FIXED BED COLUMN STUDY FOR REMOVAL OF CHROMIUM (VI) FROM AQUEOUS SOLUTION BY USING SAW DUST (*GMELINA ARBOREA)*

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Submitted By
GOUTAM GIRI
10500011
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Under the guidance
of
Prof. (Dr.) R.K.SINGH

Department of Chemical Engineering
National Institute of Technology
Rourkela
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National Institute of Technology
Rourkela

CERTIFICATE

This is to certify that the work for the thesis entitled **" FIXED BED COLUMN STUDY FOR REMOVAL OF CHROMIUM(VI) FROM AQUEOUS SOLUTION BY USING SAW DUST (*Gmelina arborea*)"** submitted by Goutam Giri in partial fulfillment of the requirements for the award of Bachelor of Technology Degree in Chemical Engineering (Session 2005-2009) at National Institute of Technology Rourkela (Deemed University) , is an authentic work which was carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/Institute for the award of any Degree or Diploma.

Date:
Rourkela

Prof. (Dr.) R.K.Singh
Department of Chemical Engineering,
National Institute of Technology,
Rourkela – 769008, Orissa.

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Goutam Giri
Roll No. 10500011
B.Tech., Final Year,
Dept. of Chem. Engg.,
N.I.T Rourkela, Orissa.

CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

The study on performance of low-cost adsorbent such as saw dust of *Gmelina arborea* (Ghambhari tree) in the removal of Chromium (VI) ion from aqueous solution is performed. The adsorbent material adopted was found to be an efficient media for removal of Chromium (VI) ion in continuous mode using fixed bed column. A comparative study has also been done on the adsorption capacity of saw dust of different mesh sizes. The column studies were conducted with a fixed column of diameter 7cms and a bed height of 50cms. The flow rate of solution passing through the adsorbent bed was maintained at a fixed value of 1litre/min. It was found that the metal uptake capacity (amount of removal) of Chromium (VI) ion decreased but the adsorption capacity (percentage of removal) increased with the decrease in the concentration of chromium (VI) in the initial sample solution. It was also observed that the order of metal uptake capacity & adsorption capacity of saw dust of different ISS mesh size for removal of Chromium (VI) removal was as follows: (-30 +10) > (-50 +30) > (-70 +50) .

Keywords: Adsorption, Gmelina arborea, Chromium(VI), Continuous Fixed-bed column experiments

CHAPTER – 1

INTRODUCTION

1. INTRODUCTION

Chromium exists usually in both trivalent and hexavalent forms in aqueous systems. The two-oxidation states of chromium have different chemical, biological and environmental characteristics [1]. Cr(III) is relatively insoluble and required by microorganisms in small quantities as an essential trace metal nutrient [2], while Cr(VI) is a great concern because of its toxicity. Cr(VI) has been reported to be a primary contaminant to humans, animals, plants and microorganisms and it is known to be carcinogenic [3–5]. Chromium is used in a variety of industrial applications; hence, large quantities of chromium are discharged into the environment. Sources of chromium waste leading to water pollution includes electroplating, steel fabrication, paints and pigments, mining, leather tanning, textile dyeing, aluminum conversion coating operations, plants producing industrial inorganic chemicals and wood treatment units [6–8]. Due to environmental concern, discharge limits of both Cr(III) and Cr(VI) have been instituted by most industrial countries. Their concentration in industrial wastewaters ranges from 0.5 to 270 mg/L [7]. The tolerance limit for Cr(VI) for discharge into inland surface waters is 0.1 mg/L and in potable water is 0.05 mg/L [9,10]. The Ministry of Environment and Forest (MOEF); Government of India has set minimal national standards (MINAS) of 0.1 mg/L for safe discharge of effluent containing Cr(VI) in surface water [11]. In order to comply with this limit, it is essential that industries treat their effluents to reduce the Cr(VI) concentration in water and wastewater to acceptable levels before its transport and cycling into the natural environment.

Therefore, the level of chromium in final effluent has to be reduced by the application of appropriate technology. In wastewater treatment, various methods are utilized to remove chromium. These include reduction followed by chemical precipitation [12], ion exchange [13], electrochemical precipitation [14], reduction [15], adsorption [16], solvent extraction [17], membrane separation [18], concentration [19], evaporation, reverse osmosis and bio-sorption [20,21] and emulsion per traction technology [22].

Adsorption is by far most versatile and effective method for removing any contaminants like heavy metal, especially, if combined with appropriate regeneration steps. This solves the problem of sludge disposal and renders the system more economically viable, especially if low-cost adsorbents are used [23]. In the last few years, several approaches have been reported in this direction utilizing inexpensive and effective adsorbent for removal of Cr(VI) from aqueous solutions. The advantages of the low-cost adsorbents over the conventional adsorbents are as follows:

(1) The efficiencies of various non-conventional adsorbents towards adsorbate removal vary generally between 50% and 90% depending on the characteristics and particle size of the adsorbent, and the characteristics and concentration of the adsorbate, etc. Hence, low-cost adsorbents can be employed efficiently in removal of heavy metals.

(2) Non-conventional adsorbents are much cheaper relative to conventional adsorbents, and when readily available locally lead to much reduced transportation costs.

(3) Non-conventional adsorbents require simple alkali/and or acid treatment for the removal of lignin before application in order to increase their efficiency.

(4) Non-conventional adsorbents require less maintenance and supervision.

The materials developed for this purpose range from industrial wastes to agricultural waste products, biomass and various solid substances. Some examples are hydrous concrete particles [24], paper mill sludge [16], seaweed biosorbent [25], tannin gel particles [26], sugar beet pulp [27], wheat bran [28], leaf mould [29], coniferous leaves [30], activated groundnut husk carbon [31], coconut husk and palm pressed fibers [32], coconut shell, wood and dust coal activated carbons [33], coconut tree sawdust carbon [34], used tyres carbon [35], cactus, olive stone/cake, wool, charcoal, and pine needles [36], rice husk carbon [37], moss [38], sphagnum moss peat [39], hazelnut shell carbon [40,41], almond shell carbon [42], corncob [43], cow dung carbon [44], agricultural wastes [45], waste slurry [46], carbon slurry [47], lignocellulosic solid wastes [48], charred rice husk and activated charcoal and eucalyptus bark [49] have been reported in literature.

However, to cover this problem, more work and investigations are needed to deal with other locally available and economically viable adsorbents to eliminate Cr(VI) from aqueous solutions having different composition and characteristics. In this project we have studied the efficiency of saw dust of *Gmelina arborea* (locally known as Ghambhari tree) in the removal of Cr(VI) from solution. A comparative study has also been done on the adsorption capacity of saw dust of different mesh sizes.

CHAPTER – 2

LITERATURE REVIEW

2.1. HARMFUL EFFECTS OF HEAVY METALS

Ever increasing industrial activity is the main culprit behind most environmental pollution problems and ecosystem damage, coming from the accumulation of pollutants such as toxic metals chromium, copper, lead, cadmium, zinc, nickel, etc. [48]. Contamination of soils, groundwater, sediments, surface water and air with hazardous and toxic chemicals poses significant problems for both human health and the environment [49]. Heavy metals are considered to be particularly dangerous pollutants. Their presence in the wastewater of several industrial processes, such as electroplating, metal finishing, metallurgical work, tanning, chemical manufacturing, mining and battery manufacturing, has brought about more environmental concerns due to their toxicity even at low concentrations [50−52]. In view of the human health impacts, each metal imparts different effects and symptoms. For instance, in the case of minor zinc exposure, irritability, muscular stiffness, loss of appetite and nausea are common [53]. Chromium [54], on the other hand, can cause cancer in the digestive tract and lungs [55], while manganese (Mn) triggers neurotoxicity, low hemoglobin levels, and gastrointestinal accumulation [56].As another example, copper consumption in high doses brings about serious toxicological concerns since it can be deposited in the brain, skin, liver, pancreas, and myocardium [57], and initiates intestinal distress, kidney damage and anemia [58]. Lead (Pb) has been cited as one of the three most toxic heavy metals that have latent long-term negative impacts on health, causing anemia, encephalopathy, hepatitis and nephritic syndrome [59]. Cadmium also exposes human health to severe risks, as it can provoke cancer, kidney damage, mucous membrane destruction, vomiting, diarrhea, bone damage, and itai-itai disease, as well as affect the production of progesterone and testosterone [60]. Moreover, the presence of nickel exceeding its critical level might bring about serious lung and kidney problems aside from gastrointestinal distress, pulmonary fibrosis and skin dermatitis [61]. Finally, mercury has been identified for its nervous system deterioration, including protoplasm poisoning [62].

2.2. REMOVAL OF HEAVY METALS FROM WATER AND WASTE WATER

Several contender technologies exist to eliminate heavy metals from industrial wastewater, including reduction followed by adsorption on miscellaneous adsorbents [63,64], supercritical fluid extraction [65], ion exchange [66], ion flotation[67], electrocoagulation [68], high-gradient magnetic separation[69], micellar-enhanced ultrafiltrationtc [70] etc.. Most methods seem to be almost equally effective. However, further consideration of suitability places a large portion of them outside of industrial scale applications due to the high capital investment and operational costs involved. Specifically speaking, the most effective and versatile technique for heavy metal removal, even at very low concentrations, is adsorption. However, the high price of adsorbents (usually activated carbon) is regarded as the major obstacle for industrial application. From an economic point of view, it is infeasible to utilize activated carbon for commercial wastewater treatment. To that end, the focus of heavy metal adsorption studies has been altered toward natural materials that are available in vast amounts, as well as certain waste products from industrial and agricultural operations [71].

2.3. BIOSORPTION OF HEAVY METALS

Based upon the metal binding capacities of various biological materials, biosorption can separate heavy metals from wastewater [72]. Lately, biosorption has emerged as a cost-effective and efficient alternative for application to low strength wastewaters [73]. Biosorption, a term used here to describe the removal of heavy metals using a passive binding process with nonliving microorganisms including bacteria, fungi, and yeasts [74], and other biomass types that are capable of efficiently collecting heavy metals. Obviously, some of the advantages biosorption has over conventional treatment methods include low cost, high efficiency for dilute concentration solutions, a minimal amount of chemical and/or biological sludge, no additional nutrients required and the possibility of biosorbent regeneration and metal recovery [72]. The sorption of heavy metals onto these biomaterials is attributed to their constituents, which are mainly proteins, carbohydrates and phenolic compounds, since they contain functional groups such as carboxylates, hydroxyls and amines, which are able to attach to the metal ions [75].

Heavy metal accumulation in aquatic organisms, which is an active process involving metabolic activity within living organisms, has been studied by several researchers since 1978 [76−80]. Biosorption onto biomass, an entirely different process from bioaccumulation, was pioneered by Volesky's group from McGill University in 1981 [81]. At present, the biosorption field has been enriched by a vast amount of studies published in different journals. Although in the beginning most researchers focused their efforts upon heavy metal accumulation and concentration within living organisms [82−85], upon noticing that dead biomass possesses high metal-sorbing potential [86], their interest shifted to biosorption [87−104]. This is mainly due to the abundant availability, adsorption capacity and economic value of agricultural, plant tissue and industrial wastes, which has made them the main subject for biosorption research during the last decade [105−115].

Several reviews are available that discuss the use of biosorbents for the treatment of water and wastewater containing heavy metals [116−139]. One of the most productive biosorption research groups is Volesky's group. During the last three decades, his group has written several review papers, of which some are cited within this paper [117,121,127,131,134]. Their review papers cover a multitude of aspects affecting heavy metal removal using biosorbents. For example, in 1995, Volesky and Holan [117] compiled more than 110 papers published between 1943 and 1995. Their review contains an assessment of adsorption performance, biosorption by industrial biomass types and biosorption by seaweed materials. Examples of biosorption of several heavy metals on several types of biosorbents are also mentioned.

