

Technical Report No 112
Biosorption of Heavy Metals by Low cost Adsorbents

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LIST OF NOTATIONS AND ABBREVIATIONS

q	Amount of adsorbate adsorbed at equilibrium time t (mg of adsorbate / gram of adsorbent)
q_e	Amount of adsorbate adsorbed at equilibrium time (mg of adsorbate / gram of adsorbent)
$q_{\max}$	Langmuir constant (adsorption capacity) (mg/g)
b	Langmuir constant (energy of adsorption) (L/mg)
R_L	Equilibrium parameter
k_f	Freundlich constant
n	Freundlich constant
C_{eq}	Adsorbate concentration in solution at equilibrium (mg/L)
k_{ad}	Lagergren adsorption rate constant (l/min)
LC_{50}	Lethal concentration for 50 percent mortality of the animal
BGH	Bengal gram husk
TDH	Tur dal husk
TH	Tamarind husk
CH	Coffee husk
AM	Amaranth
FG	Fast green
MB	Methylene blue
RB	Rhodamine B

1.0 Introduction

Freshwater ecosystems are aquatic systems which contain drinkable water or water of almost no salt content. Freshwater resources include lakes and ponds, rivers and streams, reservoirs, wetlands, and groundwater. . They provide the majority of our nation's drinking water resources, water resources for agriculture, industry, sanitation, as well as food including fish and shellfish. They also provide recreational opportunities and a means of transportation. In addition, freshwater ecosystems are home to numerous organisms (e.g., fish, amphibians, aquatic plants, and invertebrates). It has been estimated that 40% of all known fish species on Earth come from freshwater ecosystems

Human activities are causing species to disappear at an alarming rate. It has been estimated that between 1975 and 2015, species extinction will occur at a rate of 1 to 11 percent per decade. Aquatic species are at a higher risk of extinction than mammals and birds. Losses of this magnitude impact the entire ecosystem, depriving valuable resources used to provide food, medicines, and industrial materials to human beings. While freshwater and marine ecosystems face similar threats, there are some differences regarding the severity of each threat. Runoff from agricultural and urban areas, the invasion of exotic species, and the creation of dams and water diversion have been identified as the greatest challenges to freshwater environments (Allan and Flecker 1993; Scientific American 1997). Overfishing is the greatest threat to marine environments, thus the need for sustainable fisheries has been identified by the Environmental Defense Fund as the key priority in preserving marine biodiversity.

Other threats to aquatic biodiversity include urban development and resource-based industries, such as mining and forestry that destroy or reduce natural habitats. In addition, air and water pollution, sedimentation and erosion, and climate change also pose threats to aquatic biodiversity. Pollution has been very damaging to aquatic ecosystems, and may consist of agricultural, urban, and industrial wastes containing contaminants such as sewage, fertilizer, and heavy metals that have proven to be very damaging to aquatic habitats and species.

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

millenia. Metals are notable for their wide environmental dispersion from such activity; their tendency to accumulate in select 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 our 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 distribution of heavy metals in manufacturing industries is given in Table 1

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

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

Note: Ag - Silver,, As – Arsenic; Cd – Cadmium; Cr – Chromium; Cu –Copper; Fe – Iron, Hg – Mercury; Mn – Manganese; Ni – Nickel; Pb – Lead; Se – Selenium; Zn- Zinc.

Some metals, such as copper and iron, are essential to life and play irreplaceable roles in, for example, the functioning of critical enzyme systems. Other metals are

xenobiotics, i.e., they have no useful role in human physiology (and most other living organisms) and, even worse, as in the case of lead and mercury, may be toxic even at trace levels of exposure. Even those metals that are essential, however, have the potential to turn harmful at very high levels of exposure, a reflection of a very basic tenet of toxicology--“the dose makes the poison.”

1.1 Toxicological Aspects of Heavy metals

Due to their mobility in aquatic ecosystems and their toxicity to higher life forms, heavy metals in surface and groundwater supplies have been prioritised as major inorganic contaminants in the environment. Even if they are present in dilute, undetectable quantities, their recalcitrance and consequent persistence in water bodies imply that through natural processes such as biomagnification, concentrations may become elevated to such an extent that they begin exhibiting toxic characteristics. These metals can either be detected in their elemental state, which implies that they are not subject to further biodegradative processes or bound in various salt complexes. In either instance, metal ions cannot be mineralized. Apart from environmental issues, technological aspects of metal recovery from industrial waters must also be considered (Wyatt, 1988).

1.1.1 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. When concentrated in particular areas, however, they present a serious danger. 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. Next section presents the harmful effects to the four heavy metals that are prevalent in the environment.

- **Chromium:** Humans are exposed to chromium through breathing, eating or drinking and through skin contact with chromium or chromium compounds. The level of chromium in air and water is generally low. In drinking water the level of chromium is usually low as well, but contaminated well water may contain the dangerous chromium (VI); hexavalent chromium. For most people eating food that contains chromium (III), it is the main route of chromium uptake, as chromium (III) occurs naturally in many vegetables, fruits, meats, yeasts and

grains. Various ways of food preparation and storage may alter the chromium contents of food, as in the case of food stored in steel tanks or cans leading to enhanced chromium concentrations. Chromium (VI) is a danger to human health, mainly for people who work in the steel and textile industry. Chromium (VI) is known to cause various health effects. When it is a compound in leather products, it can cause allergic reactions, such as skin rash. Inhaling chromium (VI) can cause nose irritations and nosebleeds. Other health problems that are caused by chromium (VI) are skin rashes, respiratory problems, weakened immune systems, kidney and liver damage, alteration of genetic material, lung cancer and death. The health hazards associated with exposure to chromium are dependent on its oxidation state. The metal form (chromium as it exists in this product) is of low toxicity. The hexavalent form is toxic. Adverse effects of the hexavalent form on the skin may include ulcerations, dermatitis, and allergic skin reactions. Inhalation of hexavalent chromium compounds can result in ulceration and perforation of the mucous membranes of the nasal septum, irritation of the pharynx and larynx, asthmatic bronchitis, bronchospasms and edema. Respiratory symptoms may include coughing and wheezing, shortness of breath, and nasal itch. Carcinogenicity- Chromium and most trivalent chromium compounds have been listed by the National Toxicology Program (NTP) as having inadequate evidence for carcinogenicity in experimental animals. According to NTP, there is sufficient evidence for carcinogenicity in experimental animals for the following hexavalent chromium compounds; calcium chromate, chromium trioxide, lead chromate, strontium chromate, and zinc chromate.

- **Mercury:** Mercury is generally considered to be one of the most toxic metals found in the environment (Serpone *et al.*, 1988). Once mercury enters the food chain, progressively larger accumulation of mercury compounds takes place in humans and animals. The major sources of mercury pollution in environment are industries like chlor-alkali, paints, pulp and paper, oil refining, rubber processing and fertilizer (Namasivayam and Periasamy, 1993), batteries, thermometers, fluorescent light tubes and high intensity street lamps, pesticides, cosmetics and pharmaceuticals (Krishnan and Anirudhan, 2002). Methyl mercury causes deformities in the offspring, mainly affecting the nervous system (teratogenic effects). Children suffer from mental retardation, cerebral palsy and convulsions. Mercury also brings about genetic defects causing chromosome breaking and

interference in cell division, resulting in abnormal distribution of chromosome. Mercury causes impairment of pulmonary function and kidney, chest pain and dyspnoea (Beglund and Bertin, 2002; WHO, 1990). The harmful effect of methyl mercury on aquatic life and humans was amply brought out by the Minamata episode in Japan (WHO, 1991).

- **Nickel:** Electroplating is one important process involved in surface finishing and metal deposition for better life of articles and for decoration. Although several metals can be used for electroplating, nickel, copper, zinc and chromium are the most commonly used metals, the choice depending upon the specific requirement of the articles. During washing of the electroplating tanks, considerable amounts of the metal ions find their way into the effluent. Ni (II) is present in the effluents of silver refineries, electroplating, zinc base casting and storage battery industries (Sitting, 1976). 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 jewellery. 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 (Al-Asheh and Duvnjak 1997; Kadirvelu, 1998; Beliles 1979).
- **Iron:** Iron exists in two forms, soluble ferrous iron (Fe^{2+}) and insoluble ferric particulate iron (Fe^{3+}). The presence of iron in natural water may be attributed to the dissolution of rocks and minerals, acid mine drainage, landfill leachate sewage or engineering industries. Iron in water is generally present in the ferric state. The concentration of iron in well aerated water is seldom high but under reducing conditions, which may exist in some groundwater, lakes or reservoirs and in the absence of sulphate and carbonate, high concentrations of soluble ferrous iron may be found. The presence of iron at concentrations above 0.1mg/l will damage the gills of the fish. The free radicals are extremely reactive and short lived. The free radicals formed by the iron on the surface of the gills will cause oxidation of the surrounding tissue and this will lead to massive destruction of gill tissue and anaemia. The presence of iron in drinking water supplies is objectionable for a number of reasons. Under the pH condition existing in drinking water supply, ferrous sulphate is unstable and precipitates as insoluble ferric hydroxide, which settles out as a rust coloured silt. Such water often tastes unpalatable even at low concentration (0.3 mg/L) and stains laundry

and plumbing fixtures. Iron is an essential element in human nutrition. It is contained in a number of biologically significant proteins, but ingestion in large quantities results in haemochromatosis where in tissue damage results from iron accumulation.

1.1.2 Effects of heavy metals on aquatic organisms

Aquatic organisms are adversely affected by heavy metals in the environment. The toxicity is largely a function of the water chemistry and sediment composition in the surface water system.

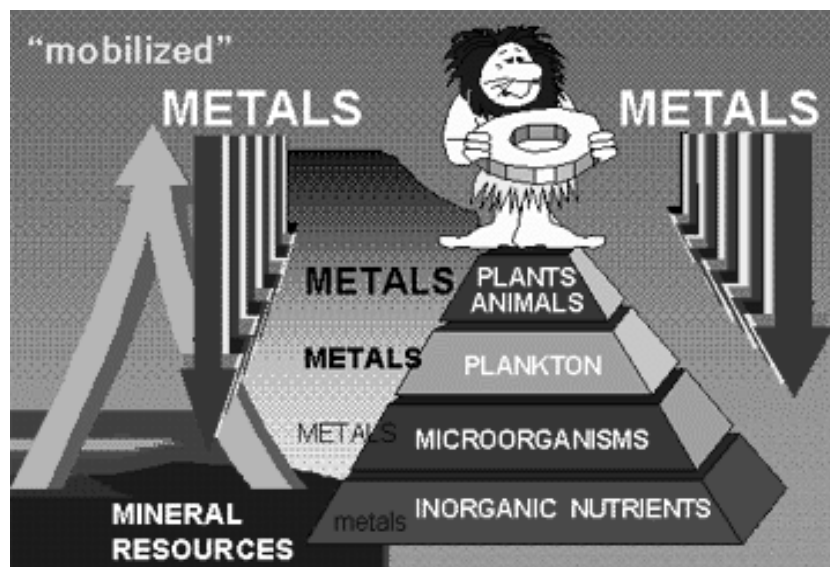


Figure 1: Biomagnification in natural systems

The above illustration (Figure 1) (Volesky, 2005) shows how metal ions can become bioaccumulated in an aquatic ecosystem. The metals are mineralised by microorganisms, which in turn are taken up by plankton and further by the aquatic organisms. Finally, the metals by now, several times biomagnified is taken up by man when he consumes fish from the contaminated water.

- i.) Slightly elevated metal levels in natural waters may cause the following sublethal effects in aquatic organisms: histological or morphological change in tissues;
- ii.) changes in physiology, such as suppression of growth and development, poor swimming performance, changes in circulation;
- iii.) change in biochemistry, such as enzyme activity and blood chemistry;

- iv.) change in behaviour; and
- v.) changes in reproduction (Connell *et al.*, 1984).

Many organisms are able to regulate the metal concentrations in their tissues. Fish and crustacea can excrete essential metals, such as copper, zinc, and iron that are present in excess. Some can also excrete non-essential metals, such as mercury and cadmium, although this is usually met with less success (Connell *et al.*, 1984). Research has shown that aquatic plants and bivalves are not able to successfully regulate metal uptake (Connell *et al.*, 1984). Thus, bivalves tend to suffer from metal accumulation in polluted environments. In estuarine systems, bivalves often serve as biomonitor organisms in areas of suspected pollution (Kennish, 1992). Shellfishing waters are closed if metal levels make shellfish unfit for human consumption.

In comparison to freshwater fish and invertebrates, aquatic plants are equally or less sensitive to cadmium, copper, lead, mercury, nickel, and zinc. Thus, the water resource should be managed for the protection of fish and invertebrates, in order to ensure aquatic plant survivability (USEPA, 1987). Metal uptake rates will vary according to the organism and the metal in question. Phytoplankton and zooplankton often assimilate available metals quickly because of their high surface area to volume ratio. The ability of fish and invertebrates to adsorb metals is largely dependent on the physical and chemical characteristics of the metal (Kennish, 1992). With the exception of mercury, little metal bioaccumulation has been observed in aquatic organisms (Kennish, 1992). Metals may enter the systems of aquatic organisms via three main pathways:

- i.) Free metal ions that are absorbed through respiratory surface (e.g., gills) are readily diffused into the blood stream.
- ii.) Free metal ions that are adsorbed onto body surfaces are passively diffused into the blood stream.
- iii.) Metals that are sorbed onto food and particulates may be ingested, as well as free ions ingested with water (Connell *et al.*, 1984). For eg: Chromium is not known to accumulate in the bodies of fish, but high concentrations of chromium, due to the disposal of metal products in surface waters, can damage the gills of fish that swim near the point of disposal.

1.1.3 Irrigation effects of heavy metals

Irrigation water contaminated with sewage or industrial effluents may transport dissolved heavy metals to agricultural fields. Although most heavy metals do not pose a threat to humans through crop consumption, cadmium may be incorporated into plant tissue. Accumulation usually occurs in plant roots, but may also occur throughout the plant (De Voogt *et al.*, 1980).

Most irrigation systems are designed to allow for up to 30 percent of the water applied to not be absorbed and to leave the field as return flow. Return flow either joins the groundwater or runs off the field surface (tailwater). Sometimes tailwater are rerouted into streams because of downstream water rights or a necessity to maintain streamflow. However, usually the tailwater is collected and stored until it can be reused or delivered to another field (USEPA 1993a).

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

1.2 Need for the removal of heavy metals

Continuous discharge of industrial, domestic and agricultural wastes in rivers and lakes causes deposit of pollutants in sediments. Such pollutants include heavy metals, which endanger public health after being incorporated in food chain. Heavy metals cannot be destroyed through biological degradation, as is the case with most organic pollutants. Incidence of heavy metal accumulation in fish, oysters, mussels, sediments and other components of aquatic ecosystems have been reported from all over the world (Naimo, 1995; Sayler *et al.*, 1975).

Excessive amounts of some heavy metals can be toxic through direct action of the metal or through their inorganic salts or via organic compounds from which the metal can become easily detached or introduced into the cell. Exposure to different metals may occur in common circumstances, particularly in industrial setting. Accidents in some environments can result in acute, high level exposure. Some of the heavy metals are toxic to aquatic organisms even at low concentration. The problem of heavy metal pollution in water and aquatic organisms including fish, needs continuous monitoring and surveillance as these elements do not degrade and tend to biomagnify in man through food chain. Hence there is a need to remove the heavy metals from the aquatic ecosystems.

Research and development, therefore focuses on sector-specific methods and technologies to remove colour and heavy metals from different kinds of waste streams. In view of the above toxicological effects of heavy metals on environment, animals and human beings, it becomes imperative to treat these toxic compounds in wastewater effluents before they are discharged into freshwater bodies.

1.3 Conventional methods for the treatment of metals

Over the last few decades, several methods have been devised for the treatment and removal of heavy metals. Numerous industries (e.g., electroplating, metal finishing operations, electronic –circuit production, steel and non-ferrous processes and fine-chemical and pharmaceutical production) discharge a variety of toxic metals into the environment. For several years now, it is mandatory that industry is required to remove metal pollutants from liquid discharges. The commonly used procedures for removing metal ions from aqueous streams include chemical precipitation, lime coagulation, ion exchange, reverse osmosis and solvent extraction (Rich and Cherry, 1987). The process description of each method is presented below.

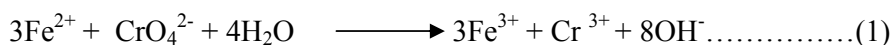
1.3.1 Chemical precipitation:

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

- **Hydroxide precipitation:** Chemical precipitation of heavy metals as their hydroxides using lime or sodium hydroxide is widely used. Lime is generally favoured for precipitation purposes due to the low cost of precipitant, ease of pH control in the range of 8.0 –10.0 and the excess of lime also serves as an adsorbent for the removal of metal ions. The efficiency of the process depends on a number of factors, which include the ease of hydrolysis of the metal ion, nature of the oxidation state, pH, presence of complex forming ions, standing time, degree of agitation and settling and filtering and characteristics of the precipitate. The limitations of this method include difference between metals in the optimum pH for hydroxide formation may lead to the problems in the treatment of effluents containing combined metal ions. Variability in metal hydroxide solubility at a fixed pH is another drawback.
- **Carbonate precipitation:** Carbonate precipitation of metals using calcium or sodium carbonate is very limited. Patterson *et al.*, 1997 reported improved results using carbonate precipitate for Cd (II) and Pb (II) from electroplating effluents. When the pH was brought to 7.5, residual concentration of Pb (II) and Cd (II) were 0.60 and 0.25 mg/L respectively.
- **Sulphide precipitation:** Since most of the heavy metals form stable sulphides, excellent metal removal can be obtained by sulphide precipitation. Treatment with sulphides is most advantageous when used as a polishing step after conventional hydroxide precipitation or when very high metal removals are required.

1.3.2 Chemical reduction

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



Another application of reduction process is the use of sodium borohydride, which has been considered effective for the removal of mercury, cadmium, lead, silver and gold (Kiff, 1987).

1.3.3 Xanthate process

Insoluble starch xanthate (ISX) is made from commercial cross linked starch by reacting it with sodium hydroxide and carbon disulphide. To give the product stability and to improve the sludge settling rate, magnesium sulphate is also added. ISX works like an ion exchanger, removing the heavy metals from the wastewater and replacing them with sodium and magnesium. Average capacity is 1.1-1.5 meq of metal ion per gram of ISX (Anon, 1978).

ISX is most commonly used by adding to it the wastewater as slurry for continuous flow operations or in the solid form for batch treatments. It should be added to the effluent at $\text{pH} \geq 3$. Then the pH should be allowed to rise above 7 for optimum metal removal (Wing, 1978). Residual metal ion level below 50 $\mu\text{g/L}$ has been reported (Hanway *et al.*, 1978, Wing *et al.*, 1978). The effectiveness of soluble starch xanthate (SSX) for removal of Cd (II), Cr (VI) and Cu (II) and insoluble starch xanthate (ISX) for Cr (VI) and Cu (II) have been evaluated under different aqueous phase conditions. Insoluble starch xanthate had better binding capacity for metals. The binding capacity of SSX and ISX respectively for different metal ions follows the sequence of Cr (VI) > Cu (II) > Cd(II) and Cr (VI) > Cu (II) (Tare *et al.*, 1988).

1.3.4 Solvent extraction

Liquid-liquid extraction (also frequently referred as solvent extraction) of metals from solutions on a large scale has experienced a phenomenal growth in recent years due to the introduction of selective complexing agents (Beszedits, 1988). In addition to hydrometallurgical applications, solvent extraction has gained widespread usage for waste reprocessing and effluent treatment.

Solvent extraction involves an organic and an aqueous phase. The aqueous solution containing the metal or metals of interest is mixed with the appropriate organic solvent and the metal passes into the organic phase. In order to recover the extracted metal, the organic solvent is contacted with an aqueous solution whose composition is such that the metal is stripped from the organic phase and is reextracted into the stripping solution. The concentration of the metal in the strip liquor may be increased, often 10 to 100 times over that of the original feed solution. Once the metal of

interest has been removed, the organic solvent is recycled either directly or after a fraction of it has been treated to remove the impurities.

1.3.5 Membrane process

Important examples of membrane process applicable to inorganic wastewater treatment include reverse osmosis and electrodialysis (EPA, 1980). These processes involve ionic concentration by the use of selective membrane with a specific driving force. For reverse osmosis, pressure difference is employed to initiate the transport of solvent across a semipermeable membrane and electro dialysis relies on ion migration through selective permeable membranes in response to a current applied to electrodes. The application of the membrane process described is limited due to pretreatment requirements, primarily, for the removal of suspended solids. The methods are expensive and sophisticated, requiring a higher level of technical expertise to operate.

A liquid membrane is a thin film that selectively permits the passage of a specific constituent from a mixture (Beszedits, 1988). Unlike solid membranes, however liquid membranes separate by chemistry rather than size, and thus in many ways liquid membrane technology is similar to solvent extraction. Since liquid membrane technology is a fairly recent development, a number of problems remain to be solved. A major issue with the use of supported membranes is the long term stability of the membranes, whereas the efficient breakup of microspheres for product recovery is one of the difficulties encountered frequently with emulsion membranes.

1.3.6 Evaporators

In the electroplating industry, evaporators are used chiefly to concentrate and recover valuable plating chemicals. Recovery is accomplished by boiling sufficient water from the collected rinse stream to allow the concentrate to be returned to the plating bath. Many of the evaporators in use also permit the recovery of the condensed steam for recycle as rinse water. Four types of evaporators are used throughout the electroplating industry (USEPA, 1979a) (i) Rising film evaporators; (ii) Flash evaporators using waste heat; (iii) submerged tube evaporators; (iv) Atmospheric evaporators. Both capital and operational costs for evaporative recovery systems are high. Chemical and water reuse values must offset these costs for evaporative recovery to become economically feasible.

1.3.7 Cementation

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

1.3.8 Ion exchange

Ion exchange resins are available selectively for certain metal ions. The cations are exchanged for H^+ or Na^+ . The cation exchange resins are mostly synthetic polymers containing an active ion group such as SO_3H . The natural materials such as zeolites can be used as ion exchange media (Van der Heen, 1977). The modified zeolites like zeocarb and chalcab have greater affinity for metals like Ni and Pb (Groffman *et al.*, 1992). The limitations on the use of ion exchange for inorganic effluent treatment are primarily high cost and the requirements for appropriate pretreatment systems. Ion exchange is capable of providing metal ion concentrations to parts per million levels. However, in the presence of large quantities of competing mono-and divalent ions such as Na and Ca, ion exchange is almost totally ineffective.

1.3.9 Electrodeposition

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

1.3.10 Adsorption

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

- (i) The direct adsorption of Cr^{6+} onto carbon surface.
- (ii) The reduction of Cr^{6+} species to Cr^{3+} by carbon on the surface.
- (iii) The adsorption of the Cr^{3+} species produced, which occurs to a much lesser extent than the adsorption of the Cr^{6+} species.

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

1.4 Disadvantages of conventional methods for treatment of wastewater containing heavy metals

Metals are a class of pollutants, often toxic and dangerous, widely present in industrial and household wastewaters. Electroplating and metal finishing operations, electronic circuit production, steel and aluminum processes to name but a few industries, produce large quantities of wastewater containing metals. Although metal precipitation using a cheap alkali such as lime (calcium hydroxide) has been the most favoured option, other separation technologies are now beginning to find favour. Precipitation, by adjusting the pH value is not selective and any iron (ferric ion) present in the liquid effluent will be precipitated initially followed by other metals. Consequently precipitation produces large quantities of solid sludge for disposal, for example precipitation as hydroxides of 100 mg/l of copper (II), cadmium (II) or

mercury (II) produces as much as 10-, 9- and 5 fold mg/l of sludges respectively. The metal hydroxide sludge resulting from treatment of electroplating wastewater has been classified as a hazardous waste. The performance characteristics of heavy metal waste water treatment technologies are identified in Table 2. The versatility, simplicity and other technology characteristics will contribute to the overall process costs, both capital and operational. At present many of these technologies such as ion exchange represent significant capital investments by industry.

Table 2 Performance characteristics of various heavy metal removal /recovery technologies

Technology	pH change	Metal selectivity	Influence of Suspended solids	Tolerance of organic molecules	Working level for appropriate metal (mg/l)
Adsorption, e.g. Granulated Activated carbon	Limited tolerance	Moderate	Fouled	Can be poisoned	<10
Electro chemical	Tolerant	Moderate	Can be engineered to tolerate	Can be accommodated	>10
Ion exchange	Limited tolerance	Chelate resins can be selective	- Fouled	Can be poisoned	<100
Membrane	Limited tolerance	Moderate	Fouled	Intolerant	>10
Precipitation (a) Hydroxide	Tolerant	Non-selective	Tolerant	Tolerant	>10
(b) Sulphide	Limited tolerance	Limited selective pH dependent	Tolerant	Tolerant	>10
Solvent extraction	Some systems pH tolerant	Metal selective extractants available	Fouled	Intolerant	>100

As seen from the table above, conventional methods are ineffective in the removal of low concentrations of heavy metals and they are non-selective. Moreover, it is not possible to recover the heavy metals by the above mentioned methods.

1.5 Biosorption

During the 1970's increasing environmental awareness and concern led to a search for new techniques capable of inexpensive treatment of polluted wastewaters with metals. The search for new technologies involving the removal of toxic metals from wastewaters has directed attention to biosorption, based on binding capacities of various biological materials.

Till date, research in the area of biosorption suggests it to be an ideal alternative for decontamination of metal containing effluents. Biosorbents are attractive since naturally occurring biomass/adsorbents or spent biomass can be effectively used. Biosorption is a rapid phenomenon of passive metal sequestration by the non-growing biomass/adsorbents. Results are convincing and binding capacities of certain biomass/adsorbents are comparable with the commercial synthetic cation exchange resins.

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

There are many types of adsorbents; Earth's forests and plants, ocean and freshwater plankton, algae and fish, all living creatures, that including animals are all "biomass/adsorbents". The renewable character of biomass that grows, fuelled directly or indirectly by sunshine, makes it an inexhaustible pool of chemicals of all kinds.

Biosorption has advantages compared with conventional techniques (Volesky, 1999). Some of these are listed below:

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

Biosorbents intended for bioremediation environmental applications are waste biomass of crops, algae, fungi, bacteria, etc., which are the naturally abundant. Numerous chemical groups have been suggested to contribute to biosorption. A review of biosorption of heavy metals by microorganisms is presented below. Biosorption by microorganisms have various disadvantages, and hence many low cost adsorbents (industrial/agricultural waste products/byproducts) are increasingly used as biosorbents. This chapter also provides review of the low cost adsorbents used for removal of heavy metals (Ahalya *et al.*, 2004)

1.5.1 Biosorption of heavy metals by microorganisms

A large number of microorganisms belonging to various groups, viz. bacteria, fungi, yeasts, cyanobacteria and algae have been reported to bind a variety of heavy metals to different extents. The role of various microorganisms by biosorption in the removal and recovery of heavy metal(s) has been well reviewed and documented (Stratton, 1987; Gadd and Griffiths, 1978; Volesky, 1990; Wase and Foster, 1997; Greene and Darnall, 1990; Gadd 1988). Most of the biosorption studies reported in literatures

have been carried out with living microorganisms. However due to certain inherent disadvantages, use of living microorganisms for metal removal and recovery is not generally feasible in all situations. For example, industrial effluents contain high concentrations of toxic metals under widely varying pH conditions. These conditions are not always conducive to the growth and maintenance of an active microbial population. There are several advantages of biosorption of using non living biomass and they are as follows:

- Growth independent nonliving biomass is not subject to toxicity limitation by cells.
- The biomass from an existing fermentation industry, which essentially is a waste after fermentation, can be a cheap source of biomass.
- The process is not governed by physiological constraints of microbial cells.
- Because nonliving biomass behaves as an ion exchanger, the process is very rapid, requiring anywhere between few minutes to few hours. Metal loading is very high on the surface of the biomass leading to very efficient metal uptake.
- Because cells are non-living processing conditions are not restricted to those conducive for the growth of the cells. Hence, a wider range of operating conditions such as pH, temperature and metal concentrations are possible. Also aseptic operating conditions are not essential.
- Metals can be desorbed readily and then recovered. If the value and the amount of metal recovered are insignificant and if the biomass is plentiful, the metal loaded biomass can be incinerated, eliminating further treatment.

Biosorption essentially involves adsorption processes such as ionic, chemical and physical adsorption. A variety of ligands located on the fungal cell walls are known to be involved in metal chelation. These include carboxyl, amine, hydroxyl, phosphate and sulphydryl groups. Metal ions could be adsorbed by complexing with negatively charged reactions sites on the cell surface. Table 3 presents an exhaustive list of microorganisms used for the uptake of heavy metals.

