Removal of Hexavalent Chromium from Aqueous Solution by Leaf Litter Biomass

A Dissertation submitted in partial fulfillment of the requirement for the award of the degree of

MASTER OF TECHNOLOGY

IN

BIOTECHNOLOGY

By

Biney Preet Kaur

Roll No.-601304004

Under the Supervision of

Dr. Dinesh Goyal

Department of Biotechnology

THAPAR UNIVERSITY,

PATIALA-147004

July, 2015

Candidate's Declaration

I, hereby declare that the work presented in the dissertation entitled "Removal of Hexavalent Chromium from aqueous solution by leaf litter biomass", in partial fulfillment of the requirement for the award of the degree of Master of Technology, Department of Biotechnology, Thapar University, Patiala, is an authentic record of my own work during the period of eleven months from July 2007 to July 2008, under the supervision of Dr. Dinesh Goyal, Associate Professor, Head of Department of Biotechnology, Department of Biotechnology, Thapar University. The thesis report has not been submitted for the award of any other degree or certificate in this or any other University.

Place: Patiala

Date: 15 July, 2015

Biney Preet

(Biney Preet Kaur)

2

Certificate

This is to certify that the Dissertion report entitled to "Removal of Hexavalent Chromium from aqueous solution by leaf litter biomass" submitted by Biney Preet Kaur in the partial fulfillment of the requirement for the award of degree of the Master of Technology in Biotechnology, Department of Biotechnology, Thapar University, Patiala, is a record of Student's own work carried out by her under my supervision and guidance. The report has not been submitted for the award of any other degree or certificate in this or any other university or institute.

Dr. Dinesh Goyal
(Supervisor and Head)
Department of Biotechnology,
Thapar University,
Patiala

Dr. S.S Bhatia
Dean
(Academic Affairs)
Thapar University,
Patiala.

Acknowledgements

My foremost thank goes to my thesis adviser Dr. Dinesh Goyal, without him, this dissertion would not have been possible. I thank him for his patience and encouragement that carried me on through difficult times, and for his insights and suggestions that helped to shape my research skills. His valuable feedback contributed greatly to his dissertion. His visionary thoughts and energetic working style has influenced me greatly.

I thank Dr. Sarabjeet Ahluwalia, Miss Jyotika and Sandeep Kaur Saggi who helped me whenever needed in various aspects of my work. They are the ones that I can always count on to discuss the tiniest details of a problem.

I thank all the students and staffs in Department of biotechnology for sharing the literature and invaluable assistance. I enjoyed all the vivid discussions we had on various topics.

Last but not the least, I thank my parents for always being there when I needed them most, and for supporting me.

Finally, and most importantly, I would like to thank the almighty God, for it is under his grace that we live, learn and flourish.

Biney Preet.

Biney Preet Kaur

CONTENTS **Page No.**

List of Figures

List of Tables

Abstract

Feasibility of eight different waste leaf litter biosorbents of plant origin were investigated for removal of hexavalent chromium from synthetic aqueous solution in batch and continuous mode of sorption. The objective was to develop inexpensive and effective metal ion adsorbents that are available in large quantity as an alternative to existing commercial adsorbents. The different leaf litter biomass, Eucalyptus, Ashoka, Bamboo, Mango, Poplar, Wheat Husk, Rice straw and Jamun were used to carry Cr (VI) sorption process under shake flask conditions at pH 5 and a temperature of 28°C and agitation rate of 120 rpm in batch mode. The effect of varied biomass concentration, pH, initial metal concentration and contact time to remove Cr (VI) from aqueous solution was studied. Maximum removal of Cr (VI) from aqueous solution by the Eucalyptus, Bamboo, Poplar, Jamun leaf litter biomass, wheat husk and Rice straw was observed in 1 hour, thereafter it reached equilibrium. Removal of Cr (VI) from aqueous solution was 94% by Eucalyptus, 94% by Bamboo, 84% by Poplar leaf litter biomass, 83% by Wheat Husk biomass, 82% by Mango leaf litter biomass, 82% by Jamun leaf litter biomass, 77% Ashoka leaf litter biomass, and 22% by Rice Straw biomass in 1 hour of contact using 4% of adsorbent. Combination of four biomasses i.e. Eucalyptus, Mango, Bamboo and Wheat husk was effective in removal of Cr (VI) from metallic solution at varying initial concentration i.e. 10 mg/l to 100 mg/l of Cr (VI) in aqueous solution. The removal efficiency at 20, 30, 40, 50 and 60 mg/l of initial metal concentration was 97, 97, 96, 96, and 94% respectively in 30 min of contact. In continuous flow sorption column packed with dry biomass of combination of four different leaf litter biomass namely, Eucalyptus, Bamboo, Mango and Poplar in the ratio of 1:1:1:1, 95% and 94% of metal removal at 10 mg/l and 20 mg/l of initial metal concentration was observed.

Adsorption isotherms Equilibrium sorption data of Cr (VI) was used to predict conventional Langmuir and Freundlich isotherm, which suggested involvement of either physico-chemical or ion exchange interaction in chromium binding. Fourier transform infrared spectral analysis

revealed that different types of functional groups, aliphatic amines, primary amines and alkanes played an important role in metal binding.

This study showed that waste leaf litter biomass generated in great quantities can be used for Cr (VI) removal in waste water treatment as an effective alternative. Leaf litter biomass used as an adsorbent has given significant results, which shows that the biosorption technology can be scaled up to industrial scale to treat chromium effluent at low cost with no generation of toxic chrome sludge.

Introduction

Advancement in science and technology has brought progress in many spheres, but it has also contributed to degradation of environment all over the globe due to little attention paid to the treatment of industrial effluents. Industrial pollution continues to be a potential threat affecting the water (Venkateswarlu et al., 2007). One of the most challenging environmental problems today is the removal of heavy metals and other toxic contaminants from industrial wastewater. Many aquatic environment face metal concentrations that exceed water quality limits designed to protect the environment, animals, and humans (Sulaymon et al., 2013). These metals cannot be degraded or readily detoxified biologically and have tendency to accumulate in living system (Khan and Mohamad, 2007).

Chromium compounds released into the environment have been increasing continuously as a result of industrial processes such as electroplating, metal finishing, leather, mining, petroleum refining, wood preservation, corrosion inhibition in power plants and nuclear facilities, manufacturing of pigments, dyeing, textiles, carpets, magnetic tapes, jet aircrafts and refractory materials etc.

Cr (III) is considered as an essential trace nutrient for human, while Cr (VI), in turn, is highly toxic (Dobrowolski and Otto, 2010; Nriagu and Nieboer, 1998). Owing to the different toxicities of Cr (VI), there is a great interest in the speciation and determination of chromium species in environment. Cr (VI) compounds are highly water soluble, having carcinogenic and nephrotoxic properties, whereas Cr (III) compounds are relatively insoluble and less harmful (Cheung and Guji, 2007; Morales and Cristiani, 2008; Wang and Chen, 2009 and Chen and Hao, 1998).

Workplace exposure to hexavalent chromium may cause the following health effects:

• Lung cancer in workers who breathe airborne hexavalent chromium.

• Irritation or damage to the nose, throat, and lung (respiratory tract) if hexavalent chromium is breathed at high levels.

• Irritation or damage to the eyes and skin if hexavalent chromium contacts these organs in high concentrations.

So, the removal of Cr (VI) from water and wastewater is important to protect the environment. Conventional methods for removing hexavalent chromium(VI) ions from wastewater are chemical reduction, electrochemical treatment, ion exchange and evaporative recovery that may sometime become ineffective and expensive when metal concentration in the effluent fall in the range of 10-100g/m^3 (Yun et al.,2001; Vijayraghvan and Yun, 2008). Heavy metals especially at trace concentrations in large volume of solution are considerably difficult to remove by conventional techniques. Current research activity in this field is focused on evaluating, whether biosorption may eventually provide such an effective and economic alternative treatment process. It is a rapid phenomenon of passive metal uptake sequestration by non-growing biomass (Beveridge and Doyle, 1989).

Work has been carried out on the use of adsorbents such as activated charcoal, low cost agriculture waste materials and microbial biomass. Functional groups such as carboxylate, hydroxyl, amide and amine groups have been identified to be responsible for metal binding present in the cell of non-living microbial biomass (Ahluwalia and Goyal, 2007; Sun et al., 2010). Among these, the amine and carboxyl group is very effective in removing heavy metals. It not only chelates cationic metal ions, but also absorbs anionic metal species through electrostatic interaction or hydrogen bonding. Health and environmental issues derived from waste effluents are universally acknowledged problems. It is therefore necessary to find cheap and simple decontamination methods (Ramirez and Holmes, 2008). The aim of this work was to study the biosorption of hexavalent chromium [Cr (VI)] from aqueous solution by using different leaf litter biomasses i.e. Eucalyptus, Ashoka, Bamboo, Mango, Poplar, Wheat husk, Rice Straw and Jamun leaves. Effect of varied adsorbent dosage, pH, initial concentration of hexavalent chromium and contact time on biosorption of metal ion from aqueous solutions was studied in batch mode and continuous sorption column.

Review of literature

The term heavy metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations. Examples of heavy metals in density criteria range from above 3.5 g/cm^3 to above $7g/cm^3$. Mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), thallium (Tl) and lead (Pb). Heavy metals exist as components of earth's crust naturally. As trace elements, some heavy metals are essential to maintain metabolism of human body. Higher concentration of heavy metals intake may leads to poisoning. They enter human bodies via food, water and air.

Heavy metals are dangerous because they tend to bioaccumulate. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted. Of the important metals, Mercury, lead, cadmium, Arsenic and Chromium (VI) are regarded as toxic; whereas, others such as copper, nickel, cobalt and zinc are not as toxic, but their extensive usage and increasing levels in the environment are of serious concerns (Brown and Absanullah, 1971; Moore, 1990 and Volesky, 1990).

Process waste streams from the mining operations, metal-plating facilities, power generation facilities, electronic device manufacturing units, and tanneries may contain heavy metals at concentrations exceeding the local discharge limits (Owlad et al., 2008).

1. What is Cr (VI)?

- Chromium with valence of positive six, in any form or chemical compound in which it occurs.
- Toxic form of chromium metal that is generally man-made.
- Exist as many type of Cr (VI) compounds that vary in their solubility and use.
- Used in many industrial applications primarily for its anti-corrosive properties.

- CR(VI) occurs in all states of matter, any solution or other mixture, even if encapsulated by other substances
- Term also includes industrial process that creates Cr (VI) fumes.

Out of the various toxic pollutants chromium and its compounds are considered as the most dangerous in organic water pollutants. Chromium occurs in a number of oxidation states, but Cr (III) (trivalent chromium) and Cr (IV) (hexavalent chromium) are of main biological relevance. Chromium occurs in the aquatic environment as both trivalent [Cr (III)] and hexavalent [Cr (VI)] states. Hexavalent chromium, which is primarily present in the form of chromate (CrO_4) and dichromate (Cr_2O_7), possesses significantly higher levels of toxicity than the other valency states (Sharma and Foster, 1995; Overview of mining and mineral industry in India, New Delhi, 2001).

2. Formation of Cr (VI)

It is created during hot work processes such as welding on stainless steel or melting of chromium metal. Chromium metal is ionized into the fume at high temperatures and chemical reactions temporarily oxidizes the chromium ion into a hexavalent (+6) state.

Hexavalent chromium may exist in aquatic media as water soluble complex anions and may persist in water (Bansode, 2002). Hexavalent chromium is a strong oxidizing agent and may react with organic matter or other reducing agents to form trivalent chromium (Raoa and Prabhakar, 2011).

3. Major sources of hexavalent chromium

Chromium is a priority metal pollutant introduced into the water bodies from many industrial processes such as tanning, electroplating, metal processing, paint manufacturing, steel fabrication and agricultural runoff. Chromium is also used in explosives, ceramics, photography (Selvi et al., 2001) and Chromate preparation (Venkateswarlu et al., 2007).

The other sources are:

- Welding on stainless steel or Cr(VI) painted surfaces
- Painting
  - Aerospace
  - Auto body repair
- Chromate pigment and chemical production

- Chromium dye and catalyst production
- Glass manufacturing
- Plastic colorant production
- Textile manufacturing
- Construction
    - Traffic painting
    - Refractory brick restoration
    - Paint removal from bridge

Chromium compounds are also present in the effluents as a result of magnetic tapes, wood preservation, pigments, and chemical manufacturing industries (Gupta et al., 2010; Wang et al., 2012). They can also be present in rocks, soils, plants, and animals.

4. Harmful effects of chromium

Hexavalent chromium, also known as chromium 6 or Cr (VI), is a heavy metal that is commonly found at low levels in drinking water (Draft Public Health Goal for Hexavalent Chromium, 2009).The discharge limit of chromium from industries is less than 1 mg/l. Chromium is hazardous to health when its limit in potable water exceeds 0.5 mg/l (ISI). When chromium enters the gastric system, epigastric pain, nausea, vomiting, severe diarrhea, corrosion of skin are noticed (Venkateswarlu et al., 2007). Because of its mutagenic and carcinogenic properties, it includes skin irritation to lung cancer, as well as kidney, liver, and gastric damage (Mansri et al., 2009).

5. Conventional methods of removal

Various methods adopted for the removal of heavy metals from industrial effluents include chemical precipitation, membrane separation, ion exchange electrochemical Treatment, Membrane Technologies, adsorption on activated Carbon etc. (Matheickal and Yu, 1999). A number of other treatment methods for the removal of chromium ions from aqueous solution have been reported, mainly reduction, electrodialysis, electrochemical precipitation, evaporation, solvent extraction, reverse osmosis and adsorption (Dulha et al., 2014).

Each of these methods has its own merits and demerits. But the search for new eco-friendly and cost-effective technology for the removal of heavy metals from wastewaters has been directed towards biosorption (Ilamathi et al., 2014).

1. Precipitation is the most common method for removing toxic heavy metals up to parts per million (ppm) levels from water. Since some metal salts are insoluble in water and which get precipitated when correct anion is added. Although the process is cost effective, efficiency is affected by low pH and the presence of other salts (ions). The process requires addition of other chemicals, which finally leads to the generation of a high water content sludge, the disposal of which is cost intensive (Gray, 1990). Precipitation with lime, bisulphide or ion exchange lacks the specificity and is ineffective in removal of the metal ions at low concentration. The addition of chemicals must be accurate, making the process sensitive and unreliable. The hazardous sludge which is left behind after the precipitation process is completed, needs to be safely disposed off.
2. Ion exchange is another method used successfully in the industry for the removal of heavy metals from effluent. Though it is relatively expensive as compared to the other methods, it has the ability to achieve ppb levels of clean up while handling a relatively large volume. An ion exchanger is a solid capable of exchanging either cations or anions from the surrounding materials. Commonly used matrices for ion exchange are synthetic organic ion exchange resins. The disadvantage of this method is that it cannot handle concentrated metal solution as the matrix gets easily fouled by organics and other solids in the wastewater. Moreover ion exchange is nonselective and is highly sensitive to pH of the solution.
3. Electro-winning is widely used in the mining and metallurgical industrial operations for heap leaching and acid mine drainage. It is also used in the metal transformation and electronics and electrical industries for removal as well as recovery of metals. Metals like Ag, Au, Cd, Co, Cr, Ni, Pb, Sn and Zn present in the effluents can be recovered by electro-deposition using insoluble anodes (Gray, 1999).
4. Electro-coagulation is an electrochemical approach, which uses an electrical current to remove metals from solution. Electro-coagulation system is also effective in removing suspended solids, dissolved metals, tannins and dyes. The contaminants presents in wastewater are maintained in solution by electrical charges. When these ions and other

charged particles are neutralized with ions of opposite electrical charges provided by electrocoagulation system, they become destabilized and precipitate in a stable form.

5. Cementation is a type of another precipitation method implying an electrochemical mechanism in which a metal having a higher oxidation potential passes into solution e.g. oxidation of metallic iron, Fe (0) to ferrous iron (II) to replace a metal having a lower oxidation potential. Copper is most frequently separated by cementation along with noble metals such as Ag, Au and Pb as well as As, Cd, Ga, Pb, Sb and Sn can be recovered in this manner.
6. Reverse osmosis and electro-dialysis involves the use of semi-permeable membranes for the recovery of metal ions from dilute wastewater. In electro-dialysis, selective membranes (alternation of cation and anion membranes) are fitted between the electrodes in electrolytic cells, and under continuous electrical current the associated ion migrates, allowing the recovery of metals.

6. Problems with conventional methods

The ultimate goal of wastewater treatment is to separate the toxic harmful materials from wastewater streams of different industries. The foremost important deciding factor for the technology to be employed as the required treatment process is the degree of concentration of metallic species in the solution to be treated. For a solution which have a high concentration of metals (hundreds/thousands of mg/l), crude metal removal processes could be employed. However such processes do not extract metals, when the solution metal concentrations range lower than hundreds of mg/l or even more less. For them to be treated, costly methods of heavy metal removal are required, which are often not employed.

Most of these conventional methods suffer from drawbacks such as high operational costs and incomplete removal or the disposal of the residual metal sludge (Demirbas et al., 2004). The main disadvantage of activated carbon is the weak mechanical properties of its surface and that it is easily burned at high operation temperature (Karakas et al., 2004). These treatment methods are not widely practiced due to their low feasibility for small-scale industries.

In case of adsorption, the generally used adsorbents like activated carbon, silica, alumina etc. are expensive. This has prompted the use of various materials as adsorbents in order to develop cheaper alternatives. Natural materials available in large quantities or waste products may have the potentiality of high uptake of metals. They can be disposed off without regeneration due to their lower cost (Venkateswarlu et al., 2007). Adsorption is by far the most effective and widely used technique for the removal of toxic heavy metals from wastewater.

7. The need for novel technology

The need for effective and economically viable technologies is driven by environmental pressures such as:

- Stricter regulations with regard to the metal discharges are being enforced, particularly in industrialized countries.
- Toxicology studies confirm the dangerous impacts of heavy metals.
- Current technologies for the removal of heavy metals from industrial effluents often create secondary problems with metal-bearing sludge.

8. Biosorption

Biosorption is an innovative technology that employs inactive and dead biomass for the removal and recovery of metals from aqueous solutions (Kim et al., 2008; Mckay et al., 1999; Romera et al., 2007). Individuals from engineering to biochemistry backgrounds can make significant contributions to the understanding of biosorption.

Biosorbents must be hard enough to withstand the application pressures, porous and/or "transparent" to metal ion sorbate species, and high and fast sorption uptake even after repeated regeneration cycles (Fourest and Volesky, 1996).

8.1. Sources of Biomass for Biosorption

Sources of biomass:

- Microorganisms (Bacteria, Fungi, Yeast, Molds)
- Seaweeds
- Activated sludge
- Fermentation waste
- Other specially propagated biomass

Pioneering research on biosorption of heavy metals has led to the identification of a number of microbial biomass types (Benedict et al., 1981) that are extremely effective in concentrating metals. Biosorption using potential metal biosorbents like algae, bacteria, fungi, and yeast can be an effective technique to decrease the concentration of heavy metal ions in solution (Volesky, 1986). Reduction of hexavalent chromium Cr (VI) to Cr (III) by bacteria such as *Pseudomonas aeruginosa* (Song et al., 2009), *Bacillus sp.* (Wang and Xiao, 1995) and *Escherichia coli* (Liu et al., 2010) is already reported. However, application of free bacterial cells at industrial scale is disadvantageous due to the difficulty of biomass/effluent separation (White et al., 1995) etc., which may be overcome by using immobilized bacterial cells with the advantages of stability, regeneration, solid–liquid separation and minimal clogging in continuous systems (Viera et al., 2003). Immobilization of microorganisms in a suitable matrix like polyvinyl alcohol, agar media and sol–gel materials has been proven to be an efficient solution to this problem (Saraj et al., 1999; Xu et al., 2011).

Adsorption processes are traditionally carried out in fixed beds (Mcdougall and Fleming, 1987) due to the high concentration of solids and the obtainable uniform residence time. However since the wastewater to be treated often contains solid impurities leading to a plugging of the fixed bed, the liquid must be clear to avoid column blocking.
Recently, many experimental studies have been conducted in fluidized beds, which allow treatment of turbid liquids while avoiding the channeling problems (Fu and Liu, 2007).

