



## Analysis and interpretation of heavy metal in reference to cost-effective adsorbents

M JudeJenita<sup>1</sup>, H Anandalakshmi<sup>2\*</sup>

<sup>1</sup> Department of Chemistry, Government College of Engineering, Bodinayakannur, Theni, Tamil Nadu, India

<sup>2</sup> Chemistry Section, FEAT, Annamalai University, Annamalainagar, Tamil Nadu, India

### Abstract

In emerging countries, heavy metal contamination is becoming more of a problem. Metal accumulation in fresh water sources has increased in emergent nations as a result of sewage water treatment, as well as increasing industrial production. This article gives an overview on various types of heavy metal pollution and elaborates on the same. It also includes data on the specific amount of pollution emitted by each heavy metal genre. Filtrations using membrane, adsorption using activated carbon, and electro-coagulation are widespread practice for removal of heavy metals from water, although they are ineffective in emerging countries. As a result, there has been much study done to determine efficacy of adsorbents with minimal fare in getting rid of these accumulated metals. The condition of heavy metal research right now on negative consequences in the human body, as well as heavy metal removal, is discussed, with a focus on cost-effective adsorbents that are viable in developing countries. It also takes into account the utilization of adsorbents derived from two major sources: agricultural waste deposits and other readily available waste materials. This article provides an overview of how these adsorbents are used in heavy metal removal, as well as information on how heavy metals and these adsorbents are influenced by different water quality circumstances. The use of agricultural goods and by-products as an alternative for present expensive ways of eliminating heavy metals from water and wastewater has received a lot of attention. Agricultural products can be utilized as low-cost sorbents in some cases. Agricultural by-products could be tweaked to improve their natural capabilities and increase their worth. The adsorption processes for heavy metal removal that have been proposed are also investigated. This article compiles a comprehensive list of adsorbents to furnish a quick overview of information on a variety of cost-effective agricultural commodities and deductible sorbents, as well as their modification for heavy metal removal from sewage water.

**Keywords:** Human exposure, toxicity, genotoxicity, carcinogenicity Green products, sorbent, cost-effective, heavy metals, sewage water

### Introduction

Heavy metals are toxic metals that have a high density, specific gravity or atomic weight. They are commonly prevalent in the earth's crustal plane, but their geochemical as well as biochemical equilibrium has been significantly altered as a result of indiscriminate human activity, and they have made their way into our drinking water supply. Some vital heavy metals, such as cobalt, copper, zinc, and manganese, are required in tiny amounts by the human body, but in excess, they can be harmful to your health. Lead, mercury, arsenic, and cadmium, among other heavy metals found in drinking water, have no good benefits on your body. In fact, its accumulation inside the body might lead to serious health issues <sup>[1]</sup>. These metals accumulate inside the body since the human body is unable to eliminate them. It has little immediate effect on the body, but it can lead to substantial long-term health problems, the majority of which are brain-related. It has the potential to wreak havoc on the brain and central nervous system <sup>[2]</sup>. Other vital organs such as the lungs, liver, and kidneys are also impacted. Carcinogens are chemicals that have the potential to cause cancer. Heavy metals are one such type. Heavy metal has polluted and poisoned water due to a variety of natural and artificial sources. Through bio magnifications, it causes harm to humans and aquatic life. However, for the vast majority of people in impoverished countries, drinking of heavy metal contaminated water is the most common cause of illness. Metals detected in recent years as a result

of activity in the manufacturing and urban areas have risen in the emerging world, contributing to an increase in heavy metal pollution. The Minamata disaster, caused by mercury poisoning, and Japan's "Itai-Itai" illness, caused by cadmium poisoning, are the common cause of contamination in heavy metal. Metals may be eminent from other dangerous contaminants and become concentrated throughout the food chain because they are perdurable and can survive in biological tissues.

Heavy metals are released into the environment by a variety of industries through their effluent such as production of iron and steel, as well as non-iron metals, mining and mineral processing, and pigment production are among them <sup>[2]</sup>.

Metal pollution is also a problem, as many of the potable water processing technologies adopted in emerging countries, such as chlorinating, disinfecting water by heat and sunlight, are unsuccessful in getting rid of heavy metals. As a result, heavy metal must be cleaned using different techniques for the sake of humanity.

### Sources of Pollution of Heavy Metals in Surface water Familiar origin

Extreme stages of heavy metals can occur in nature due to physical conditions such as rock withstanding, volcanic eruptions, and leaching out into rivers, lakes, and surface water due to water stroke <sup>[3]</sup>. Mining industry produces both direct and indirect waste into the water all over the world.

### Sources of anthropogenic pollution

During mining and wildfires, trace amounts of heavy metals are emitted, resulting in enormous masses of metal, ores, and open flames. Heavy metals spilled into the water as a result of the industrial revolution, as they were mined from natural sources and processed in industry. Traces of heavy metals are also let into the environment by waste releases, like household, agricultural, and automobile drains<sup>[4]</sup>. Some of the common human activities like Smelting or processing metal ores, exploration and mining, the combustion of petroleum-based products and fossil fuels, Disposal of production waste, Disposing of household garbage, Auto exhausts dumping, and the use of insecticides may also result in heavy metal entering the water there by polluting the environment.

### Mining activities

Heavy metals are prevalent in the earth's background information and, as a result, end up in water sources by means of natural processes. Heavy rains or flowing water, for example, might leach heavy metals from the physical background, contaminating mining activity.

### Electronic waste

Industrial corporations must offer disposal instructions for their products in their user guide book by law. Heavy metals, harmful compounds, and carcinogens have been discovered as a key source of heavy metals, dangerous compounds, and carcinogens in diseases associated to the intestinal, immunological, skin, respiratory, and endocrine CNS, as well as tumors including E-waste. By properly managing and removing E-waste, diseases associated to the intestinal, immunological, skin, respiratory, and endocrine CNS, as well as cancers can be avoided.