Table 3 Biosorbent uptake of metals by Microbial Biomass

Metal	Biomass Type	Biomass class	Metal uptake (mg/g)	Reference
Ag	Freshwater alga	Biosorbent	86-94	Brierley and Vance, 1988; Brierley <i>et al.</i> , 1986
	Fungal biomass	Biosorbent	65	Brierley <i>et al.</i> , 1986
	<i>Rhizopus arrhizus</i>	Fungus	54	Tobin <i>et al.</i> , 1984
	<i>Streptomyces noursei</i>	Filamentous bacter	38.4	Mattuschka <i>et al.</i> , 1993
	<i>Sacchromyces cerevisiae</i>	Yeast	4.7	Brady and Duncan, 1993
Au	<i>Sargassum natans</i>	Brown alga	400	Volesky and Kuyucak, 1988
	<i>Aspergillus niger</i>	Fungus	176	Kuyuack and Volesky, 1988
			15	Gee and Dudeney, 1988
	<i>Rhizopus arrhizus</i>	Fungus	164	Kuyuack and Volesky, 1988
	<i>Palmaria tevera</i>	Marine alga	164	Kuyuack and Volesky, 1988
	<i>Palmaria palmata</i>	Marine alga	124	Kuyuack and Volesky, 1988
	<i>Chlorella pyrenoidosa</i>	Freshwater alga	98	Darnall <i>et al.</i> , 1988
	<i>Cyanidium caldarium</i>	Alga	84	Darnall <i>et al.</i> , 1988
	<i>Chlorella vulgaris</i>	Freshwater alga	80	Gee and Dudeney, 1988
	<i>Bacillus subtilis</i>	Bacteria Cell wall	79	Beveridge, 1986
	<i>Chondrus crispus</i>	Marine alga	76	Kuyuack and Volesky, 1988
	<i>Bacillus subtilis</i>	Bacterium	70	Gee and Dudeney, 1988
	<i>Spirulina platensis</i>	Freshwater alga	71	Darnall <i>et al.</i> , 1988
			58	Gee and Dudeney, 1988
	<i>Rhodomenia palmata</i>	Marine alga	40	Darnall <i>et al.</i> , 1988
	<i>Ascophyllum nodosum</i>	Brown marine alga	24	Kuyuack and Volesky, 1988
Cd	<i>Ascophyllum nodosum</i>	Brown markertman ine alga	215	Holan <i>et al.</i> , 1993
	<i>Sargassum natans</i>	Brown marine alga	135	Holan <i>et al.</i> , 1993
	<i>Fucus vesiculosus</i>	Brown marine	73	Holan <i>et al.</i> , 1993

		alga		
	<i>Candida tropicalis</i>	Yeast	60	Mattuschka <i>et al.</i> , 1993
	<i>Pencillium chrysogenum</i>	Fungus	56	Holan and Volesky, 1995
			11	Niu <i>et al.</i> , 1993
	<i>Rhizopus arrhizus</i>	Fungus	30	Tobin <i>et al.</i> , 1984
	<i>Sacchromyces cerevisiae</i>	Yeast	20-40	Volesky <i>et al.</i> , 1993
	<i>Rhizopus arrhizus</i>	Fungus	27	Fourest and Roux, 1992
	<i>Rhizopus nigricans</i>	Fungus	19	Holan and Volesky, 1995
	<i>Pencillium spinulosum</i>	Fungus	0.4	Townsley <i>et al.</i> , 1996
	<i>Pantoea sp. TEM 18</i>	Bacteria	204.1	Guyen Ozdemir <i>et al.</i> , 2004
	<i>Chlamydomonas reinhardtii</i>	Alga	42.6	Tuzun <i>et al.</i> , 2005
	<i>Spirulina sp.</i>	Blue green algae	1.77 meq/g	Chojnacka <i>et al.</i> , 2005
	<i>Enterobacter cloaceae</i> (Exopolysaccharide)	Marine bacterium	16	Anita Iyer <i>et al.</i> , 2005
	<i>Padina sp.</i>	Brown seaweed	0.75	Sheng <i>et al.</i> , 2004
	<i>Sargassum sp.</i>	Brown seaweed	0.76	Sheng <i>et al.</i> , 2004
	<i>Ulva sp.</i>	Green seaweed	0.58	Sheng <i>et al.</i> , 2004
	<i>Gracillaria sp.</i>	Red seaweed	0.30	Sheng <i>et al.</i> , 2004
	<i>Gloeotheca magna</i>	Cyanobacteria	115–425 $\mu\text{g mg}^{-1}$	Zakaria A. Mohamed, 2001
Co	<i>Ascophyllum nodosum</i>	Brown marine algae	100	Kuyucak and Volesky, 1989a
	<i>Sacchromyces cerevisiae</i>	Yeast	4.7	Brady and Duncan, 1993
	<i>Ulva reticulata</i>	Marine green algae	46.1	Vijayaraghavan <i>et al.</i> , 2005
	<i>Enterobacter cloaceae</i>	Marine bacterium	4.38	Anita Iyer <i>et al.</i> , 2005
Cr	Bacillus biomass	Bacterium	118 Cr^{3+} 60 Cr^{6+}	Brierley and Brierley, 1993
	<i>Rhizopus arrhizus</i>	Fungus	31	Tobin <i>et al.</i> , 1984
	<i>Candida</i>	Yeast	4.6	Mattuschka <i>et al.</i> , 1993

Cu	<i>tropicalis</i>			
	<i>Streptomyces noursei</i>	Bacteria	1.8	Mattuschka <i>et al.</i> , 1993
	<i>Pantoea sp. TEM 18</i>	Bacteria	204.1	Guven Ozdemir <i>et al.</i> , 2004
	<i>Spirulina sp.</i>	Cyanobacteria	10.7 meq/g	Chojnacka <i>et al.</i> , 2005
	<i>Spirogyra sp.</i>	Filamentous algae	4.7	Gupta <i>et al.</i> , 2001
	<i>Bacillus subtilis</i>	Biosorbent	152	Beveridge, 1986; Brierley <i>et al.</i> , 1986; Brierley and Brierley, 1993
	<i>Candida tropicalis</i>	Yeast	80	Mattuschka <i>et al.</i> , 1993
	<i>Manganese oxidising bacteria</i>	MK-2	50	Stuetz <i>et al.</i> , 1993
	<i>Cladosporium resinae</i>	Fungus	18	Gadd <i>et al.</i> , 1988
	<i>Rhizopus arrhizus</i>	Fungus	16	Gadd <i>et al.</i> , 1988
	<i>Saccharomyces crevisae</i>	Yeast	17-40; 6.3	10; Volesky and May-Phillips, 1995; Mattuschka <i>et al.</i> , 1993; Brady and Duncan, 1993
	<i>Pichia guilliermondii</i>	Yeast	11	Mattuschka <i>et al.</i> , 1993
	<i>Scenedesmus obliquus</i>	Freshwater algae	10	Mattuschka <i>et al.</i> , 1993
	<i>Rhizopus arrhizus</i>	Fungus	10	Gadd <i>et al.</i> , 1988
	<i>Pencillium chrysogenum</i>	Fungus	9	Niu <i>et al.</i> , 1993
	<i>Streptomyces noursei sp.</i>	Filamentous bacteria	5	Mattuschka <i>et al.</i> , 1993
	<i>Bacillus sp</i>	Bacterium	5	Cotoras <i>et al.</i> , 1993
	<i>Pencillium spinulosum</i>	Fungus	0.4-2	Townsley <i>et al.</i> , 1986
	<i>Aspergillus niger</i>	Fungus	1.7	Townsley <i>et al.</i> , 1986
	<i>Trichoderma viride</i>	Fungus	1.2	Townsley <i>et al.</i> , 1986
	<i>Pencillium chrysogenum</i>	Fungus	0.75	Paknikar <i>et al.</i> , 1993
	<i>Pantoea sp. TEM 18</i>	Bacteria	31.3	Guven Ozdemir <i>et al.</i> , 2004.
	<i>Ulva reticulata</i>	Marine green alga	56.3	Vijayaraghavan <i>et al.</i> , 2005
	<i>Spirulina sp.</i>	Blue green algae	6.17 meq/g	Chojnacka <i>et al.</i> , 2005

	<i>Enterobacter cloaceae</i> (Exopolysaccharide)	Marine bacterium	6.60	Anita Iyer <i>et al.</i> , 2005
	<i>Padina sp.</i>	Brown seaweed	1.14	Sheng <i>et al.</i> , 2004
	<i>Sargassum sp.</i>	Brown seaweed	0.99	Sheng <i>et al.</i> , 2004
	<i>Ulva sp.</i>	Green seaweed	0.75	Sheng <i>et al.</i> , 2004
	<i>Gracillaria sp.</i>	Red seaweed	0.59	Sheng <i>et al.</i> , 2004
	<i>Thiobacillus thiooxidans</i>	Bacteria	38.54	Liu <i>et al.</i> , 2004
	<i>Ulothrix zonata</i>	Algae	176.20	Nuhoglu <i>et al.</i> , 2002
Fe	<i>Bacillus subtilis</i>	Bacterial cell wall preparation	201	Beveridge, 1986
	<i>Bacillus biomass</i>	Bacterium	107	Brierley and Brierley, 1993
	<i>Sargassum fluitans</i>	Brown alga	60	Figueira <i>et al.</i> , 1995
Hg	<i>Rhizopus arrhizus</i>	Fungus	54	Tobin <i>et al.</i> , 1984
	<i>Pencillium chrysogenum</i> (biomass not necessarily in its natural state)	Fungus	20	Nemec <i>et al.</i> , 1977
	<i>Cystoseira baccata</i>	Marine alga	178	Herrero <i>et al.</i> , 2005
	<i>Chlamydomonas reinhardtii</i>	Algae	72.2	Tuzun <i>et al.</i> , 2005
Ni	<i>Fucus vesiculosus</i>	Brown marine algae	40	Holan and Volesky, 1994
	<i>Ascophylum nodosum</i>	Brown marine algae	30	Holan and Volesky, 1994
	<i>Sargassum natans</i>	Brown marine algae	24-44	Holan and Volesky, 1994
	<i>Bacillus licheniformis</i>	Bacterial cell wall preparation	29	Beveridge, 1986
	<i>Candida tropicalis</i>	Yeast	20	Mattuschka <i>et al.</i> , 1993
	<i>Rhizopus arrhizus</i>	Fungus	18	Fourest and Roux, 1992
	<i>Bacillus subtilis</i>	Bacterial cell wall	6	Beveridge, 1986

Pb	<i>Rhizopus nigricans</i>	preparation Fungus	5	Holan and Volesky, 1995
	<i>Absidia orchidis</i>	Fungus	5	Kuycak and Volesky, 1988
	<i>Ulva reticulata</i>	Marine green algae	46.5	Vijayaraghavan <i>et al.</i> , 2005
	<i>Padina sp.</i>	Brown seaweed	0.63	Sheng <i>et al.</i> , 2004
	<i>Sargassum sp.</i>	Brown seaweed	0.61	Sheng <i>et al.</i> , 2004
	<i>Ulva sp.</i>	Green seaweed	0.29	Sheng <i>et al.</i> , 2004
	<i>Gracillaria sp.</i>	Red seaweed	0.28	Sheng <i>et al.</i> , 2004
	<i>Polyporous versicolor</i>	White rot fungus	57	Dilek <i>et al.</i> , 2002
	<i>Bacillus subtilis</i> (biomass not necessarily in its natural state)	Biosorbent	601	Brierley <i>et al.</i> , 1986
	<i>Absidia orchidis</i>	Fungus	351	Holan and Volesky, 1995
	<i>Fucus vesiculosus</i>	Brown marine algae	220-370	Holan and Volesky, 1994
	<i>Ascophyllum nodosum</i>	Brown marine algae	270-360	Holan and Volesky, 1994
	<i>Sargassum natans</i>	Brown marine algae	220-270	Holan and Volesky, 1994
	<i>Bacillis subtilis</i> (biomass not necessarily in its natural state)	Biosorbent	189	Brierley and Brierley, 1993
	<i>Pencillium chrysogenum</i>	Fungus	122; 93	Niu <i>et al.</i> , 1993; Holan and Volesky, 1995
	<i>Rhizopus nigricans</i>	Fungus	166	Holan and Volesky, 1995
	<i>Streptomyces longwoodensis</i>	Filamentous bacteria	100	Friis and Myers-Keith, 1986
	<i>Rhizopus arrhizus</i>	Fungus	91; 55	Tobin <i>et al.</i> , 1984; Fourest and Roux, 1992, Holan and Voleky, 1995.
	<i>Streptomyces noursei</i>	Filamentous bacteria	55	Mattuschka <i>et al.</i> , 1993
	<i>Chlamydomonas reinhardtii</i>	Algae	96.3	Tuzun, <i>et al.</i> , 2005
	<i>Padina sp.</i>	Brown seaweed	1.25	Sheng <i>et al.</i> , 2004
	<i>Sargassum sp.</i>	Brown	1.26	Sheng <i>et al.</i> , 2004

		seaweed		
	<i>Ulva sp.</i>	Green seaweed	1.46	Sheng <i>et al.</i> , 2004
	<i>Gracillaria sp.</i>	Red seaweed	0.45	Sheng <i>et al.</i> , 2004
	<i>Ecklonia radiata</i>	Marine alga	282	Matheickal and Yu, 1996
Pd	Freshwater alga(biomass not necessarily in its natural state)	Biosorbent	436	Brierley and Vance, 1988.
	Fungal biomass	Biosorbent	65	Brierley <i>et al.</i> , 1988
Pt	Freshwater alga (biomass not necessarily in its natural state)	Biosorbent	53	Brierley and Vance, 1988; Brierley <i>et al.</i> , 1988
U	<i>Sargassum fluitans</i>	Brown algae	520	Yang and Volesky 1999; Yang and Volesky, 1999
	<i>Streptomyces longwoodensis</i>	Filamentous bacteria	440	Friis and Myers-Keith, 1986
	<i>Rhizopus arrhizus</i>	Fungus	220; 195	Volesky and Tsezos, 1981; Tobin <i>et al.</i> , 1984
	<i>Sacchromyces crevisae</i>	Yeast	55-140	Volesky and May Phillips, 1995
	<i>Bacillus sp.</i>	Bacterium	38	Cotoras <i>et al.</i> , 1993
	<i>Chaetomium distortum</i>	Fungus	27	Khalid <i>et al.</i> , 1993.
	<i>Trichoderma harzianum</i>	Fungus	26	Khalid <i>et al.</i> , 1993.
	<i>Pencillium chrysogenum</i> (biomass not necessarily in its natural state)	Fungus	25	Nemec <i>et al.</i> , 1977
	<i>Alternaria tenuilis</i>			Khalid <i>et al.</i> , 1993.
Th	<i>Rhizopus arrhizus</i>	Fungus	160; 93	Tsezos and Volesky, 1981; Gadd <i>et al.</i> , 1988
	<i>Sacchromyces cerevisae</i>	Yeast	70	Gadd <i>et al.</i> , 1988
Zn	<i>Bacillus subtilis</i> (biomass not necessarily in its natural state)	Biosorbent	137	Brierley <i>et al.</i> , 1986
	<i>Sargassa sp.</i>	Brown algae	70	Davis <i>et al.</i> , 2003; Davis <i>et al.</i> , 2000; Figueira <i>et al.</i> , 1995; Figueira <i>et al.</i> , 1997; Figueira <i>et al.</i> , 2000; Figueira <i>et al.</i> , 1999;

			Schiewer <i>et al.</i> , 1995; Scheiwer and Volesky, 1996; Scheiwer and Volesky 1997; Scheiwer and Wong, 1999. Stuetz <i>et al.</i> , 1993
Manganese oxidising bacteria	(MK-2)	39	
<i>Sacchromyces cerevisae</i>	Yeast	14-40	Volesky and May-Phillips, 1995
<i>Candida tropicalis</i>	Yeast	30	Mattuschka <i>et al.</i> , 1993
<i>Rhizopus arrhizus</i>	Fungus	20; 14	Tobin <i>et al.</i> , 1984; Gadd <i>et al.</i> , 1988
<i>Pencillium chrysogenum</i>	Fungus	6.5	Niu <i>et al.</i> , 1993; Paknikar <i>et al.</i> , 1993
<i>Bacillus sp.</i>	Bacterium	3.4	Cotoras <i>et al.</i> , 1993
<i>Pencillium spinulosum</i>	Fungus	0.2	Townsley <i>et al.</i> , 1986
Padina sp.	Brown seaweed	0.81	Sheng <i>et al.</i> , 2004
<i>Sargassum sp.</i>	Brown seaweed	0.50	Sheng <i>et al.</i> , 2004
<i>Ulva sp.</i>	Green seaweed	0.54	Sheng <i>et al.</i> , 2004
<i>Gracillaria sp.</i>	Red seaweed	0.40	Sheng <i>et al.</i> , 2004
<i>Thiobacillus thiooxidans</i>	Bacteria	43.29	Liu <i>et al.</i> , 2004

Among micro-organisms, fungal biomass offers the advantages of having high percentage of cell wall material, which shows excellent metal binding properties (Gadd, 1990; Rosenberger, 1975; Paknikar, Palnitkar and Puranik, 1993). Many fungi and yeast have shown an excellent potential of metal biosorption, particularly the genera *Rhizopus*, *Aspergillus*, *Streptoverticillum* and *Sacchromyces* (Volesky and Tsezos, 1981; Galun *et al.*, 1984; de Rome and Gadd, 1987; Siegel *et al.*, 1986; Luef *et al.*, 1991, Brady and Duncan, 1993 Puranik and Paknikar, 1997).

2.0 Low cost adsorbents for metal removal

The disadvantages of using microorganisms can be overcome by using low cost adsorbents. In general, a sorbent can be assumed to be “low cost” if it requires little processing and is abundant in nature, or is a by product or waste material from another industry, which has lost its economic or further processing values. There have

been several low cost adsorbents that have been used for the removal of heavy metal. The following Section presents a detailed discussion on the low cost adsorbents that have been used for the removal of heavy metals.

Cost is an important parameter for comparing the sorbent materials. However, cost information is seldom reported, and the expense of individual sorbents varies depending on the degree of processing required and local availability. Research pertaining to low cost adsorbents is gaining importance these days though most of the work is at laboratory levels. Some of the low-cost sorbents reported so far include: Bark/tannin-rich materials; lignin; chitin/chitosan; seaweed/algae/alginate; xanthate; zeolite; clay; flyash; peat moss; modified wool and modified cotton; tea waste; maize cobs etc., efficacy of which are discussed next

2.1 Bark and other tannin – rich materials

Timber industry generates bark a by-product that is effective because of its high tannin content. The polyhydroxy polyphenol groups of tannin are thought the active species in the adsorption process. Ion exchange takes place as metal cations displace adjacent phenolic hydroxyl groups, forming a chelate (Randall *et al.*, 1974a; Vasquez *et al.*, 1994).

Another waste product from the timber industry is sawdust. Bryant *et al.* (1992) showed adsorption of Cu and hexavalent chromium (Cr (VI)) by red fir sawdust to take place primarily on components such as lignin and tannin rather onto cellulose backbone of the sawdust (Table 4). While bark is the most likely choice due to its wide availability, other low cost byproducts containing tannin show promise for economic metal sorption as well.

Table 4 Reported adsorption capacities (mg/g) for tannin containing materials

Material	Source	Cd	Cr (III)	Cr (VI)	Hg	Pb
Activated carbon	Teles de Vasconcelos and Gonzàlez Beça, 1994					2.95
Black oak bark	Masri <i>et al.</i> , 1974	25.9			400	153.3
Douglas fir bark	Masri <i>et al.</i> , 1974				100	
Exhausted coffee	Orhan and Büyükgüngör, 1993	1.48		1.42		
Formaldehyde – polymerised	Randall <i>et al.</i> , 1978	74				205
peanut skins						
Hardwickia binata bark	Deshkar <i>et al.</i> , 1990	34				
Nut shell	Orhan and Büyükgüngör, 1993	1.3		1.47		
Pinus pinaster bark	Teles de Vasconcelos and Gonzàlez Beça, 1993, 1994 and Vázquez <i>et al.</i> , 1994	8.00	19.45		3.33, 1.59	
Redwood bark	Masri <i>et al</i> 1974, Randall <i>et al</i> 1974a, b	27.6, 32			250	6.8, 182
Sawdust	Bryant <i>et al.</i> , 1992; Dikshit, 1989; Zarraa, 1995			10.1, 16.05, 4.44		

Turkish coffee	Orhan and Buyukgungor, 1993	1.17	1.63
Treated Pinus sylvestris bark	Alves <i>et al.</i> , 1993	9.77	
Untreated Pinus sylvestris bark	Alves <i>et al.</i> , 1993	8.69	
Walnut shell	Orhan and Buyukgungor, 1993	1.5	1.33
Waste tea	Orhan and Buyukgungor, 1993	1.63	1.55

2.2 Chitosan

Among various biosorbents, chitin is the second most abundant natural biopolymers after cellulose. However, more important than chitin is chitosan, which has a molecular structure similar to cellulose. Presently, chitosan is attracting an increasing amount of research interest, as it is an effective scavenger for heavy metals. Chitosan is produced by alkaline N-deacetylation of chitin, which is widely found in the exoskeleton of shellfish and crustaceans. It was estimated that chitosan could be produced from fish and crustaceans (Rorrer and Way 2002). The growing need for new sources of low-cost adsorbent, the increased problems of waste disposal, the increasing cost of synthetic resins undoubtedly make chitosan one of the most attractive materials for wastewater treatment.

Various researches on chitosan have been done in recent years and it can be concluded that chitosan is a good adsorbent for all heavy metals (Table 5). It is widely known that the excellent adsorption behaviour of chitosan for heavy metal removal is attributed to: (1) high hydrophilicity of chitosan due to large number of hydroxyl groups, (2) large number of primary amino groups with high activity, and (3) flexible structure of polymer chain of chitosan making suitable configuration for adsorption of metal ions.

Table 5 Reported adsorption capacities (m/g) for chitosan

Material	Source	Cd	Cr (III)	Cr (VI)	Hg	Cu	Pb
Chitin	Masri <i>et al.</i> , 1974				100		
Chitosan	Jha <i>et al.</i> , 1988; Masri <i>et al.</i> , 1974, McKay <i>et al.</i> , 1989; Udhaybhaskar <i>et al.</i> , 1990	6.4, 558.92	27.3		1123, 815		796
Chitosan (from lobster shell)	Peniche- Covas <i>et al.</i> , 1992				430		
Chitosan powder	Rorrer <i>et al.</i> , 1993	420					
Chitosan beads	Rorrer <i>et al.</i> , 1993	518					
N-acylated chitosan beads	Hsien and Rorrer, 1995	216					
N-acylated cross linked chitosan beads	Hsien and Rorrer, 1995	136					
Thiol-grafted chitosan gel	Merrifield, <i>et al.</i> , 2004				8.0 mmol/g		
Aminated chitosan	Jeon and. Höll, 2003				2.23 mmol/g		
Chitosan derived from prawn shells	Chu, 2002						0.266 mmol/g
Chitosan	Wan Ngah <i>et al.</i> , 2002					80.71	
Chitosan beads cross- linked with	Wan Ngah <i>et al.</i> , 2002					59.67	

glutaraldehyde		
Chitosan beads cross-linked with epichlorohydrin	Wan Ngah <i>et al.</i> , 2002	62.47
Chitosan beads cross-linked with thylene glycol diglycidyl ether	Wan Ngah <i>et al.</i> , 2002	45.62

2.3 Zeolites

Basically zeolites are a naturally occurring crystalline aluminosilicates consisting of a framework of tetrahedral molecules, linked with each other by shared oxygen atoms. During 1970s, natural zeolites gained a significant interest, due to their ion-exchange capability to preferentially remove unwanted heavy metals such as strontium and cesium [Grant *et al.*, 1987]. This unique property makes zeolites favorable for wastewater treatment (Table 6). The price of zeolites depending on the quality is considered very cheap and is about US\$ 0.03–0.12/kg, [Virta, 2001].

Table 6 Reported adsorption capacities (mg/g) for zeolite

Material	Source	Cd	Cr (III)	Cr (VI)	Hg	Pb	Zn	Cu
CETYL-amended zeolite	Santiago <i>et al.</i> , 1992			0.65				
EHDDMA-amended zeolite	Santiago <i>et al.</i> , 1992			0.42				
Zeolite	Leppert, 1990	84.3	26.0		150.4	155.4		
Clinoptilolite zeolites	Erdem <i>et al.</i> , 2004						133.85	1
							41.12	

2.4 Clay

It is widely known that there are three basic species of clay: smectites (such as montmorillonite), kaolinite, and micas; out of which montmorillonite has the highest cation exchange capacity and its current market price is considered to be 20 times cheaper than that of activated carbon [Virta, 2002]. Therefore, a number of studies

have been conducted using clays, mainly montmorillonite, to show their effectiveness for removing metal ions such as Zn^{2+} , Pb^{2+} , and Al^{3+} from aqueous solutions (Brigatti *et al.*, 1996; Staunton and M. Roubaud, 1997 and Turner *et al.*, 1998) (Table 7). Although the removal efficiency of clays for heavy metals may not be as good as that of zeolites, their easy availability and low cost may compensate for the associated drawbacks.

Fly ash, an industrial solid waste of thermal power plants located in India, is one of the cheapest adsorbents having excellent removal capabilities for heavy metals such as copper ions (Panday *et al.*, 1985). It was reported that an adsorption capacity of 1.39 mg of Cu^{2+} /g was achieved by fly ash at a pH of 8.0. It is also known from various studies that fly ash could be easily solidified after the heavy metals are adsorbed. However, since it also contains heavy metals, the possibility of leaching could be considered and evaluated.

Table 7 Reported adsorption capacities (mg/g) for clays

Material	Source	Cd	Cr (VI)	Pb	Cu^{2+}	Hg^{2+}	Zn
Bentonite	Khan <i>et al.</i> , 1995; Cadena <i>et al.</i> , 1990; Kaya and Ören, 2005	0.512, 55	6				0.921
Na rich bentonite	Kaya and Ören, 2005						8.271
Tailored bentonite	Cadena <i>et al.</i> , 1990		57, 58				
Acid treated bentonite	Pradas <i>et al.</i> , 1994	4.11					
Heat treated bentonite	Pradas <i>et al.</i> , 1994	16.50					
China clay	Yadava <i>et al.</i> , 1991			0.289			
Wollastonite	Yadava <i>et al.</i> , 1991			0.217			
Wollastonite-fly ash mixture	Panday <i>et al.</i> , 1984a		2.92		1.18		
Fly ash	Panday <i>et al.</i> , 1985; Sen and Arnab				1.39		
Fly ash-China clay	Panday <i>et al.</i> , 1984a	0.31					
Palygorskite clay	Potgieter, <i>et al.</i> , 2005	58.5		62.1	30.7		
Fly ash	Cho <i>et al.</i> , 2005	5.0		10.0	2.8		3.2

2.5 Peat moss

Peat moss, a complex soil material containing lignin and cellulose as major constituents, is a natural substance widely available and abundant, not only in Europe (British and Ireland), but also in the US. Peat moss has a large surface area (>200

m²/g) and is highly porous so that it can be used to bind heavy metals. Peat moss is a relatively inexpensive material and commercially sold at US\$ 0.023/kg in the US [Jasinski, 2001]. Peat moss is a good adsorbent for all metals (Table 8). It is widely known that peat moss exhibited a high CEC and complexities towards metals due to the presence of carboxylic, phenolic, and hydroxylic functional groups.

Table 8 Reported adsorption capacities (mg/g) for peat moss

Material	Source	Cd	Cr (III)	Cr (VI)	Hg	Cu	Pb
Irish sphagnum moss peat	Sharma and Forster, 1993, 1995			119.0, 43.9			
Modified peat	Kertman <i>et al.</i> , 1993		76				230
Rastunsuo peat	Tummavuori and Aho, 1980a, b	5.058	4.63		16.2		20.038
Sphagnum moss peat	McLelland and Rock, 1988	5.8	29				40
Sphagnum peat	Fattahpour Sedeh <i>et al.</i> , 1996					40	
Carex peat	Fattahpour Sedeh <i>et al.</i> , 1996					24 to 33	

2.6 Industrial waste

Several industrial by-products have been used for the adsorption of heavy metals. Table 9 summarises some of the industrial wastes.

Table 9 Adsorption capacities of industrial waste (mg/g)

Material	Sources	Ni ²⁺	Pb ²⁺	Hg ²⁺	Cr ⁶⁺	Zn ²⁺	Cd ²⁺	Cu ²⁺
Waste slurry	Srivastava <i>et al.</i> , 1985 Lee and Davis, 2001	1030	560	640			15.73	20.97
Iron (III) hydroxide	Namasivayam and Rangnathan, 1992				0.47			
Lignin	Aloki and Munemori, 1982	1865				95		
Blast furnace slag	Srivastava <i>et al.</i> , 1997	40			7.5			
Sawdust	Ajmal <i>et al.</i> , 1998							13.80
Activated red mud	Zouboulis and Kydros, 1993	160						
	Pradhan <i>et al.</i> , 1999				1.6			
Bagasse fly ash	Gupta <i>et al.</i> , 1999				260			

2.7 Miscellaneous Adsorbents

Table 10 lists some of the miscellaneous adsorbents used for the removal of heavy metals.

