2

Literature review

The term heavy metal is designated for the group of elements that have atomic density value more than 6 g/cm^3 (O' Connell *et al.*, 2008). Jarup (2003) described heavy metals as those elements that exhibit specific gravity at least five times the specific gravity of water. 90 elements occur naturally in the environment and of these, 21 are non-metals, 16 are light metals and 53, including arsenic are considered as heavy metals. The heavy metals bear the significance of acting as trace metals in intricate biochemical reactions (Nies, 1999). Majority of the heavy metals can be categorized into transition elements with partially filled d-orbitals, which enable the heavy metal cations to form co-ordination complexes, which may or may not be redox active (Chakravarty, 2011).

2.1 Natural sources of heavy metals

The heavy metals occur naturally as constituents of the earth crust, largely dispersed in rock formations. Table 2.1 shows the concentrations of heavy metals in different igneous and sedimentary rocks. The type of rock, the prevalent environmental conditions and the activating weathering processes majorly determine the composition and the concentration of the heavy metal present in the rock cropping (Nagajyoti *et al.*, 2010). In general, high

concentrations of Cr, Mn, Co, Ni, Cu, Zn, Cd, Sn, Hg and Pb are found in the geological parent material. Although soil formation mostly takes place from the sedimentary rocks, it is mostly the igneous rocks like olivine, augite and hornblende that help in the contribution of considerable concentrations of Mn, Co, Ni, Cu and Zn. In addition to the igneous rocks, sedimentary rocks like shale has highest concentrations of Cr, Mn, Co, Ni, Cu, Zn, Cd, Sn, Hg and Pb, and is succeeded by limestone and sandstone (Nagajyoti *et al*., 2010). It has been reported that volcanoes emit large amounts of Al, Zn, Mn, Pb, Ni, Cu and Hg along with poisonous and hazardous gases (Seaward and Richardson, 1989). The worldwide emission of heavy metals as estimated by Pacyna (1986) is shown in table 2.2. Some major eruptions have extensive effects e.g. emissions from Mount Etna, Sicily, give rise to 10×10^6 kg per year of Cd, Cr, Cu, Mn and Zn (Climino and Ziino, 1983).Significant rise in Hg levels in the plants growing in the surrounding area was observed due to the activity of Mount Etna (Barghiani *et al*., 1987).

Sea sprays and mists often contribute elements to the ecosystem. Cu and Mn, arising from marine sources have been detected in rain water input to terrestrial environment (Vermette and Bingham, 1986). Bubble bursting is a natural process and a source of Cd, Cu, Ni, Pb and Zn (Pacyna, 1986). Airborne emissions of heavy metals can occur during forest and prairie fires. Carbonaceous matter generated during fire is sources of volatile heavy metals like Hg and Se (Ross, 1994). Through processes like decomposition, volatilization and leaching from leaves and stems, natural vegetation can emit heavy metals into the environment (Nagajyoti *et al*., 2010).

2.2 Biological importance of heavy metals

It is considered that a total number of 30 elements are essential to life. These 30 elements can be grouped as 6 structural elements, 5 macro minerals and 19 trace elements

(Florence, 1986). Some of the heavy metals like Cu and Zn act either as cofactors and activators of enzyme reactions like formation of enzymes/substrate metal complex (Mildvan, 1970) or initiate a catalytic property such as prosthetic group in metalloproteins. The essential heavy metals (Fe, Mn and Mo) have biochemical and physiological importance in plants and animals. Two principal functions of essential heavy metals are: (i) participation in redox reaction and (ii) direct participation as an integral part of several enzymes. (Sharma and Agrawal, 2005). However, certain heavy metals like Cd, Hg and As, etc are potentially toxic to metal sensitive enzymes which further culminate in growth inhibition and death of organisms. It has been authenticated that, all metals, irrespective of being essential or inessential to living organisms can prove to be toxic beyond a certain threshold concentrations, which can be extremely low for highly noxious metal species (Gadd, 1992).

2.3 Sources of heavy metal contamination and toxicity

Heavy metal contamination generally refers to the aberrantly high concentrations of hazardous heavy metals in the ecosystem. Heavy metals are stable and persistent environmental pollutants and hence cannot be degraded or destroyed. As a result they have a tendency to accumulate in the soil, seawater, freshwater, and sediment.

Nriagu (1989) noted the prominent number of ways through which heavy metals can enter the atmosphere from natural sources like wind blowing of dust from the soil surface, volcanic activity, and formation of sea salt particles. Degassing from soils forms a major source of Hg in the environment. The glacier samples taken in Greenland on being analyzed demonstrated that the beginning of human activity impact on the heavy metal atmospheric cycle could be dated back to the Rome Empire epoch (Hong *et al*., 1997). The origin of manifestation of this impact, however, coincides with the emergence of industrial revolution in the mid nineteenth century. From that period till the eighties of the twentieth century, an

exponential growth of heavy metal emission to the atmosphere was observed (Sarma, 2004). With the advent of the Industrial Revolution, the production of heavy metals such as Pb, Cu, and Zn has increased by leaps and bounds. Nearly a ten folds increase in the production of these three metals was recorded between 1850 and 1990, which further led to augmented emission. Heavy metals have been utilized in numerous ways for at least two millennia. For example, lead has been used in plumbing, and lead arsenate has been used to control insects in apple orchards. The Romans added lead to wine to improve its taste, and mercury was used as a salve to alleviate teething pain in infants (Sarma, 2004).The environment is contaminated by heavy metals metals during mining, refining of ores, burning of fossil fuels, industrial processes and the disposal of industrial and domestic wastes (Xie *et al.*, 1996). Anthropogenic activities also generate circumstances in which the heavy metals are integrated into new compounds and may be dispersed worldwide.

Table 1.1 Range of heavy metal concentrations (mg/kg) in igneous and sedimentary rocks (Cannon *et. al.*, 1978)

Metals	Basaltic igneous	Granite igneous	Shales and clays	Black shales	Sandstones
Pb	2-18	6-30	16-50	7-150	<1-31
Cu	30-160	4-30	18-120	20-200	---
Cd	0.006-0.6	0.003-0.18	0.0-11	<0.3-8.4	---
As	0.2-10	0.2-13.8	---	---	0.6-9.7
Cr	40-600	2-90	30-590	26-1000	---
Co	24-90	1-15	5-25	7-100	---
Mo	0.9-7	1-6	---	1-300	---
Ni	45-410	2-20	---	1-300	---
Zn	48-240	5-140	18-180	34-1500	2-41

Table 2.2 Worldwide emissions of heavy metals from natural sources (Pacyna, 1986)

Sources	Annual emission (kg x 10^6)								
	Pb	Cu	Cd	Co	Cr	Hg	Mn	Ni	Zn
Windblown dust	10	12	0.25	4	5	0.03	425	20	25
Volcanogenic particles	6.4	4	0.5	1.4	3.9	0.03	82	3.8	10
Forest wild fires	0.5	0.3	0.01	---		0.1	---	0.6	0.5
Vegetation	1.6	2.5	0.2	---		---	5	1.6	10
Sea salt	0.1	0.1	0.002	---		0.003	4	0.04	0.02
Total	18.6	18.9	0.96	5.4	8.9	0.16	516	26	45.52

Inorganic and organic fertilizers, liming, sewage sludge, irrigation water and pesticides are the prime source of heavy metals in agricultural soils. Varying concentrations of Cd, Cr, Ni, Pb and Zn are found in fungicides and phosphate fertilizers. Cd is specifically important in plants as it gets accumulated in the leaves at very high concentrations which in turn can be ingested by animals or human beings. Cd enrichment is also possible due to application of sewage sludge, manure and lime (Nriagu, 1988, Yanqun *et al*., 2005). Although agricultural soils have very low concentrations of heavy metals, repetitive usage of phosphate fertilizers and the persistent nature of heavy metals can lead to the dangerously high accretion of heavy metals in some soils (Verkleji, 1993). The prolonged usage of pesticides like lead arsenate in Canadian orchards resulted contamination of the orchard soil with Pb, As and Zn which further lead to food contamination (Ross, 1994). Animal manure enriches the soil by addition of Mn, Zn, Cu, Cr and Co and sewage sludge by addition of Zn, Cr, Pb, Ni, Cd and Cu (Verkleji, 1993).

Mining and refinement (spoil heaps, tailings, transport of ores, smelting and metal finishing and recycling of metals) are the primary industrial sources of heavy metal contamination. As, Cd, Fe, generated from coal mines enrich the nearby soil directly or

indirectly. Metals are emitted in the form of vapor and particulate from high temperature metal processing operations like smelting and casting. The vapors of As, Cd, Cu, Pb, Sn and In form aerosols by combining with water vapor in the atmosphere. These aerosols are either subjected to dry deposition (dispersed by wind) or wet deposition (precipitated as rain) leading to contamination of water and soil (Sharma and Agrawal, 2005). Contamination of soil and water ecosystems can also occur through runoff from erosion of mine wastes, dusts generated during the transport of crude ores, corrosion of metals, and leaching of heavy metals to soil and ground water. Power stations that operate on burning of coal and petroleum for power generation, nuclear power stations and high tension lines contribute many heavy metals such as Se, B, Cd, Cu, In, Cs and Ni to the environment (Verkleji, 1993). Other industrial sources include plastic manufacturing units, textiles, microelectronics, preservation of wood and paper processing. Contamination with high concentrations of Cu is observed in plants growing beneath the power line and this is reported to be toxic to the grazing animals (Kraal and Ernst, 1976). Hg utilized in gold mining has proved to be a significant source of environmental pollution due to mobilization of large quantities of Hg from the gold mines (Lacerda, 1997).

The domestic waste water comprises the largest single source of enhanced concentrations of heavy metals in natural water bodies. The domestic effluents may include the following.

i.   Untreated or entirely mechanically treated waste waters

ii.   Substances which have passed through the filters of biological treatment plants

iii.   Waste substances passed over sewage outfalls and discharged into receiving water bodies (Nagajyoti *et al*., 2010)

Angino *et al*. (1970) identified that trace amounts of Fe, Mn, Cr, Co, Zn, Sr and B are present in most enzyme detergents. Thus use of house hold detergents can have hazardous effects on the water quality of water bodies into which the effluents are discharged.

Intensive industrial operations are not the only source of heavy metal contamination. Today, roadways and automobiles are also contemplated as one of the largest sources of heavy metals. Zn, Cu, and Pb are three of the most common heavy metals released from road travel, accounting for at least 90 of the total metals in road runoff (Chakravarty, 2011). However with the introduction of unleaded gasoline, there has been a decline in the concentrations of lead. Trace amounts of many other metals, such as Ni and Cd, are also present in road runoff and exhaust. Cd and Cu are primarily released from diesel engines and Ni and In are added to the atmosphere through aerosol emissions. Lubricants, particularly in inefficient engines, emit Cd, Cr, Hg, Ni, Pb and In. Automobiles contribute to about half of the Zn and Cu to the environment. Cu is also released from the brakes whereas wearing of tire wear gives rise to Zn contamination. Motor oil on being exposed to surrounding parts when the engine operates, begins to build up metals. Thus oil leaks have also become a method by which heavy metals can find an entry into the environment.

Other sources of heavy metals include refuse incineration and landfills. Two significant anthropogenic sources that cause heavy metal contamination are fly ash originated due to combustion of coal and the corrosion of commercial waste products, which results in the addition of Cr, Cu, Pb and galvanized metals (primarily In) (Al-Hiyaly *et al*., 1993). Incineration of municipal wastes generates significant concentrations of In, Pb, AI, Sn, Fe and Cu.