Some types of biomass are waste byproducts of large-scale industrial fermentations (e.g., the mold *Rhizopus* or the bacterium *Bacillus subtilis*). Other metal binding biomass types, such as certain abundant seaweeds (brown algae, *e.g.*, *Sargassum, Ecklonia*), can be readily harvested from the oceans.

The other natural adsorbents include:

- Wood charcoal (Deepak, 1990).

- Green pea skin dust (Samantaray et al., 1999).
- Rice straw (Samanta et al., 1999).
- Paper mill sludge (Ahluwalia and Goyal, 2004).
- Rice husk, sawdust, coir pith ad charcoal (Sumathia et al., 2005).
- Waste tea leaves (Ahluwalia and Goyal, 2005).
- Bagasse (Rao et al., 2006).

These biomass types can accumulate in excess of 25% of their dry weight in deposited heavy metals. Research on biosorption is revealing that it sometimes is a complex phenomenon where the metallic species could be deposited in the solid biosorbent through various sorption processes, such as ion exchange, complexation, chelation, microprecipitation, etc. Granulation of biomass materials into suitable cost effective biosorbents is a crucial step for successful application of biosorption processes.

Main objectives of granulation are:

- Establish the behavior of native biomass in a packed-bed reactor
- Establish the effectiveness of biomass granulation and reinforcement
- Determine the effect of size reduction on sorption capacity
- Determine the feasibility of biomass processing

8.2 Biomass types

The assessment of the metal binding capacity of some types of biomass has gained importance since 1985. Some biomass types have been proven to be very effective in accumulating heavy metals (Crist et al., 1993).

Availability is a major factor to be taken into account to select biomass for clean-up purposes. The economics of environment remediation dictate that the biomass must come from nature, or even be a waste material. Seaweeds, molds, yeasts, bacteria, and crab shells, among other kinds of biomass, have been tested for metal biosorption with very encouraging results.

Some biosorbents can bind and collect a wide range of heavy metals with no specific priority, whereas others are specific for certain types of metals. When choosing the biomass for metal biosorption experiments, its origin is a major factor to be considered.

Biomass can come from:

- Industrial wastes which should be obtained free of charge.
- Organisms that can be obtained easily in large amounts in nature e.g. bacteria, yeast, algae.
- Fast growing organisms that are specifically cultivated or propagated for biosorption purposes e.g. crab shells, seaweeds.

8.3 Various biosorbents

Biomass from various sources such as bacteria, yeast, algae, fungi and plants have been used to adsorb metal ions from the environment (Sulaymon et al., 2012; Kratochvil, 1997; Brady et al., 1999; Romera et al., 2006). Various biomasses such as bacteria (Ridha, 2011), sludge (Ali, 2011), yeast (Sulaymon et al., 2010) and plants (Melcakova and Ruzovic, 2010) have been used to adsorb metal ions from the environment. The functional groups involved are carboxyl, hydroxyl and sulphate, which can act as binding sites for metals (Crist et al., 1994).

Diniz et al., 2008, studied the fixed bed biosorption of lanthanum (La^{3+}) and europium (Eu^{3+}) using protonated *Sargassum* polycystum biomass (brown algae). The sorption mechanism was based on the ion exchange mechanism. The experimental results were fitted with an ion exchange model; good matching and high regression coefficient were obtained. The calculated affinity constants were 2.7 and 4.7 for La^{3+} and Eu^{3+} respectively, demonstrating a higher affinity of biomass towards Eu^{3+}. Column experiments were carried out in fixed bed system to estimate the mass transfer coefficient for each metal. A series of consecutive sorption/desorption runs demonstrated that the two metals could be recovered. Rathinam et al., 2010 studied the batch biosorption of cadmium onto *Hypnea valentiae* biomass (red algae). The results showed that the biosorption capacity was low at pH 3.0, but increased considerably from 4.30 to 14.54 mg/g as the pH solution increased to 5.0. On further increase in pH to 6.0 and 7.0 the biosorption capacity remained almost stable at 16.89 and 17.02 mg/g, respectively. Wang et al., 2011 studied the removal of emulsified oil from water by inverse fluidization of hydrophobic silica aerogels (Nanogel).

Algal biomass has been reported to have a good metal binding capacity due to the presence of polysaccharides, proteins or lipids on the cell wall structure which contain functional groups such as amino, carboxyl, hydroxyl, sulfate, and others (Hossain et al., 2012). These groups have the ability to bind heavy metals by donation of an electron pair from these groups to form complexes with the metal ions in solution (Fiu and Liu, 2007). Recently, biosorption in columns and its modeling have been receiving more attention. Fixed and fluidized bed reactors have been used widely by the chemical industry, pharmaceutical industry, food industry, wastewater treatment and for recovery of different substances (Schiewer and Volesky, 1996). Fluidized bed systems are common and important reactors in process engineering because of the good mass and heat transfer rate between the fluid and the particles, and between the particles and the side wall of the column (Diniz and Volesky, 2005).

Table 1: Fungal biomass used for removal of heavy metals from aqueous solution

Biosorbent	Metal removed	Adsorption capacity(mg/g)	References
R. oligoporus	Cr	126	Ariff et al., .1999
Pleurotus sapidus	Cd, Hg	127,287	Yalcinkaya et al., 2002.
Rhodotorula glutinis	Pb	73.5	Cho and Kim, 2003.
Aspergillus foetidus	Cr (VI)	2	Prasanjit and Sumanthi, 2005.
Phanerochaete chrysosporium	Cr	11.2	Ahluwalia and Goyal, 2010.
Cladosporium resinae	Cr	10.69	Ahluwalia and Goyal, 2010.

Paecilomyces variotii	Cr	10.35	Ahluwalia and Goyal, 2010.
Aspergillus niger	Cr	-	Goyal et al., 2003; Ahluwalia and Goyal, 2010.

Biosorbent	Metals	Adsorption capacity(mg/g)	References
Pseudomonas fluorescens	Th, U	15,6	Tsezos and Volesky, 1981.
Thiobacillus ferrooxidans	Zn	82	Baillet *et al*., 1998.
B.megatarium	Cr(VI)	30.7	Srinath *et al*,. 2002.
B.coagulans	Cr(VI)	39.9	Srinath et al., 2002.
Bacillus firmus	Pb,Cu,Zn	467,381,418	Salehizadeh and Shojaosadati, 2003.

Table 2: Bacterial biomass used as adsorbent

Table 3: Plant biomass used as biosorbents

Biosorbent	Metals	Adsorption	References

		capacity(mg/g)	
Alfalfa	Cu, pb	20,43	Tiemann et al., 1999.
Cupressus female cone	Cr(VI)	119	Murugan & Subramanian, 2003.
Larrea tridenta	Cu	24	Gardea-Torressdey et al., 2004.
Ceratophylum demersum	Cu, Pb, Zn	6.17,45,14	Keskinkan et al., 2004.
Grape stalk waste	Cu, Ni	15.9,18.1	Villaescusa et al., 2004.

Table 4: Various adsorbents used for chromium removal

Adsorbent	Maximum uptake capacity (mg/g)	References
Cupress female cone	119.4	Chand et al., 1994
Eucalyptus bark	45	Hamadi et al, 2001.
Pine needles and wool	5.36 and 8.66	Dakiky et al., 2002.
Chitosan, cross linked and non cross linked	50 and 78	Murugan and Subramaniyan, 2003.
Tyres activated carbon	58.5	Demirbas et al., 2004.
Cement kiln dust	33	Karthikeyan et al., 2005.
Neem leaf powder	7.43	Venkateshwarlu et al., 2007

8.4 Mechanisms of metal uptake

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, the later is attracted and removed 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.

Various metal binding mechanisms have been postulated to be active in biosorption (Volesky, 1990).

- Chemisorption
    1. Ion Exchange
    2. Complexation
    3. Coordination
    4. Chelation
- Physical Adsorption
- Microprecipitation

1. Ion Exchange

   Ion exchange is a reversible chemical reaction wherein an ion in a solution is exchanged for a similarly charged ion attached to an immobile solid particle. These solid ion-exchange particles are either naturally occurring inorganic zeolites or synthetically produced organic resins. Synthetic organic resins are the predominant type used today because their characteristics can be tailored to specific applications. Several researchers have independently concluded that the major mechanism of heavy metal uptake by algae (Kratochvil et al., 1995) is ion exchange. Cell wall of microbes contains polysaccharide salts and metal ions exchange with the counter ions of the polysaccharides. e.g, the alginate of marine algae occurs as salts of K^+, Na^+, Ca^{2+} and Mg^{2+} ions. These ions can exchange with counter ions such as Co^{2+}, Cu^{2+}, Cd^{2+} and Zn^{2+} resulting in the biosorptive uotake of heavy metals (Kuyucak and Volesky, 1989). Ion exchange reactions are stoichiometric and reversible, and as such they are similar to other solution-phase reactions.

2. Microprecipitation

   Microprecipitation is the deposition of the electrically neutral material (Metal or Metal Salts) at the surface of the biomass, and doesnot necessarily involve a bond between the biomass and the deposited layer. It may be facilitated by initial binding of metal ions to reactive sites of the biomass, which serve as nucleation sites for further precipitation (Mayers and Beveridge, 1989). Microprecipitation is based on interaction between the solute (dissolved solid) and solvent, occurs when the local solubility is exceeded.

3. Chelation

The word chelation means claw, and is defined as the firm binding of a metal ion with an organic molecule (ligand) to form a ring structure. Some ligands are attached to a metal atom by more by more than one donor atom in such a manner as to form a heterocyclic ring. This type of ring has been given a specific name- Chelating agent or chelator. The process of forming a chelate ring is known as chelation. Thus, metal chelates are metal complexes where there is an organic compound bound to the metal by at least two available sites.

4. Coordination (Complex Formation)

It has been suggested that numerous chemical groups contribute to biosorption metal binding by either whole organisms such as algae and bacteria or by molecules such as biopolymers. These include hydroxyl, carboxyl, carbonyl, sulfhydryl, thioether, sulfonate, amine, imine, amide, imidazole, phosphonate, and phosphodiester groups. The importance of any given group for biosorption of a certain metal by a certain biomass depends on such factors as the number of sites in the biosorbent material, the accessibility of the sites, the chemical state of the sites (availability), and the affinity between the site and the metal (binding strength). For covalent metal binding, even an occupied site is theoretically available; the extent to which the site can be used by a given metal depends on its binding strength and concentration compared to the metal already occupying the site.

5. Physical Adsorption

Physical adsorption takes place with the help weak forces such as vanderwaals forces and electrostatic interactions. It was hypothesized that adsorption of uranium, cadmium, zinc, copper and cobalt by dead biomass of algae, fungi and yeasts take place through electrostatic interactions between the metal ions in solution and the cell walls of microbial cells (Kuyucak and Volesky, 1989).

9. Bioremoval of heavy metals

Selection of a metal for its removal depends on the extent of their impact on the environment. There may be:

a) Toxic heavy metals

b) Strategic metal
c) Precious metal
d) Radio nuclides.

Removal of metals from aqueous solution is mainly for toxicity removal, an environmental aspect and recovery of metals of commercial value, a technological aspect. Heavy metals pose a threat not only to aquatic life but also endanger to the whole food chain consequently influencing the human health. The second category includes metals of technological importance, strategic significance and of high value. Technologically important heavy metals, in many cases, also act as pollutants because of their increasing concentration beyond safe limits in the environment caused by anthropological activities.

10. Development of biosorbent material

Biosorption is a complex process, mainly comprising of ion exchange, chelation and adsorption by physical forces and entrapment in inter and intra-fibrillar capillaries and space of the structural polysaccharide network as a result of the concentration gradient and diffusion. There are many chemical groups that would sequester the metals in biomass. Acetamide groups of chitin, structural polysaccharides of fungi, amino and phosphate groups of nucleic acids, amide, amine, sulfhydral and carboxyl groups in the proteins and hydroxyls in polysaccharide of marine algae belonging to Phaeophyceae, Rhodophyceae and Chlorophyceae are some of the examples. Apart from functional groups phenomenon of biosorption can perhaps occur due to steric, conformational or other effects.

11. Equilibrium Modeling

Biosorption has been studied as simplified sorption systems, usually containing one heavy metal. This is an appropriate simplification for effective experimentation. In order to evaluate feasibility and effectiveness of biosorption in wastewater treatment, it is essential to make predictions of the sorption performance (e.g., for facilitating process design). Therefore it is necessary to develop appropriate mathematical models of biosorption.

The amount of metal M (sorbate) bound per mass of sorbent is called the binding (uptake), q_e. The binding is not only dependent on the sorbent material but also on the equilibrium concentration (C_e) of the sorbate in the solution and on other parameter, such as, pH and equilibrium concentration of other ions in the solution. The relationship between equilibrium binding and the concentration of ions (at constant temperature) is depicted in an isotherm plot of q_e versus (C_e). With increasing metal concentration in solution its binding increases from zero to the maximum. It is desirable for the sorbent to possess a high sorption capacity and high affinity for the sorbate species, which is reflected in a steep slope of the isotherm curve at low equilibrium concentrations.

The equilibrium of the biosorption process is often described by fitting the experimental data with models (Gadd et al., 1988) used for the representation of the equilibrium adsorption isotherm. The two most widely used linearized equilibrium adsorption isotherm models for the single solute systems are given by Langmuir and Freundlich isotherm.

Langmuir model:

$q_e/q_m = bC_{eq}/ (1+bC_e)$

Where q is milligram metal accumulated per gram of the biosorbent material, Ceq is the metal residual concentration in solution, q_{max} is the maximum specific uptake corresponding to the site saturation and b is the ratio of adsorption and desorption rates. Langmuir model has few assumptions such as

- The surface consists of adsorption sites
- All adsorbed species interact only with the sites and not with each other
- Adsorption is limited to monolayer
- Adsorption energy of all sites is identical and independent of the presence of adsorbed neighbouring species.

Freundlich Model:

$$q_e = k_f C_e^{\ n}$$

Where, k_f and n are constants.

These models are applied at a constant pH and represent mathematically the biosorption equilibrium over a given period of metal-ion concentration range. It can provide information on differences in metal uptake capacities between various species.

12. Metal elution and biosorbent regeneration

The success of biosorption technology is largely attributed to the regeneration of the biosorbent. If biosorption process is to be used as an alternative to the conventional wastewater treatment, then the regeneration of the biosorbent is crucially important for the keeping the process cost low with possible recovery of the adsorbed metals. It is therefore, necessary to standardize simple and cost effective methods to desorb the sorbed metals and regenerate the biosorbent material for another cycle of application. Desorption process should

a) yield the metal in a concentrated form
b) Restore the biosorbent very close to the original form without any physical or chemical change.
c) Undiminished metal uptake upon re-use.

Regeneration or desorption of the biosorbent may be accomplished by washing the metal-laden biosorbent with appropriate solution, the type and strength of which would depend on the extent of binding of the deposited metal, therefore emphasizing the need for effective regenerating solution. The objective of desorption is to weaken the biomass–metal binding. The eluant used for desorption must have a higher binding affinity for metal than the biomass-metal binding. Desorption is similar to ion exchange process and is based on eluting metal by small volume of an appropriate solution called desorbent. Dilute solution of mineral acids like sulphuric acid, hydrochloric acid, acetic acid and nitric acid can be used for metal desorption from the biomass. Among all these, dilute HCl has been reported to be the most effective eluant (Modak and Natarajan, 1995). The selectivity of the elution- desorption operation may be different, which may serve as another means of eventually separating metals from one another if desirable.

13. Types of biosorption

Biosorption can be carried out as a batch process, a continuous process, or a two-stage process with continuous metal recovery. Biomass should be defrosted and washed with

deionized water. To ensure equal quality of the biomass during all experiments, different kinds of biomass should be mixed together to obtain a uniform mixture.

- Batch Process

  Batch biosorption experiments can be done in a stirred vessel with a working volume of approximately 100 ml. The decreasing metal concentration can be recorded as a function of the initial metal concentration (C_i) and the biomass loading.

- Continuous Process

  Continuous process experiments can be carried out in a glass column having an inner diameter of 2-8 cm and filled with a packed bed of dried biomass of varying heights (10, 20, 40, 55 cm). The effluent solution of metal ions can be fed from the top of the column with the help of a pump using varying flow rates. An inert bed of glass spheres can be placed at the bottom of the column below the active biomass bed to ensure homogenous distribution of the feed. The breakthrough curves can be recorded as a function of the flowrate and bed height.

  Measurements of metal ion concentrations in the solution can be made online with metal-detecting electrodes or ion-selective electrodes, and may be verified with an atomic absorption spectrometer.

14. Applications of metal biosorption

The term biosorption commonly refers to the passive binding of metal ions by biomass, which may even be dead. It must be distinguished from bioaccumulation, which is usually understood to be an active, metabolically mediated process occurring in living organisms.

It has been known for decades that different type of microbial biomass bind trace metal ions, achieving very high concentration factors. The biomass metal uptake phenomenon has been made use of in, for example electron microscopy, to visualize cellular components. The focus on early studies of microbial uptake has been almost exclusively on the nutritional and toxicological aspects of metal presence.

It is suited as a polishing water treatment step because it is possible to reach drinking water quality of the treated water, especially in the packed bed flow-through sorption column applications. To prevent unnecessarily rapid exhaustion of the sorption capacity when the metal concentration of the wastewater to be treated is high, it may be desirable to use a different pretreatment technique, such as precipitation or electro-recovery, for removal of the bulk of the metal content. However, generation of toxic sludge during pretreatment must be considered, since these represent another type of hazard and the eventual recovery of metal from them may not be feasible.

The metal laden biosorbent can be regenerated, incinerated or stored in landfills. The biosorption process basically serves to reduce the waste volume. Alternatively and preferably, regeneration of the biosorbent material or multiple reuses is desirable to increase the process economy. It can be accomplished by metal desorption with, for example, acids or salt solutions. The resulting high concentrated metal solution can be proceed by other technique such as precipitation or electro winning to remove or concentrate the metal, which could be recovered and resold. The latter process, in particular, is aimed at recuperation of the metal. The overall achievements of biosorption (complete adsorption + desorption cycle) process is to concentrate the metal solution, possible at least a factor of 100 or more.

Advantage of biosorption is not only that it can be operated under broad range of conditions (pH, temperature), but especially that it may be economically attractive due to cheap raw material that can be used as biosorbent (Kuyucak and Volesky, 1990).

It is particularly economical and competitive for environmental applications in detoxifying effluents from:

- Metal plating and metal finishing operations
- Mining and ore processing operations
- Metal processing
- Battery and accumulator manufacturing operations
- Thermal power generation (Coal-fired plants)
- Nuclear power generation

15. Feasibility of biosorption

The successful application on a large scale of any operation depends on its economical viability. The feasibility depends on the following factors:

- Biosorbent uptake performance
- The source of raw biomass
- Biomass granulation and treatment
- The desorption and regeneration processes used

The source of the biosorbent has a major impact on the feasibility of the operation. It should always be obtained from the least-expensive source, such as from the effluent of a fermenter, seaweeds from nearby bodies of water, algae, etc. The spent biosorbent can be regenerated at very low cost, so the material can be used many times. Hence, considering the overall unit operations involved in biosorption, we can conclude that the process is generally economically viable (Park et al., 2006).

16. Advantages of biosorption

- Growth-independent, non-living biomass is not subject to toxicity limitation of cells. No requirement of costly nutrients required for the growth of cells in feed solutions. Therefore, the problems of disposal of surplus nutrients or metabolic products are not present.
- Biomass can be procured from the existing fermentation industries, which is essentially a waste after fermentation.
- The process is not governed by the physiological constraint of living microbial cells.
- Because of non-living biomass behave as an ion exchanger, the process is very rapid and takes place between few minutes to few hours. Metal loading on biomass is often very high, leading to very efficient metal uptake.
- Because cells are non-living, processing conditions are not restricted to those conducive for the growth of cells. In other words, a wider range of operating conditions such as pH, temperature and metal concentration is possible. No aseptic conditions are required for this process.
- Metal can be desorbed readily and then recovered if the value and amount of metal recovered are significant and if the biomass is plentiful, metal-loaded biomass can be incinerated, thereby eliminating further treatment.

