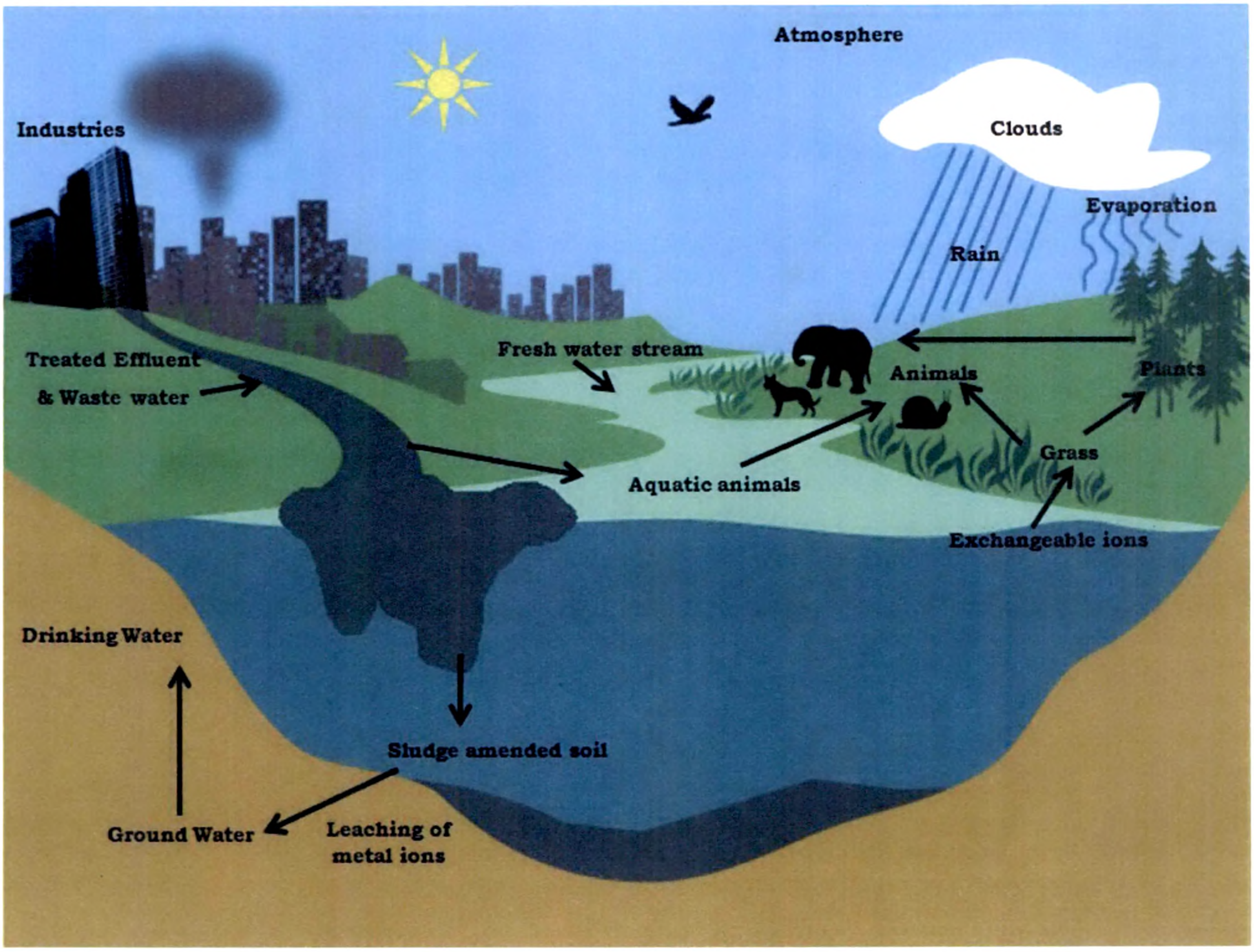
Chapter 1

Introduction



'Heavy metals' is a general collective term applied to the group of metals and metalloids with an atomic density greater than 6 g/cm^3. Although it is only a loosely defined term it is widely recognized and usually applied to the elements such as Cd (cadmium), Cr (chromium), Cu (copper), Hg (mercury), Ni (nickel), Pb (lead) and Zn (zinc) which are commonly associated with pollution and toxicity problems.

Unlike most organic pollutants, heavy metals occur naturally in rock-forming and ore minerals and so a range of normal background concentrations is associated with each of these elements in soils, sediments, waters and living organisms. On an annual basis, significant quantities of various heavy metals are produced from the mining of their respective ores.

Industrial uses of metals and other domestic processes (e.g. burning of fossil fuels, incineration of wastes, automobile exhausts, smelting processes and the use of sewage sludge as landfill material and fertilizer) have introduced substantial amounts of potentially toxic heavy metals into the atmosphere and into the aquatic and terrestrial environments. Discharged toxic metals typically include Cd, Cu, Ni, Cr, Co, Zn and Pb [1].

