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Heavy Metals: Sources, Health Effects, Environmental Effects, Removal Methods And Natural Adsorbent Material As Low-Cost Adsorbent: Short Review

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Abstract: Industrial activities have experienced rapid growth producing an increase in the volume and toxicity of residues. Among these residues, liquid effluents containing heavy metals are of special interest. Metals have a high degree of toxicity, which can be prejudicial even at low concentrations for both human beings and the environment. Discharge and treatment of industrial wastewater containing heavy metals are important issues in environmental protection. Chemical precipitation, ion exchange, reverse osmosis process, electro dialysis, ultra filtration, coagulation–flocculation, flotation and adsorption processing techniques are used to reduce the concentrations of heavy metals in industrial wastewater. Use of adsorption contacting systems for industrial and municipal wastewater treatment has become more prevalent during recent years. Adsorption is often used at the end of a treatment sequence for pollution control due to high degree of purification that can be achieved. The adsorption abilities of a number agricultural by-products as low-cost adsorbents (e.g., rice husk, rice straw, tea factory waste, spent leaves tea, fly ash, sawdust, pomegranate husk, nut shell, several tree leaves,…etc.) have been determined for the removal of heavy metals from water.

Keywords: Heavy Metals, Toxicology, Adsorption, Natural Materials And Low-Cost Adsorbent.

I. INTRODUCTION

One of the most challenging environmental problems is the removal of heavy metals and other toxic contaminants from industrial wastewater. Heavy metals are toxic pollutants released into the environment as a result of different activities such as industrial, mining, and agricultural activities. Many aquatic environments face metal concentrations that exceed water quality criteria designed to protect the environment, animals and human (Gin, et al., 2002) [1]. Metals can be distinguished from other toxic pollutants, since they are non-biodegradable and can accumulate in the living tissues, thus becoming concentrated throughout the food chain. The most direct potential routes of human exposure to such discharged metals into a river would be any consumption of water or fish or other food derived from the river (Watson, et al., 2002) [2]. The objective of this study is Identify the serious effects of heavy metals on humans and the environment, and the most important methods of treatment and review of agricultural wastes which can be used as low-cost adsorbents material**.**

Heavy Metals: Heavy metals are elements having atomic weights between (63.5 and 200.5) and an atomic density greater than 5.0) gm/cm^3 ((Kennish, 1992; Raut et al., 2012) [3, 4]. Living organisms require trace amounts of some heavy metals, including cobalt, copper, iron, manganese, molybdenum, vanadium, strontium, and zinc. Excessive levels of essential metals, however, can be detrimental to the organism. Non-essential heavy metals of particular concern to surface water systems are cadmium, chromium, mercury, lead, arsenic, and antimony. All heavy metals exist in surface waters in colloidal, particulate, and dissolved phases, although dissolved concentrations are generally low (Kennish, 1992) [3]. The colloidal and particulate metal may be found in:

- Hydroxides, oxides, silicates, and sulfides; or
- Adsorbed to clay, silica, or organic matter.

Sources of Heavy Metals in Wastewater: With the development in industrialization and human activities, the discharge of waste and wastewater containing heavy metals to environment has increased. Mine drainage, metal industries, petroleum refining, tanning, photographic processing, and electroplating are some of the main sources of heavy metals (Beszedits, 1983) [5]. Electroplating and metal surface treatment processes generate significant quantities of wastewaters containing heavy metals (such as cadmium, zinc, lead, chromium, nickel, copper, vanadium, platinum, silver, and titanium) from a variety of applications (Chuah et al., 2005) [6].In addition, domestic effluents, landfill leachate, agricultural runoff, and acid rain also contribute to heavy metals in wastewater (Pradhan and Levine., 1992) [7].

Health Effects of Heavy Metals: Heavy metals are dangerous because they tend to bio-accumulate.

Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted (Howari, et al., 2004) [8].. Only a relatively small number of heavy metals such as cadmium, copper, iron, cobalt, zinc, mercury, vanadium, lead, nickel, chromium, manganese, molybdenum, silver, and tin as well as the metalloids arsenic and selenium are associated with environmental, plant, animal, or human health problems. Appropriate selection of metals for bio-sorption studies is dependent on the angle of interest and the impact of different metals; they would be divided into four major categories: toxic heavy metals, strategic metals, precious metals and radio nuclides (Vole sky, 1986; Bishop, 2002) [9, 10].