Kratochvil and Volesky discussed accomplishments in the biosorption area from 1978 to 1997 [121]. They summarize metal binding capacities for numerous biomass types under different tested operation parameters. Accordingly, the most encountered mechanism is the ion exchange mechanism. Recognition of ion exchange between protons and heavy metals, contribution of surface functional groups in ion exchange processes and ion exchange isotherm development are presented in their review.

Reliable sorption equilibria and kinetic data are of substantial value for adsorption separation system design. A majority of biosorption studies have been devoted to this end. Furthermore, a combination of basic equilibrium sorption data, sorbate behavior in solution, sorbate uptake mechanisms, mass transfer characteristics and fluid dynamic characteristics is required for the design of adsorption systems [131]. Illustrations and descriptions of how to employ this information simultaneously within suitable mathematical models for predicting sorption column performance were given in Volesky's review published in 2003 [131].

Recently, Volesky wrote a review titled "Biosorption and me" [134]. This interesting paper covers almost all of the author's work. Taking into account his experience in biosorption, Volesky classified his work into several sections, namely biosorption and its interdisciplinary challenge, metal's threat to the environment, the mystery of biomass-metal interactions, sorption equilibrium and where mistakes are made, process considerations and sorbent regeneration, and how to model and optimize biosorption performance, including the future of biosorption. Later in this review, he also made an analogy that the current state of heavy metal biosorption is only the "tip of the iceberg" to express its unlimited prospects. Likewise, biosorption is predicted to be of exceptional advantage for the purification and recovery of high-value products, including proteins, steroids, pharmaceuticals, and drugs.

Apart from Volesky's groups, other researchers also provide several reviews that are worthy of mention. For instance, structural modifications of bacteria through alteration of their polysaccharide backbone or side chains or through sugar modification for biosorption purposes have been performed by many research groups. Progress on this topic was covered by Gutnick and Bach [123]. They focus their discussion on several issues, namely cation binding to specific bacterial biopolymers, binding of cations by amphipathic biopolymers, molecular approaches to biopolymer modification and preparations, and also potential application for metal sequestration. This review presents useful information on polymer engineering applications within the biosorption area [123]. They further remark that the benefits associated with enhanced specificity and cation-binding capacity should be examined to judge the economic competitiveness of polymer engineering for industrial applications.

Further on, Ahluwalia and Goyal [133] condensed more than a few studies about applications of microbial- and plant-derived biomass to sequester metal ions from solutions. Some conventional techniques utilized to remove heavy metals from industrial effluents, as well as the advantages and disadvantages of biosorption processes, were mentioned. They also added sections explaining the use of different surface and structural characterization methods, such as SEM, XPS, and EDAX, to determine biosorption mechanisms.

Shukla et al. [126] put emphasis on the role of sawdust for water treatment. The adsorption mechanism, influencing factors and favorable conditions for different sawdust materials were discussed. A statistical review on the biosorption of Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II) using algae was also provided by Romera et al. [128]. Their review covered 54 studies on 37 different algae (20 brown algae, 9 red algae and 8 green algae). Another review on the utilization of brown algae for heavy metal biosorption was done by Davis et al. [127]. The focus of Davis's review was the biochemistry of biosorption, which revolved around a detailed description of the macromolecular conformation of the alginate biopolymers, metal binding mechanisms and the role of cellular structure, storage polysaccharides and cell wall and extracellular polysaccharides on metal sequestration [127].

The state-of-the-art review in the field of heavy metal biosorption employing *Saccharomyces cerevisiae* was compiled by Wang and Chen [129], and stemmed from an immense number of publications from1990 to 2005. Yeast-utilized biosorption depends largely on pH, the initial metal ion to biomass concentration ratio, culture conditions, the presence of various ligands and competitive metal ions in solution, and, to a more limited extent, temperature. Still, another equally good review has been presented by Lodeiro et al. [130] that stressed the importance of thermodynamic and kinetic aspects to fully understand the biosorption process.

Finally, a summary paper on the performance of agricultural waste materials as biosorbents for heavy metals is written by Sud et al. [135]. They compiled quite a lot of work on heavy metal biosorption using cellulosic agricultural wastes. Another paper with similar content by Nurchii and Villaescusa should also be referred to interested readers [137].

2.4. AGRICULTURAL WASTE AND OTHER CELLULOSIC MATERIALS AS ALTERNATIVE ADSORBENTS

Despite the availability of numerous techniques for the treatment of effluents with heavy metals, adsorption is constantly viewed as a highly effective technique for this purpose, especially in low metal concentration solutions.

Agricultural by-products are mostly composed of lignin and cellulose, as well as other polar functional group-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 an electron pair from these groups to form complexes with metal ions in solution [140].

The capability of several cheap agro-based materials, namely almond shell (AS), crushed coconut shell (CS), ground nut shell (GS), *Tamarindus indica* seed (TS), and walnut shell (WS), for Cr(VI) subtraction have been evaluated [24]. By comparing the adsorption capacity of five low cost sorbents, Agarwal et al. [71] concluded that the use of tamarind seed as an alternative adsorbent is more economical and worthwhile than other conventional methods. They also noted that the removal of Cr(VI) ions by tamarind seed is significantly reduced with a pH increase, slightly decreased with ionic strength enhancement and enhanced with rising temperature. It is suggested that chemisorption is the most plausible mechanism involved.

Azadirachta indica (neem) is a typical tree in the mahogany family of *Meliciae*. Products derived from neem have proven to possess therapeutic value such as anthelmintic, antifungal, antidiabetic, antibacterial, antiviral, anti-infertility and sedative activities. Several researchers have investigated the prospects of neem leaf as an alternative adsorbent for Cr(VI), Cd(II) and Pb(II) [141−146]. Sharma and Bhattacharyya [142] utilized *Azadirachta indica* (Neem Leaf Powder) to extract chromium(VI) from solution. The adsorption was carried out in a batch process using different concentrations of metal ions in aqueous solution 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. On the basis of the Langmuir model, they obtained an adsorption capacity of neem leaf powder for Cr(VI) of 0.0028 mmol/g. A relatively low amount of *Azadirachta indica* (Neem Leaf Powder) (1.6 g dm−3) could remove as much as 87% of Cr(VI) from a dilute solution (0.137 mmol/L) during a 300 min period at 300K. The optimum pH range in their study was 4.5−7.5. In a separate study, Babu and Gupta [141] also exploited activated *Azadirachta indica* (Neem Leaf Powder) as a biosorbent. By modifying the physical structure and surface chemistry of the neem leaf via an activation process, the adsorption capacity could be significantly enhanced.

Azadirachta indica (Neem Leaf Powder) was considered as a good adsorbent for cadmium from simulated wastewater [146]. In the adsorption of Cd(II) on *Azadirachta indica* (Neem Leaf Powder), pH had a considerable effect upon the removal percentage. A rise of pH from 4 to 9.5 resulted in an 11-fold enhancement of removal efficiency (8.8−93.6%). While the removal performance was better at higher pH, the effectiveness of *Azadirachta indica* (Neem Leaf Powder) to remove Cd(II) is still questionable, since no further information about the Cd(II) removal percentage caused exclusively by adsorption or precipitation is given. At high pH (above 8.6), it is likely that Cd(II) precipitates into its hydroxide, since the initial concentration used in their study (0.325 mmol/L) already surpasses the thermodynamic solubility limit of Cd(II) (around 0.07mmol/L) [147]. Therefore, the 11-fold enhancement of removal efficiency of Cd(II) would be better attributed to the higher extent of Cd(II) precipitation as its hydroxide at higher pH rather than the adsorption process.

Chaff is an agricultural by-product that contains fiber and protein along with some functional groups, and is mainly given to livestock and poultry as food [148]. Numerous functional groups such as carboxylates, hydroxyls, amidogens, etc. are also encountered within chaff. Han et al. [148] 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 cellwall polysaccharide based on a-(1−4) linked d-galacturonic acid, which is commercially available by extraction from pectin-rich sugar-beet pulp, apple pomace and citrus peels [149]. Some degree of similarities exists between pectin structures and alginate, denoting its potential as an alternative sorbent. Schiewer and Patil [149] 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 biosorbent for cadmium removal from wastewater [150]. The initial pH of the solution and cadmium concentration, in particular, significantly affects cadmium sorption onto copra meal.

Pino et al. [48,151] examined the capability of green coconut shell powder to adsorb three heavy metals. Coconut shell accommodates 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 probed at different particle sizes (0.044−0.297 mm), initial metal concentration (0.385−19.232 mmol/L) and pH values (2−9) in batch mode. In their study, as-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 models.

It is revealed that a major rice bran fraction contains 12%-13% oil and highly unsaponifiable components. In view of its abundant availability and ease of retrieval as an unused by-product, Wang et al. [152] conceived the possibility of using this material as an alternative adsorbent for zinc removal from synthetic wastewater. They also studied the influence of 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.

Plant materials are comprised of cellulose materials that are capable of adsorbing heavy metal cations within aqueous medium. The treatment of agricultural waste materials have been and still are a vital environmental concern, since they represent unused resources that need to be disposed of properly. The impending use of teawaste from Srilankan tea as a biosorbent for Cu(II) and Pb(II) removal from wastewater has been studied by Amarasinghe and Williams [153]. Their assessment on the adsorption capacity of tea waste-based granular activated carbon confirms these materials potential.

Likewise, another biodisposability material commonly acquired as by-products from the industrial treatment of wheat bran is also worthy of mention. This material has been employed as a media for detoxification of two heavy metal ions, Cu(II) and Zn(II), from aqueous solution [154]. Batch experimental results showed that the retention capacity of the lignocellulosic substrate was 0.199mmol/g at pH 4.5 for Cu(II) and 0.239 mmol/g at pH 6.5 for Zn(II). Furthermore, the metallic cations were found attached in a complexation reaction to the lignin and fatty acid functional groups within the lignocellulosic substrate, i.e., alcohols, ketones and carboxylic acids.

Other low cost and widely available natural materials are represented by almond shell, hazelnut and walnut [114], birch wood [108], *Cassia fistula* (Golden Shower) biomass [156], coconut fiber [157], lemon peel [158], *Moringa oleifera* seeds [159], neem oil cake [160], olive pomace

[161], orange peel [162], palm flower [115], pine bark [163], pomegranate peel [164], ponkan peel [165], reed [166], rice husk [167], rice straw[168], sour orange residue [169], and yellow passion fruit shell [170], and they have lucratively been applied as biosorbents to eliminate metals from aqueous media. With the aim of increasing biosorption capacity, modifications of the biosorbent surface have been carried out [157,161−163,166,167,169]. For instance, Igwe et al. [157] conducted a thiolation of coconut fiber, whereas Argun and Dursun [163] altered the surface properties of pine bark using the Fenton reagent. Alteration of the surface of olive pomace by phosphoric acid and hydrogen peroxide exposure was claimed to improve the sorption properties of this material as well [161]. These modification processes tend to improve the adsorption capacity of the biosorbents.

CHAPTER – 3

EXPERIMENTAL METHODS

3.1. PREPARATION OF ADSORBATE SOLUTION

The stock solutions of Cr(VI) of concentration 1000 ppm was prepared by dissolving 0.2828 grams of analytical grade of $K_2Cr_2O_7$ in 100ml of RO distilled water. The stock solution was further diluted with RO distilled water to desired concentration for obtaining the standard solutions for absorbance measurement. The sample solutions which were to be treated with the adsorbent were also prepared similarly by dissolving required quantity of the above mentioned salt in RO distilled water.