### Heavy Metals Toxicity and the Environment

Each year, over 300,000 persons are expected to be exposed to chromium and chromium-containing compounds at work. [Cr (III)] is an essential nutrient in humans and animals that assists glucose, lipid, and protein digestion by increasing the effect of insulin<sup>[5]</sup>. Workplace exposure, Environmental poisoning by these metals has become a major environmental and hygienic concern in recent years. Further, as a result of their aggressive growth in a variety of industrial, agricultural, residential, and technical applications, human exposure has increased dramatically<sup>[6]</sup>. Disintegration of rocks and volcano bursting, for example, have been shown to add notably to heavy metal pollution. Industrial sources such as metal clearing in purifier, coal burning in power plants, petroleum ignition, atomic furnace, power cables, polymers, textiles, microelectronics, wood preservation, and paper processing are reasons for increased metal toxicity.

### Arsenic

#### Occurrences in the Environment and Industrial Production

Arsenic is a never-present element that can be found in trace amounts in almost all habitat matrices. The two most frequent inorganic forms of arsenic are trivalent arsenate and pentavalent arsenate. Agricultural items such as pesticides, defoliant, antifungal agents, organophosphorous compounds, creosote, and colorants contain arsenic-containing compounds, which are generated industrially.

Arsenic trioxide was recently licensed by Food and Drug Administration as an antitumor drug for the therapy of blood cancer<sup>[7]</sup>. The healing effects of cancer cells are assumed to be due to the medicated cell death (apoptosis).

### Human Exposure Risk

Mass population are likely to be persistently exhibited to arsenic around the globe, particularly in nations where arsenic levels in groundwater are high, such as Bangladesh, India, Chile, Uruguay, Mexico, and Taiwan. In the open air, arsenic concentrations range from 1 to 3 mg/m<sup>3</sup>, but in cities, concentrations range from 20 to 100 mg/m<sup>3</sup>.<sup>[8]</sup> Although larger amounts can be found around common mineral reserves or excavation sites, most water contains less than 10g/L. Personal liability might transpire through breathing-in of dust in the air, consumption of polluted water or soil, or exposure via the food web. A strong link has been identified between exposure to arsenic and an elevated risk of mutagenic and fundamental health effects in several epidemic investigations.

### Cadmium

#### Occurrences in the Environment and Industrial Production

Cadmium is a highly hazardous heavy metal that can affect both workers and the environment. With an average content of 0.1 mg/kg, it's widely spread throughout the earth's crust<sup>[9]</sup>. Cadmium compounds are most plentiful in sedimentary rocks, with roughly 15 mg/kg of cadmium in marine phosphates. Cadmium is also emitted during unearthing, heating, and the production of batteries, paint, soother, and alloys. Cadmium can also be found in negligible quantity in leafy greens, potatoes, grains, and seeds, as well as the liver and kidneys, crustaceans, and mollusks in minute proportions.

### Potential for Human Exposure

Inhalation of cigarette smoke and consumption of food are the two most common ways to be exposed to cadmium. Absorption through the skin is uncommon. Working in major metal-producing industries, consuming tainted food, smoking cigarettes, and working in a cadmium-polluted environment are all potential sources of cadmium exposure, with smoking being the most common<sup>[10]</sup>. Inhalation for long durations of time cadmium particle exposure is typically connected to emphysema-like alterations in pulmonary function and chest radiography. At elier exposure to cadmium particles has been correlated to improved olfactory function. Cadmium can harm the kidneys, bones, liver, and blood if exposed to it for long periods of time at high levels.

### Chromium

#### Occurrences in the Environment and Industrial Production

Chromium is a commonly appearing element found in the surface of the earth in various oxidation levels, ranging from chromium (II) to chromium (VI). The element chromium [Cr(0)] does not exist in nature. Chromium enters the environment via a variety of natural and anthropogenic (air, water, and soil) sources, with industrial firms releasing the most toxic agent<sup>[11]</sup>. Metal recycling, leather industry, chromate manufacture, chrome steel binding, and ferrochrome and chrome coloring matter manufacture- are

the industries that contribute the most to chromium release.

### Potential for Human Exposure

On the other hand, Chromium is also one of the major sources that could lead to high risk of illness to the employees working in factory <sup>[12]</sup>. When inhaled or absorbed through the skin, chromium can cause bronchogenic carcinoma, sore in the nasal cavity, and intolerance such as contact allergy and asthma. Chromium affects many immune system constituents, causing immunostimulation or immunosuppression.

### Mercury

#### Industrial Production and Occurrences in the Environment

Mercury is a heavy metal that can be found in three different forms in nature (organic form, inorganic form and elemental form), has its own toxicological information <sup>[13]</sup>. Mercury in its elemental statesubstists as a liquid with a high vapour pressure at room temperature, and it is emitted into the atmosphere as mercury vapors. Mercury is a common environmental toxin and contaminant that causes significant changes in human tissues as well as a variety of negative health impacts. Mercury enters the water by toxious gas emission from the earth's crust, as well as pollution from industry.

#### Exposure Risk to Humans

Accidents, environmental pollution, food poisoning, tooth treatment, proactive medical practices, activities in industries and agriculture, and activities in workplaces are all ways in which humans are exposed to various forms of mercury. Dental amalgams and fish intake are the two most common reasons for persistent, low-level mercury exposure. Mercury in the streams is methylated by algae and bacteria. Methyl mercury then travels up the food chain, ending up in fish, shellfish, and eventually people <sup>[14]</sup>. Breathing of mercury vapors can harm the nervous, digestive, and immune systems, as well as the lungs and kidneys, and it can be lethal. Mercury in drinking water has the potential to affect the nervous system and kidneys.

