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Review article

HEAVY METAL CU, NI AND ZN: TOXICITY, HEALTH HAZARDS AND THEIR REMOVAL TECHNIQUES BY LOW COST ADSORBENTS: A SHORT OVERVIEW

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ABSTRACT: Electroplating and metalworking industries discharge large amounts of heavy metals, including copper (Cu), nickel (Ni) and zinc (Zn) ions, in their effluents have been recognized as a major problem to human health and aquatic life. Copper is highly toxic because it is non biodegradable and carcinogenic, Copper has been reported to cause neurotoxicity commonly known as "Wilson's disease" due to deposition of copper in the lenticular nucleus of the brain and kidney failure, Nickel exposure vary from skin irritation to damage of the lungs, nervous system, and mucous membranes and Zinc toxicity from excessive ingestion is uncommon but causes gastrointestinal distress and diarrhea. The current regulation of waste water and drinking water standards are require contamination of heavy metal reduced up to few parts per million. Several processing techniques are available to reduce the concentrations of heavy metals in wastewater, including precipitation, flotation, ion exchange, solvent extraction, adsorption, cementation onto iron, membrane processing, and electrolytic methods. Adsorption onto activated carbon is a well-known method for removing toxic metal ions, but the high cost of activated carbon restricts its use in developing countries, so cheap and effective alternatives for the removal of heavy metals should reduce operating costs, reduce the prices of products, improve competitiveness, and benefit the environment. The adsorption abilities of a number of low-cost adsorbents (e.g., cheap zeolites, clay, coal fly ash, sewage sludge, agriculture waste, tea waste, rice husk, coconut husk, neem leaves and biomass) have been determined for the removal of heavy metals from water.

Key words: Copper, nickel, zinc, toxicology, adsorption and low cost adsorbents like rice husk, tea waste, coconut husk, neem leaves etc.

INTRODUCTION

The term "heavy metal" is collectively applied to a group of metals (and metal-like elements) with density greater than 5 g/cm^3 and atomic number above 20[73]. Removal of heavy metals from industrial wastewater is of primary importance. The use of natural materials for heavy metals removal is becoming a concern in all countries. 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 [2]. Water of high quality is essential to human life and water of acceptable quality is essential for agriculture, industrial, domestic and commercial uses. All these activities are also responsible for polluting the water. Billions of gallons of waste from all these sources are thrown to freshwater bodies every day. The requirement for water is increasing while slowly all the water resources are becoming unfit for use due to improper waste disposal. The task of providing proper treatment facility for all polluting 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 adsorption technique is economically favourable and technically easy to separate as the requirement of the control system is minimum. In this article, the technical feasibility of various low-cost adsorbents for heavy metal removal from contaminated water has been reviewed [75].

Heavy metals have been excessively released into the environment due to rapid industrialization and have created a major global concern. Cadmium, zinc, copper, nickel, lead, mercury and chromium are often detected in industrial wastewaters, which originate from metal plating, mining activities, smelting, battery manufacture, tanneries, petroleum refining, paint manufacture, pesticides, pigment manufacture, printing and photographic industries, etc[96]. Adsorption is one the physico-chemical treatment processes found to be effective in removing heavy metals from aqueous solutions. Adsorbent can be considered as cheap or low-cost if it is abundant in nature, requires little processing and is a by product of waste material from waste industry. Plant wastes are inexpensive as they have no or very low economic value [17]. Adsorption studies mostly focused on untreated plant wastes such as grape stalk wastes [54], Neem bark, rice husk ash [51], pellets of peanut hull [102]. Sago waste [98], Imperata cylindrical leaf [109], papaya wood [37], Moringa oleifera pods [4], tea waste [42[. etc. Industries carries out operations like electroplating, metal/surface finishing and solid-state wafer processing, generate wastewater contaminated with hazardous heavy metals. The concentrations of some of the toxic metals like Cu, Ni, and Zn etc. are higher than permissible discharge levels in these effluents. It, therefore, becomes necessary to remove these heavy metals from these wastewaters by an appropriate treatment before releasing them into the environment [58].

Toxicity of Heavy metals:

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 [102].