Most heavy metals become bound to the surfaces of road dust or other particulates present on the surface of the road. During precipitation, the bound metals will either be

dissolved in rain water or be swept off the roadway with the dust. From the statistical summary of Bradford (1977), it is revealed that the urban storm water run- off is also a major source of heavy metal contamination in the surface water. Bolter (1974) studied the leaching of Pb by humic and other acids resulting in its increase of availability for run-off rather than its seepage into the upper layer of the soil. The metals thus, either enter the soil or are conducted into a storm drain. Metals can be dispersed by several processes whether it is in the terrestrial environment or in the aquatic environment. These procedures are dictated by not only the chemical characteristics of metals, soil and sediment particles but also the pH of the surrounding environment.

The toxicity of the heavy metals has been recorded throughout the history of human civilization. Even before toxicology became a science, the Greek and Roman physicians diagnosed the prodromes of acute lead poisoning. Today, a huge database is available on the health effects of heavy metals. Exposure to heavy metals has been deduced as a primary reason for developmental retardation, various cancers, renal failure, and even death in some cases of exposure to very high concentrations. Exposure to high levels of Hg and Pb has also been related with the development of autoimmunity which can further lead to the development of rheumatoid arthritis, or diseases of the circulatory or central nervous systems.

Essential elements can prove to be poisonous if ingested in excess quantities. However, safe limits have been prescribed so as to demarcate the levels of deficiency and toxicity. Some elements such as Ca and Mg have wide range whereas others such as Se and F have a relatively narrower window where even a minute increase in concentration can progressively deteriorate human health and can also cause death. Metal toxicity can be manifested in three different ways, viz. blocking the essential biological functional groups of molecules, displacing the essential metal ion in biomolecules, and modifying the active conformation of biomolecules (Florence, 1986). The level and length of exposure to heavy

metals determine the possible health hazards. In general, exposures are divided into two classes: acute exposure in which the subject is exposed to high concentrations of heavy metals for a short period of time and chronic exposure where the contact with low concentrations of heavy metals takes place over a long period of time. In some cases, the health effects are immediately apparent; in others, the effects are delayed (Young, 2000).

2.4 Sources of the heavy metals undertaken in the current study and their effect on human health

The current research investigates the biosorption of lead, copper and cadmium. The sources, toxicity and effect on human health are described in the following paragraphs.

2.4.1 Lead

Atomic Symbol: Pb

Atomic Number: 82

Atomic Mass: 207.2 amu

Melting Point: 327.5°C (600.65 K, 621.5 °F)

Boiling Point: 1740.0°C (2013.15 K, 3164.0 °F)

Density at 293 K: 11.34 g/cm^3

Lead is a malleable, bluish- gray, lustrous metal with a high density and low melting point. It occurs naturally in small amounts in the earth's crust and do not possess a specific taste or odor. The most economically important lead ore is called galena where lead is present as lead sulfide (PbS). Some amounts of zinc and silver are also present and all of these can be extracted and refined to obtain metals in their pure forms. Other ores that are mined for lead

include anglesite and cerussite. Most of the lead is introduced into the environment through anthropogenic activities like mining, manufacturing, and the combustion of fossil fuels.

The Greeks were the first to identify the corrosion resistant properties of lead and used it as a protective covering on ship hulls. As a result, the Romans began extracting large quantities of lead for their expansive water systems and also to manufacture water pipes and earthenware (Kazantzis, 1989). Today lead is most importantly used in the production of batteries. Lead is also used in ammunition, metal products like solder and pipes, roofing, and devices to shield x-rays. Earlier lead was vastly used in gasoline, paints and ceramic products, caulking, but due to its deleterious effects on human health the use of lead has been dramatically declined in recent years (Landsdown and Yule, 1986).

Break down of lead is not a spontaneous process but under the influence of sunlight, air and water, lead compounds undergo changes. When released into the air from an industrial source or burning of fossil fuels and waste, it persists in air for about 10 days. Majority of the lead in soil comes from particles falling out of the air. Lead in water is distributed into three different fractions: dissolved, bound to suspended particulate matter (SPM) and sedimented (Zarazua *et al*., 2006). Lead has the ability to adhere to soil particles and unless the water is acidic or "soft", lead remains immobile in soil and do not get transferred to underground water or drinking water (Chrastny *et al*., 2006). The amount of lead dissolved in the aqueous medium is increased by several factors such as high dissolved organic matter (Linnik, 2003) and low pH. Thus the metal has a long residence time in both terrestrial and aquatic environment. Humans are exposed to the metal through the following processes;

i.   Inhaling workplace air (lead smelting, refining, and manufacturing industries),

ii.   Ingesting lead-based paint chips,

iii.   Drinking water circulated by lead pipes or lead soldered fittings,

iv.   Inhaling or ingesting contaminated soil, dust, air, or water near waste sites,

v.   Active or passive smoking of tobacco,

vi.   Consuming contaminated food grown on soil containing lead or food enveloped with lead-containing dust,

vii.   Breathing fumes or ingesting lead from hobbies that use lead (leaded-glass, ceramics) (Tong, 1998; Tong *et al*., 2000)

Lead pollution is considered to be a grave issue globally because of the presence of this metal in several industrial waste waters (Davydova, 2005). The presence of even low concentrations of lead in water can lead to its bio accumulation in the food chain (Prasad *et al*., 2008).

Lead poses a threat to almost every organ and system in the human body. The central nervous system, particularly in children is most vulnerable to lead poisoning (Deng *et al*., 2006). Exposure to lead is more hazardous for young and unborn children who are exposed to lead through their mothers. The detrimental effects include premature births and decreased mental ability in the infant, deficiency of cognitive development, and reduced growth in young children (Davis, 1990; Schwartz, 1994; Pocock *et al*., 1994). These effects are more prominent when exposed to high levels of lead in the childhood years. It has been reported that an increase in blood lead concentration from 10 to 30 µg/dL leads to a decrease in intelligence quotient (IQ) of about 1-4 points (Pocock *et al*., 1994; Wasserman *et al*., 1997). Canfield *et al*. (2003) reported a similar minute decline in IQ when blood lead concentrations increased from 1 to 10 µg/dL.

In adults, exposure to lead for a prolonged duration can culminate in memory deterioration, prolonged reaction time and reduced ability to understand. In severe cases of lead poisoning, the affected person may suffer from acute psychosis, confusion and reduced consciousness (Jarup, 2003). Lead interrupts with several enzymatic processes involved in heme synthesis (Barbosa *et al*., 2005) and elevated lead concentrations in blood have been correlated with reduced hemoglobin synthesis and red blood cell number (Schwartz *et al*., 1994; Factor-Litvak *et al*., 1999; Tripathi *et al*., 2001) resulting in anemia in worst cases. Increased levels of lead in blood can also lead to renal dysfunction, which is demonstrated by urinary excretion of small molecular proteins (Ehrlich *et al*., 1998; Factor-Litvak *et al*., 1999; Weaver *et al*., 2005).

The World Health Organization (WHO, 2006) prescribed guideline of 10 µg/L (0.01 mg/L) for lead concentrations in drinking water. Natural lead concentrations of water bodies are generally low, and background concentrations of < 0.45 to 14 µ/L in groundwater has been reported (Smedley *et al*., 2002). The Centers for Disease Control and Prevention (CDC) recommends all children be screened for lead poisoning at least once a year. This is especially important for children between 6 months and 6 years old. The United State Environmental Protection Agency (USEPA) requires lead in air not to exceed 1.5 micrograms per cubic meter (0.0015 mg/L) averaged over 3 months. The sale of leaded gasoline is stopped from December 31, 1995 in USA. USEPA limits lead in drinking water to 15 micrograms per liter (0.015 mg/L). The Occupational Safety and Health Administration (OSHA), USA limits the concentration of lead in workroom air to 50 µg/cubic meter (5×10^{-5} mg/L) for an 8-hour workday. If a worker has a blood lead level of 40 µg/dL (0.4 mg/L), OSHA requires that, that particular worker has to be removed from the workroom.

2.4.2 Copper

Atomic Symbol: Cu

Atomic Number: 29

Atomic Mass: 63.546 amu

Melting Point: 1083.0 °C (1356.15 K, 1981.4 °F)

Boiling Point: 2567.0 °C (2840.15 K, 4652.6 °F)

Density at 293 K: 8.96 g/cm^3

Copper is an iridescent reddish brown metal that corrodes when exposed to environment and develops a greenish patina. It is highly ductile and malleable and has effective electrical conductivity. Copper is conventionally extracted from sulfide and oxide ores that contain between 0.5 and 2.0% copper. The sulfide ores of copper include chalcocite (Cu_2S), chalcopyrite ($CuFeS_2$) and covellite (CuS). These ores are treated by smelting. The oxide ores include azurite ($2CuCO_3.Cu$ $(OH)_2$), brochantite ($CuSO_4(OH)_6$), chrysocolla ($CuSiO_3.2H_2O$) and cuprite (Cu_2O). The techniques applied for refining the copper ores, depend on the type of ore as well as the economic and environmental factors. Copper ores may also contain molybdenum, lead, gold and silver as impurities.

Copper is believed to be one of the first metals used by human civilization. Although use of copper as tools and decorative items dates back to as early as 9000 B.C., evidence from archaeological studies suggest that it was actually the early Mesopotamians, 5000 to 6000 years ago, who could completely harness the ability to extract and exploit copper. The most common oxidation state of copper is copper (I), (Cu^+) state which is less stable and copper (II) state, (Cu^{2+}), which is more stable. Under atypical conditions it can also exist in a +3 state and even in +4 state in exceptionally rare conditions. The industrial sources of

copper emission include mining, smelting, metal electroplating, surface finishing, electrolysis, manufacturing electrical appliances, electric boards and circuits. The agricultural sources encompass mostly the use of fertilizers and pesticides (Bilal *et al*., 2013).

Copper is redox-active transition element essential for the growth of plants and is an important micronutrient. The average concentration of copper in plant tissue is 10 µg/g dry weight (Yruela, 2005). Copper helps in activating enzyme necessary for lignin synthesis and is also an essential component of photosynthesis. Deficiency of copper in plants can cause chlorosis and in some cases can cause wilting of leaves (Marschner and Rimmington, 1988). In human beings copper is required in trace quantities for its function in synthesis of enzymes, tissues and in development of bones (Akar *et al*., 2009). However, when ingested in excessive amounts, divalent copper (Cu (II)) can be toxic and carcinogenic. Consumption of excessive divalent copper can lead to its accumulation in liver which can further induce vomiting, headache, nausea, respiratory problems, abdominal pain, hepatic insufficiency and renal disorders and finally gastrointestinal bleeding (Akar *et al*., 2009). Application of copper salt to the skin may develop itching, dermatisation, and keratinisation of the hands and soles of feet (Huang *et al*., 2007). Workers involved in the use of fungicides containing copper sulphate ($CuSO_4$), develop a respiratory affliction called "Vineyard sprayer's lungs" which is characterized by the development of interstitial pulmonary lesions and nodular fibro-hyaline scars leading to respiratory failure (Shrivastava, 2009). Inhalation of copper spray increases the risk of lung cancer among exposed workers (Aydin *et al*., 2008).

