C and 40±5˚C.**

### 4.1.3 Rate Kinetics for Cr (III) removal by leaves and barks biomass of *Taxus baccata*

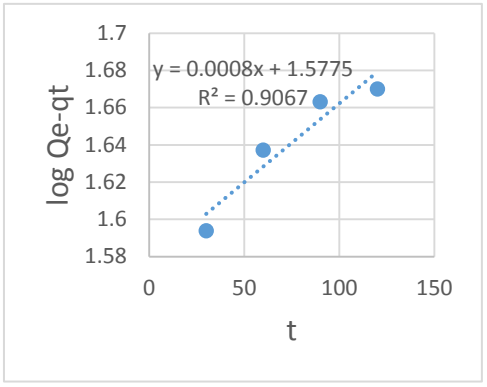
Study of rates of chemical processes is known as chemical kinetics. How different experimental conditions influence speed of a chemical reaction and yield information about the reaction's mechanism and transition states. In order to further expose the adsorption mechanism of Cr (III) on to biosorbent biomass and rate-controlling steps, a kinetic investigation was conducted. The rate kinetic models for removal of chromium (III) ions by leaves and bark of ***Taxus baccata*** contact timings from 30 to 120 min., initial metal ion concentration (1ppm and 2ppm), temperature (25°C and 40°C), biomass dosage (1g and 2g) and pH (4.2, 7 and 9) during biosorption process. Pseudo first order, Pseudo-second order and Elovich kinetic models have been used for testing experimental data. The criteria upon which the suitability of the model to fit the experimental data is determined by including both the correlation coefficient ($R^2$) and the calculated Qe value. When the model's $R^2$ value approaches unity and its Qe calculated is equal to Qe experimental, then the model gives the best fit to the experimental data. In the present study the criteria used for fitting the suitable model is only based on $R^2$ value. **Fig.4.7 and 4.8** represents regression correlation coefficient ($R^2$) value for pseudo first order, pseudo second order and Elovich kinetic model.

**Table 4.6: $R^2$ value for Pseudo-first order, Pseudo-second order and Elovich correlation coefficients for Cr (III) removal by leaves and bark of *Taxus baccata* at cold and hot temperature**

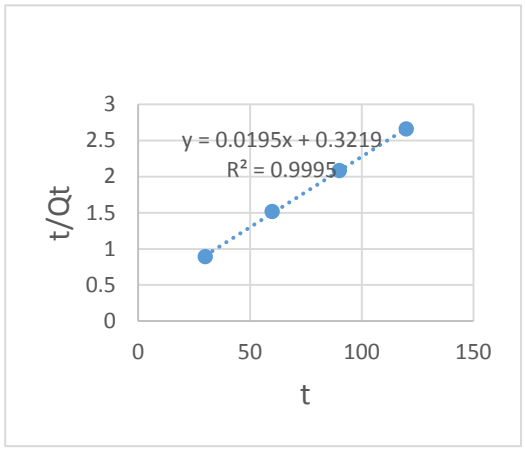
| Sample | Pseudo first order kinetic | Pseudo second order kinetic | Elovich adsorption kinetic |
|---|---|---|---|
| **TBL-C** | 0.896 | 0.999 | 0.998 |
| **TBL-H** | 0.906 | 0.999 | 0.987 |
| **TBB-C** | 0.905 | 0.997 | 0.963 |
| **TBB-H** | 0.967 | 0.998 | 0.952 |



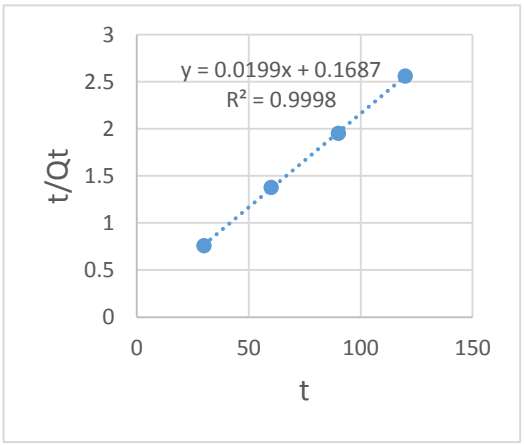

A



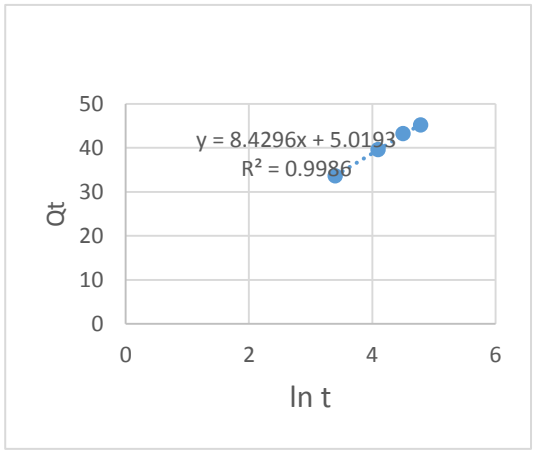

B



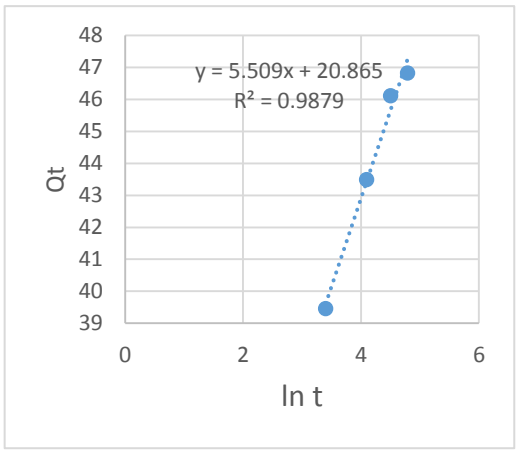

C




D

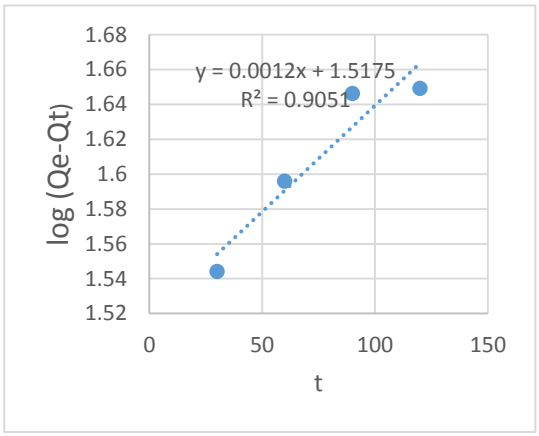



E

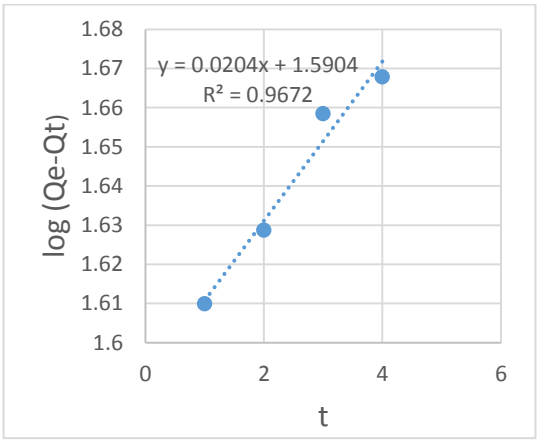



F

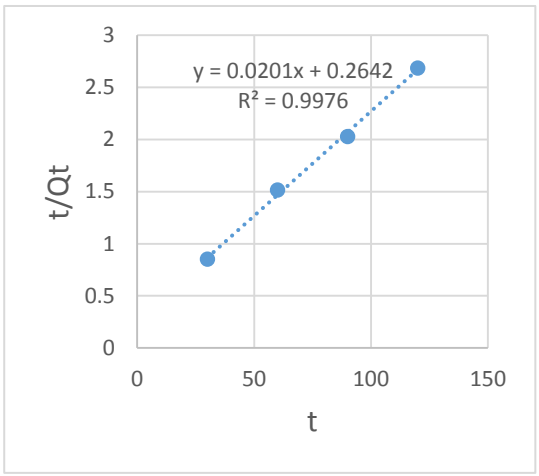
**Fig. 4.7: Pseudo-first order (A, D), Pseudo-second order (B, E) and Elovich (C, F) adsorption kinetic models for biosorption of Cu (II) on leaves of *T. baccata* at 25˚C and 40˚C**



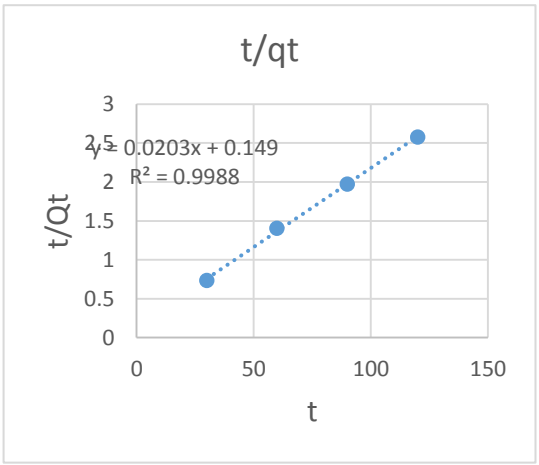

A



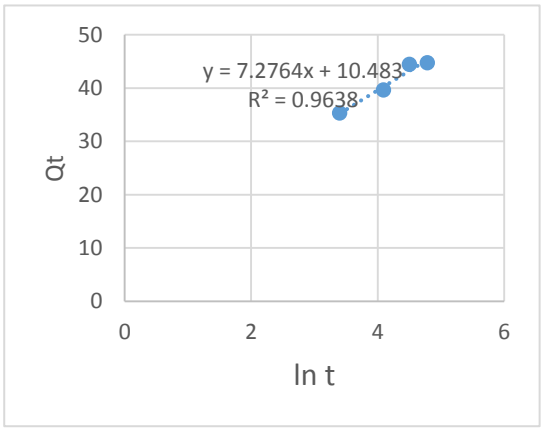

B



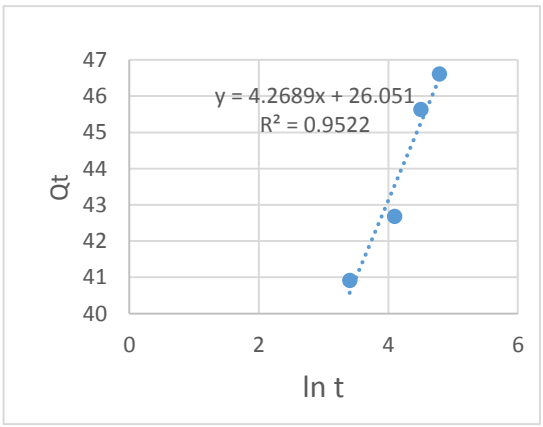

C




D




E




F

**Fig. 4.8: Pseudo-first order (A, B), Pseudo-second order (C, D) and Elovich (E, F) adsorption kinetic models for biosorption of Cr (III) on bark of *T. baccata* at 25˚C and 40˚C**

### 4.1.4 FT-IR study of leaves and bark of *Taxus baccata*

Infrared absorption frequencies of leaves of *Taxus baccata* and chromium loaded leaves of *Taxus baccata* are discussed and presented in **Table 4.7 and Fig 4.9**. Certain changes in peak intensity and frequency were observed in the FT-IR spectrum of unloaded leaves and metal loaded leaves of *Taxus baccata* at acidic, neutral and basic pH. A broad band intense band at 3420.00 $cm^{-1}$ was assigned for hydrogen bonding between N-H of amines and O-H of acids and alcohols but there was slight changes in the frequencies with less intensity and little broadness in peaks were observed after the biosorption of chromium ions at acidic and basic pH treatments and bands of H-bonded N-H streching shifted at 3404.72 $cm^{-1}$ and 3407.18 $cm^{-1}$. At neutral pH this band found to be completely absent and a new band is generated at 3314.18 $cm^{-1}$ assigned for –OH associated frequency. Sharp peak of C-H streching of alkanes at 2922.33 $cm^{-1}$ and –CH alkyl symmetrical stretching at 2854.144 $cm^{-1}$ is shifted to 2925.29 $cm^{-1}$, 2924.00 $cm^{-1}$, 2925.52 $cm^{-1}$, 2851.7 $cm^{-1}$, 2853 $cm^{-1}$, 2858.7 $cm^{-1}$ respectively at acidic, neutral and basic pH treatments. Along with C-H stretching vibrations, bending vibrations of alkyl groups found to be present at 1442.45 $cm^{-1}$ in unloaded leaves and at 1444 $cm^{-1}$ , 1443.3 $cm^{-1}$ and 1440.3 $cm^{-1}$ in the spectra of adsorbed leaves at acidic, neutral and basic pH respectively.

A small peak at 1622.88 $cm^{-1}$ indicates asymmetric streching of C=O of acids and amino group of amines and carboxylate ions of acids is represented by peak at 1373.83 $cm^{-1}$. After biosorption there were no significant shifts in the frequencies and peaks situated in the range for C=O stretching vibrations from 1622.62 $cm^{-1}$ to 1623.20 $cm^{-1}$ and for carboxylate ions from 1373.83 $cm^{-1}$ to 1375 $cm^{-1}$. The peak at 1721.32 $cm^{-1}$ assigned for free C=O of carboxylic acid group shifted to higher frequency in case of acidic and neutral pH while completely absent at basic pH. New band of -C-C- Streching at 1520.4 $cm^{-1}$ are generated in loaded spectrum of leaves at acidic and basic pH, and absent in neutral pH and unloded leaves. C-O stretching vibrations of acids and esters were also present at 1245.83 $cm^{-1}$ and at 1059.67 $cm^{-1}$ before biosorption, but after biosorption significant shifts were observed, on acidic pH theses were at 1245 $cm^{-1}$ and 1067.96 $cm^{-1}$. On neutral pH at 1236.3 $cm^{-1}$ and 1075 $cm^{-1}$ and on basic pH

frequencies shifted at 1238.1 $cm^{-1}$ and 1059.20 $cm^{-1}$ respectively. Small peaks attributed to -C-O Streching in tertiary alcohols found to be present at 1160.7 $cm^{-1}$, 1158.8 $cm^{-1}$ and 1154.5 $cm^{-1}$ after biosorption process. Similarly three new peaks (1106, 1104.57 and 1109.2 $cm^{-1}$) of C-O Streching of ether appears after biosorption mechanism at acidic, neutral and basic pH.

The peaks in the range from 1317.3 $cm^{-1}$ to 1317.89 $cm^{-1}$ present in all the spectra assigned for O-H stretching of alcohols and acids of sugars. It may be proved by presence of C-H bending vibrations of pyranose rings at 829.43 $cm^{-1}$ and 778.34 $cm^{-1}$ in unloaded leaves, at 781.6 $cm^{-1}$ on acidic pH, at 831.16 $cm^{-1}$ and 780.68 $cm^{-1}$ at neutral pH and at 781.6 $cm^{-1}$ and 896.61 $cm^{-1}$ at basic pH before and after biosorption. A wide band at 670.34 $cm^{-1}$ indcated N- H bending vibrations of amines having large shifts after biosorption of metal ions, on acidic and basic pH at 659.63 $cm^{-1}$ and 663.74 $cm^{-1}$ but on neutral pH slight shift was observed toward peak situated at 668.63 $cm^{-1}$. Interaction between metal and ligands were present at 526.78 $cm^{-1}$ with significant shift after biosorption towards lower frequency region at 518.91 $cm^{-1}$ and 511.89 $cm^{-1}$ in acidic and neutral pH solutions while at basic pH this peak resolved completely.

The FTIR spectra of dried unloaded bark and nature of possible interactions between the functional groups of bark with chromium metal ions at acidic, neutral and basic pH are presented in Fig. and Table. The broad and intense peak in spectra of unloaded leaves at 3411.11 $cm^{-1}$ corresponded to H-bonded N-H stretching with O-H band with free O-H stretching at 1319.27 $cm^{-1}$ of alcohols, carboxylic acid and phenols of cellulose, pectin, absorbed water, hemicelluloses and lignin, present in plant materials **(Feng *et al.*, 2009).** Along with this associated O-H frequency also present at 3359.01 $cm^{-1}$ in dried unloaded bark which is shifed to 3346.51 $cm^{-1}$, 3384.45 $cm^{-1}$ and 3359.67 $cm^{-1}$ at acidic, neutral and basic pH conditions. The peak at 2925.80 $cm^{-1}$ assigned for –CH alkyl asymmetric stretching showed slight shifting in loaded bark at at acidic, neutral and basic pH conditions. New peaks 2853.2 $cm^{-1}$ and 2851.7 $cm^{-1}$ generated at acidic and basic pH conditions assigned for -CH alkyl symmetric stretching.

**Table 4.7 FT-IR spectral analysis of *Taxus baccata* leaves before and after the biosorption of Cr (III) metal ions**

| Peak assignment | Frequency before adsorption ($cm^{-1}$) | Frequency after adsorption of Cr(III) $cm^{-1}$ | | | Differences in frequencies before and after adsorption ($cm^{-1}$) | | |
|---|---|---|---|---|---|---|---|
| | | pH=4 | pH=7 | pH=9 | pH=4 | pH=7 | pH=9 |
| -OH bonded N-H Streching | 3420.00 | 3404.72 | - | 3407.18 | 15.28 | Disappear | 12.82 |
| -OH associated | - | - | 3314.18 | - | Disappear | New band | Disappear |
| -CH alkyl asymm. Streching | 2922.33 | 2925.29 | 2924.00 | 2925.52 | -2.96 | -1.67 | -3.19 |
| -CH alkyl symm. Streching | 2854.14 | 2851.7 | 2853 | 2858.7 | 2.44 | 1.14 | -4.56 |
| Free –C=O of –COOH gp. | 1721.32 | 1733 | 1729.5 | - | -11.68 | -8.18 | Disappear |
| V $C=O_{(assym.)}$, $NH_2$ Bending | 1622.88 | 1622.86 | 1623.20 | 1622.62 | 0.02 | -0.32 | 0.26 |
| -C-C- Streching | - | 1520.4 | - | 1520.4 | New band | Disappear | New band |
| -CH Bending (Methyl) | 1442.45 | 1444 | 1443.3 | 1440.3 | -1.55 | -0.85 | 2.15 |
| $COO^-$ in Acids and Alcohols | 1373.83 | 1375 | 1374.9 | 1374 | -1.17 | -1.07 | -0.17 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| -O-H Streching | 1317.82 | 1317.7 | 1317.3 | 1317.89 | 0.12 | 0.52 | -0.07 |
| C-O Streching Of –COOH gp. | 1245.83 | 1245 | 1236.3 | 1238.1 | 0.83 | 9.53 | 7.73 |
| -C-O Streching in $t^0$ -OH | - | 1160.7 | 1158.8 | 1154.5 | New band | New band | New band |
| C-O Streching of ether | - | 1106 | 1104.57 | 1109.2 | New band | New band | New band |
| =C-O-CH Streching in ethers | 1059.67 | 1067.96 | 1075 | 1059.20 | -8.29 | -15.33 | 0.47 |
| -CH Bending of Pyranose sugar | 829.43 | - | 831.16 | 896.61 | Disappear | -1.73 | -67.18 |
| Bending viberation of Pyranose | 778.34 | 781.6 | 780.68 | 781.6 | -3.26 | -2.34 | -3.26 |
| N-H Bending (Amines) | 670.34 | 659.63 | 668.83 | 663.74 | 10.71 | 1.51 | 6.6 |
| Metal- Ligand Bonding (M-O) | 526.78 | 518.91 | 511.89 | - | 7.87 | 14.89 | Disappear |

