

**Review Article**

The Sources, Toxicity, Determination of Heavy Metals and Their Removal Techniques from Drinking Water

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Abstract: Heavy metals (Cr, Cd, Hg, As, Zn, Cu, Fe, Al, Ba, Ca, Mg, Pb, Mn, Ag, Na, and Se) contamination in drinking and irrigation water are much toxic for living organisms that are present in excess amount or in less than their requirement in the body. Their major sources are from different industries as dyeing, textiles, leather, mining, pesticides, plastic, wood, and pharmaceuticals. The industrial processes release these metals in air, surface water, soil, groundwater, and crops and ultimately target human beings. Groundwater contamination occurs through the anthropogenic activities by man-made products such as gasoline, oil, road salts, mining, pesticides, and fertilizers, etc. discharge into groundwater. Copper, zinc, and selenium are heavy metals that are needed in trace amounts for humans. On the other hand, some other metals like lead, arsenic, and mercury are extremely dangerous for human beings even if consumed in small amounts. There is a big challenge to remove heavy metals from drinking water. Different diseases like nervous system damage, kidney failure, blood pressure, hypertension, diabetes, growth inhibition are mostly caused by their contamination in drinking water. Various modern and conventional techniques are used for the determination of heavy metals and water treatment.

Keywords: Drinking Water, Heavy Metals, Toxic, Sources, Diseases

1. Importance of Water

Drinking water is important that it is the second most essential material for human life. We know there is no existence of life without water. However, it is so much difficult for the availability of pure water for human use and hence now a day it is a big problem worldwide. It is considered that the pollution of drinking water (freshwater) is a problem for about half of the world population. United Nations report is that about 2.7 billion people will face deficiency of water by 2025. As we know that only 3% freshwater of total water is available for us and 0.06% available for human use only. Approximately, over 80 countries in the world are suffering a deficiency of water and 1.2 billion people using contaminated water. About

2.5 billion cases are noted from water pollution and rough The important chemical ingredients that present in water are also beneficial for human health effect mainly in two ways: Firstly, by providing essential micro and macro elements that food cannot supply in proper amount of these elements (for example zinc, iodine, and Magnesium); and secondly, by supplying the micro and macro elements that prevents the absorption and toxic effects of elements such as cadmium (Cd), Mercury (Hg) and Lead (Pb). By taking the excess amounts of these beneficial elements also exhibits harmful effects on health. Because the concentration of macro and microelements that found in natural, portable water is totally different depending upon the source and geographical location of a specific area [1].

Estimation is that 5 to 10 million people's deaths have been taken place due to the contamination of water. The serious diseases caused by contaminated and poor-quality water are dysentery, cholera, and schistosomiasis, typhoid, and diarrheal diseases [2].

2. Sources of Heavy Metals

Various types of heavy metals are released from different industrial manufacturing processes, such as Cr, Cd, Ni, Cu, Zn, As, and Pb are considered most toxic among them. These metals are highly soluble in water and can be taken by aquatic organisms. The large concentration of these metals may accumulate in the human body through the food chain. If the concentration of heavy metals is ingested more than the required concentration, they can cause toxic health diseases [3].

The treatment of wastewater, therefore, must be important before its discharge to the environment. For the treatment of wastewater, conventional processes such as ion exchange, chemical precipitation, and electrochemical removal can be used for the removal of heavy metals from industrial effluent. The disadvantages of these processes are that there is incomplete removal of heavy metals, high-energy resources, and toxic sludge is produced [4].

There is a wide range of processes that emit heavy metals in the environment including in air during combustion, extraction, and processing and to surface water via runoff from storage and transport and to the soil hence into groundwater and crops. Human health is profoundly affected by the emission of these metals in environments. The cadmium, lead, and mercury spatial distribution to the environment due to the Meteorological Synthesis Centre [5].

