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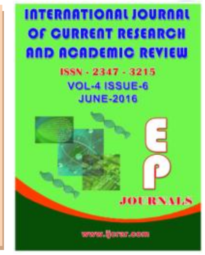

Heavy Metal Pollution, Sources, Toxic Effects and Techniques Adopted for Control

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A B S T R A C T

Heavy metals, a major category of globally distributed pollutants, discharged by various industries in their effluents, have tendency to accumulate in selected tissues of the human body and their potential to be toxic for all life forms even at relatively minor levels of exposure. Several processing techniques like chemical precipitation, ion exchange, flotation, solvent extraction, adsorption, membrane filtration and dialysis are available to reduce the concentration of heavy metals in wastewater. Adsorption onto various natural and synthetic adsorbents has become well known method for the removal of toxic metal ions. This study gives an account of the role played by adsorption phenomena in reducing heavy metal pollution by using various types of adsorbents. Heavy metals removal efficiencies through various techniques has been studied and found that adsorption is more promising, more efficient, eco-friendly and widely adopted technique in reducing heavy metal pollution. A large number of low cost natural and synthetic adsorbents such as agricultural waste, minerals, clays, activated carbon, sludge and coal ash can be employed in removing heavy metals from wastewater streams.

Introduction

Heavy metal is a general collective term, which applies to the group of metals and metalloids with atomic density greater than 4 g/cm^3 or 5 times greater than the density of water and has atomic numbers above 20 (Duruibe *et al.*, 2007, Raut *et al.*, 2012). Heavy metals include lead (Pb), chromium (Cr), copper (Cu), iron (Fe), zinc (Zn), mercury (Hg), arsenic (As), silver (Ag), and platinum group elements. Heavy metals can be emitted into environment by both natural and anthropogenic activities including mining, smelting, combustion of fuels, etc. (UNEP/GPA, 2004).Some metals, such as copper and iron are essential to life and play irreplaceable role in biological processes, for example the functioning of critical enzyme systems (Halliwell and Gutteridge, 1999).Other metals are xenobiotics, i.e., they have no useful role in human physiology (and most of other living organisms) but may be toxic even at trace levels of exposure. The excess levels of heavy metals cause severe toxicity. The toxicity of heavy metals and their salts depends on several factors such as nature and stability of cation and that of anion (Duruibe*et al*., 2007). The heavy metals, viz., As, Cd, Pb and Hg are considered most toxic to humans, animals, fishes and environment. They destabilize ecosystems because of their bioaccumulation in organisms, and exhibit toxic effects on biota and even death via metabolic interference and mutagenesis (Zhitkovich, 2005). These pollutants have a unique property to accumulate in food chain for a long period of time. Even very low concentration of a metal ion in wastewater, causes accumulation in food chain to a higher level. The toxic heavy metals have direct effects on man and animals (Renge *et al*., 2012). Environmental pollution by heavy metals is very prominent in areas of mining and old mine sites. It decreases with increasing distance from mining sites. These metals are leached out and in sloppy areas are carried by acid water downstream or run-off to the sea. Wells located near mining sites have been reported to contain heavy metals exceeding drinking water criteria (Duruibe*et al*., 2007).

Water of high quality is essential to human life and water of acceptable quality is required for agriculture, industrial, domestic and commercial uses. Requirement of water is increasing while slowly all major water resources are becoming unfit for their use due to improper waste disposal. Therefore removal of heavy metals from wastewater is of primary concern. The use of natural and waste material as adsorbent in heavy metal removal has become a requirement for their control. The task of providing proper treatment facility for all the polluted sources is difficult and also expensive, hence there is pressing demand for innovative technologies which are low cost, require low maintenance and are energy efficient. The removal of heavy metals from polluted water by all major techniques such as chemical precipitation, ion exchange, flotation, solvent extraction, membrane filtration and dialysis (Wang *et al*., 2004**;** O'Connel *et al*., 2008;Kurniawan *et al*., 2006) except adsorption have some drawbacks. Adsorption is more promising technique in treating polluted water as it is economically favourable, technically easy and eco-friendly (Kurniawan *et al*., 2005).