Other key features:

- Cost-effectiveness
- Performance
- Heavy metal selectivity
- Regenerative
- No sludge generation
- No additional nutrient requirement

Material and Methods:

1. **Collection and processing of adsorbent**

   Leaf litter biomass from 8 different tree species Eucalyptus, Ashoka, Bamboo, Mango, Poplar, Wheat Husk, Rice straw and Jamun Leaves were obtained from Thapar University campus located at 30°19'48"N, 76°24'0"E and 310 m above the sea level. Leaf litter biomass collected from 8 different tree species were washed to remove adhered debris, dried at a temperature of 110°C, grounded and sieved to particle size of 0.5 mm. Sieved samples were stored in an air tight containers at room temperature for further use.

2. **Preparation of heavy metal solution**

   The aqueous stock solution (1000 mg/l) of hexavalent chromium (Cr (VI)) was prepared by dissolving 2.857 gm of analytical grade of potassium dichromate (sd fine chem. Ltd., Mumbai) in 1000 ml of distilled water. The stock solution was further diluted with distilled water to reach the desired concentration for adsorption measurement. Solution pH was adjusted with dilute 0.1 N HCl or 0.1 N NaOH.

3. **Optimization of parameters**

   Batch sorption experiments were carried out for optimization of pH (2-6), adsorbent concentration (0.05-4 g/100 ml) and metal concentration (10-100 mg/l).

4. Batch sorption Experiments

Batch sorption studies were conducted with dried leaf litter biomass, in 250 ml of Erlenmeyer flask with different biomass concentrations (0.05-4% of biomass) at 10 mg/l of metal concentration and different hexavalent chromium concentrations (10-100 mg/l) using 1% of combination of 4 different leaf litter biomasses namely, Eucalyptus, Mango, Bamboo and Wheat Husk, separately along with control without any metal at pH 5.0 adjusted using 0.1 N HCl or 0.1 N NaOH, agitated at orbitek open shaker at 120 rpm and at 28±2°C. Experiments were conducted at different pH 2, 4 and 6 for metal removal from 10 mg/l aqueous solution by using 2% Eucalyptus leaf litter biomass at 28±2°C and 120 rpm. After constant time intervals (0-300 min), the samples were filtered (Whatman filter paper No.42) and the filtrate was analyzed by UV-VIS spectrophotometer (*Hitachi Japan*) for the residual metal content.

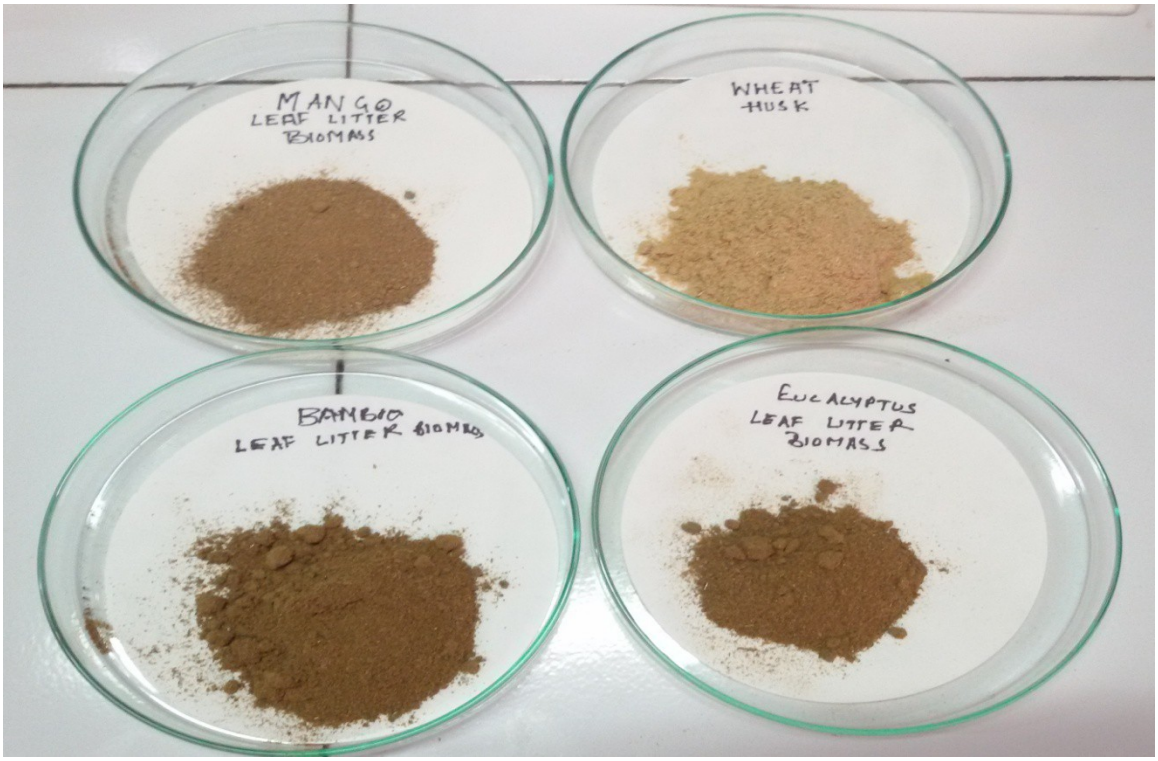


Fig.1: Mango leaf litter biomass, wheat husk biomass, Bamboo leaf litter biomass and Eucalyptus leaf litter biomass.

5. Continuous flow Column Sorption Studies

Column of 11.4 cm length and 1.75 cm of diameter was packed with combination of dried leaf litter biomass to study the removal of chromium (VI) in a continuous flow sorption mode. The aqueous solution containing 10-20 mg/l of chromium (VI) (pH 5) was passed manually from the top continuously. The fractions of the elutant were collected at different time intervals from the column outlet (bottom) for the analysis of residual metal content.

6. Determination of Residual Metal content

For the determination of residual Cr (VI), the samples were filtered and centrifuged if necessary and analyzed by colorimetric method using 1, 5 diphenyl-carbazide reagent (250 mg of 1, 5 diphenyl-carbazide in 50 ml of acetone) in acid solution as complexing agent, which reacts with chromate, forming colour complex that absorbs light at 540 nm (Clesceri et al., 1998). The absorbance was measured by UV-VIS spectrophotometer (*Hitachi, Japan*).

Residual concentration R (%) was calculated [Zhang et al., 1998] as:

$$R\ (\%) = (C_i - C_f)/C_f * 100 \qquad (1)$$

7. Metal Uptake by Biomass

Specific metal uptake was calculated as follows:

$$Q = (C_i - C_f)/m*V, \qquad (2)$$

Where C_i and C_f are the initial and final metal concentrations in mg/l respectively, initially and at a given time t, respectively, V is the volume of the metal solution in ml, m is the weight of the biomass in g.

8. Adsorption isotherms

Adsorption isotherm evaluates the amount of solute adsorbed per unit of adsorbent. Two commonly used adsorptive isothermal models, Langmuir and Freundlich equations, were used to evaluate the experimental data and described as:

8.1 Langmuir isotherms

This isotherm represents one of the first theoretical treatments of nonlinear sorption and suggested that uptake occurs on a homogenous surface by monolayer sorption with interaction between adsorption molecules.

$$q_e = q_{max}\, b\, C_e / 1 + bC_e \qquad (3)$$

Where q_{max} (mg/g) and b is Langmuir constants related to adsorption capacity and the energy of adsorption respectively.

Eq(3) is usually linearized to obtain the following form (kinniburgh, 1986).

$$1/q_e = 1/C_e(1/q_{max}\, b) + (1/q_{max})$$

q_{max} and b can b determined from the linear plot of $1/q_e$ versus $1/C_e$.

8.2 Freundlich model

This isotherm also considers monolayer sorption with a heterogenous distribution of active sites of the sorbent (Freundlich, 1907).

$$q_e = k_f C_e^{\,n} \qquad (4)$$

Where K_f stands for the adsorption capacity and n for adsorption intensity.

Logarithmic form of Eq (4)

$$\text{Log } eq_e = \log_e (K_f C_e^{\,1/n})$$

$$= \log_e K_f + \log_e C_e^{\,1/n}$$

$$\text{Log } eq_e = \log ek_f + 1/n \log_e C_e$$

Where K_f and 1/n can be determined from the linear plot of $\log_e(qe)$ vs $\log_e(C_e)$.

Experimental values obtained for the adsorption capacity experiments were used to calculate the parameters.

9. FTIR analysis

Fourier transform infrared spectra of the native as well as metal laden biomass were obtained after drying the biomass at 70°C. The finely powdered samples (10 mg) were encapsulated with 200 mg of potassium bromide (KBr) and compressed to prepare translucent sample disks and spectra were recorded by Nicolet Instrument (Model: MAGNA 550, USA). Each spectrum was the average of 64, co-addition of scans with a total scan time 15s in the IR range of 400-4000 cm^{-1}.

Result and discussion

1. Collection and processing of leaf litter biomass

Leaf litter biomass from 8 different tree species Eucalyptus, Ashoka, Bamboo, Mango, Poplar, Wheat Husk, Rice straw and Jamun were used as biosorbents for removal of hexavalent chromium [Cr(VI)] from synthetic solution containing different concentration of Cr (VI). Effect of biomass concentration, time and pH was studied on percentage removal of Cr (VI) and its specific uptake by plant biomass.

Agricultural waste biomass from wheat and rice straw and leaf litter biomass from different trees viz. *Mangifera indica, Populus deltoides, Polyalthia longifolia, Eucalyptus globules, Bambuseae* and *Syzygium cumini* were collected from Thapar University campus located at 30°19'48"N,76°24'0"E and 310 m above the sea level. Samples were washed to remove adhered debris, dried, grounded and sieved to particle size of 0.5 mm. Sieved samples were stored in an air tight containers at room temperature for further use.

Table 5: Classification of the tree species used as adsorbents.

Common name	Family	Genus	Scientific name
Wheat straw	Poaceae	Triticum	*Triticum aestivum*
Rice straw	Poaceae	Oryza	*Oryza sativa*
Mango leaf litter	Anacardiaceae	Mangifera	*Mangifera indica*
Poplar leaf litter	Salicaceae	Populus	*Populus deltoides*
Ashoka leaf litter	Annonaceae	Polyalthia	*Polyalthia longifolia*
Eucalyptus leaf litter	Myrtaceae	Eucalyptus	*Eucalyptus globulus*
Bamboo leaf litter	Poaceae	Acidosasa	*Bambuseae*
Jamun leaf litter	Myrtaceae	Syzygium	*Syzygium cumini*

2. Removal of hexavalent chromium by leaf litter biomass in batch mode

Biosorption of heavy metal ions is affected by various physico-chemical parameters and surface properties. Therefore, the effect of varying biomass concentration, initial metal concentration and initial pH on the removal of hexavalent chromium by the leaf litter biomasses was investigated.

2.1. Effect of Eucalyptus leaf litter biomass

Specific uptake capacity and removal efficiency of Cr (VI) by Eucalyptus leaf litter biomass was studied with the adsorbent dosage of 0.05 to 4 % at 0 to 300 min time interval (Table 6, Fig.1). It was observed that both specific metal uptake capacity and removal efficiency increased from 0 to 300 min time interval. It was found that at 0.05 % adsorbent dosage, the specific metal uptake capacity increased from 0.8 mg/g at 0 min to 4.8 at 60 min and thereafter it reached saturation in 120 min with specific metal uptake of 5 mg/ g and it remained constant upto 300 min time interval. At the adsorbent dosage of 0.1 %, the specific metal uptake increased from 0.4 mg/g at 0 min to 3.4 mg/g at 300 min interval of time with no clear saturation point, although the specific metal uptake became constant at 240 min time interval. Similarly, with the adsorbent dosage of 0.5 %, no fixed pattern for saturation point of specific metal uptake was observed but it increased from 0.06 mg/g to 0.74 mg/g from 0 to 300 min time interval. At the adsorbent dosage of 1 %, initially the specific metal uptake was 0.04 mg/g at 0 min but it rose to 0.41 mg/g at 30 min, attaining saturation at 60 min time interval with specific metal uptake capacity of 0.61 mg/g. With the adsorbent dosage of 1.5 %, the metal uptake capacity enhanced from 0.02 mg/g at 0 min to 0.22 mg/g at 30 min with final saturated uptake of 0.28 mg/g at 60 min time interval. Specific metal uptake increased from 0.02 mg/g at 0 min to 0.25 mg/g at 60 min, later on attaining saturation point at 120 min time interval. At the adsorbent dosage of 2.5, 3 and 4 % respectively, the initial uptake is 0.01 mg/g at 0 min time. It increased to 0.32 mg / g, 0.3 mg / g at 120 min time interval, getting saturated thereafter at 2.5 and 3 % adsorbent dosage respectively. However the saturation point at 4 %

adsorbent dosage was attained at 60 min time interval with 0.23 mg/g specific metal uptake.

The removal efficiency of Cr (VI) by 0.05 % adsorbent dosage increased upto 25 % at 120 min time interval, thereafter saturation point was attained. No fixed pattern for achieving saturation point for removing Cr (VI) was observed for 0.1 and 0.5 % adsorbent dosage, however, the maximum removal efficiency was achieved at 240 min time interval which was 34 and 37% at 0.1 and 0.5 % adsorbent dosage respectively. At 1 % of adsorbent dosage, the removal efficiency by eucalyptus leaf litter biomass increased from 4 to 41 % at 0 to 30 min time interval, after which it became saturated with the removal efficiency of 61% at 60 min time interval. Removal of Cr (VI) increased to 43, 53, 84, 91 and 95 % at 60, 180, 120, 180 and 120 min of time interval for adsorbent dosage of 1.5, 2, 2.5, 3 and 4 % respectively (Table 6, Fig. 2)

At 1 % adsorbent dosage, the maximum specific metal uptake was found to be 0.61 mg/g and maximum removal efficiency to be 61% at 60 min time interval. However, the maximum specific uptake by eucalyptus leaf litter biomass was found to be 5 mg/g at 0.05 % adsorbent dosage after 120 min of incubation. The maximum removal efficiency was found to be 95% at 4 % of adsorbent dosage at 120 min.

Table 6: Effect of Eucalyptus leaf litter biomass dosage on removal and uptake of Cr (VI) from aqueous solution (C_i=10 mg/l, Rpm=120, Room temperature)

Time (min)	Adsorbent dosage (%)																	
	0.05		0.1		0.5		1		1.5		2		2.5		3		4	
	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)
0	0.8	4	0.4	4	0.06	3	0.04	4	0.02	3	0.02	5	0.01	4	0.01	3	0.01	5
10	1.8	9	1.1	11	0.24	12	0.19	19	0.07	11	0.07	15	0.06	16	0.06	18	0.04	16
20	3.8	19	2.2	22	0.26	13	0.31	31	0.21	32	0.16	33	0.10	26	0.13	39	0.12	48
30	4	20	3.1	31	0.66	33	0.41	41	0.22	33	0.21	43	0.21	54	0.16	49	0.19	78
60	4.8	24	3.2	32	0.68	34	0.61	61	0.28	43	0.25	51	0.26	66	0.22	68	0.23	94
120	5	25	3.3	33	0.72	36	0.61	61	0.28	43	0.26	52	0.32	82	0.3	90	0.23	95
180	5	25	3.3	33	0.72	36	0.61	61	0.28	43	0.26	53	0.32	82	0.3	91	0.23	95
240	5	25	3.4	34	0.74	37	0.61	61	0.28	43	0.26	53	0.32	84	0.3	91	0.23	95
300	5	25	3.4	34	0.74	37	0.61	61	0.28	43	0.26	53	0.32	84	0.3	91	0.23	95

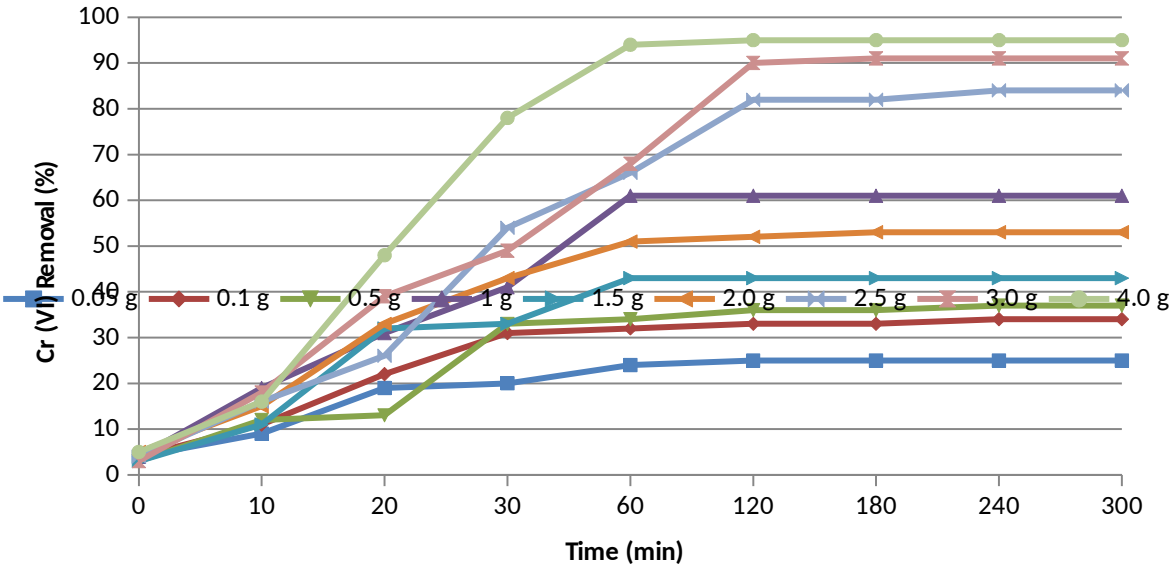


Fig 2: The Effect of Eucalyptus leaf litter biomass concentration on the removal efficiency of Cr (VI) from aqueous solution (Room temperature; Agitation rate=120 rpm, C_i=10 mg/l).

2.2 Effect of Bamboo leaf litter biomass

The specific metal uptake capacity and removal efficiency of Cr (VI) by bamboo leaf litter biomass was studied for 0 to 300 min time interval at adsorbent dosage of 0.05 to 4 % (Table 7, Fig. 2). Both specific metal uptake and removal efficiency increased from 0 to 300 min time interval. The specific metal uptake increased from 0.8 to 7.2 mg/g at time interval of 0 to 60 min, thereafter saturation point came with the maximum uptake being 7.8 mg/g at 120 min of time of incubation with 0.05 % of adsorbent dosage. At 0.1% adsorbent dosage, specific metal uptake increased to 5.1 mg/g at 120 min from 0.4 mg/g at 0 min. The adsorbent at 0.5, 1, 1.5 and 2% was observed to be saturated at 60 min of time of incubation with specific uptake of 1.04, 0.58, 0.4 and 0.33 mg/g respectively. At 2.5 % of adsorbent dosage, the initial specific metal uptake increased from 0.01 to 0.31 mg/g at the time of incubation from 0 to 300 min. Saturation point was achieved after 120 min of incubation. The specific metal uptake capacities at adsorbent dosages of 3 and 4% were found to be maximum after 60 min of incubation i.e. 0.29 and 0.23 mg/g. Thereafter saturation point was attained (Table 7).

The removal efficiency of Cr (VI) at 0.05% dosage of bamboo leaf litter biomass was found to be 39% at 120 min which increased from 4% at 0 min, after which saturation was achieved. The maximum removal efficiency at 0.1% adsorbent dosage was found to be 51% after 120 min of time of incubation. After this, saturation point was attained. For 0.5, 1, 1.5 and 2% adsorbent dosages, the maximum removal was found after 60 min of incubation, which was 52, 58, 61 and 66 % respectively. The maximum removal at 2.5% adsorbent dosage increased from 4% at 0 to 78% after 120 min of incubation thereafter which, it eventually achieved its saturation point. At 3 and 4 % of bamboo leaf litter biomass dosage, the maximum removal was found to be 89 and 94% respectively after 60 min. Thereafter saturation was achieved (Table 7, Fig. 3).

