CHAPTER 1

1. INTRODUCTION

1.1 Statement of pollution problem

Several necessities arise from continuous human population growth that causes rapid industrialization and urbanization and these have resulted in the generation of large quantities of harmful substances. Aqueous toxic substances are mainly heavy metals, dyes and organic compounds generated as industrial effluents. Although heavy metals are mostly found in nature, they are artificially discharged at much higher concentrations, which significantly accumulate in both soil and water systems. Different heavy metals are generated from various types of industries and finally discharged into the environment. Some metals are emerging as an important class of human carcinogens. At least five transition metals: arsenic, cadmium, chromium VI, beryllium, and nickel are accepted as human carcinogens in one form or another or in particular routes of exposure. Metal ions in their soluble form pose a great threat, as these are easily transported and taken up by living ecosystems. The regular accumulation even at low concentrations from different sources into the human organs may cause different diseases and disorders as shown in Table 3. The toxicity of metal ion is owing to their ability to bind with protein molecules and prevent replication of DNA and thus subsequent cell division [1], it is essential to remove heavy metals from industrial wastewater before being discharged into the environment. Numerous physico-chemical and biological processes are generally employed to remove pollutants from industrial wastewater before discharging into the environment [2]. Different conventional treatment processes such as membrane separation, electrodialysis, precipitation, coagulation, ion exchange, carbon adsorption have been used for the separation of heavy metals. Particularly precipitation and coagulation become less effective and more expensive when adsorbates are at a low concentration range [3-5]. Although activated carbons and ion exchange resins have been recognized as effective commercial adsorbents for the removal of industrial pollutants, the former due to its high cost, low efficiency and non-selective nature has reduced its popularity as adsorbent. On the other hand, ion exchange resin is effective for large volume operations, since such resins are made up of plastic materials their disposal after exhaustive use make difficult owing to the generation of dioxane in the incineration process. To date, bio-adsorption has been recognized as an alternative and effective process of metal ion removal from aqueous solutions.

Adsorption processes may be classified as physical or chemical. Physical adsorption does not involve the sharing or transfer of electrons and is essentially reversible. It has a low degree of specificity; thus, adsorbed molecules are free to cover the entire surface of the adsorbent. A physisorbed molecule keeps its identity and upon desorption returns to the fluid phase in its original form. Chemisorption, on the other hand, involves chemical bonding and is essentially irreversible. Chemisorbed species are fixed at specific sites and are linked to reactive parts of the adsorbent surface, confining the adsorption to a monolayer. The extent of chemical adsorption is dependent on the reactivity of the adsorbent and adsorbate. Many cases are actually an intermediate of physical and chemical adsorption, with both pore structure and reactive functional groups contributing to metal removal. Such is the case with peat which had been found to be effective for the wastewater treatment. The efficiency and adsorption capacity depends on the nature of both bio-sorbents and metal ions in the wastewater. Although various conventional methods have been used to sequester heavy metals from contaminated water, however, these methods have some disadvantages like incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste products that need careful disposal [6]. With increasing environmental awareness legal constraints being imposed on discharge of effluents, a need for cost-effective alternative technologies are essential. In this endeavor, agricultural biomass has emerged as an option for developing low cost and eco-friendly wastewater treatment processes.

Metals, a major category of globally-distributed pollutants, are natural elements that have been extracted from the earth and harnessed for human industry and products for millennia. Metals are notable for their wide environmental dispersion from such activity; their tendency to accumulate in certain tissues of the human body; and their overall potential to be toxic even at relatively minor levels of exposure. Today heavy metals are abundant in drinking water, air and soil due to our increased use of these compounds. They are present in virtually every area of modern consumerism from construction materials to cosmetics, medicines to processed foods; fuel sources to agents of destruction; appliances to personal care products. It is very difficult for anyone to avoid exposure to any of the many harmful heavy metals that are so prevalent in our environment. The distributions of heavy metals in manufacturing industries are given in Table 1.

Industries	Ag	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Se	Ti	Zn
General Industry and Mining													
Plating													
Paint Products													
Fertilizers													
Insecticides / Pesticides													
Tanning													
Paper Products													
Photographic													
Fibers													
Printing / Dyeing													
Electronics													
Cooling Water													
Pipe Corrosion													

 Table 1: General Distribution of Heavy metals in Particular Industrial Effluents

Highly poisonous cadmium does not exist in nature as the native metal but mainly found as sulphide ore greenockite (CdS), which is strongly associated with zinc sulphide ore sphalerite. It enters into the environment from the wastewater of industries using cadmium, but also discharged from the iron and steel industry.

Various soluble forms of cadmium exist in water. It exist mainly as Cd^{2+} , also as $[CdCO_3]^0$, $[CdCl]^+$, $[Cd(OH)]^+$ and $[CdSO_4 (aq)]$. Free Cd^{2+} ion occur at pH level below 8. At higher pH values, $[Cd(OH)]^+$ is formed and in very alkaline solutions $[Cd(OH)_3]^-$ and $[Cd(OH)_4]^{2-}$ are formed [7].

Lead is rarely found as the free metal in nature, but it is present in several minerals, principally in galena (PbS) the main source for lead production. It is also found as anglesite (PbSO₄) and cerrusite (PbSO₃).

Metals	At.wt. (g/mol)	Pauling Electronegativity	Polarizability (10 ⁻²⁴ cm ³)	LogK _{MOH}	R _{ionic} (Å)	R _{covalent} (Å)	R _{hydrated} (Å)
Cd	112.41	1.69	7.20	3.92	0.97	1.48	4.26
Pb	207.20	2.33	6.80	5.20	1.33	1.47	4.01
Ni	58.69	1.91	6.80	4.14	0.83	1.21	4.29
Zn	65.39	1.65	6.26	3.69	0.74	1.22	4.30
Cu	63.55	1.90	6.10	6.00	0.71	1.38	4.19

Table 2: Different properties of some heavy metals of interest

Lead is commonly used as non-ferrous metals. It has many applications; its largest use is in making storage batteries, most of which as is recycled. As a result of its resistance to corrosion and its malleability nature, it is found in building constructions, storage tank lining and corrosive liquid containers. Other uses of this metal are for radiation shielding, ammunition, solder, and cable sheathing and pipe work. Lead compounds are used as pigments in paints and ceramics, catalysers, antibacterial substances and wood preservatives. A major use in the production of anti-knock compounds for addition to petrol, is particularly tetraethyl lead, $Pb(C_2H_5)_4$. The exhausts gases mainly contain oxides, halides and alkyl compound of lead generated from vehicles which are a major source of the environmental contamination by lead. Other source of lead emissions are copper and nickel smelters, iron and steel production.

Lead exit in the oxidation states Pb^{2+} and Pb^{4+} , with the divalent form being the more stable in most aquatic environments. The speciation of lead compounds in water is complicated and depends upon a number of factors, principally pH, dissolved oxygen and the concentration of organic and inorganic compounds. In surface waters, lead is presents as hydrated Pb^{2+} , or $[PbCO_3]^0$ in the pH range 7-9. At pH 6, Pb^{2+} and $[Pb(OH)]^+$ are in equal concentration, whereas at higher pH values there is an increase on Pb in the form of $Pb(CO_3)_2^{2-}$, $Pb(OH)^+$ and concentration of lead in waters is usually limited by the solubility of $PbCO_3$, and by its adsorption onto particulate matter [7].

The average concentration of nickel in earth's crust is about 75 mg/g and it constitutes about 0.016% of the total mass. Its principal ores are pentlandite ($(FeNi)_6 S_8$), millerite (NiS) and garnierite ($(NiMg)_6Si_4O_{10}(OH)_8$). It occurs as the natural metal only in meteorites. It is used in the production of alloys, nickel plating for corrosion resistance and in the manufacture of nickel- cadmium batteries. The metal or its compounds are also used as catalysts, dye, fungicides and pigments.

Nickel is present in crude oil in varying concentrations and burning of petroleum products, either in combustions processes or in vehicle fuel, thereby introduces the metal into the environment. It also enters surface water by the natural weathering and leaching processes of minerals and rocks. Nickel can exist in the oxidation states ranging from -1 to +4, but its aqueous chemistry are dominated by the +2 (nickelous) states. This ion forms stable complexes with both organic and inorganic ligands and also adsorbed onto particular matter. The commonest inorganic ligands are halides, sulphate, phosphate, carbonate and carbonyls, whilst the organic ones are those containing oxygen, nitrogen or sulphur in their structures [7].

Higher concentrations of nickel cause cancer of lungs, nose and bone. Dermatitis (Ni itch) is the most frequent effect of exposure to Ni, such as coins and jewelers. Acute poisoning of Ni (II) causes headache, dizziness, nausea and vomiting, chest pain, tightness

of the chest, dry cough and shortness of breath, rapid respiration, cyanosis and extreme weakness [8-10].

Zinc makes up about 0.0075% of the Earth's crust making it the 24th most abundant element. The important zinc ores are zinc blende (ZnS), franklinite (ZnO.Fe₂O₃), willimite (Zn₂SiO₄), calamine (ZnCO₃), and zincite (ZnO).

Brass, which is an alloy of copper and zinc, has been used since at least the 10th century BC. It is used in the preparation of certain alloys, principally for galvanizing iron; more than 50% of metallic zinc goes into galvanizing steel. The element is normally found in association with other base metals such as copper and lead in ores. It is used for the negative plates in some electric batteries and for roofing and gutters in building construction. Zinc oxide is used as a white pigment in watercolors or paints, and as an activator in the rubber industry. As a pigment, zinc is used in plastics, cosmetics, photocopier paper, wallpaper, and printing inks. With a standard reduction potential of -0.76 volts, zinc is used as an anode material for batteries. Powdered zinc is used in this way in alkaline batteries and sheets of zinc metal form the cases for and act as anodes in zinc–carbon batteries [7].

Copper is widely distributed in nature as free metal and more commonly, as compounds in various chief ores such as copper pyrites(CuFeS₂), cuprite (Cu₂O), copper glance (Cu₂S), and malachite (Cu₂CO₃(OH)₂). Copper is mainly used in the production of alloys with zinc, nickel and tin, as a catalyst in the chemical industry and electrochemical industry. It is used as in wires, generators, transformers and heat exchangers, and of course in the production of piping for water supply. Copper salts are used as pigments and fungicides, and also biocides for controlling slime and in human and animal waste.

Copper can exist in four valance states- the native element Cu^0 and the ions Cu^{1+} , Cu^{2+} , and Cu^{3+} . The most common form is as Cu^{2+} . In water, most cupric (Cu^{2+}) salts readily dissolve to form an aqua complex $Cu(H_2O)_4^{2+}$, and the water molecules can then be replaced by a variety of ligands to form different complexes. The different forms of copper complexes found in water are $[CuCO_{3(aq)}]^0$, $[Cu(CO_3)_2]^{2-}$, $[CuOH]^+$, $[Cu(OH)_3]^-$ and $[Cu(OH)_4]^{2-}$ [7].

In this study, the charred xanthated and aminated sugarcane bagasse were prepared by chemical modification from agricultural waste-materials of sugarcane after extraction of its juice. Sugarcane bagasse is a lignocellolusic materials that have several organic components, such as lignin, cellulose and hemicelluloses, which have specific influences on the adsorption of metals. Chemical modification after charring of sugarcane bagasse, the heterogeneity of its surface and pore structure provide numerous adsorption sites which may also act selectively in terms of affinity for certain metals. The nature of the attractive forces of molecules to the solid surface determines the characteristics of the binding sites and gives rise to the classification. Different properties of metal ions of interest such as cadmium, lead, copper, nickel and zinc are depicted in the Table 2 for the convenience of their study in the adsorption processes.

In order to reduce the pollution problem in environment that is caused by these heavy metals, their concentrations must be reduced before discharge into the wastewater stream. In this study, biosorption is considered as an effective treatment process that must be applied to obey the WHO standards listed in Table 3.

1.2 Effects of Heavy Metals on Human Health

The heavy metals hazardous to humans include lead, mercury, cadmium, arsenic, copper, zinc, and chromium. Such metals are found naturally in the soil in trace amounts, which pose few problems. Heavy metals can enter a water supply by industrial and consumer waste, or acid rain breaking down soils and releasing heavy metals into streams, lakes, rivers, and groundwater. When concentrated in particular areas, however, and they present a serious danger. Heavy metals are dangerous because they tend to bio-accumulate. They accumulate in living beings at any time they are taken up and stored faster than they are broken down or excreted.

Table	3:	Major	sources,	health	effects	of heav	y metals	and	WHO	drinking	water
standa	ard	s (Sour	ce: APHA	, AWW	VA, WE	F: 167)					

Metal	N7 '		Permissible		
ions	Major sources	Effect on human health	limit (mg/L)		
	Electroplating, PVC stabilizer,	Kidney damage, renal disorder,			
C4(II)	pigments, pesticide, fertilizer,	Itai-Itai, bronchitis, bone	0.002		
Cu(II)	Cd-Ni batteries, nuclear fission	marrow cancer, gastrointestinal	0.003		
	plant	disorder			
	Paint, pesticide, smoking,	Liver, kidney, gastrointestinal			
Pb(II)	automobile emission, mining,	damage, depression, lethargy,	0.01		
	burning of coal	mental retardation in children			
	Ni-Cd batteries, catalysts,	Dermatitis, nausea, chronic			
Ni(II)	metal plating, dyes and	netal plating, dyes and asthma, coughing, human			
	pigments	carcinogen			
		Pancreas damage,			
$\mathbf{7n}(\mathbf{H})$	Brass manufacture, plumbing,	arteriosclerosis, respiratory	2.0		
Zn(11)	metal plating, refineries	disorder, disturbance of protein	5.0		
		metabolism			
Cu(II)	Alloys, catalysts, wires,	Liver damage, Wilson disease,	1.0		
	fungicide and biocides	insomnia, lung cancer	1.0		
1	1		1		

Metals are released into the environment by different human activities and high concentration of these metals constitutes a great risk for the aquatic and terrestrial ecosystem. Arsenic and cadmium, for instance, can cause cancer. Mercury can cause mutations and genetic damage, while copper, lead, and mercury can cause brain and bone damage. The main sources of exposure and harmful effects of five heavy metals such as Cd, Pb, Cu, Ni, and Zn on human health are depicted in Table 3.

1.3 Common Methods Used for the Treatment of Heavy metals from Wastewater

1.3.1 Chemical Precipitation

Chemical precipitation is a process of formation of a separable solid substance from a solution, either by converting the substance into an insoluble form or by changing the composition of the solvent to diminish the solubility of the substance in it. This method can be used to remove metals, fats, oils and greases, suspended solids and some organics. It can also to be used to remove phosphorus, fluoride, ferrocyanide and other inorganics. In practice, chemical precipitation is commonly employed to separate the most of metals from wastewater if their concentration is high. Lime and caustic soda are common precipitants which are used to precipitate metals in the form of hydroxides.

 $M^{2+} + 2(OH)^{-} \qquad \longrightarrow \qquad M(OH)_2$

However, this method is inappropriate for large solution volumes with very low concentrations of metal ions. In spite of its advantages, chemical precipitation requires a large amount of chemicals to reduce metals to an acceptable level for discharge (Jutner et al. 2000). Other drawbacks are its excessive sludge production that requires further treatment, the increasing cost of sludge disposal, slow metal precipitation, poor settling, the aggregation of metal precipitates, and the long term environmental impacts of sludge disposal [11-13]

1.3.2. Coagulation–Flocculation

Coagulation–flocculation can be employed to treat wastewater laden with heavy metals. Principally, the coagulation process destabilizes colloidal particles by adding a coagulant and results in sedimentation [14]. To increase the particle size, coagulation is followed by the flocculation of the unstable particles into bulky floccules [15]. The general approach for this technique includes pH adjustment and involves the addition of ferric/alum salts as the coagulant to overcome the repulsive forces between particles [16]. In spite of its advantages, coagulation–flocculation has limitations such as high operational cost due to chemical consumption. The increased volume of sludge from coagulation–

flocculation may hinder its adoption as a global strategy for treatment. This can be attributed to the fact that the toxic sludge must be converted into a stabilized product to prevent heavy metals from leaking into the environment [17]. To overcome such problems, electro-coagulation may be a better alternative than the conventional coagulation, as it can remove the smallest colloidal particles and produce just a small amount of sludge [18, 19]. However, this technique also creates a floc of metallic hydroxides, which requires further purification, making the recovery of valuable heavy metals impossible.

1.3.3 Reverse Osmosis

Reverse osmosis is used for the removal of dissolved constituents from wastewater remaining after advanced treatment. When two solutions having different solute concentrations are separated by a semipermeable membrane, a difference in chemical potential will exist across the membrane. Water will tend to diffuse through the membrane from the lower concentration side to the higher concentration side. In a system having a finite volume, flow continues until the pressure difference balances the chemical potential difference. This balancing pressure difference is termed the osmotic and is a function of the solute characteristics and concentration and temperature. If a pressure gradient opposite in direction and greater than the osmotic pressure is imposed across the membrane, flow from the more concentrated to the less concentrated region will occur and is termed reverse osmosis [20]. Reverse osmosis has been proposed for treatment for recovery of heavy metals. To protect the reverse osmosis membranes, feed solution pH must be adjusted. Reverse osmosis alone will not achieve complete recovery and reuse of the solutions. Pretreatment required prior to the reverse osmosis unit includes equalization, media filtration, pH adjustment and anti-precipitant additions.

1.3.4 Ultrafiltration

Ultrafiltration technologies can be used in a variety of ways in wastewater treatment and water reuse systems. Ultrafiltration can reduce the amount of treatment chemicals, has smaller space requirements, and reduce labor requirements. On the contrary in this method uses more electricity, may need pretreatment, and requires replacement of membranes [21].

1.3.5 Electrodialysis

In the electrodialysis process, ionic components of a solution are separated through the use of semipermeable ion-selective membranes. This process may be operated in either a continuous or a batch mode. Problems associated with the electrodialysis process for wastewater renovation include chemical precipitation of salts with low solubility on the membrane surface. To reduce the membrane fouling, activated carbon pretreatment, possibly preceded by chemical precipitation and some form of multimedia filtration may be necessary [20]. The process has not been widely utilized in full-scale treatment of metal wastes.

1.3.6. Flotation

Flotation is employed to separate solids or dispersed liquids from a liquid phase using bubble attachment [22]. The attached particles are separated from the suspension of heavy metal by the bubble rise. Flotation can be classified as: (i) dispersed-air flotation, (ii) dissolved-air flotation (DAF), (iii) vacuum air flotation, (iv) electro-flotation, and (v) biological flotation. Among the various types of flotation, DAF is the most commonly used for the treatment of metal-contaminated wastewater [23]. Adsorptive bubble separation employs foaming to separate the metal impurities. The target floated substances are separated from bulk water in a foaming phase. Although it is only a kind of physical separation process, heavy metal removal by flotation has the potential for industrial application [24]. Low cost materials such as zeolite and chabazite have been found to be effective collectors with removal efficiency of higher than 95% for an initial metal concentration ranging from 60 to 500 mg/L. Other advantage, such as a better removal of small particles, shorter hydraulic retention times and low cost is one of the most promising alternatives for the treatment of metal-contaminated wastewater [25].