#### Heavy metal removal and water quality features

When it comes to heavy metal removal, it's important to consider how the heavy metals behave, as well as the adsorbent's properties, under various water quality situations. Temperature, pH and ionic strength are three of the most critical properties of water for poisonous metal removal <sup>[15]</sup>. Table -1 list some typical heavy metals in developing countries. Heavy metal contamination is most commonly connected with industrial sewagewater, although it has also been found in a variety of water sources in poor countries, including domestic wastewater effluent groundwater, rivers, and lakes. The water quality factors of various water sources influence an adsorbent's ability to effectively get rid of metal pollution from these water sources.

Toxic metals are constantly released into the surroundings due to various undertakings of industries, agronomy, and improper waste management. Because of their long-term environmental impact, heavy metals are extremely hazardous. These toxic metals are imperishable, and they pile up in living beings as a result of consuming polluted comestibles <sup>[16]</sup>. Human beings, like all biological creatures,

require different percent of toxic metals such as iron, zinc, copper, and chromium for enrichment, too much of these metals can be lethal. Table -2 lists the chemical characteristics of some toxic metals found in the surroundings.

#### The pH Effect

The existence of heavy metals and their properties are affected by the pH of the water supply. The pH of aqueous solutions has a criticeffect on the speciation of heavy metals. Heavy metals are more dispersible and adaptable in water sources when they are in their cationic state, which occurs at 7 to <7 pH values <sup>[19]</sup>. As the pH of the water rises, complexes form with hydroxides and other anions. In addition to the impacts of heavy metals, pH can affect the charge of the surface assimilative, the assemblage of ions on the functional groups of the surface assimilative, and the ionization state of the adsorbent. The effect of pH on heavy metal speciation and removal has been demonstrated in several researches. Copper, for example, has been demonstrated to have increased stability and mobility when pH decreases. As the pH rises, heavy metals form complexes with hydroxide ions, changing the heavy metal's oxidation state. Heavy metals precipitate out of the water as the pH rises above neutral. Lower pH values raise the accumulation of free lead ions in the water origins, whereas higher pH values cause immobilization, which is primarily caused through precipitation. Overall, pH affects how heavy metals behave and how easily they may be eliminated.

#### Effect of temperature

Another significant element to consider when examining the behavior of heavy metals and their eventual elimination is temperature. Many ways for toxic metal removal that have been found, such as surface association reactions and other forms of anion and cation interchange reactions, are improved at higher temperatures <sup>[17]</sup>. When the temperature was raised from 25 to 60 degrees Celsius, the removal of Ni (II) utilizing tea waste by roughly 20%, owing to enhanced movement of the toxic metals as well as raised number of assimilation sites due to breaking of bonds. Cu (II) surface assimilation on filberts enhanced due to raise in temperature, which contribute to the shells' possible expansion in stoma dimension and Cu (II) ions' higher kinetic energy, allowing for more contact with the adsorbent. The surface assimilation procedure has been presented to continue more swiftly at increasing temperatures due to elevated propulsion through the outer surface and higher diffusion rate within the adsorbent. On the other hand, higher temperatures have usually resulted in poorer heavy metal removal rates. Furthermore, when the temperature rises, several scientists have noticed a decline in the removal of toxic metals like Pb(II) and Ni(II), which they attribute to lower superficial activity. When analyzing the consequences of temperature on the removal of toxic metals, each adsorbent and the matching metal ion must be analyzed separately to ascertain the total effect of temperature variations on the surface.

#### Effect of ionic strength

Heavy metals and their capacity to be removed are affected by the ionic strength of water origin. The existence of chloride produce the formation of soluble and difficult-to-remove neutral or negatively charged metal-chloride

complexes. As the ionic strength increased, the dismissal effectiveness of Cu(II) and Ni(II) decreased significantly, owing to the increasing production of heavy metal-chloride complexes with low adsorption affinity. Enhanced ionic strength in a suspension can have a considerable impact on the removal of heavy metals when their interactions with other surfaces are highly effected by coulomb's force. According to surface chemistry theories, when ionic strength rises, the electric double layer shrinks, changing electrostatic interactions and reducing heavy metal adsorption [18]. When we looked over the effect of ionic strength on the withdrawal of heavy metals such as Cu (II), Pb(II), and Zn(II) from plant fertilizers, we discovered that as ionic strength increased, the overall withdrawal of heavy metals decreased.

