Chapter–1

INTRODUCTION
The *American Heritage Dictionary of the English Language* (1992 edition) defines pollution as, “the act or process of polluting or the state of being polluted, especially the contamination of soil, water or the atmosphere by the discharge of harmful substances” [Rana, 2007]. An introductory college text book defines pollution in its glossary as a process, to make foul, unclean, and dirty; any physical, chemical, or biological change that adversely affects the health, survival, or activities of living organisms or that alters the environment in undesirable ways (Saigo and Cunningham, 1992). In 21st century the definition of pollution becomes wider and more complex as to include natural and social system affecting the quality of our environment. An expanded definition of pollution includes terms such as ecological restoration, ecosystem rehabilitation and revitalization as well as aesthetic pollution, cultural eutrophication and anthropogenic impacts. Human activities increased dramatically, frequently and chronically resulting into unforeseen problems of diverse nature. Anthropogenic activities “aesthetically” polluted natural landscapes, “culturally” eutrophied lakes and deliberately allowed poisonous gasses to enter the atmosphere. Beginning with the industrial revolution in the 18th century, pollution became a more noticeable phenomenon in the middle of 19th century, particularly following the American civil war. The phenomenon of acid rain was first described in the 17th century. The major events, one in the Meuse valley in Belgium in 1930 and the other in Donora, Pennsylvania in 1948 were responsible for raising alarm against air pollution in scientific community. Bhopal gas tragedy (1984) affected 3.5 lacks peoples of Bhopal (India).

Environmental pollution in general can be classified as follows.

1. **Air pollution**

The presence of one or more contaminants in the atmosphere in such quality and for such duration as is injurious, or tends to be injurious to human health or welfare, animal or plant life. It is the contamination of air by the discharge of harmful substances. Air pollution can cause health problems and it can also damage the environment and properties. It has cause thinning of the protective ozone layer of the atmosphere. Industries, vehicles, increase in the population, and urbanisation are some of the major factors responsible for air pollution. The following industries are among those that emit a large quantity of pollutants into the air: thermal power plants, cement, steel, refineries, petrochemicals and mines. The source of pollution may be in one country but the impact of pollution may be felt elsewhere.
Carbon monoxide is a toxic gas. It is a product of incomplete combustion of organic matter due to insufficient oxygen supply to enable complete oxidation to carbon dioxide. Exposures at 100 ppm or greater can be dangerous to human health [Prockop and Chichkova, 2007]. Carbon monoxide mainly causes adverse effects in humans by combining with hemoglobin to form carboxyhemoglobin (HbCO) in the blood. This prevents oxygen binding to hemoglobin, reducing the oxygen-carrying capacity of the blood, leading to hypoxia. Inhaling even relatively small amounts of the gas can lead to hypoxic injury, neurological damage, and even death. Carbon dioxide is a naturally occurring atmospheric gas that is considered safe at levels below 0.5% according to OSHA standards [CCOH S, 2005]. It is also produced by human activities. CO$_2$ is considered to be a potential inhalation toxicant and a simple asphyxiate [Aerias, 2005; NIOSH, 1976; Priestly, 2003]. It enters the body from the atmosphere through the lungs, is distributed to the blood, and may cause an acid-base imbalance, or acidosis, with subsequent CNS (Central Nervous System) depression [Nelson 2000; Priestly 2003]. Chlorofluorocarbon (CFC) released mainly from air conditioning system and refrigeration. When released into the air, CFC rise to the stratosphere, where they come in contact with other gases like ozone and lead to a reduction of the ozone layer. Ozone occurs naturally in the stratosphere of the atmosphere. This important gas shields the earth from the harmful ultraviolet rays of the sun. However at the ground level it is a pollutant with highly toxic effects. Ground level ozone is powerful oxidant and eye irritating. Nitrogen oxide causes smog and acid rain. It is produced from burning fossil fuels like petroleum and coal. Nitrogen oxide can make children susceptible to respiratory diseases in winters. Suspended Particulate matter (SPM) consists of solids in the air in the form of smoke, dust, and vapours that can remain suspended for extended period and is also the main source of haze which reduce visibility. The finer of these particles, when breathed in can lodged in lungs and causes lung damage and respiratory problems. Sulphur dioxide (SO$_2$) gas is produced from burning coal, mainly in thermal power plants. Some industrial processes, such as production of papers and smelting of metals, produce sulphur dioxide. It is a major contributor to smog, acid rain and can lead to lung diseases.

2. Land pollution
It is the pollution of the earth’s natural land surface by industrial, commercial, domestic and other agricultural activities. Some of the common sources of land pollution are chemical and
nuclear plants, industries, oil refineries, human sewage, mining, littering, debris from construction work and deforestation.

3. Water pollution

The indiscriminate disposal of water after use in the form of wastewater causes water pollution. Water pollution could be in the form of any change in the physical, chemical and biological properties of water which has harmful effect on living things. It could take place in various water sources, like ponds, lakes, rivers, seas and oceans. Water is the most abundant compound on earth, covering nearly three quarters of the planet’s surface. Although the total amount of water on earth is enormous, only a small percentage is fresh water and much of that is not readily available for human use. Over 97% of the world’s total supply of water is found in oceans which is too salty for drinking, irrigation, and most industrial and household needs. Lakes and rivers, which are the major sources of the world’s drinking water, account 1% of earth’s total water (Fig. 1.1).

![Fig. 1.1. Distribution of water on earth’s surface](image)

One of the causes of water pollution is the release of waste into the water bodies, for example domestic waste, industrial effluents, agricultural wastes. In addition infection agents, plant
nutrients, exotic organic chemicals, inorganic materials and compounds sediments and heat totally spoil the quality of water. Several legislations starting from 1899 till date have been passed in various states (Including Maharashtra India since 1964) to preserve the quality of water because the water quality is of major concern for everyone. Other causes of pollution in the sea include events such as oil spills and atmospheric deposition (where pollutants enter water bodies through falling particles, dissolving in rain, snow, or direct dissolving in water.

**Types of water pollution**

The growing human population is putting undue pressure on the planet’s water resources resulting in various type of water pollution. The qualities of major water bodies such as rivers, lakes, oceans and ground water is greatly reduced by human activities. Ground water is important to man since a large section of people in every country, including the developed nations depends on it. Moreover, this recourse is an integral component of hydrologic cycle.

Ground water pollution falls into two broad categories: **Point source and Non-Point source pollution.** Point source pollution refers to contamination originating from a single tank or a single disposal site. Leakage of gasoline from a storage tank is an example of point source pollution. Non-point source pollution also called diffuse source pollution refers to contamination that is spread out over an extensive area. For example, fertilizers and pesticides that are spread over large fields may percolate into groundwater at a number of places, causing non-point source pollution. Since non-point source pollution affects a larger area, it is generally considered to be more hazardous than point source pollution.

Chemical pollutants are subdivided into organic and inorganic pollutants (Table 1.1 and 1.2). Organic pollution is the most common form of water pollution. It is caused by the naturally occurring compounds like proteins, fats, carbohydrates etc, as well as by synthetic compounds like dyes pesticides herbicides etc. The synthetic organic derivatives cause more harm to the environment than the naturally occurring one. Some important organic pollutants, along with the sources of their origin, are listed in Table 1.1. These pollutants can be classified into two groups named **biodegradable** in which naturally occurring compounds are placed and **non-biodegradable** which includes synthetic compounds. When a biodegradable organic polluting load is discharged into a water body it is decomposed or degraded by aerobic bacteria. However non-biodegradable pollutants like detergents, pesticides, herbicides, paints, plasticizers, pharmaceuticals, industrial effluents and aromatic derivatives are resistant to microbial decomposition and also toxic in nature. Their biodegradation occurs
extremely slowly, consuming massive amount of dissolved oxygen [Sodhi, 2009]. For such reactions, the rate of oxygen consumption is greater than the rate of oxygen replenishment. Under these circumstances, depletion of dissolved oxygen occurs, resulting in severe consequences for the aquatic biota and before they are acted upon by micro-organisms they manifest their toxic effects on the aquatic living community. Thus such compounds elicit a wide range of environmental hazards.