1.3.7. Ion Exchange

The ion-exchange process can be defined as a chemical reaction between ions in a liquid phase and ions in solid phase. The ion-exchanger solid preferentially adsorbs certain ions in the solution. Since electro-neutrality must be maintained, the exchanger solid releases replacement ions back into the solution. Ion-exchange is one of the methods used for the removal of several toxic substances including heavy metals, from industrial and municipal wastewater. Ion exchangers are materials that can exchange one ion for another, hold it temporarily, and release it to a regenerant solution. Ion-exchange is used extensively in both water and wastewater treatment. The most common applications are water softening, demineralization, desalting, ammonia removal, treatment of heavy metals containing wastewaters, and treatment of some radioactive wastes [26]. Materials used for the exchange of metals include zeolites, weak and strong anion and cation, chelating resins. Ion exchange processes are highly pH-dependent. Solution pH has a significant impact on the metal species present and the interaction between exchanging ions and the resin [21].

1.4. Scope of the Study

Adsorption has become one of the promising treatment techniques for wastewater laden with heavy metals. Basically, adsorption is a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid, and becomes bound by physical and/or chemical interactions [27]. The aim of this study is the preparation and characterization of charred xanthated and aminated biopolymer, from sugarcane bagasse in controlled experimental condition to investigate the uptake performance for heavy metal ions (Cd²⁺, Pb²⁺, Cu²⁺, Ni²⁺, and Zn²⁺). Characterization of charred xanthated and aminated sugarcane bagasse were carried out with Scanning Electron Microscopy (SEM), Elemental Analysis, IR Spectroscopy, X-Ray Diffraction (XRD), Zeta Potential Analysis, and Thermal Gravimetric Analysis (TGA/DTA). Batch experiments were carried out in the adsorption of heavy metal ions Cd²⁺, Pb²⁺, Cu²⁺, Ni²⁺, and Zn²⁺, Cu²⁺, Ni²⁺, and Zn²⁺ onto CXSB and CASB biopolymers. The primary parameters investigated include pH, contact time, concentration

and temperature. Moreover the best fitting adsorption isotherm models are examined using the most widely applied isotherm models. Adsorption isotherms are helpful in demonstrating the extent of homogeneity of the adsorption sites and the affinity of these sites towards the adsorbed cations. The thermodynamic parameters, ΔH° , ΔG° and ΔS° are also calculated, that can help in testing whether or not electrostatic binding forces are involved in adsorption. Concentration of the metal ions solutions was analyzed using Flame Atomic Absorption Spectro-photometer (AAS).

CHAPTER 2

2. OBJECTIVES OF THE STUDY

The main objective of this study was to develop two new chemically modified biosorbents that is superior to other adsorbents reported in the literatures. The increasing number on publications in the adsorption of toxic compounds by modified polysaccharides shows that there is recent increasing interest in the synthesis of new low-cost adsorbents used in wastewater treatment. Industrial wastewater is a complex wastewater containing different chemicals and dyestuffs. The effluent treatment in developing countries is expensive and major cost is associated with the dependence on imported technologies and chemicals. The indigenous production of treatment techniques and chemicals locally, or use locally available non-conventional materials to treat pollutants seems to be the solution to the increasing problem of treatment of effluents. In this regard, there has been a focus on the use of appropriate low cost technology for the treatment of wastewater in developing countries in recent years. Technically feasible and economically viable pretreatment procedures with suitable biomaterials based on better understanding of the metal biosorbent mechanisms are gaining importance. Activated carbon of agricultural waste products as low cost adsorbents has been reported till now. However, there is an additional cost involved in the processing of the agricultural wastes to convert the same to activated carbon, which is posing economic difficulties necessitating research on alternate adsorbents with equivalent potential of activated carbon.

In this study, charred xanthated sugarcane bagassse (CXSB) and aminated sugarcane bagassse (CASB) has been investigated whether the modification have been taken place or not. Most of the studies were carried out by using synthetic wastewater containing single metal ion solutions adjusting the pH, where chemically modified bio-adsorbent are used to sequester the heavy metal ions. Therefore, it is necessary to determine behavior of treatment systems operating with real wastewater. The major objectives of this thesis can be summarized as follows:

14

The objective of the present research is to find out the adsorption capacity of the chemically modified CXSB and CASB for the removal of heavy metals from aqueous solutions so as to facilitate comparison with other adsorbents. The raw biomass used to prepare the modified adsorbents (CXSB and CASB) in the present study is available and can be found almost free of cost in terai regions of Nepal. Adsorption properties of such modified adsorbents have not yet been reported in literature. The adsorbents CXSB and CASB in the present study were tested for their adsorption capacity on the five heavy metals namely; cadmium (II), lead (II), nickel (II), zinc (II) and copper (II),

Exploratory studies reveal that wastewater solutions are contaminated with heavy metals cadmium (II), lead (II), nickel (II), zinc (II) and copper (II). Growing problem of water and soil contamination due to untreated effluents has necessitated focusing on these heavy metals in the current endeavor. The heavy metals have proven to be hazardous not only for human life, but also to the aquatic flora and fauna, requiring remediation of the heavy metals using appropriate techniques.

Keeping these environmental, ecological and societal health issues, it is considered necessary to attempt and provide an easy, feasible, economical and reliable method for the removal of heavy metals. Hence, adsorption by locally available, environmentally-friendly and cost effective adsorbents have been explored. Actually, the aim of this work is to develop chemically modified biosorbents which would be novel sorbent to compare results found in literature. The objective is achieved through:

- 1. Characterisation of the adsorbents through elemental analysis of their carbon, nitrogen and sulphur content.
- 2. Characterisation of functional groups on the surface of the adsorbent that contributes to the biosorption of heavy metals used in the present study through infrared spectroscopy.
- 3. Determination of the equilibrium time, pH and effect of adsorbent at different initial metal ions concentrations.
- 4. Determination of the adsorption capacity and intensity using Langmuir and Freundlich isotherm models,

- 5. Desorption of metals from metal loaded adsorbents to determine the mechanism of adsorption.
- 6. Comparison among the adsorbents for their adsorption capacity with those found in the literature.

CHAPTER 3

3. LITERATURE REVIEW

3.1.1 Fundamentals of adsorption

Adsorption is the process through which a substance, originally present in one phase, is removed from that phase by accumulation at the interface between that phase and a separate solid phase. In principle adsorption can occur at any solid liquid interface. Here, example include liquid-solid interface as in the adsorption of toxic metals on modified biosorbent. Various technologies and processes are currently used for the sequestration of heavy metal ions from natural and wastewater. Advanced oxidation processes, membrane separations, biological treatments, chemical and electrochemical techniques, and adsorption procedures are the most widely used for the removal of metals and organic compounds from industrial effluents. Amongst all the treatments proposed, bio-adsorption is one of the promising methods for the separation of metal ions from the contaminated water. Biosorption is defined as the removal of metal or metalloid species, compounds and particulates from solution by biological materials [28]. Bohumil Volesky, a pioneer in the field, defined 'biosorption' as the property of certain biomolecules to bind and concentrate selected ions or other molecules from aqueous solutions [29]. Bioaccumulation is a much more complex phenomenon, based on active metabolic transport whereas biosorption by dead biomass is passive and occurs primarily due to the 'affinity' between the biosorbent and adsorbate. The use of dead biomass is generally preferred since it limits the toxicity effects of heavy metals as they may accumulate at the surface of cell walls and /in the cytoplasm. The polysaccharides found in sugarcane bagasse are biopolymers having many hydroxyl and/or phenolic groups (Figure 1) that can be chemically modified to form more pronounced functionality with changed properties [30]. The different hetero atoms and functional groups found on carbon surface [Figure 2] of any biomaterials have important role for the adsorption process.



Figure1. Cellulosic structure of sugarcane bagasse



Figure 2: Hetero atoms and Groups on Carbon Surface

Adsorption is a well-known equilibrium separation process. It is now recognized as an effective, efficient, and economic method for water decontamination applications and for separation analytical purposes. The adsorbents may be of mineral, organic or biological origin: activated carbons [2-3], zeolites [4-5], clays [8, 31-32], silica beads [33-34], low cost industrial by-products [35-40], agricultural wastes [41] and organic polymeric resins [42-43] are some significant examples.

In recent years, the search for low cost adsorbents that have metal-binding capacities has been intensified. Various locally available materials such as inorganic materials, agricultural wastes, forest by-products, fishery wastes and industrial by-products can be utilized as low cost adsorbents. Zeolites, clay, fly ash and natural oxides are extensively used inorganic adsorbents to sequester heavy metals from the contaminated water.

Zeolites

Basically zeolites are a naturally occurring crystalline aluminosilicates consisting of a framework of tetrahedral molecules, linked with each other by oxygen atoms. During 1970s, natural zeolites gained a significant interest among scientists due to their ionexchange capability to remove strontium and cesium [44]. This unique property makes zeolites favorable for wastewater treatment.

Zeolite consists of a wide variety of species such as clinoptilolite and chabazite. Clioptilolite is most abundant in nature and is readily available from more than 40 natural zeolites species [45]. Among the most frequently studied natural zeolites, clinoptilolite, has shown to have high selectivity for certain heavy metal ions such as Pb^{2+} , Cd^{2+} , Zn^{2+} , and Cu^{2+} . Table 4 shows that adsorption capacities of zeolites for some heavy metals available in the literature.

Clay

It is widely known that there are three basic species of clay: montmorillonite, kaolinite, and micas; out of which montmorillonite has the highest cation exchange

capacity and that its current market price is considered to be 20 times cheaper than that of activated carbon. Therefore, a number of studies have been conducted using clays, mainly montmorillonite, to show their effectiveness for removing metal ions and Table 4 shows adsorption capacity of clay for some heavy metals.

Peat moss

Peat moss, a complex material containing lignin and cellulose as major constituents, is a natural substance widely available. It has a large surface area (>200 m²/g) and is highly porous so that it can be used to bind heavy metals. In 1986, the use of peat to remove heavy metals was investigated [46]. The adsorption capacity of peat moss for heavy metals is depicted in Table 4 from literature.

Fly Ash

Fly ash, an industrial solid waste of thermal power plants, is one of cheapest adsorbents having excellent adsorption capabilities for heavy metal. The adsorption capacities of fly ash for some metals are shown in Table 4.

Natural Oxide

In 1985, a study on the use of aluminium oxide to remove Cr^{3+} from aqueous waste was conducted [47]. It was reported that the ultimate adsorption capacity of 11.7 mg of Cr^{6+}/g alumina was observed at pH of 4.0. It is important to note that the adsorption capacity of alumina was significantly reduced in the presence of CN^{-} anions. This may be due to the fact that cyanide has a strong anionic influence upon the sorption characteristics of alumina. Therefore, CN^{-} anions are competitively adsorbed covering the surface sites of alumina, which in turn prevent the Cr^{6+} to be adsorbed on the internal surface of adsorbent.

The removal of Pb^{2+} and Cd^{2+} from aqueous solutions using aluminium oxide and goethite, an iron oxide was also explored [48]. Goethite exhibited a better sorption capacity

for both ions than aluminium oxide and the uptake of Pb^{2+} was higher than that of Cd^{2+} . The sorption capacities of natural oxides for some metals are shown in Table 4.

Activated carbon

Amongst the adsorbent materials, activated carbons are unique and versatile adsorbents and it has been found the most popular and widely used adsorbents in wastewater treatment application throughout the world. It shows the maximum adsorption capacity to adsorb pollutants from the aqueous solutions. The higher capacity is mainly due to their structural characteristics and porous texture, which gives them a large surface area. A large number of adsorbents have been tested by researchers for removal of heavy metals from pure and complex solutions. The effectiveness of activated carbon has been evaluated by several researchers [49-51] for the removal of metal ions from wastewater.

Many cheap, easily available agricultural/or plants- based materials such as silk cotton hull, banana pith, maize cob, jute fiber, palm kernel shell, date pits, rice bran, coir pith, rice husk, mango seed kernel powder, rubber wood sawdust, rosewood sawdust, corncob wastes, straw, coconut coir dust have been used as a source of the production of activated carbon for the removal of heavy metals and textile dye effluents.

There are several chemical groups that could attract and sequester the metals in biomass: acetamido groups of chitin, structural polysaccharides of fungi, amino and phosphate groups in nucleic acids, amino, amido, sulfhydryl, and carboxyl groups in proteins, hydroxyls in polysaccharides, and mainly carboxyls and sulfates in the polysaccharides of marine algae that belong to the divisions Phaeophyta, Rhodophyta, and Chlorophyta. However, it should be stressed that the presence of some functional groups found in lower plants like bacteria, fungi and algae have major role for the separation of heavy metals.

Adsorbents	Pb ²⁺	Ni ²⁺	Zn ²⁺	Cu ²⁺	Cd ²⁺ Cr ⁶⁺	References
	1.6	0.48	0.50	1.64	2.40	[52]
Clinopatite	62.0			3.80	70.0	[53]
Chilopatite	6.00	0.90	2.70		3.70	[54]
	1.40				1.20	[55]
Chabazite	175				137	[53]
	6.00	4.50	5.50	5.10	6.70	[54]
Chabazite –phillipsite		0.56	0.04	0.37		[56]
Montmorillonito	0.68				0.72	[57]
Wontmormonite			4.98		4.78	[58]
			1.25			[59]
Kaolinite	0.12				0.32	[57]
	1.41					[60]
Bentonite			4.54		11.41	[61]
Dentomite			52.91			[62]
Illite	4.29					[60]
Eutrophic peat		11.15	11.12	12.07	20.23	[46]
Lui opine pour				19.56		[63]

Table 4: Adsorption capacities (mg/g) of some inorganic substances for some heavy metals removal

Olizatranhia naat	11.74	13.08	12.07	22.48		[46]
Ongotrophic peat			6.41			[63]
Sphagnum					1.32	[64]
Fly ash			1.39			[65]
Fly ash-wollastonite			1.18	2.92		[66]
Fly ash-China clay				0.31		[66]
Aluminium oxide					11.7	[46]
230				72		[48]
Synthetic resins66.3						[43]

Biosorption of heavy metals using bacteria, fungi and algae

Bio-sorbents primarily fall into the following categories: agricultural wastes, industrial wastes, natural residues, algae, fungi and bacteria. Agricultural by-products are mostly composed of lignin and cellulose, as well as polar functional groups containing compounds which include alcohols, aldehydes, ketones, carboxylates, phenols and ethers. These groups are able to bind heavy metals through replacement of hydrogen ions with metal ions in solution or by donation of electron pair from these groups to form complexes with metal ion in solution [67].

Bacteria are the most abundant and versatile of microorganisms and they were used as biosorbents because of their small size, their ubiquity, their ability to grow under controlled conditions as well as a wide range of environmental situations [68]. Bacterial species such as Bacillus, Pseudomonas, Streptomyces, Escherichia, and Micrococcus have tested for uptake metals or organic compounds. Some of the important results of the metal biosorption using bacterial biomasses, according to some published references [69-70] are given in Table 5. This table also provides the basic information to evaluate the possibility of using bacterial biomass for the removal of metal ions.

Bacteria may either possess the capacity for biosorption of many elements or, alternatively, depending on the species, may be element specific. It is likely that, in the future, microorganisms will be tailored for a specific element or a group of elements, using recombinant DNA technology which is based on genetic modification using endores-trictive nucleases [71].

Although fungi are a large and diverse group of eukaryotic microorganisms, three groups of fungi have practical importance: the molds, yeasts and mushrooms. The importance of metallic ions to fungal and yeast metabolism has been known for long time [27]. The presence of heavy metals affect the metabolic activities of fungal and yeast cultures, and can affect commercial fermentation processes, which created interest in relating the behavior of fungi to the presence of heavy metals. The yeast biomass has been successfully used as biosorbent for the removal of Ag, Au, Cd, Co, Cr, Cu, Ni, Pb, U, Th and Zn from aqueous solution. The selectivity and competitive biosorption of Saccharomyces cerevisiae were depicted in detail by Wang and Chen [72]. Numerous researchers studied heavy metal removal by fungi, and some of the results reported in literatures are summarized in Table 5. The fungus Aspergillus niger, which is commercially and economically essential in fermentation for citric acid production due to its efficiency and high yield outcome. The waste products utilization of this fungus to sequester toxic metals from aqueous solution has been reported by Dursun [73]. He carried out the sorption experiment with sodium hydroxide pretreated Aspergillus niger and found good results than untreated biomass for the separation of Cu (II) and Pb (II). A similar study was conducted by Mungasavalli and coworkers [74] pre-treating with sodium hydroxide, sulphuric acid, acetone, formaldehyde, and ethyl trimethylammonium bromide to modify the surface of Aspergillus niger. Another comparison study of biosorption capacity between Saccharomyces cerevisiae and Aspergillus niger for Mn (II) sorption was also reported by Pavarthi [75] and they found Aspergillus niger was a better Mn (II) biosorbent.

Algae are a large and diverse group of lower plants ranging from unicellular to multicellular forms, which are found in aquatic and terrestrial environments. In the pollution control field, algae are used in waste water treatment facilities to reduce hazardous organic and inorganic contaminants. Studies of biosorptions using diverse types of algae for heavy metal removal in aqueous solutions have been conducted by various research groups [76-84]. The carboxyl, hydroxyl, sulphate, and amino groups in algal cell wall polysaccharides act as binding sites for the removal of metals. The biomass characteristics, physical, chemical properties of the target metals, and solution pH have a large impact on the biosorption performance.

Caulerpa lentillifera is a marine green macroalgae cultivated mainly as a food for animals and humans is used to treat wastewater from shrimp farm [82]. Some particular types of algae have been employed in the treatment of ponds to balance the nitrogen compound [79]. Its excessive amount as a result of its rapid growth has often created problems. For that reason, their application as a biosorbent for metals is quiet attractive. Pavasanta and his co-workers [82] studied the sorption of Cu (II), Cd (II), Pb (II) and Zn (II) onto dried marine green macro algae *Caulerpa lentillifera* at different pH and particle size. From the FTIR analysis, they denoted that the possible functional groups involved in metal sorption using these algae were carboxylic acids, amines, amides, sulfonyl and sulfonate groups.

The seaweed *Laminaria japonica* harvested in Hokkaido Island, Japan; contain water soluble components like amino acids and alginic acid. The adsorbent was prepared by crosslinking with epichlorohydrin in strongly basic medium in order to increase adsorption capability [85]. They evaluated maximum uptake capacity by using the chemically modified alga for the adsorption of various heavy metal ions from contaminated water that is depicted in Table 5.

Biosorptions of Pb(II) and Cu(II) onto *Cladophora fascicularis* was analyzed as a function of initial pH, metal ion concentrations, temperature and other co-existing ions by Deng and coworkers [80]. They decided that pH could affect the protonation of the functional groups on the biomass as well as the metal chemistry. The cellular ligands

become protonated under acidic conditions and consequently there is repulsion between the metal ions and the protonated biosorbents. With the rise of pH, more ligands with phosphate, carboxyl and amine groups containing negative charge would be exposed to the metal ions resulting in an attractive force.