Heavy Metal pollution

Water pollution through heavy metals occurs when toxic heavy metals or metals beyond permissible limit has been discharged into the water bodies. Industrial effluent isone of the main source of heavy metal pollution in water bodies. Heavy metals poses serious threat to both environment and human health and tends to accumulate in the tissues and organs of living organism causing various diseases and long term disorders.Heavy metal ions exposure to newborn babies may damage brain memory, disrupt the function of red blood cells, the central nervous system, physiological and behavioural problems (Loutseti *et al*., 2009). These metals can have toxic effects on different organsshown in fig. 1. The toxic effects caused by mercury, cadmium and zinc on soil microbial population have been reported by (Bhat *et al*., 1979). Severe toxicity from these metals may cause cancer. When volatile vapours of these metals are inhaled; they cause gastrointestinal disorders, paralysis, vomiting, convulsion, depression and pneumonia (Duruibe*et al*, 2007). Effects of various heavy metals on human health and their maximum contamination limit by different agencies is given in the table 1 and 2 respectively. Exposure of plants to heavy metals may lead to physiological and morphological changes and damage to cell function and reduce photosynthesis rates. Mutagenic changes have also been observed in several plant species. Metal ion toxicities may lead to chlorosis, bleaching, nutrient deficiencies and increased oxidation stress in plants. Heavy metals obstruct the growth of microbes (Nagajyoti *et al*., 2010). The toxic effects of chromium on both lower and higher plants and humans have been investigated (Shanker *et al*., 2005; Zhitkovich, 2005).

Sources and health hazards through heavy metals

Heavy metals are the most common pollutants found in wastewater and pose a serious threat to all forms of life even at low concentration.

Lead

Lead is a pollutant of major concern as it is used as one of the raw materials for battery manufacturing, printing, pigments, fuels, photographic materials and explosive manufacturing. Airborne lead may cause the poisoning of agricultural products by their deposition on fruits. Lead is extremely toxic to the nervous system, kidney and reproductive system. Higher doses may damage the foetus. (Owen and sandhu 2000; Moreira *et al*., 2001)

Cadmium

Cadmium being one of the most toxic elements, even at low concentration in the food chain has been found to cause itai-itai disease killing scores of population of Japan. It is used widely in electroplating industries, solders, batteries, television sets, ceramics, photography, insecticides, electronics, metal-finishing industries and metallurgical activities. It is introduced into the environment by metal-ore refining, cadmium containing pigments, alloys and electronic compounds, cadmium containing phosphate fertilizers, detergents and refined petroleum products (Zufiaurrer *et al*., 1998; Alkorta *et al*., 2004; Hu, 2008).Cadmium exposure causes renal dysfunction, bone degeneration, liver and blood damage. It has been reported that there is sufficient evidence for the carcinogenicity of cadmium (Zufiaurrer *et al*., 1998).

Copper

Copper has been used by man since prehistoric times. It is used in the production of utensils, electrical wires, pipes and in the manufacture of brass and bronze. Mining, metallurgy and industrial applications are the major sources of copper exposure in the environment (Barrell, 1975).Copper, as an essential trace element, is required by biological systems for the activation of some enzymes during photosynthesis but at higher concentrations it shows harmful effects on the human body. It is also toxic to a variety of aquatic organisms even at very low concentrations. High-level exposure of copper dust causes nose, eyes and mouth irritation and may cause nausea, vomiting and diarrhoea. Continuous exposure may lead to kidney damage and even death. (Wagoner and Soffioti, 1979; Onundi *et al*., 2010)

Zinc

Zinc is also an essential element in our diet. Too much of it, however, can also be damaging to health. Mining and metallurgical processing of zinc ores and its industrial application are the major sources of zinc in the air, soil and water. It also comes from the burning of coal. Zinc toxicity in large amounts causes nausea and vomiting in children. A higher concentration of zinc may cause anaemia and cholesterol problems in human beings (Plum *et al*., 2010).

Nickel

Nickel occurs naturally in soils and volcanic rocks. Nickel and its salts are used in several industrial applications such as electroplating, automobile and aircraft parts, batteries, coins, spark plugs, cosmetics, stainless steel, and is used extensively in the production of nickel–cadmium batteries on an industrial scale (Mishra *et al*., 2005). Paint formulation and enamelling industries discharges nickel containing effluents to the nearby bodies of water (USEPA, 2009a).Nickel is also found in cigarettes, as a volatile compound commonly known as nickel carbonyl (WHO 2004). Nickel plays an essential role in the synthesis of red blood cells; however, it becomes toxic when taken in higher doses. Trace amounts of nickel do not damage biological cells, but exposure to a high dose for a longer time may damage cells, decrease body weight and damage the liver and heart. Nickel poisoning may cause reduction in cell growth, cancer and nervous system damage (Duvnjak and Al-Asheh, 1997). The water soluble salts of nickel are the major problems of contamination in aquatic systems (Hu, 2008).

Arsenic

Arsenic is found naturally in the deposits of earth's crust worldwide and enters the environment through natural weathering of rocks and anthropogenic activities, mining, smelting processes, pesticide use and coal combustion. Arsenic has been found naturally at high concentration in groundwater in countries such as India, Bangladesh, Taiwan, Brazil and Chile. The toxicity of arsenic as a result of the contamination of groundwater bodies and surface waters is of great concern. Its high concentration in drinking water causes toxicity in the blood, central nervous system, lung and skin cancer, breathing problems, vomiting and nausea (Ratnaike, 2003).