**Biological pollutants**
Those aquatic organisms which either multiplied excessively or are otherwise undesirable, harmful or injurious are classified as biological pollutants. These pollutants generally arise as secondary result of pollution by sewage or trade wastes. Excessive growth of fresh water weeds like chest nuts is because of the discharge of untreated sewage or effluents into water. Algae multiply at an accelerated pace, causing odours in water. When they die, their cell decompose, encouraging the growth of bacteria and fungi which thrive on dead cell constituents, moreover, the decomposition of algae cells consume oxygen. The depletion of dissolve oxygen causes eutrophic conditions in water bodies likes lacks. High density of algae may also produce toxins which are lethal to animals for example; *Prymnesium parvum* produces a toxin which is harmful to the fish. The faecal contamination of water can introduce a variety of pathogenic bacteria in water. *Salmonella* can cause acute gastro-enteritis with diarrhea, fever and vomiting. *Escherichia coli* produce diarrhea in children. *Salmonella typhi* causes typhoid while *Vibrio cholerae* causes cholera. Viruses are inducted into natural water through faeces. Although these organisms are present in water in much lower number than bacteria, yet they pose a considerable health hazards because they cause greater resistance to disinfection. Many of the common infection of man are viral diseases. Influenza, small pox, poliomyelitis and yellow fever are some of the common ailments caused by viruses. Hepatitis A is transmitted by virus contaminated water. Faecal contamination of drinking water is the major source of transmission of pathogenic protozoa. Amoebic dysentery is caused by the parasitic protozoan, *Entamoeba histolytica*. It is endemic in the tropical and subtropical region. Another parasitic protozoan, *Naegleria fowleri* causes *amoebic meningoencephalitis*, a fatal disease.
Table. 1.1. Common organic pollutants.

<table>
<thead>
<tr>
<th>Pollutants</th>
<th>Representative Examples</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proteins</td>
<td>Gelatin, Keratin Casein</td>
<td>Food processing, Cannery waste, Slaughter house waste, tannery waste</td>
</tr>
<tr>
<td>Fats</td>
<td>Glycerol palmitate, glycerol stearate.</td>
<td>Fat refining, wool scouring waste, edible oil waste.</td>
</tr>
<tr>
<td>Carbohydrates</td>
<td>Starch, Cellulose</td>
<td>Paper and pulp industry, textile industry</td>
</tr>
<tr>
<td>Resins</td>
<td>Amber, Rosin</td>
<td>Paint manufacture, textile industry, lacquer industry</td>
</tr>
<tr>
<td>Soaps</td>
<td>Sodium palmitate, potassium stearate</td>
<td>Laundry waste, textile waste</td>
</tr>
<tr>
<td>Detergents</td>
<td>Sodium lauryl sulphate, polyglycol ether</td>
<td>Laundry waste, textile waste</td>
</tr>
<tr>
<td>Dyes</td>
<td>Fluorescein magenta</td>
<td>Dyeing and printing textile, paper, leather</td>
</tr>
<tr>
<td>Agro chemicals</td>
<td>DDT, 2,4-D</td>
<td>Agricultural run-off</td>
</tr>
</tbody>
</table>

Table.1.2. Common inorganic pollutants.

<table>
<thead>
<tr>
<th>Pollutants</th>
<th>Representatives examples</th>
<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acids</td>
<td>Sulphuric acids, phosphoric acids</td>
<td>Mine run-off, wool scouring waste, iron pickle liquor.</td>
</tr>
<tr>
<td>Alkalis</td>
<td>Caustic soda, lime</td>
<td>Tannery waste, cotton processing waste.</td>
</tr>
</tbody>
</table>

Both acids and alkalis destroy bacteria and so inhibit self purification of stream.

**Heavy metal pollution**

Bjerrum’s definition of “Heavy Metal” is based upon the density of the elemental form of the metal and he classifies “heavy metals” as those metals with elemental densities above 7 g cm$^{-3}$. A little later, in 1989, 1991 and 1992, Parker [Parker, 1989], Lozet and Mathieu [Lozet and Mathieu, 1991] and Morris [Morris, 1992] chose a defining density “greater than
5 g cm$^{-3}$. However, Streit [Streit, 1994] used a density of 4.5 g cm$^{-3}$ as his reference point, and Thornton [Thornton, 1995] chose 6 g cm$^{-3}$. In terms of atomic weights, heavy metals are the metals with high atomic weight; (e.g. Chromium, Cadmium and Lead) can damage living things at low concentration and tends to accumulate in the food chain [USEPA, 2000] or those metals which have atomic weight greater than Sodium (23) that forms soaps on reaction with fatty acid [Lewis Sr, 1993]. In terms of atomic number, metals with an atomic number greater than 20 [Hale and Margham, 1988] or those metals having atomic number between 21 and 92 [Lyman, 1995] are termed as heavy metals. Heavy metals are natural components of the earth’s crust. They cannot be degraded or destroyed. To a small extent, they enter in human bodies via food, drinking water and air. As trace elements, some heavy metals are essential to maintain the metabolism of the human body. However, at higher concentration they can lead to poisoning [Vinodh et al., 2011]. They can enter a water supply by industrial and consumer waste, or even from acidic rain breaking down soils and releasing heavy metals into streams, lakes, rivers and groundwater. Heavy metal pollution has become a serious problem with the rapid increase of global industrial activities. The pollution of water by toxic heavy metals is considered as a threat due to their immense toxicity and their non-biodegradability. These heavy metal ions can be accumulated through the chain even at lower concentration, leading to a threat to aquatic life as well as to animal, plant life and human health as shown in Table 1.3.
Table 1.3. Some important heavy metals with their toxic effects and sources.

<table>
<thead>
<tr>
<th>Heavy Metals</th>
<th>Health Effects</th>
<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>Wilson disease, cancer, gastrointestinal catarrh, cramps in calves, anaemia, diarrhea, fatigue, loss of hair colour, low hormone production, osteoporosis, atherosclerosis, demyelination of nerve, alopecia, anxiety, arthritis, cancer, diabetes, migraine.</td>
<td>Electroplating industries, pulp and paper mills, fertilizer plants, petroleum refineries, copper water pipes, and copper cookware.</td>
</tr>
<tr>
<td>Chromium</td>
<td>Severe mucosal irritation, cancer, renal failure, haemolysis, Lung cancer, Long-term exposure can cause kidney and liver damage and damage too circulatory and nerve tissue.</td>
<td>Metal alloys and pigment for paints, cement, paper, rubber and other materials, cooling towers, leather tanning industries.</td>
</tr>
<tr>
<td>Nickel</td>
<td>Haemorrhages, intestinal cancer, oral cancer, lung cancer, respiratory symptoms, nausea, dermatitis.</td>
<td>Industrial waste, tobacco smoke, Nuclear device testing, etc.</td>
</tr>
<tr>
<td>Zinc</td>
<td>Abdominal pain, vomiting, diarrhea, sideroblastic anaemia, leukopenia, hypochromic microcytic anaemia, red urine, icterus, liver failure, kidney failure.</td>
<td>Galvanized coating on iron and steel, automotive parts, batteries, fungicides, zinc oxides based skin cream (such as diaper rash cream and sun screen) etc.</td>
</tr>
<tr>
<td>Lead</td>
<td>In children low level of lead can cause learning disabilities, nervous system damage, speech and language impairment, decreased muscle and bone growth, kidney damage; high level of lead can cause seizures, unconsciousness and death. In adults it causes increased chance of illness</td>
<td>Lead paint, industries that use lead (battery manufacturing, pipe fitting, firing ranges, demolition glass production, smelting operations etc), imported glazed pottery and</td>
</tr>
</tbody>
</table>
Mercury during pregnancy, harm to fetus, including brain damage or death, fertility problem in both men and women, high blood pressure, digestive issue, nerve disorder, Abdominal pain, arthritis, blindness, Parkinson’s disease, schizophrenia. Adrenal dysfunction, allergy, alopecia, brain damage and the central nervous system, hearing loss, vision loss, etc. Minamata disease, at high exposure there may be kidney effects, respiratory failure, and death. leaded crystal. Drinking contaminated water, eating fish contaminated with mercury, leaching of mercury from badly fitting dental filling, from vaccinations containing thimerosal, air conditioner filters, and broken thermometers.

