# Chapter 7
# Environmental and Health Effects of Heavy Metals and Their Treatment Methods

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**Abstract** Heavy metals (HMs) are natural constituent that exist in ecosystem and are used for various industrial and economics purposes. Mercury is the naturally occurring heavy metal, mostly use in industries. It is commonly present in the form of elemental mercury, methyl-mercury, and inorganic mercury. The main sources of mercury and cadmium are earth crust, volcanoes, and vaporization from natural water bodies. Mostly mercury is used in producing dental amalgams, thermometer, and some batteries. It can be found in some chemicals, electrical equipment, metal processing, and building industries. Mercury is released into the ecosystem by different ways such as agriculture sources in the form of seed preservation, pharmaceuticals, speeding organic reactions, and in chlorine and caustic soda production. It has also many negative impacts on environment as well as human health.

Mercury and cadmium are the deleterious substances which have indirect role in human chemical and physiochemical processes and do not naturally occur in living bodies. Mercury and cadmium contamination occur in human beings through anthropogenic activities such as municipal and industrial wastewater discharge and through agricultural runoff. Mercury and cadmium produced during metal processing and building industries can cause many health hazards such as blindness, deafness, and digestive problems. Fetal exposure to mercury will causes miscarriages, inborn diseases, and mental retardation.

Mercury is present in an unreactive form in the air. Workers and residents living near the mercury extraction sites have greater chances of exposure. According to the U.S. Environmental Protection Agency, HMs are possible carcinogens. Methyl-

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mercury is made primarily by minute organisms present in water and soil. The current standard of mercury by EPA and WHO for drinking water is 0.002 mg/L, and for industrial effluent, it is 0.001 mg/L.

Removal of HMs from wastewater can be carried out by precipitation, coagulation, ionic exchange, electrochemical operation, and biological treatment, while removal of mercury from drinking water can be done by using coagulation, granulated activated carbon, lime softening, and reserve osmosis. HMs pose serious health issues and also have economic impacts such as decrease in working productivity, increase in health expenditure per person, and increase in mortality and morbidity. Health is the basic right of every human, so strict protective measure should be taken by workers which are mostly exposed to mercury. Hence, major research is needed to further explicate the public health impact associated with human exposure to such toxic metal.

## 7.1 Introduction

Increasing industrialization results in the generation of heavy metals, which causes environmental pollution as a global issue (Usman et al. 2019). Heavy metals are actually elements having atomic number and density greater than 20 and 5 g/cm$^3$, respectively (Ali and Khan 2018). Arsenic (As), lead (Pb), copper (Cu), cadmium (Cd), nickel (Ni), chromium (Cr), and mercury (Hg) are a few examples of heavy metals and are toxic, bioaccumulative, and persistent in nature. They are released into various components of the environment, i.e., water, air, and soil, from various natural and anthropogenic sources like volcanic eruptions, weathering of rocks, mining, industries, domestic, and various agricultural activities (Ali et al. 2019; Usman et al. 2019).

Some heavy metals are known as essential metals as they play a vital role in various biological functions of living organisms and are harmful beyond a certain dose and exposure time. However, nonessential heavy metals are toxic even at a very low concentration. Heavy metals are mutagenic, teratogenic, and carcinogenic, which have serious effects on public health as well as on the environment (Mohamed et al. 2017). They result in the generation of ROS (reactive oxygenic species) and cause oxidative stress. Oxidative stress in living organisms results in the development of various abnormalities and diseases like renal, brain, and neurological disorders (Ali et al. 2019).

Chronic or long-term exposure to heavy metals is a real hazard for the environment and living organisms (Wieczorek-Dąbrowska et al. 2013). The most common routes of chronic exposure of heavy metals to human beings and animals are through inhalation of pollutants, utilization of contaminated food and water, or exposure to contaminated soil and industries (Mohammadi et al. 2019a; Shen et al. 2019). Contamination of various sources of food like vegetables, fruits, fishes, and grains can also occur by the accumulation of heavy metals in them from polluted water and soil sources (Sall et al. 2020). Heavy metals' exposure can result in various diseases in humans like cancers, respiratory, neurological, and kidney problems. For instance, carcinogenic chromium can aggravate skin abrasions, cancer, and respiratory problems (Mohammadi et al. 2019a).