Mercury

Mercury is a very toxic element in its organic form. It occurs naturally in volcanic eruption, weathering of rocks and soils, whereas anthropogenic mercury comes from the extensive use of the metal in industrial applications, its mining and processing, applications in batteries and mercury vapour lamps. The toxicity of mercury has been recognized worldwide, such as in Minamata Bay episode of Japan. Mercury toxicity has been found to be associated with physiological stress, abortion and tremors. The exposure to mercury causes toxicity to the brain, blindness, mental retardation and kidney damage. Mentally disturbed and physically deformed babies were born to mothers who were exposed to toxic mercury due to consumption of contaminated fish (Karagas *et al*., 2012; Kirk *et al*., 2012).

Chromium

Chromium compounds are extensively used in industrial applications which discharge huge amounts of wastewater containing toxic chromium species into water bodies. Hexavalent chromium is known to be more toxic than trivalent chromium (Mungasavalli *et al*., 2007). Volcanic eruptions, geological weathering of rocks, soils and sediments are the natural sources of chromium, whereas anthropogenic contributions of chromium originate from the burning of fossil fuels, production of chromates, plastic manufacturing, electroplating of metals and extensive use in the leather and tannery industries (Shrivastava and Majumdar, 2008). High levels of exposure cause liver and kidney damage, skin ulceration and also affect the central nervous system. In plant species it reduces the rate of photosynthesis (Shanker *et al*., 2005). It is also associated with the toxic effects on haematological problems and immune response in freshwater fish.

Iron and Manganese

The undesirable presence of iron and manganese in drinking water may pose a toxicity threat to health. However, iron and manganese are required by the biological system as they play major roles in the haemoglobin synthesis and functioning of cells. The major concerns focus on the dietary intake of iron because a high dose may pose acute toxicity to newborn babies and young children. The gastrointestinal tract rapidly absorbs iron that may pose a toxicity risk to the cells and cytoplasm. The liver, kidneys and cardiovascular systems are the major toxicity targets of iron. Neurological disturbances and muscle function damage are the result of toxic effects of manganese in human bodies (Shahid *et al*., 2014).

Effects of heavy metals pollution on Aquatic organisms

Aquatic organisms are adversely affected by heavy metals in the environment. The toxicity of the water chemistry and sediment composition in the surface water system has been studied (Baby *et al*., 2010). The metals are mineralized by microorganism, which in turn are taken up by plankton and further by the aquatic organisms. Finally the metals, which are several times biomagnified is taken up by man when he consumes fish from the contaminated water.Among animal species, the fishes are inhabitants which can be highly affected by these toxic pollutants leading to serious problems and ill-effects. With increasing heavy metals in the environment, these elements enter the biogeochemical cycle leading to toxicity in animals, including fishes. They enter into water bodies via drainage, atmosphere, soil erosion and human activities. As the heavy metals concentrate more in the environment, they enter biogeochemical cycle, leading to toxicity in animals and fishes (Pandey and Madhuri, 2014).

The chlorinated hydrocarbon as well as oil products and heavy metals have become toxicants of global abundance. The heavy metals have a high degree of accumulation through the food chain. This process can intensify the toxic effects directly on both the hydrobionts and on humans eating marine products. Various combinations of metals and also metals and other ions in domestic and industrial waste waters present a potential hazard for aquatic ecosystems (Shesterin and Ivan, 2001).

Techniques for the removal of Heavy metals

Severe toxic effects and poisoning by heavy metal ions worldwide and strict discharge regulations for wastewater effluents to aquatic bodies requires more intensive treatment techniques. Environmental scientists have developed several procedures such as co-precipitation, coagulation, reverse osmosis, ion-exchange, electro-dialysis, ultraviolet treatment, membrane filtration and adsorption for treatment of wastewater effluents containing heavy metals**.** Mukesh and Lokendra, 2013 have reviewed the techniques such as precipitation, cementation, electro-dialysis, reverse-osmosis, ion exchange and adsorption for the removal of heavy metals from wastewater. Although these techniques can be employed for the treatment of wastewater laden with heavy metals, but the selection of the most suitable treatment for metal contaminated wastewater depends on some basic parameters such as pH, initial metal concentration, contact time, amount of adsorbent, the overall treatment performance compared to other technologies, environmental impact as well as economics parameter such as the capital investment and operational costs. Finally, technical applicability, plant simplicity, and cost-effectiveness are the key factors that play major roles in the selection of the most suitable treatment process for waste water effluent. All the factors mentioned above should be taken into consideration in selecting the most cost effective treatment techniques in order to protect the environment and human health from toxic and hazardous contaminated waste water.