Human Health & Hazards:

The heavy metals hazardous to humans include Copper, Zinc, Nickel, Lead, Mercury, Cadmium, Arsenic, and Chromium. Such metals are found naturally in the soil in trace Amounts, which pose few problems. When concentrated in particular areas, however, they present a serious danger. Arsenic and cadmium, for instance, can cause cancer. Mercury can cause mutations and genetic damage, while copper, nickel, and zinc can cause brain and bone damage [83].

Toxic effect on aquatic organisms:

Aquatic organisms are adversely affected by heavy metals in the environment. The toxicity is largely a function of the water chemistry and sediment composition in the surface water system [93]. The metals are mineralised by microorganisms, which in turn are taken up by plankton and further by the aquatic organisms. Finally, the metals by now, several times biomagnified is taken up by man when he consumes fish from the contaminated water.

i.) Slightly elevated metal levels in natural waters may cause the following sublethal effects in aquatic organisms: histological or morphological change in tissues;

ii.) Changes in physiology, such as suppression of growth and development, poor swimming performance, changes in circulation;

iii.) Change in biochemistry, such as enzyme activity and blood chemistry;

iv.) Change in behaviour; and

v.) Changes in reproduction [28].

Source of waste heavy metals

Industrial wastewater streams containing heavy metals are produced from different industries. 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 [27].

These include electroplating, electro less depositions, conversion-coating, anodizing-cleaning, milling, and etching. Another significant source of heavy metals wastes result from printed circuit board (PCB) manufacturing. Tin, lead, and nickel solder plates are the most widely used resistant over plates. Other sources for the metal wastes include; the wood processing industry where a chromate copper-arsenate wood treatment produces arsenic containing wastes; inorganic pigment manufacturing producing pigments that contain chromium compounds and cadmium sulfide; petroleum refining which generates conversion catalysts contaminated with nickel, vanadium, and chromium; and photographic operations producing film with high concentrations of silver and ferrocyanide. All of these generators produce a large quantity of wastewaters, residues, and sludge's that can be categorized as hazardous wastes requiring extensive waste treatment [72].

Table1: General Distribution of Heavy metals in Particular Industrial Effluents

Industries	Cu	Ni	Zn
General Industry and Mining	X		X
Plating	X	X	X
Paint Products			
Fertilizers	X	X	X
Insecticides / Pesticides	X		
Tanning			
Paper Products	X	X	X
Photographic			
Fibers	X		X
Printing / Dyeing			
Electronics			
Cooling Water			
Pipe Corrosion	X		

Source: Alves M. M et al 1993; [10].

Copper: Electroplating and metalworking industries discharge large amounts of heavy metals, including copper (Cu) and nickel (Ni) ions, in their effluents [87]. Environmental contamination due to copper is caused by mining, printed circuits, metallurgical, fibre production, pipe corrosion and metal plating industries [20]. The other major industries discharging copper in their effluents are paper and pulp, petroleum refining and wood preserving. Agricultural sources such as fertilizers, fungicidal sprays and animal wastes also lead to water pollution due to copper. Copper may be found as a contaminant in food, especially shell fish, liver, mushrooms, nuts and chocolates. Any packaging container using copper material may contaminate the product such as food, water and drink [69]. Copper has been reported to cause neurotoxicity commonly known as "Wilson's disease" due to deposition of copper in the lenticular nucleus of the brain and kidney failure [18]. In some instances, exposure to copper has resulted in jaundice and enlarged liver. It is suspected to be responsible for one form of metal fume fever [94]. Copper-containing sprays are linked to an increase in lung cancer among exposed workers [68].

Zinc: Zinc is the 23rd most abundant element in the Earth's crust and its concentrations are rising unnaturally, due to addition of zinc through human activities [65]. Zinc is a lustrous bluish-white metal and found in group IIB of the periodic table. It is brittle and crystalline at ordinary temperatures, but it becomes ductile and malleable when heated between 110°C and 150°C. It is a fairly reactive metal that will combine with oxygen and other non-metals, and will react with dilute acids to release hydrogen. Most zinc is added during industrial activities, such as mining, coal and waste combustion and steel processing [73]. Zinc is widely used in industries such as galvanization, paint, batteries, smelting, fertilizers and pesticides, fossil fuel combustion, pigment, polymer stabilizers, etc, and the wastewater from these industries is polluted with zinc, due to its presence in large quantities [34]. Electroplating is one important process involved in surface finishing and metal deposition for better life of articles and for decoration. Although several metals can be used for electroplating, nickel, copper, zinc and chromium are the most commonly used metals, the choice depending upon the specific requirement of the articles. During washing of the electroplating tanks, considerable amounts of the metal ions find their way into the effluent [8]. When it is present in less quantity in human's body, it affects considerably human's health. Although humans can handle large extent of zinc, too much of it can still cause eminent health problems [43].