### Heavy metal removal with cost - effective materials Green waste

Scientists all over the world have looked into the utilization of green waste to withdraw toxic metals. Agricultural waste is abundant and an excellent adsorbent to get rid of heavy metals from water treatment systems in emerging. Plant compost, for example, is a one-of-a-kind product that has been demonstrated to remove heavy metals effectively, with peak surface assimilation capacities of 15.5, 27.2, and 95.3 mg g<sup>-1</sup> for Zn (II), Cu (II), and Pb (II), respectively. These wastes include all kinds of rice roughages like rice bran, rice husk and rice straw. All these materials though considered as waste, have been proven to be effective in removing heavy metals from damp solutions. The straw and bran of rice, for instance, have maximum surface assimilation capacities of 19.4 and 20.0 mg g<sup>-1</sup>, respectively, shown to be very effective in eliminating Cu (II). Rice husk has been shown to be capable of eliminating toxic metals from water sources in a variety of tests. According to the study conducted by (Lesley Joeph *et al.*) utilizing rice husks to eliminate Cu (II). found a high surface assimilation scope of 17.5 mg g<sup>-1</sup>. Heavy metals can be successfully extracted from aqueous solutions using a variety of fruit wastes. Divalent zinc, copper, nickel, cadmium and lead have all been successfully removed using lemon peels, with maximal adsorption capacities of 26.8, 35.9, 53.6, 70.9, and 79.0 mg g<sup>-1</sup>, respectively. Orange peel, removes 97.5 percent of Ni(II), whereas removal efficiency for Cu(II), Pb(II), Zn(II), and Cr(VI) are lower. Cd<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, and Zn<sup>2+</sup>, adsorption on citrus peel exhibited appreciable elimination, with maximal adsorption capacities of 40.8, 61.3, 80.3, 26.1, and 25.1 mg g<sup>-1</sup>, respectively. (Byung-Moon Jun *et al.*,) proposed that banana peel had maximum adsorption capacities of 20.0, 24.2, 33.1, 52.4, and 54.2 mg g<sup>-1</sup> for the removal of Cd<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, and Zn<sup>2+</sup>. Heavy metals can be removed from water sources using various other vegetable wastes also. Heavy metals have been found to be removed by mushroom remnants. Divalent Cu, Zn, and Hg removal efficacy ranged from 39.7% to 81.7 percent in a study of four different types of mushroom wastes. (Joseph R.V. Flora *et al.*,) showed that the four distinct types of mushroom residues, removal efficiency for Cu<sup>2+</sup>, Zn<sup>2+</sup> and Hg<sup>2+</sup> ranged from 39.7 to 81.7 percent. (Chang Min Park *et al.*,) in their study the author used three distinct mushrooms to eliminate Cd<sup>2+</sup> and Pb<sup>2+</sup>, with maximum surface assimilation capabilities of 35.0 and 33.8 mg g<sup>-1</sup>, respectively. Table-3 summarizes a number of researches that looked at the possibilities of green wastes to eliminate

toxic metals.

### Removal of Heavy metals using other waste materials.

The efficiency of nearby accessible garbage in eliminating toxic metals from damp solutions has been studied extensively. Some variety of garbage may be generated in excess than others due to differences in geographical conditions, energy sources, farming practices, and civilizations [19]. Tea trash have been demonstrated to eliminate a number of toxic metals successfully. Cu (II) may be removed from black tea garbage using laundering, steaming, and using ultrasonography. Cu(II) elimination increased with each treatment when compared to untreated adsorbents, with tea throw-away treated with any base obtaining the maximum adsorption. Changes in the physical and chemical features of the adsorbent, such as increased surface area and porosity, as well as a higher number of functional groups, have been linked to the enhanced removal accomplished employing these modification processes.

Heavy metals can be extracted from aqueous solutions using coal ash, a common by-product of fossil fuel burning [20]. Due to the heavy metals' electrostatic interaction with the charged surface of the adsorbent, (Byung-Moon Jun *et al.*,) proposed that employed coal fly ash to remove Cr<sup>3+</sup>, Pb<sup>2+</sup>, and Zn<sup>2+</sup> and found high adsorption capacities of 21.0, 44.1, and 16.3 mg g<sup>-1</sup>, respectively. A summary of selected studies evaluating the ability of locally available wastes to remove heavy metals can be found in Table 4 Olive cake, garbage from the olive oil production was discovered to have a high surface assimilation capability of 65.4 mg g<sup>-1</sup> and was proven to be effective in removing Cd<sup>2+</sup>. (Yeomin Yoon *et al.*,) in Palestine looked at how well olive cake, cactus leaves, coal, and wool could extract Cr from a range of locally available materials (VI). Wool (40.5 mg g<sup>-1</sup>) had the greatest adsorption capability in this investigation, followed by olive cake (33.4 mg g<sup>-1</sup>), cactus leaves (8.3 mg g<sup>-1</sup>), and coal (8.3 mg g<sup>-1</sup>) (7.2 mg g<sup>-1</sup>). The wool's loose structure was attributed to its efficacy in removing Cr (VI), allowing for physisorption, whereas the other surface assimilators were more firm, hence less effective.

### Low-cost adsorbents from agricultural products and by-products

For the elimination of heavy metals in minute amounts, active charcoal surface assimilation seems to be a highly aggressive and successful technique. However, because of its high cost, activated carbon is not appropriate for developing countries. Hence, the use of cost-effective materials as viable source for removal of metal from wastewater has gained importance. The constituent polymers determine the native exchange capacity and general sorption characteristics of these materials like cellulose, hemicelluloses, pectin, lignin, and protein (in roughly decreasing order of abundance). When immersed in water, the cellulose surface becomes somewhat negatively charged, resulting in columbic interaction with cationic species in the water [21]. Columbic interactions are primarily responsible for the high binding capabilities of cationic species on adsorbents. Crop residues have been demonstrated to be an excellent adsorbent for a variety of solutes, particularly divalent metal cations, but they have some primary drawbacks: low exchange or sorption capacity and poor physical stability (i.e. partial solubility). Also, some

substances may percolate into solution; for example, peanut skin may percolate a deep red color into suspension when it comes in touch with water. Low molecular weight tannins represented the majority of the soluble coloured compounds. Peanut skin also tends to disintegrate when exposed to water over an extended period of time. To address these issues, raw adsorbents must be chemically modified and/or activated. Agricultural wastes and by-products are plentiful and must be properly disposed of. It emits CO<sub>2</sub> and other pollutants when burned in place. As a result, agricultural products and by-products must be converted into usable and promising high added value. One possibility is to use a cost-effective ion exchange or sorbent material that can eliminate hazardous metals from damp solutions. The nature of the adsorbent and adsorbate metal concentration, temperature and pH of the aqueous solution, adsorption kinetics, adsorption isotherm, and the types of contacting system of the adsorbent with the adsorbate, as well as the contact time, have all been studied in order to optimise the use of adsorbent in wastewater treatment. The metal adsorption capabilities (mg/g) of some green products and by-products are compared to active charcoal and several ion exchange resins (Table 5).