While many of the heavy metals are needed by plants at the micronutrient level, higher concentrations are known to produce a range of toxic effects. At high exposure levels, lead causes encephalopathy, cognitive impairment, behavioural disturbances, kidney damage, anaemia and toxicity to the reproductive system [2]. Chromium is widely recognised to exert toxic effects in its hexavalent form [3]. Human exposure to Cr(VI) compounds is associated with a higher incidence of respiratory cancers [4]. Cadmium is associated with nephrotoxic effects particularly at high exposure levels; long-term exposure may cause bone damage as well [5]. High concentrations of mercury can lead to neuro behavioural disorders and developmental disabilities including dyslexia, attention deficit hyperactivity disorder, and intellectual retardation [6]. Excessive copper concentrations can lead to weakness, lethargy and anorexia, as well as damage to the gastrointestinal tract [7]. The toxic effects of nickel and other heavy metals are discussed in some detail by Nordberg et al. [8].

Pollutants like uranium arise into the wastewaters as a result of different industrial activities like: mining, production of nuclear fuels, laboratory investigations, etc.. Uranium contamination poses a threat in some surface and ground waters. The chemical toxicity of uranium is predominantly caused by the highly reactive hexavalent uranyl ions [9]. Uranium disposed into the environment can reach the top of the food chain and be ingested by humans

[10], causing kidney or liver damage to humans [11-13]. Removal of radioactive ions from the wastewaters is a huge problem because these ions are extremely dangerous for the environment and human health by their high toxicity even at very low concentrations and long half lives. Hence, the removal of uranium from waste water is important not only for the nuclear industry, but also for environmental remediation [14].

Presence of metals in water streams and marine water causes a significant health threat to the aquatic community which is most common for the damage of the gill of the fish [15, 16]. Consequently, in many countries, more strict legislation has been introduced to control water pollution. Various regulatory bodies have set the maximum prescribed limits for the discharge of toxic heavy metals in the aquatic systems. However, the metal ions are being added to the water stream at a much higher concentration than the prescribed limits by industrial activities, thus leading to the health hazards and environmental degradation. Table 1.1 shows the permissible limits and health effects of various toxic heavy metals [17-20].

Removal of metal ions from wastewater in an effective manner has thus become an important issue today. Various methods exist for the removal of heavy metal ions from wastewater which include chemical precipitation/coagulation, membrane technology, electrolytic reduction, ion exchange and adsorption [21, 22]. The advantages and disadvantages associated with each method are listed in Table 1.2.

The most widely used method of removing heavy metals from solution is to increase the pH of the effluent, thus converting the soluble metal into an insoluble form (i.e. its hydroxide). Ion exchange is the second most widely used method for heavy metal removal from aqueous streams [23]. During removal, recovery, or processing of metals, ion exchange acts as a concentrator of metals. The chemistry of the influent stream becomes very important to the success of the ion exchange application.

Coagulation–flocculation can also be employed to treat wastewater laden with heavy metals wherein the coagulation process destabilises colloidal particles by adding a chemical agent (coagulant) and results in sedimentation [24]. Coagulation is followed by flocculation of the unstable particles in order to increase their size and form into bulky floccules which can be settled out. Flotation is employed to separate solids or dispersed liquids from a liquid phase using bubble attachment [24]. Adsorptive bubble separation employs foaming to separate the metal impurities. Ion flotation, precipitate flotation and sorptive flotation are the main flotation process mechanisms for removal of metal ions from solution. Membrane filtration has received considerable attention for the treatment of inorganic effluent, since it is capable of removing not only suspended solids and organic compounds, but also inorganic contaminants such as heavy metals.

Table 1.1. Permissible limits, source and health effects of various toxic metal ions [88]

Metal	Source	Permissible limits for discharge of industrial effluent to inland surface water (mg/L)		Permissible limits by International bodies for potable water (mg/L)		Health hazards
		Indian Standard	WHO	Indian standard	WHO	
As	Electronics, paints & pigments, metallurgical industries	0.20	-	0.01	0.010	Carcinogenic, producing liver tumors, skin & gastrointestinal effects
Hg	Batteries, manure sewage sludge & electronics	0.01	-	0.001	0.001	Corrosive to skin, eyes and muscle membrane, dermatitis, anorexia, kidney damage & severe muscle pain
Cd	Fertilisers, Manure Sewage sludge, batteries, electronics & Metallurgical industries	2.00	0.10	0.01	0.003	Carcinogenic, causes lung fibrosis, dyspnea & weight loss
Pb		0.10	0.10	0.05	0.010	Suspected carcinogen, loss of appetite, anemia, muscle & joint pains, diminishing IQ, cause sterility, kidney problem &high blood pressure
Cr	Metalliferous mining, Paints & pigments, Electroplating, Electronics	0.10	-	0.05	0.050	Suspected human carcinogen, producing lung tumors, allergic dermatitis
Ni	Metalliferous mining, Electroplating, Electronics, metallurgical industries	3.00	-	0.02	-	Causes chronic bronchitis, reduced lung function, cancer of lungs and nasal sinus
Zn	Metalliferous mining, Paints & pigments, Electroplating, Batteries	5.00	5.0-15.0	5.0	-	Causes short-term illness called metal fume fever & restlessness
Cu	Metalliferous mining, Electroplating, metallurgical industries	3.00	0.05-1.5	1.5	-	Long term exposure causes irritation of nose, mouth, eyes, headache, stomachache, dizziness, diarrhea
Fe	Metallurgical industries	3.00	0.1-1.0	0.30	0.20	Excess amounts cause rapid pulse rates, congestion of blood vessels, hypertension
U	Metallurgical industries	-	-	-	0.03	Dermatitis, renal damage, acute necrotic arterial lesions, respiratory irritants, with coughing, shortness of breath.