Nickel: Nickel is generally considered to be one of the most toxic metal found in environment, ones its enter in the food chain progressively larger accumulation of nickel compounds takes place in humans and animals. Ni (II) is present in the effluents of silver refineries, electroplating, zinc base casting and storage battery industries [58]. Higher concentration of nickel causes cancer of lungs, nose and bone. Dermatitis (Ni itch) is the most frequent effect of exposure to Ni, such as coins and jewellery. Acute poisoning of Ni (II) causes headache, dizziness, nausea and vomiting, chest pain, tightness of the chest, dry cough and shortness of breath, rapid respiration, cyanosis and extreme weakness [29].

Table2: The Maximum Contamination Limit (MCL) standards

Heavy metal	Atomic Number	Toxicities	MCL(mg/l)
Arsenic	33	Skin manifestations, visceral cancers, vascular disease	0.050
Cadmium	48	Kidney damage, renal disorder, human carcinogen	0.01
Chromium	24	Headache, diarrhea, nausea, vomiting, carcinogenic	0.05
Copper	29	Liver damage, Wilson disease, insomnia	0.25
Nickel	28	Dermatitis, nausea, chronic asthma, coughing, human carcinogen	0.20
Zink	38	Depression, lethargy, neurological signs and increased thirst	0.80
Lead	82	Damage the fetal brain, diseases of the kidneys, circulatory system, and nervous system	0.006
Mercury	80	Rheumatoid arthritis and diseases of the kidneys, circulatory system.	0.0003

Source: established by USEPA and web link: www.periodictable.com [88, 103]

Need for the removal of heavy metals: Continuous discharge of industrial, domestic and agricultural wastes in rivers and Lakes causes deposit of pollutants in sediments. Such pollutants include heavy metals, which endanger public health after being incorporated in food chain. Heavy metals cannot be destroyed through biological degradation, as is the case with most organic Pollutants. Incidence of heavy metal accumulation in fish, oysters, mussels, sediments and other components of aquatic ecosystems have been reported from all over the World [80]. Excessive amounts of some heavy metals can be toxic through direct action of the metal or through their inorganic salts or via organic compounds from which the metal can become easily detached or introduced into the cell. Exposure to different metals may occur in common circumstances, particularly in industrial setting. Accidents in some environments can result in acute, high level exposure. Some of the heavy metals are toxic to aquatic organisms even at low concentration. The problem of heavy metal Pollution in water and aquatic organisms including fish, needs continuous monitoring and surveillance as these elements do not degrade and tend to biomagnified in man through food chain. Hence there is a need to remove the heavy metals from then Aquatic ecosystems [61]. Research and development, therefore focuses on sector-specific methods and Technologies to remove colour and heavy metals from different kinds of waste Streams. In view of the above toxicological effects of heavy metals on environment, Animals and human beings, it becomes imperative to treat these toxic compounds in Wastewater effluents before they are discharged into freshwater bodies [42].

Treatment methods for removal of heavy metals: several methods have been devised for the treatment and removal of heavy metals, the commonly used procedures for removing metal ions from aqueous streams include chemical precipitation, lime, coagulation, ion exchange, reverse osmosis and solvent extraction [5].

Chemical precipitation: Chemical precipitation is the most widely used for heavy metal removal from inorganic effluent. The conceptual mechanism of heavy metal removal by chemical precipitation is presented in Equation [19].

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

Precipitation of metals is achieved by the addition of coagulants such as alum, lime, iron salts and other organic polymers. The large amount of sludge containing toxic compounds produced during the process is the main disadvantage [5]. Lime precipitation can be employed to effectively treat inorganic effluent with a metal concentration of higher than 1000 mg/L. Other advantages of using lime precipitation include the simplicity of the process, inexpensive equipment requirement, and convenient and safe operations. However, chemical precipitation requires a large amount of chemicals to reduce metals to an acceptable level for discharge. Other drawbacks are its excessive sludge production that requires further treatment, slow metal precipitation, poor settling, the aggregation of metal precipitates, and the long-term environmental impacts of sludge disposal [19]. In spite of its advantages, chemical precipitation requires a large amount of chemicals to reduce metals to an acceptable level for discharge [40]. Other drawbacks are its excessive sludge production that requires further treatment, the increasing cost of sludge disposal, slow metal precipitation, poor settling, the aggregation of metal precipitates, and the long-term environmental impacts of sludge disposal [22].