The detrimental effects of copper on soil biota are also extensively studied. Lamb *et al*. (2012) studied the damages initiated by copper on Australian endemic plant species like *Acacia holosericea* and *Eucalyptus creba*. The disruption of osmo-regulatory mechanism of fresh water animals due to exposure to copper was studied by Lee *et al.* (2010). United State Environmental Protection Agency (USEPA) has set the permissible limits for copper (II) as

1.3 mg/L in industrial effluents (Shawabkeh *et al*., 2004) where as the permissible limits for copper (II) in drinking as recommended by World Health Organization (WHO) is 1.5 mg/L (Kalavathy, 2005).

2.4.3 Cadmium

Atomic Symbol: Cd

Atomic Number: 48

Atomic Mass: 112.411 amu

Melting Point: 320.9 °C (594.05 K, 609.62 °F)

Boiling Point: 765.0 °C (1038.15 K, 1409.0 °F)

Density at 293 K: 8.65 g/cm^3

Cadmium occurs in the earth's crust in association with lead, copper and zinc ores. Pure cadmium is bluish-white in color and is ductile and malleable. Cadmium is generally retrieved as a byproduct from zinc concentrates. The ratio of zinc to cadmium in zinc ores commonly range from 200:1 to 400:1. Sphalerite (ZnS) is the most economically viable zinc mineral and commonly contains minor amounts of other elements. Cadmium, being similar in certain chemical properties to zinc often substitutes for zinc in the sphalerite crystal lattice. The cadmium mineral, greenockite (CdS), is frequently associated with weathered sphalerites and wurtzites (ZnS), but usually at microscopic levels.

Cadmium is mainly utilized for the production of rechargeable nickel cadmium batteries. Other uses of cadmium comprise manufacture of pigments, coatings and plating and stabilizers for plastics. Solar cell manufacturing may become another significant market for cadmium in the future. Cadmium telluride thin-film photovoltaics serve as a substitute to the traditional silicon-based solar cells. These are a more preferable photovoltaic technology for

commercial rooftop arrangement and for ground-mounted utility systems involving larger areas. Metallic cadmium has mostly been used as an anticorrosion agent (cadmiation) (Chakravarty, 2011). Cadmium is also present in high concentrations in the phosphate fertilizers used in agriculture. Cadmium production, consumption, and emissions to the environment worldwide have increased dramatically during the 20th century (Jarup, 2003).

Cadmium enters air from mining, industries, and combustion of coal and household wastes. Cadmium particles in air can travel long distances before falling to the ground or water (ATSDR, 1999). Waste disposal and spills at hazardous waste sites can release cadmium into water and soil environment. Most of the cadmium remains undissolved in water and also do not undergo environmental degradation, but go through transformation and finally is uptaken by fishes and plants. Cadmium can enter the human body by the following modes of exposure.

i.   Inhaling workplace air contaminated by cadmium (battery manufacturing, metal soldering or welding)

ii.   Eating foods containing cadmium (highest in shellfish, liver, and kidney meats)

iii. Smoking cigarette and breathing cadmium in cigarette smoke (doubles the average daily intake)

iv.   Drinking contaminated water

v.   Breathing contaminated air near the burning of fossil fuels or municipal waste (WHO, 1992; Jarup *et al*., 1998; Sarma and Bhattacharyya, 2005)

Exposure to cadmium through diet has been reported to cause adverse health effects in the kidneys, liver, bone, peripheral vascular tissues, mammary glands, placenta, prostates, breasts, pancreas and colon (Satarug and Moore, 2004; Satarug *et al*., 2006). The kidneys are the primary target of cadmium, and approximately one third of body's cadmium is stored in the cortex part of the kidneys (WHO, 1992). The half-life of cadmium in the kidney is reported to be decades and this cadmium is gradually excreted in urine. Consequently the first adverse indications induced by chronic oral exposure to cadmium are revealed in the kidneys. Exposure to higher concentrations may even lead to renal failure (Fanconi syndrome), but usually it causes renal tubular dysfunction which further leads proteinuria, calciuria, aminoaciduria, glucosuria and tubular necrosis (WHO, 1992; Jarup *et al*., 1998).Degenerative effects in bones, osteomalacia and osteoporosis (itai-itai syndrome), have been associated with long term cadmium exposure (Staessen *et al*., 1999; Alfven *et al*., 2000; Nordberg *et al*., 2002; Jarup and AlfVen, 2004). Bone degradation may be a consequence of hypercalciuria which again results from cadmium-induced tubular dysfunction (Wu *et al*., 2001) and delayed activation of precursors of vitamin D_3 in the kidney (Chalkley *et al*., 1998) decline in blood calcium concentration and increasing bone desorption. Occupational exposure to high concentrations of cadmium, mainly through the pulmonary route, has been reported to cause at least lung cancer (WHO, 1992).

The United State Environmental Protection Agency (USEPA) allows 0.005 mg/L of cadmium in drinking water. The USEPA also limits the levels of cadmium in lakes, rivers, waste sites, and cropland. The USEPA prohibits the use of cadmium in pesticides. The Food and Drug Administration (FDA), USA limits the amount of cadmium in food colors to 15 parts of cadmium per million parts of food color. The Occupational Safety and Health Administration (OSHA) now limits workplace air to 100 $\mu g/m^3$ (0.0001 mg/L) cadmium as fumes and 200 $\mu g/m^3$ (0.002 mg/L) cadmium dust (Sarma, 2004).

2.5 Conventional methods for removal of heavy metals from water and waste water

Several methods for treatment of water and waste water have been developed over the last two decades. Most frequently used techniques for removal of heavy metals are chemical precipitation, chemical oxidation and reduction, ion exchange, filtration, electrochemical treatment, reverse osmosis (membrane technologies), evaporative recovery, solvent extraction, electrolysis, and adsorption (Xia and Liyuan, 2002; Ramachandra *et al*., 2005; Sadrzadeh *et al*., 2008; Gavrilescu *et al*., 2009). Some of these classical methods are elaborated in the following paragraphs.

2.5.1 Chemical precipitation

Chemical precipitation is a very frequently used technique for the removal of heavy metals from industrial waste water. Here the metals are precipitated by addition of coagulants like alum, lime, iron salts and other organic polymers. The particles formed are then separated from the solution using methods like settling or filtration and sometimes through both. Unit operations like neutralization, precipitation, coagulation or flocculation, separation of solids or liquid and dewatering are normally involved in this technology.

Several factors like the type and the concentration of ionic metals present in the system, the coagulant used, the reaction system conditions mainly pH of the solution and also the presence of interfering constituents that might cause inhibition f the precipitation process, determines the overall effectiveness of the process. Precipitation is used as the treatment method to extract metals ions from solutions by almost 75 percent of plating companies. The most common precipitation methods used by industries are carbonate precipitation, sulphide precipitation and sodium hydroxide precipitation (Joshi, 2017). Since majority of the heavy metals form stable sulfides, sulfide precipitation is considered to be more suitable as it helps in removal of large quantities of contaminants and encounter less interference with the

chelating agents in the system (Veeken *et al*., 2003). Carbonate precipitation is applied where it contributes excellent precipitation properties or lesser effluent concentrations. The disadvantage of precipitation is the production of sludge, which constitutes a solid waste disposal problem (Chakravarty, 2011).

2.5.2 Chemical reduction

Chemical reduction is an advanced and efficient waste treatment technology. Reduction of hexavalent chromium to decrease its toxicity and facilitate precipitation can be achieved 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). The most significant advantages of using chemical reduction in order to reduce hexavalent chromium comprise working in an ambient state, automatic controls, increased reliability, and basic process instrumentation. The reducing agents like sulfur dioxide and sodium meta bisulfate are added after adjusting pH of the aqueous solution to 2.0 using hydrochloric and sulphuric acid. The trivalent chromium is precipitated on being increasing the pH to 8.5 by adding lime. 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 (Ramchandra *et al*., 2005). The excessive use of chemicals throughout the process is the primary disadvantage of the process.

2.5.3 Chelation/complexation

Chelation involves the formation or presence of two or more separate coordinate bonds between a ploydentate ligand and a central atom. Matlock *et al.* (2002a) reviewed and examined the efficiency of three extensively utilized commercial heavy metal precipitants, trimercaptotriazine, potassium/sodiumthiocarbonate and sodiumdimethyldithiocarbamate.

Commercial heavy metal precipitants either lack the necessary binding sites or pose to be too hazardous to the environment to be safely utilized. Thus it becomes necessary to explore and synthesize new and more effective precipitants to meet the discharged requirements (Fu and Wang, 2011).

2.5.4 Solvent extraction

Solvent extraction is also known as liquid-liquid extraction of metals. This method is useful in removal of metals from solutions on a large scale and has witnessed astounding advancements in the recent years due to the introduction of selective complexing agents (Beszedits, 1988). Solvent extraction has gained popularity beyond the dimension of hydrometallurgical applications due to its capacity of waste reprocessing and treatment of the effluent.

Solvent extraction comprises of two phases: organic and aqueous. The metal is allowed to pass to the organic phase by mixing the aqueous solution which contains the metal or metals, with the congruous organic solvent. The recovery of the extracted metal is accomplished by contacting the organic solvent with an aqueous solvent whose composition is such that it initiates stripping of the metal in the organic phase and enable its re-extraction into the stripping solution (Ramachandra *et al*., 2005). Often there may be an increase in the concentration of metals in the strip liquor by 100 to 110 times than that in the original feed solution. On removal of the metal of interest, the organic solvent is recycled either directly or in fractions after removing impurities from it.

2.5.5 Membrane process

Membrane technologies involve reverse osmosis and electrodialysis. These processes are commercially employed to retrieve dissolved metals from the effluents that are produced

by electroplating or metal etching processes (USEPA, 1980). The technology involves pretreatment steps like removal of suspended and dissolved solids so as to ensure the lifetime of the membranes followed by ionic concentration using selective membrane with a definite driving force. While reverse osmosis is carried out by generating a pressure difference so as to initiate transport of solvent across a semi-permeable membrane, electro dialysis on the other hand involves the migration of metal ions through semi-permeable membranes induced by the application of current to the electrodes. The limitations of the membrane process is inherent with the pretreatment techniques, fundamentally, with the removal of suspended particles. In addition to this, the method involves exorbitant costs and is highly sophisticated, which requires high level of technical skills to manoeuvre the treatment process.

A liquid membrane is a thin film that selectively permits the passage of a specific constituent from a mixture (Beszedits, 1988). Unlike solid membranes, liquid membranes take in to account the chemistry for separation rather than the size and thus liquid membrane technology is similar to solvent extraction in a number of aspects. Liquid membrane technology is a recently evolved procedure and so a wide range of problems are yet to be addressed. Longevity of the supported membranes in terms of stability and the efficient breakup of microspheres for product recovery have emerged as a major issue with the emulsion membranes (Ramachandra *et al.*, 2005).

2.5.6 Ion exchange

Ion exchange is a multifaceted separation technique which is beneficial in treating waste water of metal contaminants and to either recycle or discharge the treated solution. The ion exchange resins are selective for a particular metal ion. The cations are exchanged for H^+ or Na^+. There are mainly three basic types of resins: cation exchange resins, anion exchange resins, and metal selective chelating resins. The cation exchange resins are primarily

synthetic polymers containing an active ion group such as SO_3H. The natural materials such as zeolites can be used as ion exchange media (Heen, 1977). The modified zeolites like zeocarb and chalcarb have greater affinity for metals like Ni and Pb (Groffman *et al*., 1992). The resin enables the selective exchange of toxic ions in the solution with the ions held by electrostatic forces on the resin. The toxic compound as a result is removed while the non-toxic ions remain in the solution. Ion exchange can extend an efficient pollution control measure in a variety of operations such as water purification and chemical recovery. However, involvement of high capital investments and huge consumption of electricity per volume of water treated, ion exchange does not offer a cost effective solution to abate heavy metal contamination. Ion exchange is also totally ineffective for large quantities of competing mono and divalent ions Na (I) and Ca (II) (Joshi, 2017).