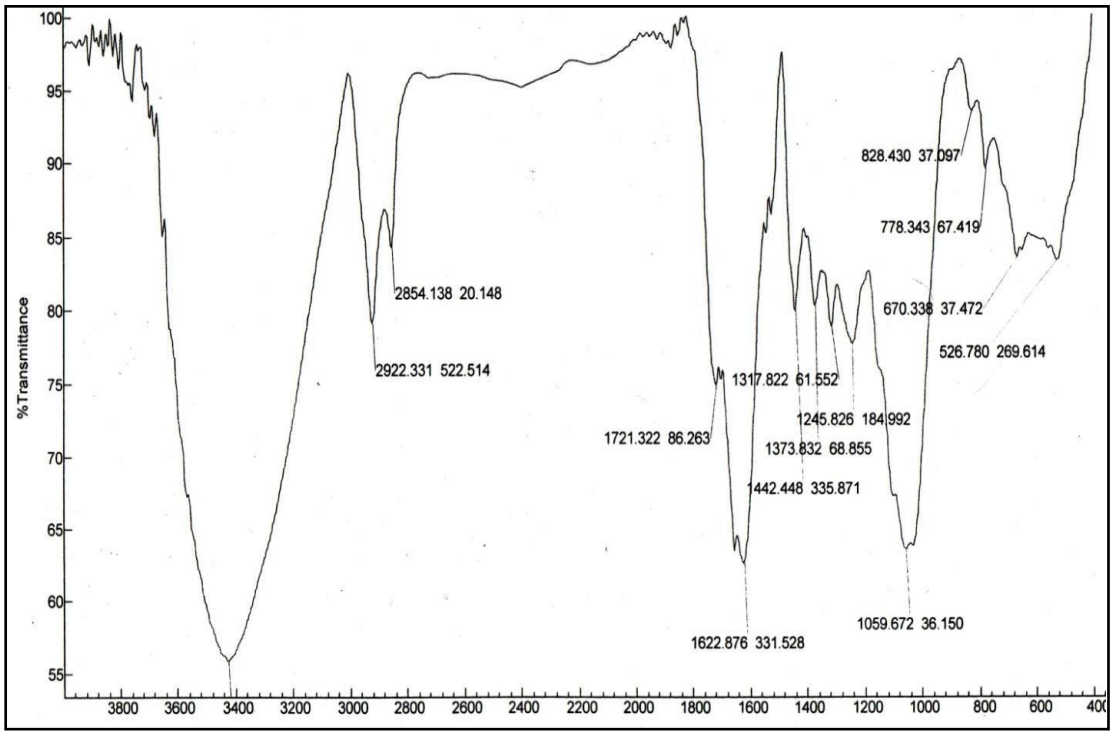
Peaks at 1621.82 $cm^{-1}$, 1620.41 $cm^{-1}$ and 1621.69 $cm^{-1}$ regarding to biosorption at acidic, neutral and basic pH donot have any significant shifts in asymmetric stretching vibrations of free carbonyl group (C=O) and amino group bands due to participation of free carbonyl group of acids and esters in biosorption mechanism as compared to unloded bark peak at 1621.05 $cm^{-1}$. Frequency of C-C stretching shifted from 1516.05 $cm^{-1}$ to 1518 $cm^{-1}$ and 1520.4 $cm^{-1}$ after adsorption mechanism on neutral and basic pH with complete disappearance of peak at acidic pH. At acidic, neutral and basic pH treatments, significant differences were obsereved in peaks at 1443.83 $cm^{-1}$, 1439.6 $cm^{-1}$ and 1442.06 $cm^{-1}$ respectively. The weakened intensity peak of carboxylate group (-COO) of acids (1372.14 $cm^{-1}$) donot any large changes at different pH solutions.

The peak at 1260.53 $cm^{-1}$ and 1096.80 $cm^{-1}$ assigned for streching vibrations for C-N bond of amines and double bonded C-N bands. Large shifting of frequencies were found in case of streching vibrations for C-N bond at acidic, neutral and basic pH. Bonded C-N bands shifted from 1096.80 $cm^{-1}$ to 1059.18 $cm^{-1}$, 1061.46 $cm^{-1}$ and 1057.29 $cm^{-1}$ after biosorption mechanism. Bands of C-O stretching of ethers appeared at 1109.3 $cm^{-1}$, 1109.2 $cm^{-1}$ and 1108.7 $cm^{-1}$ at acidic, neutral and basic pH conditions and resolved in case of metal unloaded bark. Esters C-O stretching band at 1063.76 $cm^{-1}$ in unloaded bark material shifted to 1032.2 $cm^{-1}$ and 1032 at acidic and basic pH while absent in case of neutral pH. –CH bending of pyranose sugars shifted in the range of 814.85 $cm^{-1}$ to 892.63 $cm^{-1}$ while bending vibration of pyranose shifted in the range of 780.97 $cm^{-1}$ to 781.81 $cm^{-1}$. N-H bending of amines shifted from 656.99 $cm^{-1}$ to 662.84 $cm^{-1}$, 668.31 $cm^{-1}$ and 667.54 $cm^{-1}$ at acidic, neutral and basic pH. Metal ligand bonds with oxygen atom were observed with slight shifting from 519.68 $cm^{-1}$ to 518.76 $cm^{-1}$, 516.8 $cm^{-1}$ $^{a}$nd 521.0 $cm^{-1}$ at acidic, neutral and basic pH respectively with low intensity peaks.

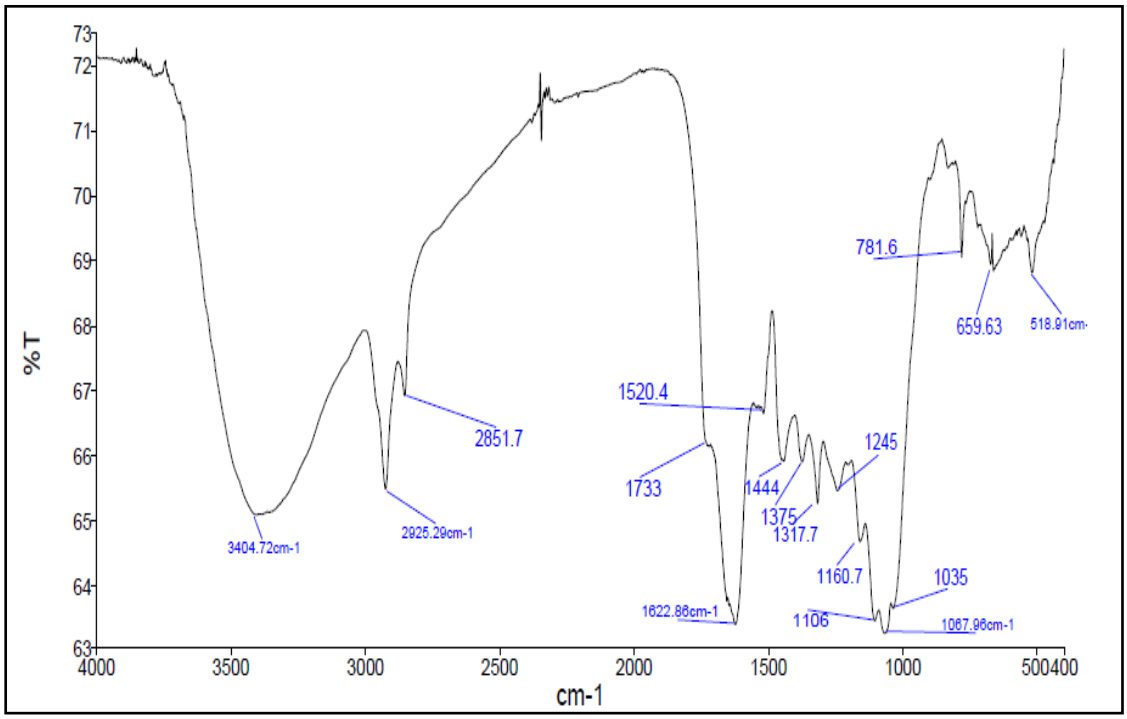
**Table 4.8 FT-IR spectral analysis of *Taxus baccata* bark before and after the biosorption of Cr (III) metal ions**

| Peak assignment | Frequency before adsorption ($cm^{-1}$) | Frequency after adsorption of Cr(III) $cm^{-1}$ | | | Differences in frequencies before and after adsorption ($cm^{-1}$) | | |
|---|---|---|---|---|---|---|---|
| | | pH=4 | pH=7 | pH=9 | pH=4 | pH=7 | pH=9 |
| -OH bonded N-H Streching | 3411.14 | - | - | - | Disappear | Disappear | Disappear |
| -OH associated | 3359.01 | 3346.51 | 3384.45 | 3359.67 | 12.5 | -25.44 | -0.66 |
| -CH alkyl asymm. Streching | 2925.80 | 2927.12 | 2928.75 | 2928.78 | -1.32 | -2.95 | -2.98 |
| -CH alkyl symm. Streching | - | 2853.2 | - | 2851.7 | New band | Disappear | New band |
| V $C=O_{(assym.)}$, $NH_2$ Bending | 1621.05 | 1621.82 | 1620.41 | 1621.69 | -0.77 | 0.64 | -0.64 |
| -C-C- Streching | 1516.05 | - | 1518 | 1520.4 | Disappear | -1.95 | -4.35 |
| -CH Bending (Methyl) | 1444.09 | 1443.83 | 1439.6 | 1442.06 | 0.26 | 4.49 | 2.03 |
| $COO^-$ in Acids and Alcohols | 1372.14 | 1373.94 | 1373.5 | 1372.81 | -1.8 | -1.36 | -0.67 |
| -O-H Streching | 1319.27 | 1317.88 | 1317.82 | 1318.06 | 1.39 | 1.45 | 1.21 |

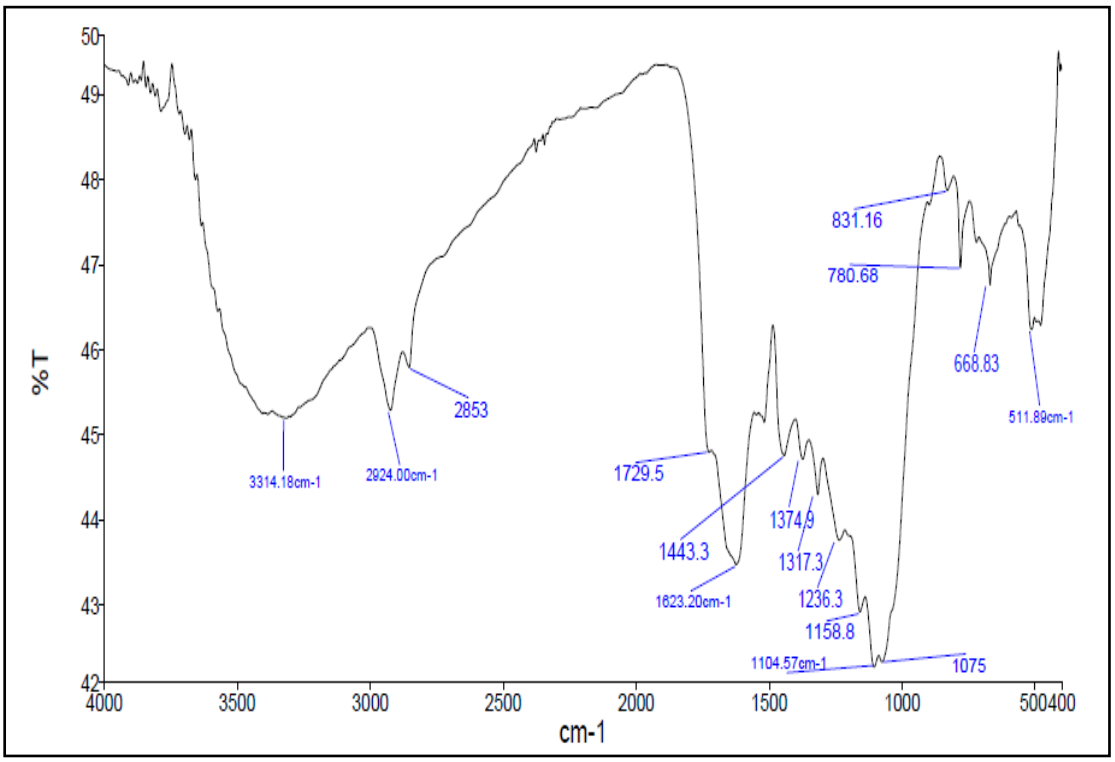
| | | | | | | | |
|---|---|---|---|---|---|---|---|
| -C-N Streching | 1260.53 | 1241.6 | 1236.2 | 1250.4 | 18.93 | 24.33 | 10.13 |
| -C-O Streching in $t^0$ -OH | 1148.93 | 1159 | 1158.8 | 1159.2 | -10.07 | -9.87 | -10.27 |
| C-O Streching of ether | - | 1109.3 | 1109.2 | 1108.7 | New band | New band | New band |
| =C-N bending in amines | 1096.80 | 1059.18 | 1061.46 | 1057.29 | 37.62 | 35.34 | 39.51 |
| =C-O-CH Streching in ethers | 1063.76 | 1032.2 | - | 1032 | 31.56 | Disappear | 31.76 |
| -CH Bending of Pyranose sugar | 814.85 | 891.93 | 891.97 | 892.63 | -77.08 | -77.12 | -77.78 |
| Bending viberation of Pyranose | 781.81 | 780.97 | 781.31 | 780.97 | 0.84 | 0.5 | 0.84 |
| N-H Bending (Amines) | 656.99 | 662.84 | 668.31 | 667.54 | -5.85 | -11.32 | -10.55 |
| Metal- Ligand Bonding (M-O) | 519.68 | 518.76 | 516.8 | 521.0 | 0.92 | 2.88 | -1.32 |


%Transmittance
828.430 37.097
778.343 67.419
2854.138 20.148
670.338 37.472
526.780 269.614
2922.331 522.514
1317.822 61.552
1245.826 184.992
1721.322 86.263
1373.832 68.855
1442.448 335.871
1622.876 331.528
1059.672 36.150

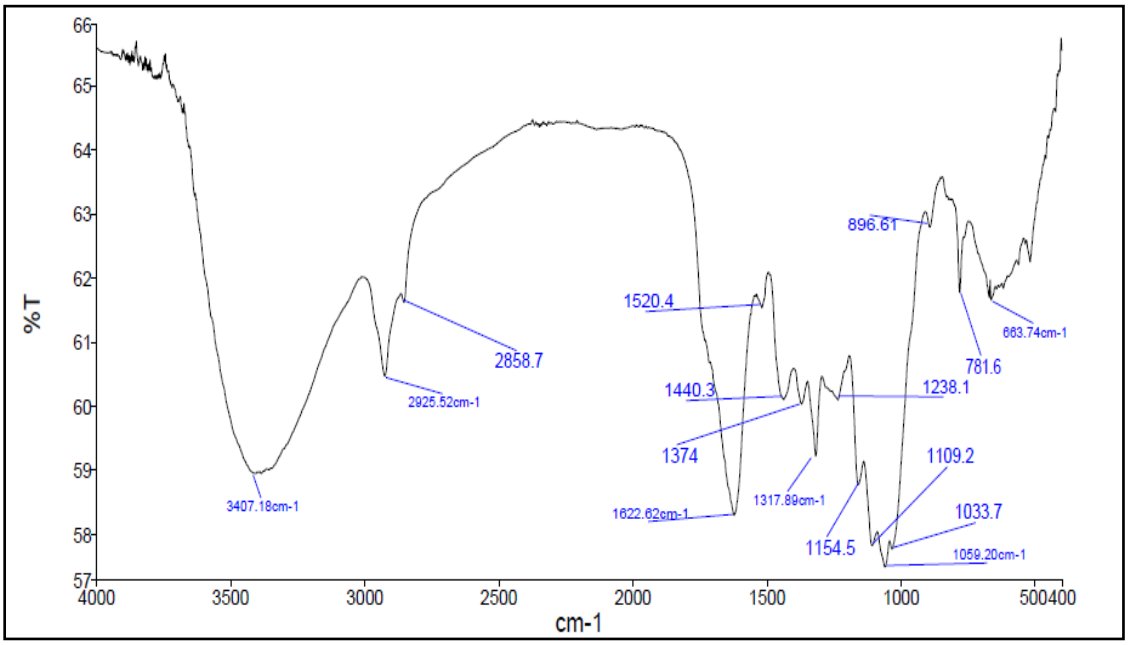
**(A)**


%T
781.6
659.63
518.91cm-
1520.4
2851.7
1245
1733
1444
1375
1317.7
3404.72cm-1
2925.29cm-1
1160.7
1035
1622.86cm-1
1106
1067.96cm-1
cm-1