Ingestion of metals such as lead (Pb), cadmium (Cd), mercury (Hg), arsenic (As), barium (Ba), and chromium (Cr), may pose great risks to human health. Trace metals such as lead and cadmium will interfere with essential nutrients of similar appearance, such as calcium (Ca^{2+}) and zinc (Zn^{2+}). The toxic effect of heavy metals appears to be related to production of reactive oxygen species (ROS) and the resulting unbalanced cellular redox status (Emani et al., 2003) [11]. In terms of environmental threats, it is mainly categories toxic heavy metals and radio nuclides that are of interest for removal from the environment and/or from point source effluent discharges. The interest in specific metals may be based on how representative their behavior is in terms of eventual generalization of results of studying their bio-sorption. The toxicity and interesting solution chemistry of elements such as lead, copper and cadmium make them interesting to study (Ahalya et al., 2003) [12].

II. HEAVY METAL TOXICITY

Environmental pollution particularly from heavy metals and minerals in the wastewater is the most serious problem in India. Due to extensive anthropogenic activities such as industrial operations particularly mining, agricultural processes and disposal of industrial waste materials; their concentration has increased to dangerous levels. Most of the heavy metals are dangerous to health or to the environment. Heavy metals in industrial wastewater include lead, chromium, mercury, uranium, selenium, zinc, arsenic, cadmium, silver, gold, and nickel. The main threats to human health from heavy metals are associated with exposure to lead, cadmium, mercury and arsenic. These metals have been extensively studied and their effects on human health regularly reviewed by international bodies such as the WHO. Acute heavy metal intoxications may damage central nervous function, the cardiovascular and gastrointestinal (GI) systems, lungs, kidneys, liver, endocrine glands, and bones. Chronic heavy metal exposure has been implicated in several degenerative diseases of these same systems and may increase the risk of some cancers.

Due to their mobility in aquatic ecosystems and their toxicity to higher life forms, Heavy metals in surface and groundwater supplies have been prioritised as major contaminants in the environment. Even if they are present in dilute, Undetectable quantities, their recalcitrance and consequent persistence in water bodies Imply that through natural processes such as biomagnification, concentrations may become elevated to such an extent that they begin exhibiting toxic characteristics. These metals can either be detected in their elemental state, which implies that they are not subject to further biodegradative processes or bound in various salt complexes. In either instance, metal ions cannot be mineralized. Apart from environmental issues, Technological aspects of metal recovery from industrial waters must also be considered [2].

III. VARIOUS CONVENTIONAL METHODS OF HEAVY METAL REMOVAL

The quality of our environment is deteriorating day by day with the largest cities reaching saturation points and unable to cope with the increasing pressure on their infrastructure. Industrial effluents, sewage and farm wastes are the major pollutants contaminating the environment. Most of the industries discharge wastewater and their effluents containing toxic materials into rivers without adequate treatment. Environmental pollution particularly from heavy metals and minerals in the waste water is the most serious problem in India. Heavy metals are major pollutants in marine, ground, industrial and even treated wastewater. Most of the point sources of heavy metal pollutants are industrial wastewater from mining, metal processing, tanneries, pharmaceuticals, pesticides, organic chemicals, rubber and plastics, lumber and wood products.

The heavy metals are transported by runoff water and contaminate water sources downstream from the industrial site. To avoid health hazards it is essential to remove these toxic heavy metals from waste water before its disposal. Most of the heavy metals discharged into the wastewater are found toxic and carcinogenic and cause a serious threat to the human health. The release of large quantities of hazardous materials into the natural environment has resulted in a number of environmental problems and due to their non-biodegradability and persistence, can accumulate in the environment elements such as food chain, and thus may pose a significant danger to human health and removal of these wastes cannot be achieved using secondary methods. Hence, tertiary/advanced wastewater treatment methods various conventional methods of metal removals are given below [12].

A. Chemical Precipitation

Chemical precipitation processes involve the addition of chemical reagents, followed by the separation of the precipitated solids from the cleaned water. Precipitation of metals is achieved by the addition of coagulants such as alum, lime, iron salts and other organic polymers. Found 80% removal, and Pb, and up to 96.2% removal of oil from industrial wastewaters by using a joint hydroxide precipitation and air floatation system.