Table 10 Reported adsorption capacities (mg/g) for several miscellaneous sorbents

Material	Source	Cd	Cr	Hg	Pb	Ni	Zn	Cu
Dry pine needles	Masri <i>et al.</i> , 1974			175				
Dry redwood leaves	Masri <i>et al.</i> , 1974			175				
Dyed bamboo pulp (C.I. Reactive orange 13)	Shukla and Sakhardande, 1992			15.6	15			
Undyed bamboo pulp	Shukla and Sakhardande, 1992			9.2	8.4			
Dyed jute (C.I. Reactive orange 13)	Shukla and Sakhardande, 1992			13.7	14.1			
Undyed jute	Shukla and Sakhardande, 1992			7.6	7.9			
Dyed sawdust (C.I. Reactive orange 13)	Shukla and Sakhardande, 1992			18.0	24.0			
Undyed sawdust	Shukla and Sakhardande, 1992			8.5	7.3			
Milogranite (activated sewage sludge)	Masri <i>et al.</i> , 1974			460	95.3			
Modified wool	Masri and Friedman, 1974	87	17	632	135			
Moss	Low and Lee, 1991	46.5						
Orange peel (white inner skin)	Masri <i>et al.</i> , 1974		12 5					
Orange peel (outer skin)	Masri <i>et al.</i> , 1974		27 5					
PEI wool	Freeland <i>et al.</i> , 1974		33 0.9 7					

Senna leaves	Masri <i>et al.</i> , 1974	250						
Unmodified jute	Shukla and Pai, 2005				3.37	3.55	4.23	
Modified jute	Shukla and Pai, 2005				5.57	8.02	7.73	
Papaya wood	Saeed <i>et al.</i> , 2005	17.35				14.44	19.99	
Activated carbon from apricot stone	Kobyia <i>et al.</i> , 2005	3.08	34.70	6.69	2.50		4.86	
Lignocellulosic fibres – unmodified	Shukla <i>et al.</i> , 2005				7.49	7.88		
Lignocellulosic fibres oxidised with hydrogen peroxide	Shukla <i>et al.</i> , 2005				2.51	1.83		
Carbon aerogel	Meena <i>et al.</i> , 2005	400.8	45.62	0.70	12.85	1.84	561.71	
Dye loaded groundnut shells	Shukla and Pai, 2005				9.87	17.09	8.07	
Unloaded sawdust	Shukla and Pai, 2005				8.05	10.96	4.94	
Siderite	Erdem and Özverdi, 2005			14.06				
Diatomite	Khraisheh, 2004	16.08		24.94			27.55	
Manganese treated diatomite	Khraisheh, 2004	27.08		99.00			55.56	
Wheat shell	Basci <i>et al.</i> , 2004						10.84	
Wheat bran	Farajzadeh <i>et al.</i> , 2004	21	93	70	62	12	15	
Tea industry waste	Cay <i>et al.</i> , 2004	11.29					8.64	
Sawdust of <i>P. sylvestris</i>	Taty-Costodes, <i>et al.</i> , 2003	19.08		22.22				
Cork biomass	Chubar <i>et al.</i> , 2003					0.34 meq./g	0.76 meq/g	0.63 meq/g
Cocoa shells	Meunier <i>et al.</i> , 2003			6.2				
Vermicompost	Matos and Arruda, 2003	33.01		92.94		28.43	32.63	
Peanut hulls	Johnson <i>et al.</i> , 2002						9	

Peanut pellets	Johnson <i>et al.</i> , 2002							12
poly(ethylene glycol dimethacrylate-co-acrylamide) beads	Kesenci <i>et al.</i> , 2002	0.370 mmol/g		0.270 mmol/g	1.825 mmol/g			
Activated carbon derived from bagasse	Dinesh Mohan and Kunwar P. Singh, 2002	49.07					14.0	
Polyacrylamide-grafted iron(III) oxide	Manju <i>et al.</i> , 2002	151.47		163.21	218.53			
Carboxylated alginic acid	Jeon <i>et al.</i> , 2002				3.09 mmol/g			
Petiole felt sheath of palm	Iqbal <i>et al.</i> , 2002	10.8	5.32		11.4	6.89	5.99	8.09
Sheep manure waste	Munther Kandah, 2001						13.8	
Peanut husk carbon	Ricordel <i>et al.</i> , 2001	0.45			0.55	0.28	0.20	
Kudzu (Pueraria lobata ohwi)	Brown <i>et al.</i> , 2001	15					35	32
Turkish coal	Arpa <i>et al.</i> , 2000	0.008 mmol/g		0.039 mmol/g	0.041 mmol/g			
Peanut hulls	Brown <i>et al.</i> , 2000	6			30		9	8
Peanut hull pellets	Brown <i>et al.</i> , 2000	6			30		10	10
Commercial grade ion exchange Resin	Brown <i>et al.</i> , 2000	50					90	85
Carrot residue	Nasernejad <i>et al.</i> , 2005		45.09				29.61	32.74

The results of many biosorption studies vary widely because of the different criteria used by the authors in searching for suitable materials. Some researchers have used easily available biomass types, others specially isolated strains, and some processed the raw biomass to different extents to improve its biosorption properties. In the

absence of uniform technology, results have been reported in different units and in many different ways, making quantitative comparison impossible.

Certain waste products, natural materials and biosorbents have been tested and proposed for metal removal. It is evident from the discussion so far that each low-cost adsorbent has its specific physical and chemical characteristics such as porosity, surface area and physical strength, as well as inherent advantages and disadvantages in wastewater treatment. In addition, adsorption capacities of sorbents also vary, depending on the experimental conditions. Therefore, comparison of sorption performance is difficult to make. However, it is clear from the present literature survey that non-conventional adsorbents may have potential as readily available, inexpensive and effective sorbents for both heavy metals. They also possess several other advantages that make them excellent materials for environmental purposes, such as high capacity and rate of adsorption high selectivity for different concentrations, and also rapid kinetics. There is a need to look for viable non-conventional low-cost adsorbents to meet the growing demand due to the enhanced quantum of heavy metals in the environment, despite the number of published laboratory data.

3.0 Objectives of the Present Study

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 mechanism(s) 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.

The objective of the present research is to find out the adsorption capacity of the four husks namely Tur dal (*Cajanus cajan*) husk (TDH); bengal gram husk (BGH), seed coat of *Cicer arietinum*; coffee (*Coffea arabica*) husk (CH) and tamarind (*Tamarindus indica*) pod shells (TH) for the removal of heavy metals from aqueous solutions so as to facilitate comparison with other adsorbents and provide a sound basis for further modification of the adsorbent to improve its efficiency. .

The four adsorbents chosen for the present study is available in plenty in tropical regions. Adsorption properties of these adsorbents have not yet been reported in literature. The adsorbents in the present study were tested for their adsorption capacity on the four heavy metals namely chromium (VI), iron (III), mercury (II) and nickel (II).

Exploratory studies reveal that lakes of Bangalore are contaminated with heavy metals chromium (VI), iron (III), mercury (II) and nickel (II). Growing problem of water and soil contamination due to untreated effluents has necessitated to focus on these heavy metals in the current endeavour. 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 through biosorption using low cost adsorbents.

Keeping these environmental, ecological and societal health issues in view, 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 and exploited. The objective is achieved through:

- 1) Characterisation of the adsorbents for 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 agitation/equilibrium time, pH and effect of adsorbent at different initial metal concentrations.

- 4) Calculation 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 between the adsorbents for their adsorption capacity with those found in literature.

4.0 Materials and Methods

In this Section methods for using viable non-conventional low-cost adsorbents like tur dal husk (TDH); bengal gram husk (BGH), coffee husk (CH) and tamarind husk (TH) for removal of metals such as chromium (VI), iron (III), mercury (II) and nickel (II) are discussed.

4.1 Materials

Tur dal (*Cajanus cajan*) husk (TDH) and bengal gram (*Cicer arietinu*) husk (BGH), was collected from a legume seed-splitting mill. The coffee husk (CH) was collected from coffee processing unit and tamarind pod shells (TH) were obtained from a de-hulling unit. The four husks were washed extensively in running tap water to remove dirt and other particulate matter. This was later subjected to colour removal through washing and boiling in distilled water repeatedly. Subsequently the husks were oven dried at 105°C for 24 hours, stored in a desiccator and used for biosorption studies in the original piece size.

4.2 Preparation of Adsorbate Solutions

Metal solutions

- **Iron [Fe (III)] solution:** An aqueous stock solution (1000mg/l) of Fe (III) ions was prepared using Ferrous ammonium salt as follows: 7.022 g of crystallized ferrous ammonium sulphate was dissolved in 500 ml of water and 50 ml of 1:1 sulphuric acid was added. The solution was warmed and oxidized with approximately 0.1% potassium permanganate solution until the solution remained faintly pink. The solution was diluted and made upto 1l. The pH of

the solution was adjusted using 0.1N HCl or NaOH. Fresh dilutions were used for each study.

- **Chromium [Cr (VI)] solution:** A stock solution of 1000 mg/l of Cr (VI) was obtained by dissolving 3.734 g of Potassium dichromate in 1 l of distilled water. To this is added 5 ml of HNO₃
- **Nickel [Ni (II)] solution:** Dissolved 4.477 g of nickel sulphate in 1000ml of distilled water to this is added 5 ml of 1:1 HNO₃
- **Mercury [Hg (II)] solution:** A stock solution of 1000mg/l of Hg (II) was prepared by dissolving 1.354 g of mercuric chloride in 700 ml of distilled water. Added 10 ml of concentrated nitric acid and diluted to 1000ml.

4.3 Determination of Carbon, Nitrogen and Sulphur in the four husks

Total carbon, nitrogen and sulphur were determined, in order to understand the metal binding mechanisms of four agricultural byproducts. Elemental analysis was carried out with a C.H.N. 1106 Carlo Erba MicroAnalysing device equipped with inductive furnace analyzer. Samples of the four husks were put in an oven at 1000°C under oxygen in order to obtain a quick and complete combustion. N₂, H₂O and CO₂ were released and conducted in a copper oven at 650°C, then passed through a 2 m column with helium vector gas, and analyzed by a catharometer detector.

4.4 Infrared spectroscopic analysis

FT-IR spectra of the four adsorbents namely BGH, TDH, CH and TH were obtained using shimadzu, Model FTIR – 8201PC. The infrared spectral analysis was done to determine the functional groups responsible for the adsorption of metals. As chemical bonds absorb infrared energy at specific frequencies (or wavelengths), the basic structure of compounds can be determined by the spectral locations of their IR absorptions. The plot of a compound's IR transmission vs. frequency is its "fingerprint", which when compared to reference spectra identifies the material.

4.5 Analysis of adsorbates

Estimation of metals: The metals were estimated using standard methods as described in literature (Snell and Snell, 1961; Eaton et al., 1995). Iron as Fe (III) was determined spectrophotometrically at 530 nm after complexation with sodium

salicylate (Snell and Snell, 1961). Chromium as Cr (VI) was determined spectrophotometrically at 540 nm after complexation with 1, 5 diphenylcarbazide (Eaton et al., 1995). The residual concentration of nickel was determined spectrophotometrically after complexation with dimethylglyoxime at 440 nm (Snell and Snell, 1961). Mercury (II) was estimated by the di-beta-naphthylthiocarbazone method at 515 nm as described by Snell and Snell, 1961.

4.6 Batch mode adsorption studies

Batch mode adsorption studies for individual metal compounds were carried out to investigate the effect of different parameters such as adsorbate concentration, adsorbent dose, agitation time and pH. Solution containing adsorbate and adsorbent was taken in 250 mL capacity beakers and agitated at 150 rpm in a mechanical shaker at predetermined time intervals. The adsorbate was decanted and separated from the adsorbent using Whatman No.1 filter paper. To avoid the adsorption of adsorbate on the container walls, the containers were pretreated with the respective adsorbate for 24 hours.

4.6.1 Effect of agitation time

For the determination of rate of metal biosorption by BGH, TDH, TH and CH from 100 ml (at 10, 20, 50, 100 mgL⁻¹), the supernatant was analysed for residual metal at different time intervals. The pH and the adsorbent dosage was kept constant, which varied according to the adsorbent and adsorbate under consideration.

4.6.2 Effect of adsorbent dosage

The effect of adsorbent dosage i.e., the amount of the four husks on the adsorption of metals was studied at different dosages ranging from 1 to 40 g/l with varied metal concentrations of 10, 20, 50 and 100 mg/L. The equilibrium time and the pH were kept constant depending on the metal under consideration.

4.6.3 pH effect

To determine the effect of pH on the adsorption of metal solutions (100 mL) of different concentration ranges (0-100 mgL⁻¹) were adjusted to desired pH values and mixed with known weight of adsorbent and agitated at preset equilibrium time. The

equilibrium time and adsorbent dosage varied with the metal and adsorbent under consideration.

4.6.4 Desorption studies

After adsorption, the adsorbates – loaded adsorbent were separated from the solution by centrifugation and the supernatant was drained out. The adsorbent was gently washed with water to remove any unadsorbed adsorbate. Regeneration of adsorbate from the adsorbate – laden adsorbent was carried out using the desorbing media – distilled water at pH ranges 4.0 to 12.0 using dilute solutions of NaOH and HCl. Then they were agitated for the equilibrium time of respective adsorbate. The desorbed adsorbate in the solution was separated and analyzed for the residual heavy metals.

5.0 Results

This Section presents the results obtained from the batch studies of biosorption of metals by the four agricultural by products namely bengal gram husk, coffee husk, tur dal husk and tamarind husk. The metals studied include chromium (VI), iron (III), mercury (II) and nickel (II).

5.1 Characteristics of the Adsorbent

The approximate percentages of total carbon, nitrogen and hydrogen in the four husks are shown in Table 11. The greater percentage of carbon content in all the four husks reveal that carbon compounds might be responsible for adsorption of heavy metals [Chromium (VI), Mercury (II), Iron (III) and Nickel (II)]. The protein content is less in all the four husks, as revealed by low nitrogen values. The approximate percentages of total carbon, nitrogen and hydrogen in the four husks are listed in Table 11.

Table11 Percentage content of carbon, hydrogen and nitrogen in the four husks

Adsorbent	Carbon	Hydrogen	Nitrogen
Bengal gram husk	38.57	6.31	0.86
Tur dal husk	40.66	6.35	1.13
Coffee husk	45.33	6.21	0.63
Tamarind husk	46.01	6.14	0.94

5.2 Infrared spectroscopic studies

Unreacted samples of BGH, TDH, TH and CH were subjected to Fourier transform infrared spectroscopy and the percentage transmissions for various wavenumbers are presented in Figures 3 to 6 respectively. The absorption bands identified in the spectra and their assignment to the corresponding functional groups are discussed in detail in the discussion section.

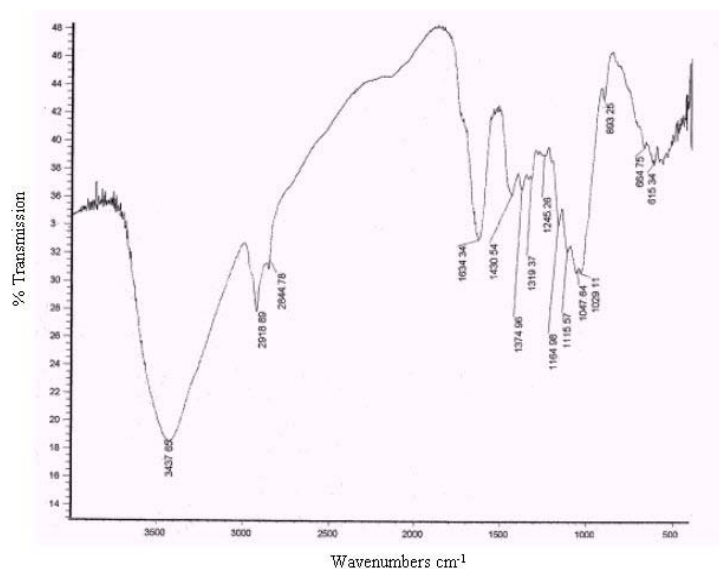


Figure 2 Infrared spectra of BGH

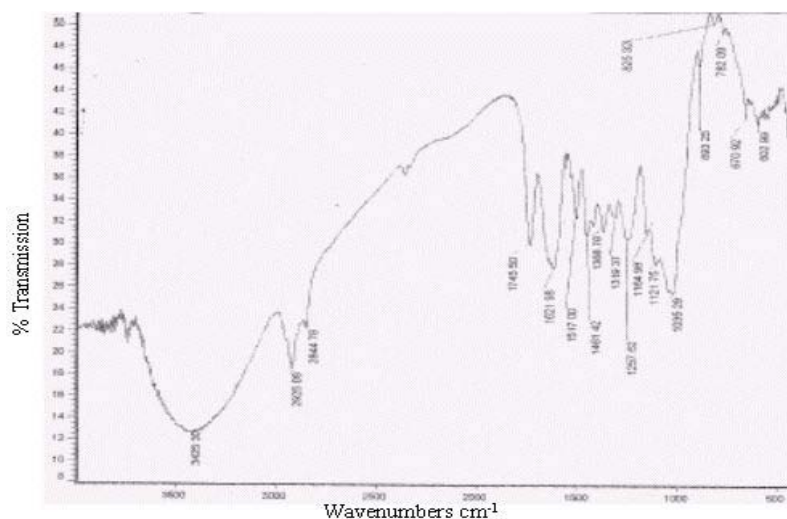


Figure 3 Infrared spectra of TDH

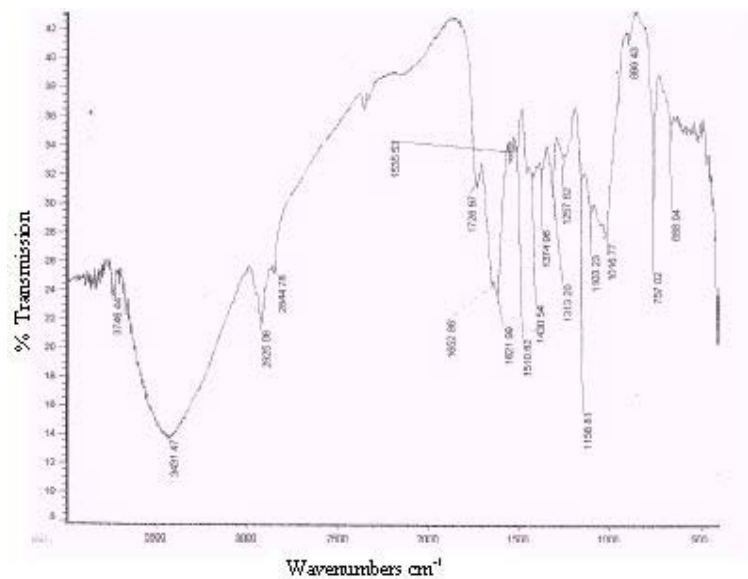


Figure 4 Infrared spectra of CH

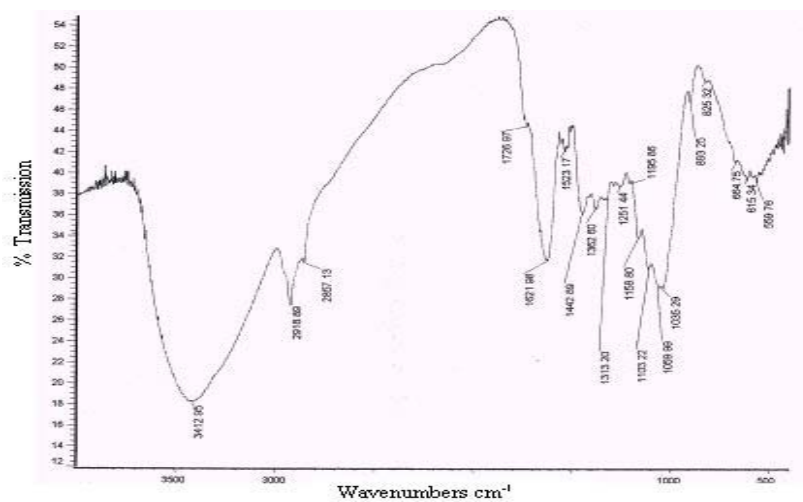


Figure 5 Infrared spectra of TH

5.3 Batch mode adsorption studies

5.3.1 Effect of agitation time

Results on the agitation time of chromium (VI) at different initial metal ion concentrations by bengal gram husk, tur dal husk, coffee husk and tamarind husk in Tables 12 to 15 and Figures 6 to 9. Tables 16-19 and Figures 10 to 13 present the results of agitation time of Iron (III) by bengal gram husk; tur dal husk; coffee husk and tamarind husk. Similarly, Figures 14 to 17 and Tables 20 to 23 represent the agitation time of adsorption of mercury (II). Adsorption of nickel (II) by the various husks is given in Figures 18 to 21 and Tables 24 to 27.

The time required to reach equilibrium for chromium (VI) adsorption by BGH is 180 minutes for all initial metal ion concentrations. The time taken for Cr (VI) adsorption by TDH, TH and CH was dependent on initial metal ion concentration and increased with increase in concentration of Cr (VI). The biosorption of iron by all the four husks were dependent on initial metal ion concentration. Similar results were obtained for the adsorption of mercury and nickel. The amount of metal ions adsorbed increased with increase in initial metal ion concentration. Most of the metal ions at all initial concentrations were optimally adsorbed within 180 to 200 minutes of contact between the husks and metals. For all the metal ions, tur dal husk exhibited the maximum uptake (mg of metal/g of adsorbent) and the order of adsorption among the metals in increasing order are mercury >chromium>iron>nickel. For BGH, it was nickel>chromium>iron>mercury. CH exhibited maximum removal of mercury followed by chromium, nickel and iron. Tamarind husk was efficient in biosorption of mercury followed by nickel, chromium and iron.

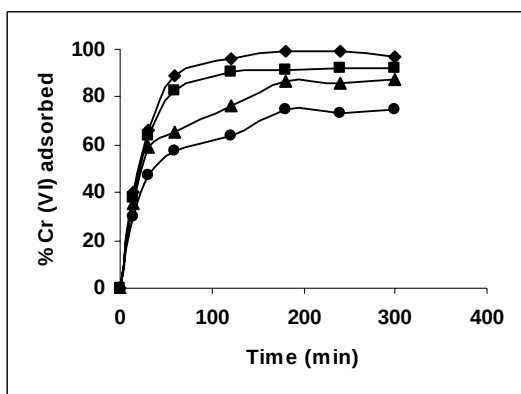


Figure: 6

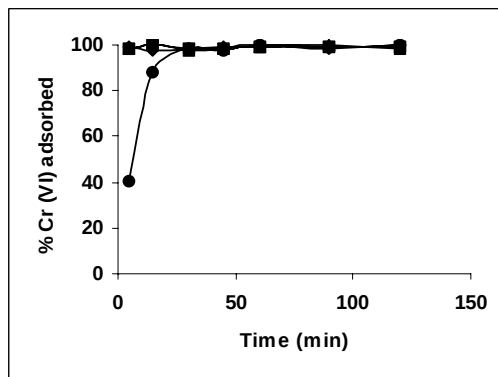


Figure: 7

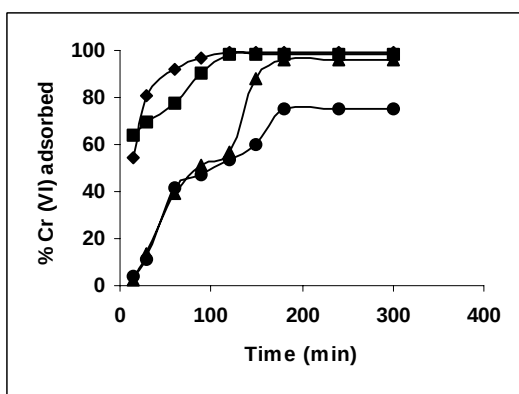


Figure: 8

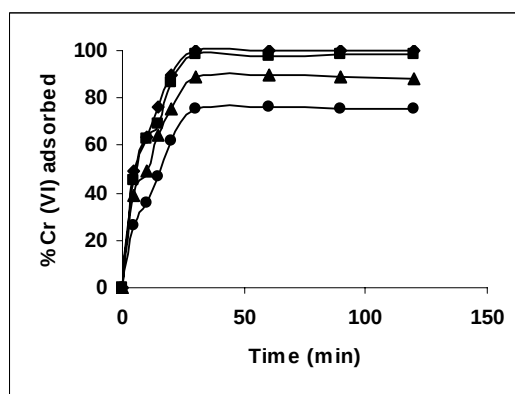


Figure: 9

Figure 6-9 Effect of agitation time on the Chromium biosorption by BGH, TDH, CH and TH respectively (♦ 10 mg/L ■ 20 mg/L ▲ 50 mg/L ● 100mg/L)

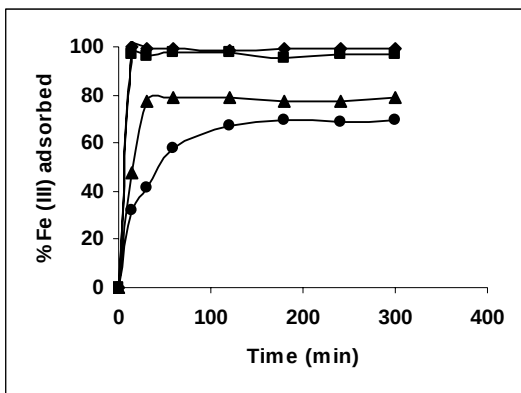


Figure: 10

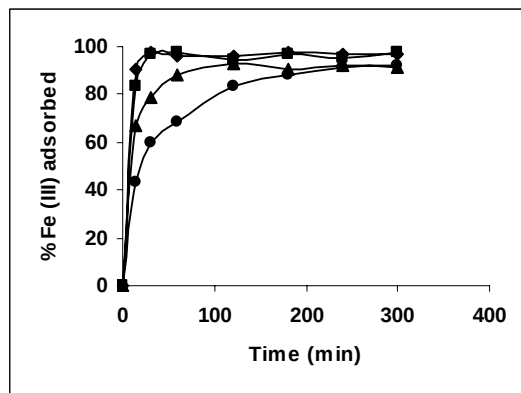


Figure: 11

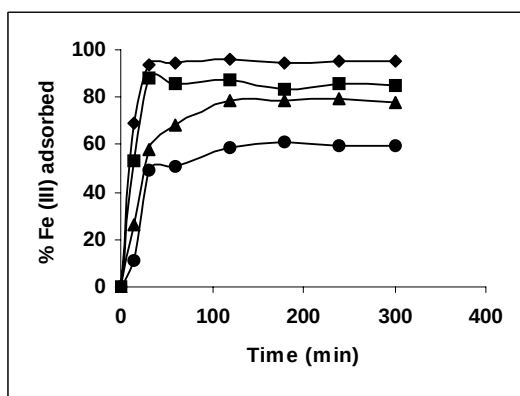


Figure: 12

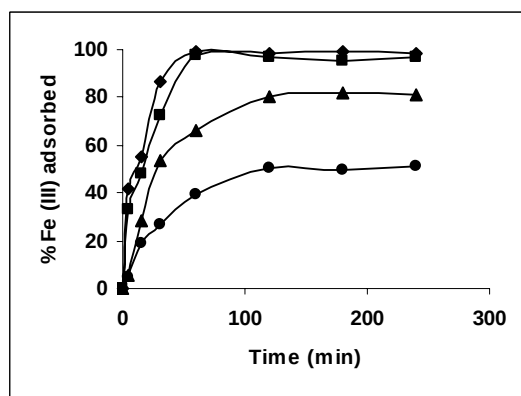


Figure: 13

Figure 10-13 Effect of agitation time on the Iron biosorption by BGH, TDH, CH and TH respectively (♦ 10 mg/L ■ 20 mg/L ▲ 50 mg/L ● 100mg/L)

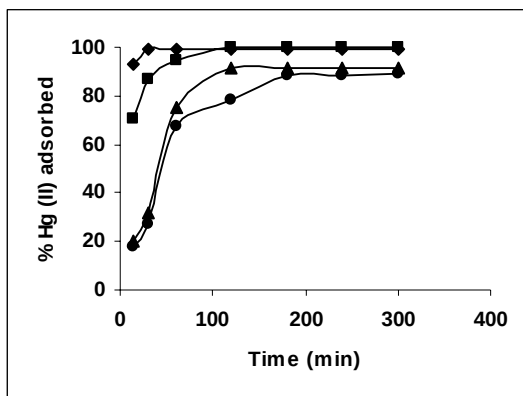


Figure: 14

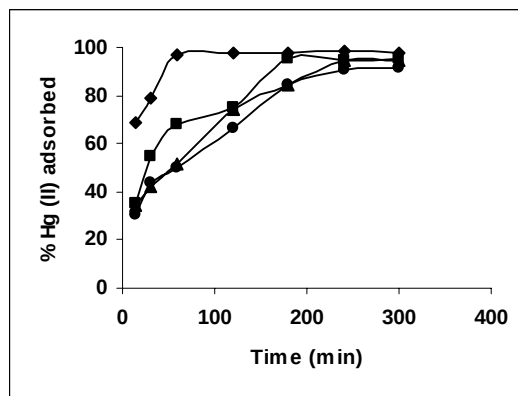


Figure: 15

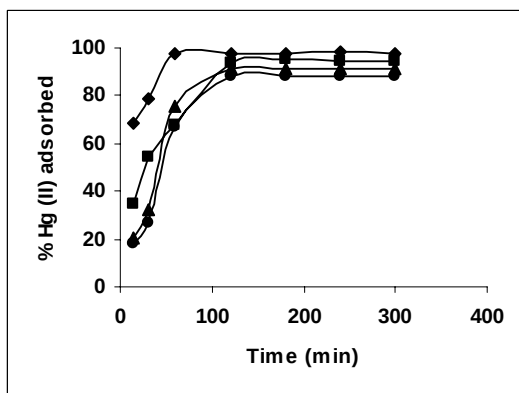


Figure: 16

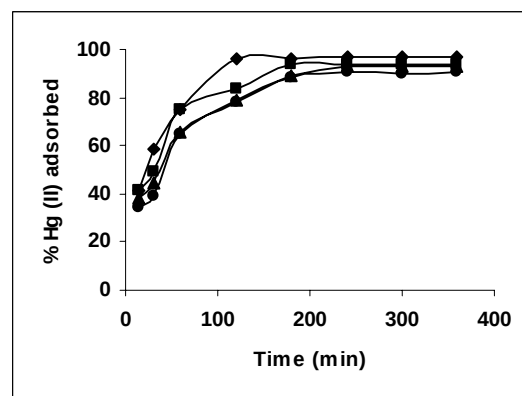


Figure: 17

Figure 14-17 Effect of agitation time on the Mercury biosorption by BGH, TDH, CH and TH respectively (♦ 10 mg/L ■ 20 mg/L ▲ 50 mg/L ● 100mg/L)