**(B)**

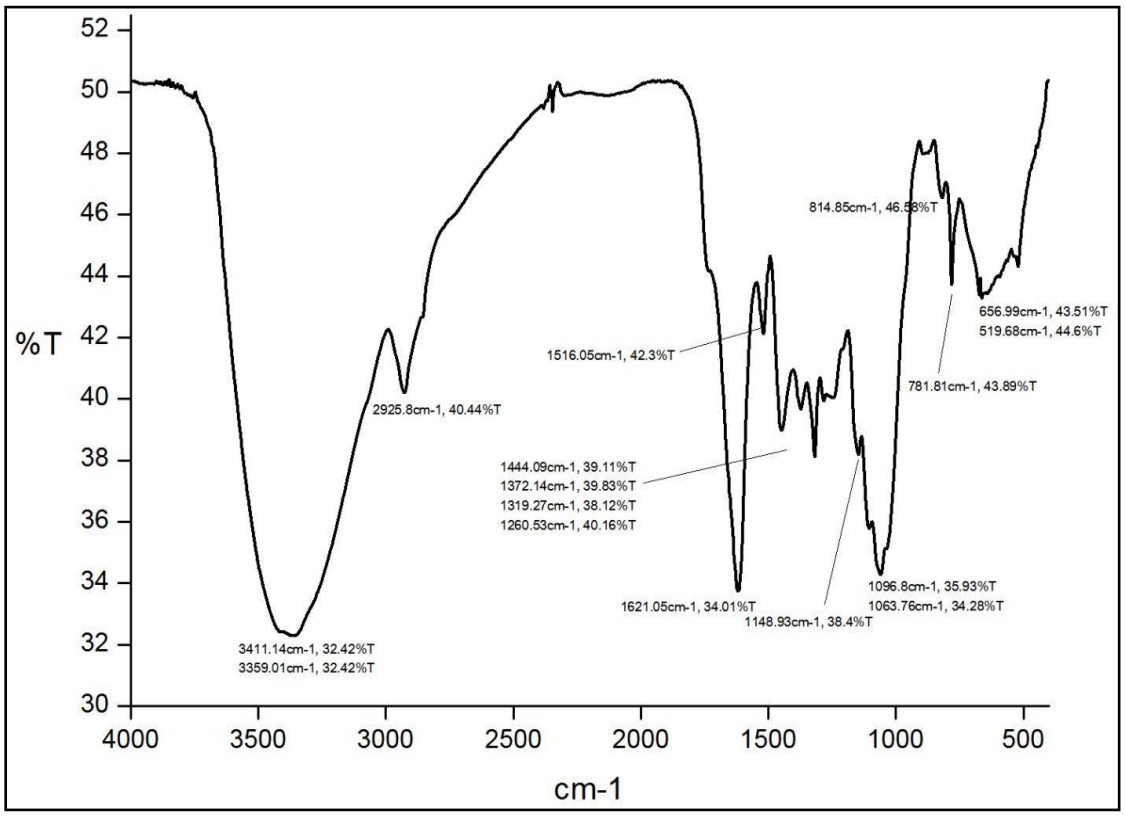



**(C)**

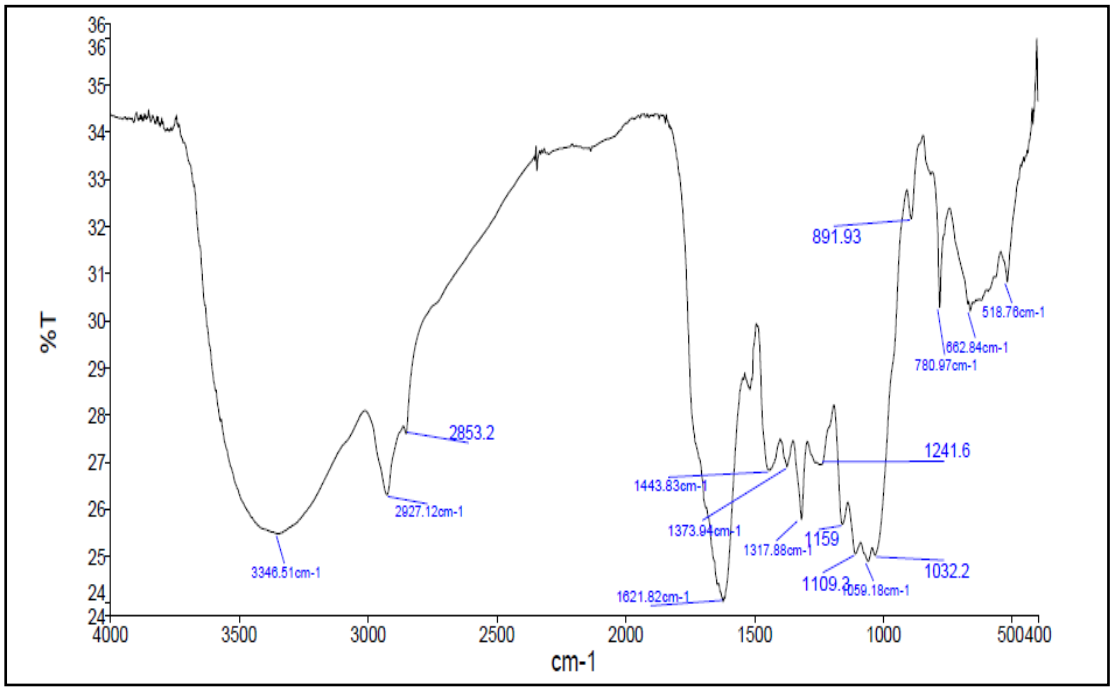



**(D)**

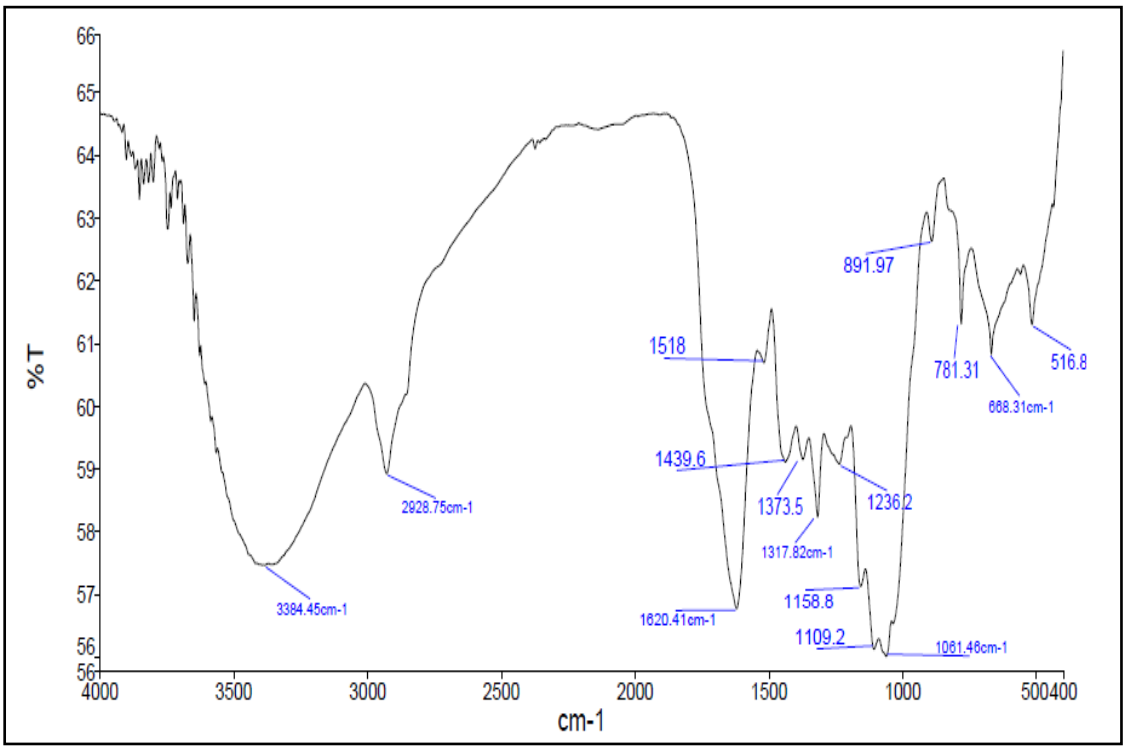
**Fig. 4.9: FT-IR spectra of *Taxus baccata* leaves before (A) and after the biosorption of Cr (III) metal ion at pH 4.2 (B), pH 7.0 (C) and pH 9.0 (D)**


%T
cm-1
3411.14cm-1, 32.42%T
3359.01cm-1, 32.42%T
2925.8cm-1, 40.44%T
1516.05cm-1, 42.3%T
1444.09cm-1, 39.11%T
1372.14cm-1, 39.83%T
1319.27cm-1, 38.12%T
1260.53cm-1, 40.16%T
1621.05cm-1, 34.01%T
1148.93cm-1, 38.4%T
814.85cm-1, 46.58%T
1096.8cm-1, 35.93%T
1063.76cm-1, 34.28%T
781.81cm-1, 43.89%T
656.99cm-1, 43.51%T
519.68cm-1, 44.6%T

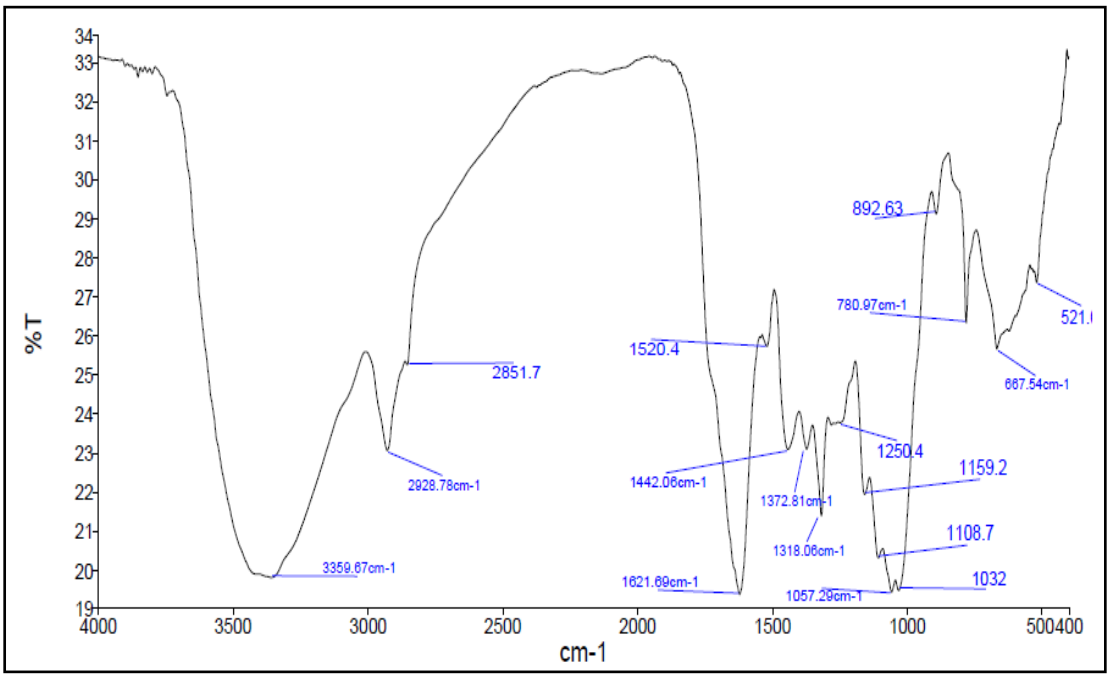
**(A)**


%T
cm-1
3346.51cm-1
2927.12cm-1
2853.2
1621.82cm-1
1443.83cm-1
1373.94cm-1
1317.88cm-1
1159
1109.2
1059.18cm-1
1032.2
1241.6
891.93
780.97cm-1
662.84cm-1
518.76cm-1

**(B)**




**(C)**




**(D)**

**Fig. 4.10: FT-IR spectra of *Taxus baccata* bark before (A) and after the biosorption of Cr (III) metal ion at pH 4.2 (B), pH 7.0 (C) and pH 9.0 (D)**

### 4.2.1 Biosorption potential of *Cupressus torulosa*

The data pertaining to effects of reaction time, pH, concentration of Chromium (II) ions, adsorbent dose and temperature on the sorption of Cr (III) by leaves and barks of *Cupressus torulosa* plant from aqueous solution.

#### 4.2.1.1 Effect of contact time

The effect of contact time was observed at initial metal concentration (1mg/L), acidic pH (4.2), biomass amount (1g) and cold (25±5˚C) to hot (40±5˚C) temperature conditions. Leaves showed maximum adsorption at 120 min and bark showed maximum absorption at 120 min when measured at the interval of 30min, visualized in **Table 4.9**

It can be visualized by **Fig**. **4.11** that the maximum removal by *C. torulosa* leaves were 85.60 and 97.83 % at cold and hot temperature conditions while bark showed 90.53 and 93.66% removal at cold and hot temperature conditions respectively at 120 min. Biomass of bark at hot temperature had highest efficiency for chromium metal removal, followed by leaves of *C.torulosa* at hot temprature. Bark have greater potential than leave. At 30 min leaves showed 79.60, 88.60 % while bark showed 84.3.20 and 88.63 % removal at cold and hot temperature. So as the contact time increased bark showed sharply removal potential but leaves at cold temperature have steady potential while at hot temperature leaves showed sharp increase in percentage removal

The **Fig**. **4.11** also represented that the removal percentage and removal capacity per 1 g of adsorbent biomass. The data showed that at 120 min leaves and bark of *C. torulosa* adsorbed 42.80, 48.91, 45.26 and 49.33 mg of chromium ions at cold and hot temperature conditions respectively. It was the maximum removal capacity for leaves and bark biomass at 120 min while at 30 min these showed minimum capacity with 39.76, 44.33, 42.26 and 44.31 8 mg of Chromium ions. There was an increasing trend of Chromium adsorption by leaves and bark at different temperature condition with increase in contact timings but after 120 min,

adsorption of Chromium decreased which could be due to the unavailability and saturation of metal binding sites present in *C. torulosa* biomass.

### 4.2.1.2 Effect of pH

To analyze the effect of pH on biosorption, experiment was conducted at different pH (4.2, 7.0 and 9.0) with initial metal ion concentration of 1 mg/L, contact time (2 hrs), biomass dosage 1g/50mL and temperature (25±5˚C and 40±5˚C). **Table 4.10** describes the biosorption data of Cr (III) removal by *Cupressus torulosa* leaves and barks biomass at varying pH.

Maximum removal of Cr (III) by leaves and bark biomass was observed at neutral pH (7.0) at higher temperature followed by acidic pH and basic pH and at lower temperature it is highest for acidic pH (4.2) followed by removal at ac pH (9.0) and neutral pH (7.0). The leaves of *C.torulosa* showed maximum removal at neutral pH (87.50) at cold temperature followed by removal at basic pH (82.10%) and removal at acidic pH (85.60%) while at hot temperature maximum removal by leaves observed at acidic pH (95.70%), followed by removal at neutral pH (95.20%) and at basic pH (85.83%). The bark of *C. torulosa* showed different trend than leaves. While at hot temperature, removal of Chromium ions at acidic pH(93.66) followed by neutral pH (89.40 and )basic pH(83.20). At lower temperature it is highest for neutral pH (91.66) followed by acidic pH (90.53) and basic pH (89.40%).

A graphical representation of adsorption capacity of *C. torulosa* plant for Chromium at different pH also observed in **Fig**. **4.12.**

### 4.2.1.3 Effect of initial metal ion concentrations

The data presented in **Table 4.11** shows sorption of Cr (III)by leaves and barks of *Cupressus torulosa* at different metal concentrations (1.0 and 2.0ppm) with a contact time of 2 hrs, biomass amount of 1g, acidic pH (4.2) and different temperatures (25±5˚C and 40±5˚C).

**Table 4.9: Biosorption efficiency of leaves and bark of *Cupressus torulosa* plant at different temperature and time interval for Cr(III)**

| Plants / Time | CTL-C | | CTL-H | | CTB-C | | CTB-H | |
|---|---|---|---|---|---|---|---|---|
| | Qe (mg/g) | % Removal | Qe (mg/g) | % Removal | Qe (mg/g) | % Removal | Qe (mg/g) | % Removal |
| **30 min** | 39.76±0.29 | 79.53±0.58 | 44.33±0.03 | 88.66±0.06 | 42.26±0.07 | 84.53±0.15 | 44.31±0.14 | 88.63±0.15 |
| **60 min** | 40.85±0.08 | 81.70±0.17 | 45.30±0.08 | 90.60±0.17 | 43.40±0.08 | 86.80±0.17 | 45.41±0.23 | 90.83±0.11 |
| **90 min** | 42.08±0.10 | 84.16±0.20 | 47.48±0.07 | 94.66±0.15 | 45.36±0.05 | 90.23±0.11 | 47.36±0.26 | 93.33±0.15 |
| **120 min** | 42.80±0.1 | 85.60±0.20 | 48.91±0.06 | 97.83±0.11 | 45.26±0.07 | 90.53±0.15 | 49.33±0.43 | 93.66±0.11 |

**Table 4.10: Biosorption efficiency of leaves and bark of *Cupressus torulosa* plant at different temperature and pH for Cr (III)**

| Plants / pH | CTL-C | | CTL-H | | CTB-C | | CTB-H | |
|---|---|---|---|---|---|---|---|---|
| | Qe (mg/g) | % Removal | Qe (mg/g) | % Removal | Qe (mg/g) | % Removal | Qe (mg/g) | % Removal |
| **Acidic (4.2)** | 42.80±0.1 | 85.60±0.20 | 47.85±0.06 | 95.70±0.11 | 45.26±0.07 | 90.53±0.15 | 49.33±0.43 | 93.66±0.11 |
| **Neutral (7.0)** | 43.75±0.12 | 87.50±0.29 | 47.60±0.09 | 95.20±0.17 | 45.83±0.13 | 91.66±0.24 | 44.70±0.10 | 89.40±0.08 |
| **Basic (9.0)** | 41.29±0.20 | 82.10±0.28 | 43.26±0.02 | 85.33±0.06 | 44.55±0.08 | 89.10±0.09 | 42.30±0.06 | 83.20±0.04 |

It is evident, visualized in **Fig**. **4.13** that there was different trend observed for Cu(II) removal by leaves and bark at different temperature. At cold and hot temperature leaves removed 89.40% and 93.66% Chromium respectively from 1ppm of Chromium ion solution that was maximum removal by leaves at hot temperature but at low temperature it was minimum percentage of removal. At 1ppm concentration bark showed maximum removal of 90.33.10% and 93.23% at cold and hot conditions respectively. At 2ppm leaves shows minimum efficiency towards Chromium removal with 92.50% at hot temperature while at cold temperature showed maximum removal of 93.31 % and bark showed minimum removal 91.65 and 93.40% at hot and cold temperature conditions respectively.

Among the leaves and barks of *C. torulosa*, bark have highest adsorption capacity at cold temperature followed by leave at cold temperature while bark at cold temperature showed highest percentage removal followed by leaves and bark at hot temperature and bark at hot temperature showed minimum percentage removal for Chromium. The increasing trend was may be due to availability of binding sites in biosorbent material while decreasing trend may be due to fulfilling of functional groups sites at biosorbent surface.

#### 4.2.1.4 Effect of biosorbent amount

To analyze the effect of biosorbent amount on biosorption of Chromium, an experiment was conducted at different amounts of leaves and barks of *Cupressus torulosa* (1.0 and 2.0g), initial metal ion concentration (1ppm), contact time (2h), pH (4.2) and different temperature conditions (25±5˚C and 40±5˚C). **Table 4.12** describes the adsorption capacity and biosorption of Cr (III)by leaves and bark biomass at varying biomass amounts.

Maximum removal of Chromium metal by 2.0g of *C. torulosa* bark was 97.30% at hot temperature followed by bark with 95.96 % removal at cold temperature while at hot temperature leaves showed 92.50% removal and leaves at (89.3)% removal of Chromium at cold temperature Among the leaves and barks at various temperature leaves and bark at hot temperature condition showed maximum percentage removal. Removal of Cr (III)by leaves biomass at hot temperature was observed sharply when the biomass amount raged between 1.0 g to 2.0g/50ml.

**Table 4.11: Biosorption efficiency of leave and bark of *Cupressus torulosa* plant at different temperature and Cr (III) metal ion concentration**

| Plants concentration | CTL-C | | CTL-H | | CTB-C | | CTB-H | |
|---|---|---|---|---|---|---|---|---|
| | Qe (mg/g) | % Removal | Qe (mg/g) | % Removal | Qe (mg/g) | % Removal | Qe (mg/g) | % Removal |
| **1.0 ppm** | 45.16±0.47 | 89.40±0.16 | 46.83±0.06 | 93.66±0.12 | 44.70±0.08 | 90.33±0.94 | 46.61±0.48 | 93.23±0.96 |
| **2.0 ppm** | 46.5±0.03 | 93.31±0.07 | 46.29±0.05 | 92.50±0.01 | 46.72±0.06 | 93.4 ±0.13 | 45.82±0.23 | 91.65±0.0 |

**Table 4.12: Biosorption efficiency of leave and bark of *Cupressus torulosa*plant at different temperature and biomass amount for Cr (III)**

| Plants amount | CTL-C | | CTL-H | | CTB-C | | CTB-H | |
|---|---|---|---|---|---|---|---|---|
| | Qe (mg/g) | % Removal | Qe (mg/g) | % Removal | Qe (mg/g) | % Removal | Qe (mg/g) | % Removal |
| **1 g** | 45.16±0.47 | 89.40±0.16 | 46.83±0.06 | 93.66±0.12 | 44.70±0.08 | 90.33±0.94 | 46.61±0.48 | 93.23±0.96 |
| **2 g** | 44.56±0.79 | 89.13±1.59 | 46.63±0.10 | 92.73±0.20 | 47.98±0.08 | 95.96 ±0.15 | 48.65±0.10 | 97.30±0.20 |

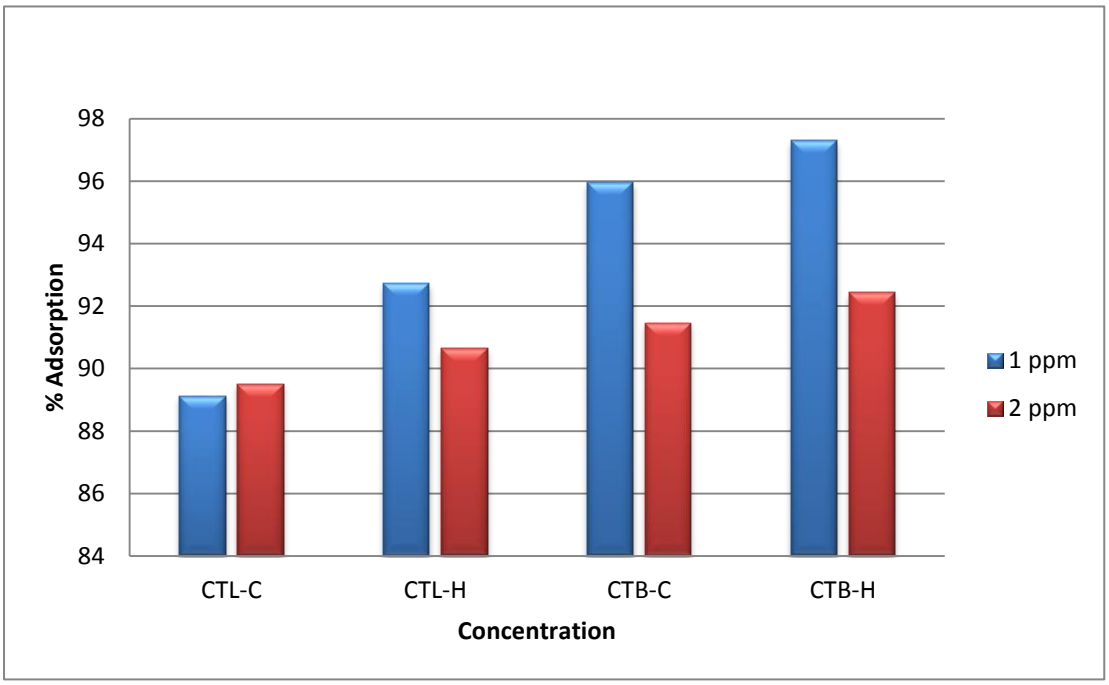



**Fig. 4.13: Effect of initial metal concentarations on biosorption of Cr (III) by leaves and barks of *Cupressus torulosa* at different temperatures (25±5˚Cand 40±5˚C) (contact time= 120min, pH = 4.2 and biomass = 1g)**