Due to the long-term use of wastewater for irrigation as a result of the buildup of heavy metals in cultivation soil and plants. These metals are absorbed both in edible and non-edible parts of vegetables. Some metals like Ni, Mn, Cu, and Zn present in small amounts and considered as micronutrients and, they become highly toxic to human health when their concentration is more and hence cause health risks diseases [6].

Various human activities and processing of different applications are the major sources of the metals contaminations into the environment. Hence, metals are not affected by microorganisms (non-biodegradable) and accumulated in the environment and disturb the food chain. The extraction from ores and processing for various applications, the mobility of heavy metals by man has led to the emission of these elements into the environment. Heavy metals are non-biodegradable and thus collected in the environment and finally contaminate the food chain. Their pollution causes hazardous effects on the environment. Carcinogen, teratogenic and endocrine disruptors effects are observed of heavy metals and especially behavior changes in children [7].

The dyeing industry is one of the largest water utilizing industries. Various chemicals and coloring compounds contaminants are existing in their effluent and hence proper treatment is necessary before its discharge into any aquatic

body. It is very difficult to treat household effluents completely because they are contaminated in variable compound composition [8].

For the proper working of biological systems, heavy metals are very important but their large amount could cause a number of diseases. The discharged effluents from the textile and tannery industry possess more amount of metals particularly cadmium (Cd) and Copper (Cu). These discharged metals are dumped into the surface water as well on the land and as results of the accumulation of toxic metallic components because dangerous diseases in living things seen. The reason is that they are not degraded entirely. In this way, discharged industrial effluent has a big effect on the people living in developing countries as well as in developed ones [9].

Major pollutants in industrial, ground, marine, and wastewater are heavy metals. The major sources of heavy metals pollutants from the processing of metals, leather industries, medicines manufacturing units, chemicals manufacturing industries, mining, pesticides, plastics and rubber, wood and lumber products. The transportation of heavy metals is by runoff water and contaminated water sources. The discharged metals into the wastewater are mostly carcinogen and toxic and lethal to human health [10]. Environmental pollution by pollutants like heavy metals mainly is due to anthropogenic activities [11].

3. Toxicity of Some Heavy Metals

The general mechanism of heavy metals toxicity is considered the generation of reactive oxygen species, causes oxidative damage, and consequently effects on health [12].

3.1. Cadmium

It is one of the most toxic metals mostly produced as a by-product during zinc manufacturing and is absorbed by humans and it is stored inside the body whole life. This metal is inhaled and ingested from the environment, thus causing several serious diseases. It is present in the environment and persists for several years. Plants also absorb this metal from the environment predominantly, which is accumulated in them and disturb the food chain and ultimately affect human life. Due to the high transfer of this metal from soil to plants, fruits and vegetables contain much amount of cadmium. Cadmium is a non-essential toxic metal which influences the cellular enzymatic system, oxidative stress and cause the deficiency of essential nutrients in plants. Cadmium causes a liver disease called hepatotoxicity by bind to cysteine-rich protein such as metallothionein. A complex of cysteine- metallothionein causes hepatotoxicity and then it moves towards the kidney and where it is accumulated in renal tissue causes nephrotoxicity. It also has a tendency to join with glutamate, histamine and aspartate ligands and as a result, iron deficiency occurred [13].

3.2. Chromium

This metal is found in variable oxidation states, hence

shows different geometry shapes as tetrahedral, octahedral, square planar, and distorted shapes. Cement manufacturing units, ore refining industries, automobiles, refractory plants, catalytic converters, and chemical processing units, chrome pigments, and leather tanneries release much amount of chromium in the environment. It has been seen that chromium that has oxidation state +6 is more toxic than the chromium has oxidation state +3. Because hexavalent chromium is more water-soluble and hence causes chronic and acute health effects. The high concentration of chromium will affect and damage liver function, respiratory system, excretory system, digestive system, immune system, and also disturb blood pressure. Ulcer and sensitivity of the skin and many more skin diseases are caused mostly by hexavalent chromium [14].