Biosorbents	Metal ions	Biosorption capacity (mg/g)	References
Pseudomonas putida	Pb(II)	270.4	[86]
	Cu(II)	96.9	
Streptomyces rimosus	Pb(II)	135	[87]
	Zn(II)	80	[88]
Thiobacillus ferooxidans	Zn(II)	172.4	[89]
Streptomyces rimosus	Fe(III)	122	[90]
Bacillus thuringiensis	Ni (II)	45.9	[91]
Penicillium canescens	Cd(II)	102.7	
	Pb(II)	213.2	[92]
	Hg(II)	54.8	
	As(III)	26.4	
Penicillium chrysogenum	Pb(II)	116	[93]
	Cd(II)	56	[94]
Penicillium chrysogenum (modified)	Cd(II)	210.2	
	Cu(II)	108.3	[95]
	Pb(II)	204	[]
	Ni(II)	55	
	Ni(II)	260	[96]
Penicillium chrysogenum	Pb(II)	116	
	Th	142	[97]
	U	70	

Table 5: Sorptions of heavy metals by bacteria, fungi and algae

Penicillium purpurogenum	Cr(II)	36.5	[98]
	Cd(II)	110.4	[99]
Aspergillus niger	Pb(II)	93	[73]
Aspergillus terreus	Cu(II)	224	[100]
	Fe(III)	164.5	[101]
	Cr(III)	96.5	[101]
Phanerochaete chrysosporium	Pb(II)	70.7	
	Cu(II)	43.7	[102]
	Cd(II)	70.8	
Caulerpa lentillifera	Cd(II)	318.61	[79]
	Pb(II)	310.8	
	Cu(II)	190.5	
	Cd(II)	4.72	
	Pb(II)	28.8	[103]
	Cu(II)	5.58	
	Zn(II)	2.68	
Laminaria japonica	Cd(II)	123.65	
U A	Pb(II)	279.72	[85]
	Fe(III)	85.45	

Bio-sorption

The term biosorption commonly refers to the passive binding of metal ions or radioactive elements by dead biomass. It has to be distinguished from bio-accumulation which is usually understood to be an active, metabolically mediated metal-accumulation process occurring specifically in living organisms.

It is evident from our literature survey that polysaccharide based bio-materials have demonstrated outstanding removal capabilities for metal ions as compared to other low cost sorbents and commercial activated carbons. Abundant natural materials, particularly of cellulosic nature, have been suggested as potential biosorbents for heavy metals. However, little work has been done in this respect. The meaningful search for metalsorbent biomaterials would be expedited greatly if the phenomenon of metal biosorption were better understood. That knowledge could serve as a guide in the search of potentially high organic materials in the natural domain. However, with the state of the art being in its infancy as it is, tedious experimental screening of selected readily available types of biomass is still the basis for discovering new biosorbents. Considering the number of candidate biomass types and the number of metals of interest, all multiplied by the number of variable experimental or process parameters, the scope of the task of prospecting for new and potentially feasible metal biosorbents is rather large. Biosorption of metals is not based on only one mechanism. It consists of several mechanisms that quantitatively and qualitatively differ according to the species used, the origin of the biomass, and its processing. Metal sequestration follows complex mechanisms, mainly ion exchange, chelation, adsorption by physical forces; and ion entrapment in inter- and intra-fibribular capillaries and spaces of the structural polysaccharide network as a result of the concentration gradient and diffusion through cell walls and membranes.

Biosorption removal of toxic heavy metals is especially suited as a 'polishing' wastewater treatment step because it can produce close to drinking water quality (from initial metal concentrations of 1-100 mg L⁻¹, final concentration < 0.01 - 0.1 mg L⁻¹), especially in packed bed flow-through applications. In order to prevent unnecessarily rapid exhaustion of the sorption capacity when the metal concentrations in the waste water to be treated are very high (> 100 mg L⁻¹) a pretreatment by different techniques (such as precipitation or electrolytic recovery) may be desirable to remove the bulk of the metal [104]. Although there are numerous techniques available for the treatment of heavy metals from wastewater, bio-sorption is effective technique for the heavy metals sequestration even at low concentration. Many researchers have studied the heavy metals adsorption properties using low cost agricultural byproducts and natural fibers as compiled in Table 6.

The adsorption capability of several agro-based materials, namely groundnut shell (GS), crushed coconut shell (CS), walnut shell (WS), almond shell (AS) and *Tamarindus indica* (TS) for Cr(VI) have been evaluated [105]. They concluded that tamarind seed has more adsorption capacity out of above mentioned five and is more economical than other conventional methods. They also noted that the removal of Cr (VI) ions by tamarind seed

is significantly reduced with the increase of pH whereas the removal slightly decreases with increasing ionic strength. They noticed that the removal capacity enhanced with rise in temperature. It has been suggested that chemisorption is the most plausible mechanism involved.

Several researchers have investigated the removal performance of neem leaf (*Azadirachta indica*) as an alternative adsorbent for Cr (VI), Cd (II) and Pb (II) [106-108]. Sharma and Bhattacharya [107] utilized powdered neem leaf and got good result to extract Cr (VI) from aqueous solution. The adsorption was carried out in batch process using different concentrations of metal ions in aqueous solutions in parallel with variation in the adsorbent amount, pH, agitation time and temperature. The suitability criteria of the adsorbent were checked by the Langmuir and Freundlich isotherms and also by various equilibrium kinetic data. In a separate study, Babu and Gupta [109] exploited activated Azadiractha indica as a bioadsorbent. They observed that the adsorption capacity could be significantly enhanced by modifying the physical structure and surface chemistry of the neem leaf via an activation as shown in Table 2. Sharma and Bhattacharya [110] investigated that Azadiractha indica is a good adsorbent for Cadmium, from simulated wastewater. The increase in removal efficiency (8.82-93.6%) with a rise of pH from 4 to 7 was due to the considerable effect of pH upon the removal percentage.

Chaff is an agricultural by-product that contains fiber and protein along with some functional group and is mainly given to livestock and poultry as food [111]. Numerous functional groups such as carboxylates, hydroxyls, and amidogens are also encountered within chaff. Han and his co-worker performed a sorption process with chaff in a fixed bed column. Several operation variables, represented by pH, flow rate, influent concentration of solution and co-existing ions were varied to reveal its effect on the removal performance. In addition, adsorption and desorption recycles of chaff were tried to arrive at a conclusion that their reuse would be feasible.

Another study has also included pectin, an anionic plant cell wall polysaccharide based on α -(1-4) linked D-galacturonic acid, which is commercially available by extraction from pectin-rich sugar-beet pulp, apple pomace and citrus peels[112]. Some degree of similarities exists between pectin structures and alginate, denoting its potential as an alternative sorbent. They compared Cd (II) uptake capacities and stability of several pectin rich fruit wastes. Citrus peels were identified as the most superior alternative adsorbent for its high metal uptake in conjunction with physical stability.

Coconut copra meal is a by-product of coconut oil production and is characterized by the presence of functional groups such as alcohols and carboxylic acids, on its surface. This material has been employed as a bioadsorbent for cadmium removal from wastewater [113]. The initial pH of the solution and cadmium concentration, in particular, significantly affects cadmium sorption onto copra meal.

Pino and his coworkers [114] examined the capability of green coconut shell powder to adsorb three heavy metals. Coconut cell contains lignin acid and cellulose, which bears various polar functional groups for metal binding, namely carboxylic and phenolic acid groups. The sorption capacities of coconut shell for cadmium, chromium and arsenic were studied at different initial metal ion concentration and pH values (2-9) in batch mode. The obtained experimental data for each metal were also evaluated and fitted with Langmuir and Freundlich isotherms, while the kinetic data were interpreted with pseudo-first and second order model.

Rice bran is a by-product of the rice milling process which can be used as an alternative adsorbent for zinc removal from synthetic wastewater [115]. They also studied the influence of the parameters such as pH, temperature, particle size and adsorption time on sorption capacity. The results underscore the importance of pH on zinc sorption capacity while to a certain extent the capacity also relies upon sorbent size.

Amarasinghe and Williams [116] studied with tea leaves from Srilankan tea as a bioadsorbent for Cu (II) and Pb (II) removal from wastewater. They confirmed the high potential adsorption capacity of tea waste-based granular activated carbon. Another agricultural by-product such as wheat bran has been employed as a sobent for detoxification of two heavy metal ions, Cu (II) and Zn (II) from aqueous solution [117]. The metallic cations were found to be attached in a complexation reaction to the lignin and

fatty acid containing functional groups of alcohols, ketones and carboxylic acid within lignocellulosic substrate of wheat bran.

Other low cost and widely available natural materials represented almond shell, hazelnut and walnut [118], birch wood [81], Cassia fistula(Golden Flower) biomass [119], coconut fiber [120], lemon peel [121], neem oil cake [122], olive pomace [123], orange peel [124], pine bark [125], pomegranate peel [126], ponkan peel [127], reed [128], rice husk [129], rice straw [130], sour orange residue [131], and yellow passion fruit shell [132]. All these sorbents have lucratively been applied as bio-sorbents to eliminate metals from contaminated water.

Many researchers have succeeded to increase the adsorption capacity by modifying the biomass chemically. The modifications on the biosorbent surface have been carried out [120, 123-125, 128-129, 131]. For instance, Igwe and coworkers [120] conducted thiolation of coconut fiber, whereas Argun and Dursun [125] altered the surface of properties of pine bark using Fenton reagent. Martin Lara and coworkers [123] claimed to improve the sorption properties of olive pomace by the treatment of phosohoric acid and hydrogen peroxide. These modification processes tend to improve the adsorption capacity of the bio-sorbents.

Adsorbents	Heavy	Optimu	Maximum	References	
Ausorbents	Metals	m pH	adsorption capacity		
Almond Shell	Cr (VI)	4	0.424	[105]	
Azadiractha	Cd (II)	5	1.404	[110]	
indica (Neem	Cr (VI)	2	1.211	[109]	
leef powder)	Pb (II)	5	1.448	[133]	
Birch wood	Cu (II)	5	0.023	[82]	
Betula sp.					

Table 6: Sorption of heavy metals by waste-products of higher plants

Cassia fistula				
(Golden Shower)	Ni (II)	6	2.6	[119]
Biomass				
Chaff	Cu(II)	5	0.031	[111]
	Pb(II)	5	0.032	
Coconut copra	Cd(II)	7	0.047	[113]
9	Cd(II)	7	1.149	[114]
Green coconut	Cd(II)	9	2.541	
shell powder	Cr(III)	7	1.412	[134]
	Cr(VI)	2.5	0.205	
Ground Nut shell	Cr(VI)	4	0.1131	[105]
Grapefruit peels	Cd(II)	5	0.245	[112]
Hazelnut shell	Cr(VI)	4	4.432	[118]
	Cd(II)	5	0.465	[112]
Lemon peel	Pb(II)	4.7	0.869	[121]
	Mn(II)	4.8	0.429	
Lemon resin(LR)	Pb(II)	4.4	0.869	[121]
	Mn(II)	4.4	0.429	
Neem oil	Cd(II)	4	0.133	
cake(NOC)	Pb(II)	4	0.145	[122]
Cake(IVOC)	Cu(II)	4	0.157	
Orange peels	Cd(II)	5	0.335	[112]
Olive pomace	Cd(II)	5	0.1	[130]
	Cu(II)	5	0.48	[]
Palm Tree leaves	Zn(II)	4	0.225	[79]
Pine bark	Cd(II)	7	0.2687	[125]
Pomegranate	Pb(II)	5.6	0.0866	[126]
peel	Cu(II)	5.8	0.3459	
Rice bran	Zn(II)	5	0.279	[115]
	Mn(II)	4.5	0.2503	
Rice husk	Cu(II)	5	0.2175	[129]
	Zn(II)	6	0.2114	

CHAPTER 4

4. MATERIALS AND METHOD

4.1 Chemicals

All reagents and chemicals used in this study were of AR grade and purchased from Wako Pure Chemical Industries, Ltd., Japan. The stock solutions (1000 mg/L) were prepared from nitrate salts of cadmium, lead, and nickel whereas from chlorides salts of zinc and copper appropriately. The pHs of the experimental solutions were adjusted using 0.1 M hydrochloric acid, and 0.1M sodium hydroxide. In the most of experiments 0.1M solution of 2-[4-(2- Hydroxymethyl)-1-piperazinyl] ethanesulfonic acid (HEPES) was also used as a buffering agent purchased from Sigma Aldrich. All the working solutions of desired concentrations were diluted using deionized water and 0.1M HNO₃.

4.2 Preparation of Adsorbents

4.2.1 Preparation of Charred Xanthated Sugarcane Bagasse (CXSB)

Sugarcane bagasse (SB) was collected from local juice vending centre situated in Kathmandu Metropolitan city. It was dried in air oven at 70^oC for 24 h and grounded into fine particles with the help of an electric grinder. It was sieved to pass uniform size of 212 μ m. Then 100 g of SB was treated with 200 ml concentrated H₂SO₄ and stirred for 30 min and left for overnight. It is well known that acid treatment with such biopolymer creates a suitable environment for its ring opening [136]. Sulphated polysaccharide acts as a good cross-linking agent within the polymer surfaces thereby decrease the solubility of the biopolymer and enhances the active functional sites for affective adsorption. It was washed with deionized water to remove excess acid and any other soluble substances until neutrality and then dried. This material is referred as charred sugarcane bagasse (CSB). Charring is a pretreatment process, which can extract soluble organic compounds and enhance chelating efficiency. In addition to dehydrating property of concentrated sulphuric acid, such materials were found to be effective for further chemical modifications. In this regard, the charred material was subjected to xanthation. 50 gm of the CSB was added into

250 ml of 15% NaOH solution and shaken for 1 h. Further 25 ml of CS_2 was added and stirred for 3 h and then left for overnight. It was filtered and washed repeatedly until the pH of the suspension became neutral. Then the material was kept in oven at 70 °C to make it complete dryness and finally put in desiccators. This material was ready for the experiments and called as charred xanthated sugarcane bagasse (CXSB) which is shown below in scheme 3(a) and (b).

(a)



(b)



Figure 3: (a) Proposed ring opening of monomeric unit of cellulose contained in sugarcane bagasse followed by (b) xanthation.

4.2.2 Preparation of Charred Aminated Sugarcane Bagasse (CASB)

The charred sugarcane bagasse was nitrated first then aminated adding sodium dithionite in presence of pyridine and finally treated with 25 % ammonia at 20° C and stirred for 4 h then left for overnight. It was washed till neutrality and dried at 70° C and

finally kept in desiccator. This material was ready for the experiments and called as charred aminated sugarcane bagasse (CASB)

Nitrogen could be added to the carbon by the similar process as in the nitration of benzene. The mechanism would involved the formation of highly reactive nitronium ion (NO_2^+) , which would ultimately form the nitrated product as shown in the reaction (1). The amination reaction was achieved via a two stage process. The first stage is the nitration stage where nitric acid was mixed with concentrated sulphuric acid to form nitronium ions, which reacted via electrophilic substitution of the hydrogen ion of the carbon matrix. The nitro-species formed was reduced using a suitable reducing agent and in this case sodium dithionite was employed in the presence of ammonia. The effectiveness of the reduction reaction is an example of the application of a classic organic reaction on charred sugarcane bagasse. In this case, nitrogen containing surface groups made charred carbon more alkaline which leads in the increase in the adsorption of acidic agents, is expected.

4.3 Effect of pH on Metals Removal

The removal of metal ions from aqueous solution by adsorbent is dependent on the pH of the solution, as the latter affects the surface charge of the adsorbents and the degree of ionization of adsorbate. Batch adsorption tests for various metal ions removal were carried out to examine the adsorption behavior of several metals onto CXSB and CASB. Adsorption of metals as a function of pH was maintained constant (50 mg/ L) at varying pH. For this experiment, pH was adjusted by adding small amounts of 0.1M HCl and NaOH and optimum pH value can be obtained for metal ions on the CXSB and CASB. All batch tests were carried out in 50 ml Erlenmeyer flask (Fig. 4) by taking 20 mg of dry charred xanthated sugarcane bagasse together with 15 ml of different synthetic metal ions solutions. The flasks were then agitated in a thermostated shaker maintained at 30°C and 150 rpm for 24 h to attain equilibrium. After 24 h, the suspensions were filtered through a 1 μ m filter paper and their equilibrium concentrations were measured by AAS. The adsorbed amounts of metal ions were calculated from the decrease in the metal ions concentrations.

4.4 Adsorption Experiments

The main objective of isotherm is to evaluate the capacity of the modified biomass to sequester heavy metals from an aqueous solution. Several authors have studied adsorption data using Langmuir and Freundlich adsorption isotherms [137]. The test solutions of cadmium(II), lead(II), nickel(II), zinc(II) and copper(II) were prepared from corresponding standard stock solution by diluting with 0.1M nitric acid and 0.1M of HEPES as a buffering agent, respectively. The pH of the solution was maintained by adding small amount of nitric acid or sodium hydroxide.

In batch adsorption experiments known weights of CXSB and CASB samples (20mg) were added to Erlymeyar flask (Figure 4) containing 15 mL heavy metal solution with adjusted pH and shaked by thermostatic shaker at approximately 150 rpm (a speed rate at which the CXSB and CASB would not precipitate). The effect of pH on adsorption was examined by operating various pH values (1, 2, 3, 4, 5, 6 and 7) of CXSB and CASB applied to 15 ml of the solution containing 50 mg/L heavy metals at 303 K for 24 h to ensure the equilibrium to be attained. Precipitation of the metal species was observed over the pH 7. The effect of temperature on adsorption was examined by operating at various temperatures; 298K, 308K, 318 and 328 K in a temperature controlled shaker. The effect of initial concentration of heavy metal ions was examined by studying different initial concentrations changing from 25 to 1000 mg/L. Initial concentration values were chosen as 25, 50, 100, 250, 500, 750 and 1000 mg/L, respectively. At the end of each mixing period the liquid phases were separated from the solution by filtration. All adsorption experiments were performed for three times and replicate average values were used for all calculations.


Figure 4: Batch Adsorption experiments (At 30° C, 150 rpm in thermo-stated shaking Incubator).

The initial and equilibrium concentrations of the metal ions were measured by using atomic absorption spectrophotometer. The adsorption efficiency, A% of the metal ion was calculated from

$$A \% = \frac{C_i - C_e}{C_i} X 100$$
 (1)

The sorption capacity of metal ions is the concentration of the metal ions on the adsorbent and can calculated based on the mass balance principle where

$$q = \frac{C_i - C_e}{W} X \frac{L}{1000}$$
(2)

In the above equations (1) and (2), q represents the amount of metal up taken per unit mass of the adsorbent (mg g⁻¹), L is the volume of the test solution (mL), W is the dry mass of the adsorbent (g), C_i and C_e the initial and final concentrations (mg dm⁻³), respectively.

4.5 Kinetic Studies

The kinetic parameters of adsorption systems, which are helpful for the prediction of adsorption rate, provide important information for designing and modeling the processes. Thus, the effects of initial concentration, contact time, and adsorbent dosage were analyzed from the kinetic point of view. Throughout the study, the kinetics of several metal ions was investigated by using 20 mg chemically modified adsorbent with 15 ml of concentration (100 mg L⁻¹) of various metal ions solutions into a 50 ml Erlenmeyer flask. The optimum pH of each solution of different metals was kept constant for different contact time (5-240 min). The apparatus used in the kinetics experiments were similar to those used in batch experiments.