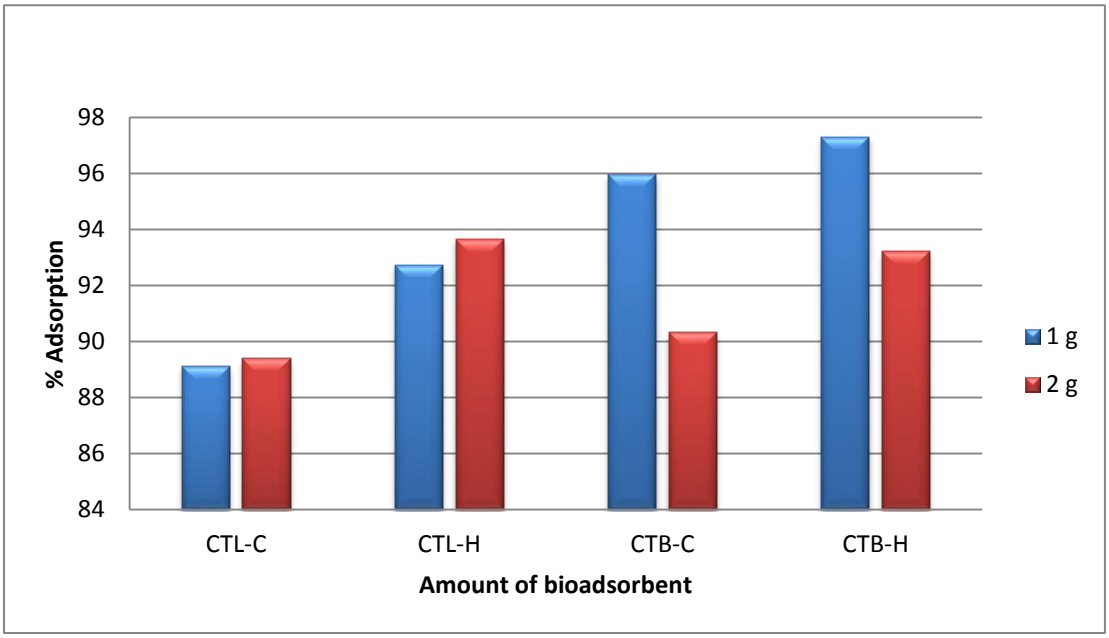
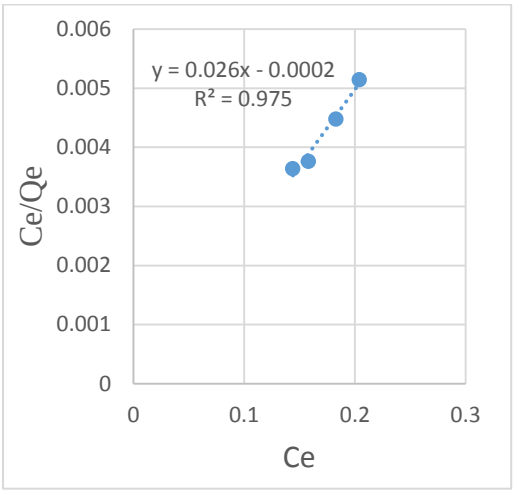
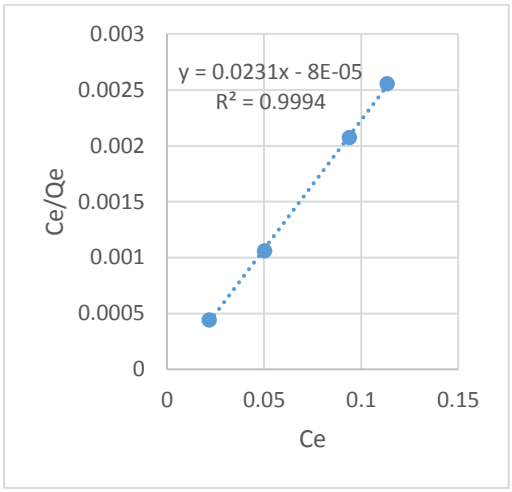


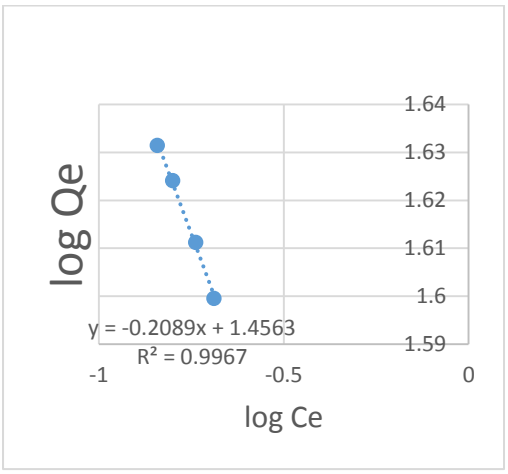

**Fig. 4.14: Effect of biomass amounts on biosorption of Cr (III) by leaves and barks of *Cupressus torulosa* different temperatures (25±5˚C and 40±5˚C) (contact time= 120min, initial metal conc. = 1ppm and pH = 4.2**



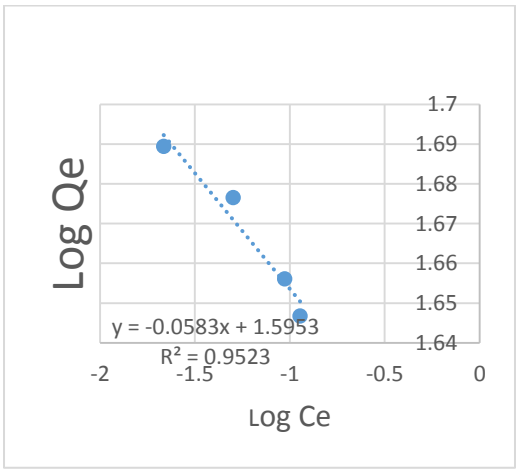

**A**



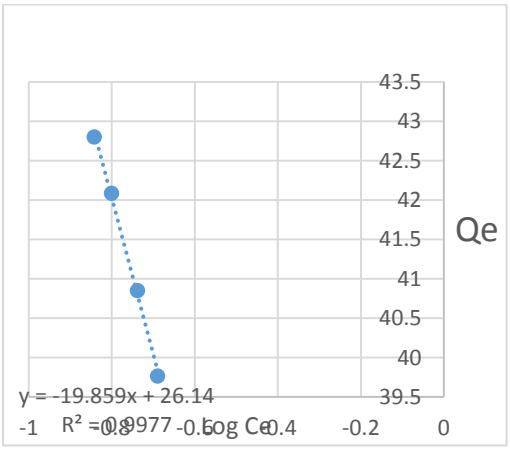

**B**



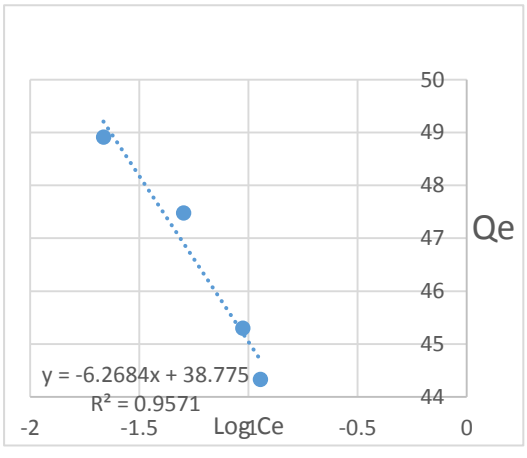

**C**




**D**

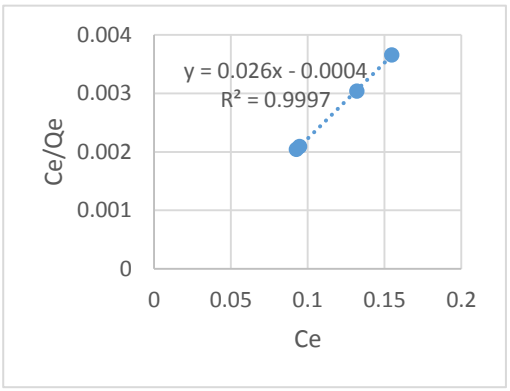


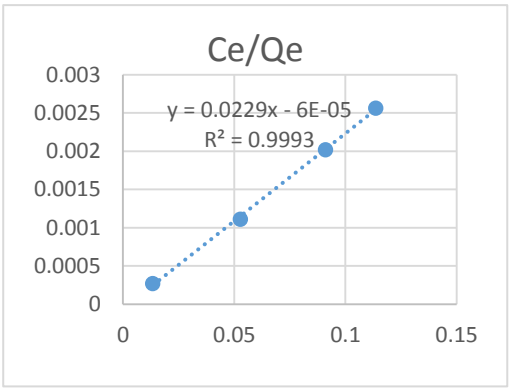

**E**



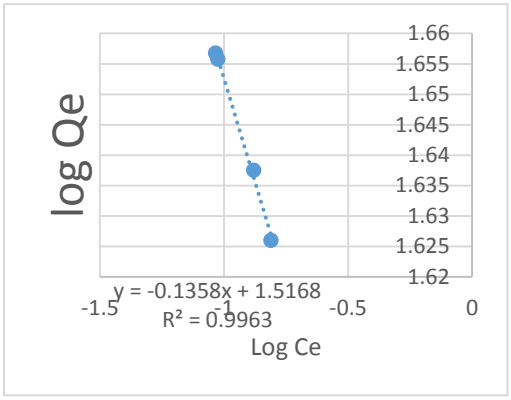

**F**

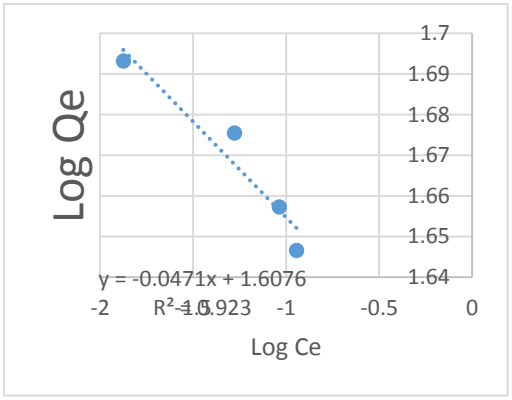
**Fig 4.15: Langmuir (A, B) Freundlich (C, D) and Tempkin (E, F) adsorption isotherms for biosorption of Cr (III) on leaves of *Cupressus torulosa* at 25±5˚C and 40±5˚C.**



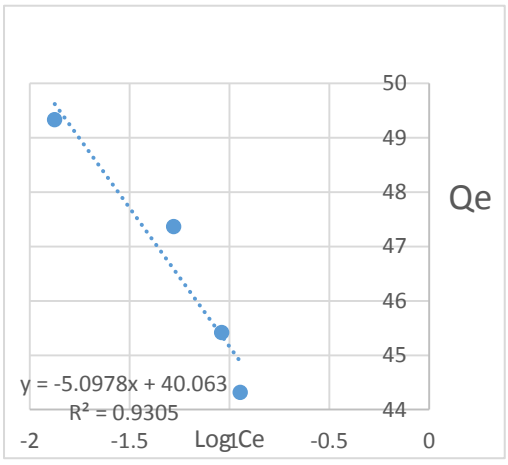



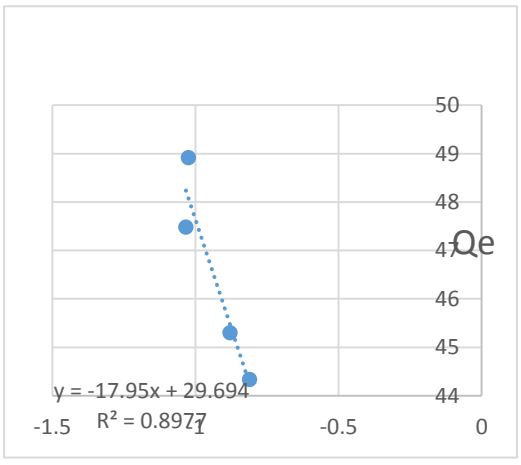

**A** **B**




**C** **D**




**E** **F**

**Fig. 4.16: Langmuir (A, B) Freundlich (C, D) and Tempkin (E, F) adsorption isotherms for biosorption of Cr (III) on bark of *Cupressus torulosa* at 25±5˚C and 40±5˚C.**

increase in biomass amount, sorption of metal increased but after equilibrium uptake of metal decreased or was constant due to unavailability of metal in solution.

The percentage removal of Cr (III)ions increased with the increasing of biosorbent at cold temprature amount.

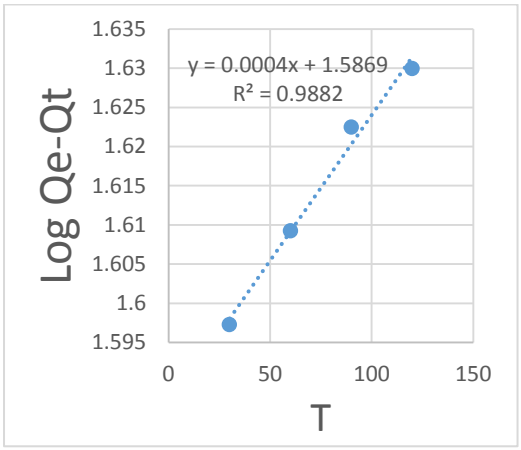
As the amount of biosorbent increased, adsorption capacity of leaves and bark was decreased significantly. These results showed that *Cupressus torulosa* have good adsorption potential for Chromium removal at different temperature conditions also.

### 4.2.1 Adsorption isotherms for Cr (III) removal by biomass of *Cupressus torulosa* plant

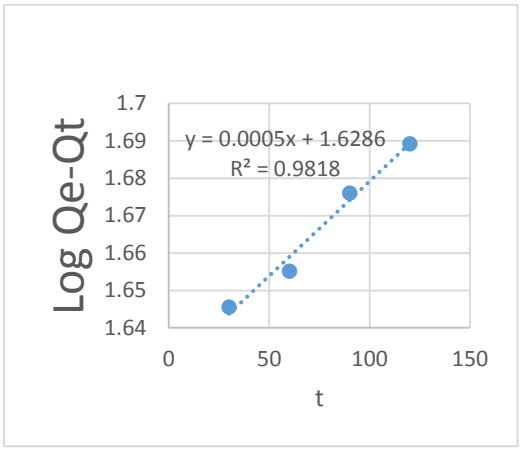
The Langmuir, Freundlich and Temkin models for leaves and bark of *Cupressus torulosa* were represented by **Fig. 4.9** and **Fig. 4.10** respectively. For leaves of *Cupressus torulosa* plant at cold temperature the $R^2$ values were 0.975, 0.996 and 0.997 while at hot temperature these were 0.994, 0.952 and 0.957 and for bark of *Cupressus torulosa* plant at cold temperature the $R^2$ values were 0.999, 0.996 and 0.897 while at hot temperature these were 0.999, 0.923 and 0.930 of Langmuir, Freundlich and Tempkin models respectively **(Table 4.5).** Langmuir isotherm model found to be most suitable at hot and cold temperature for leaves and bark shows monolayer type of adsorption chromium ions.

**Table 4.14: $R^2$ value for chromium adsorption obtained from different isotherm models**

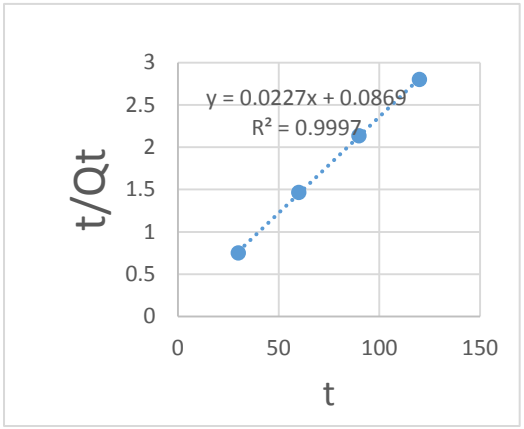
| Sample | Langmuir | Freundlich | Tempkin |
|---|---|---|---|
| **CTL-C** | 0.975 | 0.996 | 0.997 |
| **CTL-H** | 0.994 | 0.952 | 0.957 |
| **CTB-C** | 0.999 | 0.996 | 0.897 |
| **CTB-H** | 0.999 | 0.923 | 0.930 |



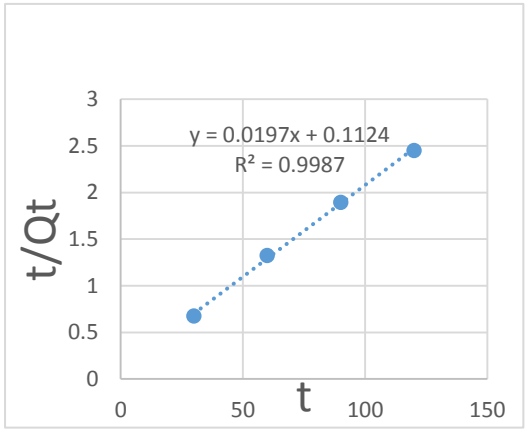

**A**



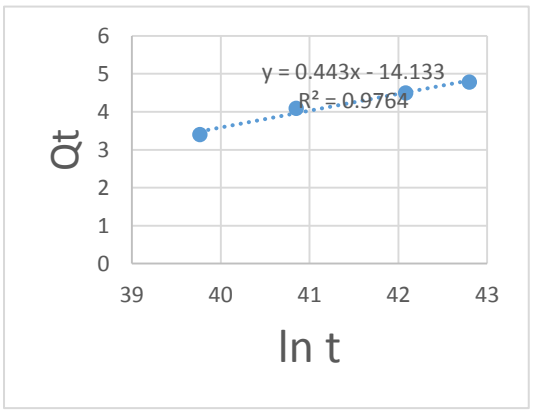

**B**



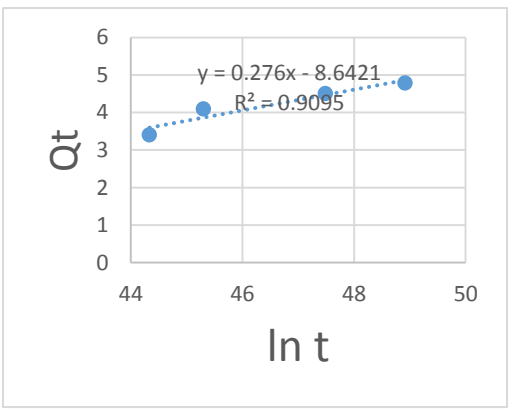

**C**




**D**

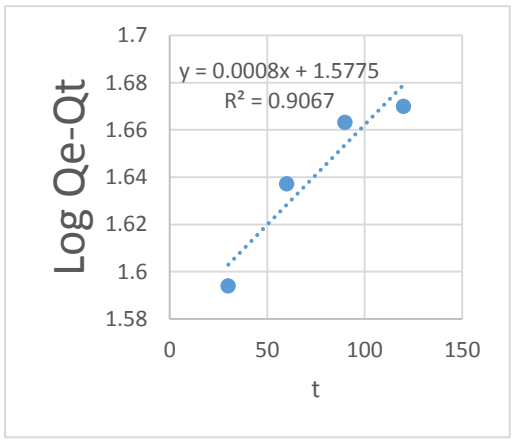



**E**

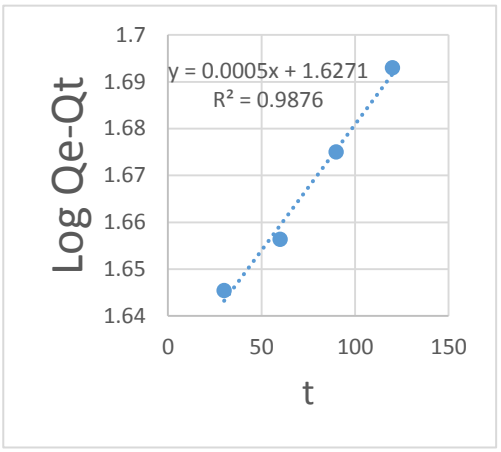



**F**

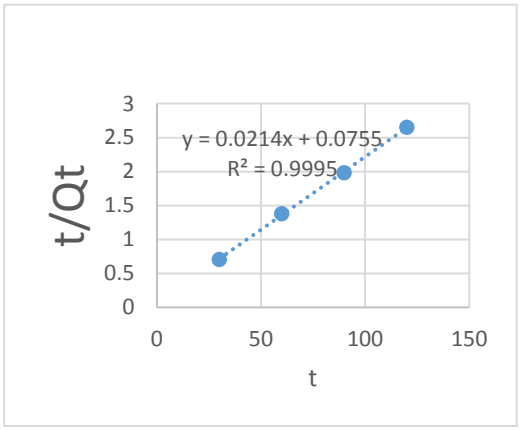
**Fig. 4.17: Pseudo-first order (A, D), Pseudo-second order (B, E) and Elovich (C, F) adsorption kinetic models for biosorption of Cr (III) on leaves of *Cupressus torulosa* at 25˚C and 40˚C**