2.5.7 Electrolytic process

In order to remove dissolved metals from waste waters generated from metal plating and etching industries, electrolysis has proved to be a promising technique. In this case the electrolytic cell employ potential values in such a way that the metal reduction reaction occur under mass transport (Bertazzoli *et al*., 1997). The dissolved metals are reduced or deposited in their elemental form, as the solution is circulated through the cell, thereby achieving separation. Various designs of electrolytic cells are available and the choice of design to be used is completely dependent on the application. While noble metals like gold and silver can be conveniently removed electrolytically using flat plate electrode, metals like copper, tin, lead and cadmium is more strenuous to remove and occasionally demand the use of the more complex electrolytic cell designs.

2.5.8 Electrodeposition

While electrolysis is a proces which uses a direct electrical current to break chemical compounds, electrodeposition, also known as electroplating, is the process of depositing material onto a conducting surface from a solution containing ionic species (salts). Insoluble anodes are used to recover metals from effluents containing heavy metals. Metal ions from solutions are reduced on the cathode at a rate determined by the metal ion concentration in the electrolyte, the current, cathode area and the species of metal being recovered. There is no sludge generation but this technology suffers from many restrictions (Joshi, 2017).

2.5.9 Floatation

Floatation comprises the hetero-phase system i.e., suspensions and liquid emulsions detached from dispersed phase) using air bubbles. The resultant flock is collected and separated from the top (Sudilovsky *et al*., 2008). Separation of heavy metals through floatation can be achieved in three ways: dissolved air floatation (DAF), ion floatation and precipitate floatation. In dissolved air floatation micro-bubbles attach with the suspended particles in the water which form agglomerates having a density lower than the aqueous medium. This facilitates their removal by pushing air through the solution (Lundh *et al*., 2007). The ionic species are made hydrophobic by introducing surfactants succeeded by associating with air bubbles. The polar head of the surfactant attaches with the cation whereas the non-polar hydrocarbon chain is directed towards the solution. Interaction with the pumped air bubbles with the non-polar end leads to the formation of flocks. Majority of the copper, zinc, chromium and silver metal ions are removed from waste water through ion floatation under optimum pH (Polat and Erdogan, 2007). The approach of precipitate floatation is based on using chemical reagents and ultimately removing heavy metals attached to the air bubbles. The precipitation progresses through the formation of metal hydroxide or

as a set with specific anions (S^{2-}, CO_3^{2-}), depending on the concentration of the metal ions (Bilal *et al*., 2013).

2.5.10 Coagulation/flocculation

This technique involves two phases: the first phase involves destabilizing the particles by neutralizing the forces that separates them (coagulation) followed by the second phase where aggregation of neutralized particles take place (flocculation). Stabilization of colloids and their sedimentation are accomplished by adding coagulants like alum into the waste water system. This is followed by flocculation so that large sized flocks which can be easily removed are formed. The ambient pH for this process is maintained at 11. Due to high operational costs and huge volume of toxic sludge generation, the method is not considered to be environmentally sustainable (Kurniawan *et al*., 2006). Moreover the traditional coagulants and flocculants are not feasible for soluble heavy metals.

2.5.11 Evaporators

Evaporators are fundamentally used in electroplating industries in order to concentrate and recover the high-priced plating chemicals (Ramachandra *et al*., 2005). Retrieval of these chemicals is achieved by boiling adequate volume of water from the accumulated rinse stream to permit the recovery of the condensed steam to be recycled as rinse water. Four types of evaporators are operated throughout the elctroplating industry (USEPA, 1979) (i) rising film evaporators; (ii) flash evaporators that use waste heat; (iii) submerged tube evaporators and (iv) atmospheric evaporators.

Evaporative recovery system involves high capital and operational costs. Thus in order to make this process economically practicable, both chemical and water reuse values must neutralize the costs for evaporative recovery.

2.5.12 Cementation

In cementation, a metal in its aqueous solution is displaced by another metal having higher electromotive force. This method is best suited for treating waste waters containing reducible metal ions. A substantial difference in electromotive force between the metals is desirable to achieve successful cementation. Scrap iron is the most widely used metal for its low cost and high availability. Cementation is appropriate for treating small volume of waste water because of the requirement of long contact duration. Some common examples of cementation in waste water 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 (Ramachandra *et al.*, 2005). Removal and recovery of lead by replacing by a less toxic and harmful metal has been reported by Angelidis *et al.* (1988, 1989).

2.5.13 Adsorption

Adsorption is regarded as a surface or interface phenomenon, which arises due to interactions between the individual atoms, ions or molecules of an adsorbate and those present in the adsorbent surface. The forces responsible for these interactions have their origin in electromagnetic interactions (Weber and Van Vliet, 1978). The process of adsorption was first detected by Lowitz in 1785 and its application was executed in the process of removal of color from sugar during refining (Ahmad *et al.*, 2009). The first granular activated carbon units were utilized in the treatment of water supplies in Hamm, Germany in 1929 and at Bay City, Michigan in 1930.

Depending on the nature of the interactions, four types of adsorption can be distinguished (Weber J, 1985):

i.   Exchange adsorption: This involves electrostatic bonding of ions to sites bearing opposite charges on the surface of the adsorbent with successive removal of these species by other ionic adsorbates possessing greater electrostatic affinity.

ii.   Physical adsorption or physisorption: Here the adsorption is a resultant of the activity of the Van der Waals forces which include weak intermolecular force like London dispersion forces and classical electrostatic forces.

iii.   Chemical adsorption or chemisorptions: In chemisorptions, the adsorbate reacts with the adsorbent as a result of the adsorbate changes its chemical form. The chemisorptive bond formed as a result is stronger than those obtained from the physical Van der Walls forces.

iv.   Specific adsorption: Specific adsorption is referred to the specific interactions which do not contribute to transformation of the adsorbate but can help in the attachment of adsorbate molecules at functional groups on the surface of the adsorbent. These type of adsorption manifest binding energies ranging from those identified for physiorption to higher values associated with chemisorption. The net dispersion, electrostatic, chemisorptive, and functional-group interactions broadly define the ability of an adsorbent for a specific adsorption (Sarma, 2004).

The application of activated carbon as adsorbent for removal of heavy metals from waste water is a well-recognized method. Adsorption on activated carbon incorporates the sequestration of a substance from one phase, most commonly an aqueous solution, followed by its accumulation on the surface of an activated carbon adsorbent. Adsorption is a comparatively a simple method for the removal of heavy metals compared to other sophisticated conventional methods. Activated carbon, silica gel, and alumina are the important adsorbents used in industries. Adsorption of Cr (III) and Cr (VI) on activated

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carbon from aqueous solutions has been studied (Toledo, 1994). Granular activated carbon columns have been used to treat waste waters containing lead and cadmium (Reed and Arunachalam, 1994, Reed *et al*., 1994). Granular activated carbon was also used for the removal of Pb (II) from aqueous solutions (Cheng *et al*., 1993). Although adsorption has showed encouraging prospects, its use is limited by the high cost of the adsorbents, which further increases the overall expenses of waste water treatment.

2.6 Biosorption of heavy metals

The increase in the awareness and concern towards removal of pollutants from the environment during 1970s, have led to the emergence of biosorption technologies. Biosorption is the property of certain biomolecules (or types of biomass) to bind and concentrate selected ions or other molecules from aqueous solutions. It is an expeditious, reversible, economical and green technology in comparison to the traditional methods employed for removal of heavy metals from aqueous streams (Gavrilescu, 2004; Tunali and Akar, 2006; Volesky, 2007).

Numerous studies have been conducted in order to determine the efficient, appropriate and low-cost materials as sorbents (Li *et al*., 2008). A biosorbent can be considered cost effective if it demands little processing, is copiously available in nature, or is a by-product or a waste generated from another industry (Gadd, 2009). The advantages of biosorption over other conventional techniques are listed below in table 2.3 (Gavrilescu, 2010).

A variety of biomaterials for removal of heavy metals are abundantly available in nature. These include microorganisms like bacteria, fungi, algae etc. and forest, agricultural wastes and by-products. Extensive studies have been conducted to estimate the potentiality of these biosorbents for removal of heavy metals from both simulated and field solutions. Some of the studies of metal ion removal are briefed below.

Generally an affinity for metal species exists in all biomaterials. While selecting a biological material for heavy metal biosorption, their origin must be put under consideration. These include microorganisms as by-product of fermentation industry, organisms naturally available in abundance and organisms cultivated or propagated for biosorption purposes using inexpensive media (Ahluwalia and Goyal, 2007). The practicability of the biosorption procedure is highly influenced by the source of the biosorbent. It is preferable that the biomass is obtained from the least expensive source such as the effluent of the fermenter, seaweeds from neighboring water bodies etc. (Gupta *et al*., 2000).

In addition to cellular products such as polysaccharides, both living and dead biomass can be used for metal sequestration (Gadd, 1993). Each biosorbent has its characteristic physical and chemical properties such as, porosity and surface area. Moreover, the sorption capacities also vary with the changes in experimental conditions. Sorption capacity is the most important characteristic of an adsorbent and is defined as the "amount of adsorbate taken up by the adsorbent per unit mass of the adsorbent" (Gavrilescu, 2010). Properties like pore and particle size distribution, specific surface area, cation exchange capacity, solution pH, surface functional groups and temperature govern the sorption capacity of the absorbent.

Table 2.3 Some advantages of biosorption

Features	Advantages
Cost	Most biosorbents used are industrial, agricultural and waste biomass of different origin and so usually involves low cost. Cost is incurred mainly for transportation and other simple processing charges.
pH	Although the solution pH greatly influences metal uptake capacity of the biomass, the process can be operated under a wide range of pH conditions.
Temperature	Temperature does not influence the biosorption process since the biomass is inactive. In fact, several studies have reported that uptake capacity of the biosorbent is enhanced with the increase in temperature.
Maintenance or storage	Biomass can be easily stored and used.

Selectivity	Selectivity can be improved by modification or processing of biomass without much effort and additional expenses.
Versatility	Reasonable versatile. A variety of ionic species can be accommodated in the binding sites.
Degree of uptake	Very high. Accommodation of an amount of toxicant almost equivalent to the dry weight of the biomass has been reported by some researchers.
Rate of uptake	Most biosorption mechanisms are rapid.
Toxicant affinity	High under favorable conditions
Regeneration and reuse	High prospect for regeneration. The biomass can be reused over a number of cycles.
Toxicant recovery	With the application of suitable elutant, toxicant recovery can be achieved. Generally, acidic or alkaline solutions enable efficient recovery of toxicants.

2.6.1 Microbial biosorption

Multitude of microbial organisms belonging to groups like bacteria, fungi, yeast, cyanobacteria, algae etc. have been reported to potentially bind with a wide range of heavy metals. The biosorptive properties of various microorganisms in the removal and recovery of heavy metals have been well reviewed and documented (Gadd and Griffiths, 1978; Volesky, 1990; Wase and Foster, 1997; Gadd 1988; Mehta and Gaur, 2005; Romera *et al.*, 2006).