The maximum specific uptake of Cr (VI) by Bamboo leaf litter biomass was observed to be 7.8 mg/g by 0.05% of adsorbent dosage after 120 min. The maximum removal efficiency of the same was found to be 94% at 4 % of adsorbent dosage after 60 min. However at 1% of adsorbent dosage, 0.58 mg/g of the specific metal uptake capacity was observed with removal efficiency of 58% after 60 min.

Table 7: Effect of Bamboo leaf litter biomass dosage on removal and uptake of Cr (VI) from aqueous solution (C_i=10 mg/l, Rpm=120, Room temperature)

Time (min)	Adsorbent dosage (%)																	
	0.05		0.1		0.5		1		1.5		2		2.5		3		4	
	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)
0	0.8	4	0.4	4	0.06	3	0.04	4	0.02	3	0.02	5	0.01	4	0.01	3	0.00	3
10	2.8	14	1.5	15	0.42	21	0.23	23	0.11	17	0.1	21	0.11	29	0.06	19	0.1	40
20	5	25	2.6	26	0.7	35	0.31	31	0.14	29	0.19	39	0.19	49	0.17	51	0.14	58
30	6.2	31	2.9	29	0.82	41	0.43	43	0.3	45	0.27	54	0.24	62	0.21	63	0.2	80
60	7.2	36	4.3	43	1.04	52	0.58	58	0.4	61	0.33	66	0.30	76	0.29	89	0.23	94
120	7.8	39	5.1	51	1.04	52	0.58	58	0.4	61	0.33	66	0.31	78	0.29	89	0.23	94
180	7.8	39	5.1	51	1.04	52	0.58	58	0.4	61	0.33	66	0.31	78	0.29	89	0.23	94
240	7.8	39	5.1	51	1.04	52	0.58	58	0.4	61	0.33	66	0.31	78	0.29	89	0.23	94
300	7.8	39	5.1	51	1.04	52	0.58	58	0.4	61	0.33	66	0.31	78	0.29	89	0.23	94

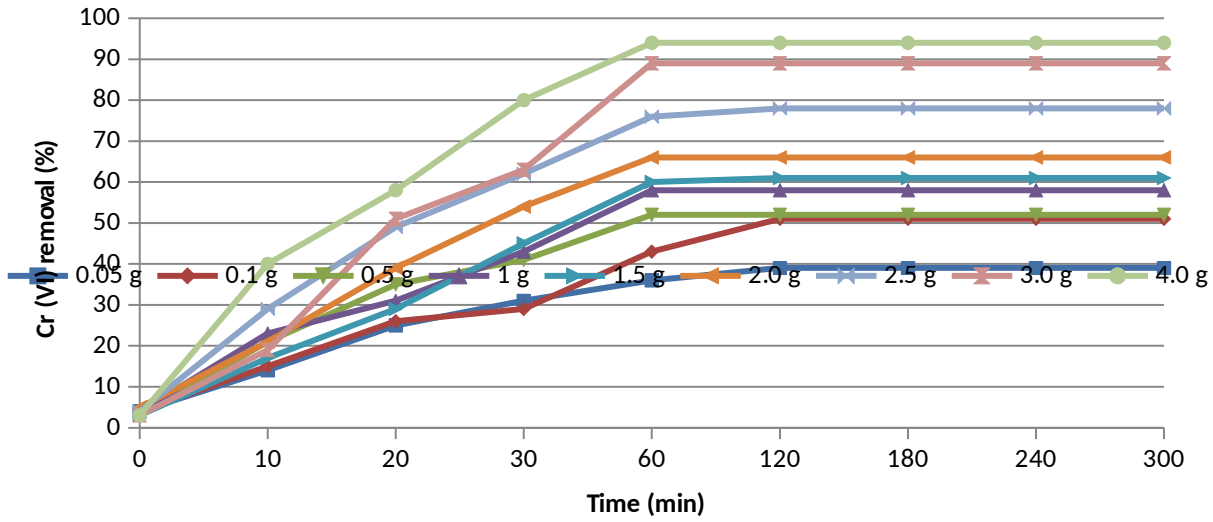


Fig 3: The Effect of Bamboo leaf litter biomass concentration on the removal efficiency of Cr (VI) from aqueous solution (Room temperature; Agitation rate=120 rpm, C_i=10 mg/l)

2.3 Effect of Poplar leaf litter biomass

The specific metal uptake and removal efficiency of Cr (VI) by poplar leaf litter biomass was studied at 0.05 to 4% from 0 to 300 min of time interval (Table 8, Fig. 3). The specific metal uptake capacities were found to increase with increase in time of incubation from 0 to 300 min. At adsorbent dosage of 0.05%, the specific metal uptake increased from 0.6 mg/g at 0 min to 6.2 mg/g at 60 min, the maximum being 6.8 mg/g at 120 min after which it became saturated. Similarly, at 0.1% of poplar leaf litter biomass dosage, the saturation point for specific metal uptake came after 120 min, which was 3.5 mg/g. The specific metal uptake at 0.5% adsorbent dosage increased from 0.06 to 0.8 mg/g after 60 min, thereafter saturation point was achieved. For the adsorbent dosages of 1, 1.5, 2, 2.5, 3 and 4%, the saturation point was achieved after 60 min with specific metal uptake capacities of 0.43, 0.33, 0.28, 0.25, 0.25 and 0.21 mg/g respectively (Table 8).

The removal efficiency of Cr (VI) by poplar leaf litter biomass was also studied and found to increase with increase with increase in adsorbent dosage and time of incubation. The removal efficiency of Cr (VI) at 0.05% adsorbent dosage increased from 3 to 34% after 120 min, thereafter saturation point came. At 0.1% adsorbent dosage, the maximum

removal, 35% was observed at 120 min of time interval, after this saturation point was achieved. The maximum removal of Cr (VI) at 0.5, 1, 1.5, 2, 2.5, 3 and 4% of adsorbent dosage achieved its saturation point after 60 min. The maximum removal efficiencies observed were 40, 43, 50, 56, 64, 75 and 84% respectively (Table 8, Fig. 4).

The maximum specific metal uptake of Cr (VI) by poplar leaf litter biomass was found at 0.05% of adsorbent dosage. The removal efficiency was found to be 84% at 4% of adsorbent dosage after 60 min. At 1% of adsorbent dosage and after 60 min, the maximum specific metal uptake and maximum removal of CR (VI) was 0.43 mg/g and 43% respectively.

Table 8: Effect of Poplar leaf litter biomass dosage on removal and uptake of Cr (VI) from aqueous solution (C_i=10 mg/l, Rpm=120, Room Temperature)

Time (min)	Adsorbent dosage (%)																	
	0.05		0.1		0.5		1		1.5		2		2.5		3		4	
	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)
0	0.6	3	0.4	4	0.06	3	0.04	4	0.02	3	0.01	3	0.01	3	0.01	3	0.00	3
10	2.8	14	1.4	14	0.3	15	0.17	17	0.10	16	0.08	17	0.07	18	0.05	15	0.06	26
20	3.2	16	1.9	19	0.62	31	0.31	31	0.18	27	0.23	47	0.14	36	0.13	41	0.12	49
30	4.6	23	2.4	24	0.74	37	0.40	40	0.28	43	0.26	52	0.2	50	0.22	66	0.16	67
60	6.2	31	2.8	28	0.8	40	0.43	43	0.33	50	0.28	56	0.25	64	0.25	75	0.21	84
120	6.8	34	3.5	35	0.8	40	0.43	43	0.33	50	0.28	56	0.25	64	0.25	75	0.21	84
180	6.8	34	3.5	35	0.8	40	0.43	43	0.33	50	0.28	56	0.25	64	0.25	75	0.21	84
240	6.8	34	3.5	35	0.8	40	0.43	43	0.33	50	0.28	56	0.25	64	0.25	75	0.21	84
300	6.8	34	3.5	35	o.8	40	0.43	43	0.33	50	0.28	56	0.25	64	0.25	75	0.21	84

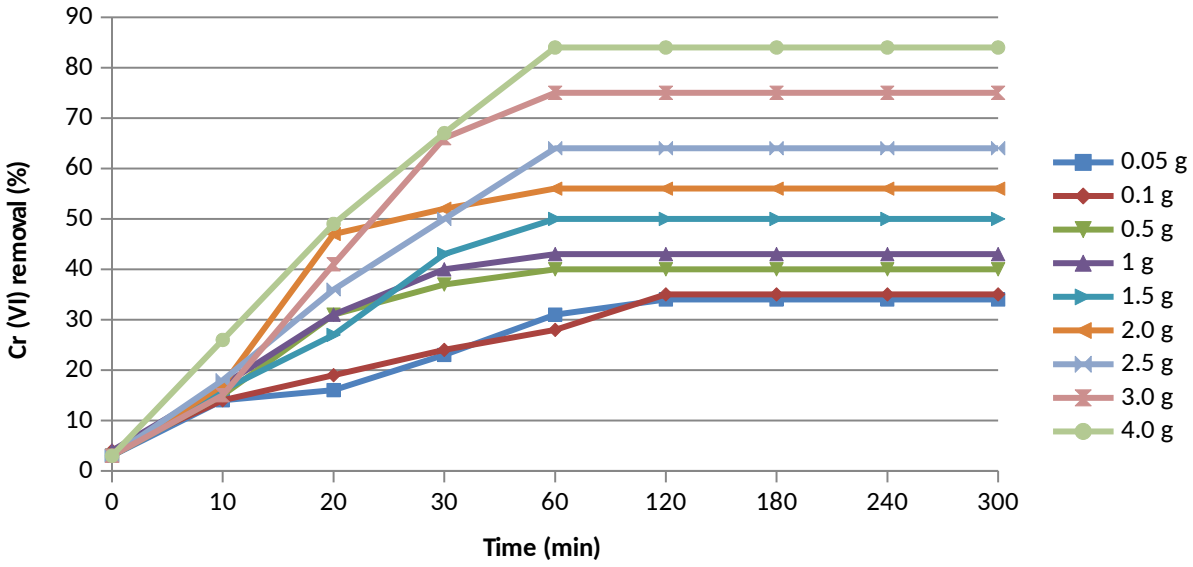


Fig 4: The Effect of Poplar leaf litter biomass concentration on the removal efficiency of Cr (VI) from aqueous solution (Room temperature; Agitation rate=120 rpm, C_i=10 mg/l)

2.4 Effect of wheat husk biomass

The specific metal uptake capacities and removal efficiency of Cr (VI) by wheat husk as adsorbent was studied with adsorbent dosage from 0.05 to 4% and time of incubation of 0 to 300 min (Table 9, Fig. 4). At 0.05% of adsorbent dosage, the specific metal uptake increased from 0.6 to 8.4 mg/g from 0 to 300 min of time interval. The saturation point was achieved after 120 min. Similarly the saturation point for specific metal uptake at 0.1% of adsorbent reached after 120 min with uptake of 4.4 mg/g. For the adsorbent dosage of 0.5, 1 and 1.5%, the maximum specific metal uptake was 1.02, 0.57 and 0.42 mg/g at 60 min of time interval, after which it became saturated. The specific metal uptake capacity at 2% adsorbent dosage increased from 0.01 to 0.33 mg/g at 120 min of time of incubation, after it achieved its saturation point. For adsorbent dosage of 2.5 %, saturation point with specific metal uptake capacities of 0.27 mg/g reached after 60 min, which initially started from 0.01 mg/g at 0 min of time interval. The specific capacities at 3.5 and 4% adsorbent dosage increased to 0.26 and 0.21 mg/g after 180 min, thereafter it became saturated (Table 9).

The removal efficiency of Cr (VI) at 0.05% dosage of wheat husk increased from 3 to 38% after 60 min, thereafter it reached maximum removal of 42%. Saturation point was achieved after 120 min. With adsorbent dosage of 0.1%, the maximum removal was observed to be 44% after 120 min. The removal efficiencies for 0.5, 1 and 1.5% adsorbent were found to be 51, 57 and 63% at 60 min time interval. The maximum removal at 2% adsorbent dosage was 67% at 120 min time interval, after which saturation point was attained. The maximum removal with 2.5% adsorbent dosage was 68% at 60 min time interval. Saturation was achieved after 60 min. The removal efficiencies by 3.5 and 4% were 78 and 84% respectively (Table 9, Fig. 5).

The maximum specific uptake capacity for Cr (VI) was 8.4 mg/g at 0.05% of wheat husk dosage. The maximum removal efficiency was 84% at 4% of adsorbent dosage. At 1% adsorbent dosage, the maximum specific metal uptake and removal efficiency was 0.57 mg/g and 57% respectively at 60 min.

Table 9: Effect of Wheat husk biomass dosage on removal and uptake of Cr (VI) from aqueous solution (C_i=10 mg/l, Rpm=120, Room temperature)

Time (min)	Adsorbent dosage (%)																	
	0.05		0.1		0.5		1		1.5		2		2.5		3		4	
	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)
0	0.6	3	0.4	4	0.1	5	0.03	3	0.02	3	0.01	3	0.01	3	0.01	4	0.00	3
10	3	15	1.6	16	0.34	17	0.12	12	0.1	15	0.10	21	0.08	22	0.07	21	0.06	26
20	4.2	21	2.2	22	0.42	21	0.21	21	0.26	39	0.14	29	0.16	40	0.08	25	0.10	41
30	5	25	2.9	29	0.6	30	0.29	29	0.3	46	0.26	53	0.19	48	0.17	51	0.15	62
60	7.6	38	4.3	43	1.02	51	0.57	57	0.42	63	0.31	63	0.27	68	0.25	76	0.20	83
120	8.4	42	4.4	44	1.02	51	0.57	57	0.42	63	0.33	67	0.27	68	0.25	76	0.20	83
180	8.4	42	4.4	44	1.02	51	0.57	57	0.42	63	0.33	67	0.27	68	0.26	78	0.21	84
240	8.4	42	4.4	44	1.02	51	0.57	57	0.42	63	0.33	67	0.27	68	0.26	78	0.21	84
300	8.4	42	4.4	44	1.02	51	0.57	57	0.42	63	0.33	67	0.27	68	0.26	78	0.21	84

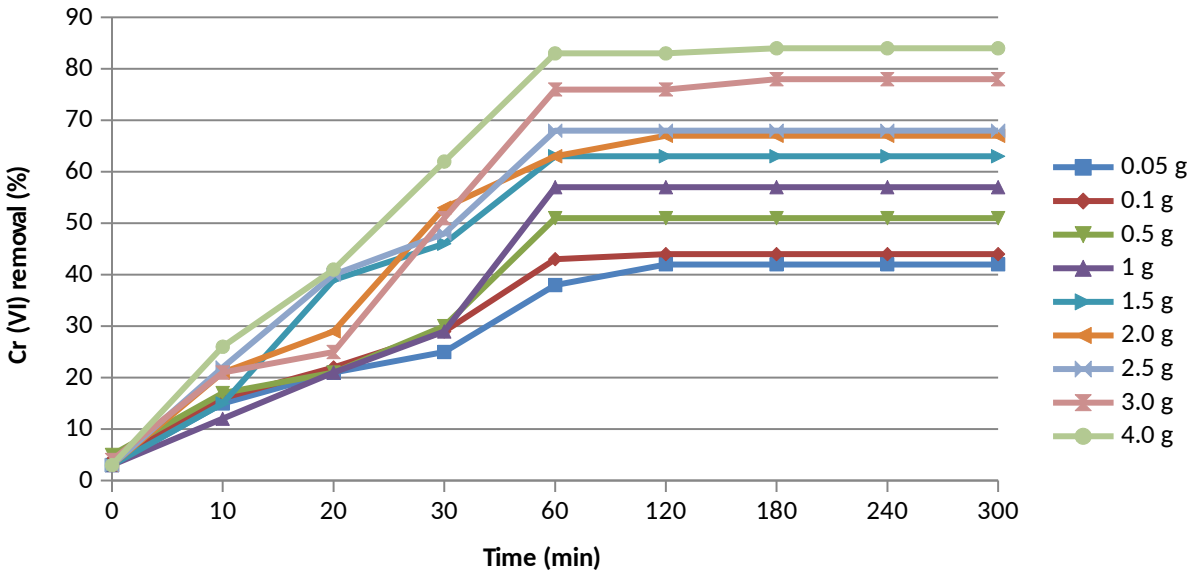


Fig 5: The Effect of Wheat husk biomass concentration on the removal efficiency of Cr (VI) from aqueous solution (Room temperature; Agitation rate=120 rpm, C_i=10 mg/l)

2.5 Effect of Mango leaf litter biomass

The specific metal uptake and removal efficiency of Cr (VI) by mango leaf litter biomass was studied at different adsorbent dosage, 0.05 to 4% and time interval of 0 to 300 min (Table 10, Fig. 5). With increase in time of incubation, an increase in specific metal uptake and metal removal efficiency was observed. The specific metal uptake at 0.05% adsorbent dosage was 5 mg/g after 60 min. At adsorbent dosage of 0.1%, specific metal uptake of 3.3 mg/g was achieved after 120 min of time interval. The specific metal uptake of maximum of 0.76 mg/g was attained at 60 min at 0.5% adsorbent dosage. The specific metal uptake at 1% of dosage of wheat husk was 0.49 mg/g at 180 min of time interval, after which it got saturated. At adsorbent dosage of 1.5%, the specific metal uptake increased to 0.37 mg/g at 300 min of time interval. At 2% of mango leaf litter dosage, the specific metal uptake of 0.28 mg/g was achieved at 120 min of time interval. The specific metal uptake at 2.5% adsorbent dosage increased from 0.01 to 0.22 mg/g at 60 min, after which, saturation point was achieved. For adsorbent dosage of 3 and 4%, specific metal uptake was 0.24 and 0.2 mg/g at 120 and 60 min of time interval respectively. After this, saturation point was achieved (Table 10).

The removal efficiency by wheat husk dosage increased with increase in time of incubation and adsorbent dosage. At 0.05% adsorbent dosage, removal of Cr (VI) increased to 5% after 60 min. The maximum removal of 33% was observed at 0.1% adsorbent dosage at 120 min, after which saturation point was achieved. At 0.5% adsorbent dosage, 38% of Cr (VI) was removed after 60 min. The saturation point at 1% of adsorbent dosage came after 180 min with removal efficiency of 49%. The removal efficiency at 1.5% adsorbent dosage increased from 3 to 56% till 300 min. No saturation point was observed. The removal efficiency at 2, 2.5, 3 and 4% adsorbent dosage was 56, 57, 72 and 82% at 120, 60, 120 and 60 min of time interval respectively, thereafter saturation point was achieved (Table 10, Fig. 6).

The maximum specific metal uptake of Cr (VI) by mango leaf litter biomass was 5 mg/g at 0.05% of the adsorbent dosage. The maximum removal efficiency was 82% at 4% of adsorbent dosage. At 1% dosage of mango leaf litter biomass, 0.41 mg/g of specific metal uptake and 41% of metal removal efficiency was observed.

Table 10: Effect of Mango leaf litter biomass dosage on removal and uptake of Cr (VI) from aqueous solution (C_i=10 mg/l, Rpm=120, Room temperature).