Chromium is widely used in various industries and thought a serious pollutant in the environment. Recently, found that soil and water are contaminants by chromium. The tetravalent chromium is more toxic than trivalent hence, the toxicity of chromium depends on the valence state. The plant growth and development that is alternation in the germination processes and other effects on the growth of leaves, stems, and roots. It also affects photosynthesis, water, and minerals nutrition [15].

Chromium in the oxidation states from +3 to +6 is the contaminant of drinking water. The animals that take drinking water containing Cr (VI) cause the tumors in the alimentary tract. The DNA is also affected by Cr (VI), forms Cr-DNA adduct as a result of mutation and chromosomal breakage take places [16].

3.3. Arsenic

According to WHO and EPA, the standard concentration of arsenic in drinking water is 10 mg per liter. The main sources of arsenic from natural (Young sediments with low flushing, black shale, geothermal environment and, gold mineralization) and anthropogenic (livestock feed additives, mining activities, arsenic trioxide wastes, stockpiles, and pesticides). Therefore, due to high pH, more than 8.5 the solubility and mobility of arsenic increased [17].

Arsenic oxidation states are trivalent (+3,-3), and pentavalent (+5) hence forms different inorganic and organic complexes, but small numbers occur naturally. The wastes containing arsenic are frequently produced from mining industries. The wood preservatives for example chrome arsenate and copper chrome also are the source of soil contamination as their direct contact with it. In the treatment of halide, arsenic was widely used as pesticides [18].

Arsenic mostly release from the anthropogenic activities and as well as natural sources in the environment. Different autonomous processes that contribute to the contamination of arsenic in the environment are dust storm, pedogenesis, hydrothermal, geothermal, forest fire, and volcanic eruptions. There are more than 200 minerals forms of it naturally occur of which 20% sulfides and sulfosalts and 60% are arsenate and the remaining 20% consisting arsenates, arsenides oxides, and silicates [19].

Groundwater and surface water are mainly contaminated from diffuse and point resources. The arsenic contamination

sources are unprocessed domestic sewage, discharge industries effluents and sewage treatment units. The anthropogenic activities like use and manufacturing of fertilizers, application of pesticides on crops, or naturally contamination of groundwater from arsenic, dissolved salts, fluorides, and geothermal processes are the main reason of diffuse pollution [20].

3.4. Aluminium

It has been seen that Aluminium is a very strong neurotoxicant. It is also observed that Al can cause Alzheimer's disease (AD) [21]. Aluminum concentration in drinking water is associated with Alzheimer's ailment or dialysis encephalopathy [22]. Crapper and Boni in 1980 also observed a relationship between Alzheimer's illness and dialysis encephalopathy from humans [23]. It is seen that kidney dialysis patient caused by dementia when the dialysis solution contained 80 $\mu\text{g/l}$ [24]. was observed the dialysis patients who take high Al may be caught by encephalopathy, and or bone mineralization diseases like dialysis osteodystrophy [22]. Al also interferes with phosphorous and as a result causes weakness, anorexia, and bone pain. Baker and Schofield saw that the OH and F complexes of Al are extremely labile (inorganic) can be more bioavailable and toxic than organic or particulate forms of Al. It has also been proved in Al toxicity studies that positive carrying charge Al hydroxyl species are much more lethal and toxic to fish than that of organic complexes [25].

3.5. Barium

In drinking water, the maximum amount of barium is about one milligram per liter. The extraordinary amount of barium in drinking water does not elevate the blood pressure significantly both in males and females [26]. Cardiovascular problems can be seen in those people who drink water containing a high level of barium as compared to those people who use drinking water containing a low level of barium [27]. The intake of barium has profound effects on human health including the excretory system, metabolic change, and nervous system [28].