Most of the biosorption experiments catalogued in literature involve the use of living organisms for the removal of heavy metals. However use of microorganisms for biosorption of heavy metals suffers from certain intrinsic disadvantages and hence the technique is not feasible in certain scenarios. For example, industrial effluents have a wide range of pH and are loaded with high concentrations of noxious metals. The culture and maintenance of an active microbial population under these parameters cannot be always feasible. Although the technique is cost effective and do not generate pollutants, it is however relatively new and requires expertise in handling the microbial consortia for remediating the metal contaminated effluent. The long term impacts of majority of strains are yet unknown and thus it generates

doubts which further promotes intensive research prior to the utilization of such microorganisms in environmental processes.

An integration of metal binding mechanisms like physiorption, ion exchange, complexation or chelation and precipitation are incorporated in the biosorption of heavy metal ions onto microorganisms (Ahalya *et al*., 2003). Complex formation takes place between different categories of ligands on the fungal cell walls and the metal ions. These include carboxyl, amine, hydroxyl, phosphonic and sulphonic groups (Le Cloirec *et al*., 2003). Tables 2.4, 2.5 and 2.6 demonstrate the lists of diversified microorganisms including algae, bacteria, fungal and yeast exploited for the removal of metal ions from their aqueous solutions. Adsorption of Pb(II), Cu(II) and Cd(II) from waste water have been accomplished by both active (living) and inactive (dead) cells of each microorganisms. Biosorbents tabulated in these tables are focused only on Pb(II), Cu(II) and Cd(II) ions as the current study emphasizes on their removal.

2.6.2 Biosorption using plant materials and agricultural by-products

Agriculture is one of the largest sources of low-cost biosorbent. The agricultural products, by-products and wastes have been investigated as an alternative for the expensive conventional methods of metal removal from water and waste water (Kumar, 2006). Being conveniently available in abundance, agricultural wastes demand little economic value. Moreover the disposal of agricultural wastes also poses to be a concern (Kurniawan *et al*., 2006; Tilman *et al*., 2002). Cellulosic content of plant materials facilitates the efficient biosorption of heavy metals. Thus due to their high metal biosorption capacity, a variety of agro-based materials have proved to be productive and potent in removal of toxic heavy metal ions like Pb(II), Cd(II), Cu(II), Ni(II), Zn(II), Cr(III), Cr(VI) and Hg(II) (Demirbas, 2008).

The basic biomolecules that constitute the agricultural waste biomass include hemicellulose, lignin, extractives, lipids, proteins, simple sugars, water, hydrocarbons, and starch. These biomolecules contain variety of functional groups that enable metal complexation, which further helps for the sequestration of heavy metals (Sud *et al.*, 2008, Dhir, 2014). A survey of the available literature shows that the ecological utilization of biomass for metal removal is widely distributed among different countries across the world and is being under the process of constant development. This initiates a great interest in emerging countries such as India, Brazil, Turkey, Argentina and Nigeria (Demirbas, 2008; Kurniawan *et al.*, 2008; Nurchi and Villaescusa, 2008; Sud *et al.*, 2008).

Agricultural based plant material adsorbents are economic, renewable, and abundant and thus stand as a viable option for waste water treatment (Jain *et al.*, 2016). Modification of agricultural by-product can enhance their natural metal uptake capacity and add efficacy to the adsorbent (Kumar, 2006). Biosorbents are either prepared from the untreated natural biomass or by treating the waste biomass by washing with acids or bases, and in some cases even both, before final desiccation and granulation. Studies on biosorption using plant materials for biosorption of heavy metals include ordinary biomaterials like seed (Gutha *et al.*, 2011; Hadi *et al.*, 2011; Jayaram and Prasad, 2009; Rao and Rehman, 2012), leaf (Shafique *et al.*, 2012; Reddy *et al.*, 2012), root (Li *et al.*, 2013a, 2013b), bark (Munagapati *et al.*, 2010; Aoyama *et al.*, 2005; Reddy *et al.*, 2011) and peel (Owamah, 2014; Feng *et al.*, 2011; Saha *et al.*, 2013). Most of the studies showed that quite high percentage of removal of heavy metals can be achieved through biosorption by agricultural waste materials and by-products. Biosorbent used in the current study focuses only on biosorption of Pb(II), Cu(II) and Cd(II) ions as these are the metals taken under the scope of this study. Tables 2.7, 2.8 and 2.9 demonstrate some relevant works reported in the literature for the biosorption of Pb(II), Cu(II), and Cd(II) ions by using various agricultural wastes and other bio-materials.

Table2.4 Maximum Pb(II) uptake capacities by microbial biomass

Biomass	Biomass class	Q_m (mg/g)	References
Sargassum natans	Brown macro algae	1.22	Holan and Volesky, 1994
Fucus vesiculosus	Brown marine algae	220-370	Holan and Volesky, 1994
Absidia orchidis	Fungus	351.00	Holan and Volesky, 1995
Ecklonia radiate	Marine algae	282.00	Matheickal and Yu, 1996
Aspergillus niger	Fungus	10.19	Kapoor *et al*., 1999
Gracilaria corticata	Algae	54.00	Jalali *et al*., 2002
Ulva lactuca	Algae	126.50	Jalali *et al*., 2002
Ulva sp	Green seaweed	1.46	Sheng *et al*., 2004
Chlamydomonas reinhardtii	Algae	96.30	Tuzun *et al*., 2005
Laminaria japonica	Algae	250.70	Luo *et al*., 2006
Enterobacter sp. J1	Bacteria	50.90	Lu *et al*., 2006
Bacillus cereus	Bacteria	54.80	Pan *et al*., 2006
Bacillus sp. ATS	Bacteria	92.27	Tunali *et al*., 2006
Saccharomyces cerevisiae	Fungus	85.60	Chen and Wang, 2007
Fasarium solani	Fungus	196.07	Bhatti *et al*., 2008
Bacillus pumilus	Bacteria	28.06	Colak *et al.* 2011
Chlorella vulgaris	Algae	178.50	Edris *et al*., 2013
Anabaena sphaerica	Algae	121.95	Abdel-Aty *et al*., 2013
Curtobacterium sp. FM01	Bacteria	186.60	Masoumi *et al*., 2016
Chara aculeolata	Algae	105.30	Sooksawat *et al*., 2016
Nitella opaca	Algae	104.20	Sooksawat *et al*., 2016
Aspergillus nidulans	Fungus	25.67	Kumar *et al*., 2017
Lepiota hystrix	Fungus	3.90	Kariuki *et al*., 2017

Table 2.5 Maximum Cu(II) uptake capacities by microbial biomass

Biomass	Biomass class	Q_m (mg/g)	References
Cladosporium resinae	Fungus	18.00	Gadd *et al*., 1988
Pichia guilliermondii	Yeast	11.00	Mattuschka *et al*., 1993
Scenedesmus obliquus	Algae	10.00	Mattuschka *et al*., 1993
Ulothrix zonata	Algae	176.20	Nuhoglu *et al*., 2002
Thiobacillus thiooxidans	Bacteria	38.54	Liu *et al*., 2004
Enterobacter cloaceae	Bacteria	6.60	Iyer and Jha., 2005
Padina sp	Brown sea weed	1.14	Sheng *et al*., 2007
Ulva sp	Green seaweed	0.75	Sheng *et al*., 2007
Gracillaria sp	Red seaweed	0.59	Sheng *et al*., 2007
Fasarium solani	Fungus	208.33	Bhatti *et al*., 2008
Cladyspoium cladosporioides	Fungus	7.74	Li *et al*., 2009
Aspergilus niger	Fungus	17.60	Tsekova *et al*., 2009
Trametes versicolor	Fungus	60.98	Sahan *et al*., 2010
Bacillus subtilis YB886	Bacteria	8.90	Allievi *et al*., 2010
Bacillus sphaericus 1593	Bacteria	22.70	Allievi *et al*., 2010
Lactobacillus sp. (DSM 20057)	Bacteria	0.046	Schut *et al*., 2011
Trichoderma asperellum	Fungus	0.959	Iskandar *et al*., 2011
Pleurotus ostreatus	Fungus	8.06	Javaid *et al*., 2011
Spirogyra sp	Algae	0.027	Rajfur *et al*., 2012
Sargassum angustifolium	Marine brown algae	0.94 mmol/g	Ahmady-Asbchin *et al*., 2013
Rhodotorula mucilaginosa	Yeast	26.20	Salvadori *et al*., 2014
Fumaria indica	Fungi	6.618	Iqbal and Khera, 2015
Cystoseira crinitophylla	Algae	160.00	Christoforidis *et al*., 2015
Candida krusei	Yeast	2.418 mmol/g	Luk *et al*., 2017
Spirulina platensis	Algae	817.70	Gunasundari and Kumar, 2017
Lessonia nigrescens	Brown seaweed	54.50	Hansen *et al*., 2017

Table 2.6 Maximum Cd(II) uptake capacities by microbial biomass

Biomass	Biomass class	Q_m (mg/g)	References
Ascophyllum nodosum	Algae	215.00	Holan *et al*., 1993
Citrobacter strain MCM B-181	Bacteria	43.50	Puranik and Paknikar, 1999
Aspergillus niger	Fungus	4.38	Kapoor *et al*., 1999
Sargassum filipendula	Algae	74.20	Davis *et al*., 2000
Sargassum fluitans	Algae	79.80	Davis *et al*., 2000
Sargassum vulgare	Algae	88.80	Davis *et al*., 2000
Escherichia coli	Bacteria	11.20	Kulczycki and Ferris, 2002
Pseudomonas putida	Bacteria	8.00	Pardo *et al*., 2003
Mucor rouxii	Fungus	20.31	Yan and Viraraghavan, 2003
Bacillus laterosporous	Bacteria	159.50	Zouboulis *et al*., 2004
Bacillus licheniformis	Bacteria	142.70	Zouboulis *et al*., 2004
Saccharomyces cerevisiae	Fungus	31.80	Goksungur *et al*., 2005
Phomopsis sp	Fungus	29.20	Saiano *et al*., 2005
Botrytis cinerea	Fungus	18.60	Akar and Tunali, 2005
Caulerpa lentillifera	Algae	4.60	Pavasant *et al*., 2006
Pseudomonas aeruginosa	Bacteria	97.00	Komy *et al*., 2006
Saccharomyces cerevisiae	Fungus	15.40	Chen and Wang, 2007
Trichoderma viride	Bacteria	0.139	Singh *et al*., 2010
Trametes versicolor	Fungus	166.60	Subbaiah *et al*., 2011
Anabaena sphaerica	Cyanobacteria	111.10	Abdel-Aty *et al*., 2013
Halomonas sp.	Bacteria	12.023	Rajesh *et al*., 2014
Aspergillus niger	Fungus	43.33	Hajahmadi *et al*., 2015
Saccharomyces Cerevisiae	Yeast	68.78	Farhan and Khadom, 2015
Scenedesmus obliquus AS-6-1	Microalga	144.93	Zhang *et al*., 2016
Sun dried algal biomas	Green algae	72.46	Khan *et al*., 2016
Agaricus bisporus	Fungus	3.49	Nagy *et al*., 2017
Gracilaria corticata	Red algae	226.9	Nasab *et al*., 2017
Escherichia coli	Bacteria	284.69 mmol/g	Tafakori *et al*., 2017
Thamnidium elegans	Fungus	123.76	Celik *et al*., 2017