Time (min)	Adsorbent dosage (%)																	
	0.05		0.1		0.5		1		1.5		2		2.5		3		4	
	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)
0	1	5	0.3	3	0.08	4	0.03	3	0.02	3	0.02	4	0.01	3	0.01	4	0.07	3
10	2.6	13	1.9	19	0.2	10	0.2	20	0.13	20	0.11	22	0.08	22	0.07	21	0.05	21
20	3.4	17	2.3	23	0.34	17	0.23	23	0.16	24	0.12	25	0.16	40	0.13	40	0.09	37
30	4.6	23	2.4	24	0.62	31	0.24	24	0.23	35	0.20	41	0.17	43	0.17	52	0.13	55
60	5	25	2.7	27	0.76	38	0.41	41	0.34	51	0.23	47	0.22	55	0.21	64	0.20	82
120	5	25	3.3	33	0.76	38	0.42	42	0.34	52	0.28	56	0.22	57	0.24	72	0.20	82
180	5	25	3.3	33	0.76	38	0.49	49	0.34	52	0.28	56	0.22	57	0.24	72	0.20	82
240	5	25	3.3	33	0.76	38	0.49	49	0.34	52	0.28	56	0.22	57	0.24	72	0.20	82
300	5	25	3.3	33	0.76	38	0.49	49	0.37	56	0.28	56	0.22	57	0.24	72	0.20	82

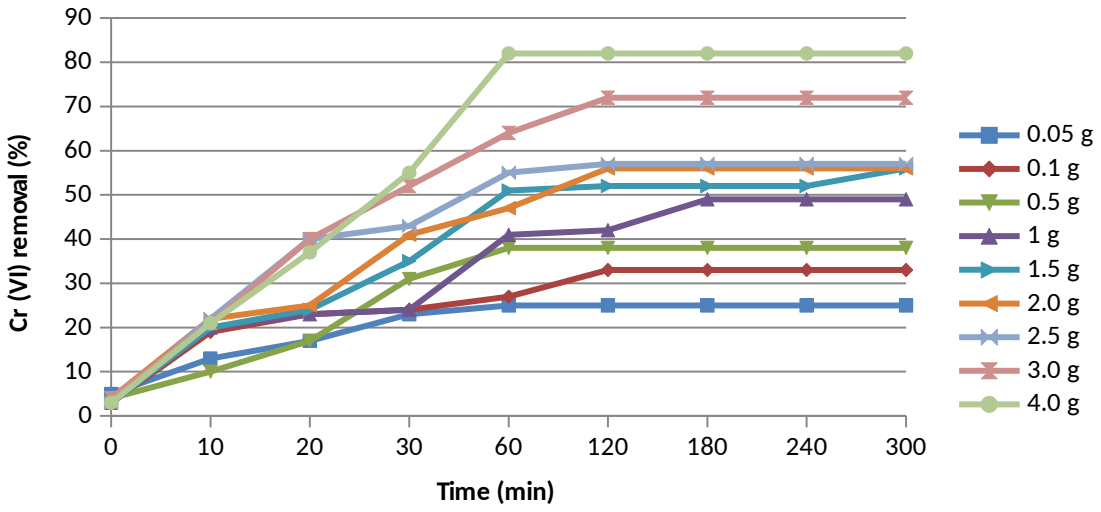


Fig 6: The Effect of Mango leaf litter biomass concentration on the removal efficiency of Cr (VI) from aqueous solution (Room temperature; Agitation rate=120 rpm, C_i=10 mg/l).

2.6 Effect of Jamun leaf litter biomass

The specific metal uptake capacities and removal efficiency of Cr (VI) by Jamun leaf litter as adsorbent was studied with adsorbent dosage from 0.05 to 4% and time of incubation of 0 to 300 min (Table 11, Fig. 6). At 0.05% of adsorbent dosage, the specific metal uptake increased from 0.6 to 6.6 mg/g from 0 to 300 min of time interval. The saturation point was achieved after 120 min. Similarly the saturation point for specific metal uptake at 0.1% of adsorbent reached after 120 min with uptake of 3.7 mg/g. For the adsorbent dosage of 0.5, 1 and 1.5%, the maximum specific metal uptake was 0.8, 0.43 and 0.33 mg/g at 60 min of time interval, after which it became saturated. The specific metal uptake capacity at 2% adsorbent dosage increased from 0.01 to 0.27 mg/g at 30 min of time of incubation, after it achieved its saturation point. Similarly, for adsorbent dosage of 2.5 %, saturation point with specific metal uptake capacities of 0.19 mg/g reached after 30 min of time of incubation, which initially started from 0.01 mg/g at 0 min of time interval. The specific capacities at 3.5 and 4% adsorbent dosage increased to 0.25 and 0.20 mg/g after 60 min, thereafter it became saturated (Table 11).

The removal efficiency of Cr (VI) at 0.05% dosage of Jamun leaf litter increased from 3 to 29% after 60 min, thereafter it reached maximum removal of 33%. Saturation point

was achieved after 120 min of time of incubation. With adsorbent dosage of 0.1%, the maximum removal was observed to be 37% after 120 min. The removal efficiencies for 0.5, 1 and 1.5% adsorbent were found to be 40, 43 and 50% at 60 min time interval. The maximum removal at 2 and 2.5% adsorbent dosage was 54 and 48% at 30 min time interval, after which saturation point was attained. The removal efficiencies by 3.5 and 4% were 76 and 82% respectively (Table 11, Fig 7).

The maximum specific uptake capacity for Cr (VI) was 6.6 mg/g at 0.05% of Jamun leaf litter dosage. The maximum removal efficiency was 82% at 4% of adsorbent dosage. At 1% adsorbent dosage, the maximum specific metal uptake and removal efficiency was 0.43 mg/g and 43% respectively at 60 min.

Table 11: Effect of Jamun leaf litter biomass dosage on removal and uptake of Cr (VI) from aqueous solution (C_i=10 mg/l, Rpm=120, Room temperature).

Time (min)	Adsorbent dosage (%)																	
	0.05		0.1		0.5		1		1.5		2		2.5		3		4	
	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)
0	0.6	3	0.3	3	0.06	3	0.04	4	0.02	3	0.01	3	0.01	4	0.01	3	0.00	3
10	2.6	13	1.4	14	0.28	14	0.16	16	0.11	17	0.08	16	0.07	19	0.04	14	0.06	24
20	3	15	2.1	21	0.44	22	0.3	30	0.17	26	0.25	50	0.14	37	0.14	42	0.1	42
30	4.4	22	2.5	25	0.74	37	0.39	39	0.29	44	0.27	54	0.19	48	0.22	67	0.15	63
60	5.8	29	2.9	29	0.8	40	0.43	43	0.33	50	0.27	54	0.19	48	0.25	76	0.20	82
120	6.6	33	3.7	37	0.8	40	0.43	43	0.33	50	0.27	54	0.19	48	0.25	76	0.20	82
180	6.6	33	3.7	37	0.8	40	0.43	43	0.33	50	0.27	54	0.19	48	0.25	76	0.20	82
240	6.6	33	3.7	37	0.8	40	0.43	43	0.33	50	0.27	54	0.19	48	0.25	76	0.20	82
300	6.6	33	3.7	37	0.8	40	0.43	43	0.33	50	0.27	54	0.19	48	0.25	76	0.20	82

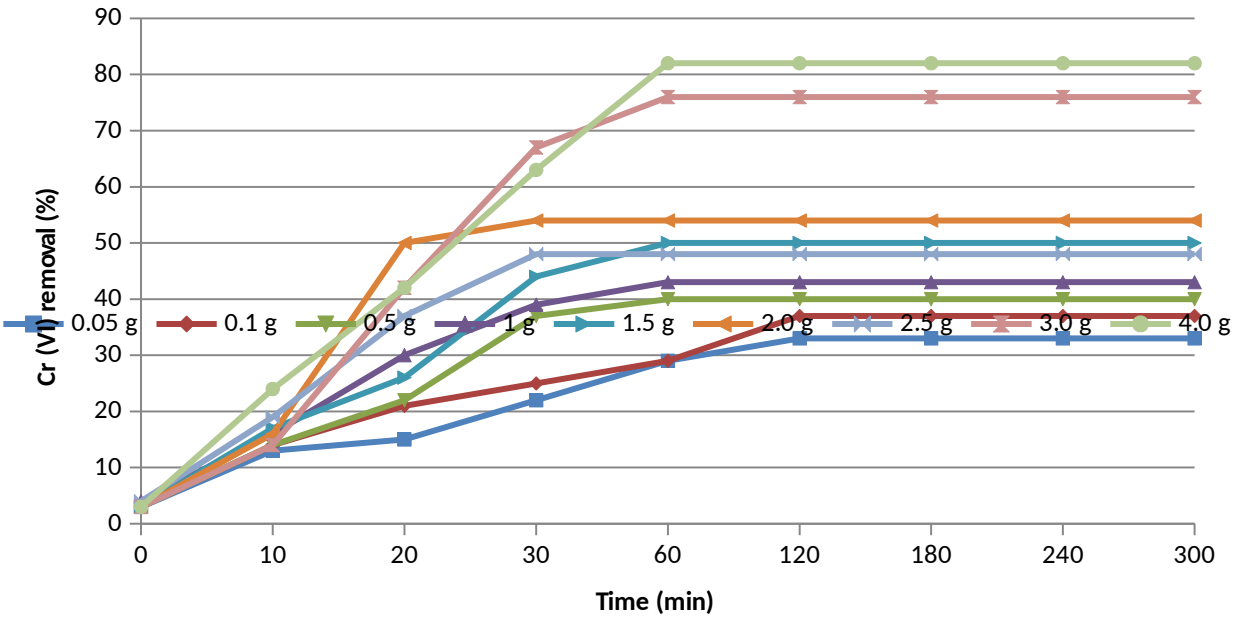


Fig 7: The Effect of Jamun leaf litter biomass concentration on the removal efficiency of Cr (VI) from aqueous solution (Room temperature; Agitation rate=120rpm, C_i=10mg/L)

2.7 Effect of Ashoka leaf litter biomass

Specific uptake capacity and removal efficiency of Cr (VI) by ashoka leaf litter biomass was studied with the adsorbent dosage of 0.05 to 4 % at 0 to 300 min time interval (Table 12, Fig. 7). It was observed that both specific metal uptake capacity and removal efficiency increased from 0 to 300 min time interval. It was studied that at 0.05 % adsorbent dosage, the specific metal uptake capacity increased from 0.8 mg/g at 0 min to 7.4 at 60 min and thereafter it reached saturation at 120 min with specific metal uptake of 8.2 mg/ g and it remain constant till 300 min time interval.

At the adsorbent dosage of 0.1 %, the specific metal uptake increased from 0.7 mg/g at 0 min to 4.7 mg/g at 60 min interval of time, thereafter saturation point was achieved. Similarly, with the adsorbent dosage of 0.5, 1 and 1.5 %, specific uptake increased to 0.98, 0.59 and 0.41 mg/g. The saturation point was achieved after 60 min of time of incubation for 0.05 and 1.5% of adsorbent dosage but after 120 min for adsorbent dosage of 1%.

At the adsorbent dosage of 2 %, initially the specific metal uptake was 0.02 mg/g at 0 min but it rose to 0.34 mg/g at 120 min, attaining saturation thereafter. With the adsorbent

dosage of 2.5 %, the metal uptake capacity enhanced from 0.02 mg/g at 0 min to 0.29 mg/g at 60 min with final saturated uptake of 0.30 mg/g at 120 min time interval. At the adsorbent dosage of 3 % respectively, the initial uptake was 0.01 mg/g at 0 min time. It increased to 0.23 mg/g at 60 min time interval, getting saturated thereafter. The saturation point at 4 % adsorbent dosage was attained at 120 min time interval with 0.22 mg/g specific metal uptake (Table 12).

The removal efficiency of Cr (VI) by 0.05 % adsorbent dosage increased upto 41 % at 120 min time interval, thereafter saturation point was attained. For 0.1 and 0.5 % adsorbent dosage, the maximum removal efficiency was achieved at 60 min time interval which was 47 and 49%. At 1% of adsorbent dosage, the removal efficiency by eucalyptus leaf litter biomass increased from 3 to 41 % at 0 to 60 min time interval, after which it became saturated with the removal efficiency of 59% at 120 min time interval. At 1.5% adsorbent dosage, maximal removal was 62% at 60 min of time interval, thereafter saturation was achieved. Removal of Cr (VI) increased to 69, 77, 82 and 91% at 120 min of time interval for adsorbent dosage of 2, 2.5, 3 and 4 % respectively (Table 12, Fig 8)

At 1 % adsorbent dosage, the maximum specific metal uptake was found to be 0.41 mg/g and maximum removal efficiency to be 41% at 60 min time interval. However, the maximum specific uptake by ashoka leaf litter biomass was found to be 8.2 mg/g at 0.05 % adsorbent dosage at 120 min. The maximum removal efficiency was found to be 91% at 4 % of adsorbent dosage at 120 min.

Table 12: Effect of Ashoka leaf litter biomass dosage on removal and uptake of Cr (VI) from aqueous solution (C_i=10 mg/l, Rpm=120, Room temperature).

Time	Adsorbent dosage (%)

(min)	0.05		0.1		0.5		1		1.5		2		2.5		3		4	
	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)
0	0.8	4	0.7	7	0.12	6	0.03	3	0.02	3	0.02	4	0.01	4	0.01	5	0.00	3
10	2.8	14	1.5	15	0.32	16	0.12	12	0.1	15	0.1	20	0.08	21	0.66	20	0.05	21
20	4	20	1.7	17	0.40	20	0.19	19	0.26	39	0.14	28	0.15	39	0.09	24	0.12	48
30	4.8	24	2.8	28	0.58	29	0.23	23	0.31	47	0.27	55	0.22	57	0.14	36	0.17	69
60	7.4	37	4.7	47	0.98	49	0.41	41	0.41	62	0.31	62	0.29	74	0.23	69	0.19	77
120	8.2	41	4.7	47	0.98	49	0.59	59	0.41	62	0.34	69	0.30	77	0.27	82	0.22	91
180	8.2	41	4.7	47	0.98	49	0.59	59	0.41	62	0.34	69	0.30	77	0.27	82	0.22	91
240	8.2	41	4.7	47	0.98	49	0.59	59	0.41	62	0.34	69	0.30	77	0.27	82	0.22	91
300	8.2	41	4.7	47	0.98	49	0.59	59	0.41	62	0.34	69	0.30	77	0.27	82	0.22	91

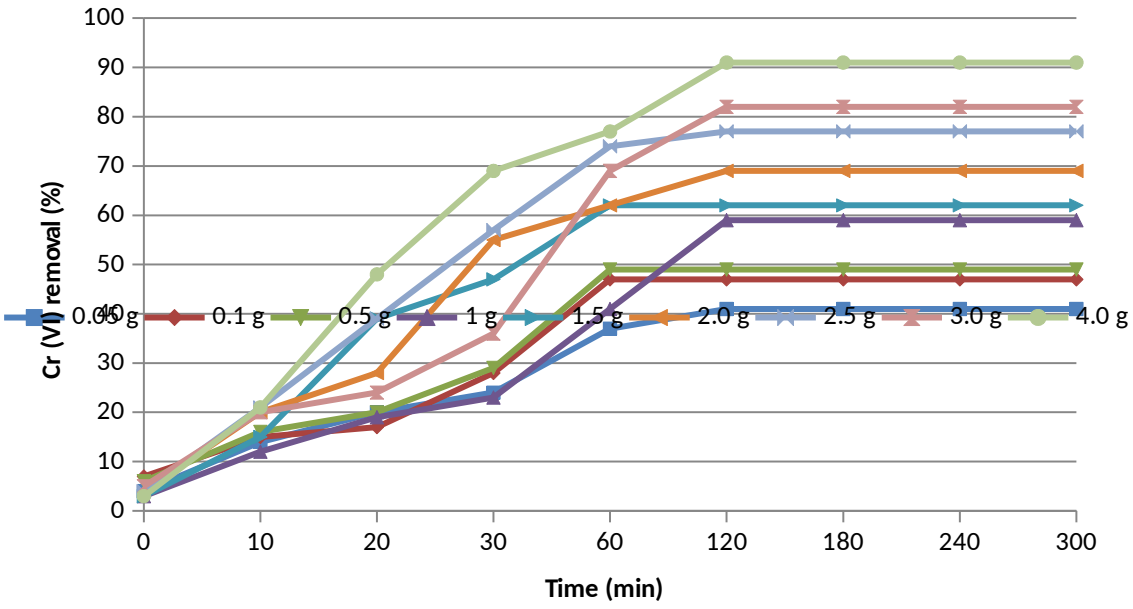


Fig. 8: The Effect of Ashoka leaf litter biomass concentration on the removal efficiency of Cr (VI) from aqueous solution (Room temperature; Agitation rate=120rpm, C_i=10mg/L)

2.8 Effect of rice straw biomass

The specific metal uptake and removal efficiency of Cr (VI) by rice straw was studied at 0 to 300 min time interval with adsorbent dosage of 0.05 to 4% (Table 13, Fig. 8). Both specific metal uptake and removal efficiency increased with increase in time of incubation. The specific metal uptake at 0.05% adsorbent concentration increased

maximally to 3 mg/g at 30 min, thereafter, it became saturated. At 0.1%, the specific metal uptake increased from 0.4 to 1.6 mg/g at 20 min, after which saturation was achieved. At 0.5% adsorbent dosage, maximum uptake at 120 min time interval was 0.32 mg/g. At 1 and 1.5% adsorbent dosage, the specific uptake was 0.18 and 0.12 mg/g at 60 and 30 min of time of incubation. After this, saturation was achieved. For adsorbent dosage of 2, 2.5, 3 and 4%, the maximum uptake increased to 0.1, 0.08, 0.07 and 0.05 mg/g respectively after 60 min, thereafter saturation point was achieved (Table13).

The removal efficiency of Cr (VI) by rice straw biomass at 0.05% concentration was 15% at 60 min of time interval, after which it got saturated. For adsorbent dosages of 0.1, 0.5 and 1%, the maximum removal was 16, 16 and 18% respectively at 20, 120 and 60 min of time of incubation. It became constant thereafter. At adsorbent dosage of 1.5%, the maximum removal was 19%. It attained its saturation point after 30 min time interval. The maximum removal by 2, 2.5, 3 and 4% was 20, 20, 21 and 23% at 60 min, thereafter saturation was achieved (Table 13, Fig. 9).

The maximum specific uptake by rice straw biomass was found to be 3 mg/g at 0.05 % adsorbent dosage at 30 min. The maximum removal efficiency was found to be 23% at 4 % of adsorbent dosage at 60 min. At 1 % adsorbent dosage, the maximum specific metal uptake was found to be 0.18 mg/g and maximum removal efficiency to be 18% at 60 min time interval.

Table 13: Effect of Rice straw biomass dosage on removal and uptake of Cr (VI) from aqueous solution (C_i=10 mg/l, Rpm=120, Room Temperature).

Time	Adsorbent dosage (%)								
	0.05	0.1	0.5	1	1.5	2	2.5	3	4

(min)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)	Q (mg/g)	R (%)
0	0.8	4	0.4	4	0.1	5	0.03	3	0.02	3	0.02	4	0.01	4	0.01	3	0.01	4
10	2.6	13	1.3	13	0.22	11	0.1	10	0.04	6	0.05	11	0.02	6	0.01	5	0.02	8
20	2.8	14	1.6	16	0.3	15	0.16	16	0.09	14	0.06	13	0.05	14	0.05	15	0.04	16
30	3	15	1.6	16	0.3	15	0.16	16	0.12	19	0.08	17	0.06	17	0.05	17	0.04	18
60	3	15	1.6	16	0.3	15	0.18	18	0.12	19	0.1	20	0.08	20	0.07	21	0.05	23
120	3	15	1.6	16	0.32	16	0.18	18	0.12	19	0.1	20	0.08	20	0.07	21	0.05	23
180	3	15	1.6	16	0.32	16	0.18	18	0.12	19	0.1	20	0.08	20	0.07	21	0.05	23
240	3	15	1.6	16	0.32	16	0.18	18	0.12	19	0.1	20	0.08	20	0.07	21	0.05	23
300	3	15	1.6	16	0.32	16	0.18	18	0.12	19	0.1	20	0.08	20	0.07	21	0.05	23

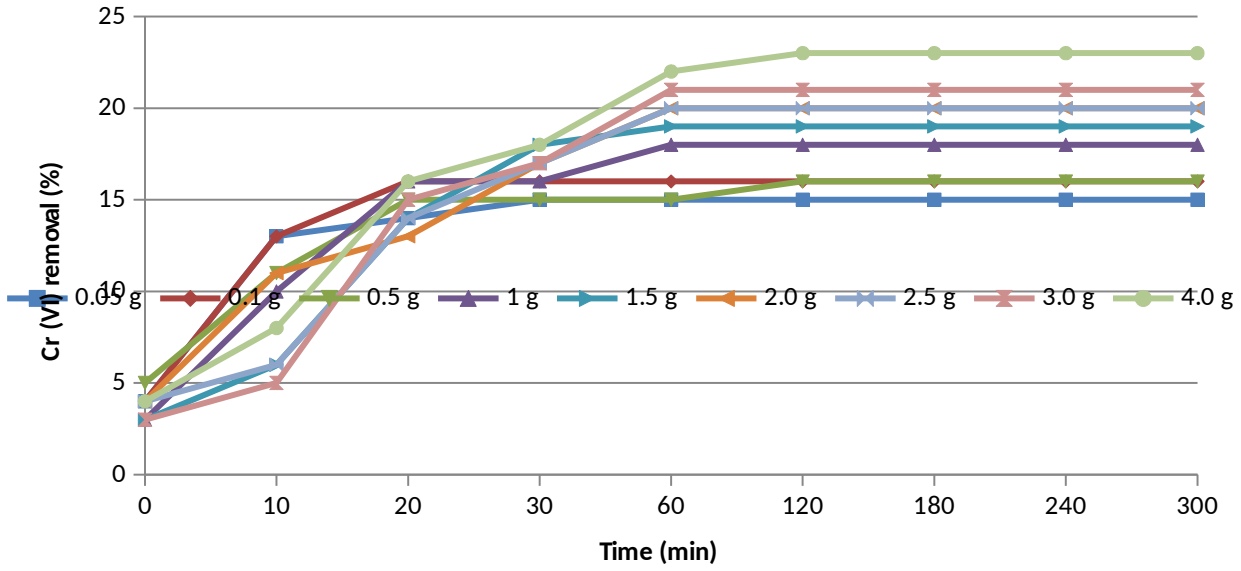


Fig. 9: The Effect of Rice straw biomass concentration on the removal efficiency of Cr (VI) from aqueous solution (Room temperature; Agitation rate=120rpm, C_i=10mg/l)

3. Comparison between different biomasses

The specific metal uptake (Q) by the different leaf litter biomasses increased with an increase in metal concentration and it amounted to be highest for Eucalyptus leaf litter biomass which was 0.61 mg/g.