4.6 Desorption Studies

Desorption experiments were carried out by metal- loaded CXSB sorbent (1.0 g) with 50 ml of 0.1 M HNO₃ as the desorbing agent in 250 ml Erlenmeyer flasks and shaken in a rotary shaker for 60 min at room temperature. The metal- loaded CXSB suspension was centrifuged and the supernatant was analyzed for metal ions desorbed. After each cycle of adsorption-desorption, CXSB sorbent was washed with distilled water and the regenerated CXSB was treated with 0.1 M CaCl₂ for 15 min, followed by washing, filtering and drying before use in further experiments. This metal-desorbed CXSB was used as the regenerated sorbent in five repeated sorption-desorption cycles to determine reusability potential of the adsorbent. The measurement was done at respective wavelength of different metals with slit width 0.7 nm using air-acetylene flame. Experimental samples were filtered using Whatman 1-mm filter paper and the filtrates were analyzed after suitable dilutions.

4.7 Analysis

The morphological characteristics of CSB and CXSB were visualized via scanning electron microscope (SEM) using an S-3000N Scanning Electron Microscope of HITACHI, Japan, at 2000x magnification. The functional groups present in the adsorbent were characterized by a Fourier transform infrared (FTIR) spectrophotometer (FT/IR-410 (JASCO, Japan), using KBr discs to prepare the CSB and CXSB samples. Thermal gravimetric analysis (TGA) was carried out on a thermal analyzer (Model TG/ DTA -6300, Seiko Instrument Inc. Extar) at a heating rate of 10° C per min under nitrogen atmosphere. The pH of the sample solution was measured using a pH meter, HM- 30R, TOA-DKK while the concentrations of the several metal ions were measured by using Shimadzu AA-6650 Atomic Absorption Spectrophotometer. Standard solutions of various metal ions of 1000 mg/L were diluted to the desired concentrations and used for AAS calibration. Each batch tests were equilibrated by shaking in a Thermostatic Shaking Incubator AT 24R, Japan.

4.7.1 Elemental Analysis

The elements such as C, H, N and S were analyzed for the chemical composition of the raw, charred and modified bio-materials. The carbon, hydrogen and nitrogen contents of the samples were determined from the quantities of CO₂, H₂O and NO₂ produced by the combustion of the dried solid in oxygen [138]. Elementar Vario Macro elemental analysis apparatus was used to determine the amount of C, H, N and S in raw, xanthated and aminated sugarcane bagasse. In this case samples were heated to a temperature of 1000°C and approximately 2mg of each respective bio-material was placed inside a silver capsule and was dropped into the furnace, where it was completely combusted. This instrument relies upon infrared detection to measure the weight percent of carbon, hydrogen, and sulfur, while nitrogen was measured using thermal conductivity detection.

4.7.2. Scanning Electron Microscope (SEM) Analysis

Scanning Electron Microscope (SEM) is commonly used to study surfaces, structures, morphologies, and forms of materials. The images viewed using SEM are created by detecting secondary electrons ejected from samples as they are bombarded by focused, high energy electron beams. Unlike optical microscopy, one does not look through lenses at the actual sample, but one observes images of the sample created by the instrument's electronics. SEM can achieve higher magnifications than optical microscopes. When samples are probed with focused electron beams, a variety of signals can be collected and displayed on the view screen. In addition to secondary electron signals, Xrays characteristic of the elemental composition of the sample can be mapped to sample images, and back-scattered electrons can also be collected and displayed. When SEMs are fitted with appropriate detectors, one can not only see images of the samples (using secondary and back-scattered electron signals) but one can also see images which map the elemental compositions of the samples. SEM analyses are conducted in vacuum environments. All non-conductive samples must be coated with electrically conductive coatings before they can be observed in SEM [138]. SEM characterization was carried out using an S-3000N Scanning Electron Microscope of HITACHI, Japan, type instruments in vacuum environment. Prior to analysis the CSB, CXSB and CASB samples were sprinkled onto Al or C tapes which are adhesive and supported on metallic disks and coated with Au. Images of the sample surfaces were recorded at different areas and magnifications.

4.7.3. Zeta Potential Analysis

The development of a net charge at the particle surface affects the distribution of ions in the surrounding interfacial region, resulting in an increased concentration of counter ions (ions of opposite charge to that of the particle) close to the surface. Thus an *"electrical double layer"* exists around each particle. The liquid layer surrounding the particle exists as two parts; an inner region, called the *"Stern layer"*, where the ions are

strongly bound and an outer, diffuse, region where they are less firmly attached. Within the diffuse layer there is a notional boundary inside which the ions and particles form a stable entity. When a particle moves (e.g. due to gravity), ions within the boundary move with it, but any ions beyond the boundary do not travel with the particle. This boundary is called the surface of hydrodynamic shear or slipping plane. The potential that exists at this boundary is known as the "*Zeta potential*".



Figure 5: Schematic representation of zeta potential. (Source: WEB_6 2007).

The magnitude of the zeta potential gives an indication of the potential stability of the colloidal system. A colloidal system is when one of the three states of matter: gas, liquid and solid, are finely dispersed in one of the others. For this technique we are interested in the two states of a solid dispersed in a liquid, and a liquid dispersed in a liquid, i.e. an emulsion. If all the particles in suspension have a large negative or positive zeta potential then they will tend to repel each other and there is no tendency to flocculate. However, if the particles have low zeta potential values then there is no force to prevent the particles coming together and flocculating. The general dividing line between stable and unstable suspensions is generally taken at either +30mV or -30mV. Particles with zeta potentials more positive than +30mV or more negative than -30mV are normally considered stable. The point where the plot passes through zero zeta potential is called the *"Isoelectric point"* and is very important from a practical consideration. It is normally the point where the colloidal system is least stable [139].



Figure 6: A typical plot of zeta potential versus pH (Source: WEB_ 6 2007).

Zeta potentials and isoelectric point (point of zero charge) determination of CXSB and CASB performed using a pH meter ZS model. A 0.1 wt % CXSB and CASB suspensions were prepared and pH adjustments made using HNO₃ or NaOH. After the pH stabilized, required amount of these solutions transferred to the beaker and duplicate values of zeta potential were measured at room temperature.

4.7.4 Infra Red Spectroscopy (IR analysis)

Infrared (IR) spectroscopy measures the absorption of IR radiation by materials as the atoms vibrate about their bonds. IR sensitive vibrations are associated with changes in dipole moments. It is primarily used for both qualitative and quantitative analysis, to identify molecules and compounds, and to determine the presence or absence of certain types of bonds, structures and functional groups. For example, double and single bonds associated with carbon-hydrogen and carbon oxygen bonding (=C-H,-C-H, C-O and C=O) can be distinguished by IR absorption. When functional groups can be bonded at different locations on molecules, IR spectroscopy can frequently identify the positions at which the functional groups are attached. The reason is that vibrational frequencies differ when functional groups are attached at different sides in molecules. When illuminated by IR radiation of the appropriate frequencies, atoms, ions, and functional groups in molecules will vibrate about their bonds and energy will be absorbed. Each bending and stretching vibration mode of a molecule or functional group will absorb at a particular frequency. When exposed to appropriate IR frequencies, energy will be absorbed from the incident radiation as vibration intensities increase. Many IR frequencies have no effect at all and will not be absorbed [138]. The functional groups present in the CSB, CXSB and CASB samples were characterized by a Fourier transform infrared (FTIR) spectrophotometer. Approximately 1mg of CXSB and CASB powder and 90 mg of KBr was blended with the help of mortar and pestle for 10 min. Approximately 40 mg of the mixture were compacted using an IR hydraulic press at a pressure of 8 tons for 60 s. The disk was conditioned in a desiccator placed in an oven at 80°C for 16 hr before analysis. The spectra of CSB, CXSB and CASB samples in the forms of KBr disk were obtained with a frequency range of 4000-400 cm⁻¹.

4.7.5. Thermal Gravimetric Analysis (TGA/DTA)

Thermal Gravimetric Analysis (TGA) measures the masses of samples as they are heated and cooled through standard firing programs. TGA analyses are very similar to DTA analyses. In the case of TGA analyses, the increase, decrease, or constancy of mass of samples at each temperature in the firing program indicates the presence or absence of reactions and the nature of each reaction that takes place. For example, phase changes occur without change of mass; some decomposition reactions are accompanied by weight loses; and oxidation reactions are accompanied by weight gains. TGA analyses require small samples (several grams) of dry powders or particulate suspensions. All such samples must be thoroughly dried before performing the analyses. Similar to the DTA analysis technique TGA analyses are also routinely used to identify during body development. Some modern instruments simultaneously perform DTA and TGA analyses [138].

4.7.6 Atomic Absorption Spectrometry (AAS) Analysis

Atomic absorption spectrometry (AAS) is a widely used and accepted technique capable of determining trace (μ g/mL) and ultra trace (sub- μ g/mL) levels of elements or metals in a wide variety of samples, including biological, clinical, environmental, food, and geological samples, with good accuracy and acceptable precision. It is arguably the predominant technique in elemental analysis, although it does have some limitations [140]. Atomic absorption spectrometry uses the absorption of radiation by free gaseous atoms in order to achieve qualitative detection and quantitative determination of elements [141]. An atomic absorption spectrometer measures the absorbance which is the logarithm of the rate of incident light power (*Po*) to transmitted light power (*P*)

$$A = \log P_0 / P \tag{3}$$

There is relationship between Po and P when a light beam is decreased by the medium through which it passes:

$$P = P_0 \exp\left(-\,\mathrm{kL}\right) \tag{4}$$

where k: Absorption coefficient which is a function of wavelength of light, number of atoms in the ground state per unit volume *L*: Path length in medium.

There are two main components in an atomic spectrometer: atom cell which creates atoms at the free gaseous ground state, optical system to measure the signal. Atom cell dissolves the liquid sample and dissociates analyte elements into their free gaseous ground state form in which the atoms are available to absorb radiation coming from light source and create a measurable signal which is proportional to concentration (143). The atomizer, in which the analyte is atomized, is flame, graphite tube or quartz tube. In flame atomization fixed aliquot of measurement solution is converted into an aerosol in nebulizer and transported into the flame which must has enough energy both vaporize and atomize the sample. The filtrate solutions obtained in the adsorption process were analyzed using flame AAS. Element content of aqueous solutions was determined with hallow cathode lamps. Table 7 shows that specific wavelengths and analysis conditions for used metal ions in our study.

Element	Wavelength (nm)	Flame Type	Hallow-Cathode Lamp
Cadmium (Cd ²⁺)	228.8	Air/acetylene	Cadmium
Lead (Pb ²⁺)	217.0	Air/acetylene	Lead
Nickel (Ni ²⁺)	232.0	Air/acetylene	Nickel
Zinc (Zn^{2+})	213.9	Air/acetylene	Zinc
Copper (Cu ²⁺⁾	324.8	Air/acetylene	Copper

 Table 7: Specific wavelengths and AAS analysis conditions for heavy metal ions

CHAPTER 5

5. RESULTS AND DISCUSSION

5.1 SEM analysis

A Scanning Electron Microscopy (SEM) was used to observe the surface morphologies of CSB before modification whereas for CXSB and CASB after chemical modification, respectively. The fiber surface of CSB was found to be relatively rough and non-uniform due to hydrolysis reaction on the surface of SB by the action of concentrated sulphuric acid. The surface morphology of CSB, CXSB and CASB was characterized by SEM images shown in Fig. 7(a), 7(b) and 7(c). It can be seen that the external surfaces of CXSB and CASB are full of cavities like a honeycomb structure. Both Xanthation and Amination processes had considerably enhanced the morphology of charred sugarcane bagasse and its physical, chemical and biodegradable characteristics, which varies with respect to the nature of synthetic side chains incorporated. SEM observations of CSB revealed its non-uniform and rough surface that changed into irregular honeycomb structure of CXSB and CASB. The CXSB and CASB showed apparently isolated and irregularly distributed pores, which are supposed to be formed due to the increase in effective diffusion surface area that helps to expose more surface active binding sites and finally enhance adsorption capacity of the modified sugarcane bagasse.



(a)



(c)

(b)



Figure 7: SEM images showing the surface morphologies of (a) CSB before modification (b) CXSB after modification and (c) CASB after modification.

5.2 FTIR Spectra Analysis

5.2.1 FTIR of Charred Xanthated Sugarcane Bagasse (CXSB)

FTIR is a useful tool to identify the presence of certain functional groups in a molecule as each specific chemical bond often has a unique energy absorption band. The spectral analysis was employed to confirm changing of functional groups for pretreated and xanthated sugarcane bagasse. The FTIR spectrum of the CXSB was recorded with KBr dispersion method where CXSB and KBr ratio was taken 1:100 to make tablet. The broad, intense absorption peaks observed at 3442 cm⁻¹ are due to the existence of bounded hydroxyl groups. The peaks observed at 2930 cm⁻¹ can be assigned to the C-H group, and peaks around 1042 cm⁻¹ are characteristics of C-O group of primary hydroxyl stretching that may be attributed to cellulose structure of the sugarcane bagasse. The band at 1754 cm⁻¹ was observed is due to the –CHO group formed during the charring process before modification of CSB. This peak disappears after modification of CSB into CXSB and an intense broad band depicted in Fig.8 is observed at 1558 cm⁻¹ revealing that xanthate group has been introduced onto the CSB. Absorption peaks appeared at 1558cm⁻¹ corresponding to the C=S stretching vibration of the xanthate unit and it may be attributed to the $-CS_2H$ deformation suggesting that CXSB has been successfully xanthated. The stretching vibration of C=S, S=O and S-S found at 1176, 1022 and 460 cm⁻¹, respectively in the spectrum of CXSB were strong indicative of the presence of xanthate group bonded to the charred materials. The major absorption bands characteristic of the C=S groups lay in the region 1563 -700 cm⁻¹ (143). This region is much more intense for CXSB in comparison to CSB. The peak corresponding to C-S-S and C-O-C symmetric stretching seemed to have merged into a broad band at 1558 cm⁻¹. The asymmetric stretching vibration of C-O-C is observed at 1176 cm⁻¹. The very weak vibration for C-S is also observed around 605 cm⁻¹.



Figure 8: (a) FTIR of CSB (before modification) and (b) CXSB (after modification).

5.2.2 FTIR of Charred Aminated Sugarcane Bagasse (CASB)

FTIR spectra in the 3500- 400 cm⁻¹ regions are for CSB and CASB where the modification of CSB with Na₂S₂O₄ and 25 % NH₃ transforms to CASB. In this transformation many characteristics bands are shifted at the maximum peak, and absorbance is changed. The peak observed at 3484 cm⁻¹ is due to the stretching vibration of the O-H groups. Although there is possibility of overlapping between the N-H and the O-H stretching vibrations, the strong broad band at the wave number region of 3300-3500 cm⁻¹ is characteristic of the N-H stretching vibration [143]. The significant decrease of transmittance in this band region after lead adsorption indicates that the N-H vibration was affected due to lead adsorption. Other changes in the transmittance can be observed at the wave number of 1720, 1644, 1457, 1251, 1049 and 902 cm⁻¹, respectively. These wave numbers are closely related to the N-H bending, C-N stretching, and N-H rocking bands. The board and strong band ranging from 3300-3500 cm⁻¹ may be due to overlapping of O-H and N-H stretching, which is consistent with the peaks at 1644 and 1047cm⁻¹ assigned to alcoholic C-O and C-N stretching vibration[143]. Prior to modification of CSB the band at 1720 cm⁻¹ is due to the –CHO group formed during the charring process. This peak disappears after modification of CSB into CASB and an intense broad band depicted in Fig. 9(b) is observed at 1592 cm⁻¹ revealing that amino group has been introduced onto CSB.



Figure 9: (a) FTIR of CSB (before modification) and (b) CASB (after modification).

Group or functionality	Assignment Regions (cm ⁻¹)	Group or	Assignment Regions	
Group of functionality	Assignment Regions (em)	functionality	(cm ⁻¹)	
C O in Ethers (stratching)	1000 1200	Lastonas	1160-1370, 1675-	
C-O III Ethers (succoming)	1000-1500	Lactones	1790	
Alcohols	1049 1276 3200 3640	Carboxylic	980 1300 1740 1880	
Aconois	1049-1270, 5200-5040	anhydrides	900-1300, 1740-1880	
Phenolic Groups		C-H (stretching)	2600-3000	
-C-OH (stretching)	1000-1220	C-N	1190	
О-Н	1160-1200, 2500-3620	C=C=N	2070-2040	
Carbonates, Carboxyl-	1100-1500 1590-1600	N-O-	1300-1000	
Carbonates	rbonates		1300-1000	
-C-C aromatic (stretching)	1585-1600	N-H, C=N	1560-1570	
Quinones	1550-1680	Cyclic amides	646, 1461, 1546, 1685	
Carboxylic acids	1120-1200, 1665-1760,	C-N aromatic ring	1000 1250 1355	
Curboxyne delus	2500-3300		1000, 1250, 1555	

Table 8: IR Assignments of Functional groups on carbon surfaces

5.3 Elemental Analysis

The amount of carbon, hydrogen and nitrogen in raw sugarcane bagasse were found to be 46.58%, 6.11% and 0.11% whereas after chemical modification 52.35%, 2.12%, and 0.22%, respectively for CXSB. The percentage of sulfur had been determined to be as 7.38% which confirmed the proper modification of charred sugarcane bagasse by the introduction of xanthate group in the xanthation process.

The amount of carbon, hydrogen and nitrogen in CASB were found to be different from the raw sugarcane bagasse (RAW) is depicted in the Table 9. After amination, the increased percentage of nitrogen confirmed that there was proper modification of charred sugarcane bagasse by the introduction of amine group.

Adsorbents	Carbon(%)	Hydrogen (%)	Nitrogen (%)	Sulphur (%)
RSB	46.58	5.95	0.23	0.32
CSB	50.24	3.14	0.51	2.46
CXSB	52.35	2.12	0.22	7.38
CASB	51.44	2.99	6.29	3.01

Table 9: Elemental analysis of sugarcane bagasse before and after modification

5.4 Thermal analysis

Thermal analysis (TG) was performed to understand the stability characteristics of the charred sugarcane bagasse (CSB) cellulose and charred xanthated sugarcane bagasse (CXSB) cellulose, which is important during the processing of fibers into composites. The experiments were carried out under continuous N2 atmosphere using a thermal analyzer with a heating rate of 10 $^{\circ}$ C min⁻¹. The charred sugarcane bagasse degraded mainly in two decomposition steps: the first at 250 °C and second one at 450 °C. Same way, CXSB also showed two decomposition steps at 300 °C and 810 °C, respectively. These results are depicted in the TGA and DTA curves shown in Fig. 10 for CSB and CXSB. The first stage started at about 100°C for all the materials with weight loss of 10-20% due to loss of physically adsorbed water on membrane surfaces. The second stage exhibited a rapid weight loss at 250-450 °C and 300-810 °C for CSB and CXSB, respectively. The maximum oxidation reached at 450 °C for CSB and 810 °C for CXSB. The second degradation stage of CXSB took place at higher temperatures than the corresponding stage of CSB indicating that CSB is less stable than CXSB. The weight loss for CSB (250-450° C) and CXSB (300-810 °C) were found to be about 90% and 80%, respectively. The DTA curves revealed interesting and more accurate differences of the thermal behavior of the CSB and CXSB than the TGA curves. The DTA peak of CXSB had shown its maximum value at about 810 °C, while it is 450°C for CSB indicating a strong evident in the increase in thermal stability of the CXSB over CSB. From the aforementioned analysis it is concluded that chemical modification has taken place within the CSB.