UV Radiation

Ultra-violet radiation method is germicidal/disinfection treatment for water that uses short wavelength ultraviolet light to kill or inactivate microorganism by destroying nucleic acid or rupturing their DNA. Mercury lamps generating 254 nm light is used for sanitizing water. Now-a-days lamps in combination of 180 and 254 nm light are used which reduces organic compounds by photo oxidation. The drawback of this purification technology is that it decreases resistivity and does not remove the colloids and ions effectively. UV radiation technique still remains a more sophisticated technique which requires greater expertise to handle. Reasons for this include the fact that the laser beam is now invisible, and that the lasers are larger, more complex, and considerably more expensive. This technique also requires specific mirror coatings, microscope objectives, diffraction gratings, and CCD detector for optimized results (Barakat, 2011).

Chemical precipitation

Precipitation is one of the oldest methods used for the removal of heavy metals from waste waters (Stinson, 1979). In ground water treatment applications, the metal precipitation process is often used as a pretreatment for other treatment technologies (such as chemical oxidation or air stripping) where the presence of metals would interfere with the other treatment processes. Chemical precipitation is the most widely used method for removal of heavy metals from inorganic effluent. The conceptual mechanism of heavy metals removal by chemical precipitation is presented by the equation**-**(Barkat, 2011)

$$M^{2+} + 2(OH)^{-} \rightarrow M(OH)^{-}$$

In this process, chemical react with heavy metal ions to form insoluble precipitate. Typically, metals precipitate from the solution as hydroxides, sulfides, or carbonates. Precipitation of metals is achieved by the addition of coagulants such as alum, lime, iron salts and other organic polymer. The precipitate formed can be separated from the water by sedimentation or filtration and the water is then decanted and discharged or reused. The hydroxide precipitation is the most widely used chemical precipitation technique because of its simplicity, low cost and ease of pH control, and it can be employed effectively to treat inorganic effluent with a metal ion concentration higher than 1000 mg/L (Huisman *et al*., 2006). The presence of complex agents such as cyanides inhibits hydroxide precipitation. The use of several reducing agents has been recommended and some of them are SO_2, sodium bisulphate and ferrous sulphate.

In spite of number of advantages, chemical precipitation has anomalies as it requires a large amount of chemicals to reduce metals to acceptable levels for discharge. Other drawbacks are its expensive sludge production that requires further treatment, thus increasing cost of sludge disposal, slow metal precipitation, poor settling, the aggregation of metal precipitates, and long term environmental impacts of sludge disposal (Bose *et al*., 2002). Chemical precipitation is usually adapted to treat wastewater containing high concentration of heavy metals ions but ineffective when metal ion concentration is low. It is uneconomical and can produce large amount of sludge to be treated with great difficulties (Fenglian and Wang, 2006).

Ion Exchange

Ion exchange is a reversible chemical reaction where an ion from solution is exchanged for a similarly charged ion attached to an immobile solid particle. In this process ions are exchanged between two electrolytes or between an electrolyte solution and a complex. These solid ion exchange particles are either naturally occurring inorganic zeolites or synthetically produced organic resins which has the ability to exchange cations with the metals in the wastewater. Ion exchangers are classified as cation exchangers and anion exchangers which has positively charged mobile ions are available for exchange (Yang *et al*., 2001). The chemical behavior of the resin is determined by the functional group present on it. The typical ion exchangers are zeolites, montmorillonite, clay and soil humus. Resins are also classified as strong or weak acid cation exchangers or strong or weak base anion exchangers. The most common cations exchangers are strongly acid resins with sulfonic acid groups ($-SO_3H$) and weakly acid resins with carboxylic acid groups (-COOH). As the solution containing heavy metals passes through the cation exchange column, metal ions are exchanged for the hydrogen ions of the resins with the following ion-exchange process;

$$nR\text{-}SO_3H + M^{n+} \rightarrow (R\text{-}SO_3^-)_n M^{n+} + nH^+$$

$$nR\text{-}COOH + M^{n+} \rightarrow (R\text{-}COO^-)_n M^{n+} + nH^+$$

The uptake of heavy metals by ion-exchange resins is affected by certain variables such as pH, temperature, initial metal concentration and contact time (Gode and Pehlivan, 2006). Ion exchange method is successfully used in industry for the removal of heavy metals from effluent. This method has been followed by many industries to treat industrial waste containing chromate.

Ion exchange is a reversible process which can be regenerated but regeneration can cause serious secondary pollution. It cannot handle concentrated metal solution as the matrix gets easily fouled by organics and other solids in waste waters. Another great disadvantage is that electrodes get corroded soon and frequently have to be replaced (Kurniawan *et al*., 2006). The process is expensive, especially when treating a large amount of waste water containing heavy metals in low concentration, so they cannot be used at large scale (Fenglian and Wang, 2011).