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. Most of the resins Used are synthetic because their characteristics can be tailored to specific applications. Synthetic resin made by polymerization of organic compounds in a porous threedimensional Structure. Ion exchange resins are classified as cation exchangers, whom it has positively charged mobile ions available for exchange, and anion exchangers [107]. Both anion and cation resins are produced from the same basic organic polymers. They differ in the ionizable group Attached to the hydrocarbon network. It is this functional group that determines the Chemical behaviour of the resin. Resins can be broadly classified as strong or weak acid Cation exchangers or strong or weak base anion exchangers [69].

Ion exchange is another method used successfully in the industry for the removal of heavy metals from effluent. Commonly used matrices for ion exchange are synthetic organic ion exchange resins. The disadvantage of this method is that it cannot handle concentrated metal solution as the matrix gets easily fouled by organics and other solids in the wastewater. Moreover ion exchange is nonselective and is highly sensitive to the pH of the solution. Electrolytic recovery or electro-winning is one of the many technologies used to remove metals from process water streams. This process uses electricity to pass a current through an aqueous metal-bearing solution containing a cathode plate and an insoluble anode. Positively charged metallic ions cling to the negatively charged cathodes leaving behind a metal deposit that is strippable and recoverable. A noticeable disadvantage was that corrosion could become a significant limiting factor, where electrodes would frequently have to be replaced [44].

Electro dialysis: Electro dialysis (ED) is a membrane separation in which ionized species in the solution are passed through an ion exchange membrane by applying an electric potential. The membranes are thin sheets of plastic materials with either anionic or cationic characteristics. When a solution containing ionic species passes through the cell compartments, the anions migrate toward the anode and the cations toward the cathode, crossing the anion exchange and cation exchange membranes [25]. The disadvantage is the formation of metal hydroxides, which clog the membrane. In the elecrodialysis process, ionic components of a solution are separated Through the use of semipermeable ion-selective membranes. This process may be operated in either a continuous or a batch mode. Problems associated with the Electro dialysis process for wastewater renovation include chemical precipitation of Salts with low solubility on the membrane surface. To reduce the membrane fouling, Activated carbon pre-treatment, possibly preceded by chemical precipitation and some Form of multimedia filtration may be necessary [50].

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 on the size of the particle that can be retained, various types of membrane filtration such as ultra filtration, nano filtration and reverse osmosis can be employed for heavy metal removal from wastewater. Unique specialties enable UF 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 [91]. The main disadvantage of this process is the generation of sludge [106].

Reverse osmosis process: The reverse osmosis process depends upon a semi-permeable membrane through which pressurized water is forced. Reverse osmosis, simply stated, is the opposite of the Natural osmosis process of water. Osmosis is the name for the tendency of water to Migrate from a weaker saline solution to a stronger saline solution, gradually equalizing the saline composition of each solution when a semi-permeable membrane separates the two solutions. In reverse osmosis, water is forced to move from a stronger saline Solution to a weaker solution, again through a semi-permeable membrane. Because Molecules of salt are physically larger than water molecules, the membrane blocks the Passage of salt particles. The end result is desalinated water on one side of the membrane and a highly concentrated, saline solution of water on the other side [19]. The disadvantage of this method is that it is expensive [5].

Ultra filtration: - Ultra filtration technologies can be used in a variety of ways in wastewater treatment and water reuse systems. Ultra filtration can reduce the amount of treatment chemicals, has smaller space requirements, and reduce labor requirements. On the contrary in this method uses more electricity, may need pre-treatment, and requires replacement of membranes [30].