3.2. PREPARATION OF ADSORBENT

Raw saw dust of *Gmelina arborea* (locally known as Ghambhari tree) was obtained from nearby saw mill. It was then screened to get particles of five different sizes i.e (+ 70) , (- 70 + 50) , (- 50 +30) , (- 30 + 10) & (- 10) ISS mesh. The above fractions of saw dust were washed with sufficient quantity of RO distilled water until it gave a clear transparent solution. Only then the prepared Cr(VI) solutions were passed through them in the bed to study their adsorption capacity. The fractions (+70) & (-10) were not used in the present study as they were found to be inconvenient due to excessive channeling effect & formation of paste like substance respectively.

Fig.1 Saw dust of (+70) ISS Mesh size

Fig.2 Saw dust of (-70 +50) ISS Mesh size

Fig.3 Saw dust of (-50 +30) ISS Mesh size

Fig.4 Saw dust of (-30 +10) ISS Mesh size

Fig.5 Saw dust of (-10) ISS Mesh size

3.3. MEASUREMENT OF Cr (VI) IN AQUEOUS SOLUTIONS

There are some components within the sawdust that may reduce the Cr(VI) to Cr(III). Therefore, oxidation of Cr(III) within the samples to Cr(VI) is necessary before the analysis of each sample. Cr ions within the samples were oxidized by using potassium permanganate in acidic medium. The violet color that forms as a result of the reaction between the Cr(VI) ions and 1,5-diphenyl carbazide in acidic medium, was measured by using JASCO V-530 UV/VIS - Spectrophotometer at 540 nm. The lowest limit of this method is 0.01 mg/L and the best suitable measurement range is 0.5 - 5.0 mg/L(ppm) . For samples containing concentrations in the range 5.0 – 100.0 mg/L, the absorbance of pure $K_2Cr_2O_7$ solution at 313nm was taken as standard .Therefore, in order to obtain the unknown concentration of treated solutions, the samples were diluted before the measurements and measured values were multiplied by the dilution factor.

3.4. COLUMN STUDIES :

The fixed-bed column had 7.0 cm internal diameter and was 60 cm in height. The bed length used in every experiment was fixed at 50 cm. The bed was filled with the saw dust upto the specified height of the column and different size of the adsorbent was used as specified for each experiment. In every experiment the metal solution of a known concentration was pumped at a fixed flow rate of 1 litre/min to the column filled with known bed height of adsorbent. The above fixed flow rate into the fixed column was maintained with the help of monitoring a bypass stream. The samples solution after passing through the adsorbent in the fixed bed column was again recycled back into the sample reservoir tank so that there is a continuous adsorption of Chromium ion. Samples for analysis of Chromium ion concentration were collected at a regular interval of 30 mins from the bottom of the sample reservoir tank. The saw dust used inside the fixed bed column was replaced by a fresh batch of saw dust at the beginning of each of experiment.

The metal uptake capacity (amount of removal of chromium ion) and the adsorption capacity (percentage of chromium ion removal) were calculated using the following equations:

Metal Uptake Capacity = Initial Chromium ion conc. – Final Chromium ion conc.

Adsorption Capacity (%) = (Metal Uptake Capacity X 100) / Initial Chromium ion conc.

3.5. EXPERIMENTAL SET - UP :

The experimental set-up and the schematic diagram of the set-up is shown as below:

Fig.6 Experimental set-up

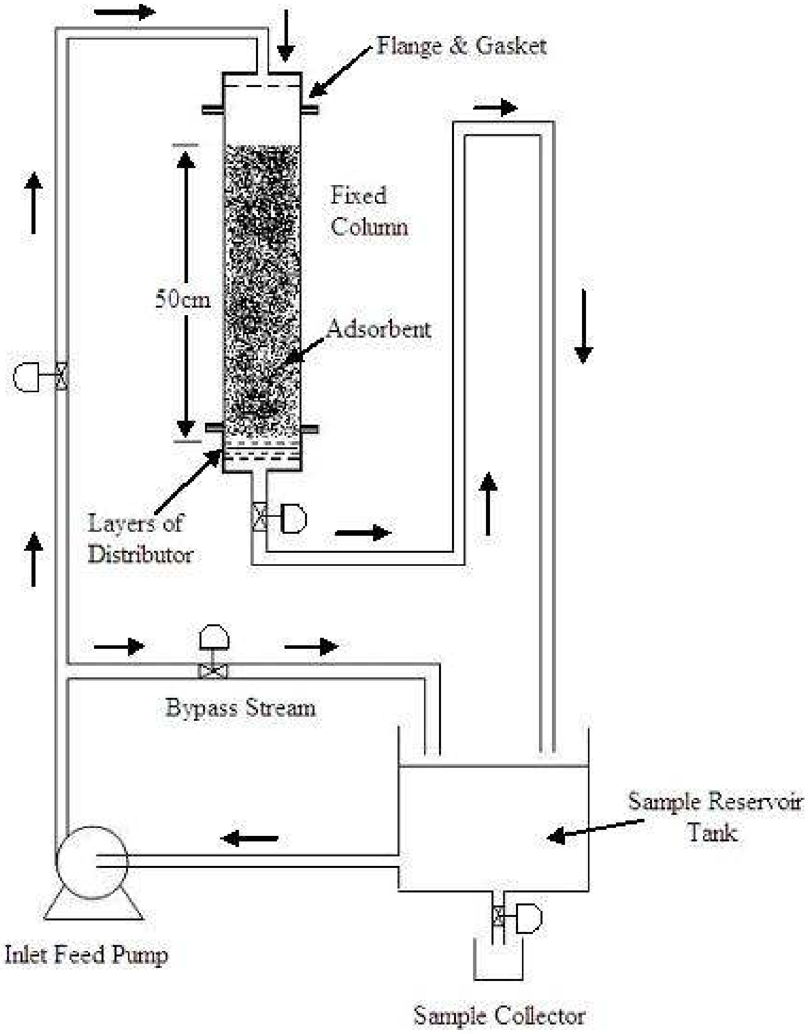

Fig.7 Schematic diagram of lab scale column study

CHAPTER – 4

RESULTS AND DISCUSSION

4.1. STUDY OF ADSORPTION CAPACITY

EXPERIMENTAL SPECIFICATIONS

Bed height of adsorbent = 50 cms

Adsorbent size used = (-50 +30) ISS Mesh size saw dust

Flow rate of solution through the bed = 1 litre/min

For 1st RUN

Initial Cr^{+6} solution conc. = 500ppm (14.14 gms of $K_2Cr_2O_7$ in 10 litres of RO distilled water)

Table – 1 Conc. of solution at different time interval (Initial solution conc = 500ppm)

Sl.No.	Time (in hr.)	Concentration (in ppm)	Sl.No.	Time (in hr.)	Concentration (in ppm)
1.	0.5	468.9	9.	4.5	387.9
2.	1.0	450.2	10.	5.0	385.3
3.	1.5	436.1	11.	5.5	382.2
4.	2.0	423.8	12.	6.0	380.0
5.	2.5	414.1	13.	6.5	377.9
6.	3.0	405.9	14.	7.0	377.1
7.	3.5	397.7	15.	7.5	375.9
8.	4.0	392.8	16.	8.0	374.9

Calculations :

Metal Uptake Capacity = 500ppm – 375ppm = 125ppm

Adsorption Capacity = (125 x 100)/500 = 25 %

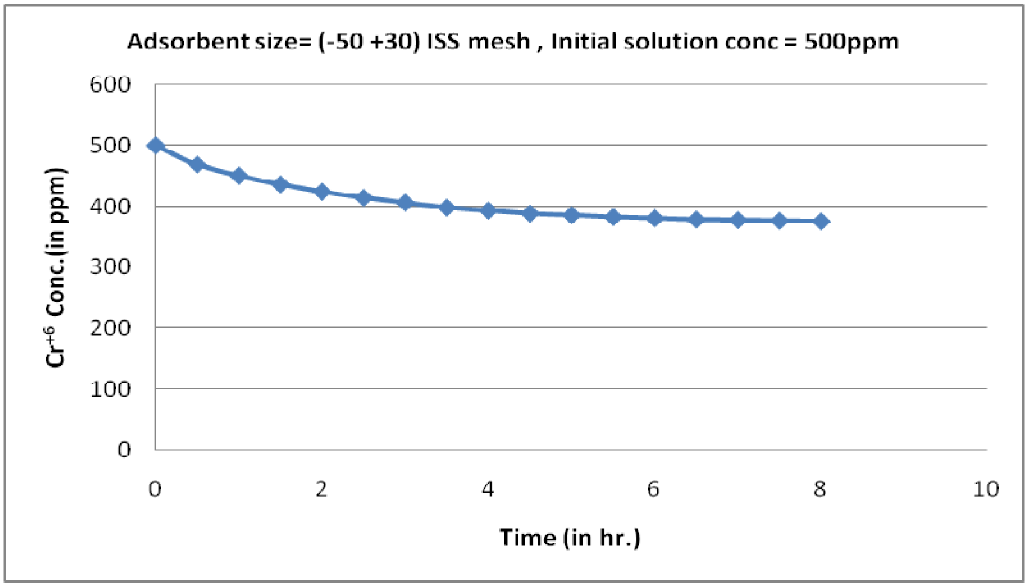

Fig 8. Cr^{+6} Conc. Vs Time plot (Adsorbent size = -50 +30 ISS Mesh, Initial solution conc = 500ppm)

For 2nd RUN

Initial Cr^{+6} solution conc. = 375ppm (10.61 gms of $K_2Cr_2O_7$ in 10 litres of RO distilled water)

Table – 2 Conc. of solution at different time interval (Initial solution conc = 375ppm)

Sl.No.	Time (in hr.)	Concentration (in ppm)	Sl.No.	Time (in hr.)	Concentration (in ppm)
1.	0.5	346.8	9.	4.5	278.8
2.	1.0	328.9	10.	5.0	276.1
3.	1.5	314.2	11.	5.5	274.1
4.	2.0	300.8	12.	6.0	272.0
5.	2.5	293.9	13.	6.5	270.1
6.	3.0	289.1	14.	7.0	269.1
7.	3.5	284.8	15.	7.5	267.9
8.	4.0	282.0	16.	8.0	266.9

Calculations :

Metal Uptake Capacity = 375ppm – 267ppm = 108ppm

Adsorption Capacity = (108 x 100)/375 = 28.8 %

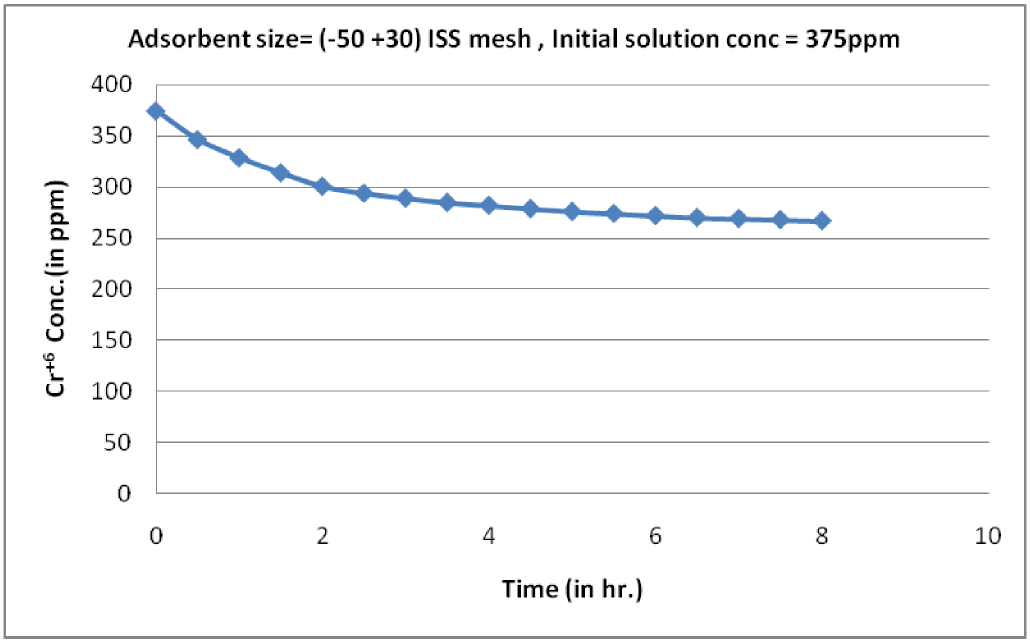

Fig 9. Cr^{+6} Conc. Vs Time plot (Adsorbent size = -50 +30 ISS Mesh, Initial solution conc = 375ppm)