Cadmium

It is a chemical element with symbol Cd(II) and atomic number 48. It prefers +2 oxidation state. The average concentration of Cadmium in the Earth’s crust is between 0.1 and 0.5 parts per million (ppm). It was discovered in 1817 simultaneously by Stromeyer and Hermann, both in Germany as an impurity in Zinc carbonate [Kirk-Othmer, 1994]. Cd(II) ions are relatively scare in the earth’s crust [Friberg et al., 1971]. Cadmium is one of the heavy metal found at the top of the toxicity list [Volesky, 1994]. The most significant use of Cadmium is in Nickel/Cadmium batteries, as rechargeable or secondary power sources exhibiting high output, long life, low maintenance and high tolerance to physical and electrical stress. Other uses of Cadmium are as pigments, stabilizers for PVC, in alloys and electronic compounds. Cadmium is also present as an impurity in several products including phosphate fertilizers, detergents and refined petroleum products. Cd(II) ions exist in the effluents produced by metal finishing industry (e.g. electroplating), battery industry and paint industry. It is fairly mobile in soil and is primarily present as an organically bound, exchangeable and water soluble species [Holm et al., 1995; Chlopecka, 1996]. It will result in the deterioration of the environment which will threaten the health and development of humans and other life form [Shao et al., 2011; Aklil et al., 2004]. Cadmium poisoning includes kidney [Nogawa et al., 2008], lung insufficiency, cancer, it changes the constitution of bone, liver and blood [Schroede, 1965]. Cadmium accumulated in the rice crops, it developed itai-itai disease and
renal abnormalities including proteinuria and glucosuria. Cadmium containing compounds are known as carcinogens [Bui et al., 1975, IARC, 1996]. Cadmium is non-biodegradable and once absorbed by an organism remains there for many years (over decades for human). The long term exposure is associated with renal dysfunction. Cadmium may also produce bone defects (Ostomalacia and Osteoporosis) in human and animals. The average daily intake for human is estimated as 0.15 µg from air and 1 µg from water. Smoking a packet of 20 cigarettes can lead to the inhalation of around 2-4 µg of cadmium, but levels may vary widely [HSDB, 1996]. The drinking water guideline value is 0.005 mg L⁻¹ [Central Pollution Control Board]. Cadmium can be removed by using three precipitation process [Islamoglu et al., 2006] which include (a) acid treatment with HNO₃ (b) alkali precipitation by NaOH (c) sulphide precipitation by Na₂S. Cadmium can also be precipitated by addition of lime and magnesium [Lin et al., 2005]. Gould et al., 1986 reported that Cadmium can be removed by cementation with magnesium while Younesi et al., 2006, Ku et al., 2002 used Zinc powder for Cadmium removal by cementation. Various types of membranes have also been used to remove cadmium from aqueous solution such as liquid membrane [Urtiaga et al., 2000], hollow fiber supported liquid membrane [Breembroek et al., 1998], emulsion liquid membrane [Mortaheb et al., 2009] and supported liquid membrane [Swain et al., 2006]. Many researchers studied Cadmium removal by ion-exchange technique using different resins like Amberlite IR 120 [Kocaoba, 2007], dolomite [Kocaoba, 2007], Dowex 50 W [Pehlivan and Altun, 2006]. Liquid-liquid extraction by using specific extractants has also been reported for separation of Cadmium [Nogueira and Delmas, 1999]. The removal of Cadmium from thiocyanate solutions with bis-2-ethylhexyl sulphoxide (EHSO) in benzene has been demonstrated by Reddy et al., 2006.

**Chromium**

Chromium takes its name from the Greek word for colour, ‘Chroma’. The element was discovered by Bauquelin in 1797. Chromium is generally found in two oxidation states. The Hexavalent Cr(VI) is toxic and a suspected carcinogen, whereas trivalent Cr(III) is much less toxic and is a nutrient. It is also the second most abundant inorganic contaminant of groundwater. Due to its acute toxicity and strong carcinogenic activity to humans, Cr(VI) has been listed as one of the priority pollutants by the United State Environmental Protection Agency (USEPA) [Keith et al., 1979; JTesta et al., 2004] and the Chinese Environmental Protection Board (EPB) [Gulay and Arica, 2008; Krishna et al., 2004]. The maximum
permissible limit of Cr(VI) in potable water, inland surface water and industrial wastewater are 0.05, 0.1 and 0.25 mg L\(^{-1}\) respectively [Bandegharaei et al., 2004]. Chromium is known as mutagen and carcinogen [Costa, 2003; Park et al., 2005]. It is highly reactive pollutant which dissipates into the ecosystems from a variety of industrial activities such as electroplating, leather tanning, mining, textile dyeing, wood preserving, chromate preparation and metal finishing [Kim et al., 2002]. Hexavalent Chromium modifies DNA transcription process causing important chromosomal aberrations. Furthermore it causes cancer in the digestive tract and lungs and may cause epigastric pain, nausea, vomiting, severe diarrhea and haemorrhage [PHSA, 1991; Mohanty et al., 2005]. According to the World Health Organization (WHO) drinking water guideline, the maximum allowable limit for total Chromium is 0.05 mg L\(^{-1}\) [WHO, 1984]. Dzyazko, 2007 used Inorganic ceramic membranes such as hydrated zirconium dioxide (HZD) for Cr(VI) removal from dilute solutions. Cr(VI) can also be removed from aqueous dilute solutions using polymer enhanced ultra filtration (PEUF) process. Nanofiltration composite polyamide membranes [Muthukrishnan and Guha, 2008] and nonmatted polyacrylonitrile fiber (PAN) membranes and aromatic polyamide thin film membranes were also used to remove Cr(VI) [Bohdziewicz, 2000]. Ion-exchange technique is a physicochemical method to remove Chromium from wastewater. Sapari et al., 1996 used Synthetic Dowex 2-X4 ion exchange resins to remove Cr(VI) from plating wastewater. Other synthetic ion exchange resin, Ambersep 132 was also explored to remove chromic acid in a four step ion-exchange process [Lin and Kiang, 2003]. Kabay et al., 2003 revealed that Aliquat 336 can be effectively used for the removal of Cr(VI) from aqueous solution. Rana et al., 2004 reported that electrochemical removal of Cr(VI) from industrial wastewater is also possible using carbon aerogel electrodes. Kongsricharoern and Polprasert, 1995 used electrochemical precipitation (ECP) process for Cr(VI) removal from an electroplating wastewater.

**Lead**

Lead has been recognized as one of the most toxic metals, mainly in ionic state. Due to its severe toxicity and great potential hazards to the environment and organisms, Lead (Pb) is regarded as one of “the big three” of the heavy metal (other are Cadmium and Mercury) Lead poisoning is also known as plumbism colica piuctonum, saturnism is a medical condition caused by increased level of Lead in the body [Volesky, 1990; Hamidpour et al., 2010]. The major sources of Lead release into the environment are industrial activities such as
electroplating, battery, manufacture, metallurgy. More than half of the world’s Lead production (at least 1.15 million metric tons) is used in automobiles, especially in car battery. Lead is a traditional base metal organ pipes, mixed with varying amounts of tin to control the tone of the pipe. The exposure of the human to Lead contamination can cause health problem including high blood pressure, anaemia, kidney damage, abdominal pain, confusion, headache, irritability, memory and learning deficiencies and in severe cases seizures, coma and death [Sgarlata et al., 2008]. Unlike other metals Lead does not naturally exists in the human body, and thus there is not a minimum Lead level which to be considered non-toxic. According to the USEPA regulation the acceptable concentration of Pb (II) in drinking water is of 0.015 mg L$^{-1}$ [USEPA, 2009]. Therefore, nowadays the removal of Lead ions from wastewater is a problem of outmost importance [Alvarez et al., 2005]. Conventional methods that have been used to remove Pb (II) ions from various industrial effluents by various researchers such as The Jordanian chabazite- phillipsite tuff and faujasite- phillipsite tuff have been used as ion exchange materials [Ibrahim and Akashah, 2004]. Emulsion liquid membrane (ELM) technique consisted of kerosene, surfactant Span 80, di-2-ethylhexyl phosphoric acid (D2EHPA) and sulphuric acid ($\text{H}_2\text{SO}_4$) was used to remove lead from battery industry wastewater (Levent et al., 2005).