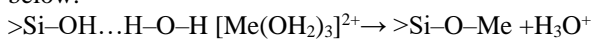
### Mechanisms of removal of heavy metal

Surface assimilation has gained the greatest notice as a elimination approach while looking into the efficacy of these cost-effective surface assimilators to eliminate toxic metals in the emerging countries. When heavy metals come into touch with certain materials, they adsorb. Toxic metal ions percolate into the adsorbent through interstitial adsorption. The ions, on the other hand, pass through the pores of the adsorbent and adsorb to the substance's interior surfaces. Micro porous adsorbents are the most common adsorbents for this sort of adsorption.

Fig1. Shows an example of interstitial adsorption. For the removal of heavy metals, several adsorption processes have been proposed. Bioadsorbents contain a variety of functional groups that can establish chemical interactions with metal ions, including amide, hydroxide, phosphates, carboxyl ate, and thiols. Surface assimilation via the ion-exchange route is very effective, and depends on the activation energy of the reaction. The proposed process is depicted in Fig 2. As a result, it was obvious that, in addition to bioadsorbents, compounds containing phenolic groups are capable of exchanging protons with metal ions, resulting in a pH reduction, as shown in the equation below.

$$\text{Me}^{2+} + 2(-\text{ROH}) = \text{Me}(-\text{RO})_2 + 2\text{H}^+$$

The transport of photo generated electrons from a metallic oxide to graphene is depicted in Fig3. Metal sulphides have also been coupled with graphene in the search for photo catalysts with better photo catalytic activity for the breakdown of organic pollutants in water. Because heavy metals cannot precipitate below pH 4.0, their adsorption in acidic solutions can be characterized using the equation below.



The mechanism of Cd(II) and Pb(II) ions is depicted in Fig4. Surface silanol sites and aluminols are ionized and hydrolyzed, resulting in this reaction. To summarise, LCSM (laser confocal scanning microscopy) removes metal ions

primarily by an ion exchange mechanism, followed by precipitation and adsorption.

According to a current study on metal adsorption by ion exchange mechanism, divalent heavy metal ions in suspension form a bond by sharing two pairs of electrons and then release 2H<sup>+</sup> or Na<sup>+</sup> ions in the solution successively in the presence of -COOH and -OH groups, as shown in Fig5. Because there are no vacant metal ion sites on the adsorbent, the ion exchange reaction mechanism predicts that when pH falls, the normality of H<sup>+</sup> ions rises, and adsorption falls [22]. Columbic forces have an impact on the adsorption mechanism. Columbic forces are the attraction between charged clouds of atoms. Working conditions, notably the pH of the aqueous solution, are quite important. Low pH causes protonation of carboxyl and hydroxyl functional groups, making it much more difficult for metal cations to accumulate on active sites of adsorbent over H<sub>3</sub>O<sup>+</sup>, resulting in electrostatic repulsion and adsorption blockage. Metal ion adsorption increases as pH rises due to a decrease in electrostatic repulsion. As a result, for pH > pHPZC, the negative charge density of the surface assimilator increases cation assimilation capability, while the opposite is true at pH < pHPZC

### Conclusions

Heavy metals, which can be found in contaminated water from both natural and manmade sources, are harmful to humans and aquatic life. As a result, removing these polluted heavy metals is critical. As a result, extensive research into the utilization of cost-effective adsorbents to eliminate toxic metals from water origins has been carried out. Different forms of agricultural waste and diverse plentiful materials have been studied as low-cost adsorbents. Heavy metals can be effectively removed by these materials, according to research. Agricultural waste and by products tend to be the most successful at eliminating heavy metals when compared to the other categories discussed in this research. The efficiency of these materials in eliminating heavy metals, however, is highly dependent on the water quality parameters, such as pH, ionic strength, and temperature, as well as the material's properties [23]. These factors can alter the heavy metals' speciation and stability, as well as the adsorbent's adsorptive properties. Furthermore, ion exchange, combined with the action of electrostatic forces, is the most commonly stated process for removing heavy metals [24]. Water quality has a significant impact on the efficiency of these systems. These adsorbents are, in general, feasible and cost-effective materials for eliminating heavy metals from water. These materials are widely available in huge numbers in the poor world, and integrating them into a water treatment process would need little technology or skill. Future research in this sector should concentrate on developing additional cost-effective materials that are successful at eliminating heavy metals from the environment around the world. Waste materials and other residual by products, which are abundant in these countries as well as nations with large production operations, should be given special attention because they typically contribute to heavy metal contamination increases [25]. No doubt, cost-effective adsorbents hold a lot of promise for future commercial uses.

**Table 1:** Characteristics of heavy metals

Heavy metal	Human health effects	Common sources	Maximum Contaminant Level	
			USEPA	WHO
Arsenic	Affects the cardiovascular or circulatory system of the body, leads to premature aging and skin cancer.	Naturally-occurring Semiconductor electronics devices	0.010mgL <sup>-1</sup>	0.010mg L <sup>-1</sup>
Cadmium	Cancer-causing agent. Premature aging and skin cancer.	Naturally-occurring Elements occur in the Earth as compounds or mixtures.	0.003mgL <sup>-1</sup>	0.002mgL <sup>-1</sup>
Chromium	<i>Atopic dermatitis</i> gastroenteritis	Naturally-occurring Steel making	0.1mgL <sup>-1</sup>	0.05mgL <sup>-1</sup>
Copper	Gastrointestinal disorder, results in hepatic disease.	Naturally-occurring Home plumbing systems	1.25mgL <sup>-1</sup>	2.0mgL <sup>-1</sup>
Lead	Kidney failure, Causes damage in Nervous system.	Lead and lead compounds, Home plumbing systems	0.01mgL <sup>-1</sup>	0.015mgL <sup>-1</sup>
Mercury	Anxiety disorders depression, or psychosis.	Air pollution from fossil fuel combustion, Electronic companies	0.002mgL <sup>-1</sup>	0.005mgL <sup>-1</sup>