For 3rd RUN

Initial Cr^{+6} solution conc. = 267ppm (7.55 gms of $K_2Cr_2O_7$ in 10 litres of RO distilled water)

Table – 3 Conc. of solution at different time interval (Initial solution conc = 267ppm)

Sl.No.	Time (in hr.)	Concentration (in ppm)	Sl.No.	Time (in hr.)	Concentration (in ppm)
1.	0.5	245.1	9.	4.5	186.9
2.	1.0	228.9	10.	5.0	184.0
3.	1.5	219.1	11.	5.5	182.0
4.	2.0	210.2	12.	6.0	179.8
5.	2.5	202.8	13.	6.5	178.1
6.	3.0	198.0	14.	7.0	177.1
7.	3.5	192.9	15.	7.5	176.0
8.	4.0	189.7	16.	8.0	174.9

Calculations :

Metal Uptake Capacity = 267ppm – 175ppm = 92ppm

Adsorption Capacity = (92 x 100)/267 = 34.45 %

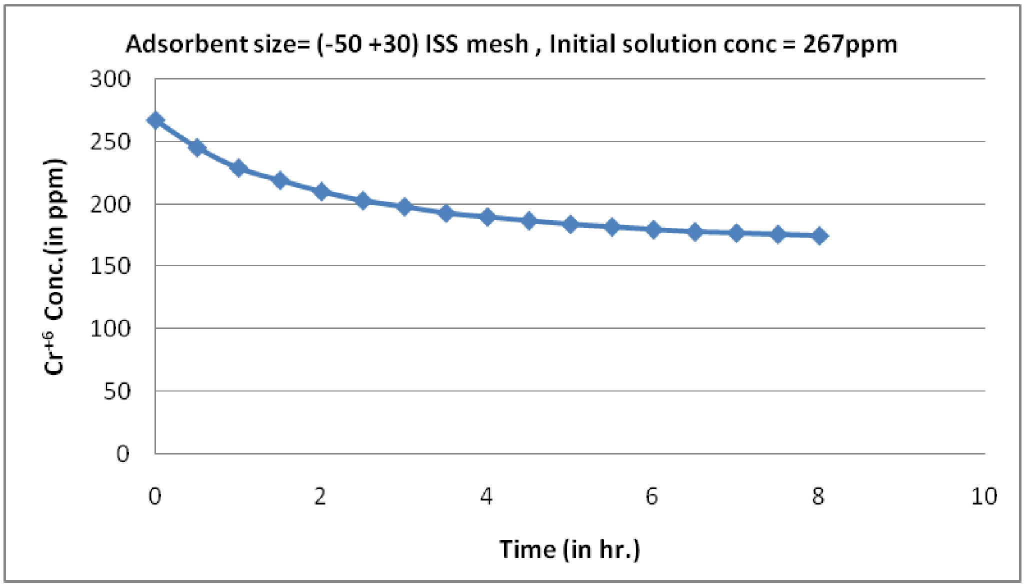

Fig 10. Cr^{+6} Conc. Vs Time plot (Adsorbent size = -50 +30 ISS Mesh, Initial solution conc = 267ppm)

For 4th RUN

Initial Cr^{+6} solution conc. = 175ppm (4.95 gms of $K_2Cr_2O_7$ in 10 litres of RO distilled water)

Table – 4 Conc. of solution at different time interval (Initial solution conc. = 175ppm)

Sl.No.	Time (in hr.)	Concentration (in ppm)	Sl.No.	Time (in hr.)	Concentration (in ppm)
1.	0.5	158.3	9.	4.5	111.0
2.	1.0	146.1	10.	5.0	107.7
3.	1.5	137.8	11.	5.5	105.8
4.	2.0	131.9	12.	6.0	104.1
5.	2.5	127.0	13.	6.5	102.2
6.	3.0	122.0	14.	7.0	101.1
7.	3.5	118.2	15.	7.5	99.9
8.	4.0	113.9	16.	8.0	98.8

Calculations :

Metal Uptake Capacity = 175ppm – 99ppm = 76ppm

Adsorption Capacity = (76 x 100)/175 = 43.42 %

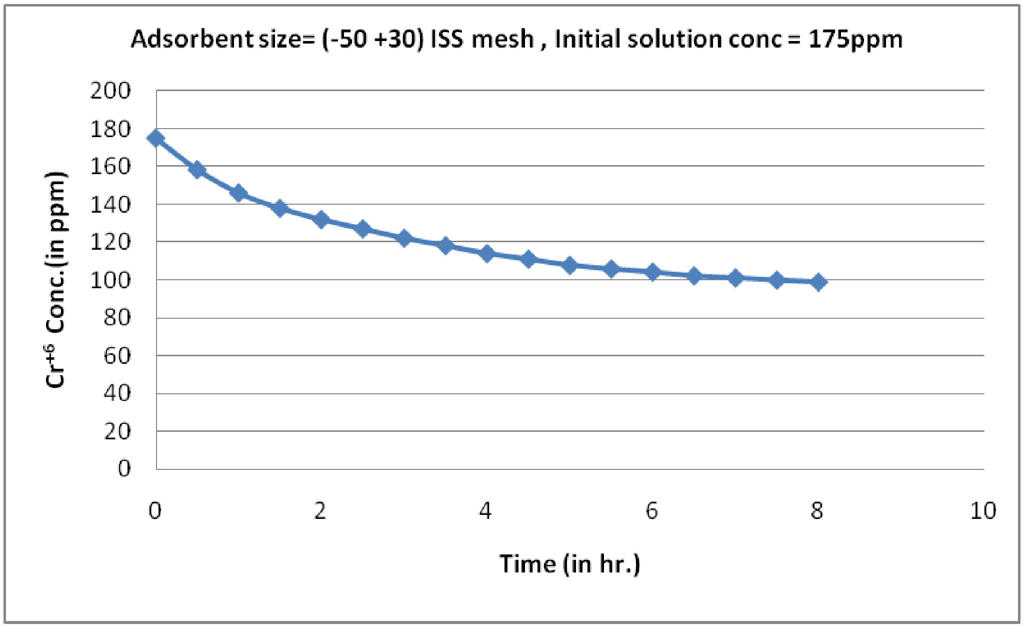

Fig 11. Cr^{+6} Conc. Vs Time plot (Adsorbent size = -50 +30 ISS Mesh, Initial solution conc = 175ppm)

For 5th RUN

Initial Cr^{+6} solution conc. = 99ppm (2.80 gms of $K_2Cr_2O_7$ in 10 litres of RO distilled water)

Table – 5 Conc. of solution at different time interval (Initial solution conc. = 99ppm)

Sl.No.	Time (in hr.)	Concentration (in ppm)	Sl.No.	Time (in hr.)	Concentration (in ppm)
1.	0.5	88.1	9.	4.5	53.8
2.	1.0	79.9	10.	5.0	52.1
3.	1.5	74.2	11.	5.5	50.2
4.	2.0	68.9	12.	6.0	47.9
5.	2.5	65.1	13.	6.5	46.1
6.	3.0	62.1	14.	7.0	45.2
7.	3.5	59.1	15.	7.5	44.0
8.	4.0	56.0	16.	8.0	43.1

Calculations :

Metal Uptake Capacity = 99ppm – 43ppm = 56ppm

Adsorption Capacity = (56 x 100)/99 = 56.66 %

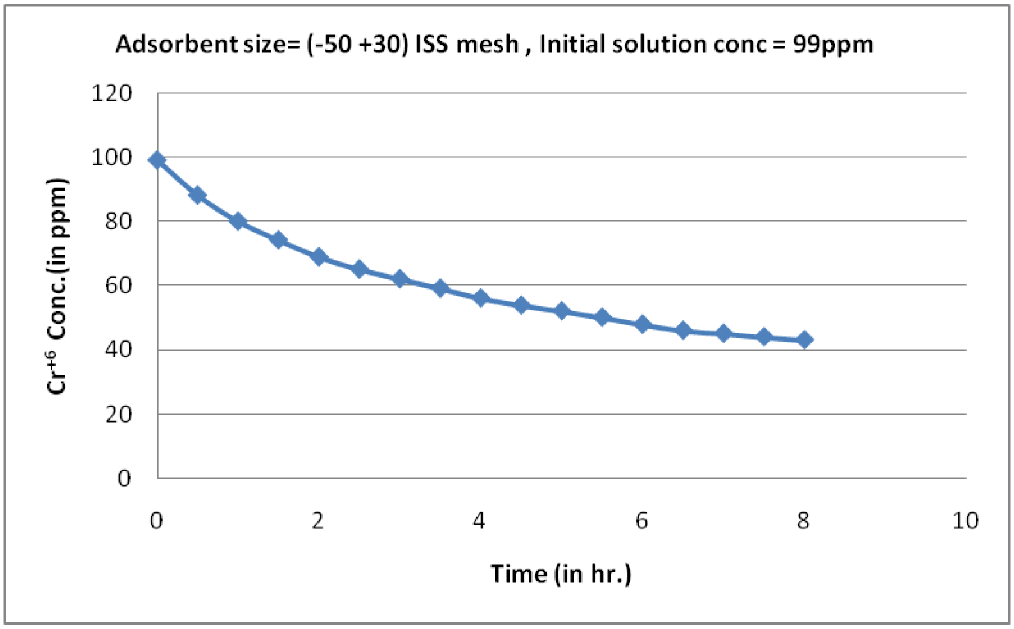

Fig 12. Cr^{+6} Conc. Vs Time plot (Adsorbent size = -50 +30 ISS Mesh, Initial solution conc = 99ppm)

For 6th RUN

Initial Cr^{+6} solution conc. = 43ppm (1.22 gms of $K_2Cr_2O_7$ in 10 litres of RO distilled water)

Table – 6 Conc. of solution at different time interval (Initial solution conc. = 43ppm)

Sl.No.	Time (in hr.)	Concentration (in ppm)	Sl.No.	Time (in hr.)	Concentration (in ppm)
1.	0.5	34.1	9.	4.5	19.0
2.	1.0	29.2	10.	5.0	18.1
3.	1.5	26.8	11.	5.5	17.0
4.	2.0	24.9	12.	6.0	15.9
5.	2.5	23.1	13.	6.5	14.8
6.	3.0	22.0	14.	7.0	13.9
7.	3.5	21.1	15.	7.5	12.8
8.	4.0	19.9	16.	8.0	11.9

Calculations :