The order followed for specific metal uptake by adsorbents at 1 g adsorbent dosage after 1 hour was: Eucalyptus>Bamboo> Wheat husk> Poplar=Jamun leaves>Mango= Ashoka >Rice straw. The specific metal uptake values for the same are 0.61, 0.58, 0.57, 0.43, 0.43, 0.41, 0.41 and 0.18 mg/g respectively (Table 14).

It was also seen that increase in adsorbent dosage to 4 % along with increase in the time of incubation from to 300 min, the specific metal uptake by various biosorbents also increased. Again the maximum being for Eucalyptus leaf litter biomass which is 0.237 mg/g, followed by Bamboo leaf litter biomass which is 0.235 mg/g, Ashoka leaf litter biomass with uptake value of 0.227 mg/g, Poplar leaf litter biomass and Wheat husk with specific metal uptake of 0.210 mg/g, Mango and Jamun leaf litter biomass with uptake value of 0.205 mg/g. The least specific metal uptake out of all the biosorbents was observed by Rice straw which corresponds to 0.057 mg/g (Table 14).

Maximum removal of Cr (VI) was by leaf litter biomass from Eucalyptus followed by Bamboo>Poplar>Wheat husk>Mango=Jamun>Ashoka>Rice straw. Maximum removal occurred almost in first hour, beyond which saturation point came. The order of removal of Cr (VI) in 1 hour by 1% biomass was:
Eucalyptus (61%)>Bamboo (58%)>wheat husk (57%)>Poplar=Jamun leaves (43%)>Ashoka=Mango (41%)>Rice straw (18%) (Table 14).The least removal efficiency was observed by rice straw biomass which is 18% (Table 13).

Removal of Cr (VI) from aqueous solution was 94% by Eucalyptus, 94% by Bamboo, 84% by Poplar leaf litter biomass, 83% by Wheat Husk biomass, 82% by Mango leaf litter biomass, 82% by Jamun leaf litter biomass, 77% Ashoka leaf litter biomass, and 22% by Rice Straw biomass in 1 hour of contact using 4% of adsorbent (Table 14).

Such behavior is obvious since the metal uptake of the adsorbent increases with the increase in dosage. This is so because the number of active sites available for metal increases with the increase in the amount of adsorbent. Malkoc et al., 2006, observed higher % removal as the dosage is increased. Garg et al., 2004 also investigated that the amount of Cr (VI) adsorbed increased with increase in dose of these adsorbents and their contact time.

Maximum removal of Cr (VI) from aqueous solution by the Eucalyptus, Bamboo, Poplar, Jamun leaf litter biomass, wheat husk and Rice straw was observed in 1 hour, after that, it reached equilibrium. However maximum removal of Cr (VI) from aqueous solution by

Mango and Ashoka leaf litter biomass was observed after 2 hours, after which it attained saturation point. This suggests that after a certain dosage of adsorbent, the maximum adsorption sets in and hence the amount of ions bound to the adsorbent and the amount of free ions remains constant even with further addition of the dosage of adsorbent.

It was also observed that the removal of hexavalent chromium increased up to 4% of biomass dosage along with increase in time of contact from 0 to 5 hour. The maximum removal of Cr (VI) from aqueous solution at 4% adsorbent dosage after 5 hour was by Eucalyptus leaf litter biomass followed by Bamboo leaf litter biomass>Ashoka> Poplar leaf litter biomass> Wheat Husk> Mango leaf litter biomass=Jamun leaf litter biomass>Rice straw which is 95, 94,91, 84, 84, 82, 82, 23 % respectively (Table 14).

Table 14: Comparison of specific metal uptake capacity and removal efficiency by 8 different leaf litter biomass at 1 and 4% of adsorbent concentration

	Q (mg/g)								R (%)							
Time (min)	20		30		60		120		20		30		60		120	
Adsorbent dosage(%)	1	4	1	4	1	4	1	4	1	4	1	4	1	4	1	4
Eucalyptus	0.31	0.12	0.41	0.19	0.61	0.23	0.61	0.23	31	48	41	78	61	94	61	95
Ashoka	0.19	0.12	0.23	0.17	0.41	0.19	0.59	0.22	19	48	23	69	41	77	59	91
Bamboo	0.31	0.14	0.43	0.2	0.58	0.23	0.58	0.23	31	58	43	80	58	94	58	94
Mango	0.23	0.09	0.24	0.13	0.41	0.2	0.42	0.02	23	37	24	55	41	82	42	82
Poplar	0.3	0.1	0.4	0.1	0.4	0.2	0.4	0.2	3	49	4	67	4	84	4	84

	1	2	0	6	3	1	3	1	1		0		3		3	
Wheat husk	0.21	0.1	0.29	0.15	0.57	0.20	0.57	0.20	21	41	29	62	57	83	57	83
Rice straw	0.16	0.04	0.16	0.04	0.18	0.05	0.18	0.05	16	16	16	18	18	22	18	23
Jamun	0.30	0.1	0.39	0.15	0.43	0.2	0.43	0.20	30	42	39	63	43	82	43	82

4. Effect of pH

The biosorption capacity of biomass is strongly influenced by the pH of the solution as it strongly affects surface charge of the adsorbent, the degree of ionization and the speciation of adsorbate species. The effect of pH was evaluated within a pH range of 2-6 to avoid precipitation of chromium.

The effect of initial pH on Cr (VI) removal by Eucalyptus leaf litter biomass is shown in Table 14, Fig. 10. The specific metal uptake at pH 2 increased from 0.02 to 0.4 mg/g after 300 min. At pH 4, the specific metal uptake increased to 0.45 mg/g after 300 min. The specific metal uptake increased to 0.42 mg/g at pH 6 at 300 min of time interval. Thus, it clearly indicated that the uptake capacity (Q) of the Eucalyptus adsorbent increased from pH 2 to 4 from 0.4 mg/g to 0.45 mg/g and then again decreased to 0.42 mg/g after 300 min of time interval at 2% of adsorbent dosage.

The removal efficiency of Cr (VI) at pH 2 increased from 4 to 80% from 0 to 300 min of time interval. At pH 4, the maximum removal was observed as 90% after 300 min. At pH 6, the removal of Cr (VI) increased from 1 to 84% after 300 min at 2% of adsorbent dosage. It was observed that with increase in contact time from 0 to 300 min, increase in Cr (VI) removal from 2 to 90 % by Eucalyptus leaf litter biomass was found and showed maximum removal at optimum pH 4 with adsorbent dosage of 2%.

Sarma and Battacharya, 2005 earlier reported that the % removal of chromium increases with an increase in pH from 3 to 7. It is conformed that adsorption increases with the decrease in acidity. At low pH, hydrogen ions compete with chromium ions for appropriate sites on the adsorbent. As pH approaches to 7, the competition of hydrogen ions becomes negligible and more chromium ions are bound to the adsorbent. The %

removal decreases as pH increases beyond 7 (Venkateswarlu et al., 2007). With chitosan as adsorbent (Sarin and Pant, 2005), the maximum uptake capacity (50 mg/g) was noted at a pH of 5. The fungi biomass (Keskinkan et al., 2004) removed 64 mg/g at a pH of 4.8. The maximum removal of chromium was reported at a pH of 4 with cationic starch maleate (Xing et al., 2006). The principal driving force for metal ion adsorption is the electrostatic interaction that is, attraction between adsorbent and adsorbate. Greater the interaction, higher will be the adsorption of heavy metal.

Table 15: The effect of pH on the removal efficiency of Cr (VI) by Eucalyptus leaf litter biomass.

Eucalyptus Biomass	Time (min)	pH					
		2		4		6	
		Q	R	Q	R	Q	R
	0	0.02	4	0.01	2	0.005	1
	10	0.05	10	0.055	11	0.115	23
	20	0.19	38	0.195	39	0.205	41
	30	0.22	44	0.295	59	0.240	48
	60	0.295	59	0.295	59	0.255	51
	120	0.3	60	0.31	62	0.30	60
	180	0.3	60	0.34	69	0.315	63
	240	0.36	72	0.435	87	0.35	70
	30	0.40	80	0.45	90	0.42	84

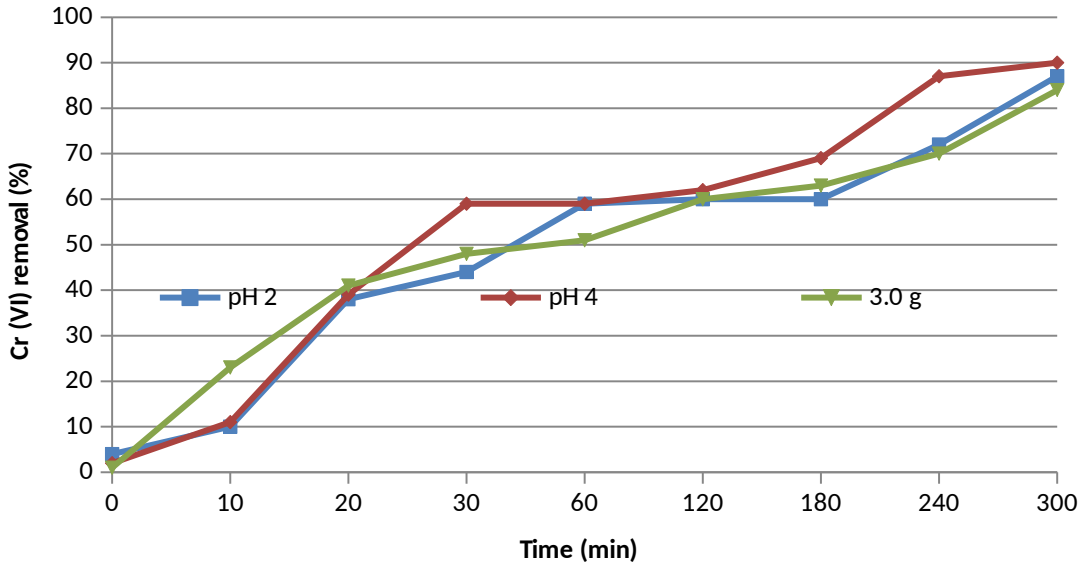


Fig 10: The effect of pH on Cr (VI) removal using Eucalyptus leaf litter biomass

5. Effect of contact time:

To study the effect of contact time, experiments were done where contact time was varied from 0 min to 300 min, for 10 to 100 mg/l of initial metal concentration, with 0.05 to 4% adsorbent dose. Solutions were freshly prepared and the pH of the solution was maintained 5 by using 0.1 N HCl or 0.1 N NaOH. It is observed that the equilibrium time for the process is 60 min. Adsorption equilibrium time is defined as the time required for heavy metal concentration to reach a constant value.

Both specific metal uptake and removal efficiency of Cr (VI) was studied from 0 to 300 min time interval. With increase in contact time (0 to 300 min), both Cr (VI) uptake as well as removal from aqueous solution was increased. The specific uptake increased from 0.8 to 5 mg/g at 0.05% adsorbent dosage by eucalyptus leaf litter biomass. It was found that maximum removal also increased from 5 to 95% (Table 6, Fig2,).

Maximum Cr (VI) removal is observed by Eucalyptus and Bamboo leaf litter biomass followed by Poplar, Wheat husk, mango and Jamun, Ashoka and least by Rice straw (Table 14).

Among all the biomasses, eucalyptus showed maximum removal of Cr (VI) from aqueous solution at pH 5, at 4 % adsorbent dosage at temperature of 28 +_2 with agitation rate of 120 rpm (Table 6, Fig 2).

Battacharya and Sarma, 2004 reported the equilibrium agitation time for adsorption of lead by neem leaf powder as 300 min. Different equilibrium agitation times are reported in literature for the removal of chromium. With the waste pomace from olive oil industry (Malkoc et al., 2006) the equilibrium agitation time is found to be 180 min. It is 90 min with neurospora crassa (Tunali et al., 2005), 120 min with activated alumina and activated charcoal (Mor et al., 2006) and 20 min with cationic starch maleate (Xing et al., 2006).

6. Effect of Combination of biomass in batch mode

6.1 Effect of initial metal concentration

The specific metal uptake capacity (Q) was studied for varied initial metal concentration of Cr (VI) at 1% of adsorbent dosage which was combination of four most efficient biomasses for the time interval of 0 to 300 min.

The specific metal uptake capacity at 10 mg/l of initial metal concentration increased from 0 to 0.98 mg/g after 30 min, after which it got saturated. At 20 and 30 mg/l of initial metal concentration, maximum metal uptake was 0.97 mg/g after 30 min. It became constant after 30 min of time interval, thereby achieving its saturation point. The specific metal uptake at 40 and 50 mg/l of initial metal concentration was 0.96 mg/g and achieved its saturation point after 30 min. Similarly, the specific uptake at 60 and 70

mg/l of initial metal concentration increased to 0.94 mg/g. The uptake capacities at 80, 90 and 100 mg/l of initial metal concentration were 0.90, 0.89 and 0.85 mg/g respectively at 30 min of time interval, after which, saturation point was achieved.

It clearly indicated that the maximum specific uptake capacity was found after 30 min of incubation. Thereafter, it reached equilibrium. The maximum uptake capacity was found at 10 mg/l concentration. Thereafter, it decreased. It was found in order of:
10 mg/l > 20=30 mg/l > 40=50 mg/l > 60=70 mg/l > 80 mg/l > 90 mg/l > 100 mg/l.

The values are 0.98, 0.97, 0.97, 0.96, 0.96, 0.94, 0.94, 0.90, 0.89, and 0.85 (Table 16).

Chromium removal by combination of 4 biomasses i.e. Eucalyptus, Mango, Bamboo and Wheat husk was studied at varying initial concentration i.e. 10 mg/l to 100 mg/l of Cr (VI) in aqueous solution.

The removal efficiency at 10 mg/l of initial metal concentration by combination of biomass increased from 0 to 98% after 30 min, after which it became constant. The removal efficiency at 20, 30, 40, 50 and 60 mg/l of initial metal concentration was 97, 97, 96, 96, and 94% at 30 min of time interval. After this, saturation point was achieved. At 70 mg/l of initial concentration the maximum removal was 94% after 20 min. The removal efficiencies were 90, 89 and 85% for 80, 90 and 100 mg/l of initial metal concentration. Saturation point for the same was achieved after 30 min of time interval. Maximum Cr (VI) removal capacities of mixture of leaf litter biomasses from aqueous solution observed at 10-50 mg/l of Chromium concentration in batch mode. At 10 mg/l, maximum specific metal uptake and removal efficiency was found, 0.98 mg/g and 98% respectively (Table 17, Fig 11).

The sorption characteristic indicated that surface saturation was dependent on the initial metal ion concentration. Evidently such a behavior can be attributed to the maintenance of fixed number of binding sites in the dosage while increasing the concentration. Mohanty et al., 2005, increased the initial concentration of chromium from 10 to 30 mg/L and noticed the decreased adsorption from 100 to 94%. Malkoc et al., 2006 also reported the decreased adsorption of chromium from 61 to 30.4%, as the initial concentration of waste pomace of olive oil factory was increased from 50 to 200 mg/L. As the initial

concentration of cationic starch maleate was increased from 10 to 45 mg/L, the uptake capacities were decreased from 33 to 24 mg/g (Xing et al., 2006).

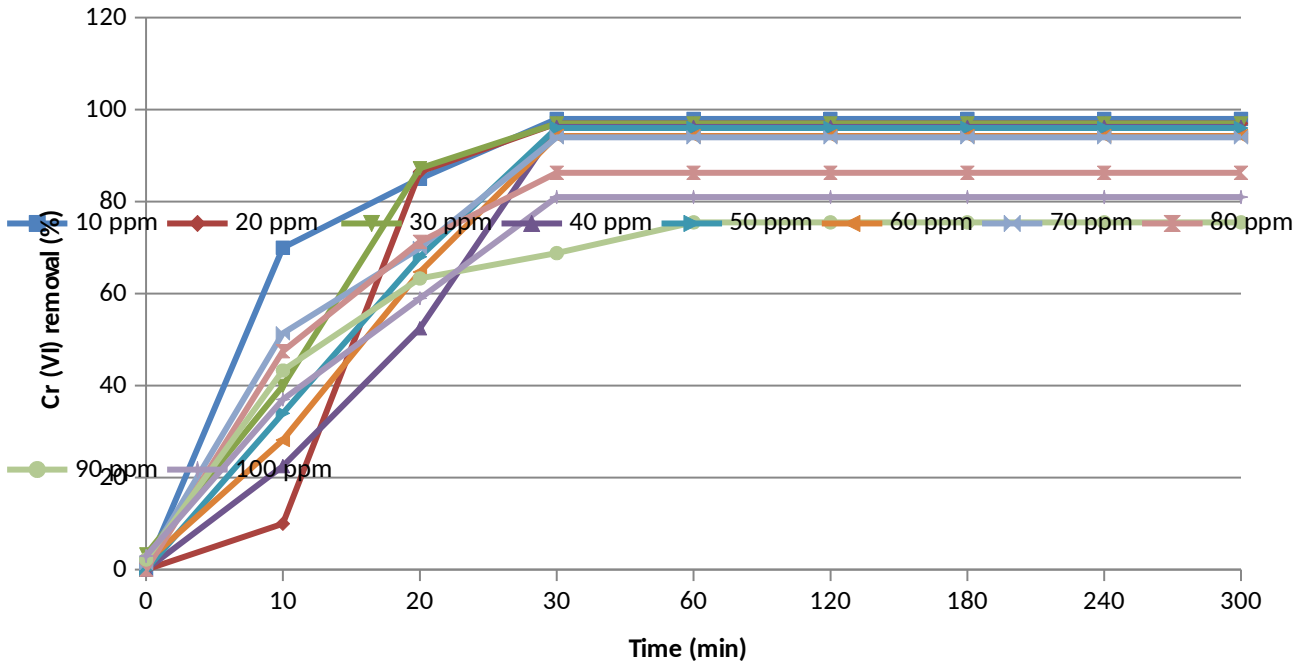
Table 16: The effect of initial metal concentration on the specific metal uptake by combination of biomass.

Time (min)	Initial metal concentration(mg/l)									
	10	20	30	40	50	60	70	80	90	100
0	0	0	0.03	0	0	0.01	0.01	0	0.02	0.03
10	0.7	0.1	0.4	0.22	0.34	0.28	0.52	0.25	0.43	0.37
20	0.85	0.86	0.87	0.52	0.68	0.65	0.94	0.52	0.48	0.59
30	0.98	0.97	0.97	0.96	0.96	0.94	0.94	0.90	0.89	0.85
60	0.98	0.97	0.97	0.96	0.96	0.94	0.94	0.90	0.89	0.85
120	0.98	0.97	0.97	0.96	0.96	0.94	0.94	0.90	0.89	0.85
180	0.98	0.97	0.97	0.96	0.96	0.94	0.94	0.90	0.89	0.85
240	0.98	0.97	0.97	0.96	0.96	0.94	0.94	0.90	0.89	0.85
300	0.98	0.97	0.97	0.96	0.96	0.94	0.94	0.90	0.89	0.85

Table 17: The effect of initial metal concentration on the Cr (VI) removal.