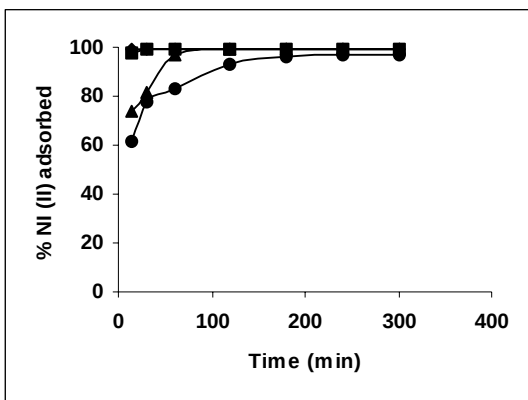


Figure: 18

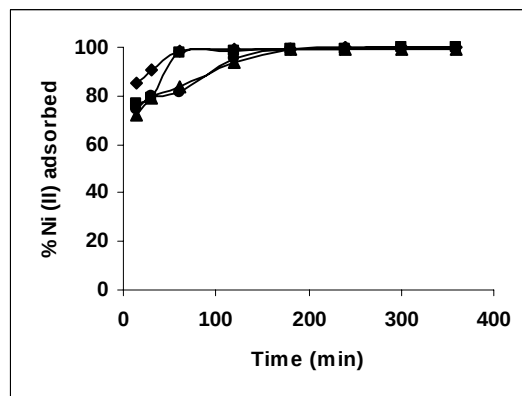


Figure: 19

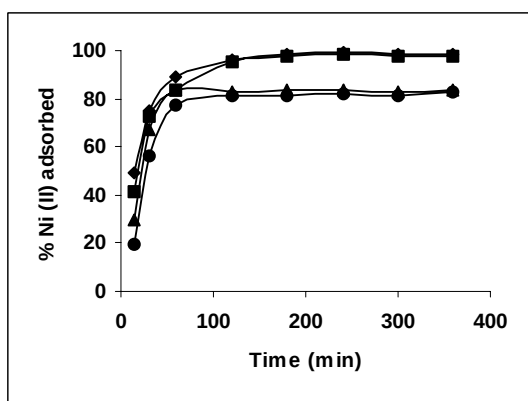


Figure: 20

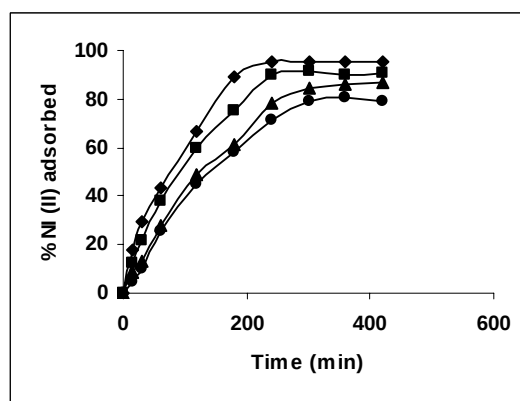


Figure: 21

Figure 18-21 Effect of agitation time on the Nickel biosorption by BGH, TDH, CH and TH respectively (♦ 10 mg/L ■ 20 mg/L ▲ 50 mg/L ● 100mg/L)

Table 12 Effect of agitation time and initial metal concentration on Chromium adsorption by bengal gram husk (Adsorbent dose = 0.2 g/100mL)

Agitation time (min)	10 mg/L			Agitation time (min)	20 mg/L		
	% adsorbed	Cr (VI) adsorbed (mg/g)	qe-q		% adsorbed	Cr (VI) adsorbed (mg/g)	qe-q
5	28.23	1.41	3.54	5	25.68	2.56	6.79
15	44.12	2.20	2.75	15	39.19	3.91	5.44
30	69.9	3.49	1.46	30	64.19	6.41	2.94
60	87.45	4.37	0.58	60	82.29	8.22	1.13
120	90.56	4.52	0.43	120	89.84	8.98	0.37
180	98.74	4.93		180	93.52	9.35	
240	98.24	4.91		240	92.88	9.28	
300	99.87	4.99		300	93.30	9.33	
360	99.12	4.95		360	92.56	9.25	
		Qe= 4.95				Qe=9.35	
Agitation time (min)	50 mg/L			Agitation time (min)	100 mg/L		
	% adsorbed	Cr (VI) adsorbed (mg/g)	qe-q		% adsorbed	Cr (VI) adsorbed (mg/g)	qe-q
5	22.56	5.64	15.8	5	18.23	9.11	28.39
15	35.45	8.86	12.6	15	30.12	15.06	22.44
30	58.78	14.69	6.81	30	47	23.5	14
60	65	16.25	5.25	60	57.85	28.92	8.58
120	76.35	19.08	2.42	120	64.02	32.01	5.49
180	86.52	21.63	0.13	180	75.08	37.54	
240	86.2	21.5		240	73.51	36.7	
300	87.21	21.80		300	74.59	37.29	
360	86.21	21.55		360	74.23	37.11	
		Qe = 21.5				Qe=37.5	

Table 13 Effect of agitation time and initial metal concentration on Chromium adsorption by Tur dal husk (Adsorbent dose = 0.2 g/100mL)

Agitation time (min)	10 mg/L			Agitation time (min)	20 mg/L		
	% adsorbed	Cr (VI) adsorbed (mg/g)	qe-q		% adsorbed	Cr (VI) adsorbed (mg/g)	qe-q
5	97.7	4.88	0.11	5	97.6	9.76	0.14
15	99.62	4.98	-	15	98.86	9.88	0.02
30	99.62	4.98		30	99.24	9.92	
45	99.89	4.99		45	99.33	9.93	
60	99.99	4.99		60	99.33	9.93	
90	99.8	4.99		90	99.24	9.92	
120	99.8	4.99		120	99.07	9.90	
	Qe=4.99				Qe=9.90		
Agitation time (min)	50 mg/L			Agitation time (min)	100 mg/L		
	% adsorbed	Cr (VI) adsorbed (mg/g)	qe-q		% adsorbed	Cr (VI) adsorbed (mg/g)	qe-q
5	99.49	24.87		5	41.09	20.54	28.93
15	99.12	24.78		15	89.63	44.81	4.66
30	99.37	24.84		30	98.37	49.18	0.29
45	99.49	24.87		45	98.6	49.3	
60	99.62	24.90		60	98.71	49.35	
90	99.24	24.81		90	98.48	49.24	
120	98.99	24.74		120	98.95	49.47	
	Qe = 24.9				Qe=49.3		

Table 14 Effect of agitation time and initial metal concentration on Chromium adsorption by Coffee husk (Adsorbent dose = 0.5 g/100mL)

10 mg/L				20 mg/L			
Agitation time (min)	% adsorbed	Cr (VI) adsorbed (mg/g)	qe-q	Agitation time (min)	% adsorbed	Cr (VI) adsorbed (mg/g)	qe-q
5	37.85	0.757	1.223	5	38.42	1.53	2.42
15	54.16	1.08	0.9	15	64.19	2.56	1.39
30	80.83	1.61	0.37	30	69.75	2.79	1.16
60	91.66	1.83	0.15	60	77.77	3.11	0.84
90	96.66	1.93	0.05	90	90.12	3.60	0.35
120	99.16	1.98	-	120	98.76	3.95	
150	99.16	1.98		150	98.38	3.93	
180	99.16	1.98		180	98.76	3.95	
240	99.16	1.98		240	98.76	3.95	
		Qe = 1.98				Qe = 3.95	
50 mg/L				100 mg/L			
Agitation time (min)	% adsorbed	Cr (VI) adsorbed (mg/g)	qe-q	Agitation time (min)	% adsorbed	Cr (VI) adsorbed (mg/g)	qe-q
5	1.38	0.138	9.46	5	1.25	0.25	14.65
15	2.52	0.252	9.34	15	4.026	0.80	14.1
30	13.29	1.32	8.28	30	10.95	2.19	12.71
60	39.09	3.90	5.7	60	41.27	8.25	6.65
90	51.1	5.11	4.49	90	46.97	9.39	5.57
120	57.04	5.70	3.9	120	53.24	10.64	4.26
150	88.16	8.81	0.79	150	59.95	11.99	2.97
180	96.01	9.60		180	74.94	14.98	
240	96.01	9.60		240	74.83	14.96	
		Qe = 9.60				Qe = 14.9	

Table 15 Effect of agitation time and initial metal concentration on Chromium adsorption by Tamarind husk. (Adsorbent dose = 0.35 g/100mL)

10 mg/L				20 mg/L			
Agitation time (min)	% adsorbed	Cr (VI) adsorbed (mg/g)	qe-q	Agitation time (min)	% adsorbed	Cr (VI) adsorbed (mg/g)	qe-q
5	49.45	1.41	1.44	5	45.12	2.57	3.02
10	63.45	1.81	1.04	10	62.4	3.56	2.03
15	76.26	2.18	0.68	15	69.36	3.96	1.63
20	89.7	2.56	0.29	20	86.21	4.92	0.67
30	99.89	2.85		30	98.52	5.62	
60	99.69	2.85		60	97.96	5.59	
90	99.92	2.85		90	98.23	5.61	
120	99.9	2.85		120	98.67	5.63	
		Qe=2.85				Qe = 5.6	
50 mg/L				100 mg/L			
Agitation time (min)	% adsorbed	Cr (VI) adsorbed (mg/g)	qe-q	Agitation time (min)	% adsorbed	Cr (VI) adsorbed (mg/g)	qe-q
5	38.65	5.52	7.18	5	26.35	7.53	13.97
10	49.21	7.03	5.67	10	35.42	10.12	11.38
15	64.3	9.18	3.51	15	46.55	13.30	8.20
20	75.15	10.73	1.96	20	62.29	17.80	3.70
30	88.95	12.70		30	75.26	21.50	
60	89.32	12.76		60	76.12	21.75	
90	88.65	12.66		90	75.6	21.60	
120	88.39	12.62		120	75.24	21.50	
		Qe= 12.7				Qe=21.50	

Table 16 Effect of agitation time and initial metal concentration on Iron adsorption by bengal gram husk (Adsorbent dose = 0.25 g/100mL)

10 mg/L				20 mg/L			
Agitation time (min)	% adsorbed	Fe(III) adsorbed (mg/g)	qe-q	Agitation time (min)	% adsorbed	Fe(III) adsorbed (mg/g)	qe-q
15	99.8	3.99		15	96.64	7.73	
30	99.35	3.97		30	96.25	7.7	
60	99.12	3.96		60	97.27	7.78	
120	98.78	3.95		120	97.62	7.80	
180	99.45	3.97		180	95.54	7.64	
240	99.21	3.96		240	96.7	7.73	
300	99.5	3.98		300	97.2	7.77	
		Qe=3.98				Qe=7.73	
50 mg/L				100 mg/L			
Agitation time (min)	% adsorbed	Fe (III) adsorbed (mg/g)	qe-q	Agitation time (min)	% adsorbed	Fe (III) adsorbed (mg/g)	qe-q
15	47.27	9.45	6.31	15	31.86	12.74	15
30	77.57	15.51	0.25	30	41.5	16.6	11.14
60	78.78	15.76		60	57.67	23.06	4.68
120	78.78	15.76		120	67.15	26.86	0.88
180	76.96	15.39		180	69.37	27.74	
240	77.57	15.51		240	69.05	27.62	
300	78.78	15.76		300	69.54	27.81	
		Qe=17.76				Qe=27.74	

Table 17 Effect of agitation time and initial metal concentration on Iron adsorption by Tur dal husk (Adsorbent dose = 0.25 g/100mL)

Agitation time (min)	10 mg/L			Agitation time (min)	20 mg/L		
	% adsorbed	Fe(III) adsorbed (mg/g)	qe-q		% adsorbed	Fe(III) adsorbed (mg/g)	qe-q
5	82.21	3.28	0.63	5	78.56	6.28	1.45
15	90.81	3.63	0.28	15	83.69	6.69	1.04
30	97.95	3.91		30	96.73	7.73	
60	96.32	3.85		60	97.82	7.82	
120	96.12	3.84		120	94.56	7.56	
180	97.95	3.91		180	96.73	7.73	
240	96.93	3.87		240	95.65	7.65	
300	96.93	3.87		300	97.82	7.82	
		Qe=3.91				Qe=7.73	
Agitation time (min)	50 mg/L			Agitation time (min)	100 mg/L		
	% adsorbed	Fe (III) adsorbed (mg/g)	qe-q		% adsorbed	Fe (III) adsorbed (mg/g)	qe-q
5	58.26	11.65	6.86	5	32.65	13.06	23.5
15	67.28	13.45	5.06	15	42.95	17.18	19.38
30	78.39	15.67	2.84	30	59.45	23.78	12.78
60	88.27	17.65	0.86	60	68.72	27.48	9.08
120	92.59	18.51		120	83.16	33.26	3.3
180	90.74	18.14		180	87.97	35.18	1.38
240	91.97	18.39		240	91.4	36.56	
300	91.35	18.27		300	92.43	36.97	
		Qe=18.51				Qe=36.56	

Table 18 Effect of agitation time and initial metal concentration on Iron adsorption by coffee husk (Adsorbent dose = 0.25 g/100mL)

Agitation time (min)	10 mg/L			Agitation time (min)	20 mg/L		
	% adsorbed	Fe(III) adsorbed (mg/g)	qe-q		% adsorbed	Fe(III) adsorbed (mg/g)	qe-q
5	54.29	2.17	1.57	5	45.37	3.62	3.43
15	69	2.76	0.98	15	52.94	4.23	2.82
30	93.56	3.74		30	88.23	7.05	
60	94.23	3.76		60	85.88	6.87	
120	95.66	3.82		120	87.05	6.96	
180	94.68	3.78		180	83.52	6.68	
240	95.06	3.80		240	85.88	6.87	
300	95.45	3.81		300	84.7	6.77	
		Qe=3.74				Qe=6.87	
Agitation time (min)	50 mg/L			Agitation time (min)	100 mg/L		
	% adsorbed	Fe (III) adsorbed (mg/g)	qe-q		% adsorbed	Fe (III) adsorbed (mg/g)	qe-q
5	16.48	3.29	12.46	5	5.29	2.11	21.46
15	25.9	5.18	10.57	15	10.78	4.31	19.26
30	58.03	11.60	4.15	30	49.47	19.78	3.79
60	68.39	13.67	2.08	60	50.78	20.31	3.26
120	78.75	15.75		120	58.94	23.57	
180	78.23	15.64		180	61.05	24.42	
240	79.27	15.85		240	59.47	23.78	
300	77.72	15.54		300	59.21	23.68	
		Qe=15.7				Qe=23.5	

Table 19 Effect of agitation time and initial metal concentration on Iron adsorption by Tamarind husk (Adsorbent dose = 0.35 g/100mL)

Agitation time (min)	10 mg/L			Agitation time (min)	20 mg/L		
	% adsorbed	Fe(III) adsorbed (mg/g)	qe-q		% adsorbed	Fe(III) adsorbed (mg/g)	qe-q
5	41.56	1.18	1.66	5	33.3	1.90	3.68
15	55.36	1.58	1.26	15	48.27	2.75	2.83
30	86.32	2.46	0.38	30	72.41	4.13	1.45
60	99.5	2.84		60	97.7	5.58	
120	98.65	2.81		120	96.55	5.51	
180	99.01	2.82		180	95.4	5.45	
240	98.62	2.81		240	96.55	5.51	
		Qe=2.84				Qe=5.58	
Agitation time (min)	50 mg/L			Agitation time (min)	100 mg/L		
	% adsorbed	Fe (III) adsorbed (mg/g)	qe-q		% adsorbed	Fe (III) adsorbed (mg/g)	qe-q
5	5.8	0.82	10.63	5	4.46	1.27	13.09
15	28.33	4.04	7.41	15	18.98	5.42	8.94
30	53.33	7.61	3.84	30	26.47	7.56	6.8
60	66.31	9.47	1.98	60	39.03	11.15	3.21
120	80.21	11.45		120	50.26	14.36	
180	81.81	11.68		180	50	14.28	
240	80.74	11.53		240	51.06	14.58	
		Qe=11.45				Qe=14.3	

Table 20 Effect of agitation time and initial metal concentration on Mercury adsorption by bengal gram husk (Adsorbent dose = 0.5 g/100mL)

Agitation time (min)	10 mg/L			Agitation time (min)	20 mg/L		
	% adsorbed	Hg (II) adsorbed (mg/g)	qe-q		% adsorbed	Hg (II) adsorbed (mg/g)	qe-q
5	85.31	1.70	0.2	5	62.14	2.48	1.51
15	93.37	1.86	0.04	15	70.57	2.82	1.17
30	99.61	1.99		30	86.92	3.47	0.52
60	99.02	1.98		60	94.7	3.78	0.21
120	99.41	1.98		120	99.77	3.99	
180	99.22	1.98		180	99.77	3.99	
240	99.61	1.99		240	99.67	3.98	
300	99.41	1.98		300	99.77	3.99	
		Qe=1.99				Qe=3.99	
Agitation time (min)	50 mg/L			Agitation time (min)	100 mg/L		
	% adsorbed	Hg (II) adsorbed (mg/g)	qe-q		% adsorbed	Hg (II) adsorbed (mg/g)	qe-q
5	11.35	1.13	7.99	5	6.75	1.53	16.09
15	20.44	2.04	7.08	15	18	3.6	14.02
30	31.89	3.18	5.94	30	27.16	5.43	12.19
60	75.23	7.52	1.6	60	67.2	13.44	4.18
120	91.23	9.12		120	77.96	15.59	2.03
180	91.35	9.13		180	88.12	17.62	
240	91.12	9.11		240	88.02	17.60	
300	91.35	9.13		300	88.83	17.76	
		Qe= 9.12				Qe=17.62	

Table 21 Effect of agitation time and initial metal concentration on Mercury adsorption by Tur dal husk (Adsorbent dose = 0.1 g/100mL)

Agitation time (min)	10 mg/L			Agitation time (min)	20 mg/L		
	% adsorbed	Hg (II) adsorbed (mg/g)	qe-q		% adsorbed	Hg (II) adsorbed (mg/g)	qe-q
5	55.68	5.56	4.16	5	20.26	4.05	14.94
15	68.68	6.86	2.86	15	34.82	6.96	12.03
30	78.75	7.87	1.85	30	54.42	10.88	8.11
60	97.25	9.72		60	67.61	13.52	5.47
120	97.8	9.78		120	74.82	14.96	4.03
180	97.98	9.79		180	94.96	18.99	
240	98.16	9.81		240	94.69	18.93	
300	97.98	9.79		300	95.23	19.04	
		Qe=9.72				Qe=18.99	
Agitation time (min)	50 mg/L			Agitation time (min)	100 mg/L		
	% adsorbed	Hg (II) adsorbed (mg/g)	qe-q		% adsorbed	Hg (II) adsorbed (mg/g)	qe-q
5	28.23	14.11	33.22	5	18.96	18.96	71.78
15	34.1	17.05	30.28	15	30.38	30.38	60.36
30	41.87	20.93	26.4	30	43.46	43.46	47.28
60	51.5	25.75	21.58	60	49.89	49.89	40.85
120	74.01	37.00	10.33	120	66.59	66.59	24.15
180	84.22	42.11	5.22	180	84.3	84.3	6.44
240	94.66	47.33		240	90.74	90.74	
300	94.43	47.21		300	91.14	91.14	
		Qe=47.33				Qe=90.74	

Table 22 Effect of agitation time and initial metal concentration on Mercury adsorption by Coffee husk (Adsorbent dose = 0.2 g/100mL)

Agitation time (min)	10 mg/L			Agitation time (min)	20 mg/L		
	% adsorbed	Hg (II) adsorbed (mg/g)	qe-q		% adsorbed	Hg (II) adsorbed (mg/g)	qe-q
5	52.32	2.61	2.25	5	25.12	2.51	6.88
15	68.68	3.43	1.43	15	34.82	3.48	5.91
30	78.75	3.93	0.93	30	54.42	5.44	3.95
60	97.25	4.86		60	67.61	6.76	2.63
120	97.8	4.89		120	93.94	9.39	
180	97.98	4.89		180	94.96	9.49	
240	98.16	4.90		240	94.69	9.46	
300	97.98	4.89		300	94.82	9.48	
		Qe=4.86				Qe=9.39	
Agitation time (min)	50 mg/L			Agitation time (min)	100 mg/L		
	% adsorbed	Hg (II) adsorbed (mg/g)	qe-q		% adsorbed	Hg (II) adsorbed (mg/g)	qe-q
5	14.23	3.55	19.25	5	9.56	4.78	39.28
15	20.44	5.11	17.69	15	18	9	35.06
30	31.89	7.97	14.83	30	27.16	13.58	30.48
60	75.23	18.80	4	60	67.2	33.6	10.46
120	91.23	22.80		120	88.12	44.06	
180	91.35	22.83		180	88.02	44.01	
240	91.12	22.78		240	87.92	43.96	
300	91.35	22.83		300	88.32	44.16	
		Qe=22.8				Qe=44	

Table23 Effect of agitation time and initial metal concentration on Mercury adsorption by Tamarind husk (Adsorbent dose = 0. 1 g/100mL)

10 mg/L				20 mg/L			
Agitation time (min)	% adsorbed	Hg (II) adsorbed (mg/g)	qe-q	Agitation time (min)	% adsorbed	Hg (II) adsorbed (mg/g)	qe-q
5	8.23	0.82	8.69	5	7.32	1.46	16.78
15	18	1.8	7.71	15	12.3	2.46	15.78
30	29.15	2.91	6.6	30	21.45	4.29	13.95
60	43.56	4.35	5.16	60	37.98	7.59	10.65
120	66.48	6.64	2.87	120	59.86	11.97	6.27
180	89.25	8.92	0.59	180	75.23	15.04	3.2
240	95.63	9.56		240	89.65	17.93	0.31
300	94.98	9.49		300	91.22	18.24	
360	95.21	9.52		360	90.21	18.04	
420	95.14	9.51		420	90.34	18.06	
		Qe=9.51				Qe=18.24	
50 mg/L				100 mg/L			
Agitation time (min)	% adsorbed	Hg (II) adsorbed (mg/g)	qe-q	Agitation time (min)	% adsorbed	Hg (II) adsorbed (mg/g)	qe-q
5	3.66	1.83	41.28	5	2.37	2.37	76.87
15	8.52	4.26	38.85	15	4.68	4.68	74.56
30	13.56	6.78	36.33	30	10.21	10.21	69.03
60	28.25	14.12	28.99	60	25.46	25.46	53.78
120	49.21	24.60	18.51	120	45.15	45.15	34.09
180	61.21	30.60	12.51	180	58.23	58.23	21.01
240	78.21	39.10	4.01	240	71.55	71.55	7.69
300	84.12	42.06	1.05	300	79.24	79.24	
360	86.22	43.11		360	80.26	80.26	
420	87.11	43.55		420	79.11	79.11	
		Qe=43.1				Qe=79.2	

Table 24 Effect of agitation time and initial metal concentration on Nickel adsorption by bengal gram husk (Adsorbent dose = 0. 2 g/100mL)

Agitation time (min)	10 mg/L			Agitation time (min)	20 mg/L		
	% adsorbed	Hg (II) adsorbed (mg/g)	qe-q		% adsorbed	Hg (II) adsorbed (mg/g)	qe-q
5	96.23	4.81		5	93.21	9.32	
15	99.019	4.95		15	97.5	9.75	
30	99.5	4.97		30	99.39	9.93	
60	99.019	4.95		60	99.39	9.93	
120	99.019	4.95		120	99.39	9.93	
180	99.019	4.95		180	99.39	9.93	
240	99.019	4.95		240	99.39	9.93	
300	99.019	4.95		300	99.39	9.93	
Agitation time (min)	50 mg/L			Agitation time (min)	100 mg/L		
	% adsorbed	Hg (II) adsorbed (mg/g)	qe-q		% adsorbed	Hg (II) adsorbed (mg/g)	qe-q
5	65.37	16.34	8.49	5	55.23	27.61	20.58
15	73.5	18.37	6.46	15	61.44	30.72	17.47
30	81.45	20.36	4.47	30	77.71	38.85	9.34
60	97.01	24.2	0.63	60	83.13	41.56	6.63
120	99.33	24.83		120	92.77	46.38	1.81
180	99.33	24.83		180	96.38	48.19	
240	99.33	24.83		240	96.98	48.49	
300	99.33	24.83		300	96.98	48.49	
		Qe = 24.83				Qe=48.19	

Table 25 Effect of agitation time and initial metal concentration on Nickel adsorption by Tur dal husk (Adsorbent dose = 0.5 g/100mL)

Agitation time (min)	10 mg/L			Agitation time (min)	20 mg/L		
	% adsorbed	Hg (II) adsorbed (mg/g)	qe-q		% adsorbed	Hg (II) adsorbed (mg/g)	qe-q
5	72.32	1.44	0.52	5	63.21	2.52	1.43
15	85.18	1.70	0.26	15	76.36	3.05	0.9
30	90.74	1.81	0.15	30	79.39	3.17	0.78
60	98.14	1.96		60	97.57	3.90	0.05
120	99.07	1.98		120	98.78	3.95	
180	99.07	1.98		180	99.39	3.97	
240	100	2		240	99.39	3.97	
300	100	2		300	100	4	
		Qe=1.96				Qe=3.95	
Agitation time (min)	50 mg/L			Agitation time (min)	100 mg/L		
	% adsorbed	Hg (II) adsorbed (mg/g)	qe-q		% adsorbed	Hg (II) adsorbed (mg/g)	qe-q
5	59.23	5.92	4.03	5	49.23	9.84	10.05
15	72.38	7.23	2.72	15	74.5	14.9	4.99
30	78.85	7.88	2.07	30	79.63	15.92	3.97
60	83.58	8.35	1.6	60	81.73	16.34	3.55
120	93.53	9.35	0.6	120	95.53	19.10	0.79
180	99.5	9.95		180	99.47	19.89	
240	99.25	9.92		240	99.6	19.92	
300	99	9.9		300	99.73	19.94	
		Qe=9.95				Qe=19.89	

Table 26 Effect of agitation time and initial metal concentration on Nickel adsorption by Coffee husk (Adsorbent dose = 0.5 g/100mL)

Agitation time (min)	10 mg/L			Agitation time (min)	20 mg/L		
	% adsorbed	Hg (II) adsorbed (mg/g)	qe-q		% adsorbed	Hg (II) adsorbed (mg/g)	qe-q
5	37.69	0.75	1.22	5	32	1.28	2.65
15	49.36	0.98	0.99	15	41.31	1.65	2.28
30	75.24	1.50	0.47	30	72.45	2.89	1.04
60	88.94	1.77	0.2	60	83.22	3.32	0.61
120	96.25	1.92	0.05	120	95.65	3.82	0.11
180	98.58	1.97		180	97.89	3.91	
240	99.58	1.99		240	98.45	3.93	
300	98.78	1.97		300	97.68	3.90	
360	98.65	1.97		360	97.51	3.90	
		Qe=1.97				Qe=3.93	
Agitation time (min)	50 mg/L			Agitation time (min)	100 mg/L		
	% adsorbed	Hg (II) adsorbed (mg/g)	qe-q		% adsorbed	Hg (II) adsorbed (mg/g)	qe-q
5	19.34	1.93	6.42	5	11.89	2.37	13.85
15	29.74	2.97	5.38	15	19.92	3.98	12.24
30	67.4	6.74	1.61	30	55.93	11.18	5.04
60	83.86	8.38		60	77.72	15.54	0.68
120	82.59	8.25		120	81.11	16.22	
180	83.54	8.35		180	80.87	16.17	
240	83.22	8.32		240	82.32	16.46	
300	83.11	8.31		300	81.35	16.27	
360	83.54	8.35		360	82.8	16.56	
		Qe=8.35				Qe=16.22	

Table 27 Effect of agitation time and initial metal concentration on Nickel adsorption by Tamarind husk (Adsorbent dose = 0.2 g/100mL)

Agitation time (min)	10 mg/L			Agitation time (min)	20 mg/L		
	% adsorbed	Hg (II) adsorbed (mg/g)	qe-q		% adsorbed	Hg (II) adsorbed (mg/g)	qe-q
5	10.28	0.51	4.27	5	8.25	0.82	8.3
15	18	0.9	3.88	15	12.3	1.23	7.89
30	29.15	1.45	3.33	30	21.45	2.14	6.98
60	43.56	2.17	2.61	60	37.98	3.79	5.33
120	66.48	3.32	1.46	120	59.86	5.98	3.14
180	89.25	4.46	0.32	180	75.23	7.52	1.6
240	95.63	4.78		240	89.65	8.96	0.16
300	94.98	4.74		300	91.22	9.12	
360	95.21	4.76		360	90.21	9.02	
420	95.14	4.75		420	90.34	9.03	
		Qe=4.78				Qe=9.12	
Agitation time (min)	50 mg/L			Agitation time (min)	100 mg/L		
	% adsorbed	Hg (II) adsorbed (mg/g)	qe-q		% adsorbed	Hg (II) adsorbed (mg/g)	qe-q
5	6.78	1.69	19.34	5	1.78	0.89	38.73
15	8.52	2.13	18.9	15	4.68	2.34	37.28
30	13.56	3.39	17.64	30	10.21	5.10	34.51
60	28.25	7.06	13.97	60	25.46	12.73	26.89
120	49.21	12.30	8.73	120	45.15	22.57	17.05
180	61.21	15.30	5.73	180	58.23	29.11	10.51
240	78.21	19.55	1.48	240	71.55	35.77	3.85
300	84.12	21.03		300	79.24	39.62	
360	86.22	21.55		360	80.26	40.13	
420	87.11	21.77		420	79.11	39.55	
		Qe=21.03				Qe=39.62	

3.2 Effect of adsorbent dosage

Results on the effect of adsorbent dosage at various initial metal concentrations are presented in this section. Adsorption of chromium (VI) by bengal gram husk, tur dal husk, coffee husk and tamarind husk at different initial metal concentrations and various adsorbent dosages are presented in Figures 22 to 25. The effect of adsorbent dosage on Ferric ion removal by bengal gram husk, tur dal husk, coffee husk and

Tamarind husk in Figures 26 to 29. Figures 30 to 33 represent the biosorption of mercury (II) by the four husks. Similarly Figures 34 to 37 represent the bioremoval of nickel by the various adsorbents at different adsorbent dosages.