Coagulation–Flocculation:- Coagulation–flocculation can be employed to treat wastewater laden with heavy metals. Principally, the coagulation process destabilizes colloidal particles by adding a coagulant and results in sedimentation [82]. To increase the particle size, coagulation is followed by the flocculation of the unstable particles into bulky floccules [81, 14]. The general approach for this technique includes pH adjustment and involves the addition of ferric/alum salts as the coagulant to overcome the repulsive forces between particles [46]. In spite of its advantages, coagulation–flocculation has limitations such as high operational cost due to chemical consumption. The increased volume of sludge generated from coagulation–flocculation may hinder its adoption as a global strategy for wastewater treatment. This can be attributed to the fact that the toxic sludge must be converted into a stabilized product to prevent heavy metals from leaking into the environment [15]. To overcome such problems, electro-coagulation may be a better alternative than the conventional coagulation, as it can remove the smallest colloidal particles and produce just a small amount of sludge [67]. However, this technique also creates a flock of metallic hydroxides, which requires further purification, making the recovery of valuable heavy metals impossible [70].

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:

(i) dispersed-air flotation, (ii) dissolved-air flotation (DAF), (iii) Vacuum air flotation, (iv)Electro-flotation and
(v) 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.

Although it is only a kind of physical separation process, heavy metal removal by flotation has the potential for industrial application [39]. Low cost materials such as zeolite and chabazite have been found to be effective collectors with removal efficiency of higher than 95% for an initial metal concentration ranging from 60 to 500 mg/L. Flotation can be employed to treat inorganic effluent with a metal concentration of less than 50 mg/L or higher than 150 mg/L. other advantages such as a better removal of small particles, shorter hydraulic retention times and low cost make flotation one of the most promising alternatives for the treatment of metal-contaminated wastewater [55].

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 (adsorbate). It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution. The term Sorption encompasses both processes, while desorption is the reverse process [56]. 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. Similar to surface tension, adsorption is a consequence of surface energy. In a bulk material, all the Bonding requirements (be they ionic, covalent or metallic) of the constituent atoms of the Material are filled. But atoms on the (clean) surface experience a bond deficiency, because they are not wholly surrounded by other atoms. Thus it is energetically favorable for them to bond with whatever happens to be available. 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 [36].

Types of adsorption:

At molecular level, adsorption is due to attractive interactions between a surface and the species being adsorbed.

- Physical adsorption: It is a result of intermolecular forces of attraction between molecules of the adsorbent and the adsorbate. In this case the molecular attractive forces that retain the adsorbent on the surface are purely physical are called Vander Walls forces. This is a readily reversible phenomenon. The energy of interaction between the adsorbate and adsorbent has the same order of magnitudes as, but is usually greater than the energy of condensation of the adsorptive. Therefore, no activation energy is needed.
- Chemical adsorption: It is a result of chemical interaction between the solid and the adsorbed substance. It is also called activated adsorption. It is irreversible. It is particularly important in catalysis. Therefore, the energy of chemisorptions considered like chemical reaction. It may be exothermic or endothermic processes ranging from very small to very large magnitudes. The elementary step in chemisoption often involves large activation energy (Activated adsorption) [79].

Low cost Adsorbents: There is increasing research interest in using alternative low-cost adsorbents. Many such materials have been investigated, including microbial biomass, peat, compost, leaf mould, palm press fiber, coal, sugarcane bagasse, straw, wool fiber and by products of rice mill, soybean and cottonseed hulls etc. [51]. The low cost agricultural waste by-products such as sugarcane bagasse [60], rice husk [84], sawdust [6], coconut husk [85]. oil palm shell [43], neem bark [15]etc., for the elimination of heavy metals from wastewater have been investigated by various researchers. Tea waste is most cost-effective adsorbent because it is available easily and it has more adsorption capacity to other natural adsorbents, Tea waste biomass can serve as a good and cheap substitute for conventional carbon- based adsorbents [47], Moringa oleifera (Drum sticks) seeds are a low cost adsorbent [4].

Source of adsorbents: In India, yearly production of tea is approximately 857000 tonnes which is 27.4% of total world production [11]. The amount of dry tea produced from 100 kg green tea leaves is 22 kg on average and approximately 18 kg tea is packed for the market. The other 4 kg of dry tea material is wasted and 18 kg tea is also wasted after using that i.e. tea waste is easily available [23]. Moringa oleifera (Drum sticks) seeds are also available easily in rural areas of India and South Africa [31].