Membrane Filtration

Membrane filtration has received considerable attention for the treatment of inorganic effluent, since it is capable of removing not only suspended solid and organic compounds but also inorganic contaminants such as heavy metals. Depending upon the types of membrane used and size of the particles that can be retained to purify water by removing different types of organic and inorganic pollutant species, various types of membrane filtration such as ultrafiltration, nanofiltration, reverse osmosis and electro dialysis have been employed. These methods have ability to clarify, concentrate and most importantly remove heavy metals from waste water (Figoli *et al*., 2010; Ahmad and Ooi, 2010). Membrane filtration has some special features unrivalled by other methods; resistance to temperature, and adverse to chemical environment and microbial attack. The specific temperature and chemical composition of the waste water determine the type and porosity of the filter to be applied. The main drawbacks of the membrane technology are the high investment cost, fouling of the membrane and the production of the effluent bath which needs to be treated (Fenglian and Wang, 2011). The major disadvantage of these methods is that it does not remove dissolved inorganic pollutants.

Ultrafiltration technique (UF) is a membrane technique working at low trans-membrane pressure for the removal of dissolved and colloidal materials. Since the pore size of UF membrane are larger than dissolved metal ions in the form of hydrated ions or as low molecular weight complexes, these ions passes easily through UF membrane. Unique specialties enable ultrafiltration to allow the passage of water and low-molecular weight solutes, while retaining the macromolecules which have a size larger than the pore size of the membrane. The main disadvantage of this process is the generation of sludge. The main parameters affecting UF are metal and polymer type, ratio of metal to polymer, pH and existence of other ions in the solution (Fenglian and Wang, 2011).

Now-a-days reverse osmosis technique is applied for treating waste waters. In this process a semi-permeable membrane is used and allows the fluid being purified to pass through it while rejecting the contaminants. It is one of the most widely used techniques which are able to remove a wide range of dissolves species from water. The cost is favourable especially when the metal to be recovered is valuable. This method has been considered to be a good treatment process for chromium removal. The spiral wound configuration of membranes support structure proves to be the best and most effective in the use when it comes to municipal wastewater reclamation. However problems that remain to be solved are membrane durability, fouling of membrane and sensitivity to hard water salts (Fenglian and Wang, 2011).

Nanofiltration is the intermediate method between UF and RO. Nanofiltration technique has been used for the removal of heavy metals ions such as nickel (Murthy and Chaudhary, 2008), chromium (Muthukrishnan and Guha, 2008), copper (Csefavay *et al*., 2009; Ahmad *et al*., 2010) and arsenic (Nguyen *et al*., 2009; Figoli *et al*., 2010) from waste water.

Electro dialysis (ED) is a membrane separation process for the separation of ionized species across charged membrane from one solution to another using an electric field as the driving force. When a solution containing ionic species is passed through the cell compartment, the anions migrate towards the anode and cations towards the cathode (Chen, 2004). The membrane is of two types: cation-exchange and anion-exchange membranes. This process has been widely used for the production of drinking and process water from brackish water and recovery of materials from effluents (Sardzadeha *et al*., 2009). Membrane filtration can remove heavy metals ions with high efficiency, but chemical precipitation of metal salts into low soluble metal hydroxides clog the membrane. Some other problems of this technique are high cost, process of complexity, membrane fouling and low permeate flux have limited their use in heavy metal removal (Fenglian and Wang, 2011).

Adsorption

Adsorption is a mass transfer process by which a substance is transferred from the liquid or gaseous phase to the surface of a solid and become bound by physical or chemical interaction (Bable and Kurniawan, 2003). The term adsorption was given by Keyser. The term adsorption is also defined as adhesion of atoms, ions, biomolecules or molecules of gas, liquid or dissolved solids to a surface. Adsorption is a surface phenomena. The substance that accumulates at the interface is called adsorbate and the solid on which adsorption occurs is called adsorbent (Dabrowski, 2001).

Adsorption is of two types, chemical adsorption (Chemisorption) and physical adsorption (Physiorption). Chemisorption is due to the formation of strong chemical association between ions of adsorbate to the functional group present on adsorbent surface (Allen and Koumanova, 2005). Chemical adsorption is a reversible process and characterized by a large heat exchange during adsorption. The physiorption is the physical process involving the intermolecular forces i.e Van der Waal's forces between adsorbate and adsorbent. It is a reversible process(Allen and Koumanova, 2005).The main physical forces controlling adsorption are Van der Waal's forces, hydrogen bond, polarity, dipole-dipole interaction, etc. (Ali, 2010). It decreases with increase in temperature and equilibrium is established between the adsorbate and the fluid phase resulting in multilayer adsorption.