The amount of adsorbent dosage required for the optimum removal of the metal ions increased with increase in the initial metal ion concentration. TDH proved efficient among all the husks for the maximum removal of metal ions followed by BGH, CH and TH.

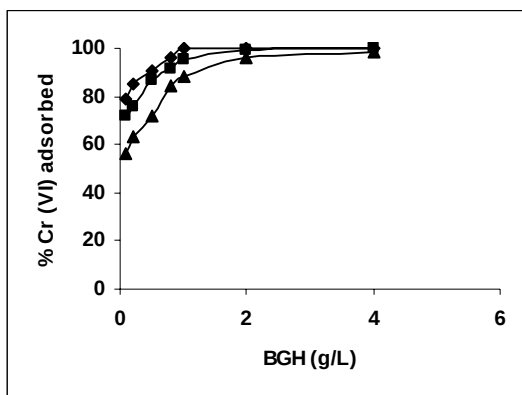


Figure: 22

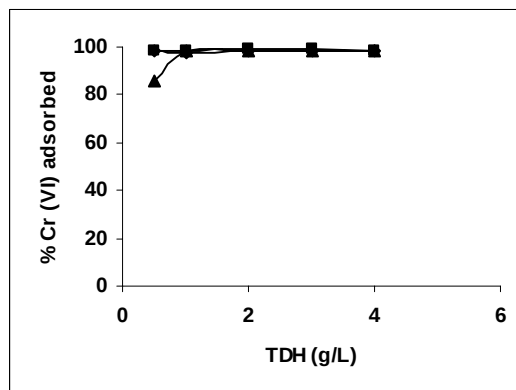


Figure: 23

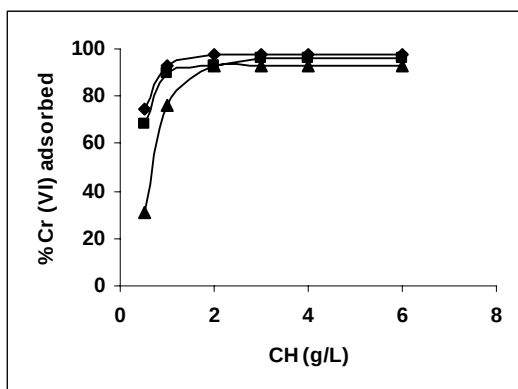


Figure: 24

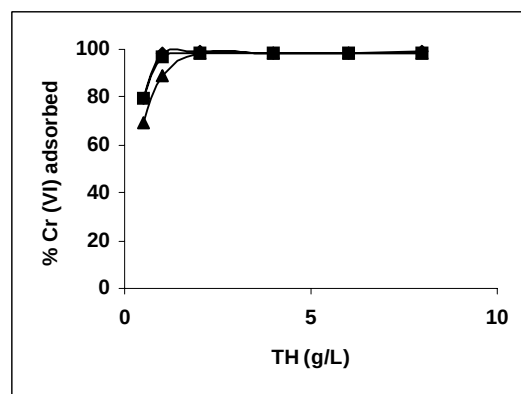


Figure: 25

Figure 22-25 Effect of adsorbent dose on the Chromium biosorption by BGH, TDH, CH and TH respectively (♦ 10 mg/L ■ 20 mg/L ▲ 50 mg/L)

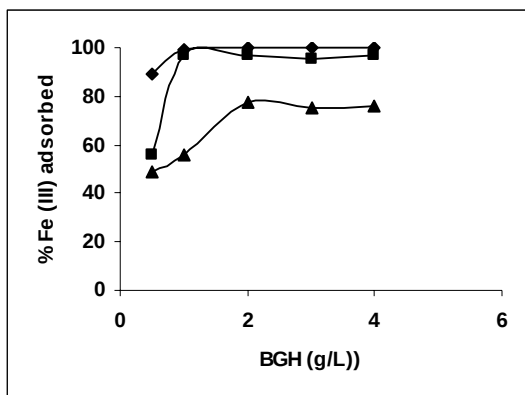


Figure: 26

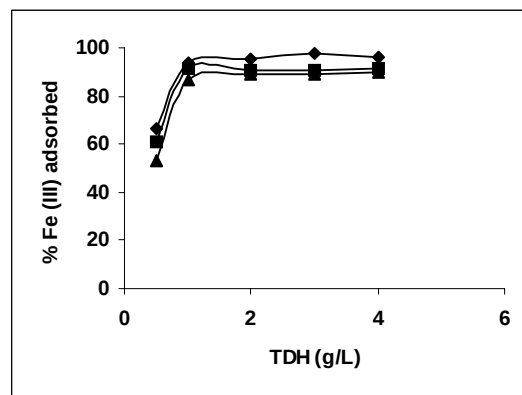


Figure: 27

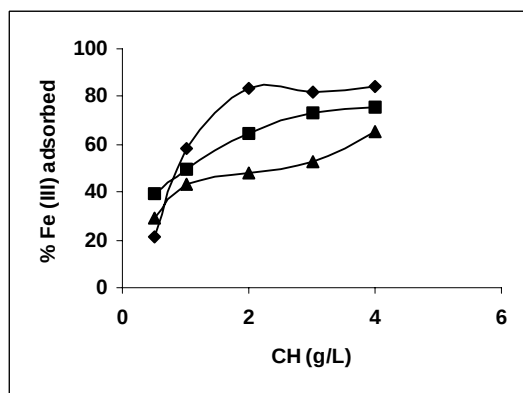


Figure: 28

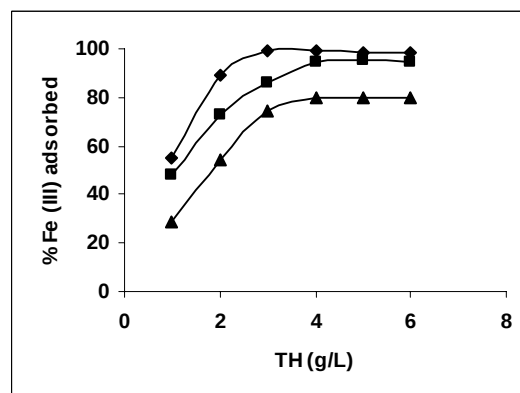


Figure: 29

Figure 26-29 Effect of adsorbent dose on the Iron biosorption by BGH, TDH, CH and TH respectively (♦ 10 mg/L ■ 20 mg/L ▲ 50 mg/L)

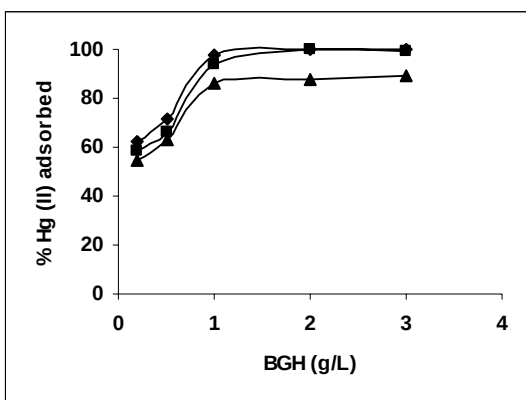


Figure: 30

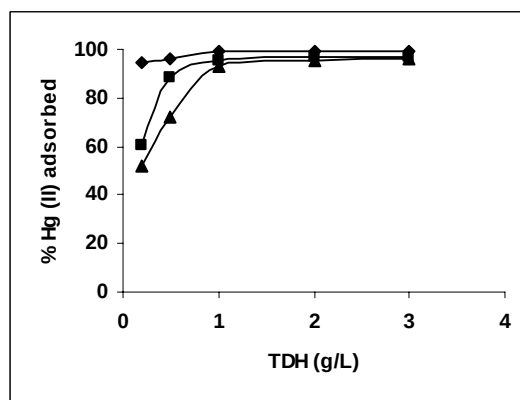


Figure: 31

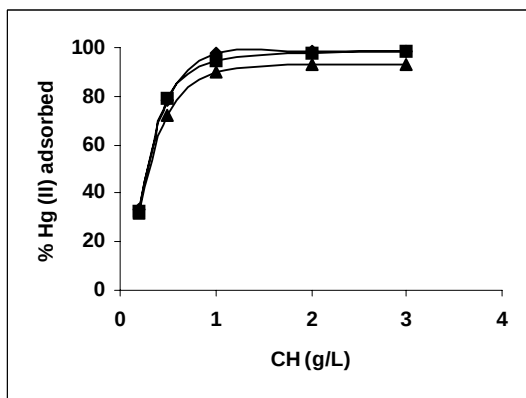


Figure: 32

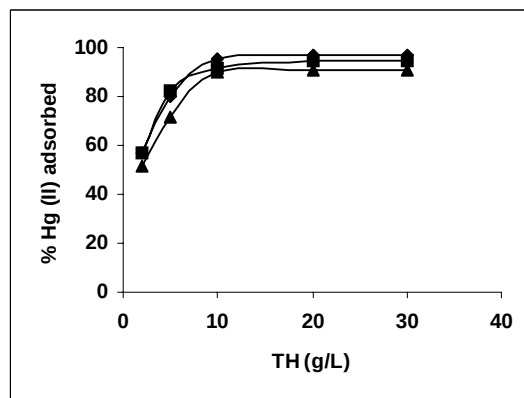


Figure: 33

Figure 30 - 33 Effect of adsorbent dose on the Mercury biosorption by BGH, TDH, CH and TH respectively (♦ 10 mg/L ■ 20 mg/L ▲ 50 mg/L)

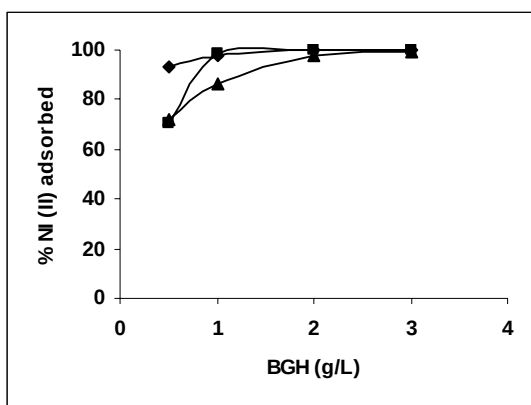


Figure: 34

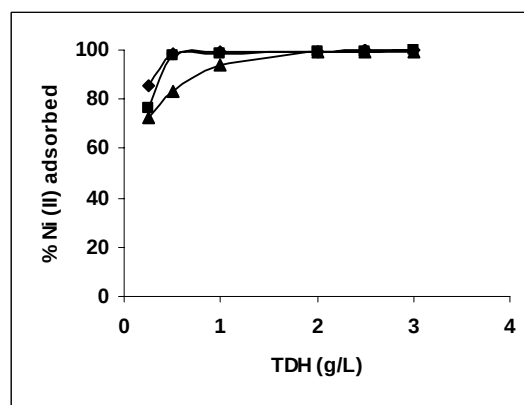


Figure: 35

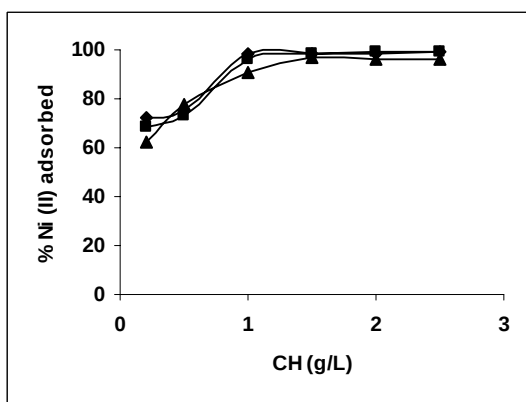


Figure: 36

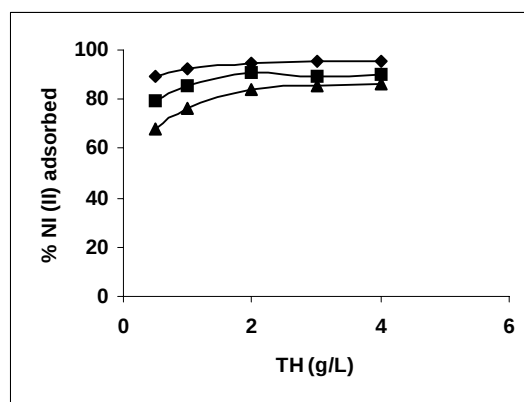


Figure: 37

Figure 34-37 Effect of adsorbent dose on the Nickel biosorption by BGH, TDH, CH and TH respectively (♦ 10 mg/L ■ 20 mg/L ▲ 50 mg/L)

5.3.3 Effect of pH

Data for the effect of pH and the effect of different initial metal ion concentration is presented in Tables 28 to 31 and Figures 38 to 41 for chromium (VI) biosorption by bengal gram husk; tur dal husk; coffee husk and tamarind husk. Tables 32 to 35 and Figures 42 to 45 show the effect of pH on biosorption of Iron by the four husks. Similarly Tables 36 to 39 and Figures 46 to 49 show biosorption of mercury and Tables 40 to 43 and Figures 50 to 53 show the adsorption of nickel at different pH and varying concentration of metal ions.

The results of effect of pH on the removal of metals reveal that irrespective of the husk (adsorbent) metal ions were adsorbed. Chromium removal was optimal at pH 2.0; iron (III) showed maximum adsorption at 2.5; mercury was adsorbed at pH 6.0 and nickel at pH 5.5.

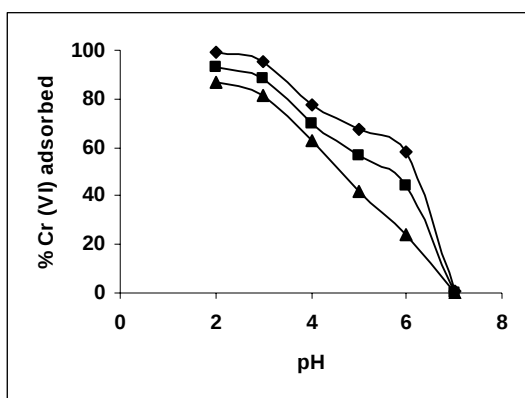


Figure: 38

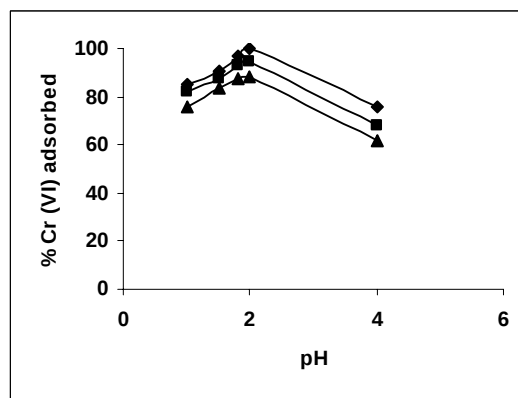


Figure: 39

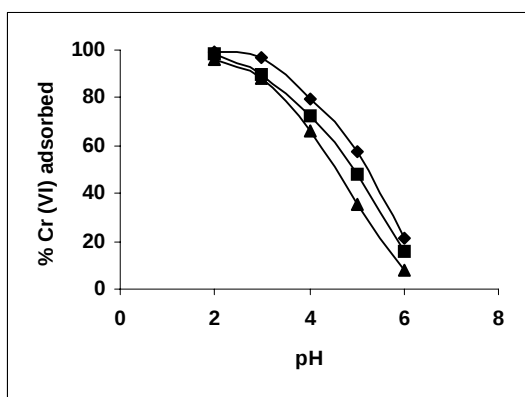


Figure: 40

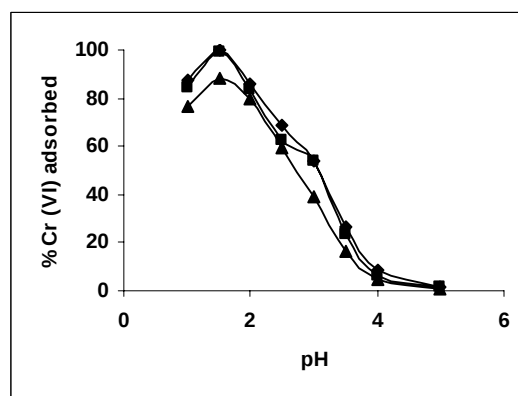


Figure: 41

Figure 38-41 Effect of pH on the Chromium biosorption by BGH, TDH, CH and TH respectively (♦ 10 mg/L ■ 20 mg/L ▲ 50 mg/L)

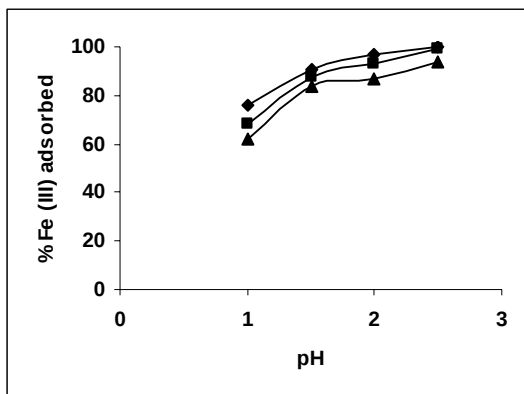


Figure: 42

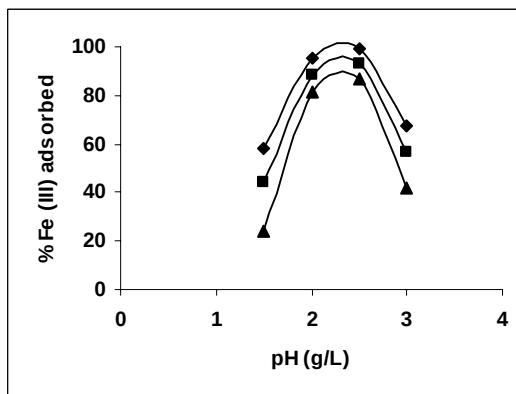


Figure: 43

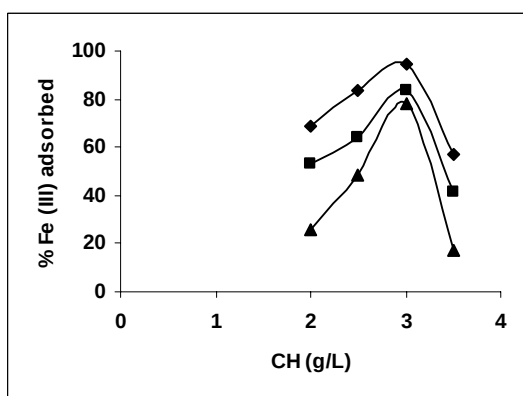


Figure: 44

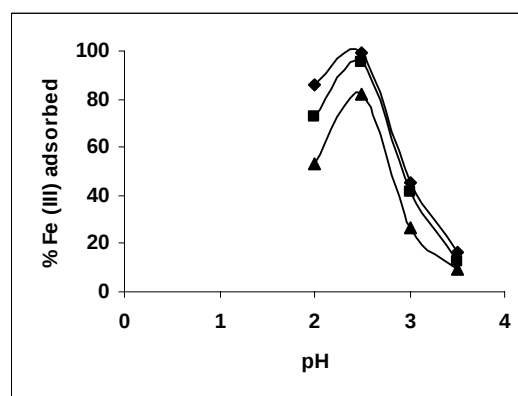


Figure: 45

Figure 42-45 Effect of pH on the Iron biosorption by BGH, TDH, CH and TH respectively (♦ 10 mg/L ■ 20 mg/L ▲ 50 mg/L)

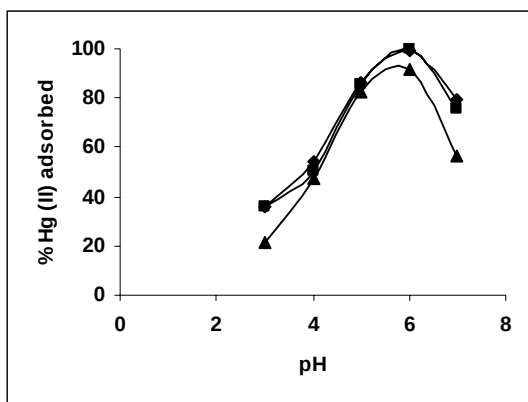


Figure: 46

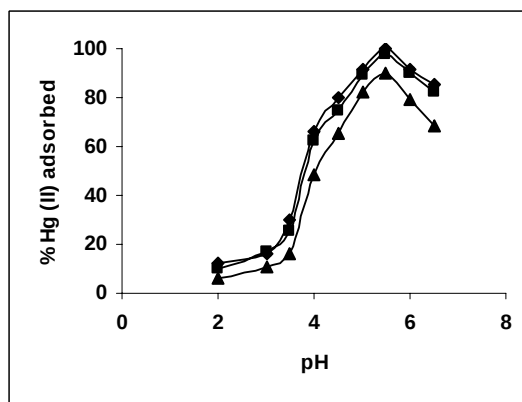


Figure: 47

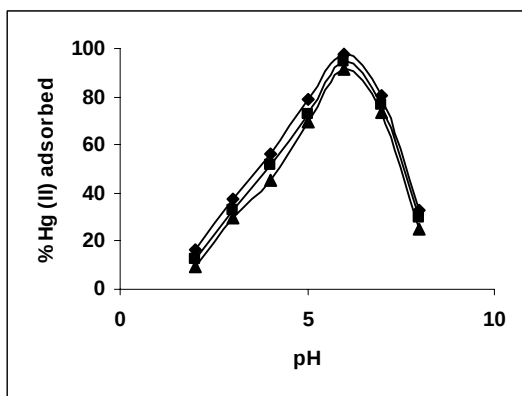


Figure: 48

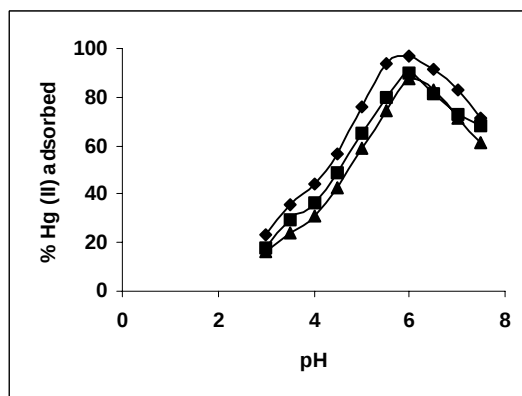


Figure: 49

Figure 46-49 Effect of pH on the Mercury biosorption by BGH, TDH, CH and TH respectively (♦ 10 mg/L ■ 20 mg/L ▲ 50 mg/L)

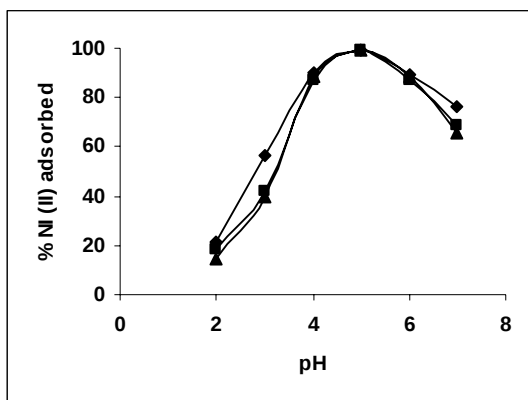


Figure: 50

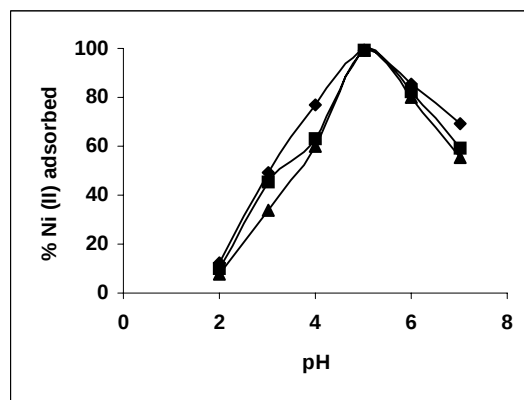


Figure: 51

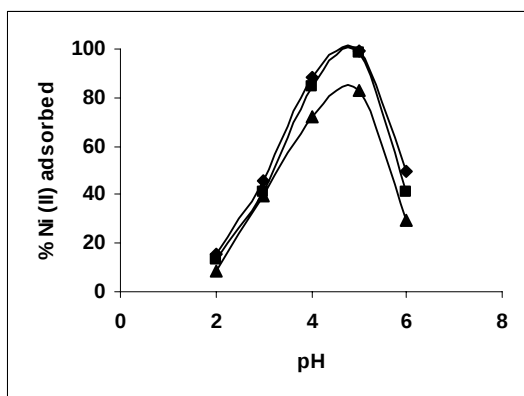


Figure: 52

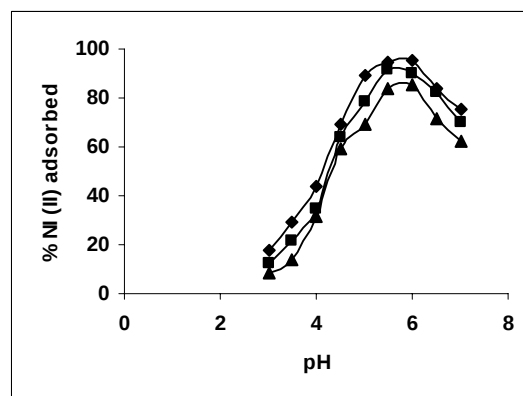


Figure: 53

Figure 50-53 Effect of pH on the Nickel biosorption by BGH, TDH, CH and TH respectively (♦ 10 mg/L ■ 20 mg/L ▲ 50 mg/L)

Table 28 Effect of pH and initial metal ion concentration on chromium adsorption by Bengal gram husk (Adsorbent dose = 0.2g/100ml)

pH	10 mg/L		20 mg/L		50 mg/L	
	% adsorbed	Cr (VI) adsorbed (mg/g)	% adsorbed	Cr (VI) adsorbed (mg/g)	% adsorbed	Cr (VI) adsorbed (mg/g)
2	99.56	4.97	93.14	9.31	87.14	21.78
3	95.48	4.77	88.15	8.81	81.23	20.30
4	77.3	3.86	69.64	6.96	62.5	15.62
5	67.36	3.36	56.7	5.67	41.65	10.41
6	58.45	2.92	44.5	4.45	24.2	6.05
7	0.5	0.02	0.2	0.02	0.2	0.05

Table 29 Effect of pH and initial metal ion concentration on chromium adsorption by Tur dal husk (Adsorbent dose = 0.2g/100ml)

pH	10 mg/L		20 mg/L		50 mg/L	
	% adsorbed	Cr (VI) adsorbed (mg/g)	% adsorbed	Cr (VI) adsorbed (mg/g)	% adsorbed	Cr (VI) adsorbed (mg/g)
1	85.3	4.27	81.72	8.17	75.45	18.86
1.5	90.32	4.52	87.4	8.74	83.6	20.90
1.8	97.24	4.86	92.65	9.27	87.2	21.80
2	99.96	5.00	94.52	9.45	88	22.00
4	76	3.80	68.3	6.83	62	15.50

Table 30 Effect of pH and initial metal ion concentration on chromium adsorption by Coffee husk (Adsorbent dose = 0.5g/100ml)

pH	10 mg/L		20 mg/L		50 mg/L	
	% adsorbed	Cr (VI) adsorbed (mg/g)	% adsorbed	Cr (VI) adsorbed (mg/g)	% adsorbed	Cr (VI) adsorbed (mg/g)
2	99.16	1.98	98.76	3.95	96.01	9.60
3	96.66	1.93	90.12	3.60	88.16	8.81
4	79.25	1.58	72.34	2.89	66.21	6.62
5	57.2	1.14	48	1.92	35.47	3.54
6	21.2	0.42	15.64	0.62	7.5	0.75

Table 31 Effect of pH and initial metal ion concentration on chromium adsorption by tamarind husk (Adsorbent dose = 0.35g/100ml)

pH	10 mg/L		20 mg/L		50 mg/L	
	% adsorbed	Cr (VI) adsorbed (mg/g)	% adsorbed	Cr (VI) adsorbed (mg/g)	% adsorbed	Cr (VI) adsorbed (mg/g)
1	87.43	2.50	84.23	4.81	76.45	10.92
1.5	99.89	2.85	98.92	5.65	88.66	12.67
2	85.74	2.45	83.29	4.76	79.34	11.33
2.5	68.41	1.95	62.12	3.55	59.29	8.47
3	54.22	1.55	53.76	3.07	38.72	5.53
3.5	26.74	0.76	23.41	1.34	16.79	2.40
4	8.3	0.24	6.33	0.36	4.5	0.64