Table 2.7 Biosorption capacity of Pb(II) by various biosorbents

Biosorbent	Q_m (mg/g)	References
Tree fern	40.00	Ho *et al*., 2004
Tea waste	65.00	Amarasinghe and Williams, 2007
Bamboo Dust carbon	2.15	Kannan and Veemaraj, 2009
Moringa Oleifera bark	34.6	Reddy *et al*., 2010
Chemically modified *Moringa oleifera* tree leaves	209.54	Reddy *et al*., 2010
Aegle marmelos (Bael) leaves	104.50	Chakravarty *et al*., 2010
Banana peels	2.18	Anwar *et al*., 2010
Hibiscus rosa sinensis dye waste (HDW)	90.909	Vankar *et al*., 2010
Heartwood powder of *Areca catechu*	11.65	Chakravarty *et al*., 2010
Sugarcane bagasse	6.366	Martin-Lara *et al*., 2010
Agave sisalana fibre	1.34	dos Santos *et al*., 2011
Tea leaves (exhausted)	120.00	Shrestha *et al*., 2012
Annona squamosa shell	90.93	Isaac and Sivakumar, 2013
Agave bagasse	36.00	Velazquez-Jimenez *et al*., 2013
Saponified musk melon peel	167.80	Huang and Zhu, 2013
Casava peel	5.80	Owamah, 2014
Maize stover (raw)	19.65	Guyo *et al*., 2015
Maize stover (treated)	27.10	Guyo *et al*., 2015
Fumaria indica biomass	39.15	Iqbal and Khera, 2015
Tephrosia purpuria Leaf	100.00	Madala *et al*., 2015
Phytolacca americana biomass	10.83	Wang *et al*., 2015
HNO_3 treated *Phytolacca americana* biomass	12.66	Wang *et al*., 2015
Sclerocarya birrea seed husk	20.00	Moyo *et al*., 2015
Rice husk	9.29	Sarma *et al*., 2015
Aspalathus linearis biomass	18.90	Kanu *et al*., 2015
Musa paradisiacal flower	3.30	Ogundipe and Barbarinde, 2017
Tinospora cordifolia biomass (batch method)	20.83	Sao *et al*., 2017
Tinospora cordifolia biomass (column method)	63.77	Sao *et al*., 2017
Cucumber peel	133.60	Basu *et al*., 2017
Adenanthera pavonina seeds	12.94	This study

Table 2.8 Biosorption capacity of Cu(II) by various biosorbents

Biosorbent	Q_m (mg/g)	References
Ceiba pentandra hulls	20.8	Rao *et al*., 2006
Tea waste	48.0	Amarasinghe and Williams, 2007
Walnut shell	6.74	Altun and Pehlivan, 2007
Hazelnut shell	6.65	Altun and Pehlivan, 2007
Almond shell	3.62	Altun and Pehlivan, 2007
Areca waste	2.84	Zheng *et al*., 2008
Coffee husks	7.50	Oliveira *et al*., 2008
Base treated rubber leaves	14.97	Wan Ngah and Hanafiah, 2008
News paper pulp	27.77	Chakravarty *et al*., 2008
Pomegranate peel	13.18	El-Ashtoukhy *et al*., 2008
Chestnut shell	12.56	Yao *et al*., 2010
Acacia leucocephala bark powder	147.1	Munagapati *et al*., 2010
Palm kernel fibre	20.12	Ofomaja, 2010
Papaya seed	212.70	Hadi *et al*., 2011
Heartwood powder of *Areca catechu*	9.578	Chakravarty *et al*., 2012
Moringa oleifera leaf	167.90	Reddy *et al*., 2012
Rice husk (activated carbon in absence of sonication)	1.046	Zakir, 2013
Rice husk (activated carbon in presence of sonication)	6.277	Zakir, 2013
Eichhornia crassipes root biomass	32.51	Li *et al*., 2013a
Casava peel	8.00	Owamah, 2014
Coconut tree sawdust	3.89	Putra *et al*., 2014
Egg shell	34.48	Putra *et al*., 2014
Sugarcane bagasse	3.65	Putra *et al*., 2014
Fumaria indica biomass	13.007	Iqbal and Khera, 2015
Watermelon based biosorbent (Ca(OH)$_2$ treated)	31.25	Gupta and Gogate, 2016
Watermelon based biosorbent (citric acid treated)	27.027	Gupta and Gogate, 2016
Portulaca oleracea biomass	85.470	Dubey and Mishra, 2017
Abelmoschus esculentus leaves	453.00	Khaskheli *et al*., 2017
Sesame seed husk	10.83	El-Araby et al., 2017
Adenanthera pavonina seeds	10.71	This study

Table 2.9 Biosorption capacity of Cd(II) by various biosorbents

Biosorbent	Q_m (mg/g)	References
Hydrilla verticillata biomass	15.00	Bunluesin *et al*., 2007
Modified rice husk	41.15	El-Shafey, 2007
Exhausted olive cake ash (EOCA	8.38	Elouear *et al*., 2008
Sugar beet pulp	46.1	Pehlivan *et al*., 2008
Abies nordmanniana leaves	6.80	Serencam *et al*., 2008
Activated Pine bark	50.0	Argun and Dursun, 2008
Coffee husks	6.85	Oliveira *et al*., 2008
Eucalyptus Bark	14.53	Ghodbane *et al*., 2008
Mushrooms	34.96	Vimala and Das, 2009
Pomelo peel	21.83	Saikaew *et al*., 2009
Scolymus hispanicus L	45.05	Barka *et al*., 2010
Banana peels	5.70	Anwar *et al*., 2010
Heartwood powder of *Areca catechu*	10.66	Chakravarty *et al*., 2010
Corn stalk (acrylonitrile modified)	12.73	Zheng *et al*., 2010
Corn stalk (raw)	3.39	Zheng *et al*., 2010
Modified orange peel	293.3	Feng *et al*., 2011
Wheat straw	14.56	Farooq *et al*., 2011
Polyalthia longifolia Seeds	20.74	Rao and Rehman, 2012
Eriobotrya japonica ash	29.24	Al-Dujaili *et al*., 2012
Moringa oleifera leaf	171.37	Reddy *et al*., 2012
Sunflower stalk	70.0	Jalali and Aboulghazi, 2013
Annona squamosa shell	71.0	Isaac and Sivakumar, 2013
Feronia acidissima shell	32.071	Suresh *et al*., 2014
Arundo donax reed	27.9	Ammari, 2014
Portulaca oleracea plant biomass	43.48	Dubey *et al*., 2014
Sesame leaf and stem	84.74	Cheraghi *et al*., 2015
Sunflower Stem Carbon	1.48	Jain *et al*., 2016
Sunflower Head Carbon	1.22	Jain *et al*., 2016
Ballota undulata biomass	121.1	Al-Shannag *et al*., 2017
Cucumber peel	107.76	Basu *et al*., 2017
Abies alba bark	11.98	Tofan *et al*., 2017
Adenanthera pavonina seeds	8.104	This study

2.7 Other natural adsorbents for heavy metal removal

2.7.1 Chitosan

Chitin is the second most popular natural biopolymer after cellulose. However, chitosan created by alkaline N-deacetylation of chitin, is currently gaining interest as an effective adsorbent for heavy metals (Babel and Kurniawan, 2003). Chitosan have a molecular structure similar to cellulose. Apart from the high adsorption capacity of chitosan for various heavy metals (Bassi *et al*., 2000), chitosan can conveniently form hydrogel (Zhao *et al*., 2007). Thus, chitosan can be considered as a suitable carrier for immobilization of biomass. However, the chitosan based hydrogel mostly have low resistance to acid and is weak in terms of mechanical strength. The weaknesses can be overcome by adopting a cross-linking approach; the disadvantage is that the sorption capacity is diminished after cross-linking (Ruiz *et al*., 2000).

2.7.2 Zeolites

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 among scientists due to their ion-exchange capability to preferentially remove unwanted heavy metals such as strontium and cesium (Babel and Kurniawan, 2003). This unique property makes zeolites favorable for waste water treatment. Zeolites comprises of a wide range of species such as clinoptilolite and chabazite. Clinoptilolite is most abundant in nature and is readily available from more than 40 natural zeolites species (Mier *et al*., 2001). Among the most frequently studied natural zeolites, clinoptilolite is found to possess high selectivity for certain heavy metal ions such as Pb(II), Cd(II), Zn(II) and Cu(II). The selectivity of the series of the heavy metals removed from waste water using clinoptilolite is determined to be Pb(II) > Cd(II) > Cu(II) > Co(II) >

Cr(III)> Zn(II) > Ni(II) > Hg(II). The results obtained from different studies indicate that zeolites sustain great potential for removal of heavy metal species from industrial waste water effluents. However, an artificial support is required when used in column operations, due to low permeability of zeolites.

2.7.3 Clay

Basically three species of clay are widely known: smectites (such as montmorillonite), kaolinite, and mica. Of these montmorillonite has the highest cation exchange capacity (Babel and Kurniawan, 2003). A number of researches have been carried out using clays, mainly montmorillonite, to verify their potentiality for removing heavy metal ions such as Zn(II), Pb(II), and Al(III) from aqueous solutions (Brigatti *et al*., 1996; Turner *et al*., 1998). The large surface area of the natural clays along with the edges and faces of clay particles enables clay minerals to be excellent adsorbent for heavy metals (Bhattacharyya and Gupta, 2008; Abollino *et al*., 2008). In case of industrial application of clay minerals, the swelling factor should be taken under consideration as the varying structural characteristics and ion-exchange mechanism may lead to tremendous pressure drop. But the easy availability and low cost of clay minerals compensate for the associated drawbacks of clay minerals as adsorbents for heavy metal sequestration.

2.7.4 Peat moss

Peat moss is a complex soil material comprising of lignin and cellulose as its major components. These constituents, especially lignin, contain polar functional groups, such as alcohols, aldehydes, ketones, acids, phenolic hydroxides, and ethers that can be engaged in chemical bonding (Bailey *et al*., 1999). Because of these characteristics, it tends to hold a high cation exchange capacity. Peat moss has a large surface area (> 200 m^2/g) and is highly porous and hence it can be utilized to bind heavy metals (Babel and Kurniawan, 2003). A

study conducted by Sharma and Forster (1993) showed that peat moss is about six times more effective than coconut-shell-based carbon for Cr (VI) removal. Peat accumulates metals in huge quatities and hence some bogs are actually mined for their metals content. For example, in Finland, it is a routine activity to sample peat bogs prospecting for metal deposits (Mineral Resources Institute, 1985). Peat, like other sorbents, can be modified to enhance its sorption capacity. Adsorption capacity and values for ion exchange and complexation by peat moss vary with conditions such as pH, ionic strength, peat type and concentration (Bailey *et al.*, 1999).

2.7.5 Fly ash

Fly ash is an industrial solid waste generated from the thermal power plants. It is one of the cheapest adsorbents having outstanding removal abilities for heavy metals such as copper ions (Babel and Kurniawan, 2003). It has been found that the adsorption capacity increases with an increase in temperature. Fly ash comprises of carbon and oxides of silica, alumina and iron. The data about the adsorption kinetics of organic compounds and reports on the increasing of adsorption capacity with increasing carbon content is presented by Banerjee *et al.* (1997). The surface area of fly ash is reported as 1 ± 6 m^2/g. Fly ash contains pozzolanic particles. These particles undergo reactions with lime in the presence of water and forms cementitious calcium-silicate hydrates. Thus easy solidification after metal adsorption is one of the important advantages of fly ash. It must be noted that fly ash may contain heavy metals and trace amounts of radioactive elements. The evaluation of the possibility of competitive displacement or leaching must also be taken under consideration (Bailey *et al.*, 1999).