Adsorbent is a material which has ability to bind the adsorbate molecules (metal ions) on its surface by means of physical or chemical forces. The adsorbent can be a natural organic or inorganic material or it can be a synthesized product. The rate of adsorption depends upon the type of adsorbent and nature of metal ions to be adsorbed. A single adsorbent can't remove all types of metal ions with equal efficiencies; therefore selection of suitable adsorbent is necessary to remove a particular type of metal ion.

The most widely used conventional adsorbent is activated carbon because of its high surface area, micro porous structure, high adsorption capacity and high degree of surface reactivity. But its widespread use in wastewater treatment is sometimes restricted due to its higher cost and poor regeneration capacity. Therefore to make adsorption an economically feasible process a considerable research work is done in search of inexpensive and easily available non-conventional adsorbent.

During the last decades various non-conventional adsorbents have been used for the removal of heavy metals from wastewater such as rice husk (Elham *et al*., 2010; Singha and Das, 2012), saw dust, wheat straw (Ajmal *et al*., 1998; 2003), wheat shell and almond shell (Dang *et al*,. 2009), hazelnut (Demirbasa *et al*,. 2004), orange peel (Kobya, 2004), sugarcane bagasse (Martin-Lara *et al*., 2010), flyash (Ahmad, A., 2012), gyttja (Dikici, *et al*., 2005), kaolinite supported zero valent iron monoparticles (Uzum *et al*., 2010), Mg oxide coated betonite (Eren *et al*., 2010) , mineral soil (Vidal *et al*., 2009) , perlite (Ghassabzadeha *et al*., 2010) , sandy soil (Yip *et al*., 2010), fired ceramic (Ahmad, S., *et al*., 2016) and roasted china clay (Ahmad, S. *et al*., 2016).

Table.1 Sources and effects of heavy metals on human body [De, 2010]

Metal	Atomic No.	Sources	Effects on human body
Chromium	24	Alloys, leather tanning, dyes pigments, wood preservatives	Affects respiration, cause kidney and liver damage, ulcers, skin allergies, pneumonia.
Copper	29	Industrial and domestic waste, metal plating, mining and mineral leaching	Essential trace elements, not very toxic to the body.
Arsenic	33	Rat poison, paints, fungicides and wood preservatives	Affects blood, kidney, central nervous system, skin and digestive system
Aluminium	13	Food additives, antacids, buffered aspirin, astringents, nasal sprays, and antiperspirants, drinking water, automobile exhaust, tobacco smoke, aluminium foil, canes, ceramics and fire works	Causes Alzheimer disease, degenerative muscular conditions and cancer, affects central nervous system.
Cadmium	48	PVC plastics, batteries, paints and pigments, insecticides, fungicides, fertilizers, dental alloys, electroplating and automobile exhaust	Affects kidney, placenta, lungs, brain and gastrointestinal system
Mercury	80	Mining operations, paper industries, thermometers, aquatic food chains and fishes in lakes	Affects brain and kidney.
Nickel	28	Electroplating industries, batteries, coins, stainless steel and magnets	Carcinogenic and cause skin allergies.
Iron	26	Drinking water, iron pipes, cookwares	Affects kidney, liver and cardiovascular system
Lead	82	Batteries, paints, PVC plastics, X-ray shielding, crustal glass production and pesticides	Affects kidney, blood, brain and thyroid gland.
Cobalt	27	Burning of coal and oil, found in soil, dust and sea water, car and truck exhaust	Affects lungs causing asthma, cancer, affects muscles.

Zinc	30	Paint industry, rubber, dye, wood, preservatives, galvanized iron objects, bronze, brass	Cause throat dryness, cough, fever, nausea, vomiting, pancreas damage, lungs and stomach aches.
Barium	56	Tiles, glass and rubber, bricks, drilling mud, oil industries	Increase blood pressure. Breathing problems, stomach irritation.

Table.2 Drinking water standards by different agencies

Heavy metal	**Agencies**
Lead	• USEPA: 0.1 mgL^{-1} • EC: 0.5 mgL^{-1} • Regulation of water quality(India) 0.1 mgL^{-1} • WHO: 0.05 mgL^{-1} • BIS: 0.1 mgL^{-1} • CPCB: No Relaxation • ICMR: 0.05 mgL^{-1}
Cadmium	• USEPA: 0.005 mgL^{-1} • EC:0.2 mgL^{-1} • Regulation of water quality(India): 0.001 mgL^{-1} • WHO: 0.005 mgL^{-1} • BIS: 0.01 mgL^{-1} • CPCB: No Relaxation • ICMR: 0.01 mgL^{-1}
Mercury	• USEPA: 0.001mgL^{-1} • EC:0.001mgL^{-1} • Regulation of water quality(India): 0.004mgL^{-1} • WHO: 0.002 mgL^{-1} • BIS: 0.001 mgL^{-1} • CPCB: No Relaxation • ICMR: 0.001 $mgL^{-}1$
Chromium	• USEPA: 0.1mgL^{-1} • EC: 0.5mgL^{-1} • Regulation of water quality(India): 0.1 mgL^{-1} • BIS: 0.5 mgL^{-1} • CPCB: No Relaxation • ICMR: No Relaxation