Figure 10: TG-DTA curves of CSB (before modification) and CXSB (after modification).



temp (°C)

Figure 11: TG-DTA curves of CSB (before modification) and CASB (after modification).

In the same way, the thermal stability and degradation behavior of CSB and CASB samples were compared by thermo-gravimetric analysis (TGA) and differential thermogravimetric analysis (DTA) in a N₂ atmosphere using a thermal analyzer. Charred sugarcane bagasse degraded mainly two stages such as devolatilization and solid decomposition, the first at 230 °C and last one at 430 °C. The first step can be assigned to decomposition of fibers and second corresponds to the complete decomposition. Same way CASB also showed two decomposition steps at 250 °C and 520 °C, respectively. These results are depicted in the TGA and DTA curves shown in Fig. 11 for CSB and CASB. The first stage started at about 100°C for all the materials with weight loss of 10-20% due to loss of physically adsorbed water on membrane surfaces. The second stage exhibited a rapid weight loss at 230-430 °C and 250- 520 °C for CSB and CASB, respectively. The

maximum oxidation reached at 430 °C for CSB and 520 °C for CASB. The second degradation stage of CASB took place at higher temperatures than the corresponding stage of CSB indicating that CSB is less stable than CASB. The weight loss for CSB (230-430° C) and CASB (250- 520° C) were found to be about 85% and 82%, respectively. The DTA curves revealed more accurate differences of the thermal behavior of the CSB and CASB than the TGA curves. The DTA peak of CASB had shown its maximum value at about 520° C in comparison to CSB (430 ° C) that indicating the increase in thermal stability of the CASB over CSB. From the above mentioned analysis it is confirmed that amination has taken place within the CSB.

5.5 Effect of pH on Adsorption of Various Metal Ions

The pH of a solution played an important role for adsorption of metal ions. At low pH, there is high concentration of H⁺ that has high mobility as compared to metal ions and competition between H⁺ with metal ions decreases their adsorption. On the other hand, as the pH value of the solution increases, adsorption also increases due to lesser number of H⁺ and greater number of surface ligands with negative charges. The low adsorption of metal ions at low pH may be due to sorbate lyophobic behavior [145]. As the pH increases, the solubility of the adsorbate decreases and surface of the adsorbent becomes negative; hence electrostatic interaction takes place, which increases adsorption. The optimum pH for Cd, Pb, Ni, Zn and Cu biosorption was found to be 5, 4, 4, 6 and 5, respectively as shown in Fig.12 and 13. The optimum pH of solution can be explained on the basis of pH_{pzc} (point of zero charge). The pH_{pzc} is the pH at which the net charge of the adsorbent surface becomes zero. The point of zero charge for CXSB was found to be 4 as shown in Fig.14. Below pH_{pzc} (pH < 4) the surface charge is positive and above pH_{pzc} (pH > 4), the surface charge of xanthated adsorbent is negative. Hence at more than pH 4, the sorption of the metal ions increased while adsorption of metal ions decreases at pH less than 4. This signifies that the adsorption of metal ion takes place according to ion exchange mechanism. The amount of adsorption above pHpzc was maximum due to the interaction of metal ions M^+ and $M(OH)^+$ with negatively charged adsorbent surface. At low pH particularly below pH_{pzc}, the positively charged M⁺ and M (OH)⁺ species may repel with

positively charged adsorbent surface having identical charge and thereby decreases the metal ion adsorption. The selectivity order in the removal of heavy metals at pH around 4 follows the order Pb > Cu > Ni > Cd > Zn. Pauling electronegativity values for these atoms are 2.33, 1.90, 1.90, 1.69 and 1.65, respectively. As the electronegativity of the atom increases, their ionic form seems to be more easily sorbed by the bioadsorbent. This is in full accord with results obtained earlier [146].



Figure 12: Effect of pH in the adsorption of Cd (II), Pb (II), Ni (II), Zn (II) and Cu (II) onto CXSB.



Figure 13: Effect of pH in the adsorption of Cd (II), Pb (II), Ni (II), Zn (II) and Cu (II) onto CASB.

pН	Cd(II)	Pb(II)	Ni(II)	Zn(II)	Cu(II)
4	99.9	99.4	99.2	99.9	99.6
5	99.4	94.3	96.1	99.1	96.3
6	95.4	59.2	52.4	93.9	77.5
7	-	9.6	12.5	88.0	19.1

Table 10: Solubility of Cd (II), Pb (II), Ni (II), Zn (II) and Cu (II) at different pHs

Table 11: Effect of pH of metal ions adsorption onto CXSB and CASB

Metal ions	Optimum pH		% Adsorption	
	CXSB	CASB	CXSB	CASB
Cd(II)	6	6	95	90
Pb(II)	4	4	98	98
Ni(II)	5	5	75	73
Zn(II)	6	6	70	66
Cu(II)	5	5	99	89

5.6 Point of Zero Charge

Depending on solution pH, the adsorbent surfaces can bear net negative, or positive, or no charge. The pH where the net total particle charge is zero is called the point of zero charge (pH_{PZC}), which is one of the most important parameters used to describe variable-charge surfaces [146,147]. If the pH of adsorbent surface is above its pH_{PZC} the adsorbent surface will have a net negative charge and predominantly exhibit an ability to exchange cations (CEC— exchange of one positive ion by another), while the modified adsorbent will mainly retain anions (electrostatically) if its pH is below its PZC (AEC— exchange of one negative ion for another). The point of zero charge for CASB was found to be 10.2 as shown in Fig.15.



Figure 14: Point of zero charge (p H_{pzc}) curve $% f(\mathbf{RSB})$ and CXSB.



Figure 15: Point of zero charge (pH $_{pzc}$) curve of RSB and CASB.

5.7 Adsorption Isotherms

The study of adsorption isotherms indicates the adsorption capacities of adsorbents at experimental condition. Isotherms help to determine the adsorptive capacity of material and further help to evaluate the mechanism of performance of the adsorption system. It is done by characterizing the equilibrium state of the functionalized adsorbent that has been allowed to react with aqueous solution of the metal of interest. Here isotherm studies were performed using various concentrations of metal ions ranging from 25 to 1000 mg dm⁻³. For batch adsorption experiment, 20 mg of adsorbent was equilibrated with 15 ml of corresponding synthetic metal solution in a 50 ml Erlenmeyer flask for 24 h to attain equilibrium. Sorption isotherms were evaluated using linearized Langmuir and Freundlich model represented by Eqs. (5) and (6), respectively.

$$\frac{C_{\rm e}}{q_{\rm e}} = \frac{1}{q_{\rm m}b} + \frac{C_{\rm e}}{q_{\rm m}}$$
(5)

$$ln q_e = ln K_F + \frac{1}{n} ln C_e$$
(6)

Where $q_e (mg/g)$ is the amount of adsorbed metal ions per gram of adsorbent; $C_e (mg/L)$ is the residual concentration of metal ion after adsorption, $q_m (mg/g)$ the maximum adsorption capacity, b (L/mg) the binding constant. In equation (4), K_F and 1/n are the Freundlich constants related to adsorptive capacity and intensity of adsorption, respectively. The Langmuir constants (q_m and b) were calculated from the plots of C_e/q_e versus C_e , and Freundlich constants (K_F and 1/n) were obtained from lnq_e versus lnC_e plots using the above linearized equation (data not given). The Langmuir constants and its correlation coefficients evaluated from the isotherm for Cd^{2+} , Pb^{2+} , Ni^{2+} , Zn^{2+} and Cu^{2+} are given in the Table 12 and 13. The high value of Langmuir correlation coefficient (R^2 = 0.99) confirmed that the Langmuir isotherm is best fitted than the Freundlich isotherm onto CXSB. The maximum adsorption capacity based on experimental results evaluated from Fig.16 and 17 to be were 225, 318, 144, 164 and 178 mg g⁻¹ for CXSB and 226, 280, 123, 137 and 128 for CASB, respectively. These results revealed that the active sites of the biomass CXSB and CASB are constant and independent of the metal solution used. The

values of b are the indicative of the affinity of the sorbent by the sorbate, and high values of b are associated with high metal adsorbed/metal desorbed ratio [148]. The b constant is higher for lead than for other metals indicating that it has higher affinity towards the active sites of the adsorbent materials. Furthermore, the affinity of CXSB by the metals followed the order: $Pb^{2+} > Cd^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+}$. On the other hand, the theoretical monolayer capacity (q_m) of CXSB for the abovementioned metal ions based on Langmuir adsorption equation as shown in Fig.18 was determined to be 250, 333, 167, 200 and 200 mg g⁻¹, respectively. Similarly, the theoretical monolayer capacity (q_m) of CASB for the above respective metal ions based on Langmuir adsorption equation as shown in Fig.19 was determined to be 248, 307, 181, 176 and 188 mg g⁻¹, respectively. These results are in close agreement against each other suggesting that heavy metals can be quantitatively sequestered onto CXSB.



Figure 16: Adsorption isotherm plot for the adsorption of several metal ions onto CXSB.



Figure 17: Adsorption isotherm plot for the adsorption of several metal ions onto CASB.



Figure 18: Langmuir isotherm plot for the adsorption of several metal ions

onto CXSB.



Figure 19: Langmuir isotherm plot for the adsorption of several metal ions onto CASB.

Table 12: Langmuir adsorption isotherm model parameters and experimental q_{max} of CXSB

Metal ions	q _{max} (mg/g)	q _{max} (mg/g)	b(L/mg)	\mathbf{R}^2	
	experimental	Langmuir			
Cd(II)	225	250	0.018	0.997	
Pb(II)	318	333	0.023	0.995	
Ni(II)	144	167	0.011	0.996	
Zn(II)	165	200	0.013	0.993	
Cu(II)	178	200	0.014	0.991	
Cd(II) Pb(II) Ni(II) Zn(II) Cu(II)	experimental 225 318 144 165 178	Langmuir 250 333 167 200 200	0.018 0.023 0.011 0.013 0.014	0.997 0.995 0.996 0.993 0.991	

Metal ions	q _{max} (mg/g) experimental	q _{max} (mg/g) Langmuir	b(L/mg)	\mathbf{R}^2
Cd(II)	226	248	0.0211	0.993
Pb(II)	280	307	0.0592	0.991
Ni(II)	123	181	0.0071	0.997
Zn(II)	137	176	0.0093	0.997
Cu(II)	128	188	0.0172	0.991

Table 13: Langmuir adsorption isotherm model parameters and experimental q_{max} of CASB

The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless constant called the equilibrium parameter R_L as expressed by Eq. (7).

$$R_{\rm L} = \frac{1}{1 + bC_{\rho}} \tag{7}$$

Where, b is the Langmuir constant and C_o is the initial metal ions concentration. R_L values represent the type of isotherm and its value between 0 and 1 indicates favorable adsorption. The R_L values evaluated (data not given) from the b values for all metal ions at various concentrations had shown that all values found to be between 0 and 1, indicating further support for the Langmuir model [149].

5.8 Sorption Kinetics

The rate of metal sorption is an important factor and a prerequisite for the determination of a successful practical adsorption application. The sorption kinetics of the metal ions onto CXSB was analyzed as the function of time at an initial concentration of 100 mg/L solutions. The concentrations of the metal ions were analyzed keeping their

optimum pH in a regular and certain interval of time by AAS. From the experimental data, it was observed that the percentage of adsorption increased with the increase in time from 5 min up to 40 min and then it became constant in the range 15 min to 240 min as shown in Fig.20 and 21. All the kinetic data of the respective metal ions were tested by using pseudo first-order rate equation and was found to be very low (data and figure not given) Lagergren correlation coefficient (\mathbb{R}^2) value. Hence the pseudo-second order kinetics model has been used to evaluate the experimental kinetic adsorption data. Adsorption kinetics was explained by the pseudo-second order model [150] given as follows in the integrated form:

$$\frac{t}{q_{t}} = \frac{1}{K_{2}q_{e}^{2}} + \frac{t}{q_{e}}$$
(8)

Where $q_t (mg g^{-1})$ is the amount of adsorption at time t (min), $K_2 (g mg^{-1} min^{-1})$ is the rate constant of the pseudo-second order kinetic adsorption. The values of K₂ and q_e can be obtained from the intercept and slope of the plot of the experimental t/q_t versus t. Figure 22 and 23 depicts the experimental data which can be explained by the pseudo-second order kinetic model, with the correlation coefficient R^2 being almost unity (0.999) for all the metal ions. The regression coefficient of above 0.999 shows that the model can be applied for the entire adsorption process and confirmed the chemisorptions [151] of all metal ions onto the CXSB and CASB. The experimental value of K_2 was found to be 3.61 x 10⁻², 3.26 x 10^{-2} , 90 x 10^{-2} , 1.28 x 10^{-2} and 9.63 x 10^{-2} g mg⁻¹ min⁻¹, respectively for the mentioned metal ions. Similarly, K₂ value for the respective metals ions onto the CASB was found to be 1.69 x 10^{-2} , 2.21 x 10^{-2} , 4.66 x 10^{-2} , 2.11 x 10^{-2} and 4.75 x 10^{-3} g mg⁻¹ min⁻¹, respectively. It is well known that higher the value of rate constant faster is the rate of adsorption. Hence the rate of adsorption for the respective metal ions onto CXSB found experimentally from K_2 values are in the order: Ni (II) > Cu (II) > Cd (II) > Pb (II) > Zn (II) with the required equilibration time 15, 20, 25, 25, and 35 min, respectively. On the otherhand the rate of adsorption of the metal ions onto CASB are in the order: Ni (II) > Pb (II) > Zn (II) > Cd (II) > Cu (II) with the equilibrium time 20, 25, 25, 30 and 35 min, respectively. The kinetics experiment thus indicated that both CXSB and CASB adsorbents might be effective for removal of heavy metals from aqueous solution within 35 minutes.

Metal ions	\mathbf{R}^2	K ₂ (g / mg /min)
Cd (II)	0.999	3.61 x 10 ⁻²
Pb (II)	0.999	3.26×10^{-2}
Ni (II)	0.999	90.0 x 10 ⁻²
Zn (II)	0.999	1.28 x 10 ⁻²
Cu (II)	0.999	9.63 x 10 ⁻²

Table 14: Sorption kinetics of pseudo-second order for several metal ions onto CXSB

Table 15: Sorption kinetics of pseudo-second order for several metal ions onto CASB

Metal ions	\mathbf{R}^2	K ₂ (g / mg /min)
Cd (II)	0.9999	1.698 x 10 ⁻²
Pb (II)	0.9999	2.213 x 10 ⁻²
Ni (II)	0.9992	4.658 x 10 ⁻²
Zn (II)	0.9998	2.113 x 10 ⁻²
Cu (II)	0.9998	4.746 x 10 ⁻³



Figure 20: Amounts of adsorption versus adsorption times for Cd (II), Pb(II), Ni(II), Zn(II) and Cu(II) onto CXSB.



Figure 21: Amounts of adsorption versus adsorption times for Cd (II), Pb(II), Ni(II), Zn(II) and Cu(II) onto CASB.



Figure 22: Pseudo second order sorption kinetics of Cd(II), Pb(II), Ni(II), Zn(II) and Cu(II) onto CXSB.



Figure 23: Pseudo second order sorption kinetics of Cd(II), Pb(II), Ni(II), Zn(II) and Cu(II) onto CASB

5.9 Adsorption Thermodynamics

The thermodynamics parameters such as Gibbis free energy change (Δ G), enthalpy change (Δ H) and entropy change (Δ S) can be applied for the study of the feasibility of the adsorption processes. The Gibb's free energy changes change indicates the degree of the spontaneity of the adsorption process and its negative value is for a better adsorption. The equilibrium constant Kc, also called the Langmuir adsorption constant, can be calculated as:

$$K_c = C_{ae} / C_e \tag{9}$$

Where, C_{ae} represents the equilibrium solute concentration on the adsorbent and C_{e} , the equilibrium concentration in the solution. Since K_C is equilibrium constant, its dependence with temperature can be used to estimate thermodynamic parameters, such as changes in the free energy (ΔG), enthalpy (ΔH), and entropy (ΔS), associated to the adsorption process and they were determined by using following equations.

 $\Delta \mathbf{G} = - \mathbf{R} \mathbf{T} \ln \mathbf{K}_{\mathbf{C}} \tag{10}$

$$\ln K_c = -\Delta H/RT + \Delta S/R \tag{11}$$

The plot of In K_c as a function of 1/T (Fig. 24 and 25) yields a straight line from which Δ H and Δ S were calculated from the slope and intercept, respectively. The results are given in Table 16. The positive value of the enthalpy change indicates that the adsorption process is endothermic. Similarly the positive entropy change corresponds to an increase in the degree of freedom of the adsorbed species which is in full accord with Gercel et al [152].

Metal s	ΔG R		R^2	ΔН		ΔS		
	CYCD	CACD	CYCD	CACD	CVCD	CACD	CYCD	CACD
	CXSB	CASB	CX2R	CASB	CXSB	CASB	CX2R	CASB
Cu	-552.49	-2994.27	0.9696	0.9772	17096.08	15033.37	59.531	60.671
Zn	-428.95	-689.27	0.996	0.9755	12089.38	20841.54	41.979	71.853

Table 16: Thermodynamic parameters of CXSB and CASB



Figure 24: Thermodynamic parameters of Cu (II) and Zn(II) for

adsorption onto CXSB.



Figure25: Thermodynamic parameters of Cu (II) and Zn (II) for adsorption onto CASB.

5.10.1. Plausible Adsorption Mechanism Metal ions onto CXSB

The probable mechanism between Metal – CXSB interaction could be electrostatic, ion exchange and / or specific chemical reaction. The xanthate groups are unprotonated above pH 4.2 and have a net negative charge. Various oxidizing agents like hydrogen peroxide, persulphate and permanganate have been reported for the oxidation of xanthate to dixanthogen and formation of metal-xanthate [154]. The corresponding value for xanthate/dixanthogen was - 0.096 V [155, 156]. These values supported the possibility of metal ions getting reduced by xanthate groups and the reduced divalent ions complexing with the unreacted xanthate. This is in agreement with the mechanism reported earlier [145]. The metal adsorption was found to be maximum at optimum pH of each respective metal ion and decreased in the pH range below the point of zero charge (pH_{nzc}). The adsorption sites for the aforementioned metals are at sulfur atoms attached to xanthate groups. The xanthate groups are unprotonated above pH 1.5 and have a net negative charge and hence the adsorption of metals with CXSB started above pH 2. Since the CXSB has very low specific surface area (~ $25m^2/g$), physical adsorption alone cannot contribute the higher metal ion uptake capacity, so the predominant mode of adsorption is the chemisorption. The cation from the xanthate group contained in the monomeric unit has

been exchanged at the cost of metal ions present in the solution. The complexation mechanism of the metal ions with the xanthate group taken place through ion exchange process is shown in Figure 26. According to HSAB theory by Pearson [157,158], both xanthate and amine groups are soft bases and they tend to form stable complexes with soft acids like heavy metal ions [159]. The metals such as Cd (II), Pb (II), Ni(II), Zn(II) and Cu(II) are larger and more polarizable and the ligands, charred xanthated sugarcane bagasse will have a much higher affinity towards the metal ions and the sorption capacity was found to be higher than its raw biomass. For example, the precipitate formation constant (K_s), which indicates the strength of metal and ligand complex, shows that the lead complex with sulfur is stronger even than the lead hydroxide complex [160]; Pb(OH)₂ $K_s = 10^{15.2}$, Pb(HPO₄) $K_s = 10^{11.36}$, PbS $K_s = 10^{27.5}$, PbSO₄ $K_s = 10^{8.0}$. This strong affinity between sulfur and lead may result in a high affinity constant.