2.7.6 Coal

The removal of Cd(II) using coal has been intensively investigated (Bhattacharya and Venkobachar, 1984). A similar study for Hg(II) sorption using bituminous coal (Babel and Kurniawan, 2003) is also reported. Significant increase in Hg(II) sorption by chemical pretreatment of the bituminous coal with nitric acid has been exhibited by activated carbon in terms of initial rate of adsorption and adsorption capacity.

2.7.7 Natural oxide

Naturally occurring iron oxide and manganese oxide have used for the removal of heavy metals like Cr (VI), As (III), As(V), Ni(II), Co(II), Mg(II) in ground water and waste water (Babel and Kurniawan, 2003).

Table 2.10 depicts the summary of the studies conducted for the removal of different heavy metals by using different natural adsorbents reported in literature.

Table 2.10 Summary of removal of different heavy metals by using natural adsorbents

Material	Metal ion	Adsorption capacity (mg/g)	Reference
	Pb(II)	16.36	Huang *et al*., 1996
Chitosan	Cu(II)	222.00	McKay *et al*., 1989
	Cd(II)	5.93	Jha *et al*., 1988
Cross-linked chitosan	Cu(II)	86.00	Schmuhl *et al*., 2001
	Pb(II)	1.60	Zamzow and Eichbaum, 1990
	Cu(II)	1.64	
Clinoptilolite	Cd(II)	2.40	
	Cd(II)	1.20	
	Pb(II)	1.40	Malliou *et al*., 1992
	Cd(II)	137.00	
	Pb(II)	6.00	Ouki and Kavanagh, 1997

	Cu(II)	5.10	
	Cd(II)	6.70	
Chabazite–phillipsite	Cu(II)	0.37	Ibrahim and Khoury, *2002*
Montmorillonite	Pb(II)	0.68	Srivastava and Tyagi, 1989
	Cd(II)	0.72	
Kaolinite	Pb(II)	1.41	Chantawong *et al*., 2001
Illite	Pb(II)	4.21	Chantawong *et al*., 2001
Bentonite	Pb(II)	20.00	Naseem and Tahir, 2001
Fly ash–wollastonite	Cu(II)	1.18	Panday *et al*., 1985
Unmodified kaolin	Pb(II)	4.2	Jiang *et al*.,2009
Modified kaolin	Pb(II)	20.00	
Magnesium oxide-coated	Cu(II)	58.44	Eren *et al*., 2010
Eutrophic peat	Cu(II)	12.07	Gosset *et al*., 1986
	Cd(II)	20.33	
Oligotrophic peat	Cu(II)	6.41	Sharma and Forster, 1986
Fly ash	Cu(II)	1.39	Panday *et al*., 1985
Aluminium oxide	Pb(II)	33.00	Srivastava *et al*., 1988
	Cd(II)	31.00	
Ferric oxide	Pb(II)	230.00	Srivastava *et al*., 1988
	Cd(II)	72.00	

2.8 Selectivity of the adsorbent

The ability of an adsorbent to separate molecule A from molecule B is known as its selectivity. The selectivity is given by the separation factor, which in turn is defined as (Thomas and Crittenden, 1998),

$$\alpha = \frac{X_i/Y_i}{X_j/Y_j} \tag{2.1}$$

where X_i and Y_i are the equilibrium mole fractions of component i and X_j and Y_j are the equilibrium mole fractions of component j, in the adsorbed and fluid phases, respectively. One or more of the following factors may lead to the selectivity of the adsorbent in separation process.

i. Equilibrium effect: Differences that exist in the thermodynamic equilibria for each sorbate-sorbent interaction.

ii. Kinetic effect: Differences that exist in the rates at which various sorbate molecules proceed into the internal structures of the adsorbent.

iii. Molecular sieving effect: Pore openings may be too constricted to permit penetration of one or more adsorbate molecule. This is an extreme case of the kinetic effect.

iv. Desorption effect: Differences that exist in the rates at which different adsorbates are desorbed from the adsorbent.

The equilibrium separation factor further depends on the properties of the adsorbent interactions, i.e. whether the surface is polar, non polar, hydrophilic, hydrophobic, etc., and on the experimental conditions such as temperature, pressure and concentration.

Kinetic separation can be achieved with molecular sieve adsorbents such as zeolites and carbon sieves and it is greatly influenced by the ratio of micropore diffusivities of the components being separated. For a suitable kinetics based separation, the size of the adsorbent micropores must be synchronous to the dimensions of the adsorbate molecules.

2.9 Sorption isotherm study

During adsorption, a relationship exists between the concentrations of metal ions in the adsorbate and the amount of metal ions adsorbed per unit mass of the adsorbent, at

equilibrium. Since equilibrium concentrations are a function of temperature, the adsorption isotherms are described as the adsorption equilibrium relationship at a given temperature (Febrianto *et al*. 2009). Though the adsorption isotherms are originally applicable to gas phase adsorption, they can be conveniently applied to investigate adsorption equilibria in biosorption study of heavy metals. The adsorbent properties like pore volume pore size or energy distribution and specific surface area can be estimated from the adsorption isotherms. The information regarding desorption mechanism that are stringently associated with the adsorbate-adsorbent interactions, can also be derived from the isotherm curves. The experimental adsorption isotherm can be precisely interpreted by some mathematical equations called adsorption isotherm model equations. An ideal physical model of the adsorption experimental system is assumed in order to derive these mathematical equations. The model assumptions are deduced from the experimental observations. The hypothesis regarding the nature of the adsorption process can be deduced from the experimental results. This hypothesis can be developed into theory if found suitable experimentally. Thus adsorption isotherms provide necessary information to determine the possibility to achieve a required purity level for a particular adsorbent. This is necessary when multiple impurities are present and one or more impurities are poorly adsorbed. Moreover, the isotherm facilitates calculation of uptake (q_e) at equilibrium, which has a significant impact on the process economy. The relative performance of different varieties of adsorbents can be predicted using adsorption isotherms.

Of the different isotherm models available in literature, the experimentally obtained equilibrium data from the present study are tested with the Langmuir isotherm (Langmuir, 1916), Freundlich isotherm (Freundlich, 1906), Temkin isotherm (Runping *et al.* Runping 2008), and Dubinin-Radushkevich isotherm (Dubinin, 1960).

2.9.1 Langmuir isotherm model

The Langmuir isotherm is applicable to monolayer sorption onto a surface with finite number of adsorption sites homogenously distributed over the sorbent surface. The isotherm is based on the assumption that the rate at which adsorbate molecules interact with a surface of an adsorbent is proportional to the product of the concentration of the solute (C) and the fraction (1-ϴ) of surface remaining uncovered by adsorbate and therefore available as adsorption sites. The isotherm model also assumes that there is only one variety of sorbate and only one sorbate molecule reacts with one active site.

The equation proposed by Langmuir is generally applicable to chemisorption with some limitations involving physiorption. This equation can be applied to the physical or chemical adsorption on solid surface with a single type of adsorption active center. As long as these restrictions are clearly demarcated, the equilibrium conditions for sorption behavior in varied adsorption systems or for different conditions within any given system can be easily illustrated using the Langmuir equation.

The isotherm equation is in the form of equation 2.2

$$\theta = \frac{q_e}{q_m} = \frac{bC_e}{1+C_e} \qquad\qquad (2.2)$$

where, b is K_a/K_d (K_a and K_d are rate constants for adsorption and desorption respectively) (L/mg), q_e (mg/g) is the amount adsorbed on unit mass of the adsorbent, q_m (mg/g) is the quantity of adsorbate required to form a single monolayer on a unit mass of the adsorbent and C_e (mg/L) is the equilibrium concentration.

A dimensionless equilibrium parameter, R_L, also known as separation factor has been developed on the basis of the Langmuir equation (Hall *et al*. 1966).

$$R_L = \frac{1}{1+bC_0} \qquad (2.3)$$

The value of R_L should be $0<R_L<1$ for favorable adsorption, while $R_L>1$ represents the unfavorable adsorption, $R_L=1$ represents linear adsorption and $R_L=0$ represents irreversible adsorption process.

The linearized equation for Langmuir isotherm model is as follows:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_m} + \frac{1}{bQ_m} \qquad (2.4)$$

The values of Q_m and b are calculated from the slope and intercept of the plot of C_e/q_e versus C_e.

2.9.2 Freundlich isotherm model

The Freundlich isotherm model (Freundlich, 1906) assumes that the metal ions are adsorbed on a heterogeneous surface forming multiple layers and that the amount of sorbate adsorbed increases infinitely with the increase in concentration. The Freundlich isotherm equation is applied to investigate the adsorption of organic and inorganic molecules on a wide range of adsorbents. The empirical equation is written in the following form.

$$q_e = K_f C_e^{\frac{1}{n}} \qquad (2.5)$$

The linearized logarithmic form of the equation is written as,

$$log\, q_e = \frac{1}{n} log\, C_e + log\, K_f \qquad (2.6)$$

where, K_f is the Freundlich constant indicating the relative adsorption capacity of the adsorbent, n is the Freundlich coefficient representing the deviation from linearity of

adsorption. K_f and $1/n$ can be calculated from the intercept and slope of the plot of log q_e versus log C_e. log K_f is equivalent to log q_e when C_e equals unity, whereas, when $1/n \neq 1$, the value of K_f depends on the units which expresses q_e and C_e. The value of Freundlich coefficient, n, tends to have a value between 1 and 10 for favorable adsorption. Stronger interaction between the adsorption sites on the biosorbent and the metal ions is indicated by larger values of n, while $1/n$ equal to 1 indicates linear adsorption which assigns identical energies of adsorption for all sites (Delle Site, 2001).

2.9.3 Temkin isotherm model

The Temkin isotherm model is based on the assumption that the heat of adsorption declines linearly with coverage rather than logarithmic decrease as stated by the Freundlich equation. The model also assumes that the adsorption is a uniform distribution of maximum binding energy. The equation for Temkin isotherm model is expressed as follows.

$$q_e = \frac{RT}{b_T} \ln(A_T C_e) \tag{2.7}$$

The equation (2.7) can be linearized as given by Equation (2.8):

$$q_e = B_T \log A_T + B_T \log C_e \tag{2.8}$$

where, $B_T = (RT)/b_T$, T is the absolute temperature in K and R is the universal gas constant (8.314J/molK). The constant b_T denotes the heat of adsorption, A_T is the binding constant (L/g) which corresponds to the maximum binding energy (Akkaya and Ozer, 2005). The slope and intercept from a plot of q_e versus log C_e gives the values of the isotherm constants A_T and b_T.

2.9.4 Dubinin-Radushkevich (D-R) isotherm model

The D-R equation is developed for sub-critical vapors in micropore solids, where adsorption involves filling pores on energetically non-uniform adsorbent. The interpretation of the equilibrium attained during sorption of organic compounds in gaseous phase onto porous solids. Liquid-phase adsorption systems are complex due to parameters like pH, ionic equilibria involved in these systems. Hence, D-R equation is rarely applicable to liquid-phase adsorption systems.