Table 32 Effect of pH and initial metal ion concentration on Iron adsorption by bengal gram husk (Adsorbent dose = 0.25g/100ml)

pH	10 mg/L		20 mg/L		50 mg/L	
	% adsorbed	Fe (III) adsorbed (mg/g)	% adsorbed	Fe (III) adsorbed (mg/g)	% adsorbed	Fe (III) adsorbed (mg/g)
1	76	3.04	68.3	5.46	62	12.4
1.5	90.32	3.61	87.4	6.99	83.6	16.72
2	97.24	3.89	92.65	7.41	87.2	17.44
2.5	99.96	4.00	99.52	7.96	93.6	18.72

Table 33 Effect of pH and initial metal ion concentration on Iron adsorption by Tur dal husk (Adsorbent dose = 0.25g/100ml)

pH	10 mg/L		20 mg/L		50 mg/L	
	% adsorbed	Fe (III) adsorbed (mg/g)	% adsorbed	Fe (III) adsorbed (mg/g)	% adsorbed	Fe (III) adsorbed (mg/g)
1.5	58.45	2.34	44.5	3.56	24.2	4.84
2	95.48	3.82	88.15	7.05	81.23	16.25
2.5	99.56	3.98	93.14	7.45	87.14	17.43
3	67.36	2.69	56.7	4.54	41.65	8.33

Table 34 Effect of pH and initial metal ion concentration on Iron adsorption by Coffee husk (Adsorbent dose = 0.25g/100ml)

pH	10 mg/L		20 mg/L		50 mg/L	
	% adsorbed	Fe (III) adsorbed (mg/g)	% adsorbed	Fe (III) adsorbed (mg/g)	% adsorbed	Fe (III) adsorbed (mg/g)
2	69	2.76	52.94	4.23	25.9	5.18
2.5	83.33	3.33	64.32	5.14	48.42	9.68
3	94.68	3.78	83.52	6.68	78.23	15.64
3.5	57.02	2.28	41.21	3.29	16.98	3.39

Table 35 Effect of pH and initial metal ion concentration on Iron adsorption by tamarind husk (Adsorbent dose = 0.35g/100ml)

pH	10 mg/L		20 mg/L		50 mg/L	
	% adsorbed	Fe (III) adsorbed (mg/g)	% adsorbed	Fe (III) adsorbed (mg/g)	% adsorbed	Fe (III) adsorbed (mg/g)
2	86.32	2.47	72.41	4.14	53.33	7.62
2.5	99.01	2.83	95.4	5.45	81.81	11.69
3	45.21	1.29	41.65	2.38	26.43	3.78
3.5	16.23	0.46	12.25	0.70	9.56	1.37

Table36 Effect of pH and initial metal ion concentration on Mercury adsorption by bengal gram husk (Adsorbent dose = 0.5g/100ml)

pH	10 mg/L		20 mg/L		50 mg/L	
	% adsorbed	Hg (II) adsorbed (mg/g)	% adsorbed	Hg (II) adsorbed (mg/g)	% adsorbed	Hg(II) adsorbed (mg/g)
3	36.23	0.72	35.8	1.43	21.22	2.12
4	54.32	1.09	50.12	2.00	47.56	4.76
5	86.23	1.72	85.42	3.42	82.1	8.21
6	99.41	1.99	99.77	3.99	91.35	9.14
7	79.32	1.59	75.23	3.01	56.32	5.63

Table 37 Effect of pH and initial metal ion concentration on Mercury adsorption by Tur dal husk (Adsorbent dose = 0.1g/100ml)

pH	10 mg/L		20 mg/L		50 mg/L	
	% adsorbed	Hg (II) adsorbed (mg/g)	% adsorbed	Hg (II) adsorbed (mg/g)	% adsorbed	Hg(II) adsorbed (mg/g)
2	12.04	1.20	9.65	1.93	6.32	3.16
3	16.32	1.63	16.56	3.31	11.11	5.56
3.5	29.65	2.97	25.12	5.02	16.23	8.12
4	65.98	6.60	62.45	12.49	48.32	24.16
4.5	79.63	7.96	74.68	14.94	65.21	32.61
5	91.54	9.15	89.02	17.80	82.12	41.06
5.5	99.65	9.97	97.58	19.52	90.21	45.11
6	91.23	9.12	90.2	18.04	79.21	39.61
6.5	85.21	8.52	82.54	16.51	68.21	34.11

Table 38 Effect of pH and initial metal ion concentration on Mercury adsorption by Coffee husk (Adsorbent dose = 0.2g/100ml)

pH	10 mg/L		20 mg/L		50 mg/L	
	% adsorbed	Hg (II) adsorbed (mg/g)	% adsorbed	Hg (II) adsorbed (mg/g)	% adsorbed	Hg(II) adsorbed (mg/g)
2	16.56	0.83	12.56	1.26	9.54	2.39
3	37.5	1.88	32.45	3.25	29.42	7.36
4	56.49	2.82	51.23	5.12	45.38	11.35
5	79.24	3.96	72.35	7.24	69.4	17.35
6	97.98	4.90	94.82	9.48	91.35	22.84
7	80.15	4.01	76.32	7.63	73.56	18.39
8	32.54	1.63	29.68	2.97	25.32	6.33

Table 39 Effect of pH and initial metal ion concentration on Mercury adsorption by Tamarind husk (Adsorbent dose = 0.1g/100ml)

pH	10 mg/L		20 mg/L		50 mg/L	
	% adsorbed	Hg (II) adsorbed (mg/g)	% adsorbed	Hg (II) adsorbed (mg/g)	% adsorbed	Hg(II) adsorbed (mg/g)
3	23.24	2.32	18.12	3.62	16.23	8.12
3.5	35.64	3.56	29.54	5.91	23.88	11.94
4	44.21	4.42	36.41	7.28	31.18	15.59
4.5	56.49	5.65	49.21	9.84	42.31	21.16
5	75.68	7.57	65.17	13.03	59.27	29.64
5.5	93.45	9.35	79.82	15.96	74.58	37.29
6	96.54	9.65	90.14	18.03	87.85	43.93
6.5	91.24	9.12	81.23	16.25	83.12	41.56
7	83.25	8.33	73	14.60	71.14	35.57
7.5	71.24	7.12	68.44	13.69	61.25	30.62

Table 40 Effect of pH and initial metal ion concentration on Nickel adsorption by bengal gram husk (Adsorbent dose = 0.2g/100ml)

pH	10 mg/L		20 mg/L		50 mg/L	
	% adsorbed	Ni (II) adsorbed (mg/g)	% adsorbed	Ni (II) adsorbed (mg/g)	% adsorbed	Ni (II) adsorbed (mg/g)
2	21.12	1.06	18.43	1.84	14.21	3.55
3	56.12	2.81	41.85	4.19	39.78	9.95
4	90.12	4.51	87.25	8.73	88.21	22.05
5	99.01	4.95	99.39	9.94	99.33	24.83
6	89.03	4.45	87.34	8.73	88.22	22.06
7	76.45	3.82	68.78	6.88	65.34	16.34

Table 41 Effect of pH and initial metal ion concentration on Nickel adsorption by tur dal husk (Adsorbent dose = 0.5g/100ml)

pH	10 mg/L		20 mg/L		50 mg/L	
	% adsorbed	Ni (II) adsorbed (mg/g)	% adsorbed	Ni (II) adsorbed (mg/g)	% adsorbed	Ni (II) adsorbed (mg/g)
2	12.05	0.24	10.22	0.41	7.44	0.74
3	49.56	0.99	45.21	1.81	34.12	3.41
4	76.57	1.53	62.89	2.52	59.85	5.99
5	99.07	1.98	99.39	3.98	99.5	9.95
6	85.41	1.71	82.31	3.29	79.65	7.97
7	69.54	1.39	59.1	2.36	55.21	5.52

Table 42 Effect of pH and initial metal ion concentration on Nickel adsorption by coffee husk (Adsorbent dose = 0.5g/100ml)

pH	10 mg/L		20 mg/L		50 mg/L	
	% adsorbed	Ni (II) adsorbed (mg/g)	% adsorbed	Ni (II) adsorbed (mg/g)	% adsorbed	Ni (II) adsorbed (mg/g)
2	15.32	0.31	13.21	0.53	8.56	0.86
3	45.63	0.91	41.32	1.65	39.41	3.94
4	88.56	1.77	84.23	3.37	72.21	7.22
5	99.58	1.99	98.45	3.94	83.22	8.32
6	49.36	0.99	41.31	1.65	29.74	2.97

Table 43 Effect of pH and initial metal ion concentration on Nickel adsorption by tamarind husk (Adsorbent dose = 0.2g/100ml)

pH	10 mg/L		20 mg/L		50 mg/L	
	% adsorbed	Ni (II) adsorbed (mg/g)	% adsorbed	Ni (II) adsorbed (mg/g)	% adsorbed	Ni (II) adsorbed (mg/g)
3	18	0.90	12.3	1.23	8.52	2.13
3.5	29.15	1.46	21.45	2.15	13.56	3.39
4	43.56	2.18	34.98	3.50	31.25	7.81
4.5	69.48	3.47	63.86	6.39	59.21	14.80
5	89.25	4.46	78.23	7.82	69.21	17.30
5.5	94.98	4.75	91.22	9.12	84.12	21.03
6	95.12	4.76	90.22	9.02	85.22	21.31
6.5	84.21	4.21	82.45	8.25	71.65	17.91
7	75.44	3.77	70.21	7.02	62.12	15.53

5.3.4 Adsorption Isotherms

Data for Langmuir isotherms for Chromium adsorption by the four adsorbents is given in Figures 54 to 57. Figures 58 to 61 give the Iron adsorption by the four adsorbents; Figures 62 to 65 present the Langmuir isotherms for mercury adsorption by the four husks and Figures 66 to 69 present the Langmuir isotherms for nickel adsorption. The plots of langmuir isotherms C_{eq}/q vs C_{eq} show that all the adsorbents followed the Langmuir isotherm with respect to the metal ions.

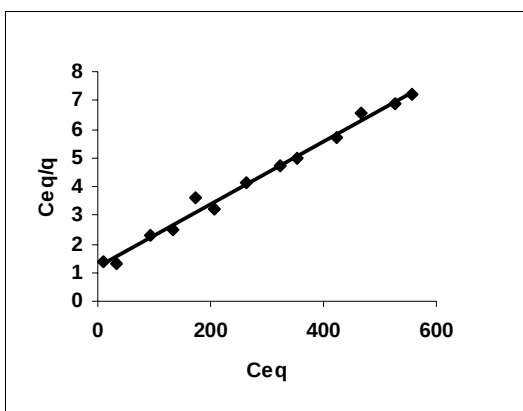


Figure: 54

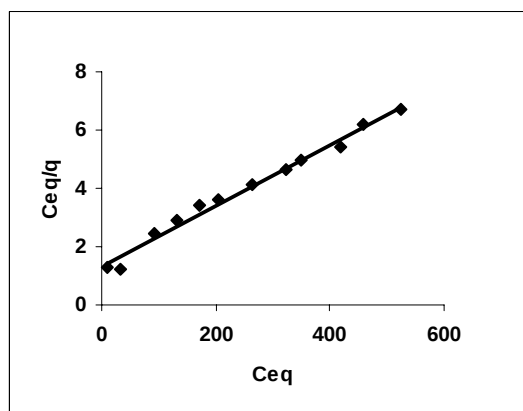


Figure: 55

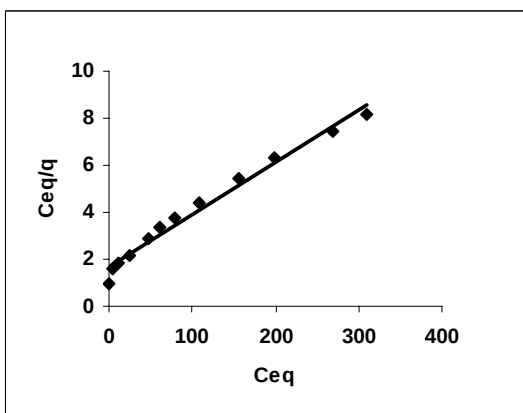


Figure: 56

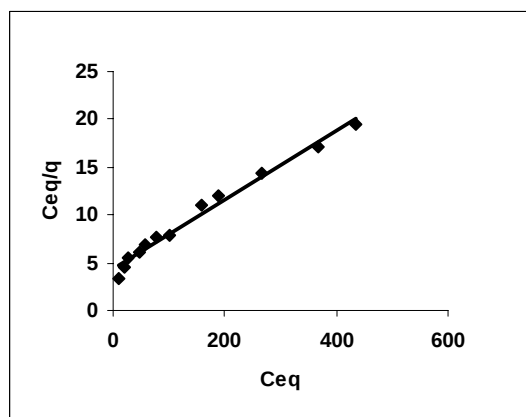


Figure: 57

Figure 54-57 Langmuir adsorption isotherm for Cr (VI) by BGH, TDH, CH and TH respectively

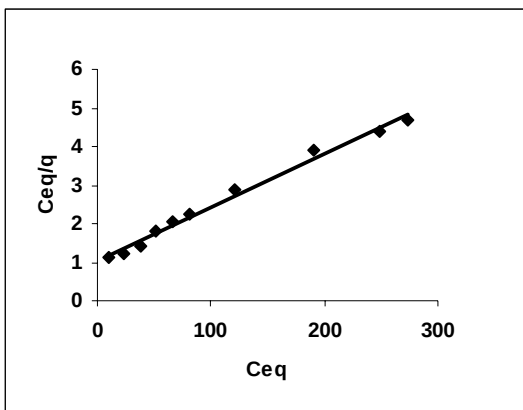


Figure: 58

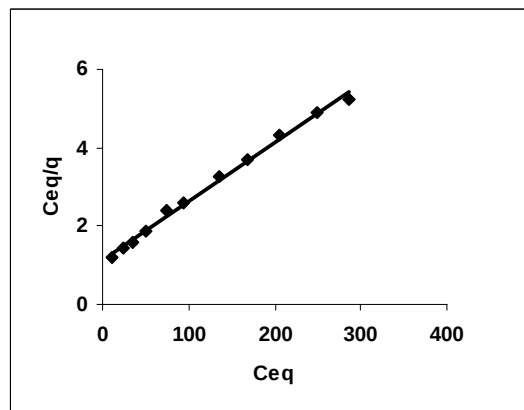


Figure: 59

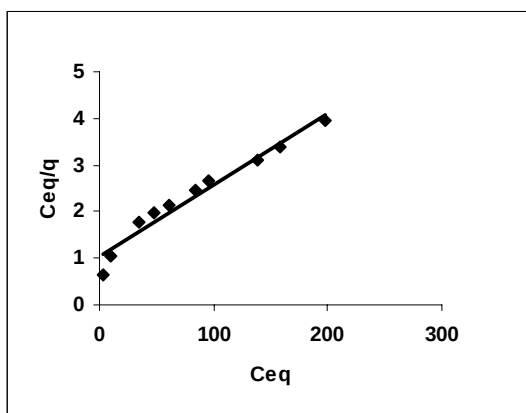


Figure: 60

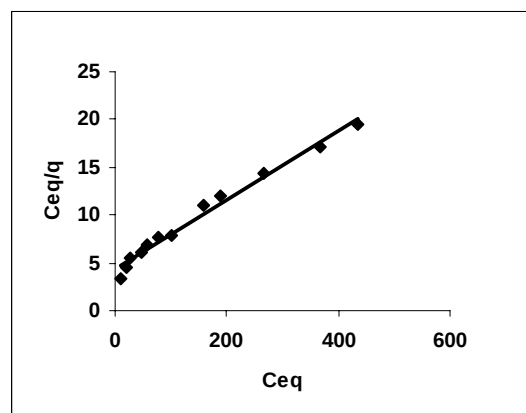


Figure: 61

Figure 58-61 Langmuir adsorption isotherm for Iron biosorption by BGH, TDH, CH and TH respectively

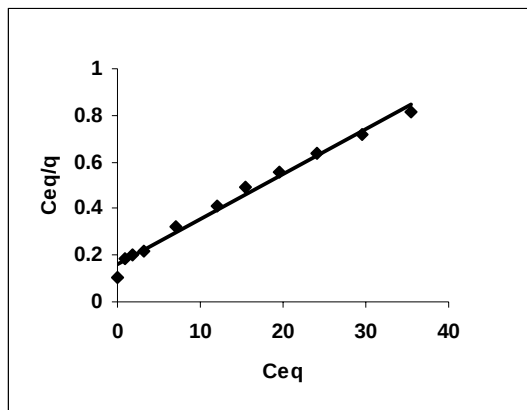


Figure: 62

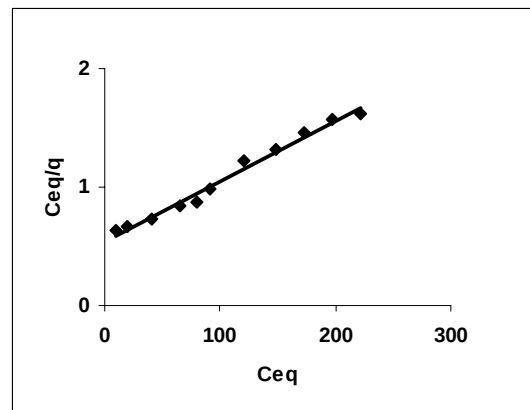


Figure: 63

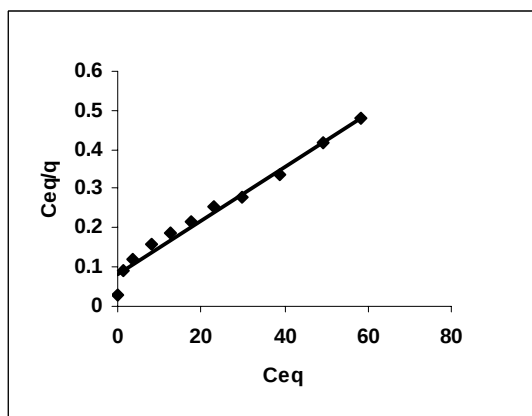


Figure: 64

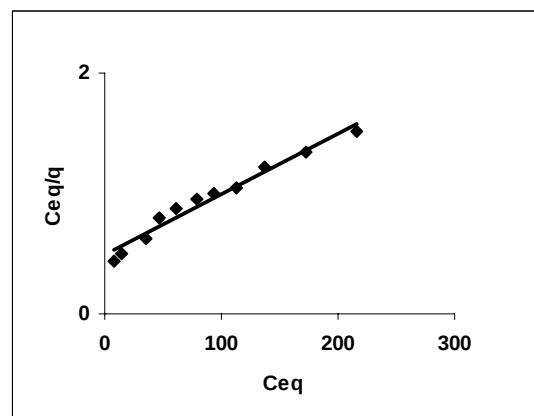


Figure: 65

Figure 62-65 Langmuir adsorption isotherm for mercury by BGH, TDH, CH and TH respectively

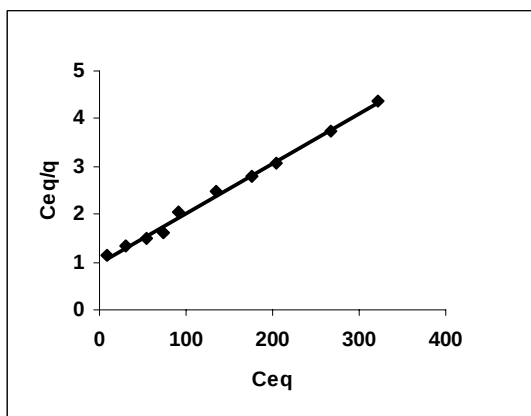


Figure: 66

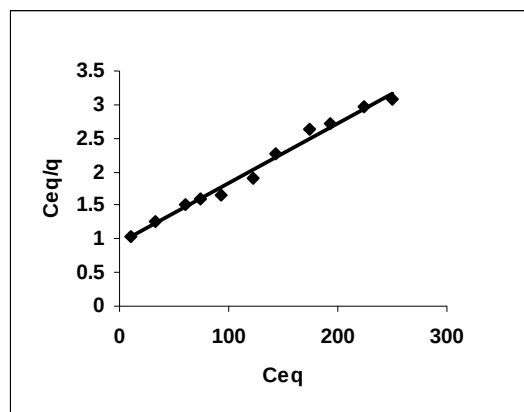


Figure: 67

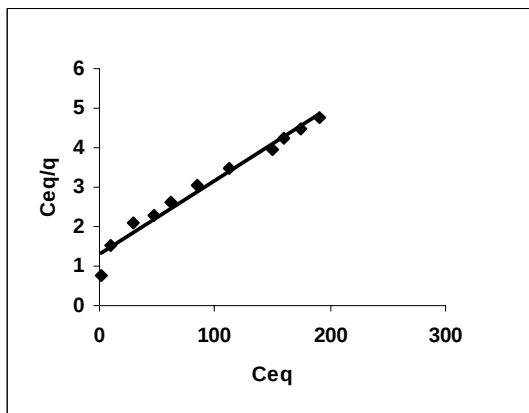


Figure: 68

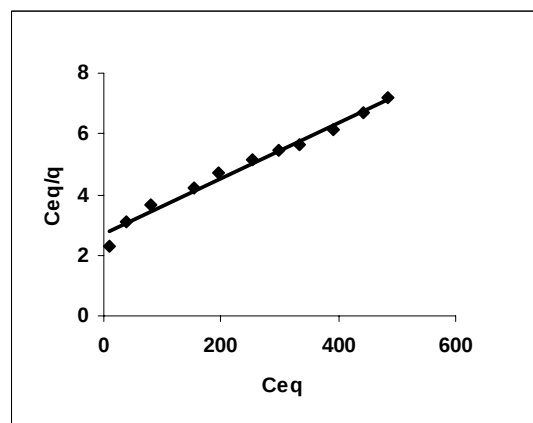


Figure: 69

Figure 66-69 Langmuir adsorption isotherm for Nickel by BGH, TDH, CH and TH respectively

Data for Freundlich plots are given in Figures 70 to 73 for chromium biosorption by BGH; TDH, CH and TH respectively. The Freundlich plots are given in Figures 74 to 77 and Figures 78 to 81 for iron and mercury biosorption by BGH; TDH, CH and TH. The Freundlich plots for nickel adsorption by the four husks are given in Figures 82 to 85. The linear plots of $\ln C_{eq}$ vs $\ln q$ for all the adsorbents showed that Freundlich isotherm was followed.

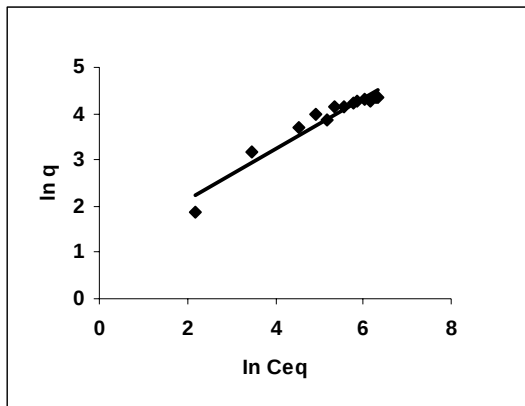


Figure: 70

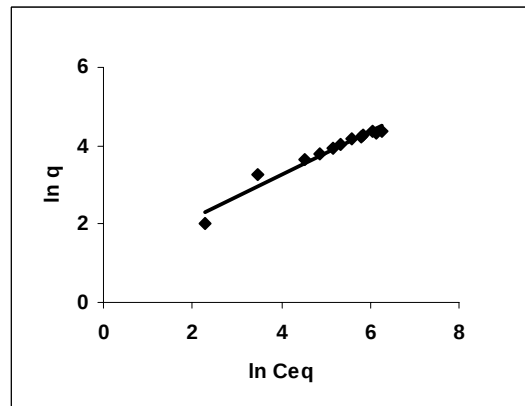


Figure: 71

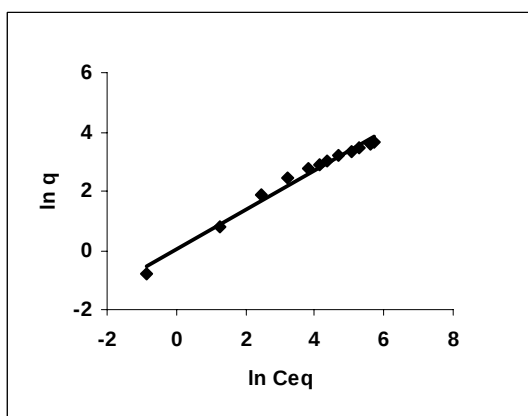


Figure: 72

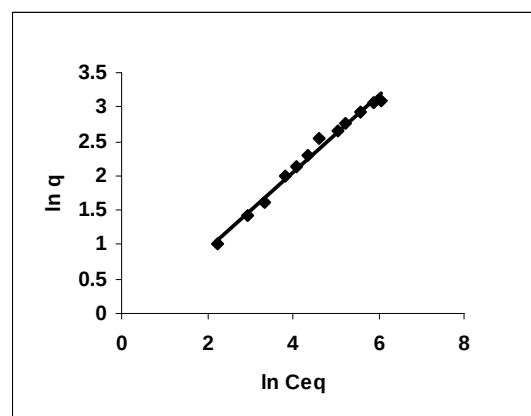


Figure: 73

Figure 70-73 Freundlich adsorption isotherm for Chromium (VI) by BGH, TDH, CH and TH respectively

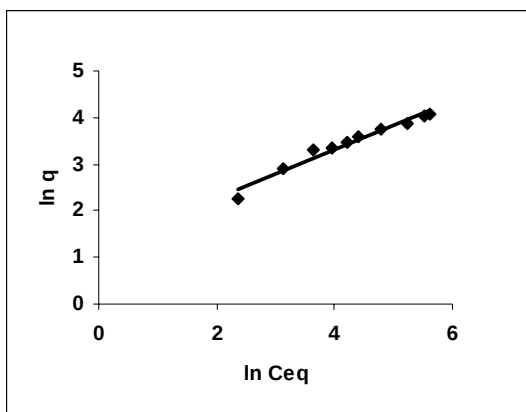


Figure: 74

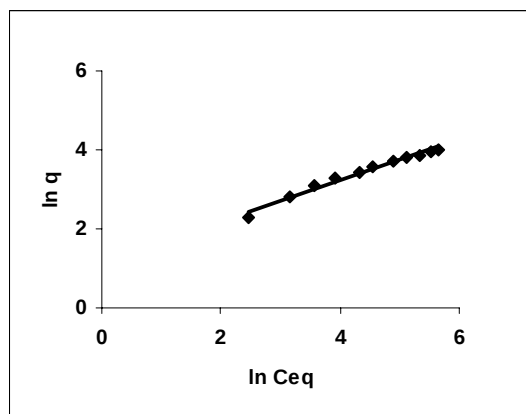


Figure: 75

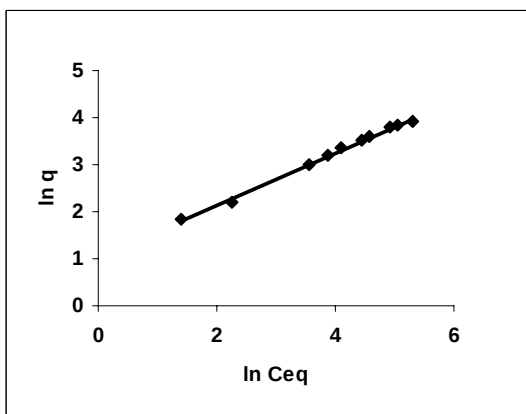


Figure 76

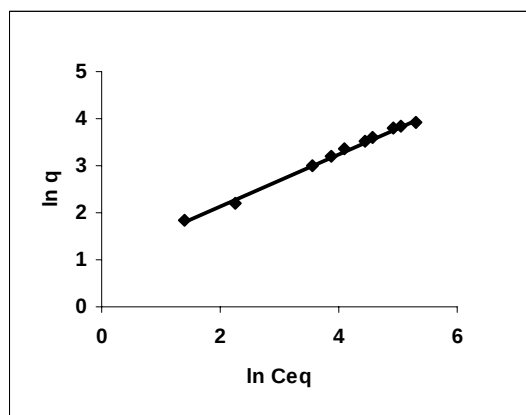


Figure: 77

Figure 74-77 Freundlich adsorption isotherm for Iron biosorption by BGH, TDH, CH and TH respectively