Figure 26: Plausible adsorption mechanism of metal ion onto monomeric cellulose unit contained in CXSB.

5.10.2. Plausible Adsorption Mechanism Metal ions onto CASB

The nitrogen atoms would have a greater tendency to donate the lone pair of electrons for sharing with metal ion to form a metal complex than oxygen atoms. On this consideration, the following chemical reactions may be proposed to account for the adsorption of metal ions on CASB [161];
$$R-NH_2 + H^+ \quad \longleftarrow \quad R-NH_3^+ \qquad (a)$$

$$R-NH_{2+}M^{2+} \longrightarrow R-NH_2 M^{2+}$$
 (b)

 $R-NH_3^+ + M^{2+} \longrightarrow R-NH_2 M^{2+} + H^+$ (c)

$$R- NH_2 M^{2+} + H_2 0 \longleftarrow MOH^+ + R-NH_3^+ \qquad (d)$$

Where, R represents all other components except $-NH_2$.

The reaction in the Eqn (a) indicates that the protonation and deprotonation of the amino groups in CASB. At the lower pH conditions, more amino groups are protonated and thus result in higher positive potentials of the CASB. At higher pH values, OH⁻ ions may be adsorbed to the surface of CASB through a hydrogen bond, which contributes to the negative potentials of the CASB, i.e.

$$R-NH_2 + OH^- \rightarrow R-NH_2 \cdots OH^- \qquad (e)$$

The negative potentials of the CASB at higher pH values may also be attributed to the following reaction

$$\mathbf{R}' - \mathbf{OH} + \mathbf{OH}^- \rightarrow \mathbf{R}' - \mathbf{O}^- + \mathbf{H}_2\mathbf{O}$$
 (f)

Where R' represents all other components except –OH in the CASB.

The equilibrium of the reaction in Eq (a) was usually established according to the initial solution pH values. When metals ions were added into the solution, the reaction in Eq (b) started, due to the sharing of lone pair of electrons from the nitrogen atom with metal ion, with a similar mechanism to that of the reaction in Eq (a). However, the binding of a metal ion to a nitrogen atom can be expected to be stronger than the binding of a H⁺ to a nitrogen atom (i.e, protonation of the amino group) since the electrical attraction force between the lone pair of electrons from the nitrogen atom and the divalent metal ion would be stronger than that between the lone pair of electrons and monovalent proton (H⁺). This

difference in the binding force drives the reaction in Eq (c) to take place through a competitive adsorption of M^{2+} over H^+ to the nitrogen atom, which may sometimes be considered as an ion exchange mechanism. The reaction in Eq (c) however can be expected to be slower than the reaction in Eq (b), attributed to the smaller attraction force between the N in R-NH₃⁺ and M^{2+} as compared to the force between the N in R-NH₂ and Pb²⁺. In addition, the complexes of R-NH₂M²⁺ are subject to the reaction in Eq (e), due to the greater binding force of M^{2+} with the OH⁻ group from water than with the nitrogen of the amino group in the CASB.

5.11 Desorption and Recycling Studies

Desorption studies are helpful to explore the possibility of recycling the adsorbent. Desorption studies was carried out by batch method for the evaluation of the adsorbed metals as well as the regeneration of the adsorbent. As for example, with 0.1 M HNO₃, as an eluting agent, Pb (II) desorbed from CXSB was found to be 93%. After three cycles of operation the adsorption capacity decreased from 97% to 78%. Regeneration of the charred carbon with 0.1 M CaCl₂ was efficient for further use. In the present study, 78% desorption was achieved for Pb²⁺ with 0.1M HNO₃ solution. Thus the study reveals that the adsorbent can be reused which makes the process more economical and eco-friendly due to minimal solid waste generation. Similarly, the regeneration and desorption aspects of the remaining metal ions onto CXSB and CASB are in progress to their further studies for real cost effectiveness.

5.12 Comparison of Adsorption Capacities

The metal uptake capacities of CXSB and CASB were found higher in the most of experimental results and some results are comparable with the capacities of different modified and / or unmodified biosorbents given in the literatures (Table 17). From these results it can be concluded that the developed bio-adsorbent CXSB and CASB would be potential adsorbents for the removal of heavy metals from wastewater.

						~
Adsorbents	Cd(II)	Pb(II)	Ni(II)	Zn(II)	Cu(II)	References
Xanthated sugarcane bagasse	225	318	144	164	178	This study
Aminated sugarcane bagasse	226	280	123	137	128	This study
Modified sugarcane bagasse	164	189	-	-	139	[162]
Modified sugarcane bagasse	195	188	-	-	113	[163]
(with succinic anhydride)						
Soluble starch xanthates	33	17	-	-	-	[143]
Sugarcane bagasse	6.79	-	-	-	-	[164]
Bacterial cellulose (diethylene		07			(2)	[165]
triamine)	-	8/	-	-	03	[103]
Modified Polyacrinitrile fiber	-	-	-	-	12.4	[166]

Table 17: Comparison of adsorption capacities (mg/g) of different biosorbents withCXSB and CASB for the removal of various metal ions reported in the literatures.

CHAPTER 6

6. CONCLUSIONS

Selective ion exchange seems to be an almost ideal method of wastewater treatment in certain applications such as purification of wastewater. There are a wide variety of different applications and possible ion exchange materials but finding the most efficient choice of exchangers is laborious because there is no basic data for modeling single and multi-component systems or the available data bases are incomplete. In view of such regard, I have investigated a novel and promising natural ion exchanger based on biopolymer, namely CXSB and CASB, respectively.

The biosorbents CXSB and CASB exchangers gave the best performance in most cases, showed performances comparable with commercially available synthetic resins. These exchangers showed high selectivity and process capacities. From a practical point of view, there are limited possibilities to adjust the chemical properties of waste effluents prior to ion exchange. The results indicated that pH value plays a significant role for the performance of exchangers, thus pH adjustment may be a feasible alternative to preparing effluent for ion exchange process. There are two parallel ways by which the pH value can affect the ion exchange equilibrium. The complexation or association of complexing ligands such as CXSB and CASB affect the solution speciation by the competition between H^+ and transition metals.

The possible adsorption mechanism onto CXSB and CASB for the binding of metal ions as discussed in the previous section may take place through a combination of physical electrostatic adsorption, ion-exchange, and complexation reactions. The extent of adsorption and the mechanisms involved are also influenced by pH, initial metal concentration, the presence and properties of competing metals in solution, and contact time with CXSB and CASB. Metal speciation is important, as the associated properties of ion charge, size and solubility determine how effectively a particular metal adsorbs. Aside from pH-dependent speciation, other properties such as electron configuration and ion size of the respective metal ions are thought to influence metal binding onto the adsorbent. Lead showed maximum adsorption onto both CXSB and CASB in comparison to cadmium, copper, zinc and nickel due to their different properties that are more favorable for binding, such as a higher electronegativity and smaller hydrated radius, that creates a greater affinity for the negatively charged adsorption sites onto CXSB and CASB.

These two specific new types of adsorbents like CXSB and CASB were successfully characterized by SEM, FTIR, TG/DTA and elemental analysis. The adsorption capacity of metal ions increased with an increase of pH value up to the optimum pH of each metal ion. Adsorption studies were compared with the Langmuir and Freudlich model in which the data fitted well only the Langmuir isotherm model. The velocity of adsorption for both adsorbents was fast and followed pseudo-second order kinetics. This signifies that the introduction of the xanthate and amino groups onto charred sugarcane bagasse is of importance in enhancing the adsorption capacities of raw sugarcane bagasse. The maximum loading capacity of CXSB for Cd, Pb, Ni, Zn and Cu were determined to be 225, 318, 144, 165 and 178 mg/g, respectively, while that for CASB were 226, 280, 123, 137 and 128, respectively. In addition, The more the adsorbent amount put into the solution, the higher the metal ions removal. Ion exchange studies indicated that, there is a strong relationship between ion exchange efficiency of biosorbent and the pH of the solution. The obtained values are far better than those available in the literature as shown in Table 17. The excellent adsorption performance of CXSB and CASB owes much to the functional groups, which has a high cation exchange capacity, thereby enabling the realization of high uptakes of metal ions. The pH and the surface chemistry, accordingly, thus facilitating enhancement of the CXSB and CASBs' adsorbate uptake. Pretreatment with concentrated sulphuric acid prior to xanthation and amination revealed to increase of the acidic surface functional groups on the cellulosic network, indicated an excellent means of producing effective adsorbents. This pertains to the low microporosities of the modified sugarcane bagasse tested thus so far.

It can be concluded that two newly prepared cation exchangers CXSB and CASB can be used as a low cost adsorbent in the purification of metal contaminated water; especially in applications where metal concentrations are low. However, the long-term efficiency of newly prepared adsorbents in terms of metal selectivity, as well as the time

and pH range of their metal binding capacity, needs to be considered in planning wastewater treatment alternatives. The possible displacement of adsorbed ions upon again used for the additional metal loadings is a material limitation that has to be addressed by eluting the adsorbed metal ions with a suitable eluent and can be again used for the treatment of toxic heavy metals.

CHAPTER 7

7. RECOMMENDATION

The raw biomass can usually be obtained relatively free of cost from the respective producers since they already present disposal problems to them. The only costs incurred should be those of modification processes and transport. The bio-sorbents are prepared from readily available bio-materials and they are relatively cheaper than synthetic resins. This field may therefore be utilized by developing countries to alleviate or at least, reduce the impacts of industrial water pollution on the aquatic environment.

Despite the number of papers published on natural adsorbents for pollutants uptake from contaminated water, there is yet little literature containing a full study comparing various sorbents. In addition, comparisons of different sorbents are difficult because of inconsistencies in the data presentation. Thus, much work is necessary to better understand adsorption phenomenon and to demonstrate the possible technology at the industrial scale.

Recommendations for future work

In many cases, tailoring of the surface chemistry is also an avenue that merits investigation for low surface area CXSB and CASB. Other recommended avenues for further research include:

- Utilization of alternative chemicals for the modification of surface active groups.
- Optimization of the most effective chemical modification techniques

- Combined use of functionalization and surface chemistry alteration techniques to produce application-specific adsorbents,
- Charring progress with concentrated H₂SO₄ help to expose the surface active sites of the biomass and it make easy for further functionalization.
- Finally, the economic viability of producing CXSB and CASBs on an industrial scale needs to be evaluated and assessed more generally in the context of sustainability measures.

The following recommendations can be made for further studies on the subject:

- 1. Effect of hydraulic retention time and sorbent age on CXSB and CASB performance in the sequential treatment system may be studied.
- 2. The influence of an immobilized system on system performance after adsorption may be evaluated.
- 3. The performance of the system may be investigated for different metal effluents like metal manufacturing industry or for different metal ion producing industries.
- 4. Wastewater recycling or reuse alternatives may be evaluated.

REFERENCES

- 1. Kar RN, Sahoo BN and Sukla CB (1992). Removal of heavy metals from pure water using sulphate-reducing bacteria (SRB), Pollut. Res.11:1-13.
- Rivera-Utrilla J, Bautista-Toledo, Ferro-Garcia MA, Moreno-Castilla C. (2003) Bioadsorption of Pb(II), Cd(II), and Cr(VI) on activated carbon from aqueous solutions. Carbon 41:323-30.
- Christopher AT, Wayne EM and Mitchell MJ (1990) Surface functional groups on acid-activated nutshell carbons. Carbon 37: 1207-1214.
- 4. Bosso ST and Enzweller J (2002) Evaluation of heavy metal removal from aqueous solution onto scolecite. Water Res. 36: 4795-800.
- Inglezakis VJ, Loizidou MD, and Grigorpoulou HP (2000) Ion exchange of Pb²⁺, Cu²⁺, and Cr^{3+,} on natural clinoptilolite: selectiveity determination and influence if acidity in metal uptake.J Colloid Int Sci. 261: 49-54.
- 6. Ahluwalia SS and Goyal D (2007) Microbial and plant derived biomass for removal of heavy matals from wastewater. Bioresour. Technol. 98: 2243-57.
- Dojlido JR and Best GA (1993) Chemistry of Water and Water Pollution. (Ellis Horwood Limited, Herts), pp.65-69, 84-91, 108-114, 201-205.
- 8. Al-Asheh S and Duvnjak Z (1997) Sorption of cadmium and other heavy metals by pine bark, *Adv. Environ. Res.*1pp.194.
- Kadirvelu K (1998) Preparation and characterization of activated carbon, from coir pith and its application to metal bearing wastewater, Ph.D. Thesis, Bharathiar University, Coimbatore, India
- Beliles RP (1979) The lesser metals. In: F.W. Oehme, Editor, Toxicity of Heavy Metals in the Environment, Part 2, Marcel Dekker, New York p. 383.
- Yang XJ, Fane AG and MacNaughton S (2001) Removal and recovery of heavy metals from wastewater by supported liquid membranes. *Water Science and Technology*. 43: 341–348.
- Bose, P., Bose, M.A. and Kumar, S. 2002. "Critical evaluation of treatment strategies involving adsorption and chelation for wastewater containing copper, zinc, and cyanide", *Advances in Environmental Research*. 7:179–195.

- Wingenfelder U, Hansen C, Furrer G and Schulin R (2005) Removal of heavy metals from mine water by natural zeolites. *Environmental. Science and Technology*. 39: 4606–4613.
- Shammas NK (2004) Coagulation and flocculation in *Physicochemical Treatment Processes*, edited by Wang LK, Hung YT and Shammas NK, (Humana Press, New Jersey), pp. 103–140.
- 15. Semerjian L and Ayoub GM (2003) High-pH-magnesium coagulation– flocculation in wastewater treatment. *Advanced Environ Research*.7: 389–403.
- 16. Licsko I (1997) Realistic coagulation mechanisms in the use of aluminium and iron (III) salt. *Water Science and Technology*. 36:103–110.
- Ayoub GM, Semerjian L, Acra AEl, Fadel M and Koopman B (2001)Heavy metal removal by coagulation with seawater liquid bittern. *Journal of Environ*. *Eng.* 127: 3: 196–202.
- Vik EI, Carlsoon DA, Eikum AS and Gjessing ET (1984) Electrocoagulation of potable water. *Water Research*. 18:1355–1360.
- Elimelech M and O'Melia CR (1990) Kinetics of deposition of colloidal particles in porous media. *Environ & Sci Technol.* 24:1528–1536.
- Metcalf and Eddy (2003) Wastewater Engineering: Treatment and Reuse. McGraw Hill International Edition, New York. pp 478-483.
- 21. Eckenfelder WW (2000) *Industrial Water Pollution Control*, McGraw-Hill Companies, pp. 451-457.
- Wang LK, Fahey EM and Wu ZC (2004) Dissolved air flotation in Physicochemical *Treatment Processes* edited by Wang LK, Hung YT and Shammas NK. Humana Press, New Jersey. pp. 431–500.
- Zabel T (1984) Flotation in water treatment in *The Scientific Basis of Flotation*, edited by Ives KJ. Martinus Nijhoff Publishers, The Hague. pp. 349–378.
- 24. Jokela P and Keskitalo P (1999) Plywood mill water system closure by dissolved air flotation treatment. *Water Science & Technology*. 40: 33–42.
- Matis KA, Zouboulis AI, Lazaridis NK and Hancock IC (2003) Sorptive flotation for metal ions recovery. *International Journal of Mineral Processing*. 70: 99– 108.

- 26. Reynolds TD (1982) Unit Operations and Processes in Environmental Engineering, PWS-Kent, Boston.
- Kurniawan TA, Chan GYS, Lo WH and Babel S (2006) Physico-chemical treatment techniques for wastewater laden with heavy metals", *Chemical Engineering Journal*.118: 83–98.
- 28. Gadd GM (1993) Interaction of fungi with toxic metals. Phytologist 124:25-60.
- 29. Volesky B (2007). Biosorption and me. Water Res. 41: 4017-4029.
- Navarro RR, Sump K, Fujii N and Matsumura M (1996) Mercury removal from wastewater using porous cellulose carrier modified with polyethyleneimine. Water Research, 30 (10): 2488-2494.
- Abollino O, Aceto M, Maladrino M, Sarzanini C and Mentasti E (2003) Adsorption if heavy metals in Na-montmorillonite: Effect of pH and organic substances. Water Res. 37: 1619-27.
- Celis R, Carmen Hermosin M and Cornejo J (2003) Heavy metal adsorption by functionalized clays. Environ Sci Technol. 34: 4593-99.
- 33. Ghoul M, Bacquet M, Morcellet M (2003) Uptake of heavy metals from synthetic aqueous solutions using modified PEI-silica gels. Water Res. 37:729-34.
- Krysztafkiewicz A, Binkowski S and Jesionowski T (2002) Adsorption of dyes on silica surface. Appl Surf Sci. 199:31-39.
- Lopez FA, Martin MI, Perez C, Lopez-Delgado A and Alguacil FJ (2003) Removal of copper ions from aqueous solution by steel – making by-product. Water Res. 37:3883-90.
- 36. Garg VK, Gupta R, Yadav AB and Kumar R (2003) Dye removal from aqueous solution by adsorption on treated sawdust, Bioresour Technol. 39:121-4.
- Gupta VK, Jain CK, Ali I, Sharma M and Saini VK (2003) Removal of cadmium and nickel from wastewater using bagasse fly ash- a sugar industry waste. Water Res. 38:71-74.
- Reddad Z, Gerente C, Andres Y and Cloirec PL (2002) Adsorption of several metal ions onto a low- cost biosorbent: kinetic and equilibrium studies. Environ. Sci. Technol. 36: 2067.

- Calace N, Nardi E, Petronio BM and Pietroletti M (2002) Adsorption of phenols by peppermill sludges. Environ Poll. 118: 315-9.
- 40. Netpradit S, Thiravetyan P and Towprayoon S (2004) Application of waste metal hydroxide sludge for adsorption of azo reactive dyes. Water Res. 38:71-78.
- Robinson T, Chandran B and Nigam P (2002) Removal of dyes from a synthetic textile dye effluent by biosorption on apple pomace and wheat straw. Water Res. 84: 2824-30.
- 42. Zang A, Asakura T and Uchiyama G (2003) The adsorption mechanism of uranium (VI) from seawater on a macroporous fibrous polymeric adsorbent containing amidoxine chelating functional group. React. Funct Polym. 57:67.
- 43. Atia A, Donia AM, Abou El-Enein SA and Yousif AM (2003) Studies on uptake behavior of copper (II) and lead (II) by amine chelating resins with different textural properties. Sep Purif Technol, 33: 295-302.
- 44. Grant DC, Skriba MC and Saha AK (1987) Removal of radioactive contaminants from west valley waste streams using natural zeolites. *Environmental Progress*.
 6: 104–109.
- 45. Vaca-Mier M, Callejas RL, Gehr R, Cineros BEJ, Alvarez PJJ (2001) Heavy metal removal with Mexican clinoptilolite: multi-component ionic exchange. *Water Research*.35: 373-378.
- 46. Gosset T, Trancart JL and Thevenot DR (1986) Batch metal removal by peat: kinetics and thermodynamics. *Water Research*. 20: 21–26.
- Gupta DC and Tiwari UC (1985) Aluminium Oxide as adsorbent for removal of hexavalent chromium from aqueous waste, Indian *Journal of Environmental Health.* 27: 205–215.
- 48. Srivastava SK, Bhattacharjee G, Tyagi R, Pant N and Pal N (1988) Studies on the removal of some toxic metal-ions from aqueous-solutions and industrial waste.(Removal of lead and cadmium by hydrous iron and aluminum oxide), *Environmental Technology Letters*. 9:1173–1185.