**Table 2:** Properties of heavy metals

Heavy metal	Molecular weight (g mol <sup>-1</sup> )	Oxidation state(s)	VanderWaals radius (10 <sup>-12</sup> m)	Electro negativity (Pauling Scale)
Copper(Cu)	63.5	+1,+2	140	1.95
Lead(Pb)	207.2	+2,+4	202	2.36
Manganese(Mn)	54.9	-1,0,+2,+3,+4,+6	205	1.56
Mercury(Hg)	200.6	+1,+2	155	2.05
Nickel (Ni)	58.7	0,+2,+3	163	1.95
Zinc (Zn)	65.4	+2	139	1.65

**Table 3:** Heavy metals removed by various agricultural waste products

Adsorbent	Heavy metal	Surface area (m <sup>2</sup> g <sup>-1</sup> )	C <sub>0</sub> (mg L <sup>-1</sup> )	q <sub>max</sub> (mg g <sup>-1</sup> )
Rice bran	Chromium(VI)	0.1	53.3	12.5
	Copper(II)	NA	5-300	20.0
Rice husk	Cadmium(II)	NA	50-200	16.4
	Chromium(VI)	0.4	53.5	11.2
	Chromium(VI)	NA	100	8.3
	Cobalt(II)	NA	5-300	9.4
	Copper(II)	NA	5-300	16.5
	Copper(II)	NA	50-200	10.7
	Lead(II)	NA	50-200	57.1
Rice straw	Mercury(II)	NA	50-200	36.3
	Chromium(VI)	1.2	53.5	12.4
Lemon peel	Copper(II)	NA	5-300	19.4
	Cadmium(II)	1.2	100-800	53.4
	Copper(II)	1.2	100-900	70.9
	Lead(II)	1.3	100-900	35.9
	Nickel(II)	1.2	100-900	79.0
Orange peel	Zinc(II)	1.3	100-900	26.8
	Cadmium(II)	2.0	100-800	40.8
	Cobalt(II)	NA	5-25	1.8
	Copper(II)	NA	5-25	3.7
	Copper(II)	2.0	100-800	61.3
	Lead(II)	NA	5-25	7.8
	Lead(II)	NA	50-1200	476
	Lead(II)	0.21	57	27.9
	Lead(II)	2.0	100-800	26.1
	Nickel(II)	NA	5-25	6.0
	Nickel(II)	NA	50-1200	80.3
Banana peel	Zinc(II)	2.0	100-800	25.1
	Cadmium(II)	NA	50-200	33.1
	Cobalt(II)	NA	5-25	2.6
	Copper(II)	1.3	100-900	51.4
	Copper(II)	NA	5-20	4.9
	Copper(II)	38.5	10-40	7.1
	Lead(II)	1.3	100-800	24.2
	Lead(II)	NA	5-20	7.2
	Nickel(II)	1.2	100-900	53.2
	Nickel(II)	NA	5-20	6.7
	Zinc(II)	1.3	100-800	20.0
	Zinc(II)	NA	5-25	5.8

NA- not available

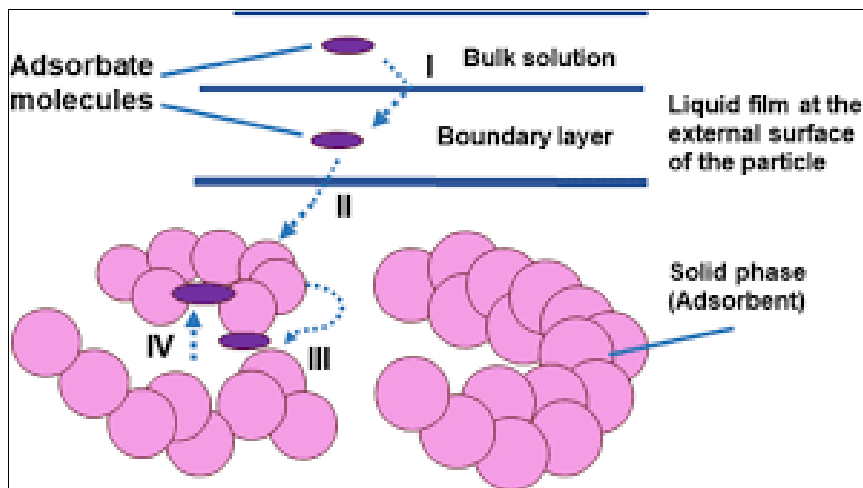
**Table 4:** Removal of Heavy metals by various locally-available waste materials

Adsorbent	Heavy metal	Surface area (m <sup>2</sup> g <sup>-1</sup> )	C <sub>0</sub> (mg L <sup>-1</sup> )	q <sub>max</sub> (mg g <sup>-1</sup> )
Tea Waste	Nickel(II)	0.39	50-300	17.4
	Zinc(II)	1.3	25-200	8.9
Coal fly ash	Chromium(III)	20	10-200	21.0
	Lead(II)	20	10-200	44.1
	Zinc(II)	20	10-200	16.3
Cactus leaves	Chromium(VI)	NA	20-1000	8.3
Coal	Chromium(VI)	NA	20-1000	7.4
Wool	Chromium(VI)	NA	20-1000	40.2
olive cake	Chromium(VI)	NA	20- 1000	32.3