Table 1.2. Advantages and disadvantages of different methods used for removal of metal ions

	Physical or Chemical Methods	Advantages	Disadvantages
Conventional Treatment processes	Adsorption	Flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants	Adsorbent requires regeneration
	Biodegradation	Economically attractive and publically acceptable treatment	Slow, necessary to create an optimal favorable environment, maintenance and nutrition requirements
	Coagulation/ Floculation	Simple and Economicaly feasible	High sludge production and formation of large particles
Established recovery Processes	Oxidation	Rapid and efficient process for toxic pollutants removal	High energy costs and formation of byproducts
	Ion exchange	Effective for a wide range of heavy metals	Adsorbent requires regeneration or disposal
	Membrane filtration technologies	Good removal of heavy metals, produces a high quality treated effluent	High pressures, expensive, incapable of treating large volumes, Concentrated Sludge production
	Electrokinetic Coagulation	Economicaly feasible	High sludge production
	Fentons Reagents	Effective and capable of treating variety of wastes and no energy input necessary to activate hydrogen peroxide	Sludge generation
	Electrochemical treatment	Rapid process and effective for certain metal ions	High energy costs and formation of byproducts
Emerging removal processes	Advanced Oxidation processes (Ozonation, Photochemical, Irradiation)	No sludge production, little or no consumption of chemicals, high efficiency, Effective at lab scale	Economically unfeasible, formation of by-products, technical constraints
	Biological Treatment	Feasible in removing some metals	Technology yet to be established and commercialised
	Selective bioadsorbents	Economically attractive, regeneration is not necessary, high selectivity	Requires chemical modification, non-destructive process
	Biomass	Low operating cost, good efficiency and selectivity, no toxic effect on microorganisms	Slow process, performance depends on some external factors (pH, salts)

In accordance with the very abundant literature data, liquid-phase adsorption is one of the most popular methods for the removal of toxic pollutants from wastewater, since proper design of the adsorption process will produce a high quality treated effluent [25]. This process provides an attractive alternative for the treatment of contaminated water, especially if the adsorbent is inexpensive and does not require an additional pre-treatment step before its application. Adsorption has been found to be superior compared to the other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants. Adsorption also does not result in the formation of harmful substances.

A number of materials have been extensively investigated as adsorbents in water pollution control. Some of the important ones include silica gel, activated alumina, zeolites, activated carbon and clays.

Activated Carbon

Activated carbon (AC) has undoubtedly been the most popular and widely used adsorbent in wastewater treatment throughout the world. There are different physical forms by which AC can be found, including: (i) granular activated carbon (GAC); (ii) powdered activated carbon (PAC); (iii) activated carbon fibers (ACF); and (iv) activated carbon cloths (ACC). GAC can be prepared from hard material, such as coconut shells, and normally includes particles retained in an 80-mesh sieve (0.177 mm); it is commonly used as column filler for gas or liquid treatments and can be regenerated after use. When small particles compose the raw material, like wood sawdust, PAC is obtained (includes particles of 0.177 mm); PAC is normally mixed with the liquid to be treated and afterwards disposed of. Due to its small particles, PAC adsorption is normally very effective, however, and for the same reasons, settling and removal tend to be slower than when using GAC. ACF can be prepared from homogeneous polymeric raw materials and, as opposed to GAC and PAC, show a monodispersed pore size distribution [26]. Their thin fiber shape enhances intra-particle adsorption and therefore improved contact efficiencies between the aqueous media and the adsorbent can be achieved [27].

ACC were initially developed in the early 1970s, using as precursors phenolic or viscose rayon [28] and are considered to be excellent adsorbents due to their low-pressure drop during process, high contact efficiency and flexibility [29]. Although many kinds of adsorbents were already prepared and tested in aqueous-phase treatments, GAC and PAC are still the most widely used.