Metal Uptake Capacity = 43ppm – 12ppm = 31ppm

Adsorption Capacity = (31 x 100)/43 = 72.09 %

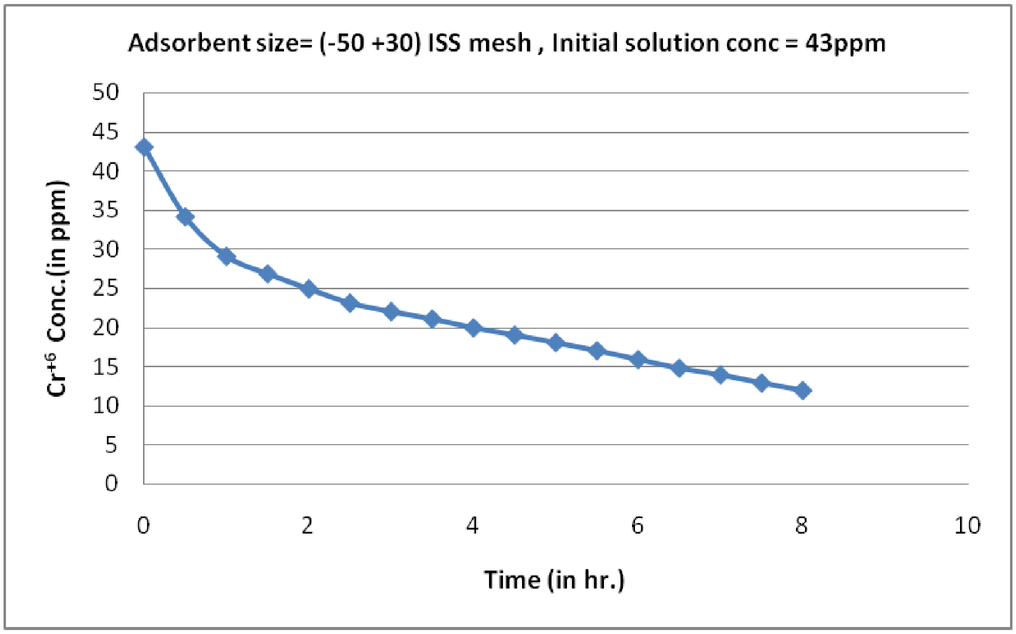

Fig 13. Cr^{+6} Conc. Vs Time plot (Adsorbent size = -50 +30 ISS Mesh, Initial solution conc = 43ppm)

For 7th RUN

Initial Cr^{+6} solution conc. = 12ppm (0.34 gms of $K_2Cr_2O_7$ in 10 litres of RO distilled water)

Table – 7 Conc. of solution at different time interval (Initial solution conc. = 12ppm)

Sl.No.	Time (in hr.)	Concentration (in ppm)	Sl.No.	Time (in hr.)	Concentration (in ppm)
1.	0.5	10.1	9.	4.5	3.9
2.	1.0	9.1	10.	5.0	3.4
3.	1.5	8.1	11.	5.5	2.9
4.	2.0	7.2	12.	6.0	2.4
5.	2.5	6.2	13.	6.5	2.2
6.	3.0	5.4	14.	7.0	2.0
7.	3.5	4.8	15.	7.5	1.9
8.	4.0	4.4	16.	8.0	1.8

Calculations :

Metal Uptake Capacity = 12ppm – 1.8ppm = 10.2ppm

Adsorption Capacity = (10.2 x 100)/12 = 85 %

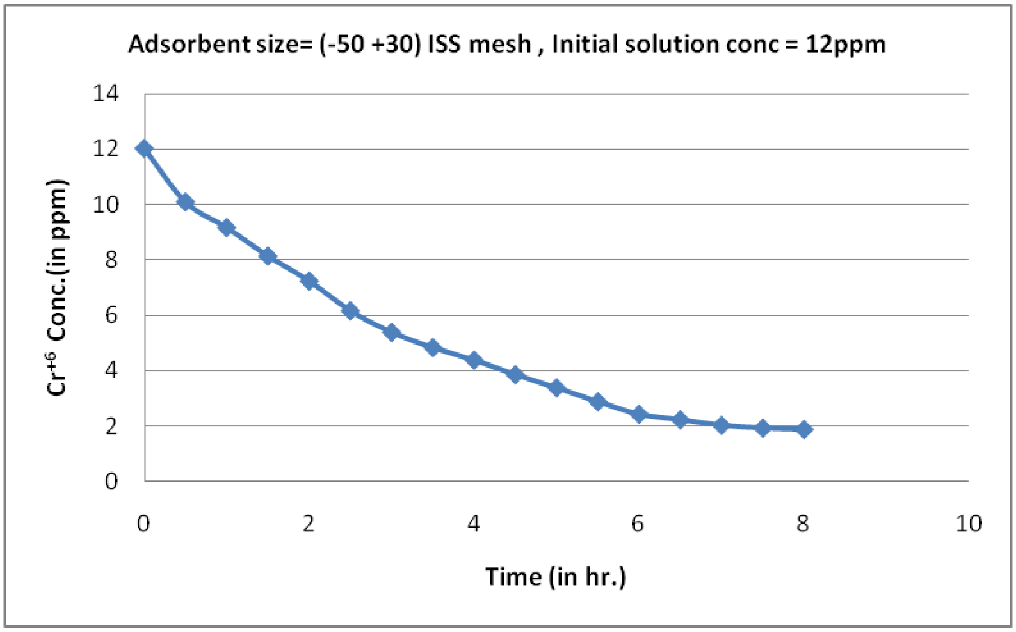

Fig 14. Cr^{+6} Conc. Vs Time plot (Adsorbent size = -50 +30 ISS Mesh, Initial solution conc = 12ppm)

4.2. STUDY OF EFFECT OF SIZE ON ADSORPTION CAPACITY

Bed height of adsorbent = 50 cms

Initial Cr^{+6} solution conc. = 500ppm (14.14 gms of $K_2Cr_2O_7$ in 10 litres of RO distilled water)

Flow rate of solution through the bed = 1 litre/min

Table – 8 Comparison of Conc. of soln. at different time interval (Initial soln. conc. = 500ppm)

Sl.No.	Time (in hrs.)	Adsorbent size : (- 30 +10) ISS Mesh	Adsorbent size : (- 50 +30) ISS Mesh	Adsorbent size : (- 70 +50) ISS Mesh
		Concentration (in ppm)	Concentration (in ppm)	Concentration (in ppm)
1	0.5	464.1	468.9	476.2
2	1.0	437.9	450.2	459.1
3	1.5	419.8	436.1	447.7
4	2.0	404.7	423.8	439.0
5	2.5	391.9	414.1	432.2
6	3.0	380.6	405.9	425.8
7	3.5	372.3	397.7	422.7
8	4.0	364.5	392.8	420.9
9	4.5	360.4	387.9	419.2
10	5.0	356.3	385.3	417.1
11	5.5	352.9	382.2	415.2
12	6.0	351.1	380.0	413.3
13	6.5	349.2	377.9	410.9
14	7.0	347.9	377.1	410.0
15	7.5	346.8	375.9	409.1
16	8.0	345.9	375.1	407.9

CALCULATIONS :

For (- 30 +10) ISS Mesh Saw Dust

Metal Uptake Capacity = 500ppm – 345ppm = 155ppm

Adsorption Capacity = (155 x 100)/500 = 30.8 %

For (- 50 +30) ISS Mesh Saw Dust

Metal Uptake Capacity = 500ppm – 375ppm = 125ppm

Adsorption Capacity = (125 x 100)/500 = 25 %

For (- 70 +50) ISS Mesh Saw Dust

Metal Uptake Capacity = 500ppm – 408ppm = 92ppm

Adsorption Capacity = (92 x 100)/500 = 18.4 %

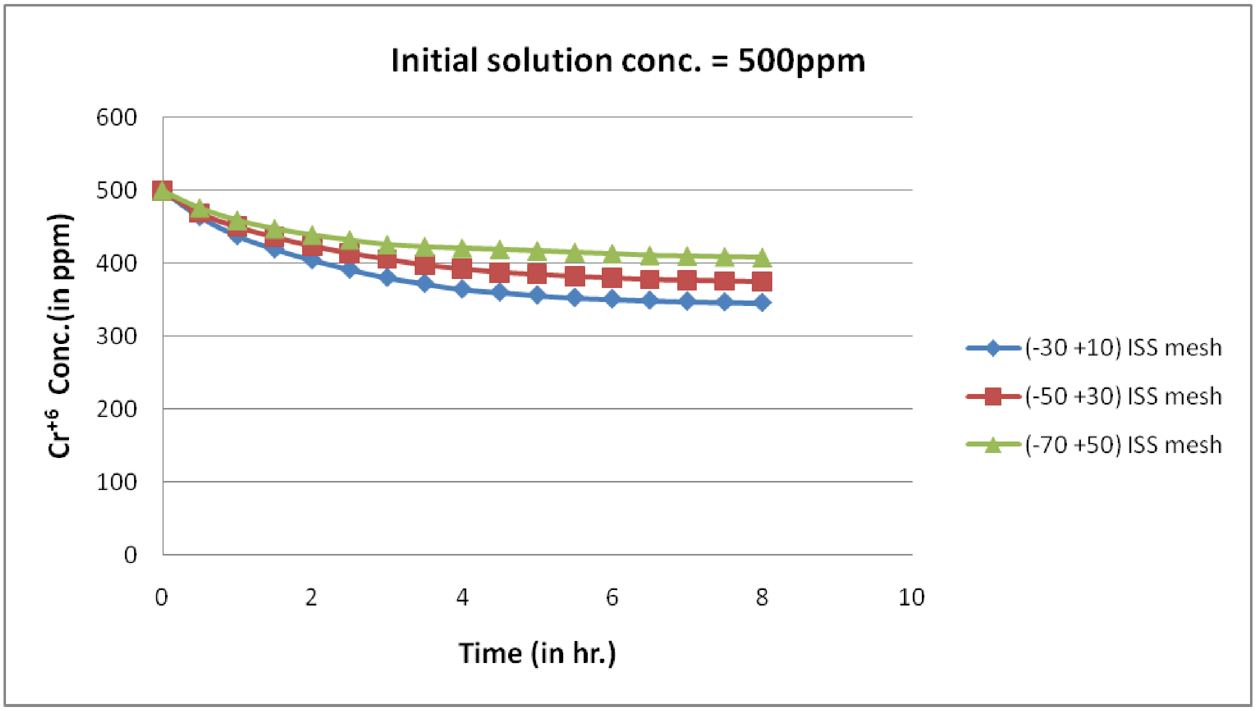

Fig 15. Comparison of Cr^{+6} Conc. Vs Time plot (Initial solution conc. = 500ppm)

CHAPTER – 5

CONCLUSION

5.1 CONCLUSION

Continuous fixed bed column studies were performed for removal of Chromium (VI) ion from water using different mesh size particles of saw dust. The study indicated the suitability of the adsorbent for removal of Chromium (VI) from aqueous solutions. The selected adsorbent may be viewed as a useful material while considering the economic aspects of wastewater treatment. The obtained results may be summarized as follows:

1. The metal uptake capacity decreases with decrease in the initial concentration of Cr^{+6} solution. However, the percentage of removal or the adsorption capacity is found to increase with lower initial concentration of chromium.
2. The saw dust particles of size (-50 +30) ISS Mesh required 7 fixed bed columns of fresh saw dust (run for 8 hours over each bed) for the removal of Chromium ion from 500ppm to a value of as low as 2ppm.
3. The observed order of metal uptake capacity as well as adsorption capacity of Cr^{+6} for saw dust of different ISS mesh size was as follows : (-30 +10) > (-50 +30) > (-70 +50) .

These experimental studies on the specified adsorbent would be quite useful in developing an appropriate technology for the removal of Cr^{+6} ions from contaminated industrial effluents.