Arsenic	• USEPA: 0.005 mgL^{-1} • EC:0.01mgL^{-1} • Regulation of water quality(India): 0.05mgL^{-1} • WHO: 0.005 mgL^{-1} • BIS: 0.05 mgL^{-1} • CPCB: No Relaxation • ICMR: 0.05 mgL^{-1}
Zinc	• USEPA: 5.0mgL^{-1} • EC: 5.0mgL^{-1} • Regulation of water quality(India): 0.1 mgL^{-1} • WHO: 5.0 mgL^{-1} • BIS: 5.0 mgL^{-1} • CPCB: 15 mgL^{-1} • ICMR: 0.1 mgL^{-1}
Nickel	• USEPA: 0.01mgL^{-1} • EC: 0.1mgL^{-1} • Regulation of water quality(India): 0.1 mgL^{-1} • BIS: 0.5 mgL^{-1}
Copper	• USEPA: 1.0mgL^{-1} • EC: 3.0mgL^{-1} • Regulation of water quality(India): 0.01 mgL^{-1} • WHO: 1.0 mgL^{-1} • CPCB: 1.5 mgL^{-1} • ICMR: 1.5 mgL^{-1}

Note: BIS: Bureau of Indian Standard**, CPCB:** Central Pollution Control Board**, ICMR:** Indian Council of Medical Research, **EC:** European Community.

Table.3 Advantages and disadvantages of various techniques to remove heavy metals

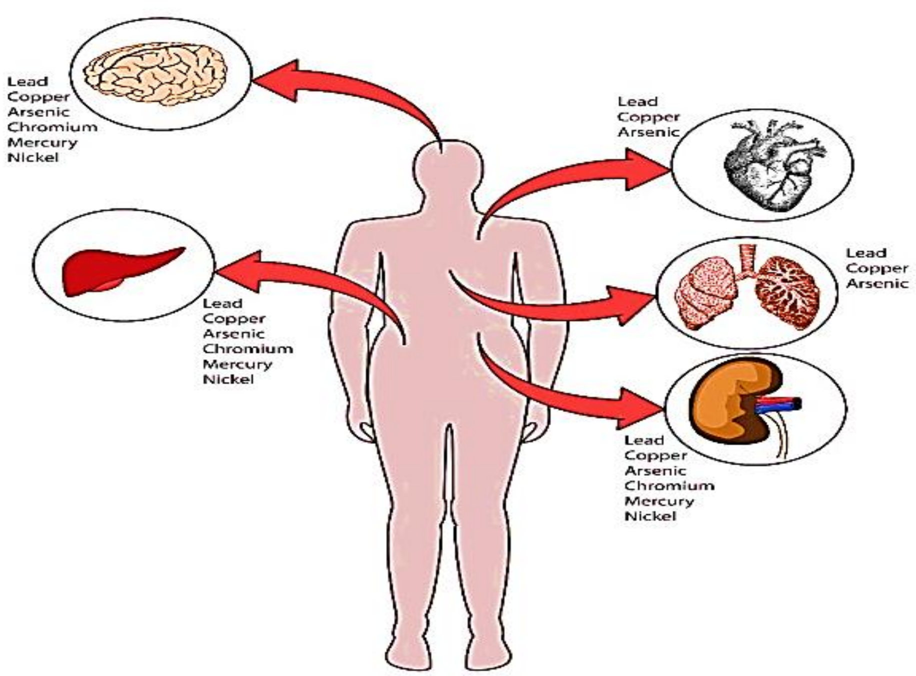
S. N	Technique	Advantages	Disadvantages	References
1.	Ion exchange	Metal selective Limited pH tolerance High regeneration	High initial capital cost High maintenance cost	Rengaraj *et al.*, 2003
2.	Coagulation and flocculation	Bacterial inactivation capacity Good sludge settling and dewatering characteristics	Chemical consumption Increased sludge volume generation	Fenglian and Wang, 2011