However, activated carbon is expensive which limits its large scale application. According to Bailey and Wan Ngah, an adsorbent can be considered as cheap or low-cost if it is abundant in nature, requires little processing and is a byproduct of waste material from waste industry [30, 31].

A potential method to reduce the cost of activated carbon production is to use low-cost materials as precursors for the production of activated carbon. AC can be prepared from a wide variety of raw materials [32], which should be abundant and cheap, with high carbon content and low inorganic content; raw materials should be easily activated and should have low degradation by aging [33]. Coal is the most commonly used precursor, mainly due to its low cost and large supply [34]. The adsorption properties of each type of coal are determined by the nature of the vegetable material and the extent of the physical–chemical changes occurring during coal formation and after its deposition [35].

The preparation of AC from waste materials has several advantages, mainly of economic and environmental nature. A wide variety of ACs have been prepared from different waste materials; conventional wastes (from agriculture and wood industry) as well as non-conventional wastes (from municipal and industrial activities) have been used.

Non-conventional wastes (from municipal and industrial activities)

The economical activities in the modern society gradually created a pattern of mass production, mass consumption as well as mass deposition [36]. As a consequence, there is an accumulation of several industrial and post-consumer waste products, which by their nature are difficult or poorly effective to be regenerated into other materials and that more currently end up in incineration plants or landfills. Due to the more restricted environmental standards, limitations on the application of such alternatives are [illegible] increasing.

The discharge of plastic wastes, such as polyethylene terephthalate (PET) and polyvinyl chloride (PVC), industrial wastes, such as oil combustion residues and fabrics, as well as the discharge of tires, sewage sludges, and fertilizers, represents a serious challenge for waste management strategies. It is therefore of main relevance to find alternatives by which such materials can be reused or recycled according to environmentally acceptable procedures [37].

The use of such non-conventional wastes as carbon source for the production of AC might be an efficient alternative for both, adoption of effective waste management practices, and production of low-cost AC. A review of the literature showed that there are a considerable amount of studies dedicated to the valorization of such wastes, namely for the production of AC. Plastic wastes, various industrial wastes like fly ashes, pitch, and polymeric residues from factories as well as other wastes such as tires and sewage sludge have been used as raw material for AC production. For instances, a waste commercial ion-exchange resin might be used to prepare AC with values of specific surface area and pore volume suggesting its application in different purposes, that might include aqueous-phase treatments [38].

Also, AC can be successfully prepared from both old newspaper and paper prepared from simulated paper sludge [39, 40]. Naturally, studies show that raw materials with higher carbon content lead to the achievement of a better AC. Generally, AC show good texture and potential to compete with commercial ones.

Conventional wastes (from agriculture and wood industry)

Due to their abundance, agricultural wastes have low economic value; additionally, their current deposition creates significant environmental degradation. Agricultural waste is a rich source for AC production due to its low ash content and reasonable hardness [35]; therefore, conversion of agricultural wastes into AC is a promising alternative to solve environmental problems and also to reduce the costs of AC preparation.

There are currently a large number of studies regarding the use of several agricultural wastes to produce AC. Most of them focus on the use of waste materials of considerable rigidity, such as the shells and/or stones of fruits like nuts, peanuts, olives, dates, almonds, apricots and cherries; however, wastes resulting from the production of cereals such as rice, coffee, soybean, maize and corn as well as olive cakes, sugar cane and sugar beat bagasse, coirpith, oil-palm shell (from oil-palm processing mills) and various seed wastes were already used.

Most of the reviewed studies show that these materials can compete with the commercial AC, and some of them have even better behavior than the commercial ones. Some relevant issues concerning different recent studies on the application of these materials in aqueous phase were summarized.

Due to their particular porous characteristics, woody materials are very relevant and challenging raw materials to prepare AC, namely for the adsorption of solutes in the liquid phase [41]. The wood industry is responsible to produce great amounts of woody waste materials that might be recycled to produce AC. Also, several forest residues can be used, additionally contributing to a better forest management and conservation. Many studies were made concerning the recycling of these materials for the production of AC. Woody materials of different types such as cedar, fir, oak, as well as from tropical trees have already been used.

The application of AC prepared from woody materials has been made for the removal of contaminants such as organic compounds, dyes, and heavy metals, from aqueous phase. These materials seem to be very effective in adsorbing heavy metals such as chromium and copper, being considered potentially good substitutes of the commercial ones. The adsorption rate is normally influenced by the proportion of AC used. On the other hand, PAC obtained from sawdust might be used to prepare GAC with the addition of a proper binder and a reinforcer; such GAC seems to have a very good behavior in adsorbing phenol, namely through physisorption mechanisms [42]. It was concluded that woody materials lead to AC showing good adsorption behaviour for adsorbates of various molecular forms.