Preparation of adsorbents

Tea waste: simple procedure to prepare the adsorbent, firstly teawaste washed and then rins with distilled water [47]. After drying in 100°C, it was ground and screened (using screen with mesh size 10). Prior to the experiments, Malkoc and Nuhoglu[50], removed other soluble dirtiness and colored components from the T.W. by washing with distilled water for much times until a colorless solution of tea waste was spectrometrically observed at room temperature. Decolorized and cleaned tea waste was dried at room temperature for a few days by spreading on gauze. Black tea produced from tea plantations from central highlands of Sri Lanka "high grown tea" was used for the experiments, Soluble and colored components were removed from tea by washing with boiling water. This was repeated until the water was virtually color less. The tea leaves were then washed with distilled water and were oven dried for 12 h at 85°C. The dried tea waste was sieved and stored in sealed polythene bags [11].

Drumstics: - After sourcing, the seeds were removed from the fruit (called drumsticks) then the seeds and pods were dried separately for about 2 weeks. When satisfactorily dried, the pods were grounded to powder using a mechanical grinder.

The method of treatment of the drumstic 80g of the biosorbent was treated with 1600ml, 0.1M HNO_3 with continuous stirring for 2 hours to remove metals from the biosorbent and increase its surface area. Then it was washed with 500ml distilled water, this was done in thrice then the sample was then sundried for about 6 hours. After the acid treatment, the adsorbent (about 50g) was extracted with 400ml methanol to remove inorganic and organic matter from the sorbent surface. This was carried out for 2 hours 30 minutes. The adsorbent pH was adjusted to 7 using 0.1M NaOH, washed with distilled water, oven – dried for about 1 hour, kept in an air – tight plastic container and put in a refrigerator at 4°C prior the analysis[62].

Rice husk- rice husk is agricultural waste mostly available in rural areas, collected their and grinding in grinders than sieved & washed with distilled water repeatly for dirt and other particulate matter removal, then dryied in hot oven at 100°C for 24 hours, then either directly used as an adsorbent or treated with H_2SO_4 and then washed again with distilled water for removing acidity, washing upto totally acidity are removed and then dried at 100°C for 12 hours then collected in air tight plastic bags and then used as an adsorbent [6].

Coconut husk- coconut easily available in all temple and religious places, collected them dried in hot oven at 80°C for 4 hours and then grinds in grinder in the powder form then sieved 120 mm sizes than washing with distilled water for dirt and other particulate matter removing, then again dried at 100°C for 24 hours then used as an adsorbent [1].

Neem leaves- The Neem belongs to the meliaceae family and is native to Indian sub-continent. Its seeds and leaves have been in use since ancient times to treat a number of human ailments and also as a household pesticide. The trees are also known as an air purifier. The medicinal and germicidal properties of the neem tree have been put to use in a variety of applications. The mature Neem leaves used in the present investigation were collected from the trees in nearby area. Neem leaves were washed thrice with water to remove dust and water soluble impurities and then dried until the leaves become crisp. The dried leaves were powdered. The powdered neem leaves were used as adsorbent. The parameters which affect wastewater treatment, such as heavy metal concentration and adsorbent dosage were investigated in batch-mode adsorption studies [15].

Various factors affecting adsorption capacity:

pH: For adsorption of heavy metal ions, ph is one of the most important environmental factors [95]. The Ph value of solution strongly influences not only the site dissociation of the biomass' surface, but also the solution chemistry of the heavy metals: hydrolysis, complexation by organic and/or Inorganic ligands, redox reactions, precipitation, the speciation and the adsorption availability of the heavy metals [38]. The adsorptive capacity of metal cations increases with increasing ph of the Sorption system, but not in a linear relationship. The percentage adsorption increases with pH to attain a maximum at pH 6 and thereafter it decreases with further increase in pH. The maximum removals of Cu (II), Zn (II) and Ni (II) at pH 6 were found to be nearly 88.8, 93.3 and 69%, respectively [58]. The maximum adsorption at pH 6 may be attributed to the partial hydrolysis of M^+, resulting in the formation of MOH^+ and M $(OH)_2$. M $(OH)_2$ would be adsorbed to a greater extend on the non-polar adsorbent surface compare to MOH^+. With increase of pH from 2 to 6, the metal exists as $M(OH)_2$ in the medium and surface protonation of adsorbent is minimum, leading to the enhancement of metal adsorption. At higher pH, that is, above optimum pH of 6, increase in OH− ions cause a decrease in adsorption of metal ions at adsorbent–adsorbate interface [41].