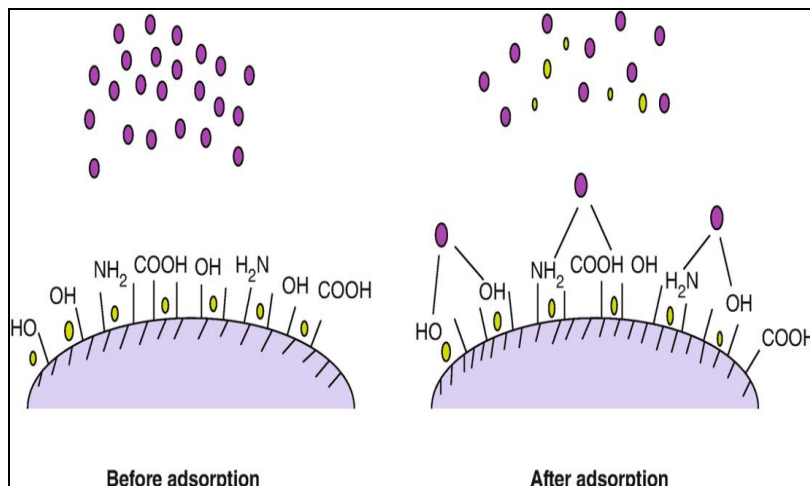
NA- not available

**Table 5:** Heavy metal adsorption capacities (mg/g) compared with activated carbon and some Cation exchange resin.

Adsorbent	Pb <sup>+2</sup>	Cu <sup>+2</sup>	Zn <sup>+2</sup>	Cd <sup>+2</sup>	Ni <sup>+2</sup>	Cr <sup>+6</sup>	Hg <sup>+2</sup>
Granular activated carbon	15.48	4.08	-	4.33	-	-	
Powdered activated carbon	24.85	3.45	-	4.31	-	-	
Activated carbon fibers	29.42	10.01	-	-	-	-	
Peanut hulls	28.10	8.01	7.96	6.96	-	-	
Corncoobs	9.25	6.62	1.96	8.89	12.5		
Pine bark -		9.49		14.13	6.24	-	
Black oak bark	-	-	-	29.4	-	-	
Lignin	173.2	-	93	-	-	-	
Leaf mould						44	
Xanthane	18			32.24			1.149
Lewatit TP 207	190.9	86.09	88.60	46.46	86.05		
Amberlite 200	350.24	87.90	84.60	124.8	119.1		



**Fig 1:** Removal of toxic heavy metal using adsorbent via interstitial adsorption (Courtesy: S0045653519308616)



**Fig 2:** Before and after adsorption of heavy metal such as lead by adsorbent via ion exchange Mechanism (Courtesy: 978-3-030-47400-

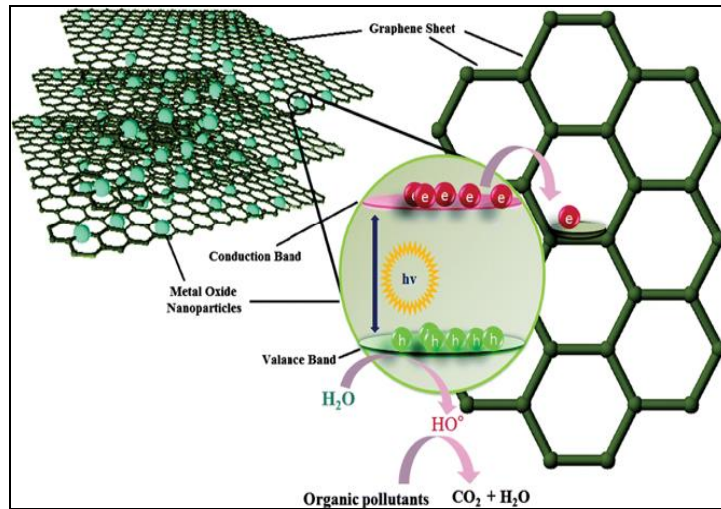


Fig 3: Schema of the mechanism of electron transfer from conduction band of metal oxide to graphene sheets. (Courtesy:) c3ra45013a

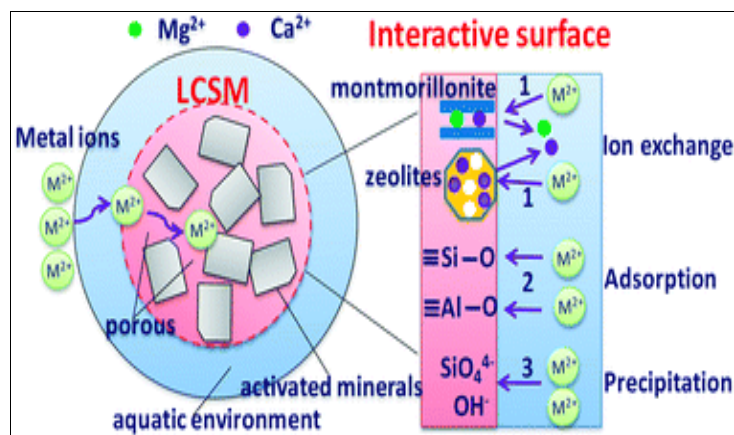


Fig 4: Mechanism of Cd (II) and Pb(II) ions removal by LCSM. (Courtesy:) c7ra08018b-s1\_hi-res