- Kadirvelu K, Kavipriya M, Kartika C, Radhika M Vennilamani N and Pattabhi S (2003) Utilization of various agricultural wastes for activated carbon preparation and application for the removal of dyes and metal ions from aqueous solutions. Bioresour. Technol 87: 129-132.
- 50. Hu Z Lei L Li Y and Ni Y (2003) Chromium adsorption on high performance activated carbon from aqueous solution. Sep. Purif. Technol.31: 13-18.
- 51. Pereira MFR, Soares SF, Orfao JMJ and Figueiredo JL (2003) Adsorption of dyes on activated carbons: influence of surface chemical groups. Carbon 41:811-21.
- Ayyappan R, Carmalin Sophia A, Swaminathan K and Sandhya S (2005) Removal of Pb (II) from aqueous solution using carbon derived from agricultural wastes. Process Biochemistry 40: 1293-1299.
- 53. Zamzow MJR, Eichbaum BR and Shanks DE (1990) Removal of heavy metals and other cations from wastewater using zeolites. Separation Science and Technology. 25: 1555–1569.
- Ouki SK, Cheeseman CR and Perry R. (1993) Effects of conditioning and treatment of chabazite and clinoptilolite prior to lead and cadmium removal. Environ Sci Technol. 27: 1108–1116.
- 55. Ouki SK and Kavanagh M (1997) Performance of natural zeolites for the treatment of mixed metal-contaminated effluents. *Waste Management and Research*.15:383–394.
- 56. Malliou E, Malamis M and Sakellarides PO (1992) Lead and cadmium removal by ion exchange. *Water Science and Technology*. 25:133-138.
- 57. Ibrahim SC, Hanafiah MAKM and Yahya MZA (2006) Removal of cadmium from Aqueous Solutions by Adsorption onto Sugarcane Bagasse. American-Eurasian J. Agric & Environ Sci. 1(3): 179-184.
- Srivastava SK, Tyagi R and Pal N (1989) The application of nature absorbents for heavy metals uptake from contaminated water, *Environmental Technology*. 10: 275–282.
- Undaybeytia T, Morillo E and Maqueda C (1996) Adsorption of Cd and Zn on montmorillonite in the presence of a cationic pesticide. *Clays and Clay Minerals*.31: 485–490.

- 60. Singh AK, Singh DP and Singh VN (1998) Removal of Zn (II) from water by adsorption on China clay, *Environmental Technology Letters*. 9: 1153–1162.
- 61. Chantawong V, Harvey NW and Bashkin VN (2001) Comparison of heavy metal adsorptions by Thai kaolin and ballclay. *Asian Journal of Energy & Environmental.* 1: 33–48.
- Panday KK, Prasad G and Singh VN (1984) Removal of Cr (VI) from aqueous solutions by adsorption on fly ash-wollastonite. *Journal of Chemical Technology* & *Biotechnology*.34:367–374.
- 63. Mellah A and Chegrouche S(1997) The removal of zinc from aqueous solutions by natural bentonite. *Water Research*. 31: 621–629.
- 64. Chen XH, Gosset T and Thevenot DR (1990) "Batch copper ion binding and exchange properties of peat. *Water Research*. 24: 1463–1471.
- 65. Sharma DC and Forster CF (1993) Removal of hexavalent chromium using sphagnum moss peat, *Water Research* 27: 1201–1208.
- 66. Panday KK, Prased G and Singh VN (1985) Copper (II) removal from aqueous solution by flies ash. *Water Research*. 19: 869-873.
- 67. Panday KK, Prasad G and Singh VN (1984) Removal of Cr (VI) from aqueous solutions by adsorption on fly ash-wollastonite. *Journal of Chemical Technology* & *Biotechnology*.34:367–374.
- 68. Ofomaja AE and Ho Y (2007) Effect of pH on cadmium biosorption by coconut copra meal, J, Hazard. Mater. B139: 3935-3948.
- Urrutia MM. General Bacterial Sorption Processes (1997) In: Froster C, editors, Biosorbents for metals ions. London, UK: CRC Press: pp 39-66.
- Ahluwalia SS and Goyal D (2007) Microbial and plant derived biomass for removal of heavy matals from wastewater. Bioresour. Technol. 98: 2243-57.
- Vijayaraghavan K and Yun YS (2008) Bacterial biosorbents and biosorption. Biotechnol Adv. 26: 266-91.
- Mann H (1990). Removal and recovery of heavy metals by biosorption. In: Volesky B, editor.biosorption of heavy metals. Boca Raton: CRC press. 93-137.
- 73. Wang JL and Chen C (2006) Biosorption of heavy metals by Saccharomyces cerevisiae: a review.Biotechnol Adv 24:427-51.

- 74. Dursun AY (2006) A comparative study on determination of the equilibrium, kinetic and thermodynamic parameters of biosorption of copper (II) and lead (II) ions onto pretreated Aspergillus niger. Biochem. Eng. J. 28: 187-195.
- 75. Mungasavalli DP, Viraraghavan T and Jin YC (2007) Bisorption of chromium from aqueous solutions by pretreated Aspergillus niger: batch and column studies. Colloids Surf. A: Physicochem. Eng. Aspects 301: 214-223.
- Parvathi K, Nareshkumar R and Nagendran R (2007) Biosorption of manganese by Aspergillus niger and Saccharmyces cerevisiae. World J. Microbiol. Biotechnol.23: 671-676.
- 77. Aksu Z and Acikel U (2000) Modeling of single-staged bioseparation process for simultaneous removal of iron (III) and chromium (VI) by using chlorella vulgaris. Biochem Eng J. 4: 229-238.
- Asku Z and Donmez G (2006) Binary biosorption of cadmium (II) and nickel (II) onto dried chlorella vulgaris: co-ion effect on mono-component isotherm parameters. Process Biochem. 41:860-868.
- 79. Al-Rub FAA (2006) Biosorption of zinc on palm tree leaves: equilibrium, kinetics, and thermodynamics studies. Sep Purif Technol. 41: 3499-3515.
- Apiratikul R and Pavasant P (2008) Batch and column studies of biosorption of heavy metals by Caulerpa letillifera. Bioresource Technol. 99: 2766-2777.
- Deng L Su Y, Su H, Wang X and Zhu X (2006) Biosorption of copper (II) and lead (II) from aqueous solutions by nonliving green algae Cladophora fasicularis: equilibrium, kinetics and environmental effects. Adsorption 2: 267-277.
- Grimm A, Zanzi R, Bjornborn E and Cukierman AL (2008) Comparison of different types of biomasses for copper biosorption, Bioresource Technol. 99: 2559-2565.
- Pavasant P, Apiratikul R, Sungkhum V, Suthiparinyanont P, Wattanachira S and Marhaba TF (2006) Biosorption of Cu²⁺, Cd²⁺, Pb²⁺ and Zn²⁺ using dried marine green macroalga Caulerpa lentillifera. Bioresource Technol 97, 2321-2329.

- Rao PS, Kalyani S, Reddy KVNS and Krishnaiah A (2005) Comparison of biosorption of nickel (II) and copper(II) ions from aqueous solution by Sphaeroplea algae and acid treated Sphaeroplea algae. Sep. Sci. Technol. 40: 3145-3165.
- 85. Vilar VJP, Botelho CMS and Boaventura RAR (2007) Modeling equilibrium and kinetics of metal uptake by algal biomass in continuous stirred and packed bed absorbers. Adsorption 13: 587-591.
- Ghimire KN, Inoue K, Ohto K and Hayashida T (2008) Adsorption study of metal ions onto crosslink seaweed Laminaria japonica. Bioresource Technology 99: 32-37.
- Uslu G and Tanyol M (2006) Equilibrium and thermodynamic parameters of single and binary mixture biosorption of lead (II) and copper (II) ions onto Pseudomonas putida: effect of temperature. J Hazard Mater. 135: 87-93.
- Selatnia A, Boukazoula A, Kechid N, Bakhti MZ and Chergui A (2004c) Biosorption of lead (II) from aqueous solution by a bacterial dead Streptomyces rimosus biomass. Biochem Eng J. 19:127-35.
- Mameri N, Boudries N, Addour L, Belhicine D, Lounicine D and Grib H. (1999) Batch zinc adsorption by a bacterial nonliving Streptomyces rimosus biomass. Water Res. 33:1347-54.
- 90. Liu HI, Chen BY, Lan YW and Chen YC (2004) Biosorption of Zn (II) and Cu (II) by the indigenous Thiobacillus thioxidans. Chem Eng J. 97: 195-201.
- Selatnia A, Boukazoula A, Kechid N, Bakhti MZ and Chergui A (2004b) Biosorption of Fe³⁺ from aqueous solution by a bacterial dead Streptomyces rimosus biomass. Biochem. 39:271-82.
- 92. Ozturk A (2007) Removal of nickel from aqueous solution by the bacterium bacillus thuringiensis. J Hazard Mater 147: 518-23.
- Say R, Yilmaz N and Denizli A (2003b) Removal of heavy metal ions using the fungus Pencillium canescens. Adsorpt Sci Technol 21: 643-50.
- 94. Niu H, Xu XS, Wang JH and Volesky B (1993) Removal of lead from aqueous solutions by Penicillium biomass. Biotechnol Bioeng; 42: 785-7.

- 95. Holan ZR and Volesky B (1995). Accumulation of cadmium, lead and nickel by fungal and wood biosorbents. Appl Environ Microbiol 53: 133-46.
- 96. Deng SB and Ting YP (2005 b) Fungal biomass with grafted poly (for acrylic acid) enhancement of Cu (II) and Cd (II) biosorption. Langmuir 21:5940-8.
- 97. Tan TW, Hu B and Su HJ (2004) Adsorption of Ni²⁺ on amine-modified mycelium of penicullium chrysogenum. Enzyme Microb Technil. 35:508-13.
- Kapoor A and Virarghavan T (1995) Fungal Biosorption an alternative treatment option for heavy metal bearing wastewaters: a review, Bioresour Technol. 53: 195-206.
- Say R, Yilmaz N and Denizli A (2004) A removal of chromium (VI) ions from synthetic solutions by the fungus Penicillium Purpurogenum. Eng. Life Sci. 4: 276-80.
- Say R, Yilmaz N and Denizli A (2003a) Biosorption of cadmium, lead, mercury and arsenic ions by the fungus Pencillium purpurogenum. Sep Sci Technol. 38: 209-53.
- 101. Gulati R, Saxena RK and Gupta R (2002) Fermentation waste of Aspergillus terrus: a potential copper biosorbent. World J Microbiol Biotechnol 18: 397-401.
- 102. Dias MA, Lecerda JCA Pimentel PF, de Castro HF and Rosa CA (2002) Removal of heavy metals by an Aspergillus terrus strain immobilized in a polyurethane matrix. Lett Appl Microbiol 34: 46-50.
- 103. Pakshirajan K and Swminathan T (2006) Continuous biosorption of Pb, Cu and Cd by phanerochaete chrysosporium in a packed column reactor. Soil Sediment. Contam. 15: 187-197.
- 104. Pavasant P, Apiratikul R, Sungkhum V, Suthiparinyanont P, Wattanachira S and Marhaba TF (2006) Biosorption of Cu²⁺, Cd²⁺, Pb²⁺ and Zn²⁺ using dried marine green macroalga Caulerpa lentillifera. Bioresource Technol 97, 2321-2329.
- 105. UNEP, Environmental aspects of the metal finishing industry: A technical guide, United Nations Environment Programme, Industry and Environment Office, Paris, 1989, pp. 19-39 and 53-57.
- 106. Agarwal GS, Bhuptawat HK and Choudhari S (2006) Biosorption of aqueous chromium (VI) by Tamarindus indica seeds.Bioresource Technol.97: 949-956.

- 107. Gupta S and Babu BV (2006) Adsorption of Cr (VI) by a low cost adsorbent prepared from neem leaves. Proc. Natl. Conf. Environ. Conserc. 175-180.
- 108. Sharma A and Bhattacharya KG (2004) Adsorption of Chromium (VI) on Azadirachta indica (neem) leaf powder. Adsorption 14: 327-338.
- 109. Athar M and Farooq U (2007) Azardichyta indica (neem): an effective biosorbent for the removal of lead (II) from aqueous solution. Bull. Environ. Contam. Toxicol. 79:288-292.
- 110. Babu BV and Gupta S. (2008) Adsorption of Cr (VI) using activated neem leaves: kinetic studies. Adsorption 14: 85-92.
- 111. Sharma A and Bhattachrya KG (2005) Azadirachta indica (neem) leaf powder as a biosorbent for removal of Cd (II) from aqueous medium. J.Hazard.Mater.B125: 102-112.
- 112. Han R, Zhang J, Zou W, Xaio H, Shi J and Liu H (2006) Biosorptions of Cu (II) and Pb (II) from aqueous solution by chaff in a fixed –bed column. J. Hazard. Mater.B133: 2062-2068.
- Schiewer S and Patil SB (2008) Pectin–Rich fruit wastes as biosorbents for heavy metal removal: equilibrium and kinetics. Bioresource Technol. 99: 1896-1903.
- 114. Ho YS and Ofo Maja AE (2006) Biosorption thermodynamics of Cadmium on coconut copra meal as biosorbent. Biochem. Eng.J.30: 117-123.
- 115. Pino GH, Mesquita LMS, Torem ML and Pinto GAS (2006) Biosorptions of Cadmium by green coconut shell powder. Miner.Eng.19:380-387.
- 116. Wang XS, Qin Y and Li ZF (2006) Biosorptions of Zinc from aqueous solutions by rice bran: kinetics and equilibrium studies, Sep. Sci. Technol. 4: 747-756.
- 117. Amarasinghe BMWPK and Williams RA (2007) Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater. Chem. Eng. J .132: 299-309.
- 118. Dupont D, Bounada J, Dumonceau M and Aplincourt M (2005) Biosorption of Cu (II) and Zn (II) onto lignocellulosic substrate extracted from wheat bran, Environ. Chem. Lett.2: 165-168.

- 119. Pehlivan E and Altun T (2008) Biosorptions of chromium (VI) ion from aqueous solutions using walnut, hazelnut and almond shell. J.Hazard.Mater.155: 378-384.
- 120. Hanif MA, Nadeema R, Bhatti HN, Ahmada NR and Ansari TM (2007) Ni(II)biosorption by cassia fistula (golden shower) biomass, J.Hazard. Mater.B 139: 345-355.
- 121. Igwe JC, Abia AA, and Ibeh CA (2008) Absorption kinetics and intraparticulate diffusivities of Hg, As and Pb ions on unmodified and thiolated coconut fiber, Int.J. Enverson.Sci. Technol.5: 83-92.
- 122. Arslanoglu H, Altundogan HS and Tumen F (2008) Preparation of cation exchanger of lemon and sorption of divalent heavy metals, Bioresource Technol.99: 2699-2705.
- 123. Rao RAK and Rao KNA (2007) Removal and recovery of Cu(II), Cd(II), and Pb(II), ions from single and multi-metal systems by batch and column operation on neemoil cake (NOC), Sep. Purif. Technol. 57: 394-402.
- 124. Martin-Lara MA, Pagnanelli F, Mainelli S, Calero M and Toro L (2008) Chemical treatment of olive pomace: effect on acid-basic properties and metal biosorption capacity. J. Hazard. Mater. 156: 448-457.
- 125. Xuan ZX, Tang YR, Li XM, Liu YH and Luo F (2006) Study on the equilibrium, kinetics and isotherm of biosorption of lead ions on to pretreated chemically modified orange peel. Biochem. Eng. J. 31: 160-164.
- 126. Argun ME and Dursun SA (2008) new approach to modification of natural adsorbent for heavy metal adsorption. Bioresource Technol. 99:2516-2527.
- 127. El-Ashtoukhy, Anima NK and Abdelwahab O (2008) Removal of lead (II) and copper (II) from aqueous solution using pomegranate peel as a new adsorbent, Desalination. 223:162-173.
- 128. Pavan FA, Mazzocato AC, Jacques RA and Dias SLP (2008) Ponkan peel: a potential biosorbent for removal of Pb (II) ions from aqueous solution, Biochem. Eng.J.40: 162-173.
- 129. Southichak B, Nakano K, Nomura M., Chiba N and Nishimura O (2006) Pb (II), biosorption of reed biosorbent derived from wetland: effect of pretreatment on functional groups, Water Sci. Technol. 54: 133-141.

- 130. Mohan S and Shreeladshmi G (2008) Fixed bed column study for heavy metal removal using phosphate treated rice husk, J. Hazard.Mater.150: 446-452.
- 131. Gao H, Liu YG, Zeng GM, Xu WH, T Li and Xia WB(2008) Characterization of Cr(VI) removal from aqueous solution by a surplus agricultural waste-rice straw. J. Hazard. Mater. 150: 446-452.
- 132. Khormaei M, Nasernejad B, Edrisi M and Eslamzadeh T (2007) Copper Biosorptions from aqueous solutions by sour orange residue.
 J.Hazard.Matter.149: 269-274.
- 133. Jacques RA, Lima EC, Dias SLP, Mazzocato AC and Pavan FA (2007) Yellow passion-fruit shell as biosorbent to remove Cr(III) and Pb(II) from aqueous solution. Sep. Purif.Technol. 57: 193-198.
- Bhattacharyya KG and Sharma A (2004) Adsorption of Pb (II) from aqueous solution by Azadirachyta indica (neem) leaf power. J. Hazard Mater. B 113: 97-109.
- 135. Pino GH, Mesquita LMS, Torem ML and Pinto GAS (2006) Biosorptions of Cadmium by green coconut shell powder. Miner.Eng.19:380-387.
- 136. Dinger DR (2005) Characterization Techniques for Ceramists. (Morris Publishing, U.S.A), pp.3-4, 71-72, 175-176, 223-224.
- Morrison RT and Byod RN (1994) Organic chemistry, 6th ed, Printice Hall of India Private Ltd. New Delhi.
- 138. Iqbal M, Saeed A and Zafar SI (2009) FTIR spectrophotometry, kinetics and adsorption isotherms modeling, ion exchange, and EDX analysis for understanding the mechanism of Cd²⁺ and Pb²⁺ removals by mango peel waste. J. Hazard. Mater. 164(1): 161.
- Dinger DR(2005) Characterization Techniques for Ceramists. (Morris Publishing, U.S.A), pp.3-4, 71-72, 175-176, 223-224.
- 140. WEB_6, 2007. The University of Wet Indies, 13/06/2007
- 141. Settle F (1997) Handbook of Instrumental Techniques for Analytical Chemistry. Prentice-Hall, New Jersey, pp. 341-342.
- Welz B, Sperling M (1998) Atomic Absorption Spectrometry. (Wiley-VCH, Weinheim), pp. 103-105, 113, 149-171.