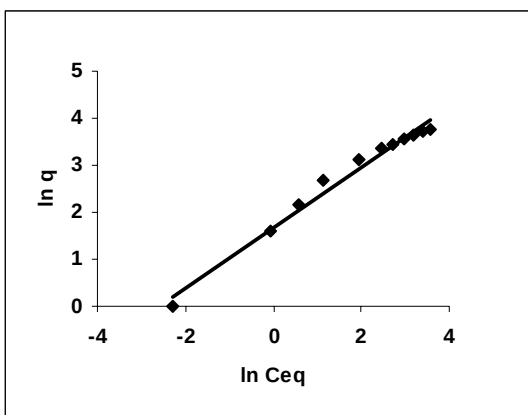


Figure: 78

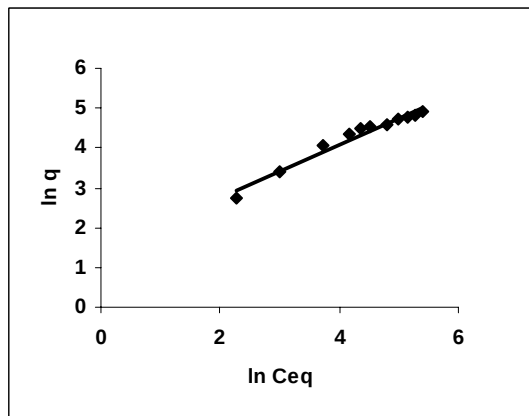


Figure: 79

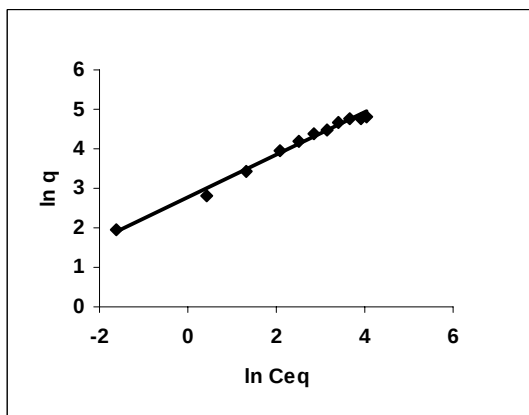


Figure: 80

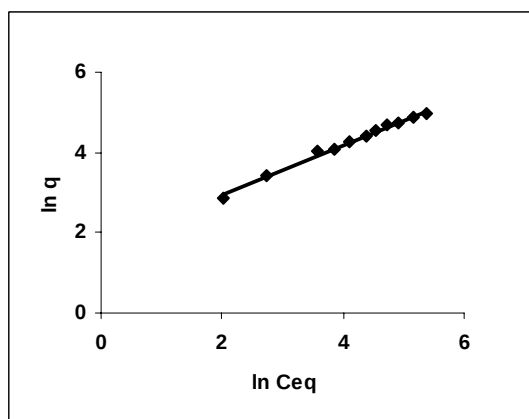


Figure: 81

Figure 78-81 Freundlich adsorption isotherm for mercury (II) by BGH, TDH, CH and TH respectively

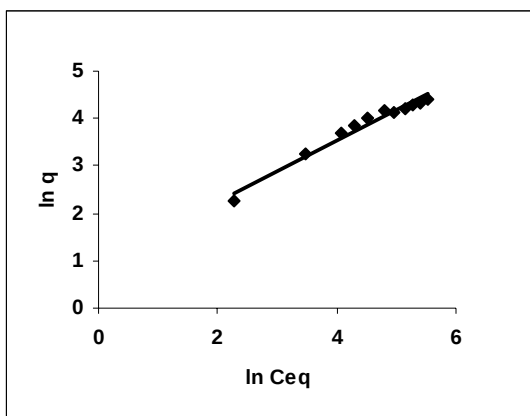


Figure: 82

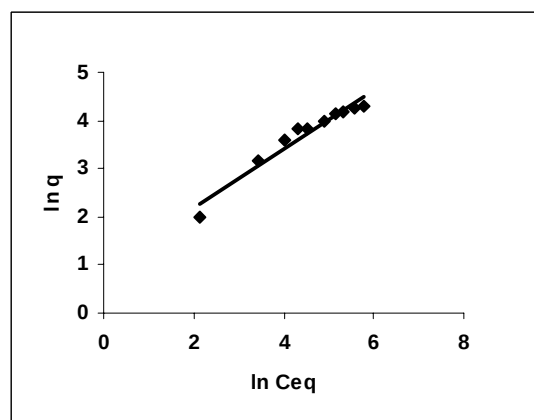


Figure: 83

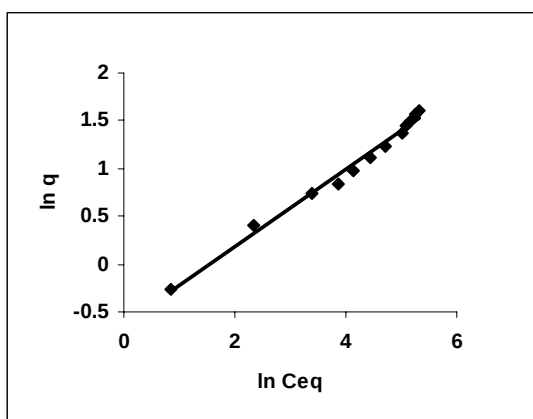


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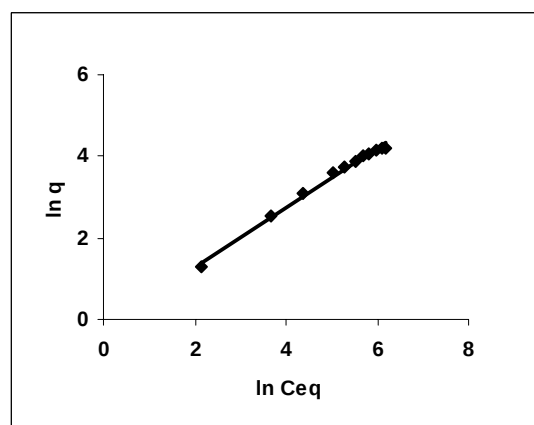


Figure: 85

Figure 82-85 Freundlich adsorption isotherm for Nickel (II) by BGH, TDH, CH and TH respectively

The Langmuir and Freundlich constants calculated from the isotherm equations are given in Tables 44 to 47 for adsorption of metals Chromium, iron, mercury and nickel by BGH, TDH, TH and CH. The maximum adsorption capacity for BGH with respect to metals were nickel>chromium>iron >mercury. Tur dal husk showed maximum adsorption capacity of mercury followed by iron, chromium and nickel. Tamarind husk was efficient in the biosorption of mercury followed by nickel, iron and chromium. Coffee husk showed least biosorption capacity for chromium and maximum for mercury.

Table 44 Sorption isotherm constants and coefficients of determination adsorption of metal ions for BGH

	Langmuir equation			Freundlich equation		
	$Q_{\max}$ (mg/g)	b (l/mg)	R^2	K_F (mg/g)	n	R^2
Iron	72.16	0.01	0.98	1.649	3.4	0.96
Chromium	91.64	0.009	0.98	2.81	1.81	0.92
Mercury	51.85	0.11	0.98	5.31	1.56	0.98
Nickel	112.22	0.009	0.98	9.19	1.56	0.97

Table45 Sorption isotherm constants and coefficients of determination for adsorption of metal ions by TDH

	Langmuir equation			Freundlich equation		
	$Q_{\max}$ (mg/g)	b (l/mg)	R^2	K_F (mg/g)	n	R^2
Iron	66.63	0.01	0.99	1.45	1.82	0.97
Chromium	96.05	0.007	0.98	2.95	1.83	0.95
Nickel	96.58	0.01	0.99	8.19	1.62	0.95
Mercury	196.32	0.009	0.98	4.05	1.49	0.96

Table 46 Sorption isotherm constants and coefficients of determination for adsorption of metal ions TH

	Langmuir equation			Freundlich equation		
	$q_{\max}$ (mg/g)	b (l/mg)	R^2	K_F (mg/g)	n	R^2
Iron	56.55	0.01	0.96	5.5	1.61	0.98
Chromium	27.73	0.008	0.98	1.17	1.8	0.98
Mercury	184.39	0.011	0.97	5.5	1.66	0.98
Nickel	111.11	0.003	0.98	1.48	1.37	0.99

Table 47 Sorption isotherm constants and coefficients of determination for adsorption of metal ions CH

	Langmuir equation			Freundlich equation		
	$q_{\max}$ (mg/g)	b (l/mg)	R^2	K_F (mg/g)	n	R^2
Iron	64.80	0.01	0.97	1.47	2.12	0.99
Chromium	44.95	0.01	0.98	1.02	1.49	0.98
Mercury	145.73	0.084	0.97	15.96	1.88	0.98
Nickel	54	0.014	0.97	4.16	2.5	0.98

Table 48 Equilibrium parameter (R_L) for adsorption of metals

Adsorbent	Adsorbate	R_L
Bengal gram husk (BGH)	Chromium (VI)	$8.4 \times 10^{-1} - 1.5 \times 10^{-1}$
	Iron (III)	$8.3 \times 10^{-1} - 1.4 \times 10^{-1}$
	Nickel (II)	$8.4 \times 10^{-1} - 1.5 \times 10^{-1}$
	Mercury (II)	$3.1 \times 10^{-1} - 1.4 \times 10^{-2}$
Tur dal husk (TDH)	Chromium (VI)	$8.7 \times 10^{-1} - 1.9 \times 10^{-1}$
	Iron (III)	$8.4 \times 10^{-1} - 1.5 \times 10^{-1}$
	Nickel (II)	$8.4 \times 10^{-1} - 1.5 \times 10^{-1}$
	Mercury (II)	$8.4 \times 10^{-1} - 1.5 \times 10^{-1}$
Tamarind husk (TH)	Chromium (VI)	$8.6 \times 10^{-1} - 1.7 \times 10^{-1}$
	Iron (III)	$8.4 \times 10^{-1} - 1.5 \times 10^{-1}$
	Nickel (II)	$9.4 \times 10^{-1} - 3.5 \times 10^{-1}$
	Mercury (II)	$8.1 \times 10^{-1} - 1.3 \times 10^{-1}$
Coffee husk (CH)	Chromium (VI)	$8.4 \times 10^{-1} - 1.5 \times 10^{-1}$
	Iron (III)	$8.4 \times 10^{-1} - 1.5 \times 10^{-1}$
	Nickel (II)	$7.8 \times 10^{-1} - 1.9 \times 10^{-2}$
	Mercury (II)	$3.7 \times 10^{-1} - 1.9 \times 10^{-2}$

5.3.5 Adsorption kinetics

Lagergren plots of $\log_{10} (q_e - q)$ vs t for the adsorption of chromium VI by BGH, TDH and TH at various initial metal ion concentrations is given in Figures 86 to 88. The kinetics of adsorption of iron by TDH, TH and CH are given in Figures 89 to 91; mercury adsorption in Figures 92 to 95 and nickel adsorption in Figures 96 to 99.

The rate constants that are derived from the Lagergren equation are given in Tables 49 to 62 for metal ions. The linear plots of $\log_{10} (q_e - q)$ vs t show that the adsorption follows a pseudo first order reaction.

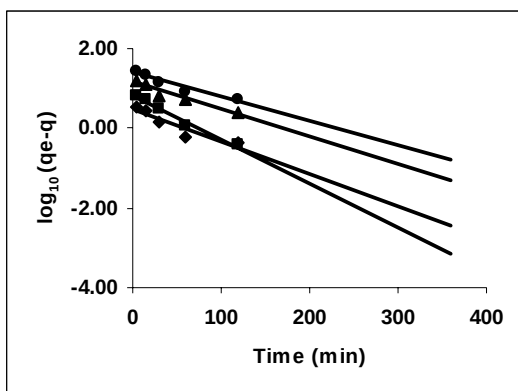


Figure: 86

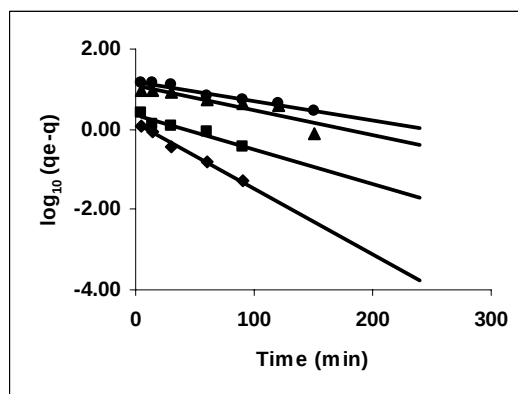


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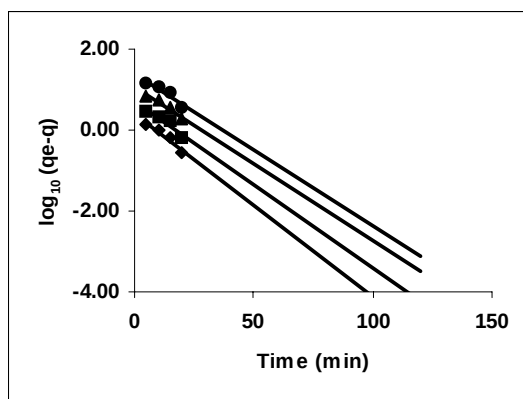


Figure: 88

Figure 86-88 Lagergren plots for Chromium by BGH, CH and TH respectively ($\blacklozenge$ 10 mg/L $\blacksquare$ 20 mg/L $\blacktriangle$ 50 mg/L $\bullet$ 100mg/L)

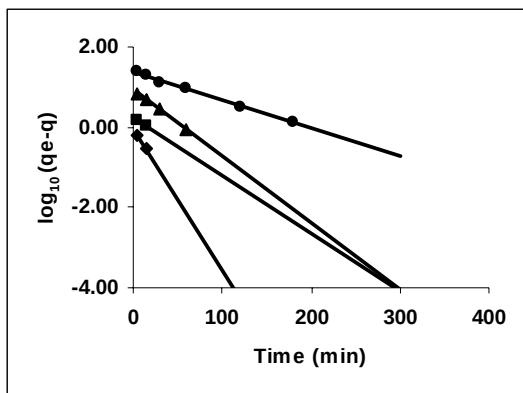


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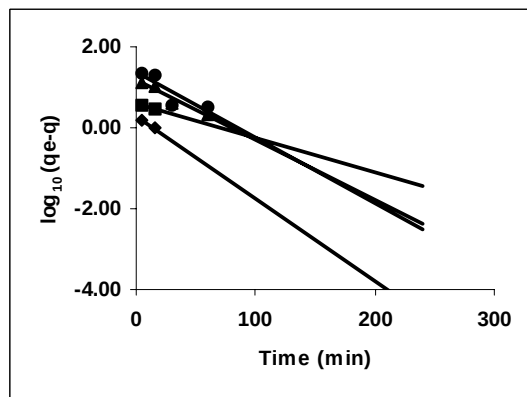


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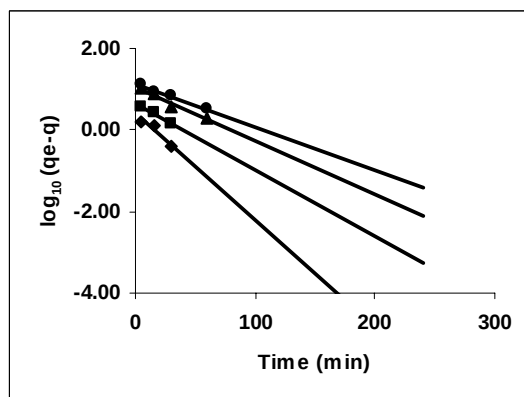


Figure: 91

Figure 89-91 Lagergren plots for Iron adsorption by TDH, CH and TH respectively (♦ 10 mg/L ■ 20 mg/L ▲ 50 mg/L ● 100mg/L)

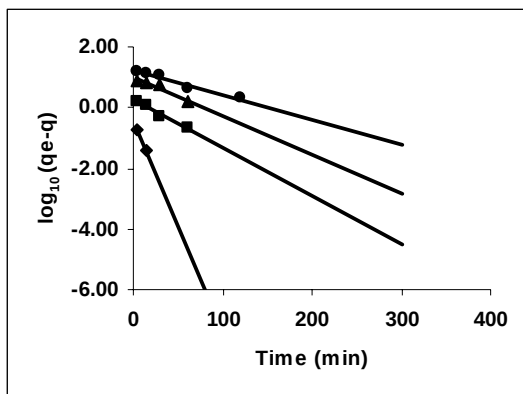


Figure: 92

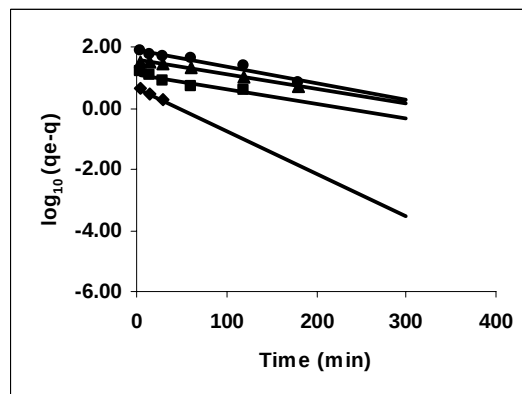


Figure: 93

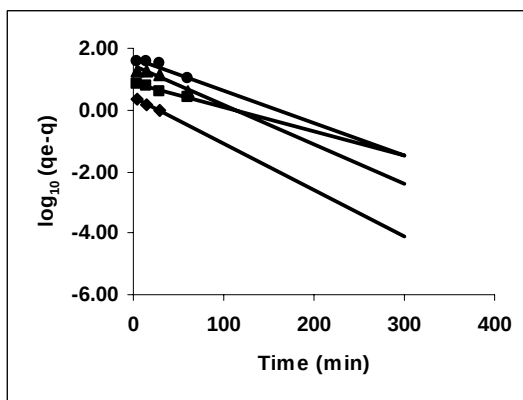


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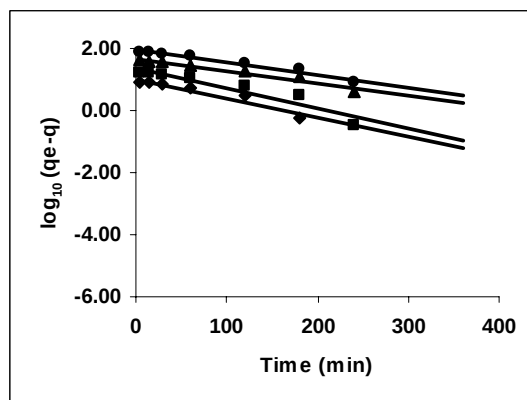


Figure: 95

Figure 92-95 Lagergren plots for Mercury adsorption by TDH, CH and TH respectively (♦ 10 mg/L ■ 20 mg/L ▲ 50 mg/L ● 100mg/L)

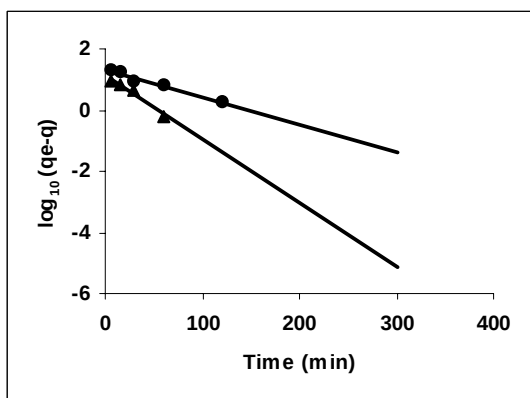


Figure: 96

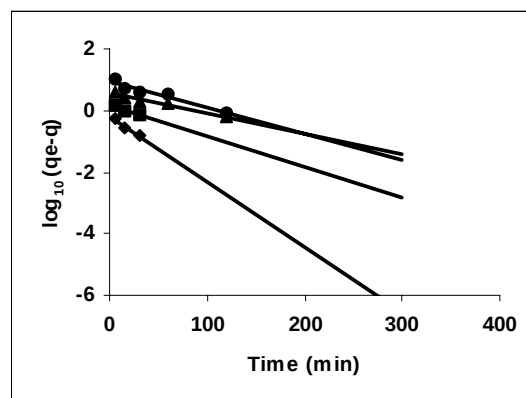


Figure: 97

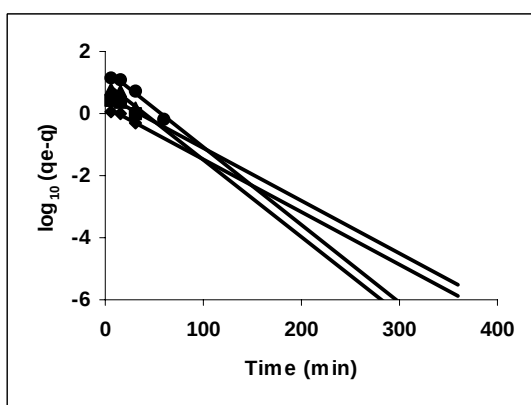


Figure: 98

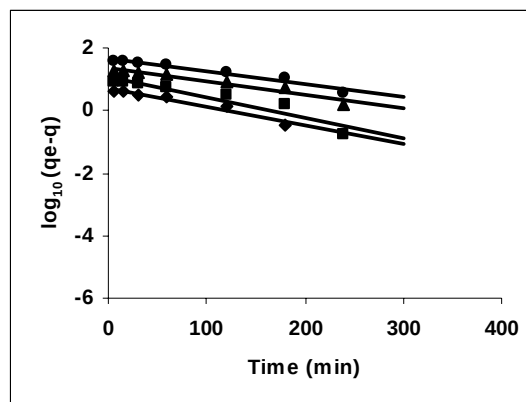


Figure: 99

Figure 96-99 Lagergren plots for Nickel adsorption by BGH, TDH, CH and TH respectively ($\diamond$ 10 mg/L $\blacksquare$ 20 mg/L $\blacktriangle$ 50 mg/L $\bullet$ 100mg/L)

Table 49 Effect of initial chromium (VI) concentration on Lagergren rate constant by bengal gram husk (Adsorbent dose – 0.2g/100 mL; pH 2.0)

Initial metal concentration (mg/L)	Kad (l/min)	R ²
10	1.85 X 10 ⁻²	0.8577
20	2.5 X10 ⁻²	0.9764
50	1.5 X 10 ⁻²	0.9403
100	1.3 X 10 ⁻²	0.9161

Table50 Effect of initial chromium (VI) concentration on Lagergren rate constant by coffee husk (Adsorbent dose – 0.5 g/100 mL; pH 2.0)

Initial metal concentration (mg/L)	Kad (l/min)	R ²
10	3.7 X 10 ⁻²	0.9911
20	1.9 X10 ⁻²	0.9438
50	1.4 X 10 ⁻²	0.8219
100	1.1 X 10 ⁻²	0.9760

Table51 Effect of initial chromium (VI) concentration on Lagergren rate constant by Tamarind husk (Adsorbent dose – 0.35g/100 mL; pH 2.0)

Initial metal concentration (mg/L)	Kad (l/min)	R ²
10	1.04 X 10 ⁻¹	0.9482
20	9.4 X10 ⁻²	0.9209
50	8.7 X 10 ⁻²	0.9686
100	8.6 X 10 ⁻²	0.9089

Table 52 Effect of initial Iron (III) concentration on Lagergren rate constant by tur dal husk (Adsorbent dose – 0.25g/100 mL; pH 2.5)

Initial metal concentration (mg/L)	Kad (l/min)	R ²
10	8.1 X 10 ⁻²	1
20	3.3 X10 ⁻²	1
50	3.8 X 10 ⁻²	0.9983
100	1.6 X 10 ⁻²	0.9952

Table 53 Effect of initial Iron (III) concentration on Lagergren rate constant by coffee husk (Adsorbent dose – 0.25g/100 mL; pH 2.5)

Initial metal concentration (mg/L)	Kad (l/min)	R ²
10	4.7 X 10 ⁻²	0.99
20	1.9 X10 ⁻²	0.8720
50	3.4 X 10 ⁻²	0.9760
100	3.7 X 10 ⁻²	0.99

Table 54 Effect of initial Iron (III) concentration on Lagergren rate constant by tamarind husk (Adsorbent dose – 0.35g/100 mL; pH 2.5)

Initial metal concentration (mg/L)	Kad (l/min)	R ²
10	6.06 X 10 ⁻²	0.9472
20	3.7 X10 ⁻²	0.9828
50	3.05 X 10 ⁻²	0.9739
100	2.4 X 10 ⁻²	0.9909

Table 55 Effect of initial mercury (II) concentration on Lagergren rate constant by bengal gram husk (Adsorbent dose – 0.5g/100 mL; pH 6.0)

Initial metal concentration (mg/L)	Kad (l/min)	R ²
10	1.6 X 10 ⁻¹	0.99
20	3.6 X10 ⁻²	0.9846
50	2.9 X 10 ⁻²	0.9244
100	1.9 X 10 ⁻²	0.9553

Table 56 Effect of initial mercury (II) concentration on Lagergren rate constant by tur dal husk (Adsorbent dose – 0.1g/100 mL; pH 6.0)

Initial metal concentration (mg/L)	Kad (l/min)	R ²
10	3.2 X 10 ⁻¹	0.9949
20	1.1 X10 ⁻²	0.8903
50	1.06 X 10 ⁻²	0.9939
100	1.25 X 10 ⁻²	0.9493

Table 57 Effect of initial mercury (II) concentration on Lagergren rate constant by coffee husk (Adsorbent dose – 0.2g/100 mL; pH 6.0)

Initial metal concentration (mg/L)	Kad (l/min)	R ²
10	3.4 X 10 ⁻²	0.9832
20	1.78 X10 ⁻²	0.9787
50	2.93 X 10 ⁻²	0.9152
100	2.4 X 10 ⁻²	0.9278

Table 58 Effect of initial mercury (II) concentration on Lagergren rate constant by tamarind husk (Adsorbent dose – 0.1g/100 mL; pH 6.0)

Initial metal concentration (mg/L)	Kad (l/min)	R ²
10	1.4 X 10 ⁻²	0.9386
20	1.49 X10 ⁻²	0.8876
50	9.1 X 10 ⁻³	0.9501
100	9.2 X 10 ⁻³	0.9683

Table 59 Effect of initial nickel (II) concentration on Lagergren rate constant by bengal gram husk (Adsorbent dose – 0.2g/100 mL; pH 5.0)

Initial metal concentration (mg/L)	Kad (l/min)	R ²
10		
20		
50	4.7 X 10 ⁻²	0.9533
100	2.07 X 10 ⁻²	0.9831

Tables 60 Effect of initial nickel (II) concentration on Lagergren rate constant by tur dal husk (Adsorbent dose – 0.5g/100 mL; pH 5.0)

Initial metal concentration (mg/L)	Kad (l/min)	R ²
10	1.4 X 10 ⁻²	0.9675
20	2.3 X10 ⁻²	0.8406
50	1.5 X 10 ⁻²	0.9742
100	1.9X 10 ⁻²	0.9291

Table 61 Effect of initial nickel (II) concentration on Lagergren rate constant by coffee husk (Adsorbent dose – 0.5g/100 mL; pH 5.0)

Initial metal concentration (mg/L)	K _{ad} (l/min)	R ²
10	3.9 X 10 ⁻²	0.961
20	3.8 X10 ⁻²	0.9347
50	5.7 X 10 ⁻²	0.9177
100	5.7 X 10 ⁻²	0.9752

Table 62 Effect of initial nickel (II) concentration on Lagergren rate constant by tamarind husk (Adsorbent dose – 0.2g/100 mL; pH 5.0)

Initial metal concentration (mg/L)	K _{ad} (l/min)	R ²
10	1.38 X 10 ⁻²	0.9688
20	1.47 X10 ⁻²	0.889
50	9.9 X 10 ⁻³	0.9314
100	9.2 X 10 ⁻³	0.9688

5.3.6 Desorption studies

Figures 100 to 103 shows the effect of pH on the desorption of metal ions Chromium (VI), Iron (III), Mercury (II) and Nickel (II) by BGH, TDH, TH and CH. Chromium showed the least desorption capacity and mercury the maximum. The metals were desorbed faster from the tamarind husk when compared to other three adsorbents.

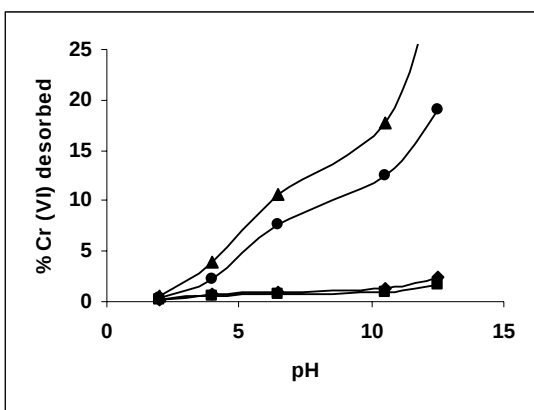


Figure: 100

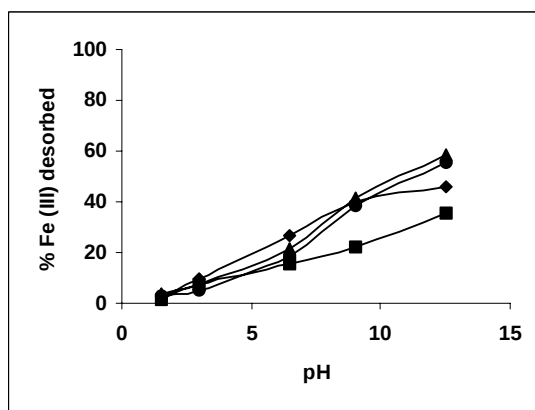


Figure: 101

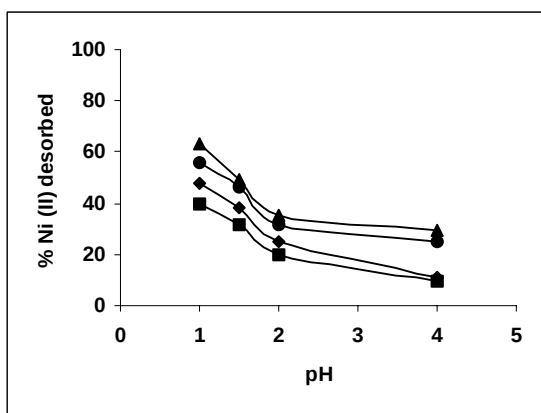


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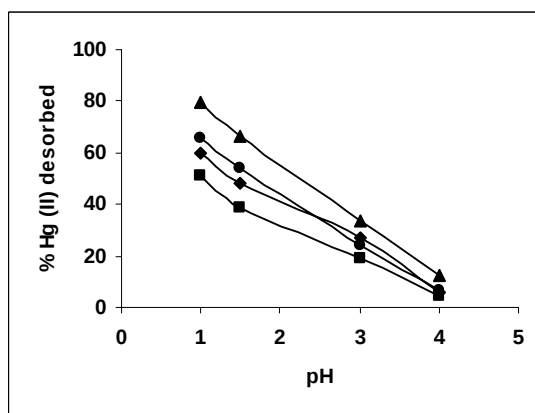


Figure: 103

Figure 100-103 Effect of pH on the desorption of Chromium (VI), Iron (III), Nickel (II) and Mercury (II) (♦ BGH ■ TDH ▲ CH ● TH)

6.0 DISCUSSION

6.1 CHARACTERISTICS OF THE ADSORBENT

The approximate percentages of total carbon, nitrogen and hydrogen in the four adsorbents namely bengal gram husk (BGH); tur dal husk (TDH); coffee husk (CH) and tamarind husk (TH) are shown in Table 11. The relatively low percentage of nitrogen (0.86% for BGH, 1.13% in TDH; 0.63 % in CH and 0.94% in TH) in comparison to the carbon quantities, indicates that few nitrogen containing compounds are involved in the adsorption of metals. A relatively larger percentage of hydrogen in comparison to nitrogen compounds indicates that carbon-hydrogen groups might be available for adsorption of metals. The relatively low percentage of nitrogen shows that very less percentage of protein might be present in the husks. This is advantageous over protein rich adsorbents since proteinous materials are likely to putrefy under moist conditions (Ahalya *et al.*, 2006).