**Zinc**

Zinc is the 24$^{th}$ most abundant element on the earth’s crust. German Chemist Andreas Sigismund Marggraf is normally given credit for discovering pure metallic Zinc in 1746. Zinc is considered as an essential trace element for life and acts as a micronutrient, it is one of the components of certain proteins inside the human body, but at elevated as well as insufficient concentrations Zinc may be detrimental on human health [Tapiero and Tew, 2003; Maret and Sandstead, 2006]. It is known as an inorganic pollutant of the priority pollutants list [Hsieh et al., 2004]. Zinc has been shown to bioaccumulate through the food chain [Kantola et al., 2000; Thompson et al., 2003]. On the other hand, although Zinc is a key element for humans, free Zinc ions in solution are highly toxic to plants, invertebrates and even vertebrates fish. Trace amounts of free Zinc ions can cause heavy damage to the environment and kill some organisms. Excessive intake of Zinc can promote deficiency in other dietary minerals. WHO recommended the maximum acceptable concentration of Zinc in drinking water as 5.0 mg L$^{-1}$ [Mohan and Singh, 2002]. Zinc toxicity to human occurs in both acute and chronic forms [I.M., F.N.B, 2001]. Zinc deficiency symptoms in human and animals are failure to eat,
severe growth depression, skin lesion and sexual immaturity [Dimirkou et al., 2002; Kiekens, 1990; Zhang et al., 2009; Haroun et al., 2007]. The main indications of Zinc poisoning are desiccating muscles, imbalance of electrolytes, stomach, vertigo and disharmony [Veli and Alyuz, 2007]. However, at large concentrations it is phytotoxic and therefore reduces soil fertility [Sawalha et al., 2007]. Also reported that Zn(II) accumulates in living organisms causing diseases and other toxic effects. Therefore there is significant interest regarding zinc removal from wastewater [Moore and Rama Moorthy, 1985; Bhattacharya et al., 2006]. In the ‘Dangerous substances Directive (76/464/EEC)’ of European Union, Zinc has been registered as list 2 dangerous substance with environmental quality standards being set at 40 g L$^{-1}$ for estuaries and marine waters and at 45-500 g L$^{-1}$ for fresh water depending on water hardness [Directive 76/464/EEC, 1976]. Zinc is a raw material for corrosion-resistant alloys and brass, and for galvanization of steel and iron products. Zinc oxide is a white pigment for rubber and paper. It is also utilized in paints, plastics, cosmetics and pharmaceuticals [Weng and Huang, 2004; Arias and Sen, 2009]. Zinc is released into aquatic and soil environments largely from various natural and anthropogenic activities. Metal mining, metallurgy industries, coating and sludge produce large quantities of wastewater containing high concentration of Zn(II) ions. Zinc has many commercial applications such as coatings to prevent rust, in dry cell batteries and in the production of die castings compounds of zinc are used in the manufacture of dyes, wood preservatives and cosmetics. Zinc occurs in the list of primary contaminant elements proposed by the U.S. Environmental Protecting Agency (EPA), since it has caused serious poisoning events. Due to its high production and application, Zinc can be found in emission, effluents, sludge and waste for instance Zinc concentrations of over 620 mg L$^{-1}$ have been recorded in drainage from abandoned Copper mines in Montana, USA [Volesky, 2003]. Zinc can be removed from electroplating wastewater by chemical coagulation and precipitation process [Charerntanyarak, 1999]. Saari et al., 1998 used Sodium xylenesulfonate (SXS) combined with Polyaluminum chloride (PAC) as new technology in Zinc removal through hydroxide precipitation. Complexation-Membrane Filtration is a conventional process to remove Zinc from industrial wastewater [Borbelya and Nagy, 2009].
Copper
The element was discovered in prehistoric times and has its name from the island of Cyprus (Latin: Cuprum). Copper is an essential trace element and necessary for the functioning of several enzymes involved in electron transfer (cytochrome oxidase), free radical defense (catalase, superoxide dismutase) and melanin formation (tyrosi wase). Copper is also essential for the utilisation of iron and formation of hemoglobin. The recommended dietary allowance (RDA) of Cu(II) for an adult male is 3.0 mg kg\(^{-1}\) of the body weight [NRC/NAS, 1980]. Exposure to copper above RDA is fatal to both vegetations and creatures [Mohan et al., 2006]. Although Copper is an essential element for life in minute amounts, at higher levels of exposure it shows magnetic and carcinogenic effect. Owing to the toxicity of Cu(II), the world health organization (WHO) recommended the maximum acceptable concentration of this element in drinking water to be 2.0 mg L\(^{-1}\) [WHO, 2008]. Cu(II) creates stress in the gastrointestinal and respiratory tracts. Excessive level of Cu(II) may damage liver and kidney, and may be responsible for anaemia, immunotoxicity and developmental toxicity. The co-carcinogenic character of Cu(II) is also implicated in stomach and lung cancer [Ahmad et al., 2009]. Cu(II) is widely used in many industries including metal cleaning and plating baths, paints and pigments, fertilizers, paper board, wood pulp etc [Aksu and Isoglu, 2005; Zhu et al., 2009]. The effluents from these industries usually contain considerable quantity of Copper, which spreads into the environment through soils and water streams and finally accumulates along the food chain which causes human health hazards. Many researchers remove Cu(II) ions from wastewater by using various techniques. Negrea et al., 2008 remove Cu(II) ions through precipitation method by using 15% NaOH and 20% Na\(_2\)CO\(_3\) solutions as precipitation agents. Liehr, 1995 removed Cu(II) through effect of pH on metal precipitation in denitrifying biofilms.

Nickel
The name of the element is derived from the German and Kupftnickle meaning ‘Old Nick’s (=Satan’s) Copper’. Nickel was discovered by Cronstedt in 1751. Enzymes of some microorganisms and plants contain Nickel as an active centre, which makes the metal an essential nutrient for them. Nickel is the 24\(^{th}\) element in order of natural abundance in earth crust [Krishnamurti and Viswanathan, 1991]. Nickel is a common metal and it is frequently used in different industries, electroplating dyeing, storage, batteries, porcelain enamelling, pigment and steel manufacturing etc. [Ewecharoen et al., 2008; Xu et al., 2006]. The
tolerance limit of Nickel in drinking water is 0.01 mg L$^{-1}$ and for industrial wastewater it is 2.0 mg L$^{-1}$ [Kadivelu et al., 2001]. Nickel is known as one of the most common toxic metal, and the US Environmental Protection Agency (EPA) has established 0.5 mg L$^{-1}$ as the permissible concentration for Nickel in drinking water [Gupta et al., 2010]. However, effluents of different industries generally contain higher concentrations of Nickel than its acceptable limit. Although Nickel is an essential micronutrient for animals and takes part in synthesis of vitamin B$\textsubscript{12}$, its higher concentration causes cancer of the lungs, nose and bones and may also cause nausea, rapid respiration, head ache, cyanosis and dry cough [Periyasamy and Namasivayam, 1995; Malkoc, 2006]. It is thus necessary to treat industrial effluents rich in Ni(II) before their discharge. Many researchers removed Ni(II) ions from wastewater by using various techniques. Papadopoulos et al., 2004 removed Ni(II) by using ion exchange and precipitation methods, Chiying et al., 1988 removed Ni(II) through precipitation treatment of spent electroless nickel plating baths.

Standards of drinking water in India are reported in Table 1.4 and 1.5.

Table 1.4. Drinking water’s standard in India (mg L$^{-1}$).

<table>
<thead>
<tr>
<th>Property</th>
<th>Level</th>
<th>Level</th>
<th>Property</th>
<th>Level</th>
<th>Level</th>
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<td>Maximum</td>
<td>Minimum</td>
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<td>Maximum</td>
<td>Minimum</td>
</tr>
<tr>
<td>Turbidity</td>
<td>5.0 (NTU)</td>
<td>25.0 (NTU)</td>
<td>Cl$^-$</td>
<td>200 (mg L$^{-1}$)</td>
<td>600 (mg L$^{-1}$)</td>
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<tr>
<td>Colour</td>
<td>5.0 (Hazen unit)</td>
<td>50.0 (Hazen unit)</td>
<td>SO$_4^{2-}$</td>
<td>200 (mg L$^{-1}$)</td>
<td>400 (mg L$^{-1}$)</td>
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<tr>
<td>pH</td>
<td>7.0–8.5</td>
<td>6.5–9.2</td>
<td>F</td>
<td>1.0 (mg L$^{-1}$)</td>
<td>1.5 (mg L$^{-1}$)</td>
</tr>
<tr>
<td>Hardness</td>
<td>100 (mg L$^{-1}$)</td>
<td>500 (mg L$^{-1}$)</td>
<td>NO$_3^-$</td>
<td>4.5 (mg L$^{-1}$)</td>
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<td>Mg</td>
<td>30 (mg L$^{-1}$)</td>
<td>150 (mg L$^{-1}$)</td>
<td>Zn</td>
<td>5.0 (mg L$^{-1}$)</td>
<td>15.0 (mg L$^{-1}$)</td>
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<td>Fe</td>
<td>0.1 (mg L$^{-1}$)</td>
<td>1.0 (mg L$^{-1}$)</td>
<td>Oils</td>
<td>0.01</td>
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<tr>
<td>Mn</td>
<td>0.05 (mg L$^{-1}$)</td>
<td>0.50 (mg L$^{-1}$)</td>
<td>Detergents</td>
<td>0.20</td>
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<td>Cu</td>
<td>0.05 (mg L$^{-1}$)</td>
<td>1.0 (mg L$^{-1}$)</td>
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Table. 1.5. Standard for potable water (as described by W.H.O.) (mg L\(^{-1}\)).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Average</th>
<th>W.H.O.</th>
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<td>Turbidity</td>
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<td>pH</td>
<td>7.0-8.5</td>
<td>6.5-9.2</td>
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<tr>
<td>Total solids</td>
<td>500.0 (mg L(^{-1}))</td>
<td>1500.0 (mg L(^{-1}))</td>
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<td>Hardness</td>
<td>100.0 (mg L(^{-1}))</td>
<td>200.0 (mg L(^{-1}))</td>
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<td>Calcium</td>
<td>75.0 (mg L(^{-1}))</td>
<td>200.0 (mg L(^{-1}))</td>
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<td>Magnesium</td>
<td>30.0-50.0 (mg L(^{-1}))</td>
<td>150.0 (mg L(^{-1}))</td>
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<td>Iron</td>
<td>0.1-0.3 (mg L(^{-1}))</td>
<td>1.0 (mg L(^{-1}))</td>
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<tr>
<td>Chloride</td>
<td>200.0 (mg L(^{-1}))</td>
<td>600.0 (mg L(^{-1}))</td>
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<td>Sulphate</td>
<td>200.0 (mg L(^{-1}))</td>
<td>400.0 (mg L(^{-1}))</td>
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<tr>
<td>Fluoride</td>
<td>1.0 (mg L(^{-1}))</td>
<td>1.5 (mg L(^{-1}))</td>
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<tr>
<td>Nitrate</td>
<td>45.0 (mg L(^{-1}))</td>
<td>45.0 (mg L(^{-1}))</td>
</tr>
<tr>
<td>Lead</td>
<td>0.05 (mg L(^{-1}))</td>
<td>0.05 (mg L(^{-1}))</td>
</tr>
</tbody>
</table>

**Characterization of wastewater**

Different quality parameters such as colour, odour, pH, temperature, taste, conductivity, transparency, turbidity, TDS (total dissolved solid), DO (dissolved oxygen), BOD (biochemical oxygen demand) and COD (chemical oxygen demand) are important to be assured before discharging water to commercial and domestic water supplies.