3.6. Calcium and Magnesium

Calcium and magnesium are collectively known as the hardness of the water. Their importance is that both these elements are also ingredients of bones and teeth. Their main role in neuromuscular excitability, contractility of muscle and heart, blood coagulation. Calcium deficiency causes blood pressure disease (hypertension), bone breakage (osteoporosis), and osteomalacia. The calcium requirement for adults is from 700 mg to 1000 mg per day. Magnesium mostly acts as a cofactor in many enzymatic reactions like in ATP metabolism, glycolysis, protein synthesis, and nucleic acids, transportation of sodium, potassium, and calcium in the cellular membrane, neuromuscular excitability and muscle contraction, also perform calcium antagonist activity. Magnesium deficiency can also cause different diseases like heart arrhythmia,

hypertension, and vasoconstriction eclampsia disease generally seen in pregnant women, disease of atherosclerotic, type II Mellitus diabetes and bones breakage such as osteoporosis disease is due to the lack of magnesium. The daily requirement of magnesium is 300-400 mg for an adult [29].

Calcium and magnesium levels in water between 24.4 and 42.3 mg/L and breast cancer and gastric cancer were seen in the deviation of permissible limits. It is considered that there is a significant relationship between nitrate amount, drinking water, and stomach cancer tolerance [30]. Many epidemiological researchers have found a very close association between cardiovascular disease, reproductive failure, growth failure, and other problems due to the hardness of the water. The acidity of water also affects the calcium & magnesium reabsorption in the kidney renal tubule. More hardness of water can cause cancer, cardiovascular diseases, central nervous system abnormality, kidneys disease, reproductive system diseases, digestive system problems, bones, and teeth weakness and many other effects can also be observed due to higher drinking water hardness [31].

3.7. Copper

Copper is also a very essential element because it is found in many enzymatic systems. Its high amount of intake has toxic effects [32]. Copper and cholesterol are very important in nutrition and brain function. Both these ingredients are important in Alzheimer's disease etiology. A very minute amount of copper in drinking water has a significant effect on individual learning and memory [33]. Copper is also part of many important enzymes of biological processes. Vitamin E and vitamin C and zinc act against Cu toxicity. Many antioxidants like Beta-carotene, alpha-carotene, and polyphenols also reduce Cu-induced oxidative damage [34].

3.8. Lead

The lead source in the environment mostly from lead-based paint, household dust, food, air, soil, certain types pottery, solder, porcelain, pewter. Lead can accumulate in the human body and may cause kidneys, brain red blood cells related diseases. It is more dangerous for young children and pregnant women. In adults, it can slow down physical development of body and normal mental growth. As in children lead contamination comes from dirt and dust and lead made toys so it is necessary to wash children's hands before taking food. Lead poisoning in drinking water has toxic effects on human health particularly the children are more affected who drink the juices and eat foods formulated by using lead-contaminated water [35].

Lead poisoning in adults by exposure through inhalation in the workplace. In pediatric lead poisoning due to the ingestion of environmental media like paint chips, soil, dust, ceramics, drinking water, and medications. Growing erythrocytes, nervous system and kidneys are affected by the lead poisoning of drinking water [36].

3.9. Mercury

Mercury is contaminated largely in various ecological compartments such as water, soil, and atmosphere.

Mercury bioaccumulation and bio-magnification in the water system food chain and the large concentration were seen among carnivorous fish [37].