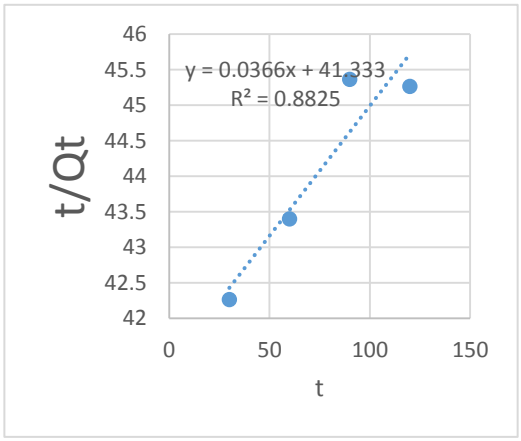

A



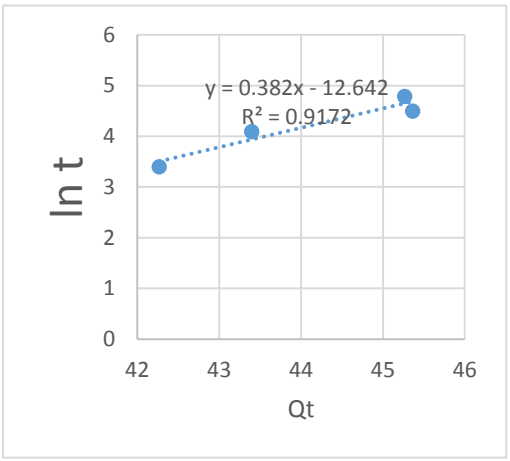

B



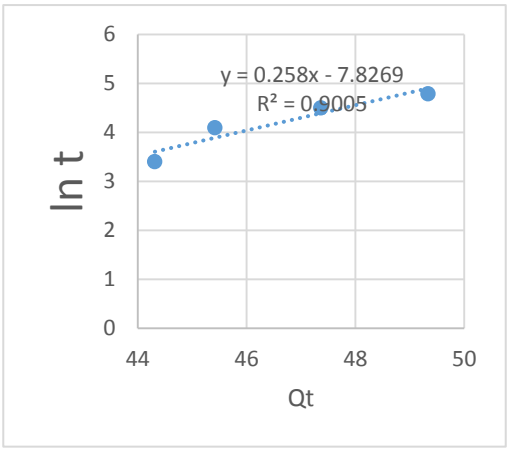

C




D




E




F

**Fig. 4.18: Pseudo-first order (A, B), Pseudo-second order (C, D) and Elovich (E, F)adsorption kinetic models for biosorption of Cr (III) on bark of *Cupressus torulosa* at 25˚C and 40˚C**

### 4.2.3 Rate Kinetics for Cr (III) removal by leaves and barks biomass of *Cupressus torulosa*

Study of rates of chemical processes is known as chemical kinetics. How different experimental conditions influence speed of a chemical reaction and yield information about the reaction's mechanism and transition states. In order to further expose the adsorption mechanism of Cr (III) on to biosorbent biomass and rate-controlling steps, a kinetic investigation was conducted. The rate kinetic models for removal of chromium (III) ions by leaves and bark of ***Cupressus torulosa*** contact timings from 30 to 120 min., initial metal ion concentration (1ppm and 2ppm), temperature (25°C and 40°C), biomass dosage (1g and 2g) and pH (4.2, 7 and 9) during biosorption process. Pseudo first order, Pseudo-second order and Elovich kinetic models have been used for testing experimental data. The criteria upon which the suitability of the model to fit the experimental data is determined by including both the correlation coefficient ($R^2$) and the calculated Qe value. When the model's $R^2$ value approaches unity and its Qe calculated is equal to Qe experimental, then the model gives the best fit to the experimental data. In the present study the criteria used for fitting the suitable model is only based on $R^2$ value. **Fig.4.11 and 4.12** represents regression correlation coefficient ($R^2$) value for pseudo first order, pseudo second order and Elovich kinetic model.

**Table 4.15: $R^2$ value for Pseudo-first order, Pseudo-second order and Elovich correlation coefficients for Cr (III) removal by leaves and bark of *Cupressus torulosa* at cold and hot temperature**

| **Sample** | Pseudo first order kinetic | Pseudo second order kinetic | Elovich adsorption kinetic |
|---|---|---|---|
| **CTL-C** | 0.988 | 0.999 | 0.976 |
| **CTL-H** | 0.981 | 0.998 | 0.909 |
| **CTB-C** | 0.906 | 0.999 | 0.917 |
| **CTB-H** | 0.987 | 0.882 | 0.900 |

### 4.2.4 FT-IR study of leaves and bark of *Cupressus torulosa*

Leaves and bark of *Cupressus torulosa* are used as biosorbent for removal of chromium metal from water at 3 different pH, *viz.* acidic, basic and neutral. FT-IR analysis was done in order to study the interactions between functional groups present in biosorbents and chromium metal ion. On comparing the spectra of unloaded leaves and bark of *Cupressus torulosa* and chromium loaded leaves and bark of *Cupressus torulosa* important distinctions are revealed.

Infrared absorption frequencies of leaves of *Cupressus torulosa* and chromium loaded leaves of *Cupressus torulosa* are summarized in Table and Fig. FT-IR spectrum of unloaded leaves shows an intense and slightly broad peak at 3424.03 $cm^{-1}$, assigned for H-bonded N-H stretching of amines. At pH 4 and 7 this peak gets completely disappear while at pH 9 it shifts to 3406.78 $cm^{-1}$. Chromium loaded leaves of *Cupressus torulosa* at pH 4 and 7 shows two new bands attributed due to -OH associated frequency at 3345.65 $cm^{-1}$ and 3344.40 $cm^{-1}$. Along with stretching vibrations, bending vibrations of OH and NH groups are also observed with slight shifts in the loaded and unloaded leaves, OH bending vibrations present at 1319.27 $cm^{-1}$ shifts to 1317.80 $cm^{-1}$, 1317.96 $cm^{-1}$ and 1317.97 $cm^{-1}$ at pH 4, 7 and 9 respectively. N-H bending vibrations present at 656.99 cm shifts to 666.79 $cm^{-1}$, 660.95 $cm^{-1}$ and 667.86 $cm^{-1}$ after adsorption at acidic, neutral and basic pH.

Bands of N-H pyranose rings are observed at 781.29 $cm^{-1}$ to 779.74 $cm^{-1}$ in all spectra of *C. torulosa* leaves. Peak at 519.99 $cm^{-1}$ shows interactions between metals and oxygen atom of ligands. After treating leaves with acidic and basic solution of chromium metal these band shifts towards lower frequency at 518.65 $cm^{-1}$ and 516.70 $cm^{-1}$, while in case of neutral solution it remain somewhat constant.

The spectra of unloaded leaves of *C. torulosa* have peak at 2923.86 $cm^{-1}$, attributed for C-H asymmetric stretching of alkyl groups with their bending vibrations at 1443.02 $cm^{-1}$ and C-H symmetric vibrations at 2853.52 $cm^{-1}$. The frequencies of C-H asymmetric stretching, symmetric and bending vibrations slightly shifts toward higher or lower frequency after biosorption mechanism. Peaks at 1654.76 $cm^{-1}$ and 2163.86 $cm^{-1}$ indicates C=C of alkenes and C=C stretching vibrations of alkynes which are found to be absent after biosorption process. In the spectrum of leaves of *C.*

*torulosa* loaded with metal ions at acidic, neutral and basic pH, new bands appears at 1517.6 $cm^{-1}$, 1516 $cm^{-1}$ and 1517 $cm^{-1}$ assigned for C-C stretching vibrations of alkanes which is absent in the spectra of leaves before biosorption.

The peaks of acids and alcoholic groups of *C. torulosa* leaves indicated by the different stretching and bending vibrations of C=O at 1623.12 $cm^{-1}$, carboxylate ions at 1376.10 $cm^{-1}$, C-O stretching of ether at 1105.84 $cm^{-1}$ and C-O of esters at 1060.01 $cm^{-1}$ before biosorption. Biosorption of chromium at different pH through *C. torulosa* leaves bring significant changes in these peaks. In the acidic neutral and basic solution peak of C=O stretching shifted to lower frequency at 1621.13 $cm^{-1}$, 1619.13 $cm^{-1}$ and 1620.82 $cm^{-1}$ with a sharp peak. New bands of free C=O group of acids appear at 1731.9 $cm^{-1}$, 1732.3 $cm^{-1}$ and 1736.5 $cm^{-1}$ in acidic , neutral and basic solution of chromium ions which is completely absent in unloded *C. torulosa* leaves. C-O stretching vibrations of acidic groups present at 1239.23 $cm^{-1}$, 1239.09 $cm^{-1}$ and 1241.6 $cm^{-1}$ and C-O stretching vibration of esters at 1060.20 $cm^{-1}$, 1059.20 $cm^{-1}$ and 1062.09 $cm^{-1}$, in acidic, neutral and basic pH solutions respectively with slight shift than unloaded leaves. The C-O stretching of ethers have high intensity to be observed in neutral and basic solutions and almost similar in acidic pH as compared to unloaded leaves.

Infrared absorption frequencies of bark of *Cupressus torulosa* and chromium loaded bark of *Cupressus torulosa* are explained and depicted in Table and Fig. The FTIR spectrum displayed a number of peaks and indicated a complex nature of the bark of *Cupressus torulosa* as a biosorbent for chromium metal ions. The broad and intense band at 3424.75 $cm^{-1}$ assigned for N-H stretching vibrations of amino groups which are H-bonded with O-H groups of alcohols and acids present in unloaded bark of *Cupressus torulosa* found to be completely absent in loaded bark of *Cupressus torulosa* at acidic, neutral and basic pH. New bands assigned for –OH associated frequency (3357.64 $cm^{-1}$, 3357.23 $cm^{-1}$ and 3354.00 $cm^{-1}$) appears in the loaded bark of *Cupressus torulosa.* Bending vibrations of amines present at 1618.58 $cm^{-1}$ shifted to higher frequency in loaded bark of *Cupressus torulosa* at acidic, neutral and basic pH while peak at and 669.19 $cm^{-1}$ shifted to higher frequency at acidic solution and lower frequency at neutral and basic solution. The vibration bands at 2928.13 $cm^{-1}$ and 1443.38 $cm^{-1}$ indicates the C-H asymmetric stretching of alkyl groups and C-H

**Table 4.16 FT-IR spectral analysis of *Cupressus torulosa* leaves before and after the biosorption of Cr(III) metal ions**

| Peak assignment | Frequency before adsorption ($cm^{-1}$) | Frequency after adsorption of Cr(III) $cm^{-1}$ | | | Differences in frequencies before and after adsorption ($cm^{-1}$) | | |
|---|---|---|---|---|---|---|---|
| | | pH=4 | pH=7 | pH=9 | pH=4 | pH=7 | pH=9 |
| -OH bonded N-H Stretching | 3424.03 | - | - | 3406.78 | Disappear | Disappear | 17.25 |
| -OH associated | - | 3345.65 | 3344.40 | - | New band | New band | - |
| -CH alkyl asymm. Streching | 2923.86 | 2921.81 | 2922.10 | 2924.33 | 2.05 | 1.76 | -0.47 |
| -CH alkyl symm. Streching | 2853.52 | 2852.3 | 2853.2 | 2855.2 | 1.22 | 0.32 | -1.68 |
| -C≡C- Streching in alkynes | 2163.86 | - | - | - | Disappear | Disappear | Disappear |
| Free –C=O of –COOH gp. | - | 1731.9 | 1732.3 | 1736.5 | New band | New band | New band |
| C=C Streching ($R_2C=CH_2$) | 1654.76 | - | - | - | Disappear | Disappear | Disappear |
| V C=O $_{(assym.)}$, $NH_2$ Bending | 1623.12 | 1621.75 | 1619.13 | 1620.82 | 1.37 | 3.99 | 2.3 |
| -C-C- Streching | - | 1517.6 | 1516 | 1517 | New band | New band | New band |
| -CH Bending (Methyl) | 1443.02 | 1446.93 | 1444.70 | 1450.7 | -3.91 | -1.68 | -7.68 |
| $COO^-$ in Acids and Alcohols | 1376.10 | 1372.30 | 1374 | 1370.6 | 3.8 | 2.1 | 5.5 |
| -O-H Streching | 1319.27 | 1317.80 | 1317.96 | 1317.97 | 1.47 | 1.31 | 1.3 |
| C-O Streching of –COOH gp. | 1247.85 | 1239.23 | 1239.09 | 1241.6 | 8.62 | 8.76 | 6.25 |
| C-O Streching of ether | 1105.84 | 1105.5 | 1107 | 1109.2 | 0.34 | -1.16 | -3.36 |
| =C-O-CH Streching in ethers | 1060.01 | 1060.20 | 1059.45 | 1062.09 | -0.19 | 0.56 | -2.08 |
| Bending viberation of Pyranose | 779.74 | 781.29 | 780.73 | 780.96 | -1.55 | -0.99 | -1.22 |
| N-H Bending (Amines) | 656.99 | 666.79 | 660.95 | 667.86 | -9.8 | -3.96 | -10.87 |
| Metal- Ligand Bonding (M-O) | 519.99 | 518.65 | 519 | 516.70 | 1.34 | 0.99 | 3.29 |

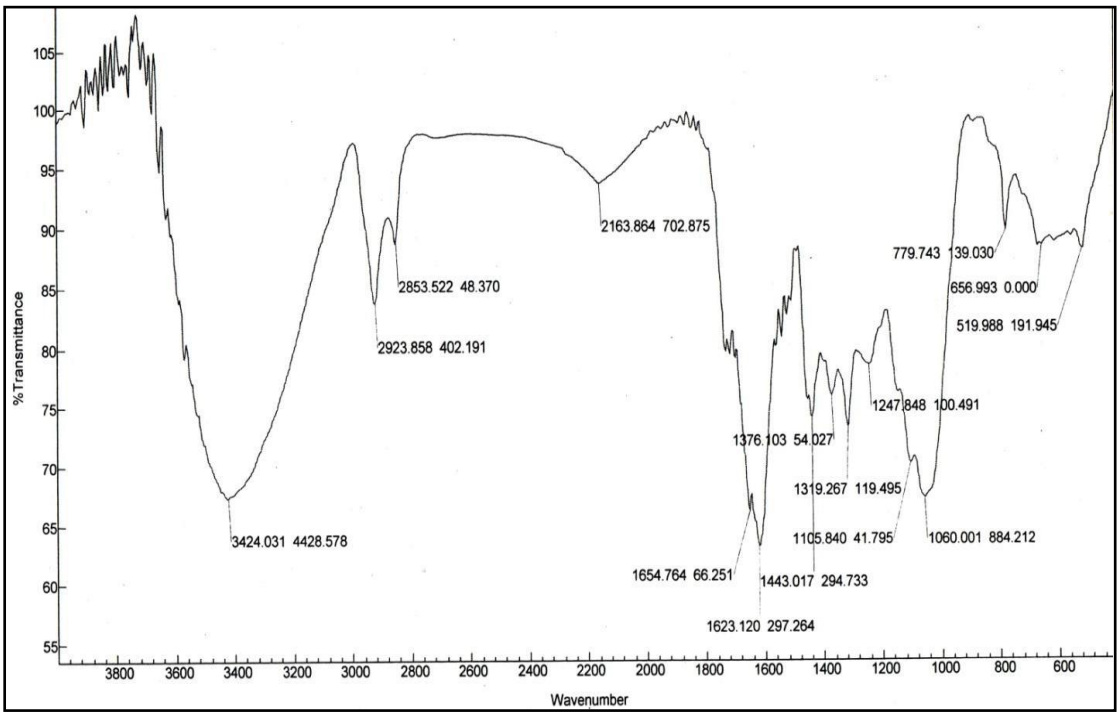
bending vibrations, which are shifted to 2928.10 $cm^{-1}$, 2924.49 $cm^{-1}$, 2927.10 $cm^{-1}$, 1443.8 $cm^{-1}$, 1444.86 $cm^{-1}$ and 1440.53 $cm^{-1}$ after biosorption of chromium metal ions on acidic, neutral and basic pH treatments respectively. A small peak of C-H asymmetric stretching of alkyl groups at 2854 $cm^{-1}$ and 2855.2 $cm^{-1}$ found to be present after biosorption process at neutral and basic pH. Before biosorption, an overtone of stretching vibrations of C≡C bonds of alkynes present at 2125.56 $cm^{-1}$ but after biosorption mechanism these overtones were absent in all spectra. A weak intense band at 1526.67 $cm^{-1}$ is indication of C-C stretching vibrations in the spectrum of unloaded material but after loading of metal ions frequency of this band shifts towards lower side at 1524 $cm^{-1}$, 1516 $cm^{-1}$ and 1520.4 $cm^{-1}$ respectively.