Temperature: Temperature has also an influence on the adsorption of metal ions, but to a limited extent under a certain range of temperature, which indicates that ion exchange mechanism exists in adsorption to some extent [32]. Adsorption process is usually not operated at high temperature because it will Increase the operational cost. It found that temperature (5–40°C) had Minor effect on the accumulation level of Cu^{2+}, Co^{2+} or Cd^{2+} by surface of wood ash in Suspension [96]. Adsorption reactions are normally exothermic, so adsorption capacity increases with Decrease of temperature. In the range of 15– 40°C, the maximum equilibrium adsorption capacity for Pb (II), Ni(II), Co(II) and Cr(VI) ions by the wood ash was reached at temperature of 25 °c. The decrease in capacity at higher temperature between 25 and 40 °C revealed that the Processes of adsorption for these metal ions by ash are exothermic. The decrease of adsorption Capacity at higher temperature may be due to the damage of active binding sites in the biomass [6].

Contact time: The adsorption process of heavy metal by wood ash usually completes rapidly for all metals. The adsorption of Metals such as copper, zinc, and nickel by wood ash is a rapid process and often reaches equilibrium within several hours [60]. The adsorbed amount of single and binary metal ions increases from 30 to 60 min time, after that a maximum removal is reached. Therefore, they selected 60 min as a suitable contact time for both metal ions in single and binary systems [23]. Studied the effect of contact time on the adsorption of Zn onto tea floor waste (TFW), Initially the removal was very rapid in first 25 minutes, then adsorption rate gradually decreases and removal reaches equilibrium in around 30 minutes. The time required to reach equilibrium was dependent on initial concentration of zinc. For the same concentration the percentage removal of zinc increases with increase in contact time till equilibrium attained in 30 minutes [100]. It is observed that in all cases the percentage removal is comparatively lower for 24 h contact time, with increasing removal efficiencies at higher contact time. In case of Ni(II) and Cd(II) ions rise sharp rise in percentage removal with increasing contact time. On other hand, percentage removal of Mn(II), Zn(II) and Cu (II) increases gradually with contact time, reaching nearly 100% removal only at around 72 h. It is evident from the results that the contact time required to attain equilibrium is dependent on the initial concentration of heavy metals. For the same concentration, the percentage removal of heavy metal increases with increase of contact time till equilibrium is attained. The optimal contact time to attain equilibrium with carbon aerogel was experimentally found to be about 48 h [58]. The effects of the contact time on the amount of Cu2+ and Ni2+ adsorbed per unit of adsorbent at three different temperatures (30, 45, and 60 .C). For Cu2+ and Ni2+, a gradual increase in adsorption occurred upon increasing the contact timeup to 120, 240 min, at which point the maximum values of adsorption were attained. Extending the contact time further had an insignificant effect on the amounts of the heavy metals adsorbed. For this reason, I used a contact time of 240 min as the optimum value in our subsequent experiments [87].

Effect of Adsorbent Dosage: in case of Cu (II) and Zn (II) ions, there is slight and gradual increase in percentage removal with increasing dose. It is apparent that the percent removal of heavy metals increases rapidly with increase in the dose of the adsorbents due to the greater availability of the exchangeable sites or surface area. Moreover, the percentage of metal ion adsorption on adsorbent is determined by the adsorption capacity of the adsorbent for various metal ions. It is observed that there is a sharp increase in percentage removal with adsorbent dose for Ni (II) ions. [58]

Effect of initial concentration of metal: The initial concentration provides an important driving force to overcome all mass transfer resistance of metal between the aqueous and solid phases [66]. An increase of the initial Ni (II) concentration from 50 to 200 mg/L, when other experimental conditions are kept constant, the corresponding adsorption bed capacity appears to increase from 7.31 to 11.17 mg/g [48, 49]. Higher initial nickel concentrations caused a faster breakthrough. A decreased inlet nickel (II) concentrations gave delayed breakthrough curves and the treated volume was also higher, since the lower concentration gradient caused slower transport due to decreased diffusion coefficient [7].At the highest Ni (II) concentration (200 mg/L) the waste tea bed saturated quickly leading to earlier breakthrough and exhaustion time. Highest uptake and low total Ni (II) removal are obtained at the highest Ni (II) concentration. Also more positive and steep breakthrough curve was obtained for 200 mg/L Ni (II). The driving force for biosorption is the concentration difference between the metal on the waste tea and the metal ion in the solution [3], removal of Zn (II) for various initial concentrations (25-200 mg/lit) of zinc by TFW (0.2 g/50 cm3) at different contact times. The percent adsorption was decreased with increase in initial concentration but actual amount of Zn (II) adsorbed per unit mass of adsorbent (TFW) increased with increase in initial concentration in test solution. This was because of the decrease in resistance for the uptake of solute from solution with increase in metal concentration [100, 99].