5.2 FUTURE SCOPE OF WORK

1. Similar continuous column studies can be performed for locally available saw dust of different trees to compare the metal uptake capacity and adsorption capacities.
2. The metal uptake capacity and adsorption capacity can also be studied at different flow rates of the solution through the column bed and by also varying the bed height.

CHAPTER – 6

REFERENCES

6. REFERENCES

[1] World Health Organization, Environmental Health Criteria 61, Chromium, WHO, Geneva, 1988.

[2] G. Saner, Chromium in Nutrition and Diesease, Alan R Liss Inc., New York, 1980.

[3] US Department of Health and Human Services, Toxicological Profile for Chromium, Public Health Services Agency for Toxic Substances and Diseases Registry, Washington, DC, 1991.

[4] M. Cieslak-Golonka, Toxic and mutagenic effects of chromium(VI), Polyhedron 15 (1995) 3667–3689.

[5] C. Raji, T.S. Anirudhan, Batch Cr(VI) removal by polyacrylamide-grafted sawdust: kinetics and Thermodynamics,Water Res. 32 (1998) 3772–3780.

[6] M.J. Udy, Chromium, Reinhold Publishing Corporation, New York, 1956.

[7] L.J. Casarett, J. Doul, Toxicology, the basic science of poisons, Macmillan, New York, 1980.

[8] J.O. Nriagu, E. Nieboer, Chromium in the Natural and Human Environment, Wiley, New York, 1988.

[9] EPA (Environmental Protection Agency, Environmental Pollution Control Alternatives. EPA/625/5–90/025, EPA/625/4-89/023, Cincinnati, US, 1990.

[10] Indian Standard, 1991. Drinking water—specification (first revision), IS 10500, 1991.

[11] MINAS, Pollution control acts, rules, and notification there under Central Pollution Control Board, Ministry of Environment and Forests, Government of India, New Delhi, 2001.

[12] X. Zhou, T. Korenaga, T. Takahashi, T. Moriwake, S. Shinoda, A process monitoring/controlling system for the treatment of wastewater containing chromium(VI), Water Res. 27 (1993) 1049–1054.

[13] G. Tiravanti, D. Petruzzelli, R. Passiono, Pretreatment of tannery wastewaters by an ion exchange process for Cr(III) removal and recovery, Water Sci. Technol. 36 (1997) 197–207.

[14] N. Kongsricharoern, C. Polprasert, Chromium removal by a bipolar electrochemical precipitation process,Water Sci. Technol. 34 (1996) 109–116.

[15] J.C. Seaman, P.M. Bertsch, L. Schwallie, In situ Cr(VI) reduction within coarse-textured, oxide-coated soil and aquifer systems using Fe(II) solutions, Environ. Sci. Technol. 33 (1999) 938–944.

[16] N. Calace, D.A. Muro, E. Nardi, B.M. Petronio, M. Pietroletti, Adsorption isotherms for describing heavy metal retention in paper mill sludges, Ind. Eng. Chem. Res. 41 (2002) 5491–5497.

[17] K. Pagilla, L.W. Canter, Laboratory studies on remediation of chromium contaminated soils, J. Environ. Eng. 125 (1999) 243–248.

[18] A.K. Chakravarti, S.B. Chowdhury, S. Chakrabarty, T. Chakrabarty, D.C. Mukherjee, Liquid membrane multiple emulsion process of chromium (VI) separation fromwastewaters, Colloids Surf. A: Physicochem. Eng. Aspects 103 (1995) 59–71.

[19] C.F. Lin, W. Rou, K.S. Lo, Treatment strategy for Cr(VI) bearing wastes, Water Sci. Technol. 26 (1992) 2301–2304.

[20] Z. Aksu, T. Kutsal, A. Comparative study for biosorption characteristics of heavy metal ions with *C. vulgaris*, Environ. Technol. 11 (1990) 979–987.

[21] Z. Aksu, D. Ozer, H. Ekiz, T. Kutsal, A. Calar, Investigation of biosorption of chromium(VI) on *C. crispate* in two staged batch reactor, Environ. Technol. 17 (1996) 215–220.

[22] I. Ortiz, M.F.S. Roman, S.M. Corvalan, A.M. Eliceche, Modeling and optimization of an emulsion pertraction process for removal and concentration of Cr(VI), Ind. Eng. Chem. Res. 42 (2003) 5891–5899.

[23] S.E. Bailey, T.J. Olin, R.M. Bricka, D.D. Adrian, A review of potentially low cost sorbents for heavy metals, Water Res. 33 (1999) 2469–2479.

[24] C.H. Weng, C.P. Haung, H.E. Allen, P.F. Sanders, Cr(VI) adsorption onto hydrous concrete particles from groundwater, J. Environ. Eng. 127 (2001) 1124–1131.

[25] D. Kratochvil, P. Pimentel, B. Volesky, Removal of trivalent and Hexavalent chromium by seaweed biosorbent, Environ. Sci. Technol. 32 (1998) 2693–2698.

[26] Y. Nokano, M. Tanaka, Y. Nakamura, M. Konno, Removal and recovery system of hexavalent chromium from wastewater by tannin gel particles, J. Chem. Eng., Japan 33 (2000) 747–752.

[27] Z. Reddad, C. Gerente, Y. Andres, P. Cloirec, Adsorption of several metal ions onto a low cost biosorbent: kinetic and equilibrium studies, Environ. Sci. Technol. 36 (2002) 2067–2073.

[28] L. Dupond, E. Guillon, Removal of Hexavalent chromium with a lignocellulosic substrate extracted from wheat bran, Environ. Sci. Technol. 37 (2003) 4235–4241.

[29] D.C. Sharma, C.F. Forster, The treatment of chromium wastewaters using sorptive potential of leaf mould, Bioresour. Technol. 49 (1994) 31–40.

[30] M. Ayoma, T. Sugiyama, S. Doi, N.S. Cho, H.E. Kim, Removal of Hexavalent chromium from dilute aqueous solution by coniferous leaves, Holzforschung, Copyright Walter de Gruyter, Berlin, 53 (1999) 365–368.

[31] K. Periasamy, K. Srinivasan, P.R. Muruganan, Studies on chromium(VI) removal by activated ground nut husk carbon, Indian J. Environ. Health 33 (1991) 433–439.

[32] W.T. Tan, S.T. Ooi, C.K. Lee, Removal of Cr(VI) from solution by coconut husk and palm pressed fibres, Environ. Technol. 14 (1993) 277–282.

[33] C. Selomulya, V. Meeyoo, R. Amal, Mechanisms of Cr(VI) removal from water by various types of activated carbons, J. Chem. Technol. Biotechnol. 74 (1994) 111–122.

[34] K. Selvi, S. Pattabhi, K. Kadirvelu, Removal of Cr(VI) from aqueous solution by adsorption onto activated carbon, Bioresour. Technol. 80 (2001) 87–89.

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

[36] M. Dakiky, M. Khamis, M. Manassra, M. Mer'eb, Selective adsorption of Chromium(VI) in industrial waste water using low cost abundantly available adsorbents, Adv. Environ. Res. 6 (2002) 533–540.

[37] K.S. Low, C.K. Lee, A.Y. NG, Column study on the sorption of Cr(VI) using quaternized rice hulls, Bioresour. Technol. 68 (1999) 205–208.

[38] C.K. Lee, K.S. Low, K.L. Kee, Removal of chromium from aqueous solution, Bioresour. Technol. 54 (1995) 183–189.

[39] D.C. Sharma, C.F. Forster, Removal of Hexavalent chromium using sphagnum moss peat, Water Res. 27 (1993) 1201–1208.

[40] G. Cimino, A. Passerini, G. Toscano, Removal of toxic cations and Cr(VI) from aqueous solution by hazelnut shell,Water Res. 34 (2000) 2955–2962.

[41] M. Kobya, Adsorption, kinetic and equilibrium studies of Cr(VI) by hazelnut shell activated carbon, Adsorpt. Sci. Technol. 22 (2004) 51–64.

[42] M.P. Candela, J.M.M. Martinez, R.T. Macia, Chromium(VI) removal with activated carbons, Water Res. 29 (1995) 2174–2180.

[43] S. Bosinco, J. Roussy, E.P. Guibal, L.E. Cloirec, Interaction mechanisms between Hexavalent chromium and corncob, Environmen. Technol. 17 (1996) 55–62.

[44] D.D. Das, R. Mahapatra, J. Pradhan, S.N. Das, R.S. Thakur, Removal of Cr(VI) from aqueous solution using activated cow dung carbon, J. Colloid Interface Sci. 232 (2000) 235–240.

[45] E. Demirbas, M. Kobya, E. Senturk, T. Ozkan, Adsorption kinetics for the removal of chromium(VI) from aqueous solutions on the activated carbons prepared from agricultural waster, Water SA 30 (2004) 533–539.

[46] S.K. Srivastava, R. Tyagi, N. Pant, Adsorption of heavy metal ions on carbonaceous material developed from the waste slurry generated in local fertilizer plants, Water Res. 23 (1989) 1161–1165.

[47] V.K. Singh, P.N. Tiwari, Removal and recovery of chromium (VI) from industrial wastewater, J. Chem. Technol. Biotechnol. 69 (1997) 376–382.

[1] G.H. Pino, L.M.S. de Mesquita, M.L. Torem, Biosorption of heavy metals by powder of green coconut shell, Sep. Sci. Technol. 41 (2006) 3141–3153.

[49] M.I. Ansari, A. Malik, Biosorption of nickel and cadmium by metal resistant bacterial isolates from agricultural soil irrigated with industrial wastewater, Bioresource Technol. 98 (2007) 3149–3153.

[50] S. Kang, J. Lee, K. Kima, Biosorption of Cr(III) and Cr(VI) onto the cell surface of pseudomonas aeruginosa, Biochem. Eng. J. 36 (2007) 54–58.

[51] F.A.A. Al-Rub, Biosorption of zinc on palm tree leaves: equilibrium, kinetics, and thermodynamics studies, Sep. Purif. Technol. 41 (2006) 3499–3515.

[52] Z. Aksu, U. Acikel, Modelling of a single-staged bioseparation process for simultaneous removal of iron(III) and chromium(VI) by using chlorella vulgaris, Biochem. Eng. J. 4 (2000) 229–238.

[53] A.K. Bhattacharya, S.N. Mandal, S.K. Das, Adsorption of Zn(II) from aqueous solution by using different adsorbents, Chem. Eng. J. 123 (2006) 43–51.

[54] B.L. Martins, C.C.V. Cruz, A.S. Luna, C.A. Henriques, Sorption and desorption of Pb^{2+} ions by dead sargassum sp biomass, Biochem. Eng. J. 27 (2006) 310–314.

[55] B. Kiran, A. Kaushik, C.P. Kaushik, Biosorption of Cr(VI) by native isolate of *lyngbya putealis* (hh-15) in the presence of salts, J. Hazard. Mater. 141 (2007) 662–667.

[56] K. Parvathi, R. Nareshkumar, R. Nagendran, Biosorption of manganese by *aspergillus niger* and *saccharomyces cerevisiae*,World J. Microbiol. Biotechnol. 23 (2007) 671–676.

[57] K. Vijayaraghavan Palanivelu, M. Velan, Biosorption of copper(II) and cobalt(II) from aqueous solutions by crab shell particles, Bioresource Technol. 97 (2006) 1411–1419.

[58] F.A.A. Al-Rub, M.H. El-Naas, I. Ashour, M. Al-Marzouqi, Biosorption of copper on chlorella vulgaris from single, binary and ternarymetal aqueous solutions, Process Biochem. 41 (2006) 457–464.