**Colour**

In natural waters is due to the presence of fulvic ions, metal ions, suspended mater, phytoplankton weeds and industrial effluents. The drinking water should be colourless, odourless and pleasant to taste.

**pH**

It is defined as a measure of hydrogen ions concentration in water or solution. The pH of natural water is nearly about 7 (neutral). According to pH scale, the water is acidic if pH is below 7 and alkaline if pH is above 7. The alkalinity of water is due to the presence of carbonates, silicates, bicarbonates and sometimes due to the presence of weak organic acids.
Temperature
Temperature of water can have a tremendous influence on aquatic environment. All the physical, chemical and biological properties are affected by temperature variation. Increase in water temperature increase oxygen demand, leading to serious oxygen depletion problem in water resources.

Transparency
Transparency is inversely proportional to the turbidity. It is important because clearer the water, the deeper sunlight will penetrate which is required for photosynthesis.

Conductivity
Conductivity is the measure of the ability or power of water to conduct electricity. Conductivity measures the concentration of dissolved ions.

Total dissolved solid (TDS)
TDS is the residue left after evaporation of water at 103°C to 105°C. It is an aggregate amount of the entire floating, suspended, separable and dissolved solids present in water. The solids may be organic or inorganic in nature.

Dissolved oxygen (DO)
DO is the amount of gaseous oxygen dissolved in an aqueous solution. When DO level in water drops below 5.0 mg L⁻¹, aquatic life is put under stress and environment shifts towards anaerobic condition.

Biochemical oxygen demand (BOD)
BOD is a standard method for indirect measurement of organic pollution. The BOD of pure water is 0–3 mg L⁻¹. If BOD is 5.0 mg L⁻¹ or more, water is said to be contaminated with organic pollutants.

Chemical oxygen demand (COD)
Biologically resistant organic compounds cannot be decomposed by bacteria. Therefore their contents cannot be determined in terms of depletion of dissolved oxygen. They are oxidized
by strong oxidizing agent like potassium dichromate and oxidant consumed is measured in terms of chemical oxygen demand.

The characteristics of industrial wastewater generated by some important industries are described below.

**Slaughter houses and meat packing industry**

Effluents from the fat and meat industry arise chiefly in slaughterhouses. Stockyard wastes mainly contain cattle manure. Slaughter house effluents and those from the quartering of carcasses, etc.; chiefly contain organic compounds such as blood, the contents of the alimentary canal, urine, pieces of flesh, hide and bowels, grease, bristles and horsehair. These wastes have a characteristic brownish, bloodlike appearance and a repugnant odour. The organic compounds occur both as suspended matter and as true solutions and colloids. Due to the large albumin content, these wastes putrefy easily. Slaughterhouse wastes are much more polluted than those from meat processing plants but are very similar in composition and characteristic. The effluents from a slaughterhouse or meat packing factory may contain pathogenic micro-organisms affecting the bowels, germs of anthrax and other animal diseases, and ovules of earthworms and bowel parasites.

**The dairy industry**

Dairy wastes, i.e. those from plants processing milk, contain typical organic pollutants, such as casein and other albuminous substances, lactose and fats. These substances impose a severe load on the receiving waters which are usually only small rivers or streams. All wastes which come directly from milk processing plants contain chemicals (e.g. soda and detergents) used in the cleaning of vessels and apparatus’. Dairy wastes (except cheese-factory wastes which usually contain small particles of casein) have only a very small content of suspended solids. They are turbid, whitish-yellow in colour and contain up to 160 mg L\(^{-1}\) of total nitrogen almost entirely converted into ammonium nitrogen during putrefaction, 2-3 mg L\(^{-1}\).

**The inorganic pigments (paint) industry**

The composition and properties of the wastes vary according to the manufacturing process. The wastes generated during the manufacture of Milori blue, for example, consist of an acid liquor from the reaction vessel and wash water; they contain free sulphuric acid (pH=1.5), sulphates, chlorides, iron compounds and cyanides. They may also contain large amounts of
suspended solids. In the manufacture of white lead, the wastes (wash waters) usually contain lead acetate, lead bicarbonate and residual acetic acid. Lead salts also occur in the waste waters from the production of chrome yellow.

**The tanning industry**

Tannery wastes are a special problem among effluents polluted with organic compounds because a high proportion of the pollutants consist of toxic inorganic compounds and chemically altered albumen. It chiefly consists of waste liquors from the technological processes (85-90% of the total), but also contain wastes from auxiliary processes which are no different from ordinary household wastes. The quantity of wastes from the tanning process average 80-100 per kg of material processed.

**The plastic industry**

The plastic industry, like that dyes and intermediates, discharges relatively small amounts of polluted water. The greater proportions of the effluents are cooling waters, which are only slightly polluted or not polluted at all. The wastes contained a number of organic acids, a tetrahydric alcohol and pentaerythritol, as well as resin acids, formaldehyde and sodium formate.

**The pharmaceutical industry**

It is difficult to make any generalizations regarding effluents discharged from pharmaceutical products factories. The problem is even more complicated by the fact that the pharmaceutical industry uses both inorganic and organic raw materials, the latter being synthetic or of vegetable and animal origin.

**The pulp and paper industry**

The composition and properties of the effluents from pulp mills differ considerably from those from paper mills, but since large plants usually produce pulp and paper, the waste are considered together. The common features of these wastes are the inevitable presence of cellulose fibres. The pulp and paper mill is a major industrial sector utilizing a huge amount of lignocellulosic materials and water during the manufacturing process, and releases chlorinated lignosulphonic acids, chlorinated resin acids, chlorinated phenols and chlorinated hydrocarbons in the effluents.
Industrial wastewater treatment technologies

a) Primary treatment

It includes screening, grinding, sedimentation, flocculation or coagulation and sedimentation. In screening the larger suspended and floating materials such as paper, rags, wooden, pieces, wires etc are removed. Screening system consists of two units. The first unit (coarse screen) consists of metal bars or heavy wires spaced 25-40 mm apart, and the second unit consists of fine screens. The materials that are removed by screening are usually incinerated. The grinding is carried out in grinders of rotating screens with cutting teeth. These are used to chop the solid materials to size smaller than 6 mm chemical treatment precipitates the solids by flocculation or coagulation. These coagulates settle down rapidly. The coagulants of importance are ferric sulphate or chloride or aluminium sulphate lime. These coagulates are then removed either by sedimentation or by filtration.

b) Secondary treatment

The next stage is a biological process which breaks down dissolved and suspended organic solids by using naturally occurring micro-organisms. These processes may be either aerobic or anaerobic. In aerobic process, bacteria and other micro-organism consume organic matter as food, at the expense of dissolved oxygen. Thus aerobic treatment reduces Biochemical Oxygen Demand (BOD). It also removes appreciable amounts of oil and phenol. However, commissioning and maintenance of aerobic treatment systems are expensive. Anaerobic treatment is mainly employed for the digestion of sludge. Generally organic liquid wastes from dairy, slaughter houses etc., are treated economically and effectively by anaerobic treatment. In anaerobic treatment process methane and carbon dioxide are the major products along with a liquid effluent that contains all the water and mineral from the upcoming material. It is used to produce heat and electricity and also reduce the overall cost of sewage treatment. The efficiency of anaerobic treatment process depends upon pH, temperature, waste loading, absence of oxygen and toxic materials.

c) Tertiary treatment

The aim of tertiary treatment is further purification of wastewater as well as its recycling. The most important purpose of tertiary treatment is an effective and efficient removal of pollutants than primary and secondary treatment and it can be applied at any stage of the total
treatment. It is the final treatment meant for “polishing” the effluent from the secondary treatment processes, to improve the quality further. Depending upon the required quality of the final effluent and the cost of treatment that can be afforded in a given situation, any of the following treatment methods can be employed.