6.2 INFRARED SPECTROSCOPIC STUDIES

Unreacted samples of the four adsorbents used in the present study namely bengal gram husk (BGH), Tur dal husk (TDH), coffee husk (CH) and tamarind husk (TH) were subjected to Fourier transform infrared spectroscopy (FTIR). The spectra obtained are presented in Figures 2 to 5 for BGH, TDH, TH and CH respectively.

The spectra of BGH sample (Figure 2) reveal the presence of several functional groups on the surface which facilitates the adsorption of metal ions. Wavenumber of 3000 and 3750 cm^{-1} for BGH indicates the presence of OH groups on the husk surface. The trough that is observed at 2918.18 cm^{-1} and 893.25 cm^{-1} indicates the presence of C-H groups. The 1634.34 cm^{-1} band is a result of CO stretching mode, conjugated to a NH deformation mode and is indicative of amide 1 band. The trough at 1115.57 cm^{-1} is due to CO or CN groups (Ahalya *et al.*, 2005).

The absorption spectra of TDH (Figure 3) display a broad, intense --OH stretching absorption trough at 3431 cm^{-1} , although the bands are dominated by the -OH stretch

due to bonded water. Weaker ---CH stretch bands are superimposed onto the side of the broad ---OH band at $3000\text{--}2800\text{ cm}^{-1}$. The strong peak at 1733 cm^{-1} is caused by the C=O stretching band of the carboxyl group. The peak at approximately 1100 cm^{-1} is due to either the C-O stretch of the ---OH bend. However, the N-H stretch (3300 cm^{-1}) and the C-N stretch (1000 cm^{-1}) are not seen in this spectra due to the dominance of the ---OH stretch (Ahalya *et al.*, 2006).

The spectrum of the pristine TH is complex due to the numerous and multifarious functional groups on the surface of the adsorbent (Figure 4). The broad and strong band ranging from 3200 to 3600 cm^{-1} may be due to the overlapping of OH and NH stretching, which is consistent with the peak at 1115 and 1161 cm^{-1} assigned to C-O and C-N stretching vibration, thus showing the presence of hydroxyl and amine groups on the adsorbent surface. The strong peak at 1674 cm^{-1} can be assigned to a C=O stretching in carboxyl or amide groups. The bands at 2936 and 1558 cm^{-1} are attributed to CH stretching and N-H bending, respectively.

The spectra of CH display a number of absorption peaks, indicating the complex nature of the material examined (Figure 5). The FTIR spectroscopic analysis indicated broad bands at 3412 cm^{-1} , representing bonded ---OH groups. The bands observed at about $2921\text{--}2851\text{ cm}^{-1}$ could be assigned to the C-H stretch. The peaks around 1733 cm^{-1} correspond to the C=O group and at $1652\text{--}1512\text{ cm}^{-1}$ C-O . This C-O band absorption peak is observed to shift to 1035 cm^{-1} . Thus, it seems that this type of functional group is likely to participate in metal binding (Ahalya *et al.*, 2006).

6.3 Batch mode studies

In order to evaluate the feasibility and economics of adsorption, laboratory batch mode studies were conducted. In this study the optimum agitation speed i.e., good contact between the adsorbent and adsorbate was established at 120 rpm . Parameters, which influence the extent of adsorption such as adsorbate concentration, agitation time, adsorbent dosage and pH were investigated. In addition to the above parameters, effect of pH on the desorption of metals were investigated. The use of the adsorbent for continuous use was also determined by regeneration studies.

6.3.1 Effect of agitation time and adsorbate concentration on adsorption

The uptake of adsorbate increased with the increase in contact time for all the metals studied and it remained constant after an equilibrium time are shown in Figures 7 to 22. The equilibrium time varied with the type of husk under consideration and it increased with the increase in initial metal concentration. Chromium adsorption by tur dal husk was independent of time and attained equilibrium within 5 minutes of contact. The equilibrium time was independent of the adsorbate concentration as seen by chromium adsorption by bengal gram husk, tur dal husk and tamarind husk. The adsorbate concentration influenced the equilibrium time of the metal uptake by rest of the adsorbents.

At any contact time, increase in initial adsorbate concentration decreased the percent adsorption and increased the amount of adsorbate uptake (q) per unit weight of the adsorbent. It is seen that for the low initial concentrations, the percent uptake of the adsorbate was high. Even though the percent uptake of the adsorbate was smaller at high initial concentrations, the actual amount of the metals adsorbed (q) increased with increase in the initial adsorbate concentration in the solution. The uptake (q) vs time curves were single, smooth and continuous leading to saturation, suggesting the possible monolayer coverage of the adsorbate on the surface of the adsorbent. Several authors have reported similar results for the adsorption of metals (Kanchana and Namasivayam, 1994; Namasivayam *et al* , 1993; Singh *et al* , 1992) Equilibrium time varied with the metals due to the difference in initial metal concentration and affinity of the adsorbent for the particular metal ion.

In all the experiments conducted, 100 ppm solutions took longer to attain equilibrium due to the presence of proportionally high amount of metal ions.

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

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

6.3.2 Effect of adsorbent dosage on adsorption

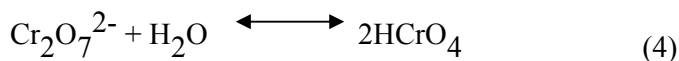
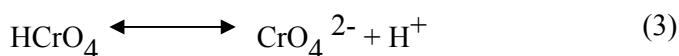
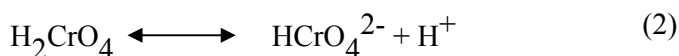
The biosorption of metal was studied at various biosorbent concentrations ranging from 0.5 to 5 mg/L. The percentage of metal removed increased with increase in adsorbent dosage due to increased adsorption surface area. For all the adsorbents studied adsorbent dosage of 1g – 2g/L was sufficient for adsorption of 90% of the initial metal concentration. Further increase in the adsorbent dosage did not show an increased removal of metal concentrations.

The percent removal of adsorbates increased with increase in adsorbent dosage and reached a particular constant value after a particular adsorbent dosage. This is also true for different pH values studied. A maximum removal of about 90% was obtained for all the adsorbates studied. However, the adsorbent dosage required for maximum percent removal varied with the concentration of initial metal ions. This is mainly due to the fact that a larger mass of adsorbent could adsorb larger amount of adsorbate due to the availability of more surface area of the adsorbent. But for each adsorbate (i.e. heavy metal) studied the amount of adsorbate adsorbed after equilibrium per unit weight of adsorbent is different.

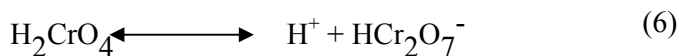
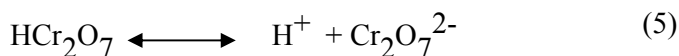
The extent of biosorption was limited by metal concentration at high adsorbent concentrations. At constant initial metal concentrations the biosorbent concentration should be low to maximize solid phase metal ion concentration at equilibrium. The results in the present study are in agreement with literature reports indicating lower biosorbed metal concentrations (q) at high adsorbent concentrations (Esposito *et al* , 2001). The primary factor explaining this characteristic is that adsorption sites remain unsaturated during the adsorption reaction, whereas the number of sites available for adsorption site increases by increasing the adsorbent dose.

6.3.3 Effect of pH on the adsorption of metal ions

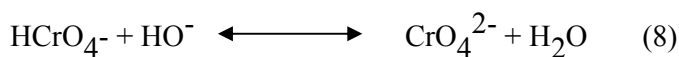
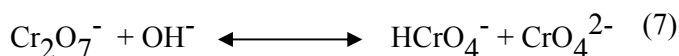
(i) **Chromium:** The percent removal of Cr (VI) increased with decrease in pH for the different concentrations of Cr (VI) which is typical of oxyanion adsorption on metal hydroxides. Similar optimum pH conditions were seen for all the four adsorbents. Chromium (VI) removal increased from 8.3% at pH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



In acidic solutions, the equilibrium is as follows:



The equilibrium in alkaline pH is given as:



The only species that can exist in solution, above pH 8.0 is CrO_4^{2-} . As the pH is shifted, the equilibrium will also shift; in the pH range 2-6, HCrO_4^- , and $\text{Cr}_2\text{O}_7^{2-}$,

ions are in equilibrium. At still lower pH (pH <2.0) values, $\text{Cr}_3\text{O}_{10}^-$ and $\text{Cr}_4\text{O}_{13}^{2-}$ species are formed. Thus the formation of more polymerized chromium oxide species occurs with the decrease in solution pH.

In highly acidic media, the adsorbent surfaces are highly protonated and favour the uptake of Cr (VI) in the anionic form HCrO_4^- . The removal of Cr (VI) by carbonaceous materials such as saw dust, sugar beet, sugar beet pulp, sugarcane bagasse and maize cob at an optimum pH 2.0 has been reported by Sharma and Forster (1994).

(ii) Nickel (II): The effect of pH on nickel biosorption is illustrated in Figures 75 to 78 for all the four husks. The percentage biosorption and the amount biosorbed are presented in Tables 66 for bengal gram husk, Tables 67 for tur dal husk, Table 69 for tamarind husk and Table 68 for coffee husk. The optimum pH for nickel adsorption for all the husks is 5 to 5.5. Adsorption is high at pH 5.0 and decreases as the pH increases or decreases. At low pH value, the H^+ ions compete with metal cation for the exchange sites in the system thereby partially releasing the metal cations (Ajmal *et al.*, 2000). pH affects both cell surface metal binding sites and metal chemistry in water. At low pH values, the functional groups of the biosorbent are closely associated with the hydronium ions and repulsive forces limit the approach of the metal ions. With increasing pH, more functional groups such as amino and carbonyl groups, would be exposed leading to attraction between these negative charges and the metals and hence increases in biosorption on to the surface of adsorbent (Aksu, 2001). The lower uptake at higher pH value is probably due to the formation of anionic hydroxide complexes (Maquieira *et al.*, 1994).

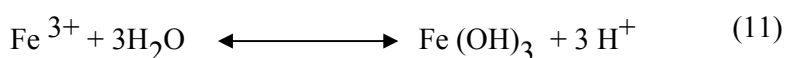
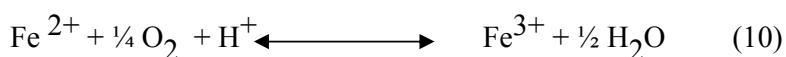
The reaction of nickel ions in the solution with the biomass can be described by the following equilibrium:



Where M represents the metal, n its charge and B the biosorptive active centers. According to reaction, the pH should influence the metal ions biosorption because of the competition between the metal and H^+ ions for the active biosorption sites.

(iii) Iron (III): The optimum pH for biosorption of ferric iron on to the four husks was observed at pH 2.5. To avoid precipitation of ferric ion as their hydroxides, all the experiments were carried below pH 3.5. The solution pH influences both the metal binding sites as well as metal chemistry in solution. The initial adsorption rates increased with increasing initial pH up to optimum pH values. At higher pH values, Fe (III) precipitated because of the high concentration of OH ions in the adsorption medium (Ozer *et al* , 1999; Sag and Kutsal, 1996) and so adsorption experiments at pH>3 could not be performed. The percentage of Ferric ions adsorbed at pH 2.5 decreased with increasing metal concentration, but the amount of metal ion adsorbed increased with increase in initial iron concentration.

Iron typically enters water bodies in the form of ferrous iron (Fe^{2+}), which can be oxidised to ferric iron (Fe^{3+}) by the oxygen dissolved in water. The rate of oxidation reaction depends primarily on the pH and on the level of dissolved oxygen in water (DO). At pH <4 and a relatively low dissolved oxygen, the oxidation process to ferric iron is very slow. At pH>4, however Fe^{2+} ions oxidise quickly to Fe^{3+} ions which then react with water producing ferric hydroxide precipitate and acidity



If the pH drops below 3, the ferric ions cease to precipitate and remain in water in partially hydrolysed forms.

(iv) Mercury (II): The optimum pH at which mercury was maximally absorbed by all the four husks is 5.5 to 6 . The percentage and the amount of mercury adsorbed increased with increase in pH. On increasing the pH from 4, the percentage removal increased and became quantitative over the pH range 5.0 –6.0. It is expected that the adsorption of metals decreases at low pH values because of competition for binding sites between cations and protons (Sahoo *et al* , 1992), while at pH higher than 7, hydroxo species of the metals can be formed and do not bind to the adsorption sites on

the surface of the adsorbent (Kaçar *et al* , 2002). Several other researchers have already reported a strong dependency of heavy metal biosorption on pH (Volesky, 2003; Wase and Forster, 1997).

6.3.5 Adsorption isotherms

Adsorption data for wide ranges of adsorbate concentrations and adsorbent doses have been treated by Langmuir (Langmuir, 1918) and Freundlich (Freundlich, 1907) isotherms, two widely used models. The Langmuir isotherm model is based on the assumption that maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface, that the energy of adsorption is constant and that there is no transmigration of adsorbate in the plane of the surface. Langmuir isotherms were obtained by agitating the adsorbent of fixed dose and the adsorbate solution of different concentrations for a contact time greater than equilibrium time. The Langmuir isotherm represents the equilibrium distribution of metal ions between the solid and liquid phases. The following equation can be used to model the adsorption isotherm:

$$q = q_{\max} b C_{\text{eq}} / 1 + b C_{\text{eq}} \quad (12)$$

where q is milligrams of metal accumulated per gram of the biosorbent material; C_{eq} is the metal residual concentration in solution; $q_{\max}$ is the maximum specific uptake corresponding to the site saturation and b is the ratio of adsorption and desorption rates (Chong and Volesky, 1995).

When the initial metal concentration rises, adsorption increases while the binding sites are not saturated. The linearised Langmuir isotherm allows the calculation of adsorption capacities and the Langmuir constants and is equated by the following equation.

$$C_{\text{eq}}/q = 1/q_{\max} \cdot b + C_{\text{eq}}/q_{\max} \quad (13)$$

Thus a plot of C_{eq}/q vs C_{eq} should be linear if Langmuir adsorption were operative, permitting calculation of $q_{\max}$. The Langmuir isotherm model was followed by all the adsorbates and adsorbents in the present study.

The comparison of sorption capacities of adsorbents used in this study with those obtained in the literature shows that the four husks namely bengal gram husk, tur dal husk, tamarind husk and coffee husk are effective for the removal of metals from aqueous solution.

Table 63 Comparison of adsorption capacity of Chromium (VI) with other adsorbents

Adsorbent	$q_{\max}$	Reference
<i>Rhizopus arrhizus</i>	23.88	Prakasham <i>et al</i> (1999)
<i>Rhizopus nigricans</i>	99.00	Bai and Abraham (2001)
<i>Chlorella vulgaris</i>	33.80	Cetinkaya <i>et al</i> (1999)
<i>Scenedesmus obliquus</i>	30.20	Cetinkaya <i>et al</i> (1999)
<i>Synechocystis</i> sp.	39.00	Cetinkaya <i>et al</i> (1999)
Cone biomass	201.81	Ucun <i>et al</i> , 2002
Bengal gram husk	91.64	Present work
Tur dal husk	96.05	Present work
Coffee husk	27.73	Present work
Tamarind husk	44.95	Present work

Table 64 Comparison of adsorption capacity of Iron (III) with other adsorbents

Adsorbent	$q_{\max}$ (mg/g)	Reference
Industrial biomass (<i>Aspergillus niger</i> grown on wheat bran)	19.2	Chandrashekar <i>et al</i> , 1998
<i>Streptomyces rimosus</i>	125	Selatnia <i>et al</i> , 2004
<i>Chlorella vulgaris</i>	24.49	Aksu <i>et al</i> , 1997
<i>Schizomeris leibleinii</i>	101.70	Ozer <i>et al</i> , 1999
<i>Zoologea ramifera</i>	65.49	Sag and Kutsal, 1995
Bengal gram husk	72.16	Present work
Tur dal husk	66.63	Present work
Tamarind husk	56.55	Present work
Coffee husk	64.80	Present work

Table 65 Comparison of adsorption capacity of Mercury (II) with other adsorbents

Adsorbent	q_{max} (mg/g)	Reference
Fly ash	2.82	Sen and Dey, 1987
Fly ash	11.0	Banerjee <i>et al</i> , 2004
Fly ash-C	0.63–0.73	Kapoor and Viraraghvan, 2004
Rice husk ash	9.3	Feng <i>et al</i> , 2004
Bengal gram husk	51.85	Present work
Tur dal husk	196.32	Present work
Tamarind husk	184.39	Present work
Coffee husk	145.73	Present work

Table 66 Comparison of adsorption capacity of Nickel (II) with other adsorbents

Adsorbent	q_{max} (mg/g)	Reference
Coir pith	15.72	Parab <i>et al</i> , 2006
Sphagnum moss peat	9.18	Ho <i>et al</i> , 1995
Baker's yeast	11.40	Padmavathy <i>et al</i> , 2003
Sheep manure waste	7.20	Abu Al-Rub, 2002
Waste tea	18.42	Malkoc and Nuhoglu, 2005
Bengal gram husk	112.22	Present work
Tur dal husk	96.58	Present work
Tamarind husk	111.11	Present work
Coffee husk	54	Present work

The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_L , which is defined by

$$R_L = 1/(1 + bC_0) \quad (14)$$

Where C_0 is the initial adsorbate concentration (mg/L) and b is the Langmuir constant (L/mg). The parameter indicates the shape of the isotherm as follows:

Table 67 Type of Isotherm for various R_L

R_L	Type of isotherm
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

The R_L values at different initial adsorbate concentrations (Tables 89 and 90) indicate favorable adsorption for all the adsorbents and adsorbates studied.

The Freundlich equation is basically empirical, but is often useful as a means for data description. Freundlich isotherms were basically obtained by agitating the adsorbate solution of a fixed concentration and the adsorbent of different doses for a contact time greater than the equilibrium time. The Freundlich isotherm is represented by the equation (Freundlich, 1907):

$$q = K_f C_{eq}^{1/n} \quad (15)$$

where C_{eq} is the equilibrium concentration (mg/l), q is the amount adsorbed (mg/g) and K_f and n are constants incorporating all parameters affecting the adsorption process, such as adsorption capacity and intensity respectively. The linearised forms of Freundlich adsorption isotherm was used to evaluate the sorption data and is represented as:

$$\ln q = \ln K_f + 1/n \ln C_{eq} \quad (16)$$

K_f and n were calculated from the slopes of the Freundlich plots. The Freundlich isotherm basically indicates whether the adsorption proceeds with ease or difficulty. Freundlich isotherm model was obeyed by all the adsorbates under the studied conditions (Figures 119 to 146). These results may be explained if adsorbent surface sites have a spectrum of different binding energies as suggested by Benjamin and Leckie, 1981.

The langmuir and Freundlich constants calculated from the isotherm equations are given in Tables 82 to 85 for the adsorption of metal ions. The magnitude of the exponent ‘n’ gives the indication of favourability and K_f, the capacity of the adsorbent/adsorbate system. Tables 82 to 85 and Tables 86 to 88 shows that n values for metals were between 1 and 10 under the studied conditions, indicating beneficial adsorption (Yoshida, 1991).

6.3.6 Adsorption dynamics – adsorption rate constant

The rate constant of adsorption is determined from the following first order rate expression given by Lagergren (1898)

$$\log_{10} (q_e - q) = \log_{10} q_e - K_{ad} t / 2.303 \quad (17)$$

where q and q_e are amounts of adsorbate adsorbed (mg/g) at time, t (min) and at equilibrium, respectively, K_{ad} is the rate constant of adsorption (l/min). The linear plots of log₁₀ (q_e-q) vs t for all the metals were studied at different concentration (Figures 147 to 172) shows the applicability of the above equation. Values of K_{ad} were calculated from the slope of the linear plots and are presented in Tables 91 to 104 for metal ions. The rate constant for the metal ions generally decreased with increase in adsorbate concentration. The rate constant for the adsorption metals is comparable with those in literature (Kadirvelu and Namasivayam, 2003; Periasamy and Namasivayam, 1994).

6.3.7 Desorption and Regeneration studies

Both incineration and land disposal represent possible options for final disposition of spent adsorbent material. However, both methods directly or indirectly pollute the environment. If regeneration of metals from the spent adsorbent were possible then it would not only protect the environment but also help recycle the adsorbate and adsorbent and hence contribute to the economy of wastewater treatment. Desorption studies help elucidating the mechanism adsorption and recovering precious metals from wastewater and adsorbent.

Desorption of Cr (VI) from chromium loaded adsorbents increased with increase in the initial pH. At pH 12.5, 32.8% of Cr (VI) was desorbed from tamarind husk;

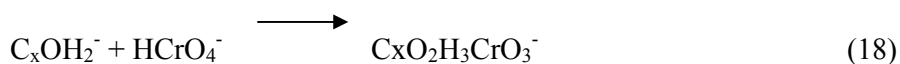
followed by 18.95% from Coffee husk and < 3% for bengal gram and tur dal husk. Among the various adsorbents, maximum desorption was seen in Tamarind husk>Coffee husk> Bengal gram husk>Tur dal husk. Iron (III) was removed maximally at an initial pH of 12.5. For the metal cations, Ni (II) and Hg (II), the percent desorption increased with decrease in pH and reached a maximum of 63.21 and 79.58% respectively at pH 1.0 for tamarind husk. At acidic conditions, H⁺ ions protonate the adsorbent surface by replacing the adsorbed metal ions on the adsorbent surface leading to the desorption of the positively charged metal ion species. Figures 173 to 176 show the effect of pH on the desorption of metal ions.

Desorption does not help to recycle the used adsorbents. Hence, utilization of dried adsorbents in an appropriate combustor such as the boiler at the dye works may be an efficient means of disposal. The gaseous products of combustion should be trapped using suitable solvents to prevent air pollution.

6.4 Mechanism of adsorption

6.4.2 Metal Adsorption:

- (i) **Chromate adsorption:** When chromate ions are introduced into the system containing the adsorbent, they may be adsorbed into the positively charged surface (Sharma and Forster, 1994).



Cr (VI) removal on the adsorbents can also probably be an anion exchange reaction:

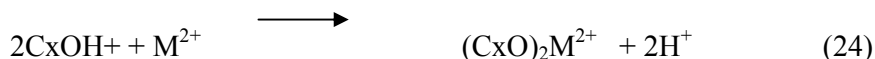
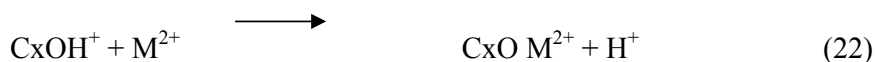


Other groups which are naturally present on the lignocellulosic wastes (like the adsorbents used in the present study), such as C_xO and C_xO₂ may remove HCrO₄⁻ by the formation of oxo functional groups on the adsorbent surface:



Very low desorption of Cr (VI) from Cr (VI) laden adsorbent at alkaline pH shows that most of the HCO₄ seems to be irreversibly bound with the adsorbent (Eq 18).

(ii) Adsorption of Fe (III), Hg (II) and Ni(II): Adsorption of metal cation on the adsorbent depends upon the nature of the adsorbent surface and species distribution of the cation. Species distribution mainly depends on the pH of the system. The metal species that exist in solution are the free metal ions and their hydroxides. The percent removal of metal ion decreased as the pH of the system was lowered, because protons compete with the metal ion for ion sorption sites on the adsorbent surface as well as the concomitant decrease of negative charge on the same surface. This is true for the adsorption of nickel and mercury ions but for ferric, the increase in pH resulted in the formation of ferric hydroxide and hence a low pH of 2.5 was found to be optimum. In the plots of percent adsorption vs pH, there is a sharp increase in adsorption over a narrow range of pH, and this is consistent with the attainment of a pH value at which the adsorption of metal hydroxides becomes possible (MOH⁺). It was proposed by Davis and Leckie, 1978 that the most likely forms of the adsorbed ions are M²⁺ and M (OH)⁻. Hence the possible adsorption reactions include the following:



From the discussion we can conclude that chemisorption is the main mode of mechanism by which metals are adsorbed to the four adsorbents – BGH, TDH, TH and CH.

7.0 CONCLUSIONS

The present investigation shows that the agricultural by-products like bengal gram husk, tur dal husk, and tamarind husk can be used as an effective adsorbent for the treatment of wastewaters containing metals like chromium (VI), iron (III), nickel (II) and mercury (II). Adsorption dynamics, isotherms, pH effect and adsorbent dosage on the removal of metals for all the adsorbates were examined. In addition desorption of the metals from the loaded adsorbents was also carried out.

The uptake of metals increased with increase in the agitation time till the equilibrium was reached. At any contact time, increase in initial adsorbate concentration decreased the percent adsorption and increased the amount of adsorbate uptake (q) per unit weight of the adsorbent.

The effect of adsorbent dosage on the adsorption of metals showed that the percentage of metal removed increased with increase in adsorbent dosage due to increased adsorption surface area. For all the adsorbents studied adsorbent dosage of 1g – 2g/L was sufficient for adsorption of 90% of the initial metal concentration.

Irrespective of the type of the adsorbent, the optimum pH for the removal of chromium (VI) was 2; for iron (III) 2.5; for mercury (II) 5.5 and nickel (II) was maximally absorbed at pH 6.0. The amount of the metal removed at optimum pH increased with increase in initial metal concentration but the percentage absorbed decreased with increase in initial metal concentration.

Adsorption data for wide ranges of adsorbate concentrations and adsorbent doses were treated by Langmuir and Freundlich isotherms. All the adsorbents and adsorbates followed the Langmuir and Freundlich isotherms. Comparison of the adsorption capacity of the four adsorbents with that cited in literature reveals that bengal gram husk, tur dal husk, tamarind and coffee husk had a higher biosorption capacity than the adsorbents reported in literature.

Values of the equilibrium parameter (R_L) from Langmuir isotherm and n values from the Freundlich isotherm indicate that the adsorption process is favorable for all the metals. The equilibrium data also fit well with the Freundlich adsorption isotherm for all the adsorbents and adsorbates (metals) studied.

The Lagergren rate constant of absorption for different concentrations for the metals by the adsorbents used in the study are generally in the range of 9.00×10^{-3} to 1.03×10^{-1} L/min.

Desorption and regeneration studies of the adsorbates showed that regeneration and recovery of the adsorbates is possible. Chemisorption/ion exchange was the main mechanism by which the adsorbates (metals) were attached to the adsorbents. Physical adsorption played a minimal role in the process. Since about 70 % of the metals still remained on sorbents, it indicates that most of metals are able to form strong bonds with the adsorbents.

The infrared spectral analysis of the adsorbents showed that Carbon bonded with hydrogen and oxygen atoms played a major role in the adsorption of metals. The absorption spectra revealed that $-C-O$, $C-N$ and $C=O$ bonds were predominant in the surface of the adsorbents and played a major role in the adsorption process.

The analysis of the carbon, hydrogen and nitrogen content of the husk, showed relatively low percentage of nitrogen, revealing the low content of protein in the adsorbents. This is advantageous over the protein rich algal and fungal biomass projected as metal biosorbents, since proteinous materials are likely to putrefy under moist conditions. Further, most metal sorption reported in literature is based on algal and fungal biomass, which must be cultured, collected from their natural habitats and pre-processed, if available as discards and transported under special conditions, thus introducing the factor of additional costs. In contrast, BGH, TDH, TH and CH as agro-industrial wastes have negligible cost and have also proved to be an efficient biosorbent for the removal of metals. Furthermore, these adsorbed metal can be easily desorbed and the biomass be incinerated for final disposal. These biosorbents are of low cost; its utility will be economical and can be viewed as a part of a feasible waste management strategy.

7.0 Acknowledgement

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