The presence of carbonyl groups of acids, esters of different constituents of bark material is indicated by the presence of peak at 1377.06 $cm^{-1}$ assigned for carboxylate ions of acids and alcohols. Along with this peak, bands at 1153.31 $cm^{-1}$, 1105.86 $cm^{-1}$ and at 1059.46 $cm^{-1}$ are corresponding to C-O stretching vibrations of tertiary alcohols, ethers and esters respectively. These bands have significant shifts in their frequencies after the biosorption of chromium metal ions due to participation of these into biosorption mechanism. Therefore, due to biosorption mechanism at acidic pH, peaks shifted from 1377.06 $cm^{-1}$ to 1374 $cm^{-1}$, 1153.31 $cm^{-1}$ to 1161.5 $cm^{-1}$, 1105.86 $cm^{-1}$ to 1109.2 $cm^{-1}$ and 1059.46 $cm^{-1}$ to 1060.29 $cm^{-1}$. At neutral pH these peaks shifted from 1377.06 $cm^{-1}$ to 1372.7 $cm^{-1}$, 1153.31 $cm^{-1}$ to 1157.9 $cm^{-1}$, 1105.86 to 1106.8 and 1059.46 to 1058.61 while at basic pH these peaks shifted from 1377.06 $cm^{-1}$ to 1373.60 $cm^{-1}$, 1153.31 $cm^{-1}$ to 1160 $cm^{-1}$, 1105.86 $cm^{-1}$ to 1108.8 $cm^{-1}$ and 1059.46 $cm^{-1}$ to 1059.36 $cm^{-1}$ respectively. A new band at 1734 $cm^{-1}$ appears at neutral pH attributed to free C=O of carboxylic group found to be completely absent in loaded bark at acidic and basic pH and unloaded bark of *Cupressus torulosa.*

Peak at 1318.71 $cm^{-1}$ assigned for O-H stretching of alcohols and acids present in bark do not show any significant changes in frequency after biosorption at acidic, neutral and basic pH. The C-N stretching band at 1264.17 $cm^{-1}$ in bark material found to be shifted to lower frequency at 1234.7 $cm^{-1}$, 1240.39 $cm^{-1}$ and 1255.6 $cm^{-1}$in acidic, neutral and basic solution of chromium metal ions. The weak and sharp band at 890.53 $cm^{-1}$ assigned for C-H bending of pyranose rings found to be absent at neutral and shifted at higher frequency in case of acidic and basic pH. The presence of sugars

**Table 4.17 FT-IR spectral analysis of *Cupressus torulosa* bark before and after the biosorption of Cr (III) metal ions**

| Peak assignment | Frequency before adsorption ($cm^{-1}$) | Frequency after adsorption of Cr(III) $cm^{-1}$ | | | Differences in frequencies before and after adsorption ($cm^{-1}$) | | |
|---|---|---|---|---|---|---|---|
| | | pH=4 | pH=7 | pH=9 | pH=4 | pH=7 | pH=9 |
| -OH bonded N-H Streching | 3424.75 | - | - | - | Disappear | Disappear | Disappear |
| -OH associated | - | 3357.64 | 3357.23 | 3354.00 | New band | New band | New band |
| -CH alkyl asymm. Streching | 2928.13 | 2928.10 | 2924.49 | 2927.10 | 0.03 | 3.64 | 1.03 |
| -CH alkyl symm. Streching | - | - | 2854 | 2855.2 | Disappear | New band | New band |
| -C≡C- Streching in alkynes | 2125.56 | - | - | - | Disappear | Disappear | Disappear |
| Aromatic –CO Streching | - | - | 1734 | - | Disappear | New band | Disappear |
| $NH_2$ Bending | 1618.58 | 1622.51 | 1620.90 | 1621.33 | -3.93 | -2.32 | -2.75 |
| -C-C- Streching | 1526.67 | 1524 | 1516 | 1520.4 | 2.67 | 10.67 | 6.27 |
| -CH Bending (Methyl) | 1443.38 | 1443.8 | 1444.86 | 1440.53 | -0.42 | -1.48 | 2.85 |
| $COO^-$ in Acids and Alcohols | 1377.06 | 1374 | 1372.7 | 1373.60 | 3.06 | 4.36 | 3.46 |
| -O-H Streching | 1318.71 | 1317.72 | 1317.94 | 1317.97 | 0.99 | 0.77 | 0.74 |
| -C-N Streching | 1264.17 | 1234.7 | 1240.39 | 1255.6 | 29.47 | 23.78 | 8.57 |
| -C-O Streching in $t^0$ -OH | 1153.31 | 1161.5 | 1157.9 | 1160 | -8.19 | -4.59 | -6.69 |
| C-O Streching of ether | 1105.86 | 1109.2 | 1106.8 | 1108.8 | -3.34 | -0.94 | -2.94 |
| =C-O-CH Streching in ethers | 1059.46 | 1060.29 | 1058.61 | 1059.36 | -0.83 | 0.85 | 0.1 |
| -CH Bending of Pyranose sugar | 890.53 | 893.13 | - | 891.84 | -2.6 | Disappear | -1.31 |
| Bending viberation of Pyranose | 779.95 | 780.73 | 779.23 | 781.01 | -0.78 | 0.72 | -1.06 |
| N-H Bending (Amines) | 669.19 | 670.46 | 661.00 | 668.83 | -1.27 | 8.19 | 0.36 |
| Metal- Ligand Bonding (M-O) | 519.71 | 520 | 520.1 | 517.49 | -0.29 | -0.39 | 2.22 |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2923.858 402.191
2853.522 48.370
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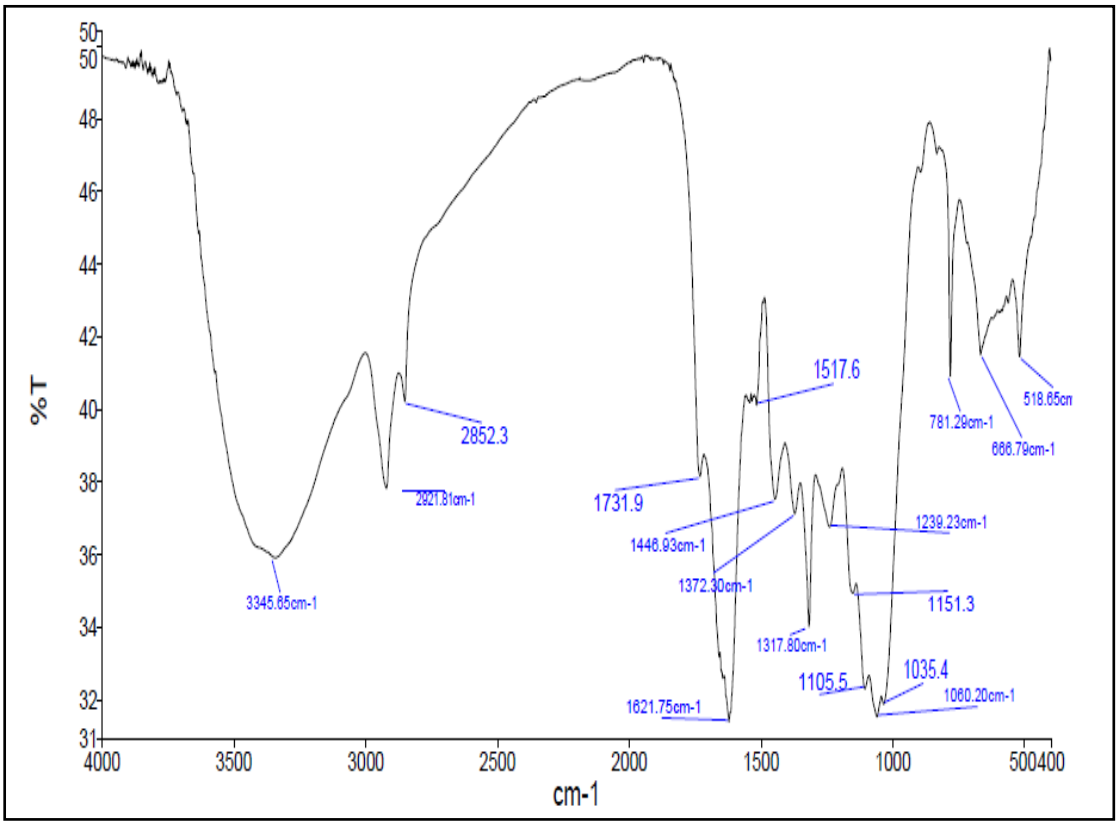
1654.764 66.251
1623.120 297.264
1443.017 294.733
1376.103 54.027
1319.267 119.495
1247.848 100.491
1105.840 41.795
1060.001 884.212
779.743 139.030
656.993 0.000
519.988 191.945

**(A)**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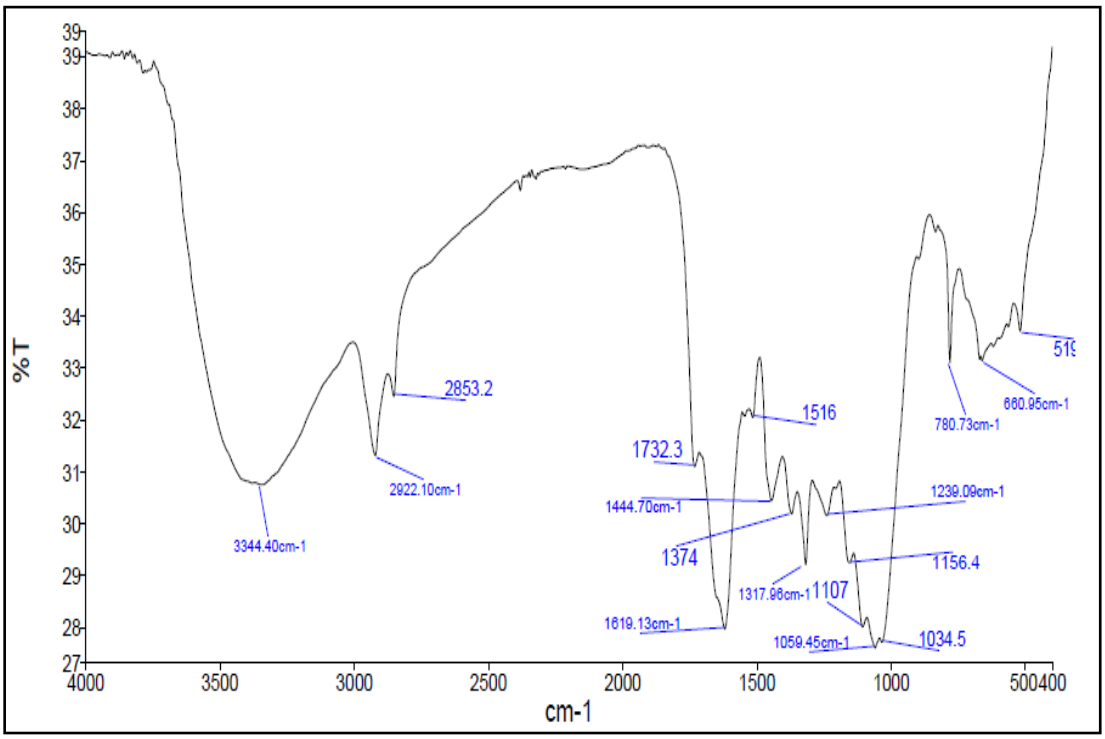
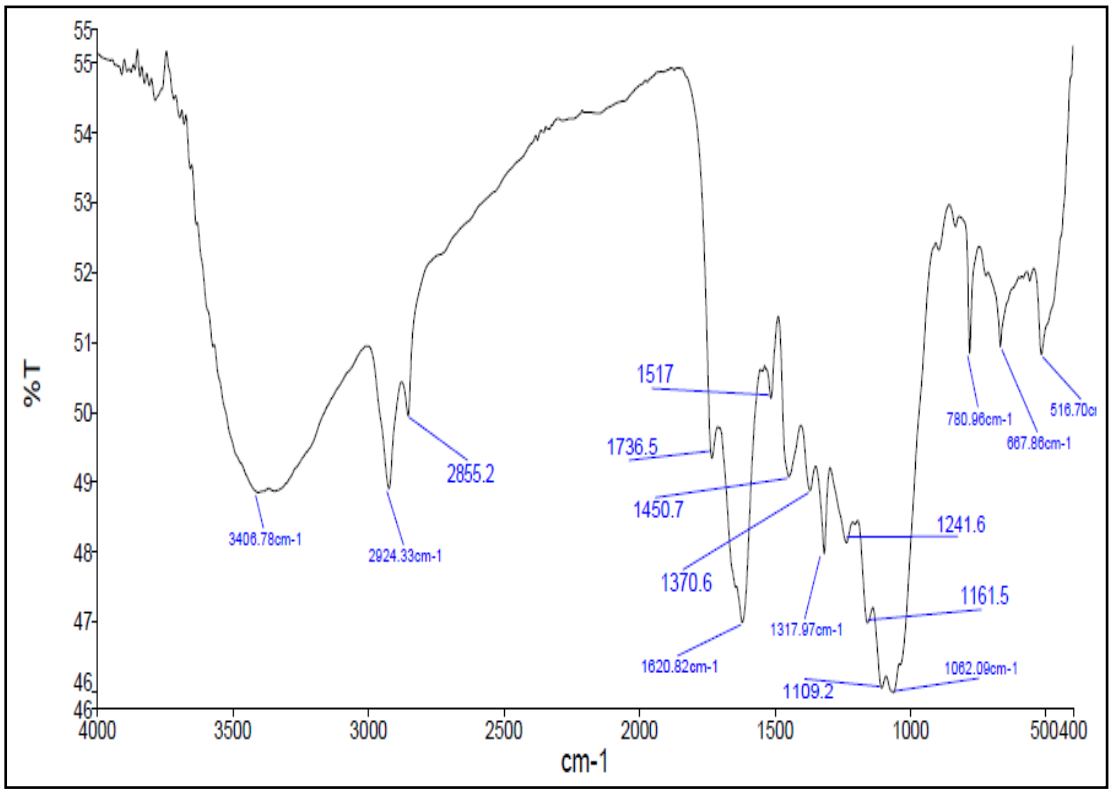
2921.81cm-1
2852.3
1731.9
1621.75cm-1
1517.6
1446.93cm-1
1372.30cm-1
1317.80cm-1
1239.23cm-1
1151.3
1105.5
1035.4
1060.20cm-1
781.29cm-1
666.79cm-1
518.65cm

**(B)**

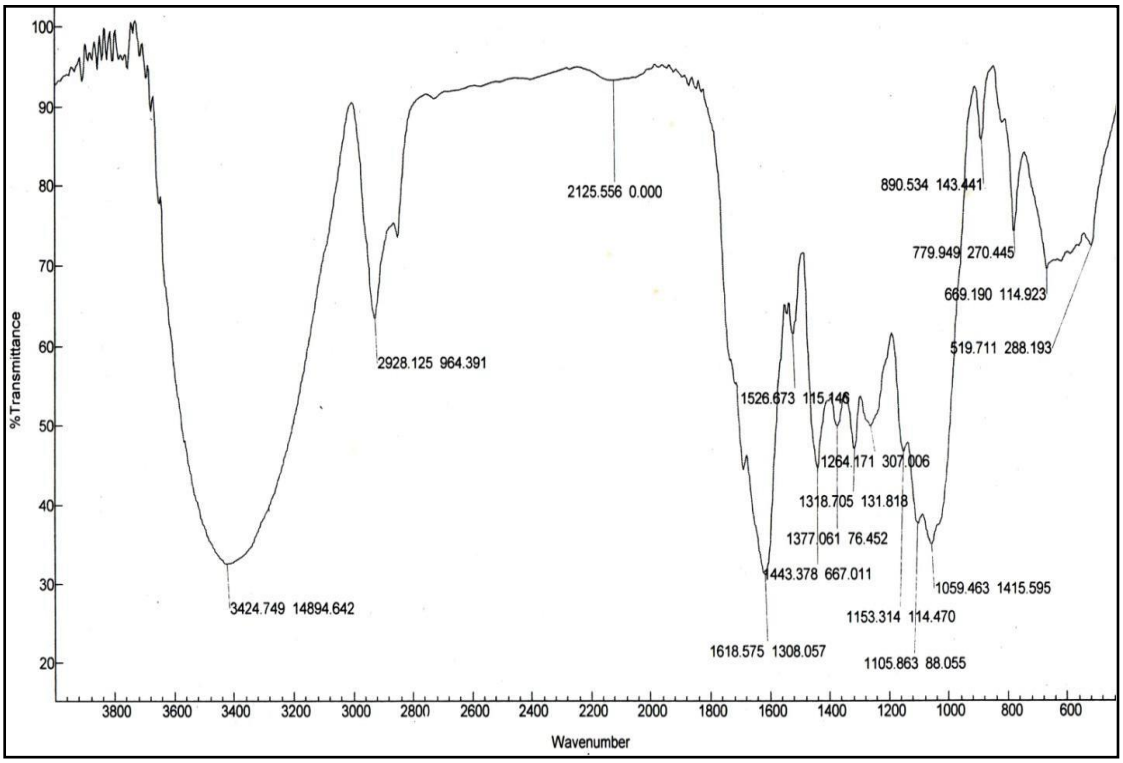



**(C)**

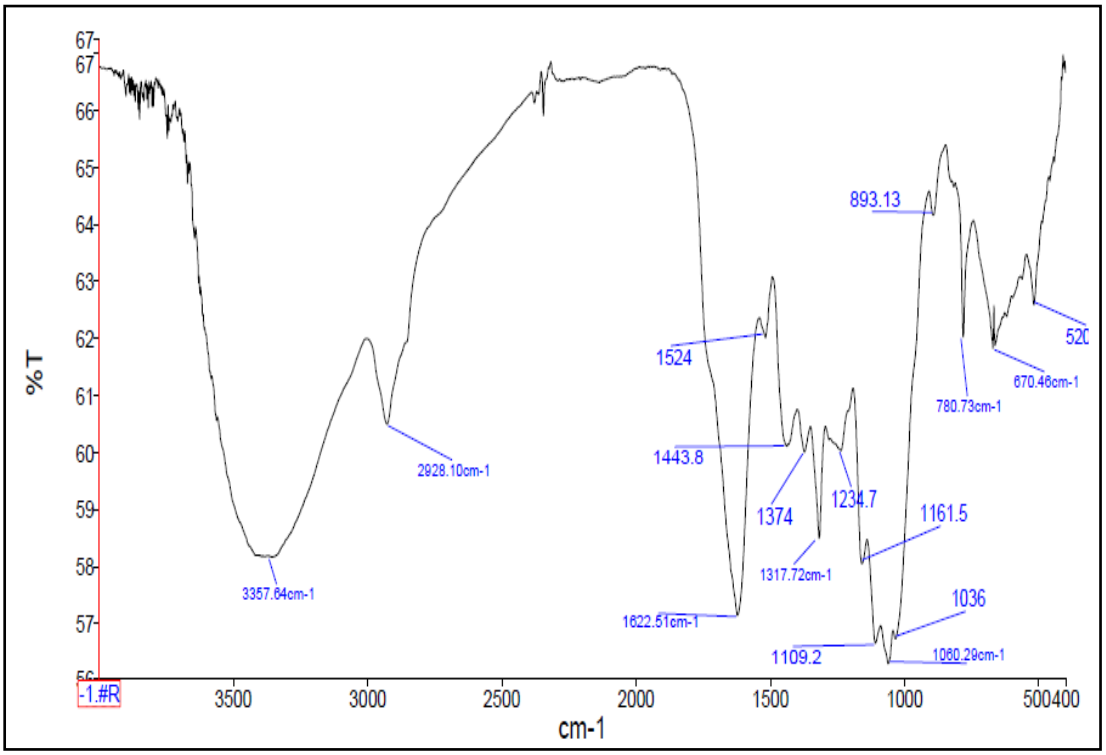



**(D)**

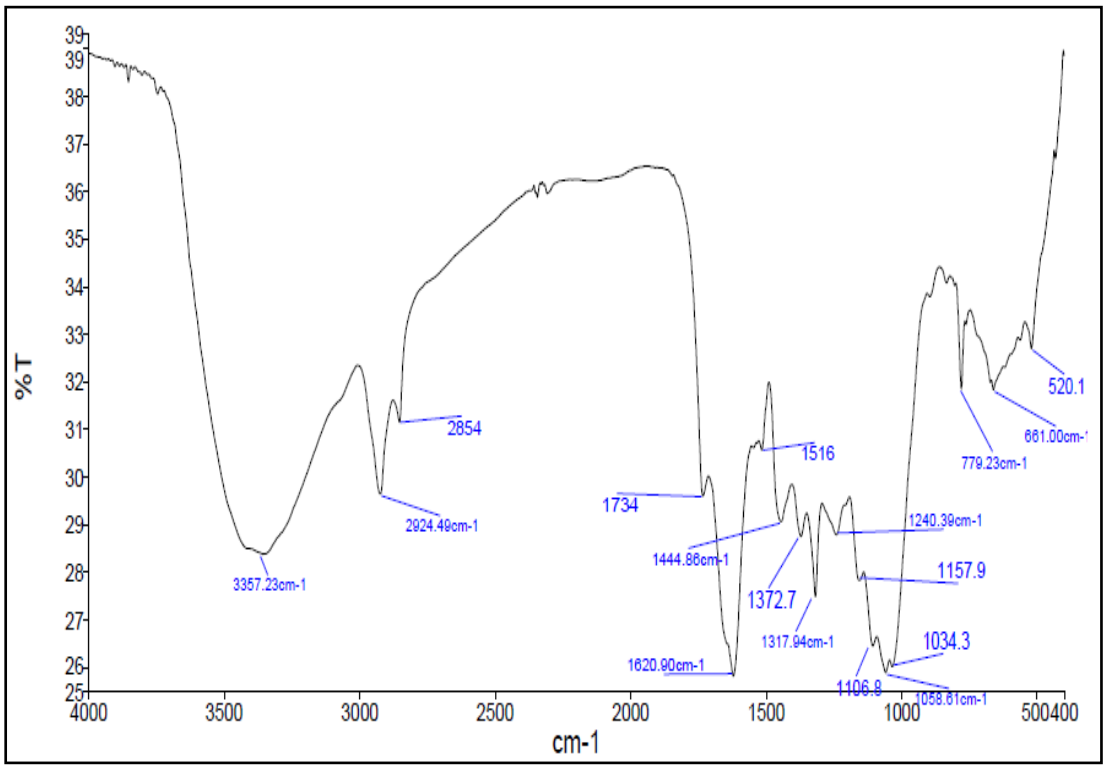
**Fig. 4.19: FT-IR spectra of *Cupressus torulosa* leaves before (A) and after the biosorption of Cr(III) metal ion at pH 4.0 (B), pH 7.0 (C) and pH 9.0 (D)**