4. Conventional Methods for the Treatment Water and Removal of Metals

4.1. Coagulation and Flocculation

Coagulation is the technology used in the treatment of water. During ancient times the coagulation method was used for the clarification of portable water by using different substances. In Egyptian, the river water was purified by using a smeared around the vessel. Alum will also be used in England as a coagulant for water purification. In recent times the coagulation and flocculation processes are used for water clarification. The coagulation method is mostly used for the treatment of water. The flocculation method, as well as the coagulation method, diminishes the intermolecular forces between suspended particles in water. In coagulation, positively charged metals are added that can destabilize and neutralize the charged particles. In coagulation the colloidal particles of 10⁻⁷ to 10⁻¹⁴ cm are targeted. There is a Brownian movement in colloidal particles in the water carrying negatively charged surface hence they repel one another, and form a stable dispersed suspension. On the addition of positive electric charged particles, the neutralization of negative charge takes place. Flocculation is the major collision that binds the destabilized particles together, agglomeration of few colloids occurs and quickly connected together to form micro flocs that appear floc masses. Coagulation in which mostly used salts is an alum, ferric and ferric compounds, lime, polymers cations, anionic and non-ionic polymers. Natural coagulation with aluminum salts mostly used as coagulants in water purification processes [38].

At lower pH, most of the metals are in higher concentration. The optimum pH for chemical coagulation should be more than 9.5 that lowers the concentration of heavy metals in water. Polymers are also used to decrease the concentration of heavy metals from water [39].

4.2. Chemical Precipitation Method

The method for the removal of inorganic effluent used due to its simple operation. In this method, undissolved precipitates of metals hydroxide as phosphate, carbonate, sulfide, and insoluble metal precipitation are obtained by reacting to the soluble metals in the solution and precipitant. When metals form solid precipitants through precipitation then removal of metals from the solution becomes easy. By altering the main parameters such as temperature, pH, ions charges, and initial concentration then the percentage of removal can be improved to the optimum. The simplest

method of precipitation technique used is hydroxide treatment, cost-effective, and ease of self pH control. Many hydroxides are minimized at a pH of 8.0 to 11.0 due to the solubility of different metals in this range [40].

4.3. Reverse Osmosis

Reverse osmosis is the water treatment method used for the purification of water which depends on the membrane development technology as the best recycling process. In this water purification technique, high pressure is applied. Cellulose, polyamide, and polyether-based membranes are used. Membranes are commercially available in different shapes. The coefficient of solutes and free energy between water and membrane is most important. Other parameters like pH, size, and molecular weight of solute and operation are also considerable factor in the treatment of water through reverse osmosis. From this method, the separation of macro and micro levels, ionic, toxic, and non-polar pollutants can be removed from the water.

The efficiency of membranes is about 99% from where TDS, organic compounds, and bacteria can be eliminated from the water. Reverse osmosis water treatment technique used almost in all industries because purified water is utilized in different manufacturing processes and other purposes. This technique is also used for the production of ultra-pure water which is free from bakeries, viruses, and other microbes. Ultra-pure water is used in the field of medicines, pharmacy, and electronic [41].

5. Determination of Metals

Heavy metals are the most important and essential in our daily lives. Further, if the amounts of heavy metals are more than the recommended limit (mentioned by WHO) in water, soil, and air they cause many diseases in the human body. For this reason, monitoring and determination of heavy metals are difficult but so much important. Hence, the assessment of the effect of each metal in human bodies is very necessary. According to WHO, NIOSH, ACGIH, EPA, and clinical chemistry, the estimation and determination of heavy metals like Mn, Zn, Cu, Hg, Cd, and Pb is very important in the human body and environmental matrixes [42].

The physical and chemical parameters analysis of natural water is necessary because water is abundantly used in our daily life. Through water analysis, environmental pollution can be studied. Various classical analytical techniques are used to check the quality of drinking water such as titrimetric, gravimetric, and now modern instrumental techniques like UV-Vis spectrometry, atomic absorption spectrometry (AAS), inductively coupled plasma-mass spectrometry (ICP-MS) [43]. The most accurate and well sensitive techniques of elemental analysis are such as atomic absorption, /emission spectrometry, mass spectrometry, catalytic kinetic methods, and nuclear techniques [11].