Effect of agitation rate: The adsorption studies with a magnetic shaker at pH 4.0 and initial nickel (II) concentration of 100 mg/L. The agitation speed varied from 3.0 to 8.0 rps (180, 360, 480 rpm). As agitating rate increased from 3.0 to 8.0 rps, adsorption capacity of low cost adsorbents increased from 7.89 to 8.59 mg/g. The adsorption removal efficiency increased weakly with increasing agitation rate because an agitation rate of 150 rpm was enough to remove nickel. When the agitation speed was increased from 180 to 480 rpm, the removal of nickel (II) ion increased from 78.9% to 85.9% [66]. Similarly increases in case of Cu (II) and Zn (II) ions up to 78% to 93% [87].

Evaluation of heavy metals removal processes: In general, physico-chemical treatments offer various advantages such as their rapid process, ease of operation and control, flexibility to change of temperature. There are numerous methods currently employed to remove and recover the metals from our environment and many physico-chemical methods have been proposed for their removal from wastewater [77]. These include chemical oxidation and reduction, membrane separation, liquid extraction, carbon adsorption, ion exchange, electrolytic treatment, electro precipitation, coagulation, flotation, evaporation, hydroxide and sulfide precipitation, crystallization, ultra filtration, electro dialysis etc. [52]. These methods differ in their effectiveness and cost. Chemical precipitation, reverse osmosis and other methods (ultra filtration, electrochemical deposition etc.) become inefficient when contaminants are present in trace concentration [63]. And do not seem to be economically feasible for such industries because of their relative high costs [71]. Therefore, there is a need to look into alternatives to investigate a low-cost method which is effective and economic. For high strength and low volumes of wastewater, heavy metal removal by adsorption technique is good proposition. Adsorption is one of the alternatives for such cases [35]. and is an effective purification and separation technique used in industry especially in water and wastewater treatments [9]. It is the tendency of molecules from an ambient fluid phase to adhere to the surface of a solid. Adsorption has advantages over other methods. The design is simple, and it is sludge-free and can involve low investment in terms of both the initial costs and land. Cost is an important parameter for comparing the adsorbent materials [67]. Activated carbon has been recognized as a highly effective adsorbent for the treatment of heavy metals in wastewater, but is readily soluble under extreme pH conditions [21]. Activated carbon is most widely used adsorbent, as it has good capacity for adsorption of carcinogenic metals. However, high cost of activated carbon and 10-15% loss during the regeneration has deterrents in the utilization of activated carbon but is replaced low cost adsorbent for the developing countries [26].

Table-3: The main advantages and disadvantages of the various physico-chemical methods for treatment of heavy metal in wastewater.

S.No.	Treatment method	Advantages	Disadvantages	References
1	Chemical precipitation	Low capital cost, simple operation	Sludge generation, extra operational cost for sludge disposal	[44]
2	Adsorption with new adsorbents	Low-cost, easy operating conditions, having wide pH range, high metal-binding capacities	Low selectivity, production of waste products	[45]
3	Membrane filtration	Small space requirement, low pressure, high separation selectivity	High operational cost due to membrane fouling	[44]
4	Electrodialysis	High separation selectivity	High operational cost due to membrane fouling and energy consumptio	[59]

CONCLUSION

Over the past two decades, environmental regulations have become more stringent, requiring an improved quality of treated effluent for removing toxic and hazards materials like Copper, Nickel Zinc and other metal ion to protection of environment, human health and aquatic life. In recent years, a wide range of treatment technologies such as chemical precipitation, adsorption, membrane filtration, and electro dialysis, have been developed for heavy metal removal from contaminated wastewater. Although many 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 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 system 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. It is evident from the literature survey. Adsorption is the most cost effective treatment method for removal of heavy metals from waste water by low cost adsorbent like tea waste, rice husk, coconut husk, drum stick, seeds powder, neem leaves etc.

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