%Transmittance
Wavenumber
2125.556 0.000
890.534 143.441
779.949 270.445
669.190 114.923
519.711 288.193
2928.125 964.391
1526.673 115.146
1264.171 307.006
1318.705 131.818
1377.061 76.452
1443.378 667.011
1059.463 1415.595
3424.749 14894.642
1153.314 114.470
1618.575 1308.057
1105.863 88.055

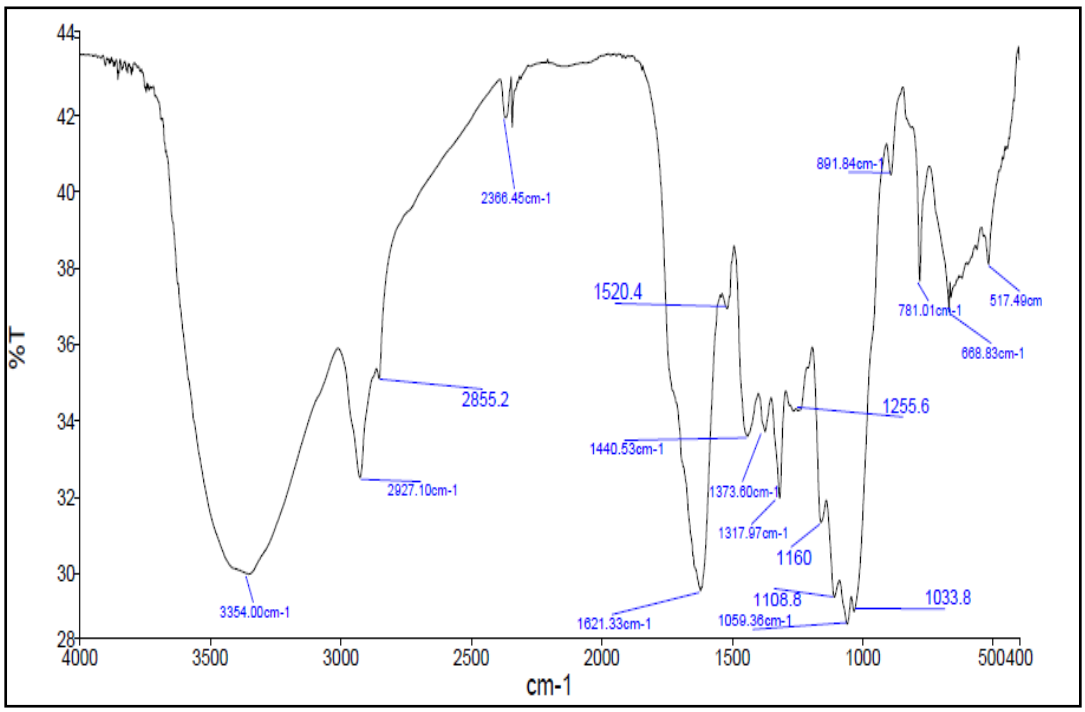
**(A)**


%T
cm-1
893.13
1524
2928.10cm-1
1443.8
1374
1234.7
1161.5
3357.64cm-1
1317.72cm-1
1622.51cm-1
1036
1109.2
1060.29cm-1
780.73cm-1
670.46cm-1

**(B)**




**(C)**




**(D)**

**Fig. 4.20: FT-IR spectra of *Cupressus torulosa* bark before (A) and after the biosorption of Cr(III) metal ion at pH 4.0 (B), pH 7.0 (C) and pH 9.0 (D)**

in the bark of *C.torulosa* can be indicated by the presence of bending vibrations of pyranose rings in the frequency region between 781.01 $cm^{-1}$ to779.23 $cm^{-1}$ in loaded as well as unloaded bark during biosorption mechanism. Metal- ligands bonding expressed by presence of band at 519.71 $cm^{-1}$ in the spectrum of unloaded bark, while peaks at 520 $cm^{-1}$, 520.1 $cm^{-1}$ and 517.49 $cm^{-1}$ in the spectra of loaded bark at acidic, neutral and basic pH solutions of chromium respectively.

### 4.2.5 Scanning Electron Microscopy (SEM) Analysis before and after the adsorption of Chromium (III) metal ions

FTIR analysis gave an indication of functional groups responsible for metal binding. Work in this content consolidates the results obtained previously as it identifies changes in surface structures and functionalities followed by metal binding. In this study, SEM allows examination of topography of biosorbent surfaces and identification of morphological changes which might take place in the biosorbent after metal exposure.

All SEM micrographs are given at magnification of 100X to 1500X. Results at higher magnifications more than 5000X were also obtained, but the focused beam at higher magnification caused thermal degradation of samples. Micrographs shown are representative of those taken over the entire sample surface.

**SEM analysis of leaves and bark of *Cupressus torulosa***

The SEM micrographs obtained for raw and chromium (III) metal loaded leaves of *Cupressus torulosa are* shown in **Fig. 4.21 A, 4.21 B & 4.21C** while those of *Cupressus torulosa* bark shown in **Fig. 4.22 A & 4.22 B.** Significant morphological changes were observed which support the binding of metal with leaves and bark surfaces. In both cases, raw leaves and bark surfaces appear smoother than that in metal-loaded samples with some rougher surface, shrinking after metal binding also apparent.

As in case of *Cupressus torulosa* leaves morphological changes can be estimated by the cavity size in raw samples as well as in metal loaded samples. Raw leaf surface of *Cupressus torulosa* is full of fibers and have small cavities between different layers, while after biosorption these fibrous layers were not observed and cavities became larger in size which may be due to multilayered metal deposition on

the epidermis of leaves after biosorption. These morphological changes in leaf surface give an idea about binding of metal ions with the biosorbent.

In **Fig. 4.22.** SEM micrographs **(A) and (B)** illustrate morphological changes between raw and chromium metal loaded bark of *Cupressus torulosa* Parenchymatous cells are irregularly distributed in the whole bark surface which could be seen in micrographs. The smoothness of bark surface has been increased after biosorption revealed the binding mechanism of metal ions and functional groups of biosorbent.

# *Chapter 5* SUMMARY AND CONCLUSION

Chromium heavy metal pollution is great concern now a days due to its health hazard effect so its removal is necessary. However there are various traditional methods are present but Biosorption is proven to be quite effective for removing heavy metals from contaminated solution in a low cost and eco-friendly manner.

The present investigation shows that the Gymnosperm like *Cupressus torulosa* and *Taxus torulosa* can be used as an effective adsorbent for the treatment of wastewaters containing metals like chromium (III). Adsorption dynamics, isotherms, pH effect and adsorbent dosage on the removal of metals for all the adsorbates were examined. The salient features of the present study are summarized as follows:

1. The gymnosperms plant species i.e., *Cupressus torulosa* and *Taxus baccata,* have been collected from high altitude of Uttarakhand hills.
2. The leaves and bark of mentioned plants are rich source of lignin, carbohydrates, minerals, cellulose, fibers, resins, etc which contains functional groups, responsible for binding of heavy metals.
3. The chromium (III) is major concern in present study because of the excessive intake of Cr (III) by human beings leads to serious health problems such as cancer, anaemia sperm, damage, renal and central nervous system damages**.**
4. The experiments were conducted at cold and hot temperatures (25±5˚C and 40±5˚C), different initial metal ion concentrations (1.0 and 2.0), acidic, neutral and basic pH (4.2, 7.0 and 9.0), different time periods i.e., 30, 60, 90, 120, 150 and 180min and different amounts of biomass of leaves and bark (1.0 and 2.0g).
5. The maximum biosorption efficiency (% removal) and biosorption capacity (Qe value) were recorded at equilibrium conditions.
6. In biosorption experiment, the maximum removal of Cr(III) by leaves and barks of *C. torulosa* was recorded at 120min, initial metal concentration (1 mg/L), acidic pH (4.2), biomass amount (1g) and cold (25±5˚C) to hot (40±5˚C) temperature conditions. The maximum removal by *C. torulosa*

leaves were 97.83 and 93.66 % at hot and cold temperature conditions while bark showed 90.53 and 93.66% removal at cold and hot temperature conditions respectively at equilibrium condition.

7. The Biosorption capacity was adsorbed 42.80, 48.91, 45.26 and 49.33 mg of chromium ions at cold and hot temperature conditions respectively mg/g by leaves and bark of *C.torulosa* at equilibrium conditions.

8. In biosorption experiment, the maximum removal of Cr (III) by leaves and barks of *Cupressus torulosa* was recorded at 120min, initial metal concentration (1 mg/L), acidic pH (4.2), biomass amount (2 g) and cold (25±5˚C) to hot (40±5˚C) temperature conditions. The maximum removal by *C. torulosa* leaves were 98.80 and 73.10% at cold and hot temperature conditions while bark showed 89.13 and 92.73% removal at cold and hot temperature conditions respectively at equilibrium conditions.

9. The leaves and bark of *Taxus baccata* adsorbed 24.70, 22.33, 17.78 and 24.05 mg of chromium ions at cold and hot temperature conditions respectively at equilibrium conditions. Among the leaves and barks of *C.torulosa*, bark have highest adsorption capacity at hot temperature followed by leaves at higher temperature while

10. In biosorption experiment, the maximum percentage removal of Cr(III) by *Taxus baccata* leaves were 89.40 and 93.23 % at cold and hot temperature conditions while bark showed 90.33 and 93.23% removal at cold and hot temperature conditions respectively and adsorption capacity of leaves and bark were 45.16, 46.83, 44.70 and 46.61 mg of chromium ions at cold and hot temperature respectively. These results observed at equilibrium conditions (initial metal concentration (1 mg/L), acidic pH (4.2), biomass amount (1 g) and contact time 120 min).

11. The increasing trend of percentage removal and adsorption capacity with contact time, initial metal ion concentration and biomass amounts, was may be due to availability of binding sites in biosorbent materials while decreasing trend may be due to fulfilling of functional groups sites at biosorbent surface or saturation of metal binding sites.

12. At lower pH, the surface of biomass is positively charged due to protonation. This protonation effect is more pronounced at low pH (below 4.0) due to presence of high concentration of H+ ions in the solution and results in more unfavorable for metal ion adsorption at a lower pH value owing to the electrostatic repulsion between both positively charged adsorbent surface and the metal ions and the functional groups transfer H+ ions which indicates that majority of the metal binding sites were occupied. When the pH increases, the concentration of H+ ions decreases and negatively charged biomass surface can interact with the positively charged metal ions and metal ions uptake increases.

13. The parameters of Langmuir, Freundlich and Temkin adsorption isotherm models were used to explain adsorption phenomenon of Cr (III) removal by leaves and barks biomass of *Cupressus torulosa* and *Taxus baccata*. The correlation coefficient ($R^2$) value greater than 0.9 explain best fitting of model among all three models. Separation factor 'RL' value is less than 1, 'n' value is greater than 1 and low value of heat of adsorption indicate favorability of Langmuir, Freundlich and Temkin models respectively and showed good affinity of chromium ions towards biomass.

14. The parameters of Pseudo first order, Pseudo-second order and Elovich kinetic models have been used for testing experimental data in order to further expose the rate-controlling steps of adsorption mechanism of Cr (III) on to biosorbent biomass of *Cupressus torulosa* and *Taxus baccata*, plants. The value of correlation coefficient ($R^2$) should be 1or near to 1, gives information about best suitable kinetic model for biosorption of Cr(III) metal ions. There should be an agreement between Qe experimental and Qe calculated values for the suitability of any kinetic model. On the observation of these parameters Pseudo-second order kinetics followed by most of the biomass at different temperature but some biomass also follow Pseudo-first order kinetic and Elovich model. Pseudo-second order kinetics represents chemisorptions.

15. To understand the nature of possible interactions between the Chromium metal ions and the functional groups of plants leaves and barks of *C. torulosa* and *T. baccata* the FT-IR spectra of dried unloaded and Cr-loaded plants biomass

were obtained. The spectra showed change in frequencies of characteristic peaks before and after the biosorption due to metal ligand interactions of chromium metal ions with oxygen, nitrogen and halogens of alcohols, carboxylic acids, amines and phenol of cellulose, pectin, absorbed water, hemicelluloses and lignin, present in plant materials.

16. In this study, Scanning Electron Microscopic (SEM) analysis, allows examination of topography of biosorbent surfaces and identification of morphological changes which might take place in the biosorbent after metal exposure. There significant morphological changes were observed which support the binding of metal with leaves and bark surfaces at 500 to 1500X magnification.

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# VITA

*The author of this manuscript was born on 05 July 1986, in Lalkua. He passed his High School and Intermediate Examination from Government inter college Lalkua in the year 2002 and 2005 respectively. He earned his B.Sc. degree in 2009 from Kumaun University, Nainital and M.Sc. Degree in Agricultural Chemicals at GBPUAT, Pantnagar, in July 2011. He joined the Department of Chemistry, College of Post-Graduate Studies, G.B. Pant University of Agriculture & Technology, Pantnagar for her Ph.D. research in July, 2011 with major in Agricultural Chemicals and minors in Environmental Science.*

**Permanent Address:**

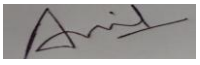
Anil Verma
S/O- Late Budhpal Verma
Ward No-5, Subhash Nagar P.O. – Lalkau
District- Nainital
Uttarakhand, Pin Code- 262402
Email- anil.verma979@gmail.com

# ABSTRACT


| | | | | | |
|---|---|---|---|---|---|
| **Name** | **:** | Anil Verma | **Id. No.** | **:** | 39376 |
| **Sem. & yearof admission:** 1st semester, 2011-2012 | | | **Degree** | **:** | Ph. D |
| **Major** | **:** | Agricultural Chemicals | **Deptt.** | **:** | Chemistry |
| **Minor** | **:** | Environmental Sciences | | | |
| **Thesis Title** | **:** | **"Equilibrium Modeling and Kinetic Studies on the Biosorption of Chromium (III) from Synthetic waste Water using *Cupressus torulosa* and *Taxus baccata*"** | | | |
| **Advisor** | **:** | Dr. Vivekanand | | | |



In recent times, Heavy metals in general and chromium in particular has received a great deal of attention because of their toxicity. Studies were undertaken to examine the biosorptive ability of Gymnosperm plant species, *Cupressus torulosa, and baccata*, , collected from high altitude of Uttrakhand hills, to remove the Chromium (III) metal ions from aqueous solution. Batch mode experiments were conducted at cold and hot temperatures (25˚±5˚C and 40˚±5˚C) to study the effects of initial Cr (III) metal ion concentrations, pH, time and amount of biomass. Thus a removal of chromium is essential from the environment by cheap and ecofriendly process. The maximum percentage removal (%removal) and biosorption capacity (Qe value) were recorded at equilibrium conditions. The maximum removal of Cr (III), at cold and hot temperature condition by by *C. torulosa* and *T. baccata,* leaves were 97.83 and 93.66, 97.83 and 93.66 while by barks were 90.53 and 93.66% , 90.33 and 93.23% respectively. Langmuir, Freundlich and Temkin adsorption isotherm models were used to explain adsorption phenomenon of Cr (III) removal. Equilibrium data agreed well for biosorption of Cr (III). The kinetic data have been analyzed using Pseudo first order, Pseudo-second order and Elovich kinetic models. The experimental data fitted very well the Pseudo second order and Elovich kinetic models. The FT-IR spectra of dried unloaded and Cr-loaded plants biomass were obtained to understand the nature of possible interactions between the chromium metal ions and the functional groups of biosorbents. The FT-IR analysis revealed that the main functional groups involved in biosorption were carboxyl, carbonyl, amino, alcoholic and phenol. Significant morphological changes were observed using SEM analysis, which support the binding of metal with leaves and bark surfaces. Thus, it can be concluded that gymnosperms can be utilized as cost-effective and environment friendly alternative over commercial methods of treatment for removal of toxic metals and contaminants of water because these plants consists high metal binding properties at different environmental conditions.