**Chemical precipitation**
Chemical precipitation method can be used to remove metals, fats, oil and greases, contaminants, suspended solids, organic and inorganic.

**Ion-exchange**
In this process, metal ions from dilute solutions are exchanged with ions held by electrostatic forces on the exchange resin. The natural materials such as zeolites can be used as ion exchange media (Vander Heen, 1977). The modified zeolites like zeocarb and chalcarb have greater affinity for metals like Ni and Pb (Groffman et al., 1992). The limitations on the use of ion exchange for inorganic effluent treatment are primarily high cost, partial removal of certain ions and the requirements for appropriate pre-treatment systems. Ion exchange is capable of providing metal ion concentrations to parts per million levels. However in the presence of large quantities of competing mono and divalent ions such as Na and Ca, ion exchange is almost totally ineffective.

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

**Reverse osmosis and ultra filtration**
Reverse osmosis uses semi permeable membrane to achieve separation of dissolved salts from the wastewater by applying pressure greater than the osmotic pressure causes by the dissolved salts using high pressure pumps. Pre-treatment steps of effluents water before going for reverse osmosis process is necessary and usually this is made possible by using ultra filtration to first remove large molecules and colloidal materials so that this will help to
protect the membranes. The spiral wound configuration of the membranes support structure proves to be the best and most effective in use when it comes to municipal wastewater reclamation. However, problems that are still needed to be solved are [Cushnie, 1994] membrane durability problems, sensitive to hard water salts, fouling of membrane.

**Electrodialysis**

In this process, the ionic components (heavy metals) are separated through the use of semi-permeable ion-selective membranes. Application of an electrical potential between the two electrodes causes a migration of cations and anions towards respective electrodes. Because of the alternate spacing of cations and anions permeable membranes, cells of concentrated and dilute salts are formed. The disadvantage is the formation of metal hydroxides which clog the membrane.

These technologies are useful but sometimes create problems like separation of sludge and disposal of secondary waste generated.

**Adsorption**

During the 1970’s increasing environmental awareness and concern led to a search for new techniques capable of inexpensive treatment of polluted wastewater with metals. The search for new technologies involving the removal of toxic metals from wastewater has directed attention to adsorption, base of binding capacities of molecules or particles to a surface. Till date, research in the area of adsorption suggests it to be an ideal alternative for decontamination of metal/dye containing effluents. Adsorbents are attractive since naturally occurring biomass/adsorbents or spent biomass can be effectively used. Adsorption is rapid phenomenon of passive metal sequestration by the non-growing biomass/adsorbents are comparable with the commercial synthetic cation exchange resins. The biosorption process involves a solid phase (sorbent or biosorbents; biological material) and a liquid phase (solvent, normally water) containing a dissolved species to be adsorbed (adsorbate, metal/dyes). Due to the higher affinity of the adsorbent for the adsorbate species, the latter is attracted and bound there by different mechanisms. The process continues till equilibrium is established between the amount of solid-bound adsorbate species and its portion remaining in the solution. The degree of adsorbent affinity for the adsorbate determines its distribution between the solid and liquid phases. Adsorption is a power tool for the environmental engineer for the removal of trace amounts of organic and inorganic contaminants present in
municipal and industrial wastewater. Adsorption is a process that occurs when a gas or a liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (the adsorbate). It is different from adsorption, in which a substance diffuses into a liquid or solid to form a solution. The term sorption encompasses both process, while desorption is the reverse process. Adsorption is operative in most natural physical, biological and chemical systems and is widely used in industrial applications. The exact nature of the bonding depends on the details of the species involved, but the adsorbed material is generally classified as exhibiting physisorption or chemisorptions. Physisorption or physical adsorption is a type of adsorption in which the adsorbate adheres to the surface only through Vander Waals (weak intermolecular) interactions, which are also responsible for the non-ideal behaviour of real gases. Chemisorption is a type of adsorption where by a molecule adheres to a surface through the formation of chemical bond. Adsorption is usually described through isotherms, that is, function which connect the amount of adsorbate on the adsorbent, with its pressure (if gas) or concentration (if liquid). One can find in literature several models describing process of adsorption, namely Langmuir, Freundlich, Temkin and Dubinin-Raduskevicvh isotherms etc. Adsorption from an aqueous solution is influenced largely by the competition between the solute and the solvent molecule for adsorption sites. The tendency of a particular solute to get adsorbed is determined by the difference in the adsorption potential between the solute and the solvent. In general the lower the affinity of the adsorbate for the solvents, the higher will be the adsorption capacity for solutes. Activated carbon and polymeric adsorbents have high adsorption capacities in water primarily because of low adsorption potential [Rai et al., 1998]. Three steps must take place for adsorption to occur.

(i) The adsorbed molecules must be transferred from the bulk phase of the solution to the surface of the adsorbent particles. In so doing, it must pass through a film of solvent that surrounds the adsorbent particles. This process is referred to as **film diffusion**.

(ii) The adsorbate molecule must be transferred to the adsorption site on the inside of the pore. This process is termed as ‘**pore diffusion**’.

(iii) The particle must be attached to the surface of the solute, i.e., be **adsorbed**.

There are many factors that influence the rate of adsorption and the extent to which a particular solute can be adsorbed for instance adsorbent characteristics; size and shape of adsorbent particles, solubility of solute, pH, temperature, agitation time and concentration. Adsorption rate usually decreases as the size of adsorbent particles becomes large. Highly
soluble compounds having strong affinity to solvent are less easily adsorbed. Adsorption capacity is inversely proportional to solubility. Adsorption rate also increases with increase in concentration. The solution pH has strong influence on adsorption primarily due to change in the ionic concentrations of water and solutes. Temperature is also a factor that affects the rate and extent of adsorption.

Conventional and non-conventional adsorbents are used in this approach. Activated carbon is a black solid substance resembling granular or powder charcoal and is carbonaceous material that has highly developed porosity, internal surface area of more than 400 m² g⁻¹ and relatively high mechanical strength. They are widely used as adsorbents in wastewater and gas treatments as well as catalyst. Activated carbon is prepared by carbonisation and activation of large number of raw materials [Rodrigues-Reinoso and linares-solano, 1998]. Activated carbon is the most widely used adsorbent, as it has good capacity towards organic molecules and heavy metals from wastewater [Bansal et.al. 1998] but high cost limits its use. Shortcoming of using activated carbon, as an adsorbent is its regeneration cost which makes it uneconomical. The increasing usage and competitiveness of activated carbon prices has prompted a considerable research work in the search of inexpensive adsorbents especially developed from various agricultural waste materials therefore to make adsorption an economically feasible process non-conventional adsorbents have come into application. Non-conventinal adsorbents include inorganic adsorbents, organic adsorbents and biosorbents. These adsorbents are capable of removing heavy metal ions and organic pollutants from wastewater. Materials like chitin, chitosan, modified cotton, keratin, flyash, oil cakes, fruit peels, barks etc. are few of the non-conventional adsorbents used for the removal of heavy metals. Some important non-conventional adsorbents studied by various researchers during the period 2000-2012 are listed in Table 1.6.
Table 1.6. Summary of various adsorbents used for the removal of heavy metals from water and wastewater (2000-2012).