3.	Chemical precipitation	Process simplicity Not metal selective Inexpensive capital cost	Large amount of sludge containing metals Sludge disposal cost High maintenance cost	Fenglian and Wang, 2011 Kurniawan *et al*., 2006
4.	Membrane filtration	Low solid waste generation Low chemical consumption	Complex process High initial capital cost High maintenance and operation costs Membrane fouling Limited flow rates	Madaeni and Masourpanah, 2003; Kurniawan *et al*., 2006 Qin *et al*., 2008
5.	Reverse Osmosis	Remove wide range of dissolved species Best and most effective to treat municipal waste water	Membrane durability Fouling of membrane Sensitive to hard water	Fenglian and Wang, 2011
6.	Electron dialysis	Recover useful materials from waste water Remove heavy metals with high efficiency	High cost Process complexity Low permeable flux	Fenglian and Wang, 2011 Mohammadi *et al*., 2005
7.	Adsorption	Wide variety of target pollutants High capacity Fast kinetics Efficient in removing metal ions even at ultra-trace level Cost effective Process simplicity Possibly selective depending on adsorbent	Performance depends upon type of adsorbents Physical or chemical activation to improve its sorption capacity.	Crini, 2005 Kurniawan *et al*., 2005

Table.4 Factors affecting adsorption of metal ions

S. No.	Factors	Effects
1.	Surface area of the adsorbent	Large surface area implies greater adsorption capacity.
2.	Particles size of the adsorbent	Smaller the particle size of the adsorbent greater is the adsorption capacity. (Krishna and Swamy, 2012)
3.	Contact time or equilibrium time	Adsorption increases with increase in time until the attainment of equilibrium. (Chen *et al*., 2011)
4.	Concentration	Rate of adsorption increases with increase in concentration. (Angelin *et al*., 2015)
5.	pH	Strong influence on adsorption due to the variation in degree of ionization of metal ion in the solution and the surface properties of adsorbent (Nandi *et al*., 2009)
6.	Temperature	Affects the rate and capacity of the adsorption. (Rani and Sud, 2015)
7.	Degree of ionization of the adsorbate molecules	Highly ionized molecules are adsorbed to smaller degree than neutral molecules.

Fig.1 Effects of heavy metals on different organs of the body



Adsorption provides an attractive alternative for the treatment of polluted waters. As for environment remediation purpose, adsorption techniques are widely used to remove certain classes of chemical contaminants from waste water, especially those that are practically unaffected by conventional biological treatments (Allen and Koumanova, 2005). Adsorption has been found to be superior to other techniques in terms of flexibility, simplicity of design, initial cost, and insensitivity to toxic pollutants and ease of operation. Adsorption also does not produce harmful byproduct (Crini, 2006). Advantages and disadvantages of various techniques discussed for the removal of heavy metals are summarized in the table 3.

Although several techniques can be employed for the treatment of wastewater laden with heavy metals, it is important to note that the selection of the most suitable treatment technique for metal-contaminated wastewater depends on some basic parameters such as pH, initial metal concentration, the overall treatment performance compared to other technologies, environmental impact as well as economic feasibility such as the capital investment and operational costs. Finally, technical applicability, plant simplicity and cost-effectiveness are the key factors that play major roles in the selection of the most suitable treatment process for wastewater; Adsorption is the only method which fulfils all the required qualities for a technique to be globalised according to its utilisation (Barakat, 2011).

Factors affecting adsorption of metal ions

The process of metals adsorption is affected by the nature of adsorbent and the solutions. It also depends upon the surface area, functional groups, pore sizes, morphology and surface charge of the adsorbents. Some factors affecting adsorption of metals are listed in table 4.

Advantages of adsorption for the removal of heavy metals: (Modak and Natranjan, 1995)

- The material used as adsorbent can be found easily as some waste material or by products used as adsorbents are available at almost no cost.
- There is no need of costly growth media.
- The process is independent of physiological constraints of living cells.
- Process is very rapid, as non-living material behaves as an ion-exchange resin. The metal loading being very high.
- The conditions of the process are not limited by the living biomass with no aseptic conditions required.
- Process is reversible and metal can be desorbed easily leading to recycling of the adsorbent.
- Chemical or biological sludge is minimized.

In conclusion, one of the most threatening environmental problems throughout the world is heavy metal pollution of wastewater. In order to meet the increased more and more stringent environmental regulations, a wide range of treatment technologies such as chemical precipitation, coagulation, flocculation, flotation, ion exchange and membrane filtration, have been developed for heavy metal removal from wastewater. It is evident from the literature survey that adsorption is the most frequently used technique for the treatment of heavy metal contaminated wastewater. In comparison to the other techniques, it was found that adsorption is the most effective, efficient, economically and technically simple method to remove heavy metal ions from water even at very low concentration by using low-cost adsorbents and biosorbents. Adsorption can also be employed on those materials as adsorbent which are itself becoming a threat to environment due to their disposal problems. The worldwide use of adsorption has made it a universally accepted and adopted technique for the proper and effective treatment of industrial wastewater.

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