When using activated carbon, the adsorption process results from interactions between the carbon surface and the adsorbate. These interactions can be electrostatic or non-electrostatic. When the adsorbate is an electrolyte that dissociates in aqueous solution, electrostatic interactions occur; the nature of these interactions, that can be attractive or repulsive, depends on the: (i) charge density of the carbon surface; (ii) chemical characteristics of the adsorbate; and (iii) ionic strength of the solution. Non-electrostatic interactions are always attractive and can include: (i) van der Waals forces; (ii) hydrophobic interactions; and (iii) hydrogen bonding.

According to Moreno-Castilla [43], the properties of the adsorbate that mainly influence the adsorption process in AC are: (1) molecular size; (2) solubility; (3) pK_a; and (4) nature of the substituents (in the case of aromatic adsorbates). The molecular size determines the accessibility of the adsorbate to the pores of the carbon, the solubility determines the degree of hydrophobic interactions between the adsorbate and the carbon surface and pK_a controls the dissociation of the adsorbate (if it is an electrolyte). When the adsorbate is aromatic, the substituents of the aromatic ring have the ability to withdraw or release electrons, which therefore affects the non-electrostatic interactions between the adsorbate and the AC surface. When the AC is in contact with an aqueous solution, an electric charge is generated. This charge results from either the dissociation of the surface functional groups of the carbon or the adsorption of ions from the solution, and strongly depends on the solution pH and on the surface characteristics of the adsorbent [44]. The central issue for ion adsorption from an aqueous medium is the understanding of the mechanisms by which ionic species become attached to the carbon surface. There are three different mechanisms by which metallic ions (or other ions) are removed from an aqueous solution. The first states that the process is based on electrostatic adsorbate–adsorbent interactions being totally dependent on the existence of carbon surfaces functionality, especially oxygen surfaces complexes (ion-exchange process). The second one suggests that enhanced adsorption potentials, as occurs in the narrowest of microporosity, may be strong enough to adsorb and retain ions. The third mechanism is based on the hard and soft acids and bases concept, a consequence of the amphoteric nature of carbon surfaces.

Variable amounts of atoms, known as heteroatoms, can be found in AC (e.g. oxygen, hydrogen, nitrogen and sulphur). These atoms, which might have origin in the raw material or could be introduced during preparation or further treatments [45], deeply influence the charge, hydrophobicity and electronic density of the AC surface. The carbon surface chemistry is, therefore, influenced by the presence of heteroatoms [46] and has a great influence on both, electrostatic and non-electrostatic interactions. Additional information regarding the surface characteristics of AC which determine the removal of pollutants from the aqueous phase can be found in a review by Moreno- Castilla and Rivera-Utrilla [33]. AC texture includes a wide range of pores that can be classified according to their width as: micropores (2 nm), mesopores (2–50 nm) and macropores (450nm) [43].

Natural materials

Because of their low cost and local availability, natural materials such as chitosan, zeolites, clay, or certain waste products from industrial operations and plant wastes are classified as low-cost adsorbents.

Chitosan has received considerable interest for heavy metals removal due to its excellent metal-binding capacities and low cost. Fishery wastes such as shrimp, lobster, and crab shells have been developed into one of the promising options to produce chitosan. These wastes could be obtained for free from local fishery industries. Since such wastes are abundantly available, chitosan may be produced at low cost. Consequently, chitosan offers a lot of promising benefits for wastewater treatment applications today. The discussion on chitosan as an adsorbent is taken up in chapter 7.

Zeolites are aluminosilicates with Si/Al ratios between 1 and infinity. There are 40 natural and over 100 synthetic zeolites. Natural zeolites also gained a significant interest among scientist, mainly due to their valuable properties such as ion exchange capability, cost efficiency since they are able to treat wastewater contaminated with heavy metal at low cost. Various zeolites have been employed for the removal of pollutants [47-50]. Recently, Wang and Peng [51] discussed the role of natural zeolites as effective adsorbents in water and wastewater treatment [52].

Clay is one of potential alternatives to activated carbon as well. Similar to zeolites, clay minerals are also important inorganic components in soil. Their adsorption capabilities come from their high surface area and exchange capacities. The negative charge on the structure of clay minerals gives clay the capability to attract metal ions [53].

Industrial wastes as an adsorbent for removal of heavy metals

Industrial waste is also one of the potentially low-cost adsorbent for heavy metal removal. It requires little processing to increase its adsorptive capacity. Generally industrial wastes are generated as by-products. Since these materials are locally available in large quantities, they are inexpensive. In India, various types of industrial wastes such as waste slurry, lignin, iron(III) hydroxide, and red mud, have been explored for their technical feasibility to remove heavy metals from contaminated water [53]. Low rank coal, such as lignite, is capable of having ion exchange with heavy metals due to its carboxylic acid and phenolic hydroxyl functional groups.