<table>
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<th>Metal Removed</th>
<th>Adsorbent</th>
<th>Remarks</th>
<th>Reference</th>
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</thead>
<tbody>
<tr>
<td>Cu(II)</td>
<td>Iron oxide coated sand</td>
<td>% Removal 74.9 %, time-20 min, conc. 5 mg/l, adsorbent 30 g/l</td>
<td>Kwak et al., 2000</td>
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<tr>
<td>Cu(II)</td>
<td>Pyrite</td>
<td>Oxidation is accompanied by the reduction of Cu(II) to Cu(I)</td>
<td>Weisener and Gerson, 2000</td>
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<tr>
<td>Cu(II)</td>
<td>Sawdust</td>
<td>Provide strong evidence to support the hypothesis of adsorption mechanism</td>
<td>Yu et al., 2000</td>
</tr>
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<td>Cu(II)</td>
<td>Tyre Rubber</td>
<td></td>
<td>Al-Asheh and Banat, 2000</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>Iron coated sand</td>
<td>Results of the study developed an innovative technology.</td>
<td>C. H. Lai et al., 2000</td>
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<td>Cu(II)</td>
<td>Pseudomonas stutzeri</td>
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<td>Hur et al., 2001</td>
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<td>Cu(II)</td>
<td>Perlite</td>
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<td>Alkan and Dogan, 2001</td>
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<td>Cu(II)</td>
<td>Activated carbons</td>
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<td>Goyal et al., 2001</td>
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<td>Cu(II)</td>
<td>Kyanite</td>
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<td>Ajmal et al., 2001</td>
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<td>Cu(II)</td>
<td>Pecan shell activated carbon</td>
<td></td>
<td>Dastgheib and D.A. Rockstraw, 2001</td>
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<td>Cu(II)</td>
<td>Peanut hull pallets</td>
<td>75% and 92% removal of copper was affected within 20 and 50 min respectively.</td>
<td>Jonson et al. 2002</td>
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<td>Cu(II)</td>
<td>Ulothrix zonata</td>
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<td>Nuhoglu et al. 2002</td>
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<td>Cu(II)</td>
<td>Material Description</td>
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<td>Cu(II)</td>
<td>Chitosan and cross-linked chitosan beads</td>
<td>WanNgah, 2002</td>
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<td>Cu(II)</td>
<td>Chitosan in prawn shell</td>
<td>Chu, 2002</td>
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<td>Cu(II)</td>
<td>Almond shell carbons and commercial carbons</td>
<td>Toles and Marshall, 2002</td>
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<td>Cu(II)</td>
<td>Natural and Modified Radiata Bark Pine</td>
<td>Montes et al., 2003</td>
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<td>Cu(II)</td>
<td>Savanna Acid Soil</td>
<td>Agbenin, J. O., 2003</td>
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<td>Cu(II)</td>
<td>Olive Mill Residues</td>
<td>Veglio et al., 2003</td>
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<td>Cu(II)</td>
<td>Sewage Sludge Ash</td>
<td>Pan et al., 2003</td>
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<td>Cu(II)</td>
<td>Organosolv Lignin</td>
<td>Acemiolu et al., 2003</td>
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<td>Cu(II)</td>
<td>Loess with high carbonate content</td>
<td>Jinren, 2003</td>
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<td>Cu(II)</td>
<td>Activated and Non-activated Oak Shells</td>
<td>Cu(II) uptake increased with decreasing sorbent concentration or with an increase in Cu(II) concentration or solution pH</td>
<td>Al-Asheh et al., 2003</td>
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<td>Cu(II)</td>
<td>Micaceous Mineral of Kenyan Origin</td>
<td>Adsorption capacity of 0.850 g/g for Cu(II)</td>
<td>Attahiru et al., 2003</td>
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<td>Cu(II)</td>
<td>Powdered Marble Wastes</td>
<td>100 % Cu(II) was attained</td>
<td>Ghazy et al., 2003</td>
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<td>Cu(II)</td>
<td>Vineyard soils of Genera</td>
<td>Celardin et al., 2003</td>
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<td>Cu(II)</td>
<td>Organic Manure</td>
<td>Bolan et al., 2003</td>
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<td>Cu(II)</td>
<td>A 1.10 Phenanthroline-grafted</td>
<td>De Leon et al., 2003</td>
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<tr>
<td>Brazilian Bentonite</td>
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<tr>
<td>Cu(II)</td>
<td>Caustic Treated Waste Baker’s Yeast Biomass</td>
<td>Goksungur et al., 2003</td>
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<td>Cu(II)</td>
<td><em>Chlorella vulgaris</em></td>
<td>Chu and Hashim, 2004</td>
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<td>Cu(II)</td>
<td>Humic substance</td>
<td>Alvarez-Puebla et al., 2004</td>
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<tr>
<td>Cu(II)</td>
<td>Chitosan</td>
<td>Wan et al., 2004</td>
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<tr>
<td>Cu(II)</td>
<td>Peat</td>
<td>Petroni and Pires, 2004</td>
<td></td>
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<tr>
<td>Cu(II)</td>
<td>Poly acrylonitrile-immobilized dead cells of <em>Saccharomyces Cerevisiae</em></td>
<td>Godjevargova and Mihova, 2004</td>
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<td>Cu(II)</td>
<td>Montmorillonites</td>
<td>Ding and Frost, 2004</td>
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<td>Cu(II)</td>
<td>Herbaceous Peat</td>
<td>Gundoan et al., 2004</td>
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<td>Sawdust</td>
<td>Larous et al., 2005</td>
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<td>Cu(II)</td>
<td>H₃PO₄-activated Rubber Wood Sawdust</td>
<td>Kalavathy et al., 2005</td>
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<td>Cu(II)</td>
<td>Cu-ZSM-5 Zeolite</td>
<td>Kazansky and Pidko, 2005</td>
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**Cr(VI) selective adsorbents (2000 to 2012)**

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Maximum Cr(VI) removal was at pH 2.0

95 % adsorption at pH 4.0
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**Pb(II) selective adsorbents (2000 to 2012)**

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**Zn(II) selective adsorbents (2000 to 2012)**