**(Vivekanand)**
Advisor

**(Anil Verma)**
Author

| | | | |
|---|---|---|---|
| नाम | : **अनिल वर्मा** | परिचयांक सं0 : | **39376** |
| सत्र एवं प्रवेश वर्ष | : **प्रथम, 2011-12** | उपाधि : | **पी0एच0डी0** |
| मुख्य विषय | : **कृषि रसायन** | विभाग : | **रसायन विज्ञान** |
| सहायक विषय | : **पर्यावरण विज्ञान** | | |
| सलाहकार | : **डॉ0 विवेकानन्द** | | |

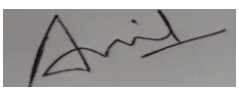

**शोध शीर्षक : " क्यूप्रस टारयूलोसा और टैक्सस बकाटा के बायोमास द्वारा Cr (III) कृत्रिम जल से अवशोषण का साम्यिक प्रारूप और गतिकी अध्ययन "**

## सारांश


वर्तमान समय में भारी धातु जिसमें मुख्यतः क्रोमियम ने अपनी जहरीली प्रवृति के कारण ध्यान आकर्षित किया है। उत्तराखण्ड की पहाड़ियो की ऊचाइयों से एकत्रित क्युप्रस टारयुलोसा और टैक्सस बकाटा की पत्तियों तथा तने की छाल से बने जैव अवशोषण अध्ययन क्रोमियम (III) धातु को जलीय विलयन से हटाने के लिए किया गया। क्रोमियम (III) धातु आयन की प्रारम्भिक सान्द्रता, pH , समय तथा जैवपदार्थ की मात्रा के प्रभाव के अध्ययन के लिए ठंडे और गर्म तापमान ($25^0 \pm 5^0$) पर बैच ($40^0 \pm 5^0$) पर बैच प्रणाली प्रयोग किये गये। अधिकतम निष्कासन प्रतिशतता तथा जैव अवशोषण क्षमता (Qe) को साम्य स्थिति पर दर्ज किया गया। क्युप्रस टोरयुलोसा तथा टेक्सस बकाटा पत्तियों के द्वारा 97.83% और 93.66%, 97.83% और 96.33% जबकि छालो द्वारा 90.53% और 93.66% और 90. 33% और 93.23% क्रमशः ठण्डे तथा गर्म तापमान पर अधिकतम निष्कासन प्रतिशतता पाई गई। क्रोमियम धातु के अवशोषण कार्यिक समूह के बीच सम्भावित पारस्परिक प्रभाव को समझने के लिए लेंग्म्यूर फ्रेड़ालिक तथा टेम्पकिन समतापी प्रारूपो का प्रयोग किया गया। साम्यिक ऑकडे **Cr** (III) अवशोषण को पूर्णतः सहमत करते हैं। क्रोमियम धातु आयन तथा जैव अवशोषण के कार्यिकी समूहो के बीच सम्भावित पारम्परिक प्रभाव को समझने के लिए शुष्क अभारीय और क्रोमियम भारीय पादपीय बायोमास के FTIR स्पेक्ट्रा प्राप्त किये गये। विश्लेषण से ज्ञात हुआ कि जैव अवशोषण मे कार्बोक्सिल, कार्बोनिल, अमीनों, एल्कोहलिक तथा फिनॉल मुख्य कार्यिकी समूह के रूप में सम्मिलित थे। SEM विश्लेषण में महत्वपूर्ण वाह्य आकृतिय परिवर्तन, धातु और पत्तियों व छालों की सतहों के मध्य बन्धनों का समर्थन करते है।

अतः यह निष्कर्षित किया गया कि अनावृतबीजीय पौधे पानी के विषाक्त धातुओं तथा सदूषणों को हटाने के लिए प्रयोग किये जाने वाली वाणिज्यिक तकनीकियों के प्रति लागत प्रभावी और पर्यावरण अनुकूल विकल्प के रूप में उपयोग किये जा सकते है क्योकिं ये पौधे विभिन्न पर्यावरण अवस्थाओ पर अधिक धातु बन्धक क्षमता रखते है।


**(विवेकानन्द)**
**सलाहकार**



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**Anil Verma**
Department of Chemistry, Govind Ballabh Pant University of Agriculture & Technology, Pantnagar, U.S. Nagar, Uttarakhand, India

**Jyotsna Dhanik**
Department of Chemistry, Govind Ballabh Pant University of Agriculture & Technology, Pantnagar, U.S. Nagar, Uttarakhand, India

**Babita Belal**
Department of Chemistry, Govind Ballabh Pant University of Agriculture & Technology, Pantnagar, U.S. Nagar, Uttarakhand, India

**Vivekanand**
Department of Chemistry, Govind Ballabh Pant University of Agriculture & Technology, Pantnagar, U.S. Nagar, Uttarakhand, India

**Om Prakash Chausali**
Department of Chemistry, Govind Ballabh Pant University of Agriculture & Technology, Pantnagar, U.S. Nagar, Uttarakhand, India

**Correspondence**
**Anil Verma**
Department of Chemistry, Govind Ballabh Pant University of Agriculture & Technology, Pantnagar, U.S. Nagar, Uttarakhand, India

# Bio sorption of heavy metal Chromium (III) from synthetic waste water using *Taxus baccata* bark as bio adsorbent

**Anil Verma, Jyotsna Dhanik, Babita Belal, Vivekanand and Om Prakash Chausali**

**Abstract**
Heavy metals are one of the most important pollutants which pollute environment by numerous ways. The present work deals with the adsorption of Cr (III) metal ions from its aqueous solution using cheap and biodegradable adsorbent prepared from *Taxus baccata*. The studies were carried out by batch method and metal ions concentrations were measured by atomic absorption spectrophotometer. The effect of pH and incubation period of Cr (III) ions on percentage adsorption of Cr (III) ions on *Taxus baccata* bark were studied. Equilibrium studies shows high percentage of biosorption at neutral pH and higher temperature.

**Keywords:** adsorbent, adsorption isotherms, *taxus baccata*, heavy metals, cr (iii) ions

## Introduction
The rapid growth in world-wide population and urbanization has driven an exponential increase in industrial activities, which is accompanied by an increase in the amount of industrial wastes being acquittal into the environment, hence the increase in heavy metals such as cadmium, mercury, lead, copper, zinc, nickel and chromium posting significant risk to soil, water and human health [1]. Heavy metals in the aquatic medium may instigate from wastewater of many industries, such as batteries, tanneries, electrical, electroplating, fertilizers, pesticides, mining, refining ores, etc [2, 3]. Due to their hazardous effects, persistency and accumulation tendency, heavy metals can pose a risk to the human and environmental health [4-5] the exposure to heavy metals can cause damage to many parts of human bodies, even at very low concentrations. Therefore, the removal of heavy metals from aqueous solutions is of extreme importance [6].

Heavy metals in general and Chromium in particular has received a great deal of attention because of their toxicity. Though the most predominant forms of chromium are Cr (VI) and Cr (III), Cr (VI) is more toxic [7]. The anthropogenic sources include, burning of oil and coal, production of ferrochromium, chromate, chromium steels, fungicides, cement, pigments, catalysts, and oxidants. It is also increasingly used in metal plating, tanneries, and oil well drilling [8, 9]. Exposure to Cr (VI) causes cancer in digestive tract and lungs [10] and may cause epigastric pain, nausea, vomiting, severe diarrhoea and haemorrhage [11].

Numerous technologies have been developed for heavy metal decontamination. Traditional treatment processes include chemical treatment, precipitation, ion exchange, membrane filtration, electroplating, adsorption [2].These methods represent significant demerits, such as high chemical and energy requirements, hazardous sludge formation, low efficiency when heavy metals concentration below 100 mg/L, high cost at large scale [12, 13]. Likewise, high price and limited reusability are key problems, obstructing the widespread application of activated carbon, a commonly used adsorbent in heavy metal treatment [14] In that context, bio sorption has emerged as a promising method, with such advantages as (1) high efficiency even with low metal concentrations, (2) low cost, (3) no supplementary nutrients requirements, (4) easy operation, (5) potential metal recovery, and (6) without detrimental effects on the environment [3, 15, 16].

## Material and Methods

### Adsorbent preparation

The barks of *Taxus baccata* was used as bioadsorbent in the present study, collected from high altitude area of kumaun hills of Uttarakhand state. The barks of all plants putted in to clean plastic bags and washed carefully in running tap water and then in deionized water to remove dirt and other particulate matter. The washed barks were air dried for 2-3 month. Barks grounded in to grinder having 2.5 mm sieve size the grounded material was sieved with the help of a sieve of pore size 2.5 mm.

### Batch Adsorption Studies

All reagents used were A.R. grade. For the preparation of 100 ppm of chromium solution, 0.469 g of chromium hexahydrate ($Cr_2$ $(SO_4)_3.6H_2O$) was dissolved into 1000 mL of triple distilled water. This solution was used as stock solution for preparation of diluted concentration of 1 ppm solution by using 1 mL dissolved In 100 ml of triple distilled water.

### Experiment I: Effect of incubation period

To a set of conical flasks, 50 mL of synthetic solution 1 ppm with pH 4.2 and 1g of bark of *Taxus baccata* was added. The solution was shaken well in an incubator shaker at 250 rpm at room temperature (25±5 ºC) and at hot temperature (40±5 ºC) for different time period. The flasks were incubated for different time period of 30, 60, 90 and 120 min.

### Experiment II: Effect of pH

To a set of conical flasks containing 1 g biomass (bark) of 50 mL of synthetic waste water solution (1 ppm Cr) was added in all flasks. The pH of effluent in different flasks was varied from acidic to basic (4.2, 7.0 and 9.0). The solution of different pH were shaken well in an incubator shaker at 250 rpm at room temperature (25±5 ºC) and at hot temperature (40±5 ºC) for different time period.

### Residual Metal Ion Analysis

After the filtration of the solution, the residual metal ion content in the filtrate was measured by using an Atomic absorption Spectrophotometer.

Calculation of removal % of metal ions: Removal percentage was expressed as a percentage of complexed metal compared to initial metal ion concentration:

$$\text{Removal } (\%) = (C_i - C_{eq}) / C_i \times 100 \quad (1)$$

Where $C_i$ and $C_{eq}$ are the initial and final concentrations of metal ion respectively.

### Metal uptake by biomass

Specific metal uptake was calculated as follows: The adsorption capacity:

$$Q_e = (C_i - C_{eq})\ V/m \quad (2)$$

Where $C_i$ and $C_{eq}$ are the initial concentration and concentration at equilibrium of metal ion respectively. V is the volume (L) of metal solution and m is the weight of biomass in gram.

## Result and discussion

### Effect of pH

To analyze the effect of pH on biosorption, experiment was conducted at different pH (4.2, 7.0 and 9.0) with initial metal ion concentration of 1 mg/L, contact time (2 hrs), biomass dosage 1g/50mL and temperature (25±5˚C and 40±5˚C). Figure 1.0 describes the biosorption data of Cr (III) removal by *Taxus baccata* barks biomass at varying pH. Maximum removal of Cr (III) by barks biomass was observed at neutral pH (7.0) followed by removal at acidic pH (4.2) and basic pH (7.0) by bark at cold and hot temperature respectively. Bark showed maximum removal at neutral pH and hot temperature (93.4%) and at cold temperature it was minimum (85.2%) at basic pH When the pH increases, the concentration of H+ ions decreases and negatively charged biomass surface can interact with the positively charged metal ions.

### Effect of incubation period

The effect of contact time was observed at initial metal concentration (1 mg/L), acidic pH (4.2), biomass amount (1g) and cold (25±5 ˚C) to hot (40±5 ˚C) temperature conditions. Bark showed maximum absorption at 120 min when measured at the interval of 30min, visualized can be visualized by Figure. 2.0 bark showed 89.40 and 93.23% removal at cold and hot temperature conditions respectively at 120 min. The interaction between contact time and *Taxus baccata* bark biomass was found significant ($P \geq 0.05$) As the contact timings increased, percentage removal also increased in significant way. At 30 min barks showed minimum removal as 70.6, 79.1, 88.6 and 89.4% removal at cold and 81.8, 85.3, 91.3 and 93.23% at hot temperature. It was the maximum removal capacity for bark biomass at 120 min while at 30 min these showed minimum 39.4, 43.5, 46.1 and 46.8mg of chromium ions removal capacity per 1.0g of biosorbents. There was an increasing trend of chromium adsorption by bark at different temperature conditions with increase in contact timings but after 120 min, adsorption of chromium decreased which could be due to the unavailability and saturation of metal binding sites present in *Taxus baccata* biomass.

### Isotherm studies

For solid–liquid adsorption system, adsorption isotherm is important model in the adsorption behaviour. When the adsorption reaction reaches equilibrium state, the adsorption isotherm can indicate the distribution of dye molecules between the solid and liquid phase [17]. It is significant for understanding the adsorption behaviour to identify the most appropriate adsorption isotherm model. In this paper, Langmuir, Freundlich, and Tempkin adsorption isotherm models were employed to investigate the adsorption behaviour. Adsorption isotherm was studied at different temperatures.

### Langmuir is otherm

The Langmuir adsorption isotherm consider the assumption that there is a finite no. of binding sited which are homogeneously distributed over the adsorbent surface of the cells, having the same affinity for adsorption of a single molecular layer and there is no interaction between adsorbed molecules (Langmuir 1916). The Langmuir equation was used to describe the observed sorption of chromium ions and is as shown by the following equation.

$$C_e / Q_e = 1/b\ Q_{max} + C_e / Q_{max} \quad (3)$$

where, $Q_{max}$ (mg/g) is the measure of maximum metal ion per unit mass of sorbent to form a complete monolayer on the surface bound at high $C_{eq}$, and b (L/mg) is a constant related

to the affinity of the biomass surface biding sites when the surface is fully covered with the metal ions and assist in the comparison of adsorption performance, particularly in the case where the sorbent didn't reach its full saturation.

**Freundlich Adsorption Isotherm**

Freundlich model is an empirical model used to describe the adsorption in heterogeneous surface [19] to explain the adsorption of chromium ions on to adsorbent. Freundlich model assumed that the adsorption energy of metal binding to a site on the adsorbent depend on whether or not the adjacent sites are already occupied. The Freundlich isotherm is shown by the following equation:

$$\log Q_e = 1/n \log C_e + \log \quad (4)$$

where $K_f$ and n are Freundlich constants, characteristics of the system. $K_f$ (mg/g) and n (L/mg) is the maximum adsorption capacity of the sorbent and **n** is the indication of how favourable the adsorption process if value 1/n is below one it indicates a normal adsorption. On the other hand, 1/n being above one indicates cooperative adsorption [20].

**Tempkin Adsorption Isotherm**

This isotherm contains into account the adsorbent-adsorbate interactions and suggested that because of these interactions the heat of adsorption of all the molecules in the layer would decrease linearly with coverage. The model is given by the following equation [21].

$$B = RT/b$$
$$Q_e = B \ln A + B \quad (5)$$

AT=Temkin isotherm equilibrium binding constant (L/g), bT = Temkin isotherm constant, R= universal gas constant (8.314J/mol/K), T= Temperature at 298K and B = Constant related to heat of sorption (J/mol)

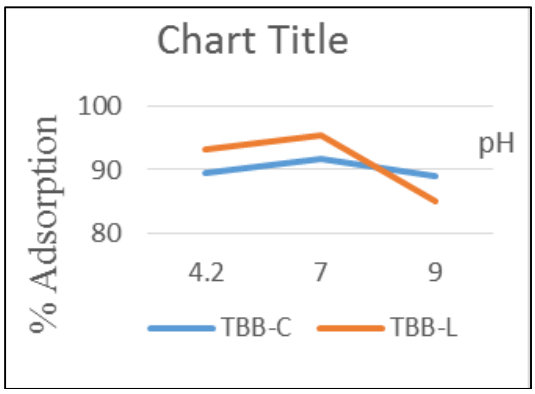



**Fig 1.0:** Effect of pH

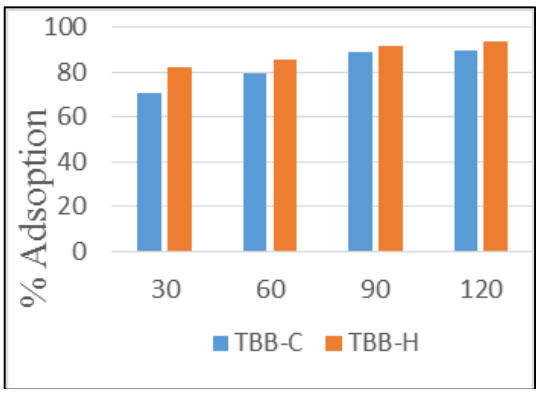
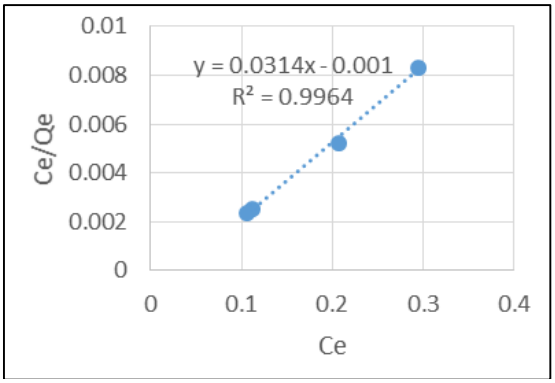
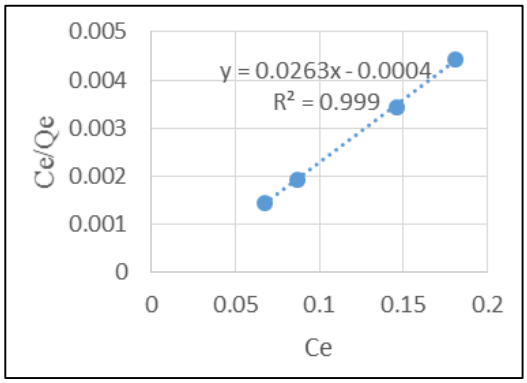


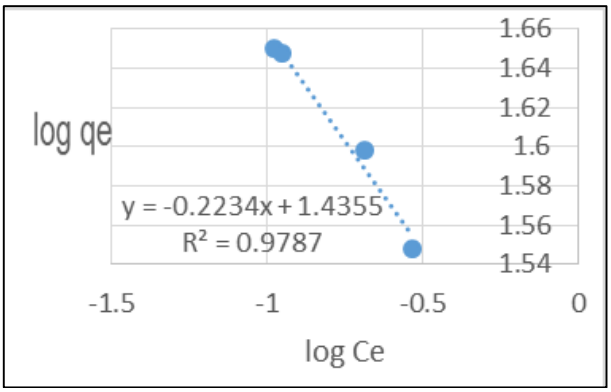

**Fig 2.0:** Effect of incubation period



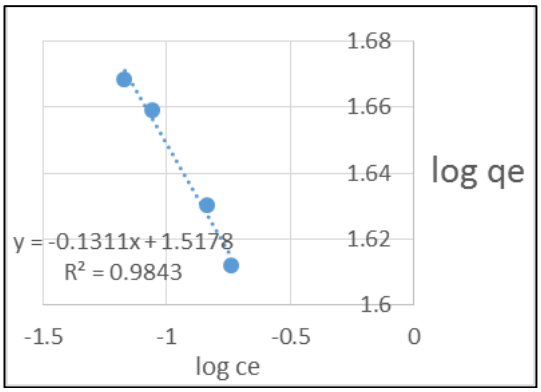

A



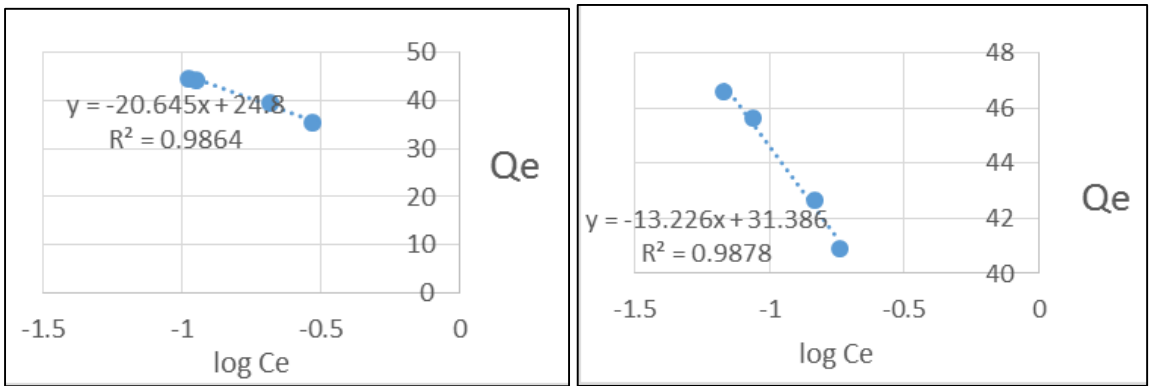

B




C




D




E F

**Fig 3.0:** Langmuir (A, B) Freundlich (C, D) and Tempkin (E, F) adsorption isotherms for biosorption of Cr (III) on bark of *T. baccata* at 25±5 ˚C and 40±5 ˚C.

The Langmuir, Freundlich and Tempkin models for bark of *Taxus baccata* were represented by Figure. 3.0. Bark of *Taxus baccata* plant at cold temperature the $R^2$ values were 0.9964, 0.9787 and 0.9864 while at hot temperature these were 0.999, 0.9843 and 0.9878 of Langmuir, Freundlich and Tempkin models respectively Figure 3.0. Langmuir model is most suitable at cold and hot temperature for bark but at the heat of adsorption was 280.75 J/mol for leaves at high temperature which explain less adsorption at high temperature while at less temperature less adsorption heat was observed by leaves. For bark at less as well at high temperature all three models are suitable but among three for bark at all temperature conditions Langmuir model is highly suitable, showed favourable homogenous adsorption of copper ions with high affinity.

## Conclusions

The batch experiment shows high percentage of biosorption at neutral pH and higher temperature. It is found that the adsorption data was well fitted to the Langmuir isotherm adsorption model then the freundlich and tempkin model. The fitness of Langmuir's model indicated the formation of monolayer coverage of the sorbate on the identical statistics surface of the adsorbent. From experiment we can conclude that *Taxus baccata* bark may be used for removal of heavy metal chromium (III) ion by biosorption.

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