Industrial waste is also one of the potentially low-cost adsorbent for the removal of heavy metals from wastewaters. It requires little processing to increase its adsorptive capacity. Generally industrial wastes are generated as by-products. Since these materials are locally available in large quantities, they are inexpensive. Various types of industrial wastes such as fly ash, blast furnace sludge, waste slurry, lignin, iron (III) hydroxide, and red mud, have been explored for their technical feasibility to remove toxic heavy metals from contaminated water. Other industrial wastes, coffee husks, Areca waste, tea factory waste, sugar beet pulp, waste pomace of olive oil factory waste, battery industry waste, waste biogas residual slurry, sea nodule residue, and grape stalk wastes have been utilized as low-cost adsorbents for the removal of toxic heavy metals from wastewater [54].

Agricultural materials particularly those containing cellulose shows potential metal biosorption capacity. The basic components of the agricultural waste materials biomass include hemicellulose, lignin, extractives, lipids, proteins, simple sugars, water hydrocarbons, starch containing variety of functional groups that facilitates metal complexation which helps for the sequestering of heavy metals [55-58]. Plant wastes are inexpensive as they have no or very low economic value. Most of the adsorption studies have been focused on untreated plant wastes such as papaya wood [59], maize leaf [60], teak leaf powder [61], lalang (*Imperata Cylindrica*) leaf powder [62], rubber (*Heveabra Siliensis*) leaf powder [63, 64], *Coriandrum Sativum* [65], peanut hull pellets [66], sago waste[67], saltbush (*Atriplexcanescens*) leaves [68, 69], tree fern [70-72], rice husk ash and neem bark [73], grape stalk wastes [74], etc. Some of the advantages of using plant wastes for wastewater treatment include simple technique, requires little processing, good adsorption capacity, selective adsorption of heavy metal ions, low cost, easy availability and easy regeneration.

However, the application of untreated plant wastes as adsorbents can also bring several problems such as low adsorption capacity, high chemical oxygen demand (COD) and biological chemical demand (BOD) as well as total organic carbon (TOC) due to release of soluble organic compounds contained in the plant materials [75, 76]. The increase of the COD, BOD and TOC can cause depletion of oxygen content in water and can threaten the aquatic life. Therefore, plant wastes need to be modified or treated before being applied for the decontamination of heavy metals.

Wan Ngah and Hanafiah [31] in their review have compiled an extensive list of adsorbents obtained from plant wastes and their methods of modification are discussed. A comparison of adsorption efficiency between chemically modified and unmodified adsorbents is also reported. The most common chemicals used for treatment of plant wastes are acids and bases. Chemically modified plant wastes vary greatly in their ability to adsorb heavy metal ions from solution. Chemical modification in general improved the adsorption capacity of adsorbents probably due to higher number of active binding sites after modification, better ion-exchange properties and formation of new functional groups that favors metal uptake.

Although chemically modified plant wastes can enhance the adsorption of heavy metal ions, the cost of chemicals used and methods of modification also have to be taken into consideration in order to produce 'low-cost' adsorbents. Many reviews are available in literature focusing on the low cost adsorbent from the natural resources [31, 77-89]. Table 1.3 shown below includes the agro-based adsorbents studied for Cu, Cd, Zn, Hg, Cr and U in the last five years and which have not been included in reviews yet.

Table 1.3. Low-Cost adsorbents with their maximum adsorption capacities

Adsorbent	q_{max} (mg g^{-1})						References
	Cu	Cd	Zn	Hg	Cr	U	
Sawdust (Poplar tree)	12.7	-	15.8	-	-	-	[90]
Cassava tuber bark waste	90.9	26.3	83.3	-	-	-	[91]
Jute fibres	8.40	-	8.02	-	-	-	[92]
Azolla filiculoides (aquatic fern)	62	86	48	-	-	-	[93]
Carrot residues	32.74	-	29.61	-	45.09	-	[94]
Sugarcane bagasse	313	139	-	-	23	-	[95, 96]
Sugarbeet pulp	0.15	-	0.18	-	-	-	[97]
Rice husk	2.48	8.82	-	-	-	-	[98]
Modified rice husk	9.36	11.03	-	-	-	-	