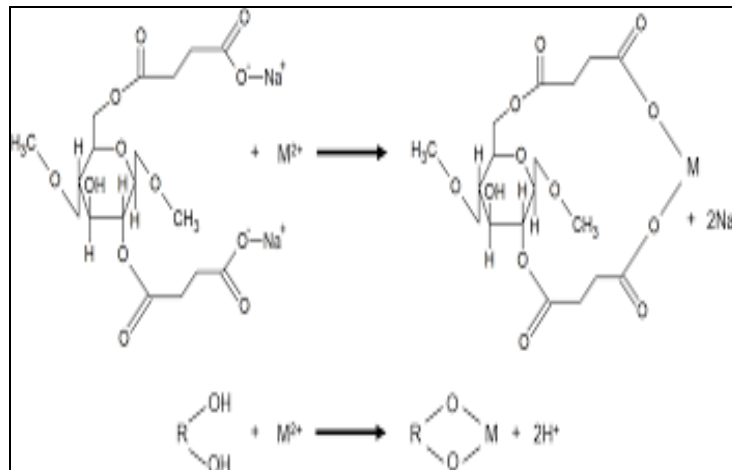


Fig 5: Adsorption of toxic divalent heavy metal cations ( $M^{2+}$ ) by exchange with  $Na^+$  and  $H^+$  ion (Courtesy:) S0045653519308616

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**References**

1. Abdelhafez AA, Li J. Removal of Pb (II) from aqueous solution by using biochars derived from sugar cane bagasse and orange peel. J. Taiwan. Inst. Chem. Eng, 2016;61:367-375.
2. Ajmal, M., Rao, R.A., Anwar, S.*et al* (2003) Adsorption studies on rice husk: removal and recovery of Cd (II) from wastewater. Bioresour. Technol. 86 (2); 147-149.
3. Al-Anber ZA, Matouq MA. Batch adsorption of cadmium ions from aqueous solution using olive cake. J. Hazard Mater,2008;151(1):194-201.
4. Annadurai G, Juang RS, Lee DJ. Adsorption of heavy metals from water using banana and orange peels. Water Sci. Technol,2002;47(1):185-190.
5. Babel S, Kurniawan TA. Low-cost adsorbents for

- heavy metals uptake from contaminated water: a review. *J. Hazard Mater*,2003;97(1-3):219-243.
6. Bansal M, Garg U, Singh D *et al.* Removal of Cr (VI) from aqueous solutions using pre-consumer processing agricultural waste: a case study of rice husk. *J. Hazard Mater*,2009;162:312-320.
  7. Boonamnuayvitaya V, Chaiya C, Tanthapanichakoon W *et al.* Removal of heavy metals by adsorbent prepared from pyrolyzed coffee residues and clay. *Separ. Purif. Technol*,2004;35:11-22.
  8. Dakiky M, Khamis M, Manassra A *et al.* Selective adsorption of chromium (VI) in industrial wastewater using low-cost abundantly available adsorbents. *Adv. Environ. Res*,2002;6:533-540.
  9. Feng N, Guo X, Liang S *et al.* Biosorption of heavy metals from aqueous solutions by chemically modified orange peel. *J. Hazard Mater*,2011;185(1):49-54.
  10. Kurniawan TA, Chan GY, Lo WH *et al.* Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metals. *Sci. Total Environ*,2006;366(2e3):409-426.
  11. Malkoc E, Nuhoglu Y. Investigations of nickel(II) removal from aqueous solutions using tea factory waste. *J. Hazard Mater*,2005;B127:120-128.
  12. Nguyen TA, Ngo HH, Guo WS *et al.* Applicability of agricultural waste and by-products for adsorptive removal of heavy metals from wastewater. *Bioresour. Technol*,2013;148:574-585.
  13. Peng W, Li H, Liu Y *et al.* A review on heavy metal ions adsorption from water by graphene oxide and its composites. *J. Mol. Liq*,2017;230:496-504.
  14. Rao R, Khan M. Biosorption of bivalent metal ions from aqueous solution by an agricultural waste - kinetics, thermodynamics, and environmental effects. *Colloids Surf. Physicochem. Eng. Aspects*,2009;332:121-128.
  15. Rashidi N, Yusup S. Overview of the potential of coal-based bottom ash as low-cost adsorbents. *ACS Sustain. Chem. Eng*,2016;4(4):1870-1884.
  16. Singha B, Das SK. Adsorptive removal of Cu (II) from aqueous solution and industrial effluent using natural/agricultural wastes. *Colloids Surfaces B Biointerfaces*,2013;107:97-106.
  17. Bryant PS, Petersen JN, Lee JM *et al.* Sorption of heavy metals by untreated red fir sawdust. *Appl. Biochem. Biotechnol*,1992;34-35:777-788.
  18. Dean JG, Bosqui FL, Lanouette KH. Removing heavy metals from wastewater. *Environ. Sci. Technol*,1972;6:518-524.
  19. Orhan Y, Buyukgungor H. The removal of heavy metals by using agricultural wastes. *Water Sci. Technol*,1993;28(2):247-255.
  20. Sharma DC, Forster CF. The treatment of chromium wastewaters using the sportive potential of leaf mold. *Bioresour. Technol*,1994;49:31-40.
  21. Friedman M, Waiss AC Jr. Mercury uptake by selected agricultural products and by-products. *Environ. Sci. Technol*,1972;6:457-458.
  22. Huang CP, Blankenship DW. The removal of mercury (II) from dilute aqueous solution by activated carbon. *Water Res*,1984;18(1):37-46.
  23. Low KS, Lee CK, Liew SC. Sorption of cadmium and lead from aqueous solution by spent grain. *Proc. Biochem*,2000;36:59-64.
  24. Tummavuori J, Aho M. On the ion-exchange properties of peat. Part I: On the adsorption of some divalent metal ions (Mn 2+, Co 2+, Ni 2+, Cu 2+, Zn 2+, Cd 2+ and Pb 2+ ) on the peat. *Suo*,1980a;31(4):79-83.
  25. Viraraghavan T, Dronamrajum Removal of copper, nickel, and zinc from wastewater by adsorption using peat. *J. Environ. Sci. Health Part A*, 1993;28:1261.