TABLE I: Sources and Toxicological Effects of Some Heavy Metals

Heavy Metal	Sources	Effects
Copper	Water pipes; Copper water heaters;; Frozen greens and canned greens using copper to produce an ultra-green color, Alcoholic beverages from copper brewery equipment; Instant gas hot water heaters; Hormone pills; Pesticides. insecticides; fungicides; Copper jewelry; Copper cooking pots	Mental disorders, Anaemia; Arthritis/rheumatoid arthritis; Hypertension, Nausea/vomiting, Hyperactivity, Schizophrenia, Insomnia, Autism, Stuttering, Postpartum psychosis, Inflammation and enlargement of liver, heart problem, Cystic fibrosis.
Chromium	Steel and textile industry	Skin rashes, respiratory problems, haemolysis, acute renal failure, weakened immune systems, kidney and liver damage, alteration of genetic material, lung cancer, Pulmonary fibrosis.
Nickel	Effluents of silver refineries, electroplating, zinc base casting and storage battery industries.	Dermatitis, Myocarditis, Encephalopathy, pulmonary fibrosis, cancer of lungs, nose and bone, headache, dizziness, nausea and vomiting, chest pain, rapid respiration.
Lead	Industries such as mining, steel, automobile, batteries and paints. Pollutants arising from increasing industrialization	Nausea, Encephalopathy, Headache and vomiting, Learning difficulties, Mental retardation, Hyperactivity, Vertigo, kidney damage, Birth defects, Muscle weakness, Anorexia, Cirrhosis of the liver, Thyroid dysfunction, Insomnia, Fatigue, Degeneration of motor neurons, Schizophrenic-like behaviour.
Mercury	Industries like chloro-alkali, paints, pulp and paper, oil refining, rubber processing and fertilizer, batteries, dental fillings adhesives, fabric softeners, drugs, thermometers, fluorescent light tubes and high intensity street lamps, pesticides, cosmetics and pharmaceuticals	Tremors, Birth defects, Kidney damage, Nausea, Loss of hearing or vision, Gingivitis, Chromosome damage, Mental retardation, Tooth loss, Seizures, Cerebral palsy , Blindness and deafness, Hypertonia - muscle rigidity, Minamata disease.

B. Ion Exchange

Ion exchange is a reversible chemical reaction wherein an ion (an atom or Molecule that has lost or gained an electron and thus acquired an electrical charge) from Solution is exchanged for a similarly charged ion attached to an immobile solid particle. These solid ion exchange particles are either naturally occurring inorganic zeolites or synthetically produced organic resins. An organic ion exchange resin is composed of High-molecular- weight polyelectrolytes that can exchange their mobile ions for ions of similar charge from the surrounding medium. Each resin has a distinct number of mobile Ion sites that set the maximum quantity of exchanges per unit of resin. Ion exchange resins are classified as cation exchangers, whom it has positively charged mobile ions available for exchange, and anion exchangers.

C. Reverse Osmosis

In the reverse osmosis process cellophane-like membranes separate purified water from contaminated water. RO is when a pressure is applied to the concentrated side of the membrane forcing purified water into the dilute side, the rejected impurities from the concentrated side being washed away in the reject water. Applications that have been reported for RO processes include the treatment of organic containing wastewater, wastewater from electroplating and metal finishing, pulp and paper, mining and petrochemical, textile, and food processing industries, radioactive wastewater, municipal wastewater, and contaminated groundwater.

D. Electro dialysis

Electro Dialysis (ED) is a membrane process, during which ions are transported through semi permeable membrane, under the influence of an electric potential. The membranes are cation or anion-selective, which basically means that either positive ions or negative ions will flow through. Cation-selective membranes are polyelectrolyte with negatively charged matter, which rejects negatively charged ions and allows positively charged ions to flow through.

E. Ultra Filtration

Ultra filtration is a separation process using membranes with pore sizes in the range of 0.1 to 0.001 micron. Typically, ultra filtration will remove high molecular-weight substances, colloidal materials, and organic and inorganic polymeric molecules. It is a pressure-driven purification process in which water and low molecular weight substances permeate a membrane while particles, colloids, and macromolecules are retained. The primary removal mechanism is size exclusion, although the electrical charge and surface chemistry of the particles or membrane may affect the purification efficiency.