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<td>Zn(II) loading on TNP was dependent on initial zinc concentration</td>
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<td>Maximum adsorption capacity 1058.2 mg/g was observed for Cd(II) Denizli et al., 2002</td>
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<td>Adsorption by kaolin was: Cr &gt; Zn &gt; Cu ≈ Cd ≈ Ni &gt; Pb by ballclay was: Cr &gt; Zn &gt; Cu &gt; Cd ≈ Pb &gt; Ni</td>
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The optimum pH for the adsorption of cobalt(II) ions onto the peanut hulls citrate was 7.0.
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<td>Immature Coal (leonardite)</td>
<td>Zeledon-Toruno et al., 2005</td>
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<td>Cr(III), Cu(II), Zn(II)</td>
<td>Carrot Residues</td>
<td>Nasernejad et al., 2005</td>
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<td>Lead, Mercury and Nickel</td>
<td>Carbon Aerogel</td>
<td>Goel et al., 2005</td>
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<td>Cd(II) and Pb(II)</td>
<td>Various Cereals from Korea</td>
<td>Park et al., 2005</td>
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<td>Pb, Cu and Cd</td>
<td>Particulate Organic Matter in Soil</td>
<td>Guo et al., 2006</td>
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<td>Pb(II) and Ni(II)</td>
<td>Chemically Modified and Unmodified Agricultural Adsorbents</td>
<td>Abia and Asuquo, 2006</td>
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<td>Cu(II) and Pb(II)</td>
<td>Dried Activated Sludge</td>
<td>Wang et al., 2006</td>
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<td>Cu(II), Zn(II) and Pb(II)</td>
<td>Calcite</td>
<td>Elzinga et al., 2006</td>
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<td>Cu(II) and Cd(II)</td>
<td>Kraft Lignin</td>
<td>Mohan et al., 2006</td>
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<td>Cu(II) and Pb(II)</td>
<td>Manganese Oxide Coated Zeolite</td>
<td>Zou et al., 2006</td>
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<td>Cr(VI) and Cr(III)</td>
<td>Natural Clino-pyrrhotite</td>
<td>Lu et al., 2006</td>
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<td>Cd(II) and Pb(II)</td>
<td>Seaweed biomass</td>
<td>Kumar and Kaladharan, 2006</td>
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<td>Metal Compounds</td>
<td>Adsorbent</td>
<td>Authors</td>
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<td>Cr(III), Ni(II), Zn(II), Co(II)</td>
<td>Phenolated Wood Resin</td>
<td>Kara et al., 2006</td>
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<td>Cu(II) and Zn(II)</td>
<td>Acid Soils</td>
<td>Arias et al., 2006</td>
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<td>Cd(II), Zn(II), Mg(II) and Cr(VI)</td>
<td>Clay Mineral</td>
<td>Fonseca et al., 2006</td>
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<td>Cu(II) and Pb(II)</td>
<td>Manganese Oxide Coated Sand</td>
<td>Han et al., 2006</td>
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<td>Cu(II), Cd(II) and Pb(II)</td>
<td>Pyrite and synthetic iron sulphide</td>
<td>Ozverdi and Erdem, 2006</td>
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<td>Pb(II), Cd(II)</td>
<td>Kaolinite Clay</td>
<td>Adebowale et al., 2006</td>
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<td>Co(II), Cr(II) and Ni(II)</td>
<td>Coir Pith</td>
<td>Parab et al., 2006</td>
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<td>Cu(II), Cd(II)</td>
<td>Ceiba Pentandra Hulls</td>
<td>Rao et al., 2006</td>
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<td>Pb(II) and Cd(II)</td>
<td>Polymer-grafted Banana (Musa paradisiacal) Stalk</td>
<td>Shibi and Anirudhan, 2006</td>
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<td>Cd(II) and Ni(II)</td>
<td>Bagasse Fly Ash</td>
<td>Srivastava et al., 2006</td>
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<td>Cu(II), Ni(II) and Co(II)</td>
<td>Methacrylic Acid/acrylamide Monomer Mixture Grafted Poly (ethylene Terephthalate) Fiber</td>
<td>Coskun et al., 2006</td>
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<td>Cd(II) and Pb(II)</td>
<td>Mesoporous Silicate MCM-41</td>
<td>Oshima et al., 2006</td>
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<td>Co(II), Fe(II) and Cu(II)</td>
<td>Modified and Unmodified Maize Husk</td>
<td>Igwe et al., 2006</td>
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<td>Zn, Cd, Pb</td>
<td>Arbuscular Mycorrhizal Maize (Zea mays L.)</td>
<td>Shen et al., 2006</td>
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<td>Pb, Fe</td>
<td>Vegetable Biomass</td>
<td>Bun-ei et al., 2006</td>
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<td>Metal(II) Combinations</td>
<td>Adsorbent</td>
<td>Authors and Year</td>
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<td>Cd(II) and Zn(II)</td>
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<td>Cu(II) and Pb(II)</td>
<td>Kaolinite-based Clay Minerals Individually and in the Presence of Humic Acid</td>
<td>Hizal and Apak, 2006</td>
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<td>Cd(II), Cu(II), Zn(II)</td>
<td>Cassava (Manihot sculenta Cranz) Tuber Bark Waste</td>
<td>Horsfall et al., 2006</td>
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<td>Pb(II), Cd(II), Cu(II) and Ni(II)</td>
<td>Anaerobic Granular Biomass</td>
<td>Hawari and Mulligan, 2006</td>
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<td>Cu(II), Zn(II), Cd(II), Pb(II)</td>
<td>Waste Tea and Coffee adsorbents</td>
<td>Utomo et al., 2006</td>
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<td>Cu(II), Cd(II), Zn(II), Mn(II) and Fe(III)</td>
<td>Tannic Acid Immobilised Activated Carbon</td>
<td>Ucer et al., 2006</td>
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<td>Ni(II), Zn(II) and Fe(II)</td>
<td>Modified Coir Fibres</td>
<td>Shukla et al., 2006</td>
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<td>Zn(II) and Cu(II)</td>
<td>Sugar Beet Pulp and Fly Ash</td>
<td>Pehlivan et al., 2006</td>
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<td>Cu(II) and Ni(II)</td>
<td>Solid Humic Acid from the Azraq Area, Jordan</td>
<td>El-Eswed and Khalili, 2006</td>
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<td>Cd(II) and Pb(II)</td>
<td>Diatom Surface</td>
<td>Gelabert et al., 2006</td>
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<td>Cu(II) and Pb(II)</td>
<td>Pretreated Aspergillus Niger</td>
<td>Dursun et al., 2006</td>
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<td>Pb(II), Cu(II), Cd(II), Zn(II) and Hg(II)</td>
<td>Multi-amine-grafted Mesoporous Silicas</td>
<td>The fresh dry samples were found to show much higher adsorption capacity than the aged ones Zhang et al., 2007</td>
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<td>Metal(s)</td>
<td>Source</td>
<td>Description</td>
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<td>Cd(II)</td>
<td>Sugarcane Bagasse</td>
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<td>Cu(II), Zn(II), Pb(II), Fe(III) and Cd(II)</td>
<td>Degreased Coffee Beans (DCB)</td>
<td>DCB behaves as a cation exchanger</td>
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<tr>
<td>Cr(VI)</td>
<td>Turkish Brown Coals</td>
<td>The adsorption reached equilibrium in 80 min</td>
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<tr>
<td>Cd(II), Pb(II) and Zn(II)</td>
<td>Unmodified and EDTA-modified Maize Husk</td>
<td>Sorption process was found to be physiosorption process</td>
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<td>Cu(II), Cd(II), Cr(VI), Zn(II)</td>
<td>Coffee husks</td>
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<tr>
<td>Pb(II), Cd(II)</td>
<td>Kaolinite clay and polyvinyl alcoal-modified kaolinite clay</td>
<td>91 % Pb and 94 % Cd were desorbed for kaolinite clay while 99 % Pb and 97 % PVA modified kaolinite clay</td>
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<tr>
<td>Cd(II), Pb(II)</td>
<td>Sugarbeet pulp</td>
<td>Maximum uptake was observed at pH 5.3</td>
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<td>Zn(II), Ni(II), Cd(II), Cu(II), Pb(II)</td>
<td>Tobacco dust</td>
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<td>Cd(II), Zn(II), Pb(II)</td>
<td>Orange wastes</td>
<td>Maximum adsorption was 0.25 mmol/g for three binary systems</td>
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<td>Cd(II), Zn(II)</td>
<td>Rice husk ash</td>
<td>Maximum adsorption at pH 6</td>
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<td>Zn(II), Cd(II), Pb(II)</td>
<td>Natural Clinoptilolitic zeolites and</td>
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<td>Sorbent</td>
<td>Adsorbate(s)</td>
<td>Maximum adsorption capacity</td>
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<tr>
<td>Commercial granular activated carbon</td>
<td>Cu(II), Mn(II), Pb(II)</td>
<td>Pecan nutshell</td>
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<td>Cr(VI), As(V)</td>
<td>HDTMA- modified zeolite</td>
<td>HDTMA- modified zeolite</td>
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<td>Cr(III), Cr(VI)</td>
<td>Modified sorbent</td>
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<td>Cu(II), Ni(II)</td>
<td>Food samples</td>
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<td>Cd(II), Pb(II), Ni(II), Zn(II), Cu(II)</td>
<td>Chemically modified sugarcane bagasse</td>
<td>Chemically modified sugarcane bagasse</td>
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<td>Cu(II), Cd(II), Pb(II), Cu(II), Cd(II), Ni(II)</td>
<td>Acacia leucocephala bark powder, Natural Kaolinite clay</td>
<td>Optimum adsorption takes place at pH 6.0, 5.0 and 4.0; Adsorption is rapid; Maximum adsorption within 30 min</td>
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<td>Cr(III), Cd(III)</td>
<td>Illitic clay</td>
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<td>Cu(II), Zn(II), Ni(II), Cd(II), Pb(II), Hg(II), Cr(VI)</td>
<td>Chitosan</td>
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<td>Pb(II), Cd(II), Cu(II), Zn(II)</td>
<td>Apricot stones</td>
<td>Apricot stones</td>
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<td>Cd(II), Cu(II), Ni(II),</td>
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<td>Metal Compounds</td>
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<td>Pb(II), Zn(II)</td>
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<td>Cu(II), Pb(II), Cd(II), Zn(II), Ni(II)</td>
<td>Green Coconut shells</td>
<td>Sousa et al., 2010</td>
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<td>Cu(II), Cr(III)</td>
<td>Vermiculite6</td>
<td>Badawy et al., 2010</td>
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<td>Cd(II), Cu(II), Pb(II), Zn(II)</td>
<td>Soils and Vegetables</td>
<td>Luo et al., 2011</td>
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<td>Cu, Pb, Cr</td>
<td>Na- Montmorillonite</td>
<td>Zhu et al., 2011</td>
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<tr>
<td>Pb(II), Cd(II)</td>
<td><em>Carpobrotus edulis</em> plant</td>
<td>Chiban et al., 2011</td>
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<tr>
<td>Zn(II), Cd(II), Pb(II)</td>
<td>Calcite mollusk shell</td>
<td>Du et al., 2011</td>
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<tr>
<td>Cr(VI), Cr(III)</td>
<td>Tea industry waste activated carbon</td>
<td>Percentage adsorption was 95-100 %</td>
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<td>Pb(II), Cr(III), Cu(II), Zn(II), Cd(II), Ni(II), Hg(II), Ba(II), Ag</td>
<td>Montmorillonite, Ca-Montmorillonite</td>
<td>De Pablo et al., 2011</td>
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<td>Pb(II), Zn(II)</td>
<td>Sulfured Orange peel</td>
<td>Maximum removal capacity was 164 mg/g for Pb (II) and 80 mg/g for Zn(II)</td>
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<td>Pb(II), Cd(II), Cu(II) and Zn(II)</td>
<td>Natural Limestone</td>
<td>It shows high removal efficiency.</td>
</tr>
<tr>
<td>Cu(II), Pb(II), Zn(II) and Cd(II)</td>
<td>Morin functionalized Merrifield’s resin</td>
<td>It retained all the studied metals with high efficiency (90–95%).</td>
</tr>
<tr>
<td>Al, Cr, Fe, Mn, Sb and V.</td>
<td>Carbon fly ash</td>
<td>The addition of lime had different effects on the column leach test (CLT)</td>
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<td>Heavy metals and dyes</td>
<td>Natural bamboo sawdust</td>
<td>Pznpc, Pzc and Iep of sawdust were characterized.</td>
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<td>Cu(II), Ni(II) and Co(II).</td>
<td>Chemically modified cellulosic adsorbent</td>
<td>Adsorbent removes metal ions with removal efficiency of 250 mg per 1 g.</td>
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</table>
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