Adsorbent	q_{max} (mg g^{-1})						References
	Cu	Cd	Zn	Hg	Cr	U	
Caulerpalentillifera	42.37	4.69	2.66	-	-	-	[99]
Dried non-living biomass (NB) of different *Pseudomonas* strains	-	-	19.6	84.25	-	-	[100]
Lignin	22.87	25.40	11.25	-	-	-	[101]
Lignocellulosic substrate (Wheat bran extract)	10.61	-	16.02	-	-	-	[102]
Neem oil cake	0.157 mmol/g	0.133 mmol/g	-	-	-	-	[103]
Olive pomace	0.480 mmol/g	0.100 mmol/g	-	-	-	-	[104]
Rice husk	0.2175 mmol/g	-	-	0.2114 mmol/g	-	-	[105]
Wheat bran	0.199 mmol/g	-	-	0.239 mmol/g	-	-	[106]
rice husk	-	3.04	14.30	9.32	-	-	[107-109]
Sulfuric acid treated rice husk (wet sorbent)	-	41.15	19.38	384.62	-	-	[110, 111]
Tea industry waste	-	0.45	0.59	-	-	-	[112]
Maize husk (unmodified)	-	4×10^{-6}	0.49	-	-	-	[113]
Maize husk (EDTA modified)	-	114.1	614.11	-	-	-	
Magnetically modified brewer's yeast	-	-	-	30.40	-	-	[114]
Sugarcane bagasse	-	38.03	31.11	-	-	-	[115]
Bacillus jeotgali	-	57.90	222.2	-	-	-	[116]
Dried non-living biomass (NB) of different *Pseudomonas* strains	-	-	19.06	84.25	-	-	[117]
*Cupriavidustaiwanensis*TJ208	19	19.6	-	-	-	-	[118]
Mimosa pudica inoculated with TJ208	25.4	42.9	-	-	-	-	
*Mimosa pudica*without inoculation	22.7	25.30	-	-	-	-	
P. chrysosporium	26.5	27.8	-	-	-	-	[119]
Trametesversicolor	116.9	109.2	-	-	-	-	[120]
Sawdust	8.07	-	17.09	-	-	-	[92]
Almond shell	-	-	-	-	0.580 mmol/g	-	[121]
AzadirachtaIndica (Neem) leaf Powder	-	1.404 mmol/g	-	-	1.211 mmol/g	-	[122, 123]
Green coconut shell powder	-	2.541 mmol/g	-	-	1.412 mmol/g	-	[124]
Waste slurry	20.97	15.73	-	560	640	-	[125, 126]
Gelidium	-	-	13	-	18	-	[127]
Algal waste	-	-	7.1	-	11.8	-	

Adsorbent	q_{max} (mg g^{-1})						References
	Cu	Cd	Zn	Hg	Cr	U	
Carboxymethyl water-insoluble dietary fiber	-	623.5 μmol/g	-	-	615.6 μmol/g	-	[128]
Terminaliaarjuna nuts Coirpith	39.7	-	-	154	28.43	-	[129]
Blast furnace sludge	16.1	-	10.15	4.3	9.55	-	
Blend coffee	2.0	2.0	-	-	-	-	[130]
Mango peel	46.09	68.92	28.21	-	-	-	[131, 132]
Red mud	19.72	10.57	12.59	-	-	-	[133]
Biogas residual slurry	-	-	-	-	7.8	-	[134]
Waste slurry	20.97	15.73	-	560	640	-	[135, 136]
ACC	-	3.75	2	65	-	-	[137]
As-received ACF	9	146	-	-	40	-	[138, 139]
Chlorella vulgaris	1.290	0.609–0.770	-	-	0.356–0.492	-	[140-142]
Risk husk ash	-	25.27	26.10	46.14	26.31	-	[143-145]
Coir pith	39.7	93.4	-	-	138.04–317.65	-	[146-148]
Chitosan coated ACSC	-	-	60.41	-	-	-	[149]
PGCP-COOH	-	-	-	4.99–31.15	-	-	[150]
TARH	29	-	-	-	-	-	[151]
RHC	-	-	-	48.31	-	-	[152]
Activated carbon	-	-	-	-	-	28.49	[153]
CR-azole	-	-	-	-	-	1.60 mol/g	[154]
CR-amine	-	-	-	-	-	1.90mol/g	
Aspergillusniger	5	-	-	-	-	29	[155]
Penicilliumchrysogenum	9	56	6.5	-	-	70	
Rhizopusnigricans	-	19	14	-	47	-	
R. arrhizus	9.5	27	14	-	36	220	
Date pits	-	-	-	-	-	10	[156]
Catenellarepens-red alga	-	-	-	-	-	303.0	[157]
Cross-linked chitosan	-	-	-	-	-	72.46	[158]
ACs-benzoylthiourea-anchored anchored	-	-	-	-	-	113.76	[159]
chitosan/clinoptilolite composite	-	-	-	-	-	562.58	[160]
Chitosan	-	-	-	-	-	482.66	
Chitosan/cotton fibers	24.78	15.74	-	104.31	-	-	[161]
Chitosan/cellulose	26.50	-	19.81	-	13.05	-	
Penicilliumcitrinum	-	-	-	-	-	274.73	[162]
Bi-functionalized biocomposite	-	-	-	-	-	43.2	[163]

Although the amount of available literature data on the use of low-cost adsorbents in water and wastewater treatment is increasing at a tremendous pace, some important issues need to be considered during the consideration of a material as a potential low cost adsorbent:

(1) Selection and identification of an appropriate low-cost adsorbent is one of the key issues to achieve the maximum removal/adsorption of specific type of pollutant depending upon the adsorbent–adsorbate characteristics.