F. Coagulation/ Flocculation

Coagulation and flocculation are an essential part of drinking water treatment as well as wastewater treatment. Coagulation is the chemical reaction which occurs when a chemical or coagulant is added to the water. The coagulant encourages the colloidal material in the water to join together into small aggregates called "flocs". Suspended matter is then attracted to these flocs. Flocculation is a slow gentle mixing of the water to encourage the flocs to form and grow to a size which will easily settle out reviews the basic mechanisms involved in the removal of organic contaminants by coagulation studied the effects of initial pH and turbidity, alum and preozonation doses, and flocculation time on the removal of dis solved organic matter during alum coagulation.

G. Flotation

Flotation is employed to separate solids or dispersed liquids from a liquid phase using bubble attachment [97]. The attached particles are separated from the suspension of heavy metal by the bubble rise. Flotation can be classified as:

- dispersed-air flotation,
- dissolved-air flotation (DAF),
- Vacuum air flotation,
- Electro-flotation and
- Biological flotation.

Among the various types of flotation, DAF is the most commonly used for the treatment of metal-contaminated wastewater [108]. Adsorptive bubble separation employs foaming to separate the metal impurities. The target floated substances are separated from bulk water in a foaming phase.

H. Adsorption

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film. Adsorption is operative in most natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resins and water purification. Among these methods, adsorption is currently considered to be very suitable for wastewater treatment because of its simplicity and cost effectiveness. Adsorption is commonly used technique for the removal of metal ions from various industrial effluents. Activated carbon is the most widely used adsorbent. It is a highly porous, amorphous solid consisting of micro crystallites with a graphite lattice, usually prepared in small pellets or a powder. It can remove a wide variety of toxic metals. Some widely used adsorbents for adsorption of metal ions include activated carbon, clay minerals, biomaterials, industrial solid wastes and zeolites [13].

I. Adsorption Process

Recently, the adsorption process has gained interest as a more promising method for the long term as it is seen to be a more effective and economic approach for heavy metal removal. Adsorption is a fundamental process today due to its flexibility in design and simple operation instead of having to perform adsorptions that are perceived as impractical by most conventional techniques. The term “adsorption” refers as heavy metals. The problems emerge during the a mass transfer process by which a substance is Instead of pH, the adsorbent dose is another factor transferred from the liquid phase to the surface of a solid which influences the adsorption process. Based on and becomes bound by physical and/or chemical assumption, when the adsorbent doses increase, the interactions. The advantages of the adsorption rate also increases. However, the adsorption process in removing or minimizing the heavy metals rate can decrease if the adsorbent dose further increases, even at low concentration enhance the application of due to the presence of more occupied active sites when adsorption as one practical treatment. The concentration gradient of adsorb ate is kept the effectiveness of the adsorption process is mainly constant. Higher adsorption rate can be obtained influenced by the nature of solution in which the once the temperature increases due to the increase of contaminants are dispersed, the molecular size and the surface area and the pore volume of adsorbent. Polarity of the contaminant and also the type of Initial metal concentration can be the driving force to adsorbent used.

Adsorption also exists due to the overcome the mass transfer between the surface of attractive interactions between a surface and the species adsorbent and the solution the initial metal being adsorbed at certain molecular level. Adsorption concentration influences the adsorption rate based on the can be categorized into two; physical adsorption and availability of the specific surface functional groups and chemisorptions. Physical adsorption is a reversible the ability of the surface functional groups to bind metal phenomenon resulting from intermolecular forces of ions (especially at high concentrations). Thus, any attraction between molecules of the adsorbent and the parameters influencing the adsorptive capacity of adsorb ate. Meanwhile, chemisorptions are a result of the adsorbent should be considered during the adsorption chemical interaction between the solid and the adsorbed process. Substance it is an irreversible phenomenon and is also called activated adsorption.