[59] L. Deng, Y. Su, H. Su, X.Wang, X. Zhu, Biosorption of copper(II) and lead(II) from aqueous solutions by nonliving green algae *Cladophora f ascicularis*: equilibrium, kinetics and environmental effects, Adsorption 2 (2006) 267–277.

[60] F.S. Johannes Godt, C. Grosse-Siestrup, V. Esche, P. Brandenburg, A. Reich, D.A. Groneberg, The toxicity of cadmium and resulting hazards for human health, J. Occup. Med. Toxicol. 1 (2006) 1–6.

[61] C.E. Borba, R. Guirardello, E.A. Silva, M.T. Veit, C.R.G. Tavares, Removal of nickel(II) ions from aqueous solution by biosorption in a fixed bed column: experimental and theoretical breakthrough curves, Biochem. Eng. J. 30 (2006) 184–191.

[62] H.K. Alluri, S.R. Ronda, V.J. Settalluri, J.S. Bondili, V. Suryanarayana, P. Venkateshwar, Biosorption: an eco-friendly alternative for heavy metal removal, African J. Biotechnol. 6 (2007) 2924–2931.

[63] L. Monser, N. Adhoum, Modified activated carbon for the removal of copper, zinc, chromium and cyanide from wastewater, Sep. Purif. Technol. 26 (2002) 137–146.

[64] E. Erdem,N. Karapinar,R. Donat, The removal of heavymetal cations by natural zeolites, J. Colloid Interface Sci. 280 (2004) 309–314.

[65] J.M. Murphy, C. Erkey, Thermodynamics of extraction of copper(II) from aqueous solutions by chelation in supercritical carbon dioxide, Environ. Sci. Technol. 31 (1997) 1674–1679.

[66] L.C. Lin, J.K. Li, R.S. Juang, Removal of Cu(II) and Ni(II) from aqueous solutions using batch and fixed-bed ion exchange processes, Desalination 225 (2008) 249–259.

[67] X.Z. Yuan, Y. Meng, G.M. Zeng, Y. Fang, J.G. Shi, Evaluation of teaderived biosurfactant on removing heavy metal ions from dilute wastewater by ion flotation, Colloids Surf. A-Physicochem. Eng. Aspects 317 (2008) 256–261.

[68] A.K. Golder, A.K. Chanda, A.N. Samanta, S. Ray, Removal of Cr(VI) fromaqueous solution: electrocoagulation vs chemical coagulation, Sep. Purif. Technol. 42 (2007) 2177–2193.

[69] P. Anand, J.E. Etzel, F.J. Friedlaender, Heavy-metals removal by high-gradient magnetic separation, IEEE Trans. Magnet. 21 (1985) 2062–2064.

[70] H. Kim, K. Baek, B.K. Kim, H.J. Shin, J.W. Yang, Removal characteristics of metal cations and their mixtures using micellar-enhanced ultrafiltration, Korean J. Chem. Eng. 25 (2008) 253–258.

[71] G.S. Agarwal, H.K. Bhuptawat, S. Chaudhari, Biosorption of aqueous chromium(VI) by tamarindus indica seeds, Bioresource Technol. 97 (2006) 949–956.

[72] V.J.P. Vilar, C.M.S. Botelho, R.A.R. Boaventura, Modeling equilibrium and kinetics of metal uptake by algal biomass in continuous stirred and packed bed adsorbers, Adsorption 13 (2007) 587–601.

[73] P. Pavasant, R. Apiratikul, V. Sungkhum, P. Suthiparinyanont, S. Wattanachira, T.F. Marhaba, Biosorption of Cu^{2+}, Cd^{2+}, Pb^{2+}, and Zn^{2+} using dried marine green macroalga caulerpa lentillifera, Bioresource Technol. 97 (2006) 2321–2329.

[74] K. Parvathi, R.Nagendran, Biosorption of chromiumfromeffluent generated in chrome-electroplating unit using saccharomyces cerevisiae, Sep. Sci. Technol. 42 (2007) 625–638.

[75] S.B. Choi, Y.S. Yun, Biosorption of cadmium by various types of dried sludge: an equilibrium study and investigation of mechanisms, J. Hazard. Mater. B 138 (2006) 378–383.

[76] P.T.S.Wong, Y.K. Chau, P.L. Luxon, Toxicity of amixture ofmetals on freshwater algae, J. Fish. Res. Board Canada 35 (1978) 479–481.

[77] B.A. Hart, P.E. Bertram, B.D. Scaife, Cadmium transport by chlorellapyrenoidosa, Environ. Res. 18 (1979) 327–335.

[78] W. Macka, H. Wihlidal, G. Stehlik, J. Washuttl, E. Bancher, Uptake of $^{203}Hg^{++}$ and $^{115M}Cd^{++}$ by chlamydomonas reinhardi under various conditions, Chemosphere 8 (1979) 787–796.

[79] G.S. Braek, D. Malnes, A. Jensen, Heavy-metal tolerance of marine phytoplankton. 4. Combined effect of zinc and cadmiumon growth and uptake in some marine diatoms, J. Exp. Marin Biol. Ecol. 42 (1980) 39–54.

[80] J.E. Duddridge, M. Wainwright, Heavy-metal accumulation by aquatic fungi and reduction in viability of gammarus-pulex fed Cd2+ contaminated mycelium,Water Res. 14 (1980) 1605–1611.

[81] M. Tsezos, B. Volesky, Biosorption of uranium and thorium, Biotechnol. Bioeng. 23 (1981) 583–604.

[82] J.F. Gipps, B.A.W. Coller, Effect of some nutrient cations on uptake of cadmium by chlorella-pyrenoidosa, Aust. J. Marine Freshw. Res. 33 (1982) 979–987.

[83] F. Glombitza, U. Iske, C. Gwenner,M.R.V. Krishnan, Biosorption of mercury by microorganisms, Acta Biotechnol. 4 (1984) 281–284.

[84] J.M. Tobin, D.G. Cooper, R.J. Neufeld, The effects of cation competition on metal adsorption by rhizopus-arrhizus biomass, Biotechnol. Bioeng. 31 (1988) 282–286.

[85] A.C.A. Costa, S.G.F. Leite, Cadmium and zinc biosorption by chlorellahomosphaera, Biotechnol. Bioeng. 12 (1990) 941–944.

[86] B. Volesky, Biosorbents for metal recovery, Trends Biotechnol. 5 (1987) 96–101.

[87] E. Fourest, J.C. Roux, Heavy-metal biosorption by fungal mycelial byproducts—mechanisms and influence of pH, Appl. Microbiol. Biotechnol. 37 (1992) 399–403.

[88] Z.R. Holan, B. Volesky, I. Prasetyo, Biosorption of cadmium by biomass of marine-algae, Biotechnol. Bioeng. 41 (1993) 819–825.

[89] B. Volesky, H. May, Z.R. Holan, Cadmium biosorption by saccharomycescerevisiae, Biotechnol. Bioeng. 41 (1993) 826–829.

[90] H. Niu, X.S. Xu, J.H.Wang, B. Volesky, Removal of lead from aqueous-solutions by penicillium biomass, Biotechnol. Bioeng. 42 (1993) 785–787.

[91] B. Volesky, I. Prasetyo, Cadmium removal in a biosorption column, Biotechnol. Bioeng. 43 (1994) 1010–1015.

[92] J.S. Chang, J. Hong, Biosorption of mercury by the inactivated cells of pseudomonas-aeruginosa pu21 (rip84), Biotechnol. Bioeng. 44 (1994) 999–1006.

[93] E. Fourest, C. Canal, J.C. Roux, Improvement of heavy-metal biosorption by mycelial dead biomasses (rhizopus-arrhizus, mucor-miehei and penicilliumchrysogenum penicillium chrysogenum) — pH Control and cationic activation, FEMS Microbiol. Rev. 14 (1994) 325–332.

[94] Y. Sag, T. Kutsal, Copper(II) and nickel(II) adsorption by rhizopus-arrhizus in batch stirred reactors in series, Chem. Eng. J., Biochem. Eng. J. 58 (1995) 265–273.

[95] P.R. Puranik, N.S. Chabukswar, K.M. Paknikar, Cadmium biosorption by streptomyces-pimprinawaste biomass, Appl. Microbiol. Biotechnol. 43 (1995) 1118–1121.

[96] S. Alasheh, Z. Duvnjak, Adsorption of copper and chromium by aspergilluscarbonarius, Biotechnol. Prog. 11 (1995) 638–642.

[97] R.K. Asthana, S. Chatterjee, S.P. Singh, Investigations on nickel biosorption and its remobilization, Process Biochem. 30 (1995) 729–734.

[98] S. Bossrez, J. Remacle, J. Coyette, Adsorption of nickel on enterococcus hirae cell walls, J. Chem. Technol. Biotechnol. 70 (1997) 45–50.

[99] J.L. Zhou, Zn biosorption by rhizopus arrhizus and other fungi, Appl. Microbiol. Biotechnol. 51 (1999) 686–693.

[100] A. Selatnia, A. Boukazoula, N. Kechid, M.Z. Bakhti, A. Chergui, Y. Kerchich, Biosorption of lead (II) fromaqueous solution by a bacterial dead streptomyces rimosus biomass, Biochem. Eng. J. 19 (2004) 127–135.

[101] U. Yetis, A. Dolek, F.B. Dilek, G. Ozcengiz, The removal of Pb(II) by phanerochaete chrysosporium,Water Res. 34 (2000) 4090–4100.

[102] R. Gupta, P. Ahuja, S. Khan, R.K. Saxena, H. Mohapatra, Microbial biosorbents: meeting challenges of heavy metal pollution in aqueous solutions, Curr. Sci. 78 (2000) 967–973.

[103] G.Y. Yan, T. Viraraghavan, Effect of pretreatment on the bioadsorption of heavy metals on mucor rouxii,Water SA 26 (2000) 119–123.

[104] A.C.A. da Costa, F.P. de Franca, Cadmium uptake by spirulina maxima: toxicity and mechanism,World J. Microbiol. Biotechnol. 14 (1998) 579–581.

[105] S. AlAsheh, Z. Duvnjak, Adsorption of copper by canola meal, J. Hazard. Mater. 48 (1996) 83–93.

[106] J.P. Chen, W.R. Chen, R.C. Hsu, Biosorption of copper from aqueous solutions by plant root tissues, J. Fermen. Bioeng. 81 (1996) 458–463.

[107] S. Samantaroy, A.K. Mohanty, M. Misra, Removal of hexavalent chromium by kendu fruit gum dust, J. Appl. Polym. Sci. 66 (1997) 1485–1494.

[108] V.M. Dronnet, C. Renard, M.A.V. Axelos, J.F. Thibault, Binding of divalent metal cations by sugar-beet pulp, Carbohydr. Polym. 34 (1997) 73–82.

[109] V.M.Dronnet, M.A.V. Axelos, C. Renard, J.F. Thibault, Improvement of the binding capacity of metal cations by sugar-beet pulp. 2. Binding of divalent metal cations by modified sugar-beet pulp, Carbohydr. Polym. 35 (1998) 239–247.

[110] S.H. Lee, J.W. Yang, Removal of copper in aqueous solution by apple wastes, Sep. Sci. Technol. 32 (1997) 1371–1387.

[111] S.Y. Quek, B. Al-Duri, D.A.J. Wase, C.F. Forster, Coir as a biosorbent of copper and lead, Process Saf. Environ. Protect. 76 (1998) 50–54.

[112] S. Senthilkumaar, S. Bharathi, D. Nithyanandhi, V. Subburam, Biosorption of toxic heavy metals from aqueous solutions, Bioresource Technol. 75 (2000) 163–165.