The D-R isotherm model can be expressed by the following equation.

$$ln\ q_e = ln\ q_D - \ B_D \varepsilon^2 \tag{2.9}$$

where, q_D is the maximum adsorption capacity (mg/g), B_D (mol^2/J^2) is the constant related to sorption energy (Ibrahim and Sani, 2014) and ε^2 can be calculated from equation 2.10

$$\varepsilon = RT\ ln\left(1 + \frac{1}{C_e}\right) \tag{2.10}$$

where R is universal gas constant (J/K mol) and T is the absolute temperature in Kelvin (K)

The mean energy of adsorption is calculated from the equation 2.11

$$E_D = \frac{1}{\sqrt{2B_D}} \tag{2.11}$$

The D-R isotherm constants, q_D and B_D are calculated from the plot between ln q_e and ε^2.

2.9.5 Characteristics of an adsorption isotherm

The information provided by an adsorption isotherm as suggested by Chakravarty (2011) can be summarized as follows.

i.   The adsorption capacity of the adsorbent

ii. The equilibrium adsorbate concentration shows the maximum amount of sorbate that can be sequestered from solution. This quantity remains unchanged with increasing adsorbent amount.

iii. The relative steepness of the isotherm can be equated to the sensitivity of the adsorbent to changes in adsorbate concentration.

However, the adsorption isotherms also suffer from certain limitations which are enumerated below.

i.   Isotherms are strictly applicative in equilibrium conditions and are devoid of any time restrictions. Thus it is difficult to ascertain the true equilibrium.

ii. The isotherm does not take under consideration any long-term chemical and biological effects.

2.10 Adsorption kinetic models

Though it is imperative to study the efficacy of adsorption, the mechanism of adsorption in a particular system must also be identified. In order to investigate the mechanism of biosorption and identify the potential rate-controlling steps including mass transport and processes involving chemical reactions, the experimental data are tested for the kinetic models. The kinetics of metal adsorption is essential to set optimum condition for removal of metal ions in batch experiments (Ho, 2006a). Three diffusive transport processes normally control any adsorption process. These are as follows,

i.   From bulk solution to the film surrounding the adsorbent

ii. From the film to the adsorbent surface

iii.   From the surface to the internal sites followed by binding of the metal ions onto the active sites.

All the above mentioned steps are assembled together under kinetic modeling. It is considered that the difference between the average solid phase concentration of the sorbate and the equilibrium concentration is the force that drives the adsorption process. It is further observed from the experimental data that at optimum agitation speed, the effects of external boundaries are nullified. Thus, application of the kinetic model is dependent solely on the initial and final concentrations of the solution at different intervals of time. It is, however, inappropriate to apply the basic kinetic models such as first and second order rate equations to an adsorption process involving a solid surface, which is hardly homogenous. Secondly, the influence of the chemical reaction is often experimentally unavoidable.

The adsorption kinetic models examined in the current study to establish the rate limiting step are, the pseudo first-order (Lagergren, 1898), pseudo-second order (Ho and McKay, 1999), Elovich (Ho and McKay, 1998) kinetic equations and the intra-particle diffusion model (Weber and Morris, 1963).

2.10.1 Pseudo first-order kinetics

The pseudo first-order or Lagergren kinetic rate equation for the sorption of liquid-solid system is derived on the basis of solid adsorption capacity. It is one of the most widely used sorption rate equations for sorption of a solute from an aqueous solution (Taqvi *et al*., 2006). According to the studies conducted, the net rate of adsorption is directly proportional to the driving force, which implies to the difference between initial and equilibrium concentrations of the sorbate (q_e-q_t). Thus the Lagergren first-order rate equation is represented by equation 2.12

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{2.12}$$

where, q_e and q_t are the adsorption capacity (mg/g) at equilibrium time and at any instant of time, t, respectively and k_1 (min^{-1}) is the rate constant of pseudo first-order adsorption process.

From the boundary conditions, $t=0$ to $t=t$, $q_t=0$ to $q_t=q_t$, equation 2.12 can be arranged into linear form as given by equation 2.13.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{2.13}$$

From the plot of log $(q_e$-$q_t)$ versus t, the adsorption rate constant, k_1, is estimated.

2.10.2 Pseudo second-order kinetics

In designing adsorption system, the rate of adsorption is an important parameter. The residence time of the adsorbate and the dimensions of the reactor are determined by the kinetics of the system (Ho, 2006b). The pseudo second-order model is based on the adsorption capacity of the adsorbent and is expressed by equation 2.14.

The pseudo second-order adsorption kinetic rate equation is expressed as,

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{2.14}$$

where, k_2 is the second order rate constant (g mg^{-1} min^{-1})

when $t=0$, $q=0$, and at $t=t$, $q=q$, equation 2.14 can be expressed linearly as,

$$\frac{t}{q_t} = \frac{1}{\square} + \left(\frac{1}{q_e}\right)t \tag{2.15}$$

where, $h=k_2q_e^2$, is the initial sorption rate as $t{\rightarrow}0$. The constants can be estimated from the straight line plot of t/q_t versus t.

2.10.3 Elovich kinetic model

In Elovich equation it is obvious to assume energetically heterogenous solid surfaces because the kinetics of the adsorption at low surface coverage remains substantially unaffected by both desorption and interactions between the adsorbate molecules. The Elovich equation (Ho and Mckay, 1998) is expressed as equation 2.16

$$\frac{dq_t}{dt} = \alpha_{exp}(-\beta q_t) \tag{2.16}$$

where, q_t is the amount of gas adsorbed in time 't', α (mg g^{-1} min^{-1}) is the initial adsorption rate and β (g/mg) is the desorption coefficient. By applying boundary conditions $q_t=0$ at $t=0$ and $q_t=q_t$ at $t=t$, and by assuming $\alpha\beta \gg t$, the equation 2.16 can be represented in the linear form as given in equation 2.17.

$$q_t = \frac{1}{\beta}ln(\alpha\beta) + \frac{1}{\beta}ln\,t \tag{2.17}$$

The kinetic constants, α, and β , are estimated from the slope and intercept of the straight line plot of q_t versus ln t.

2.10.4 Intra-particle diffusion model

Lagergren pseudo first-order and pseudo second-order rate equations are unable to ascertain the diffusion mechanisms that govern the sorption process. The mechanism governing the adsorption process can be better understood by the intra-particle diffusion model. The uptake of metal ions varies almost proportionately with the half-power of time, $t^{0.5}$, rather than time't'. The participation of two or more steps in adsorption process is revealed by the multi-linear nature of the plot of q_t versus $t^{0.5}$ (Sun *et al.* 2003). The intra-particle diffusion model can be expressed as,

$$q_t = K_{id}t^{0.5} + I \tag{2.18}$$

The linear nature of the plot of q_t versus $t^{0.5}$ indicates that intra-particle diffusion governs the adsorption process and is the rate controlling step if the line passes through the origin (Smiciklas *et al*. 2006). The intercept of the intra-particle diffusion plot, *I*, assigns the value for the thickness of the boundary layer. The larger the value of *I*, the greater is the boundary layer effect (Poots *et al*. 1978). The intra particle diffusion coefficient, K_{id} (mg g^{-1} min$^{0.5}$), can be obtained from the slope of the plot of q_t versus $t^{0.5}$.

2.11 The adsorption process

A thermodynamic equilibrium between the solid and the fluid phases in an adsorption system can be achieved through the adsorbate-adsorbent interactions. At equilibrium, adsorption and desorption take place at equal rates and there is no further increase in the net loading on the solid. This is required during regeneration of the adsorbent to achieve further adsorption. The adsorption system is designed in a way to promote maximum contact between the fluid (adsorbate) and the solid (adsorbent). The adsorption processes can be carried out in any of the following ways:

i. Batch process

ii. Fixed bed process

iii. Moving bed process

i. **Batch process**: In a batch process (Thomas and Crittenden, 1998), the adsorbent is agitated relative to the walls of the containing vessel. Here the adsorbent is mixed with a batch of fluid; most commonly a liquid, for a fixed duration and then the adsorbent is removed from the fluid by sedimentation, filtration or any other method of separation. This method is often adopted for removal of taste and odor

from waters using powdered activated carbon (PAC). Using isotherm equation, the uptake of the adsorbate by the adsorbent can be associated to the final concentration of the adsorbate in the solution when adequate time is allowed to the adsorption system to attain equilibrium. Sufficient dispersion and mixing is ensured by adding the powdered or granular adsorbent in slurry form into the equipment. The adsorbent can be removed as a settled sludge. A multiple batch or cross-flow system may be devised while using large quantities of adsorbent. On separation of the fluid from the adsorbent, the former is allowed to contact with another fresh batch of adsorbent. As the concentration of the impurity in the solution declines, the removal of impurity by the adsorbent also decreases gradually with each subsequent batch of adsorbent.

A more efficient way to accomplish the multiple batch-wise contacting process is to perform the adsorption steps counter-currently (Fox and Kennedy, 1985). Fresh adsorbent can be first employed to contact the last stage of adsorption and partially loaded adsorbent is then contacted with second-to-last stage and so with forth. The amount of adsorbent needed to remove a desired amount of sorbate is considerably smaller in a counter-current process, than that involved in a single stage process or a multiple-stage process where fresh adsorbent is utilized in each stage.

ii. **Fixed bed process:** A fixed bed process enables a degree of separation and removal that would require several steps in batch process. The columnar configuration is frequently designed as a multiple-stage batch adsorption process. The uppermost portion of bed is in continuous contact with the fresh adsorbate solution whereas the lower portion of bed is in contact with the solution containing the adsorbate that remains unadsorbed by the upper portion. Thus, the

top of the column becomes fully loaded first and then the bottom is loaded which results in the generation of an adsorption front in the column, which moves downward.

The configuration of the fixed bed process is not complicated and comparatively inexpensive to assemble and the attrition of adsorbent is negligible when it remains fixed in position. However, the process suffers from certain disadvantages as observed by Thomas and Crittenden (1998). These are as follows.

a. The transfer of adsorbate molecules from the feed to the solid takes place initially at the bed entrance, as the liquid passes through the fixed bed adsorbent. Once saturation of the adsorbent in this region sets in, the zone in which mass transfer occur, proceed through the bed towards the exit. When the occurrence of the breakthrough of the adsorbate originates, it is mandatory to take the bed off-line so that the adsorbate can be regenerated.

b. It is practicable to take the adsorption bed off-line for any time upto the breakthrough. Thus, more than one bed of adsorbent is required in the entire process in order to have a continuous stream of product. The time require for the second bed to regenerate must not exceed the time required to attain the breakthrough of the adsorbate during adsorption in the first bed.

c. Although the fixed beds are very basic in configuration, it is complicated to design accurately since time is introduced into the design equations by the process of the mass transfer zone. Several short-cut design techniques

have been developed but they have considerably varying accuracy, thereby introducing inevitable uncertainties into the system.

iii. **Moving bed process:** In this configuration, adsorption, regeneration and back washing occurs simultaneously, though in separate locations, since the adsorbent is moved around a single loop of interconnected vessels. The counter- current operation of the system with adsorbent moving in one direction and all solutions in the other is the most feasible. Usually, the moving bed process comprises of two modes; the operating mode, where the entire volume of adsorbate is contacted with the fluid for a fixed duration, and the pulse mode, during which the adsorbent is moved from one section to the other as a compacted slug.

Regeneration of the adsorbent is the first and foremost advantage of the moving bed process. In addition to this, moving bed and fluidized bed system have more improved heat transfer than fixed beds. Another advantage of this process is that the continuous nature of the process avoids duplication of holding tanks. However, this process also has certain disadvantages, as it demands higher investments than the fixed bed systems. The complicated operation process requires automatic control and wide range of process instrumentation. Attrition of the adsorbent is unavoidable during the movement of the bed which further leads to adsorbent loss and hence significant adjustment is required.