(2) The conditions for the production of low-cost adsorbents after surface modification for higher uptake of pollutants need to be optimized.

(3) Low production cost with higher removal efficiency of adsorbents would make the process economical and efficient.

(4) Mechanistic studies need to be performed in detail to propose a correct binding mechanism of aquatic pollutants with low cost adsorbents.

(5) Regeneration studies need to be performed in detail with the pollutants-laden adsorbent to recover the adsorbate as well as adsorbent. It will enhance the economic feasibility of the process.

(6) The potential of low-cost adsorbents under multi-component pollutants needs to be assessed. This would make a significant impact on the potential commercial application of low-cost adsorbents to industrial systems.

(7) The effectiveness of the treatment depends not only on the properties of the adsorbent and adsorbate, but also on various environmental conditions and variables used for the adsorption process, e.g. pH, ionic strength, temperature, existence of competing organic or inorganic compounds in solution, initial adsorbate/adsorbent concentration, contact time and speed of

rotation, particle size of adsorbent, etc. These parameters should also be taken into account while examining the potential of low-cost adsorbents.

(8) The development in the field of adsorption process using low cost adsorbents essentially requires further investigation of testing these materials with real industrial effluents.

(9) Because various heavy metal ions are often present in industrial effluents or other water resources, there is significant research and practical interest to develop the methods that can effectively remove the heavy metals and, at the same time, recover them in their individual pure form for potential reuse to avoid the second pollution problems of these heavy metals (in a more concentrated form) after they are removed from the water to a certain regulated level. A possible solution to achieve this target is to use adsorbents modified with selective ligands or ion imprinting polymers that have selectivity toward the metals to be separated and recovered.

(10) Last but not the least, environmentally safe disposal of pollutants-laden adsorbents is another important topic of concern which should not be overlooked.

If it is possible to develop such adsorbents having all the above-mentioned characteristics, then these adsorbents may offer significant advantages over currently available expensive commercially activated carbons and, in addition contribute to an overall waste minimization strategy.

A detailed critical investigation into literature and the above deliberations paved the way for us to explore the potential of palm shell (Borassus Flabellifer) as an adsorbent. *Borassus flabellifer* is a robust tree and can live 100 years or more and reach a height of 30 m, with a canopy of leaves several dozen fronds spreading 3 meters across. The large trunk resembles that of the coconut tree and is ringed with leaf scars. There are approximately 8.59 crores of palm trees all over world which produces around 80 pieces of fruits per tree per year [164].

Trees are economically useful, and widely cultivated in tropical regions. The *Borassus flabellifer* has long been one of the most important trees of India, where it has number of uses. The leaves are used for thatching, mats, baskets, fans, hats, umbrellas, and as writing material. The stalks are used to make fences and to make a strong, wiry fiber suitable for cordage and brushes. The black timber is hard, heavy, and durable and is highly valued for construction, such as for wharf pilings.

The tree also yields many types of food. The young plants are cooked as a vegetable or roasted and pounded to make meal. The fruits are eaten roasted or raw, and the young, jellylike seeds are also eaten. A sugary sap, called toddy, can be obtained from the young inflorescence, either male or female ones. The toddy is fermented to make a beverage called arrack, or it is concentrated to a crude sugar called jaggery/palm sugar. The roots can be dried to form Odiyal, a hard chewable snack. In addition, the tree sap is taken as a laxative, and medicinal values have been ascribed to other parts of the plant [164].

The recently germinated seeds form fleshy sprouts below the surface which can be boiled and eaten as a fibrous, nutritious food. The germinated seed's hard shell is also cut open to take out the crunchy kernel which tastes like a water chestnut but is sweeter. The ripe fibrous outer layer of the fruits is edible after boiling or roasting. When the fruit is tender, the kernel inside the hard shell is an edible jelly that is refreshing and rich in minerals. When the crown of the tree from which the leaves sprout is cut we get an edible cake [164].

Only the outer hard shell of the kernel has not been used and usually thrown as waste or used as fuel. We thus felt that we could study the potential of shell of kernel of *Borassus flabellifer* as adsorbent and as precursor for the development of a range of adsorbents which may provide an alternative for the commercially available expensive adsorbents.

Furthemore, chitosan is another natural material which can form chelates with a number of metals, can be derivatized because of its amino groups and can also be cross-linked to increase its rigidity. Based on the above deliberations our broad objectives were:

- To prepare low cost adsorbents using palm shell as precursor
- To evaluate the potential of these adsorbents for the removal of Hg^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+}, Cr^{6+} and U^{6+}
- Application of the materials to synthetic multi-component mixtures and effluents
- To explore the possibility of preparing adsorbents selective for mercury using barbituric acid and chitosan
- Make an attempt to prepare ion imprinting polymer for uranium

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