[113] J.L. Gardea-Torresday, K.J. Tiemann, V. Armendariz, L. Bess-Oberto, R.R. Chianelli, J. Rios, J.G. Parsons, G. Gamez, Characterization of Cr(VI) binding and reduction to Cr(III) by the agricultural byproducts of avena monida (oat) biomass, J. Hazard. Mater. 80 (2000) 175–188.

[114] E. Pehlivan, T. Altun, Biosorption of chromium(VI) ion from aqueous solutions using walnut, hazelnut and almond shell, J. Hazard. Mater. 155 (2008) 378–384.

[115] R. Elangovan, L. Philip, K. Chandraraj, Biosorption of hexavalent and trivalent chromium by palm flower (borassus aethiopium), Chem. Eng. J. 141 (2008) 99–111.

[116] A.P. McHale, S. McHale, Microbial biosorption of metals-potential in the treatment of metal pollution, Biotechnol. Adv. 12 (1994) 647–652.

[117] B. Volesky, Z.R. Holan, Biosorption of heavymetals, Biotechnol. Prog. 11 (1995) 235–250.

[118] D.R. Lovley, J.D. Coates, Bioremediation of metal contamination, Curr. Opin. Biotechnol. 8 (1997) 285–289.

[119] F. Veglio, F. Beolchini, Removal ofmetals by biosorption: a review, Hydrometallurgy 44 (1997) 301–316.

[120] A.I. Zouboulis, K.A. Matis, I.C. Hancock, Biosorption of metals from dilute aqueous solutions, Sep. Purif. Methods 26 (1997) 255–295.

[121] D. Kratochvil, B. Volesky, Advances in the biosorption of heavy metals, Trends Biotechnol. 16 (1998) 291–300.

[122] G. McKay, Y.S. Ho, J.C.Y. Ng, Biosorption of copper fromwastewaters: a review, Sep. Purif. Methods 28 (1999) 87–125.

[123] D.L. Gutnick, H. Bach, Engineering bacterial biopolymers for the biosorption of heavymetals; newproducts and novel formulations, Appl. Microbiol. Biotechnol. 54 (2000) 451–460.

[124] C. Cervantes, J. Campos-Garcia, S. Devars, F. Gutierrez-Corona, H. Loza-Tavera, J.C. Torres-Guzman, R. Moreno-Sanchez, Interactions of chromium with microorganisms and plants, FEMS Microbiol. Rev. 25 (2001) 335–347.

[125] Y. Sag, Biosorption of heavy metals by fungal biomass and modeling of fungal biosorption: a review, Sep. Purif. Methods 30 (2001) 1–48.

[126] A. Shukla, Y. Zhang, P. Dubey, J.L. Margrave, S. Shukla, The role of sawdust in the removal of unwanted materials from water, J. Hazard. Mater. B 95 (2002) 137–152.

[127] T.A. Davis, B. Voleskya, A. Mucci, A review of the biochemistry of heavy metal biosorption by brown algae,Water Res. 37 (2003) 4311–4330.

[128] E. Romera, F. Gonzalez, A. Ballester, M.L. Blazquez, J.A. Munoz, Biosorption with algae: a statistical review, Crit. Rev. Biotechnol. 26 (2006) 223–235.

[129] J.Wang, C. Chen, Biosorption of heavy metals by saccharomyces cerevisiae: a review, Biotechnol. Adv. 24 (2006) 427–451.

[130] P. Lodeiro, R. Herrero, M.E. Sastre de Vicente, Thermodynamic and kinetic aspects on the biosorption of cadmium by low cost materials: a review, Environ. Chem. 3 (2006) 400–418.

[131] B. Volesky, Biosorption process simulation tools, Hydrometallurgy 71 (2003) 179–190.

[132] S. Babel, T.A. Kurniawan, Low-cost adsorbents for heavy metals uptake from contaminated water: a review, J. Hazard. Mater. 97 (2003) 219–243.

[133] S.S. Ahluwalia, D. Goyal, Microbial and plant derived biomass for removal of heavy metals from wastewater, Bioresource Technol. 98 (2007) 2243–2257.

[134] B. Volesky, Biosorption and me,Water Res. 41 (2007) 4017–4029.

[135] D. Sud, G. Mahajan, M.P. Kaur, Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions—a review, Bioresource Technol. 99 (2008) 6017–6027.

[136] K. Vijayaraghavan, Y.S. Yun, Bacterial biosorbents and biosorption, Biotechnol. Adv. 26 (2008) 266–291.

[137] V.M. Nurchi, I. Villaescusa, Agricultural biomasses as sorbents of some trace metals, Coord. Chem. Rev. 252 (2008) 1178–1188.

[138] A. Demirbas, Heavy metal adsorption onto agro-based waste materials: a review, J. Hazard. Mater. 157 (2008) 220–229.

[139] W.S. Wan Ngah, M.A.K.M. Hanafiah, Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: a review, Bioresource Technol. 99 (2008) 3935–3948.

[140] A.E. Ofomaja, Y. Ho, Effect of pH on cadmium biosorption by coconut copra meal, J. Hazard. Mater. B 139 (2007) 356–362.

[141] B.V. Babu, S. Gupta, Adsorption of Cr(VI) using activated neem leaves: kinetic studies, Adsorption 14 (2008) 85–92.

[142] A. Sharma, K.G. Bhattacharyya, Adsorption of chromium(VI) on azadirachta indica (neem) leaf powder, Adsorption 10 (2004) 327–338.

[143] S. Guptaa, B.V. Babu, Adsorption of Cr(VI) by a low-cost adsorbent prepared from neem leaves, Proc. Natl. Conf. Environ. Conserv. (2006) 175–180.

[144] K.G. Bhattacharyya, A. Sharma, Adsorption of Pb(II) from aqueous solution by azadirachta indica (Neem) leaf powder, J. Hazard. Mater. B 113 (2004) 97–109.

[145] M. Athar, U. Farooq, B. Hussain, Azadirachata indicum (neem): an effective biosorbent for the removal of lead(II) from aqueous solutions, Bull. Environ. Contam. Toxicol. 79 (2007) 288–292.

[146] A. Sharma, K.G. Bhattacharyya, Azadirachta indica (neem) leaf powder as a biosorbent for removal of Cd(II) from aqueous medium, J. Hazard. Mater. B 125 (2005) 102–112.

[147] B. Luo, J.W. Patterson, P.R. Anderson, Kinetic of cadmium hydroxide precipitation, Water Res. 26 (1992) 745–751.

[148] R. Han, J. Zhang, W. Zou, H. Xiao, J. Shi, H. Liu, Biosorption of copper(II) and lead(II) fromaqueous solution by chaff in a fixed-bed column, J. Hazard. Mater. B 133 (2006) 262–268.

[149] S. Schiewer, S.B. Patil, Pectin-rich fruit wastes as biosorbents for heavy metal removal: equilibrium and kinetics, Bioresource Technol. 99 (2008) 1896–1903.

[150] Y.S. Ho, A.E. Ofomaja, Biosorption thermodynamics of cadmium on coconut copra meal as biosorbent, Biochem. Eng. J. 30 (2006) 117–123.

[151] G.H. Pino, L.M.S. Mesquita, M.L. Torem, G.A.S. Pinto, Biosorption of cadmium by green coconut shell powder, Miner. Eng. 19 (2006) 380–387.

[152] X.S. Wang, Y. Qin, Z.F. Li, Biosorption of zinc from aqueous solutions by rice bran: kinetics and equilibrium studies, Sep. Sci. Technol. 41 (2006) 747–756.

[153] B.M.W.P.K. Amarasinghe, R.A. Williams, Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater, Chem. Eng. J. 132 (2007) 299–309.

[154] D. Dupont, J. Bouanda, J. Dumonceau, M. Aplincourt, Biosorption of Cu(II) and Zn(II) onto a lignocellulosic substrate extracted from wheat bran, Environ. Chem. Lett. 2 (2005) 165–168.

[155] A. Grimm, R. Zanzi, E. Bjornbom, A.L. Cukierman, Comparison of different types of biomasses for copper biosorption, Bioresource Technol. 99 (2008) 2559–2565.

[156] M.A. Hanif, R. Nadeema, H.N. Bhatti, N.R. Ahmada, T.M. Ansari, Ni(II) biosorption by *cassia fistula* (golden shower) biomass, J. Hazard. Mater. B 139 (2007) 345–355.

[157] J.C. Igwe, A.A. Abia, C.A. Ibeh, Adsorption kinetics and intraparticulate diffusivities of Hg, As and Pb ions on unmodified and thiolated coconut fiber, Int. J. Environ. Sci. Technol. 5 (2008) 83–92.

[158] H. Arslanoglu, H.S. Altundogan, F. Tumen, Preparation of cation exchanger from lemon and sorption of divalent heavy metals, Bioresource Technol. 99 (2008) 2699–2705.

[159] P. Kumari, P. Sharma, S. Srivastava, M.M. Srivastava, Biosorption studies on shelled *moringa oleifera* lamarck seed powder: removal and recovery of arsenic from aqueous system, Int. J. Miner. Process. 78 (2006).

[160] R.A.K. Rao, N.A. Khan, Removal and recovery of Cu(II), Cd(II) and Pb(II) ions from single and multimetal systems by batch and column operation on neem oil cake (NOC), Sep. Purif. Technol. 57 (2007) 394–402.

[161] M.A.Martin-Lara, F. Pagnanelli, S. Mainelli, M. Calero, L. Toro, Chemical treatment of olive pomace: effect on acid-basic properties and metal biosorption capacity, J. Hazard. Mater. 156 (2008) 448–457.

[162] Z.X. Xuan, Y.R. Tang, X.M. Li, Y.H. Liu, F. Luo, Study on the equilibrium, kinetics and isotherm of biosorption of lead ions onto pretreated chemicallymodified orange peel, Biochem. Eng. J. 31 (2006) 160−164.

[163] M.E. Argun, S. Dursun, A new approach to modification of natural adsorbent for heavy metal adsorption, Bioresource Technol. 99 (2008) 2516−2527.

[164] E.-S.Z. El-Ashtoukhy, N.K. Amina, O. Abdelwahab, Removal of lead(II) and copper(II) from aqueous solution using pomegranate peel as a new adsorbent, Desalination 223 (2008) 162–173.

[165] F.A. Pavan, A.C. Mazzocato, R.A. Jacques, S.L.P. Dias, Ponkan peel: a potential biosorbent for removal of Pb(II) ions from aqueous solution, Biochem. Eng. J. 40 (2008) 357–362.

[166] B. Southichak, K. Nakano, M. Nomura, N. Chiba, O. Nishimura, Pb(II) biosorption on reed biosorbent derived from wetland: effect of pretreatment on functional groups,Water Sci. Technol. 54 (2006) 133–141.

[167] S. Mohan, G. Sreelakshmi, Fixed bed column study for heavy metal removal using phosphate treated rice husk, J. Hazard. Mater. 153 (2008) 75–82.

[168] H. Gao, Y.G. Liu, G.M. Zeng,W.H. Xu, T. Li,W.B. Xia, Characterization of Cr(VI) removal from aqueous solutions by a surplus agricultural waste–rice straw, J. Hazard. Mater. 150 (2008) 446–452.

[169] M. Khormaei, B. Nasernejad, M. Edrisi, T. Eslamzadeh, Copper biosorption from aqueous solutions by sour orange residue, J. Hazard. Mater. 149 (2007) 269–274.

[170] R.A. Jacques, E.C. Limaa, S.L.P. Dias, A.C. Mazzocato, F.A. Pavan, Yellow passion fruit shell as biosorbent to remove Cr(III) and Pb(II) from aqueous solution, Sep. Purif. Technol. 57 (2007) 193–198.