Time (min)	Initial metal concentration(mg/l)									
	10	20	30	40	50	60	70	80	90	100
0	0	0	3.33	0	0	1.66	1.42	0	2	3
10	70	10	39.96	22.5	34	28.22	51.4	25	43	37
20	85	86.5	87.24	52.5	68	64.7	94	52	48	59
30	98	97	97	96.25	96	94.28	94	90	89	85
60	98	97	97	96.25	96	94.28	94	90	89	85
120	98	97	97	96.25	96	94.28	94	90	89	85
180	98	97	97	96.25	96	94.28	94	90	89	85
240	98	97	97	96.25	96	94.28	94	90	89	85
300	98	97	97	96.25	96	94.28	94	90	89	85

Fig 11: The Effect of initial metal concentration on the Cr (VI) removal.



7. Continuous column sorption studies

Adsorption capacity of chromium by dried biomass is a function of contact time with 10% of combination of four most efficient biomass namely, eucalyptus, bamboo, mango and wheat husk in equal proportion. Removal rate of chromium was rapid during first 60 min of influent flow. This type of biosorption is typical for sorption of metals involving metabolically inert biomass, where metal removal from solution is purely due to the physico-chemical interaction between biomass and the metal in solution (Ahluwalia and

Goyal, 2013). During first hour chromium adsorption, when initial metal was 10 mg/l, specific uptake increased from 0 to 0.92 mg/g after 60 min. It further increased to 0.95 mg/g at 120 min of time interval after which it became constant, thereby getting saturated. The removal efficiency increased from 0 to 92% initially after 60 min. It then increased slowly to 95% after 120 min of time interval and thereafter attained a constant value. After a rapid sorption, chromium uptake increased slowly with time and reached equilibrium in two hour, which was consistent with the studies carried out in batch mode and then it decreased (Table 18, Fig. 12).

During influent flow of 20 mg/l chromium up to 60 min, the specific uptake increased to 0.09 mg/g and order of total chromium removed was 94%. The order of specific uptake and removal after 120 min of run time was also 0.09 mg/g and 90% respectively. Nearly 70% of Cr (VI) removal occurs within 20 min, which subsequently increased with time and nearly complete removal was obtained within 300 min (Table 18, Fig. 13).

Table 18: Effect of initial metal concentration on uptake and removal of Cr (VI) in continuous mode using combination of biomass

Time (min)	10 mg/l		20 mg/l	
	Q (mg/g)	R (%)	Q (mg/g)	R (%)
0	0	0	0	0
10	0.67	67	0.02	20
20	0.76	76	0.07	79
30	0.87	87	0.08	89
60	0.92	92	0.09	94
120	0.95	95	0.09	94
180	0.95	95	0.09	94
240	0.95	95	0.09	94
300	0.95	95	0.09	94

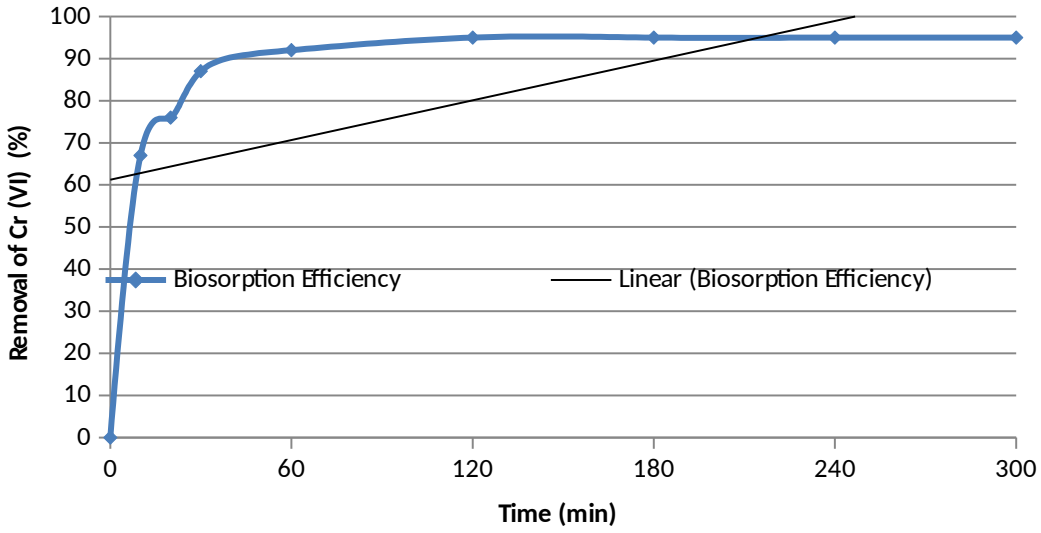


Fig. 12: Effect of initial metal concentration on Cr (VI) removal in continuous mode (CI=10 mg/l).

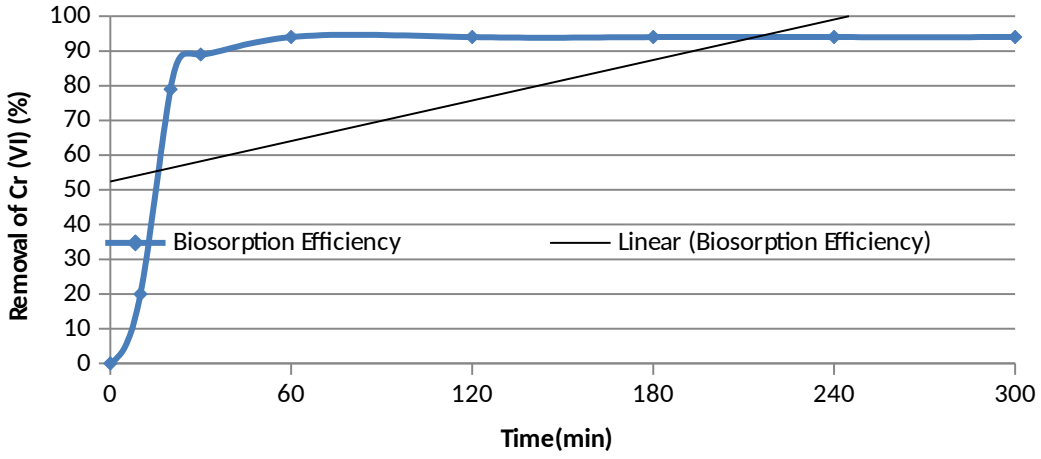


Fig. 13: Effect of initial metal concentration on Cr (VI) removal in continuous mode (Ci=20 mg/l).

8. Adsorption isotherms

The feasibility and effectiveness of the biosorption was predicted from conventional single solute adsorption isotherm models such as Langmuir and Freundlich adsorption isotherms. The degree of sorption of metal on a biosorbent at equilibrium was found to be a function of metal ion concentration in solution at constant pH and temperature.

Correlation coefficient (R^2) value indicated good correlation between the experimental data and Langmuir model, where it was found to be greater 0.9 for Ashoka, Bamboo, Mango, Poplar, wheat husk and rice straw indicating that the physico-chemical adsorption is involved in metal binding at the concentration of chromium (10 mg/l). The correlation coefficient for Eucalyptus and Jamun leaf litter biomass was found to be 0.803 and 0.897 respectively (Table 19).

Freundlich adsorption model indicates ion exchange involved in metal binding. It is greater than 0.7 for Ashoka, Mango, Poplar and Jamun leaf litter biomass. It is greater than 0.8 for Eucalyptus, Bamboo, Wheat husk and Rice straw (Table 19).

Among all the biomasses, Langmuir model fit well in ashoka, bamboo, mango, poplar, wheat husk and rice straw. Freundlich model fitted well only in eucalyptus, bamboo, wheat husk and rice straw.

Table 19: Values of experimental equilibrium constants, adsorption of hexavalent chromium by different leaf litter biomass

Biomass	Langmuir			Freundlich		
	K	b	R^2	n	K_f	R^2
Eucalyptus	0.843	0.611	0.803	2.144	0.294	0.811
Ashoka	0.227	1.11	0.940	0.693	0.121	0.735
Bamboo	0.526	0.852	0.965	0.901	0.220	0.807
Mango	0.028	3.435	0.946	0.514	0.028	0.799
Poplar	0.061	1.926	0.950	12.6	0.04	0.780
Wheat husk	-0.130	-0.501	0.991	27.7	0.011	0.837
Jamun	-0.0411	-1.676	0.897	23.74	0.018	0.789
Rice straw	-0.117	-0.047	0.934	7.55E+82	3.575E-35	0.841

9. Infrared spectroscopy

To ascertain the chemical nature of binding sites for chromium, Fourier transform infrared spectral analysis (FTIR) of native and chromium laden mixture of biomass was carried out. Combination of four most efficient leaf litter biomass namely Eucalyptus, Bamboo, Mango and wheat husk biomass were evaluated for FTIR analysis. Metal Native biomass showed number of absorption peaks, indicating the complex nature of biomass. Uptake of metal took place through a reversible association of ions with the functional groups present on the cell surface. Most prominent functional groups in biomass sample were

aliphatic amines, primary amines and alkanes, and major peaks were 1029.79, 1627.60, 2923.52 cm^{-1} (Fig. 14, 15). The peaks in fingerprint based on literature values are summarized in Table 20 (Adel *et al.,* 2011).

Table 20: Assignment of FTIR bands of functional groups in biomass sample.

S.No.	Name of characteristic group	Wavenumber (cm^{-1})
1	Alkynes	667.242
2	Aliphatic amines	1029.79
3	Primary amines	1627.60
4	Alkanes	2923.52
5	Alcohols, H-bonded phenols	3343.926

Native Biomass

FTIR spectrum of native mixture of biomass displayed a number of absorption peaks at 667.242 indicating for the presence of *C*≡*C*-H:C-H bend of alkynes , 1035.57 is designated to C-N stretch of aliphatic amines, 1320.98 is related with N-O symmetric stretch of nitro compounds, 1614.109 for N-H bend indicating primary amines, 2921.596 for C-H stretch indicating alkanes and 3334.28 cm^{-1} indicating presence of N-H stretch for primary and secondary amines and amides groups respectively on cell surface (Fig. 14).

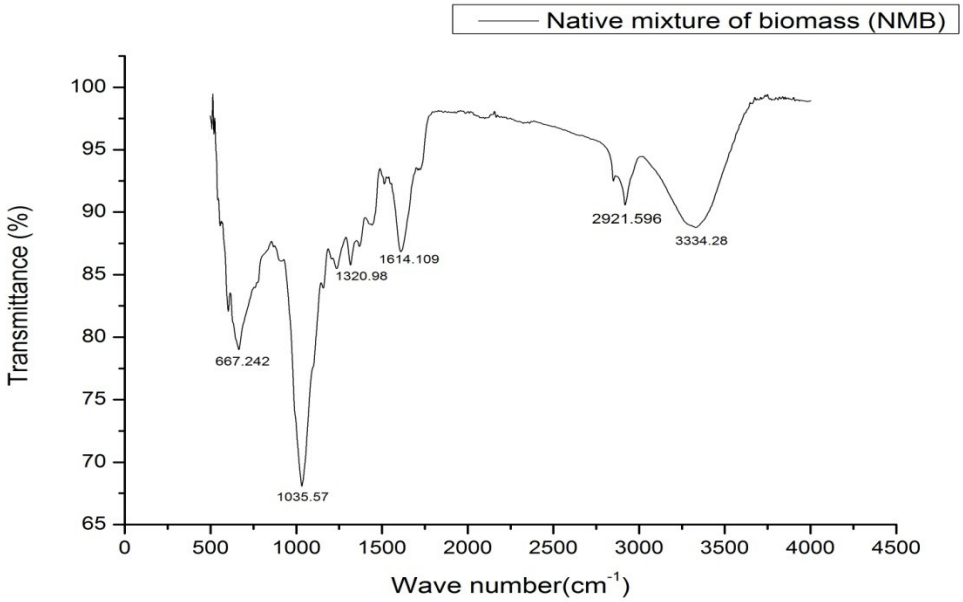


Fig. 14: FTIR of native mixture of biomass (NMB).

Metal laden mixture of biomass

FTIR spectrum of native mixture of biomass displayed a number of absorption peaks at 663.38 cm^{-1} indicating for the presence of -*C*≡*C*-H:C-H bend of alkynes, 1029.79 cm^{-1} is designated to C-N stretch of aliphatic amines, 1220.63 cm^{-1} is related with C-N stretch of aliphatic amines, 1627.60 cm^{-1} for N-H bend indicating primary amines, 1731.74 cm^{-1} for C=0 stretch for aldehydes, saturated aliphatic which was not present in native mixture of biomass, 2923.52 cm^{-1} is attributed to C-H stretching vibration. Deep band at 3343.926 cm^{-1} indicating presence of O-H stretching vibrations caused by presence of alcoholic and phenolic hydroxyl group involved in hydrogen bond (Fig. 15).

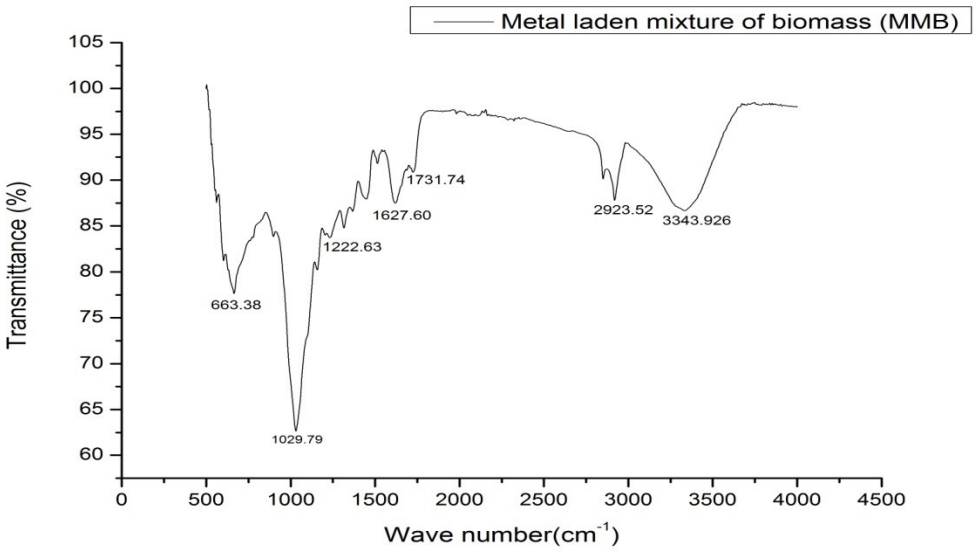


Fig 15: FTIR of metal laden mixture of biomass (MMB)

Comparison

On comparing native and metal laden mixture of biomass, the O-H stretching band was changed to higher wave number and somewhat broadened which is an indication of weaker intra and intermolecular hydrogen bonding and thereby lower crystallinity. (Jeihanipour et al., 2009). Enhancement in intensity of peak was shown in metal laden mixture of biomass at 2923.52 cm^{-1}. A study reported the similar phenomena indicating the rupturing of methyl and methylene portions in cellulose (Xiao et al., 2011). A new peak was observed at 1731.74 cm^{-1} indicating involvement of aldehydes, saturated aliphatic groups on cell surface.

CONCLUSIONS

1. Wheat husk and Ashoka showed biosorption of 8.4 and 8.2 mg of hexavalent chromium per gram of dry biomass, whereas eucalyptus and bamboo showed 95 and 94% removal of Cr (VI) from 10 mg/l of metal containing aqueous solution

2. Out of all the 8 different leaf litter biomasses used, Eucalyptus showed the maximum removal, followed by bamboo, poplar and wheat husk.

3. The highest equilibrium uptake (Q) was observed at 1 g biomass concentration after 60 min for Cr (VI) by Eucalyptus biomass (0.61 mg/g). The highest removal efficiency was observed by Eucalyptus (61%).

4. In continuous sorption column packed with dry biomass of combination of four different leaf litter biomass namely, Eucalyptus, Bamboo, Mango and Poplar in the ratio of

1:1:1:1, 95% and 94% of metal removal at 10 mg/l and 20 mg/l of initial metal concentration was observed.

5. The extent of adsorption increased with increase in the adsorbent concentration. Maximum adsorption was observed at 4g concentration of biomass. In batch mode sorption studies, adsorption increased upto 50 mg/l of initial metal concentration and after that there was decrease in the adsorption.

6. Equilibrium sorption data of Cr (VI) was used to predict conventional Langmuir and Freundlich isotherm, which suggested involvement of either physico-chemical or ion exchange interaction in chromium binding.

7. Fourier transform infrared spectral analysis revealed that different types of functional groups, aliphatic amines, primary amines and alkanes played an important role in metal binding.

8. This study showed that waste leaf litter biomass generated in great quantities can be used for Cr (VI) removal in waste water treatment as an effective alternative. Leaf litter biomass used as an adsorbent has given significant results, which shows that the biosorption technology can be scaled up to industrial scale to treat chromium effluent at low cost with no generation of toxic chrome sludge.

BIBLIOGRAPHY

1. Adel A. M., El Wahab Z .H. A., Ibrahim A. A. and Al -Shemy M. T. (2011). Characterization of microcrystalline cellulose prepared from lignocellulosic materials. Part II: Physicochemical properties. Carbohydrate Polymers, 83(2): 676-687.

2. Ahluwalia S. S. and Goyal D. (2004). Utilization of paper mill sludge for the removal of heavy metals from aqueous solution. Res. J. of Chem. And Environ, 8(2): 34-37.

3. Ahluwalia S.S. and Goyal D. (2005). Removal of heavy metals by waste tealeaves from aqueous solution. Engineering in life Sciences, 5:158–162.

4. Ahluwalia S. S. and Goyal .D. (2007). Microbial and Plant derived biomass for removal of heavy metals from wastewater. Biores. Technol, 98(12): 2243-2257.

5. Ahluwalia S.S. and Goyal D. (2010). Removal of Cr(VI) from aqueous solution by fungal biomass. Engineering in Life Sciences, 10(5):480-485.

6. Ali A.H. (2011). Performance of Adsorption/Biosorption for Removal of Organic and Inorganic Pollutants", Ph.D. Thesis, University of Baghdad, College of Engineering.

7. Ariff, A.B., Mel, M., Hasan, M.A. and Karim M.I.A. (1999). The kinetics and mechanisms of lead(II) biosorption by powderized Rhizopus olgisporus. World Journal of Microbiology Biotechnology 15: 291–298.

8. Baillet F., Magnin J..P., Cheruy A., Ozil, P. (1998). Chromium precipitation by the acidophilic bacterium Thiobacillus ferrooxidans. Biotechnology Letters 20 (1):95–99.

9. Bansode R. R. (2002). Treatment of organic and inorganic pollutants in municipal Wastewater by agricultural by-product based Granular Activated Carbons (GAC).

10. Battacharya K.G. and Sarma A. (2004). Adsorption of Pb (II) from aqueous solution by *Azardirachta indica* (neem leaf powder). J. Hazard. Mater, B113: 97-109.

11. Benedict M., Pigford T.H. and Levi H.W. (1981). The values are for Pu from fuel discharged after 33 MWth-d/Kg burnup at 80% capacity factor and 150 days of post-irradiation cooling. Nuclear Chemical Engineering, 144-145.

12. Beveridge T. C. and Doyle R. J. (1989). Metal ions and bacteria. Wiley Interscience, New York.

13. Brady J.M., Tobin J.M. and Roux J.C. (1999). Continuous fixed bed biosorption of Cu_{2+} ions: application of a simple two parameter mathematical model. J Chem Technol Biot, 74: 71-77.

14. Brown B. and Absanullah M. (1971). Effects of heavy metals on mortality and growth. Mar Pollut Bull, 2(1971): 182–187.