5.1. Titrimetric Method

5.1.1. Hardness Determination

The hardness of water is the physical and chemical parameter and calcium and magnesium ions collectively

known as the hardness of water determined by standard method EDTA titration [44]. Oxidizable substances determination in water many methods have been developed like BOD (Biological Oxygen Demand), COD (Chemical Oxygen Demand), TOD (Total Oxygen Demand) and TOC (Total Organic Carbon). These methods differ in their nature particularly in time variation for their performance. For the determination of BOD about 5 days and COD requires 2 hours and the determination of TOC and TOD needs only about 2 minutes [45].

5.1.2. Mercury Determination

An efficient analytical method is applied to directly determine the total concentration of Hg (II) and Hg (I) ions in water. It is experimentally observed that this method provides a low detection limit of 0.05mM and relatively small error within 1.5% ion an ion concentration range of 0.2-50mM. This method exhibiting several advantages, like a simple operation, good reproducibility, and low cost [46].

5.1.3. Chromium and Nickle Determination

A new method for the determination of chromium with a well-known method of Moor as modified by Johnson for the estimation of nickel was made by the discovery of Willard and Cake that boiling perchloric acid would oxidize the compounds of chromium. So, both chromium and nickel can be determined in the same solution [42].

5.2. Atomic Absorption Spectrometry (AAS) Techniques

Atomic absorption spectroscopy used in the determination of many metals in water. The determination of sodium and potassium is carried out by flame emission [47]. Metals ions in water are analyzed using an atomic absorption spectrophotometer. The elements present in the sample are aspirated in flame and atomic vapors are formed. Some of the atoms remain in the ground state and absorb the specific wavelength produced by a hollow cathode lamp specific for each analyzed metal. Metals ions of some metals like cadmium, chromium, copper, aluminum, lead, iron, silver, zinc, lead, and manganese is removed by adsorption or by ion exchange method with the wall of the glass-based container. For the preservation of metals ions high-quality nitric acid is mixed with the sample. To minimize the pH below 2.0 is necessary to avoid the precipitation and adsorption of metals on the walls of the container [48].

5.3. ICP-AES Basic Overview

It is the emission spectrophotometric technique, in which radiations are emitted from excited atoms when they return to their ground state. Each element emits characteristic radiation of a specific wavelength that shows the properties of this element. Higher the concentration of element more will be the intensity of energy emitted from it at a selected wavelength. Thus, the concentration of the element present in a sample can be detected by comparing it with its reference standard concentration. ICP- AES instrument consists of many parts but three components such as peristaltic pump, nebulizer and

spray chamber are considered main parts of the instrument. The sample is pumped into nebulizer with peristaltic pump, and aerosol mist produced by nebulizer. The mist heavy particles are wasted and the finest particles come towards torch assembly. A small amount of sample about 1% of the total sample solution goes to the torch an extra sample is wasted. The sample and mist bearing fine argon particles injected into the plasma. The Ar plasma and the radio frequency-generated maintained a temperature of about 10,000K that is used to excite the electrons. On returning back to the ground state these excited electrons emit radiation that is the property of an element present in a sample. The emitted radiation is passed through the slit by focusing a lens. The high sensitive detectors are used to detect the emitted light of each element. Photomultiplier tube (PMT) mostly used as a detector in ICP-AES. The results are displayed on a computer connected to the instrument. To get better results the spectrometer is flushed with nitrogen gas because it protects the glass parts of instruments from corrosion of atmosphere [49].

6. Conclusion

Drinking water contamination with toxic metals causes a very lethal and toxic effect on human beings. Excess limit of these metals might cause long-lasting or short term health diseases. The trace amount of heavy metals determination in drinking water contamination with toxic metals causes a very lethal and toxic effect on human beings. Excess limit of these metals might cause long-lasting or short term health diseases. The trace amount of heavy metals determination in drinking water is very important can be determined only by using sophisticated analytical techniques. The treatment of groundwater for drinking purposes can be carried out using modern and conventional techniques. The main source of heavy metals in drinking water is anthropogenic activities. To minimize the pollution of drinking water is only possible when pollution generating industries treat their waste before releasing it into the environment.

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