J. Adsorption Mechanism

Adsorption mechanisms are temperature, high physical adsorption occurs at a complicated as no simple theory adequately explains the temperature as close to the critical temperature of a given adsorption of metal ions on the adsorbent surface gas while chemical adsorption occurs at temperatures previous studies have reported on the various models much higher than the critical temperature. Under certain that describe the mechanism between the adsorbate conditions, both processes can occur simultaneously or and the adsorbent the Langmuir model and alternately. Freundlich models are commonly used to describe the Some parameters should be considered during the sorption isotherms while in terms of kinetics, the adsorption process between adsorbent and adsorb ate pseudo first order and pseudo second order kinetic including the physical and chemical characteristics of models can be used to describe the sorption kinetics. The adsorbent and adsorb ate, the concentration of adsorb ate thermodynamics of the metal ion sorption can be in liquid solution, temperature, pH and also contact time explained based on thermodynamic parameters such as. pH is the most important factors than others as pH free energy (G°), enthalpy (H°) and entropy changes controls the distribution of charge on the adsorbent (S°) based on the endothermic and exothermal sorption surface between the adsorption. However, in most processes the limitations of the adsorbent’s pH. PHzpc is the charge.

K. Adsorption Isotherm

Sorption isotherm is used to at the solid surface of adsorbent determined by describe the mechanism of how adsorb ate ions interact on protonation and deprotonation of adsorb ate ions the surface of adsorbent. There are several isotherms the surface charge density of surface depends on the equations available to analyze the experimental sorption specific metal ions which react directly with the adsorbent equilibrium parameters, but the well-known adsorption surface. For instance, when the pH value of solution is isotherm models used for single solute systems are higher than pHzpc, the surface charge of the adsorbent. Both be negatively charged and vice versa. Otherwise, the adsorption isotherm models are found to be more suitable increase of pH within a certain limit can increase the to describe the relationship between q (quantity adsorption rate but further increase in pH can adsorbed at equilibrium, mg/g) and C (concentration of decrease the adsorption rate as certain adsorbateion ions in adsorbates remained in the bulky solution at the a particular range tends to be unaffected by pH. equilibrium, mg/L) [14].

IV. NATURAL ADSORBENT MATERIAL

The greater environmental awareness in both the public and regulatory sphere in recent years has necessitated greater treatment of industrial effluent. As such there has been a great deal of research into finding cost-effective methods for the removal of contaminants from wastewater. In recent years considerable attention has been devoted to the study of removal of heavy metal ions from solution by adsorption using agricultural materials. Natural materials that are available in large quantities or certain waste from agricultural operations may have potential to be used as low cost adsorbents, as they represent unused resources, widely available and are environmentally friendly. Agricultural by-products usually are composed of lignin and cellulose as major constituents and may also include other polar functional groups of lignin, which includes alcohols, aldehydes, ketones, carboxylic, phenolic and ether groups. These groups have the ability to some extent to bind heavy metals by donation of an electron pair from these groups to form complexes with the metal ions in solution.

Several previous studies indicate to removal of heavy metal ions using other agricultural wastes low-cost abundantly available as adsorbents e.g. rice husks and rice straws, tea factory waste and spent leaves tea, fly ash, sawdust, pomegranate husks and peels, peanut husks and shells, tree fern, sunflower leaves, bael leaves, palm kernel husk, corncobs, cotton, sugar cane waste and onion skin, coffee grounds, apple waste, wool fibers, bark, orange peel, Banana peel, dried Withania frutescens plant and other cellulosic material and different agricultural by-products were used and investigated [15, 16].

V. CONCLUSION

Environmental regulations have become more stringent over the past two decades and requiring an improved quality of treated effluent for removing toxic and hazards materials like Lead, Copper, Cadmium and other metal ion to protection of environment, human health and aquatic life. Several processing techniques are available to reduce the concentrations of heavy metals in wastewater, including chemical precipitation, ion exchange, reverse osmosis process, electro dialysis, ultra filtration, coagulation–flocculation, and flotation and adsorption methods. In recent years the adsorption process has been recognized as an effective and economic method for the removal of heavy metals from wastewaters as it offers flexibility in design and operation so as to produce high quality treated effluents of desired standards for disposal. Adsorption is the most cost effective treatment method for removal of heavy metals from waste water by low cost adsorbent like sawdust, rice husk, rice straw, fly ash, bale leaves, spent leaves of green and black tea, banana peel, husk of pomegranate, peanut shell, Tree fern, sunflower leaves…etc. Many parameters such as the initial metal concentration, pH, contact time, particles size, agitation speed and temperature are very important in adsorption process.

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