15. Chand S., Agarwal V.K., Pavankumar C. (1994). Removal of hexavalent chromium from wastewater by adsorption. Indian J. Environ. Health, 36: 151-158.

16. Chen J. M. and Hao O. J. (1998). Microbial chromium (VI) reduction. Critical Reviews in Environmental Sciences and Technology, 28: 219-251.

17. Cheung K. H. and Gu Ji-D. (2007). Mechanism of heaxvalent chromium detoxification by microorganism and bioremediation application potential: A review. Intl. Biodeterioration and Biodegradation, 59: 8-15.

18. Cho, D.H. and Kim, E.Y. (2003). Characterization of Pb2+ biosorption from aqueous solution by Rhodotorula glutinis. Bioprocess Biosystem Engineering 25:271–277.

19. Crist D.R., Crist R.H., Martin J.R. and Watson J. (1993). In Metals-Microorganisms Relationships and Applications, FEMS Symposium Abstracts, Metz, France, May; Bauda, P., Societe Francaise de Microbiologie: Paris, France.13.

20. Crist R.H., Martin J.R., Carr D., Waston J.R., larke H.J. and Crist D.R. (1994). Interaction of metals and protons with algae. Environ. Sci.Technol, 28:1859-1866.

21. Dakiky M., Khamis M., Manassra A. and Mereb M. (2002). Selective adsorption of Cr (VI) in industrial waste water using low cost abundantly available adsorbents, Adv. Environ. Res, 6: 533-540.

22. Deepak B., (1990). Women and the Management of Energy, Forests and other Resources, Mountain Population and Environment Discussion Paper Series No. 3, International Center for Integrated Mountain Development (ICIMOD), Kathmandu, Nepal, March.

23. Demirbas E., Kobya M., Senturk E. and Ozkan T. (2004). Adsorption kinetics for the removal of chromium (VI) from aqueous solutions on the activated carbons prepared from agricultural wastes. Water SA, 30(4): 533–540.

24. Diniz V. and Volesky B. (2005). Biosorption of La, Eu and Yb using Sargassum biomass. Water Res, 39: 239-247.

25. Diniz, V., Weber, M.E., Volesky, B. and Naja, G. (2008). Column biosorption of lanthanum and europium by sargassum. Water Research 47:363-371.

26. Dobrowolski R. and Otto M. (2010). Study of chromium (VI) adsorption onto modified activated carbons with respect to analytical application, Adsorption 16(4-5): 279–286.

27. Draft Public Health Goal for Hexavalent Chromium. (2009). A fact sheet by the Office of Environmental Health Hazard Assessment, California Environmental Protection Agency.

28. Dula T., Siraj K. and Kitte S.A. (2014). Adsorption of Hexavalent Chromium from Aqueous Solution Using Chemically Activated Carbon Prepared from Locally Available Waste of Bamboo (*Oxytenanthera abyssinica*). Hindawi Publishing Corporation ISRN Environmental Chemistry. 9.

29. Freundlich H. 1907. Ueber die Adsorption in Loesungen. Zeitschrift fr Physikalische Chemie, 57(A): 385-470.

30. Fourest E. and Volesky B. (1996). Contribution of sulphonate groups and alginate to heavy metal biosorption by the dry biomass of *Sargassum fluitans*. Environ. Sci. Technol, 30:277-282.

31. .Fu Y. and Liu D. (2007). Novel experimental phenomena of fine-particle fluidized bed. Experimental Thermal and Fluid Science, 32: 341-344.

32. Gardea-T. J. L., Rosa D. L., Peralta G. and Videa. J. R. (2004a). Use of phytofilteration technologies to remove the heavy metals: a review.Pure and Applied Chemistry, 74 (4): 801–803.

33. Gardea T. J. L., Videa P. J. R., Montes. M. LaRosa G. and Corral-Diaz B. (2004b). Bioaccumulation of cadmium, chromium and copper by Convolvulus arvensis L.: Impact on plant growth and uptake of nutritional elementsBioresource Technology, 92:229–235.

34. Garg, D. D.,Arya, R. S. ; Sharma, T. andDhuria, R. K. (2004). Effect of replacement of sewan straw (*Lasirus sindicus*) by moong (*Phaseolus aureus*) chara on rumen and haemato-biochemical parameters in sheep. Vet. Practitioner, 5 (1): 70-73.

35. Goyal N., Jain S.C. and Banerjee U.C. (2003). Comparative studies on the microbial adsorption of heavy metals. Advances in Environmental Research, 7: 311-319.

36. Gray, N.F. (1999). Water Technology, 473–474.

37. Gupta V.K., Rastogi A. and Nayak A. (2010). Adsorption studies on the removal of hexavalent chromium from aqueous solution using a low cost fertilizer industry waste material. Journal of Colloid and Interface Science, 342(1): 135–141.

38. Hamadi N.K., Chen X.D., Farid M.M. and Lu M.G.Q. (2001). Adsorption kinetics for the removal of chromium (VI) from aqueous solution by adsorbents derived from used tyres and sawdust, Chem. Eng. J, 84:95–105.

39. Hossain M.A., Ngo H.H., Guo W.S. and Setiadi T. (2012). Adsorption and desorption of copper (II) ions onto garden grass. Bioresour Technol, 121: 386-395.

40. Ilamathi R., Nirmala G.S. and Muruganandam L. (2014). Heavy Metals Biosorption in Liquid Solid Fluidized Bed by Immobilized Consortia in Alginate beads. International Journal of ChemTech Research CODEN (USA), 6(1): 652-662.

41. ISI, Drinking water specifications (DWS), IS 10500 (1991)

42. Jeihanipour A. and Taherzadeh M.J. (2009). Ethanol production from cotton-based waste textiles. Bioresour. Technol.,100 (2), 1007-1010.

43. Karakas S. Y., Aygun A., Gunes M. and Tahtasakal E. (2004). Physical and chemical characteristics of polymer-based spherical activated carbon and its ability to adsorb organics. Carbon, 42(3): 477–484.

44. Kinniburgh D.G. 1986. General purpose adsorption isotherms, Environ. Sci. Technol.20:895-904.

45. Kim H., Baek K., Kim B. K., Shin H. J. and Yang J. W. (2008). Removal characteristics of metal cations and their mixtures using micellar-enhanced ultrafiltration. Korean J of Chemical Engineering, 25: 253-258.

46. Karthikeyan T., Rajgopal S. and Lima R.M. (2005). Chromium (VI) adsorption from aqueous solution by Hevea brasilinesis saw dust activated carbon, J. Hazard. Mater, B124: 192-199.

47. Keskinkan O., Goksu M.Z.L., Basibuyuk M. and Forster C.F. (2004). Heavy metal adsorption properties of a submerged aquatic plant (Ceratophyllum demersum). Bioresource Technolog, 92:197–200.

48. Khan N.A. and Mohamad H. (2007).Investigations on the removal of chromium (VI) from wastewater by sugarcane bagasse, Water & Wastewater Asia, Jan/Feb.

49. Kratochvil D. and Volesky B. (1995). Biosorption of copper by sargassum biomass in fixed bed column. Biotechnol. Lett, 17:777-782.

50. Kratochvil D. (1997) A study of the metal biosorption process utilizing Sargassum seaweed biomass, Ph.D Thesis, McGill University, Department of Chemical Engineering.

51. Kuyucak N. and Volesky B. 1989a. Accumulation of gold by algal biosorbent. Biorecovery. 1:1489-204.

52. Kuyucak N. and Volesky B. (1990). Biosorption by algal biomass. Biosorption of Heavy metals; Volesky, B.,ed., CRC Press: Boca Raton. FL. 173-198.

.

53. Liu G. F., Yang H., Wang J., Jin R. F., Zhou J. T. and Lv H. (2010). Enhanced chromate reduction by resting Escherichia coli cells in the presence of quinone redox mediators. Bioresour. Technol, 101: 8127–8131.

54. Malkoc, E., and Nuhoglu, Y. (2006). Removal of Ni(II) ions from aqueous solutions using waste of tea factory: Adsorption on a fixed bed column J. Hazard. Mater, B135 : 328 -336.

55. Mayers T. and Beveridge T.J. (1989). The sorption of metals to *Bacillus subtilis* walls from dilute solutions and simulated Hamilton harbour (Lake Ontario) water. Can. J. Microbial, 35:764-770

56. Mansri A., Benabadji K. I., Desbrieres J. and Francois J. (2009). Chromium removal using modified poly (4-vinylpyridinium) bentonite salts. Desalination, 245(1–3): 95–107.

57. Matheickal J. T. and Yu Q. (1999). Biosorption of lead (II) and Copper (II) from aqueous solution by pretreated biomass of Australian marine algae. Bioresour Technol, 69: 223-229.

58. McKay G., Ho Y.S. and Ng J.C.Y. (1999). Biosorption of Copper from Waste Waters: A Review. Separation & Purification Reviews, 28: 87-125

59. Melcakova I. and Ruzovic T. (2010). Biosorption of Zink from Aqueous Solution Using Algae and Plant Biomass. Nova Biotechnologica, 10(1): 33-43.

60. McDougall G. J. and Fleming C. A. (1987). Extraction of precious metals on activated carbon, in Ion Exchange and Sorption Processes in Hydrometallurgy, Ed. by Streat, M. and Naden, D. Critical Reports on Applied Chemistry, 19: 56-126.

61. Modak J.M. and Nataranjan K.A. (1195). Biosorption of metals using nonliving biomass - A review. Mineral Metallurgical Process, 12(4):189-196.

62. Mohanty, A. K., Misra, M., Drzal, L. T., Selke, S. E., Harte, B. R., and Hinrichsen, G. (2005). Natural fibers, biopolymers and biocomposites: An introduction," In:Natural Fibers, Biopolymers and Biocomposites, CRC Press, London.

63. Moore J. W. (1990). Inorganic Contaminants of Surface Water Residuals and Monitoring Priorities.New York: Springer-Verlag: 178–210.

64. Mor S, Ravindra K, Dahiya RP, Chandra A (2006). Leachate Characterization and assessment of groundwater pollution near municipal solid waste landfill site. Environ. Monit. Assess., 4: 325-334.

65. Morales B. L. and Cristiani U. E. (2008). Hexavalent chromium removal by a *Trichoderma inhamatum* fungal strain isolated from tannery effluent. Water, Air, Soil Pollut, 187: 327-336.

66. Murugan M. and Subramanian E. (2003). Biosorbent Cupressus Femail Cone in the efficient treatment of effluent containing Cr(VI). Journal of Scientific and Industrial Research, 62:1071–1078.

67. Nriagu J.O. and Nieboer E. (1988). Chromium," in *Natural and Human Environment"*. Wiley, New York, NY, USA.

68. Overview of mining and mineral industry in India New Delhi. 2001. Tata Energy Research Institute. 42:94.

69. Owlad M., Aroua M. K., Daud W. A. W. and Baroutian S. (2008). Removal of hexavalent chromium-contaminated water and wastewater. Springer science + business media b.v.

70. Park, J., Lee, S.B., Lee, S., Kim, Y., Song, S., Kim, S., Bae, E., Kim, J., Shong, M., Kim, J.M., Chung, J. (2006). Mitochondrial dysfunction in Drosophila PINK1 mutants is complemented by parkin. Nature 441(7097): 1157--1161.

71. Prasanjit B. and Sumathi S. (2005). Uptake of chromium by *Aspergillus foetidus*. Journal of Material Cycles and Waste Management, 7:88–92.

72. Ramirez O. H. and Holmes S. M. (2008). Novel and modified materials for wastewater treatment applications. Journal of Materials Chemistry.

73. Rathinam A., Maharshi B., Janardhanan S.K, Jonnalagadda R.R. and Nair B.U.(2010). Biosorption of cadmium metal ion from simulated wastewaters using *Hypnea valentiae* biomass: A kinetic and thermodynamic study. Biores. Technol, 101: 1466–1470.

74. Ridha M.J. (2011). Competitive Biosorption of Heavy Metals Using Expanded Granular Sludge Bed Reactor, Ph.D. Thesis, University of Baghdad, College of Engineering.

75. Rao R.S., Jyothi C. P., Prakasham R. S., Sarma P.N. and Rao L.V. (2006). Xylitol production from corn fiber and sugarcane bagasse hydrolysates by *Candida tropicalis*. Bioresource Technology, 97: 1974-1978.

76. Raoa L. N. and Prabhakar G. (2011). Removal Of Heavy Metals By Biosorption–An Overall Review. Journal Of Engineering Research And Studies, 0976-7916.

77. Romera E., González F., Ballester A., Blázquez M.L. and Muñoz J.A. (2006) Biosorption with algae: a statistical review. Crit Rev Biotechnol, 26: 223-235.

78. Romera E., Gonzalez F., Ballester A., Blazquez M.L. and Munoz J.A. (2007). Comparative study of biosorption of heavy metals using different types of algae. Bioresource Technol, 98: 3344-3353.

79. Salehizadeh H. and Shojaosadati S.A. (2003). Removal of metal ions from aqueous solution by polysaccharide produced from Bcillus firmus.Water Research, 17:4231–4235.

80. Samanta G., Chowdhury T.R., Mandal B.K., Biswas B.K.,Chowdhury U.K., Basu G.K., Chanda C.R., Lodh D. and Chakraborti D. (1999). Flow injection hydride generation atomic absorption spectrometry for determination of arsenic in water and biological samples from arsenic-affected districts of West Bengal, India and Bangladesh. Microchem J, 62:174-191.

81. Saraj M. A., Abdel-Latif M. S., El-Nahal I. and Baraka R. (1999). Bioaccumulation of some hazardous metals by sol–gel entrapped microorganisms. J. Non-Cryst. Solids, 248: 137–140.

82. Sarin V. and Pant K.K. (2005). Removal of chromium from industrial waste by using eucalyptus bark. Bioresour Technol, 97(1):15-20.

83. Sarma, P. M., Bhattacharya, D., Krishnan, S., & Lal, B. (2004). Degradation of Polycyclic Aromatic Hydrocarbons by a Newly Discovered Enteric Bacterium, *Leclercia adecarboxylata*. Applied and Environmental Microbiology, *70*(5), 3163–3166. doi:10.1128/AEM.70.5.3163-3166.2004

84. Schiewer S. and Volesky B. (1996). Modeling Multi-Metal Ion Exchange in Biosorption. Environ Sci Technol, 30: 2921-2927.

85. Selvi K., Pattabhi S. and Kadirvelu K. (2001). Removal of Cr (VI) from aqueous solution by adsorption onto activated carbon, Bioresource Technology, 80: 87-89.

86. Sharma D.C. and Forster C.F. (1995). Column studies into the adsorption of chromium (VI) using sphagnum moss peat. Bioresource Technol, 52: 261-267.

87. Song H. X., Liu Y. G., Xu W. H., Zeng G. M., Aibibu N., Xu L. and Chen B. B. (2009). Simultaneous Cr (VI) reduction and phenol degradation in pure cultures of *Pseudomonas aeruginosa* CCTCCAB91095. Bioresour. Technol, 100: 5079–5084.

88. Srinath T., Verma T., Ramteke P.W. and Garg S.K. (2002). Chromium (VI) biosorption and bioaccumulation by chromate resistant bacteria.Chemosphere, 48:427–435.

89. Sulaymon A.H., Ebrahim, S.E., Abdullah S.M. and Al-Musawi, T. (2010). Removal of Lead, Cadmium,and Mercury Ions Using Biosorption. Desalination and Water Treatment, 24:344-352.

90. Sulaymon A.H., Ebrahim S.E., Abdullah S.M. and Al-Musawi T.J. (2012). Removal of lead, cadmium, and mercury ions using biosorption. J Desalination and Water Treatment, 24: 344-352.

91. Sulaymon A.H., Mohammed A.A., Al-Musawi T.J. (2013). Column Biosorption of Lead, Cadmium, Copper, and Arsenic ions onto Algae. J Bioprocess Biotech, 3: 128

92. Sumathia K. M. S., Mahimairajja S. and Naidu R. (2005). Use of low-cost biological wastes and vermiculite for removal of chromium from tannery effluent. Bioresource Tecchnology, 96(3): 309-316.

93. Sun X.F., Ma Y., Liu X. W., Wang S. G., Gao B. Y. and Li X. M. (2010), Sorption and detoxification of chromium (VI) by aerobic granules functionalized with polyethylenimine. Water Research In Press.

94. Tiemann K. J., Gardea-Torresdey J.L., Gamez G., Dokken K. and Sias S. (1999). Use of X-ray absorption spectroscopy and esterification to investigate chromium (III) and nickel(II) ligand in alfalfa biomass. Environmental Science & Technology, 33:150–154.

95. Tsezos M. and Volesky B. (1981). Biosorption of uranium and thorium. Biotechnology & Bioengineering, 23:583–604.

96. Tunali S, Kiran I, Akar T (2005) Chromium (VI) biosorption characteristics of *Neurospora crossa* fungal biomass. Minerals Engineering,18:681-689.

97. Venkateswarlu P., Venkata R.M., Subba Rao D. and Venkateswara R.M. (2007). Removal of chromium from an aqueous solution using *Azadirachta indica* (neem) leaf powder as an adsorbent. International Journal of Physical Sciences, 2 (8): 188-195.

98. Villaescusa I., Fiol N., Martinez M., Miralles N., Poch J. and Serarols J. (2004). Removal of copper and nickel ions from aqueous solutions by grape stalks wastes.Water Research, 38:992–1002.

99. Viera M., Curutchet G. and Donat E. (2003). A combined bacterial process for the reduction and immobilization of chromium. Int Biodeterior Biodegrad, 52:31–34.

100. Vijayaraghavan K. and Yun Y. S. (2008). Polysulfone-immobilized *Corynebacterium glutamicum*: a biosorbent for reactive black 5 from aqueous solution in an upflow packed column. Chem. Eng. J, 145: 44-49.

101. Volesky B (1986). Biosorbent materials. Biotechnol Bioeng Symp, 16:121-126.

102. Volesky(ed). 1990. Biosorption of heavy metals. CRC Press, Boca Raton, Florida.

103. Volesky B. (1992). Biosorption of heavy metals. CRC press, 13-14.

104. Xing H, Lawrance C.B., Chambers O., Davis H.M. and Everett M.P.(2006). XB-ART-34536 Planta. April 1, 2006; 223 (5): 1024-32. Increased pathogen resistance and yield in transgenic plants expressing combinations of the modified antimicrobial peptides based on indolicidin and magainin. Planta, 223 (5): 1024-32.

105. Xu J., Song X. C., Zhang Q., Pana H., Liang Y., Fan X. W. and Li Y. Z. (2011). Characterization of metal removal of immobilized Bacillus strain CR-7 biomass from aqueous solutions. J. Hazard. Mater, 187: 450–458.

106. Wang D., McLaughlin E., Pfeffer R., Lin Y.S. (2011). Aqueous phase adsorption of toluene in a packed and fluidized bed of hydropholic aerogels. Chemical Engineering168: 1201-1208

107. Wang J. and Chen C. (2009). Biosorbent for heavy metal removal and their future. Biotech. Adv, 27:195-226.

108. Wang W. Q., Li M. Y. and Zeng Q. X. (2012). Thermodynamics of Cr (VI) adsorption on strong alkaline anion exchange fiber. Transactions of Nonferrous Metals Society of China, 22(11): 2831–2839.

109. Wang Y. and Xiao C. (1995). Factors affecting hexavalent chromium reduction in pure cultures of bacteria. WaterRes, 24:2467–2474.

110. White C., Wilkinson S. C. and Gadd G. M. (1995). The role of microorganisms in biosorption of toxic metals and radionuclides. Int Biodeterior Biodegradation, 35: 17–40

111. Yalcinkaya Y., Arica M.Y., Soysal L., Denzili A., Genc O. and Bektas S. (2002). Cadmium and mercury uptake by immobilized *Pleuritus sapidus*.Turk Journal of Chemistry, 26:441–452.

112. Yun Y.S., Park D., Park J.M. and Volesky B. (2001). Biosorption of trivalent chromium on the brown seaweed biomass. Environ. Sci. Technol, 35:4353-4358.

113. Zhang L., Zhao L., Yu Y and Chen C. (1998). Removal of lead from aqueous solution by non-living *Rhizopus nigricans.* Water Res., 32:1437-1444.