- 143. Tyson JF and Haswell SJ (1991) Basic Principles and Instrumental Requirements and optimization" in Atomic Absorption Spectrometry, edited by S.J. Haswell (Elsevier Publishing, New York), pp. 9-10, 14-17, 21-40.
- Silverstein RM, Bassler GC, Morril TC (1981) Spectrometric Identification of Organic Compounds. John Wiley & Sons., New York, 95-180.
- 145. Tare V, Chaudhari S (1987) Evaluation of soluble and insoluble xanthate process for the removal of heavy metals from wastewaters.Water Res. 21: 1109-1118.
- 146. Gaballah I, Goy D, Allain E, Kilbertus G and Thauront J (1997) Recovery of copper through decontamination of synthetic solutions using modified barks. Met. Metall. Trans. 28: 13.
- 147. Chong KH and Volesky B (1996) Metal biosorption equilibria in a ternary system. Biotechnol. Bioengineering. 49: 629.
- 148. Morais FI, Page AL and Lund LJ (1976) The effect of pH, salt concentration, and nature of electrolytes on the charge characteristics of Brazilian tropical soils. Soil Sci. Soc. Am. J. 40: 521–527.
- 149. Parks GA and de Bruyn P(1961) The zero point of charge of oxides. J. Phys. Chem. 66, 967–973. Quantachrome, 1996. Nova 1200 Gas Sorption Analyzer Manual. Quantachrome, Boyton Beach, FL
- 150. Lau PS, Lee HY, Tsang CCK, Tam NFY and Wong YS (1999) Effect of metal interference, pH and temperature on Cu and Ni biosorption by Chlorella vulgaris and Chlorella miniata. Environ. Technol. 20(9): 953.
- 151. Krishnan KA and Anirudhan TS (2008) Kinetic and equilibrium modelling of cobalt (II) adsorption onto bagasse pith based sulphuric activated carbon. Chem. Eng. J. 137: 257.
- 152. Ho YS and McKay G (1999) Pseudo-second order model for sorption process. Process Biochem. 34: 451.
- 153. Gercel O, Ozcan A, Ozcan SA and Gercel FH (2007) Preparation of activated carbon from a renewable bio-plant of Euphorbia rigida by H₂SO₄ activation and its adsorption behavior in aqueous solutions. Applied Surface Sc.253:4843-4852.

- 154. Li W, Zhang L, Peng J, Li N, Zhang S and Guo S (2008) Tobacco stems as a low cost adsorbent for the removal of Pb (II) from wastewater: Equilibrium and kinetics studies. Ind. Crops and Prod. 28: 294.
- 155. Woods R (1971) The oxidation of ethyl xanthate on platinum, gold, copper and galena electrodes. Relation to the mechanism of mineral floatation. J. Phys. Chem. 75, 354–362.
- 156. Woods R (988) Floatation of sulfide minerals. In: Somesundaram P, Moudgil BM (Eds.), Reagents in Mineral Technology Surfactant Science Series, 27. Marcel-Dekker, New York, NY, pp. 39–78.57.
- 157. Pearson RG (1963) Soft and Hard Acids and Bases Journal of American Chemical Society. 12: 3538 -3546.
- Pearson RG (1973) Ed. Hard and Soft Acid and Bases. Dowden, Hutchinson and Ross, Stroudsburg, PA.
- 159. Winter MJ (1994) In: d-Block Chemistry. Oxford University Press, New York.
- 160. Hulanicki A (1967) Complexation reaction of dithiocarbamates. Talanta, 14: 1371.
- 161. Jin L and Bai R (2002) Mechanism of Lead Adsorption on Chitosan/PVA Hydrogel Beads. Langmuir.18: 9765-9770.
- 162. Karnitz Jr O, Gurgel LVA, De Melo JCP, Borato VR, Melo TMS, De Freitas Gil RP and Gil LF (2007) Adsorption of heavy metal ion from aqueous single metal solution by chemically modified sugarcane bagasse. Bioresour. Technol. 98: 1291.
- 163. Gurgel LVA, Freitas RP and Gil LF (2008) Adsorption of Cu (II), Cd (II), and Pb (II) from aqueous single metal solutions by sugarcane bagasse and mercerized sugarcane bagasse chemically modified with succinic anhydride. Carbohydrate Polymers 74: 922.
- 164. Ibrahim SC, Hanafiah MAKM and Yahya MZA (2006) Removal of cadmium from Aqueous Solutions by Adsorption onto Sugarcane Bagasse. American-Eurasian J. Agric & Environ Sci. 3: 179-184.

- 165. Shen W, Chen S, Shi S, Li X, Zhang X and Hu W (2009) Adsorption of Cu(II) and Pb(II) into diethylenetriamine-bacterial cellulose. Carbohydrate Polymers 75: 110-114.
- 166. Deng S, Bai R and Chen JP (2003) Aminated Polyacrylonitrile Fibres for Lead and Copper Removal. Langmuir 19: 5058-5064.
- 167. Clesceri LS, Greenberg AE and Eaton AD (1998) Standard Methods for the Examination of Water and Wastewater. APHA, AWWA, WEF. 20th Edition.

PHOTOGRAPHS



Photograph 1: Me taking Scanning Electron Microscope (SEM)



Photograph 2: Me working in Saga laboratory



Photograph 3: Me working in lab taking concentration of solution by AAS



Photograph 4: Me working in CDC Lab. with Supervisor

APPENDIX

Participation in Conferences / Seminars

- 1. Presented a research paper entitled "Studies on Functionalization of Apple Waste for Heavy Metal Treatment" in The Fifth National Conference on Science and Technology, Nov.10-12, 2008, organized by Nepal Academy of Science and Technology (NAST).
- 2. Presented a research paper entitled "Development of Functionalized Bio-sorbent using Sugarcane Waste for Heavy Metal Treatment" in the Chemical Symposium-2009 organized by Nepal Chemical Society during the 26th Anniversary of NCS on Nov.21, 2009.
- 3. Presented a research paper entitled "Development and Characterization of Charred Xanthated Sugarcane Bagasse for the Treatment of Heavy Metals" in the Scientific Exhibition organized by Young Science Group, Kirtipur, on Feb. 9-12, 2010.
- 4. Presented a research paper entitled "Development of Chemically Modified Sugarcane Bagasse for the treatment of Lead ions from contaminated water" in the First National Youth Conference on Environment (NYCE-1) organized by Himalayan Alliance for Climate Change (HIMCCA) on June 3-4, 2010.
- 5. Presented a research paper entitled "Sorption of Cd(II) and Ni(II) onto Chemically Modified Sugarcane Waste for the Purification of Contaminated water" in the International Conference on Advance Materials and Nanotechnology organized by Nepal Chemical Society in co-operation with Central Department of Chemistry, Oct 21-23th, 2011, Kathmandu, Nepal.
- Presented a research paper entitled "Sorption of Cu(II) and Zn(II) onto Charred Aminated Sugarcane Bagasse for the Decontamination of Metal ions from Aqueous Solution" in The Sixth National Conference on Science and Technology Sept. 25-27, 2012, Kathmandu.

<u>Citation of my article</u> till 2012, 15th April

Google scholar	
	Advanced Scholar Search
	Search within articles citing <u>Homagai: Adsorption</u> <u>behavior of heavy metals onto chemically modified</u> sugarcane bagasse
Scholar <u>Create email alert</u>	Results 1 - 10 of about 15. (0.03 sec)

Enhanced adsorption of Methylene Blue by EDTAD-modified sugarcane bagasse and photocatalytic regeneration of the adsorbent

Y Xing, D Liu... - Desalination, 2010 - Elsevier

Ethylenediaminetetraacetic dianhydride (EDTAD) modified sugarcane bagasse (SB) was prepared, and characterized by Fourier transform infrared spectroscopy (FTIR). Due to the presence of a large number of carboxyl groups, the adsorption capacity of the EDTAD- ... <u>Cited by 3</u> - <u>Related articles</u> - <u>All 6 versions</u>

Optimization parameters for adsorption and desorption of Zn (II) and Se (IV) using rice husk ash: kinetics and equilibrium

AG El-Said, NA Badawy, AY Abdel-Aal... - Ionics, 2011 - Springer

Abstract An attempt at the use of rice husk ash, an agricultural waste, as an adsorbent of Zn (II) and Se (IV) from their aqueous solution is studied. Studies are carried out as a function of contact time, metal ion concentration, adsorbent dose, and pH at 25° C. Its adsorption ...

<u>Cited by 2</u> - <u>Related articles</u> - <u>All 2 versions</u>

<u>Sorption of methylene blue by carboxymethyl cellulose and reuse process in a</u> <u>secondary sorption</u>

H Yan, W Zhang, X Kan, L Dong, Z Jiang... - Colloids and Surfaces A: ..., 2011 - Elsevier

Abstract The sorption behaviors of carboxymethyl cellulose (CMC) for methylene blue (MB) were investigated in this work. The experimental results indicated that the sorption capacity increased from 50 mg g- 1 for unmodified cellulose (UmC) to more than 300 mg g- 1 for ...

<u>Cited by 2</u> - <u>Related articles</u> - <u>All 3 versions</u>

<u>Binary biosorption of Acid Red 14 and Reactive Red 15 onto acid treated okara:</u> <u>Simultaneous spectrophotometric determination of two dyes using partial least ...</u>

JF Gao, JH Wang, C Yang, SY Wang... - Chemical Engineering ..., 2011 - Elsevier Abstract The biosorption of Acid Red 14 (AR14) and Reactive Red 15 (RR15) by acid treated okara (ATO) in binary solutions was investigated. To overcome the severe spectral overlapping, partial least squares regression as a multivariate calibration method was ... <u>Cited by 1</u> - <u>Related articles</u> - <u>All 4 versions</u>

<u>Preparation of sugarcane bagasse modified with the thiophosphoryl function and its</u> <u>capacity for cadmium adsorption</u>

[PDF] from ncsu.edu

RA Sanchez... - BioResources, 2011 - ojs.cnr.ncsu.edu

Abstract Sugarcane bagasse (SCB) is an important by-product from the sucro-alcohol industry in Brazil, and it is a convenient raw material for new applications. In this study, SCB was modified with thiophosphoryl chloride in order to attach the P=S chelating moiety to ...

Cited by 1 - Related articles - All 3 versions

<u>Preparation and Characterization of Charred Xanthated Sugarcane Bagasse for the</u> <u>Separation of Heavy Metals From Aqueous Solutions</u>

PL Homagai, KN Ghimire... - Separation Science and ..., 2010 - Taylor & Francis Introduction of xanthate group onto sugarcane (Saccharum officinarum) bagasse has been investigated for the removal of cadmium, lead, nickel, zinc, and copper from their aqueous media. The charred xanthated sugarcane bagasse (CXSB) was found to have significant ... <u>Cited by 1</u> - <u>Related articles</u> - <u>All 5 versions</u>

COCONUT BAGASSE TREATED BY THIOUREA/AMONIUM SOLUTION FOR CADMIUM REMOVAL: KINETIC AND ADSORPTION EQUILIBRIUM

[PDF] from ncsu.edu

VOS Neto, TV Carvalho, SB Honorato... - ..., 2012 - ojs.cnr.ncsu.edu

Abstract Coconut bagasse, an agricultural solid waste was used as biosorbent for the removal of cadmium after modification with thiourea. The adsorption of Cd2+ was studied at

pH 5.5. Langmuir, Freundlich, and Temkin isotherms were used to model the adsorption ... <u>Related articles</u> - <u>All 2 versions</u>

<u>Removal of Cd (II) ions from aqueous solution using a cation exchanger derived from banana stem</u>

TS Anirudhan, NB Fernandez... - Journal of Chemical ... - Wiley Online Library

BACKGROUND: Environmental pollution and its abatement have attracted much attention

for some time. The problem of removing pollutants from water and wastewater has grown along with rapid industrialization. Formaldehyde polymerized banana stem (FPBS) having

Related articles - All 2 versions

Adsorption characterization of lead (II) and cadmium (II) on crosslinked carboxymethyl starch

YX Chen, BH Zhong... - Journal of Applied Polymer Science - Wiley Online Library The adsorption of Pb (II) and Cd (II) ions with crosslinked carboxymethyl starch (CCS) was investigated as function of the solution pH, contact time, initial metal-ion concentration, and temperature. Isotherm studies revealed that the adsorption of metal ions onto CCS better ...

Related articles

<u>Bioseparation of Pb (II) and Cd (II) from aqueous solution using cork waste biomass.</u> <u>Modeling and optimization of the parameters of the biosorption step</u>

M López-Mesas, ER Navarrete, F Carrillo... - Chemical Engineering ..., 2011 - Elsevier In this work the ability of cork wastes to remove Cd (II) and Pb (II) from aqueous solutions has been studied. The kinetics of the biosorption system, the influence of the aqueous pH and the initial metal concentration on the metal uptake were investigated, showing a pH ... <u>Related articles</u> - <u>All 4 versions</u>

[PDF] <u>Development of Chemically Modified Sugarcane Bagasse for the Treatment of</u> <u>Lead ions from contaminated water</u>

[PDF] from himcca.org

PL Homagai... - Few saying of session chairs - himcca.org

Abstract: The polysaccharides found in sugarcane (Saccharum officinarum) bagasse are natural polymers having many surface active sites containing hydroxyl and/or phenolic groups that can be chemically modified to form a new compound. The bagasse was first ... Related articles - <u>View as HTML</u> - <u>All 2 versions</u>

Potential biosorbent based on sugarcane bagasse modified with tetraethylenepentamine for removal of eosin Y

GB Jiang, ZT Lin, XY Huang, YQ Zheng... - International Journal of ..., 2012 - Elsevier Tetraethylenepentamine (TEPA) modified sugarcane bagasse (SB), a novel biosorbent (TEPA-MSB), was proved to be an effective adsorbent for anionic dyes due to the introduced functional amino groups. FTIR, TG and DSC analysis were employed to characterize the ... Related articles - <u>All 2 versions</u>

Valorization of solid waste in sugar factories with possible applications in India: A review

M Balakrishnan... - Journal of environmental management, 2011 - Elsevier

Sugar production is a major agro-based industry in India that generates various solid wastes viz. sugarcane trash, bagasse, press mud and bagasse fly ash. This work examines the state-of-the-art in innovative value added products that can be obtained from the transformation ...

Related articles - All 4 versions

[DOC] <u>Evaluation of carbon-based nanosorbents synthesised by ethylene</u> <u>decomposition on stainless steel substrates as potential sequestrating materials for</u> <u>nickel ...</u>

[DOC] from jesc.ac.cn

XJ Lee, JW Kit, SF Zakaria, KW Tan, DG Hassell... - jesc.ac.cn

Abstract: The present work covers the preparation of carbon-based nanosorbents by ethylene decomposition on stainless steel mesh without the use of external catalyst for the treatment of water containing nickel ions (Ni²⁺). The reaction temperature was varied ... <u>View as HTML</u>

[PDF] <u>Comparison of Synthetic and Natural Adsorbent for Sorption of Ni (II) Ions</u> <u>from Aqueous Solution</u>

[PDF] from sciencepub.net

AG El-Said, NA Badawy... - sciencepub.net

Abstract: Removal of Ni (II) ions from wastewater is obligatory in order to avoid water pollution. In the present study, the sorption of Ni (II) ions from aqueous solution was investigated by using lewatite S-100 (strongly cation-exchange resin) and new sorbent ..

<u>Home</u> » <u>Publications</u> » <u>White papers, newsletters, and transcripts</u> » <u>Trade newsletters</u> » <u>Science Letter</u> » <u>Apr - Jun 2011</u> » <u>May 10, 2011</u> »

New Research on Separation Science from P.L. Homagai and Co-Authors Summarized.

Newspaper Science Letter May 10, 2011 | Copyright Share

According to recent research from Kathmandu, Nepal, "Of xanthate group onto sugarcane (Saccharum officinarum) bagasse has been investigated for the removal of cadmium, lead, nickel, zinc, and copper from their aqueous media. The charred xanthated sugarcane bagasse (CXSB) was found to have significant adsorption capacity which is more than that of various bio-sorbents mentioned in the available literatures."

"The newly developed bio-sorbent was characterized by SEM, FTIR, TGA/DTA, and elemental analysis. The velocity of sorption of the tested metals was fast, reaching equilibrium within 40min. The maximum loading capacities was found to be 225 for Cd(II), 318 for Pb(II), 144....

Appendix-II

List of **Publications**

- P. L. Homagai, H. Poudyal & K. N. Ghimire, (2008/2009) Adsorption Kinetics of Pb(II), Cd(II), Zn(II) and Fe(III) onto Saponified Apple Waste, J. Nepal Chemical Society.23, 102-105.
- P. L. Homagai, D. Bashyal, H. Poudyal and K.N. Ghimire, 2009. Studies on Functionalization of Apple Waste for Heavy Metal Treatment. Nepal Journal of Science and Technology (NAST).10, 135-139.
- P. L. Homagai, K.N.Gimire & K. Inoue, 2010. Adsorption Behavior of Heavy Metals onto Chemically modified Sugarcane bagasse. Bio-resource Technology, 101, 2067-2069.
- D. Bashyal, P. L. Homagai & K. N. Ghimire, 2010. Removal of lead from aqueous medium using a novel Xanthate modified Apple juice residue, J. Nepal Chemical Society. 26, 53-60.
- P. L. Homagai and K. N. Ghimire, "Development of Chemically Modified Sugarcane Bagasse for the treatment of Lead ions from contaminated water" Published in NYCE-1 proceeding, 169-179, 2010.
- P. L. Homagai, K.N. Ghimire & K. Inoue. Preparation and Characterization of Charred Xanthated Sugarcane Bagasse for the Separation of Heavy Metals from aqueous solution. Sep. Sci. Technol, 46: 330-339, 2011.
- J. Kour, P. L. Homagai, M.R. Pokhrel and K.N. Ghimire. Kush A Potential Biosorbent in the removal of Cd (II) and Zn (II) from aqueous solution. J. Nepal Chem. Soc., 27, 107-114, 2011.
- B. Shrestha, P. L. Homagai, M.R. Pokhrel and K.N. Ghimire. Removal of Copper (II) and Zn (II) ions from Aqueous Solution by Biosorption onto Aminated Tea Waste. J. Nepal Chem. Soc., 28, 48-53, 2011.
- **9. P. L. Homagai**. Development of Natural Cation Exchanger for the Treatment of Lead ions from Aqueous Solution. J. Nepal Chem. Soc., 29, 34-43, 2012.

- 10. J. Kour, P. L. Homagai, M. R. Pokhrel and K. N. Ghimire. An Ecofriendly Alternative for the Removal of Cd (II) and Cu (II) from Aqueous Medium. J. Nepal Chem. Soc., 30, 37-44, 2012.
- 11. B. Shrestha, P. L. Homagai, M. R. Pokhrel and K. N. Ghimire. Exhausted Tea Leaves a low cost biosorbent for the removal of Lead (II) and Zinc (II) ions from their aqueous solution. J. Nepal Chem. Soc., 30, 123-129, 2012.

PUBLICATIONS