Heavy metals' concentration above the threshold limit not only reduces fertility of soil, but also affects its microbiological balance (Barbieri 2016). Bioaccumulation of heavy metals in biota of various ecosystems has different adverse effects on living organisms (Malik and Maurya 2014).

Many elements are classified into the category of heavy metals, for instance Cr, Ni, Zn, Cu, Pb, As, and Hg, but some are relevant in the environmental context (Barakat 2011). Chromium and copper are among various environmentally toxic heavy metals (Ali et al. 2019), and in the current chapter, our focus is on these two heavy metals.

### 7.1.1 Chromium and Its Oxidation States

French chemist Louis Vauquelin, in 1797, discovered chromium in the mineral crocoite (lead chromate) and named it chromium as its compounds have different colors. Chromium is derived from the Greek word (χρωα) chroma, meaning color. Chromium has the atomic and mass number of 24 and 51.99, respectively. It is present in the IV period and group VI B of the periodic table. The gemstones emerald and ruby contain chromium (chromic oxide) in their structure, so they have green and red colors, respectively. Chromium is the abundant element, i.e., on number 21 on the earth's crust, and is also the sixth most plentiful transition metal (Mohan and Pittman Jr 2006).

Chromium occurs in nature in different oxidation states from −2 to +6 (Tumolo et al. 2020). However, chromium usually exists in water in two main stable oxidation states, i.e., trivalent Cr (III) chromium and hexavalent Cr(VI) chromium, whereas other oxidation states of chromium are unstable in aqueous solution (Honnannavar and Hosamani 2014). Cr (III) has less solubility and mobility and is adsorbed by the soil particles which prevents it to enter into underground water and ultimately stops its uptake by the plants (Haroon et al. 2020).

Cr as Cr (III) is a significant element which helps in the metabolism of lipid and protein (Briki et al. 2017). However, Cr (VI) has high solubility, mobility, and oxidizing power; that's why it is 100 folds more toxic compared to the trivalent chromium and it remains available within the human body for 39 h. Cr (VI) is 1000 times more toxic, cytotoxic, mutagenic, teratogen, and cancer-causing chromium than Cr (III) in living systems (Bansal et al. 2019; Haroon et al. 2016). The United States Environment Protection Agency and International Agency for Research on Cancer classified Cr (VI) as a Group A and Group I carcinogen, respectively, for humans because of its highest toxicity level (Xia et al. 2019). Cr (VI) is included in the list of eigh most toxic chemicals for human beings and has been found commonly as a third hazardous pollutant on the waste dumping sites (Jin et al. 2016). The main focus of Erin Brockovitch, the Hollywood blockbuster movie, is on the toxicity of hexavalent chromium (Saha and Orvig 2010). Cr (VI) toxicity was linked with its oxidizing power; it strongly oxidizes various biomolecules, for instance, protein and DNA (Parlayıcı and Pehlivan 2019). High mutagenic properties of Cr (VI) can trigger the reproductive system and the DNA and can cause several birth defects (Parlayıcı and Pehlivan 2019).

According to EPA guidelines, many countries have the standard limits of Cr (VI), i.e., 0.05 mg $L^{1}$, 0.1 mg $L^{-1}$, and 0.25 mg $L^{-1}$ for drinking water, inland surface water, and industrial effluent, respectively. Cr (VI) is usually present in the form of hydrogen chromate ($HCrO_4$) and dichromate ($Cr_2O_7^{2-}$) anions in acidic conditions and as chromate ($CrO_4^{2-}$) anions in basic media (Jobby et al. 2018). These all Cr (VI) ions are highly soluble and have strong oxidizing property which make them very active in various environmental portions like water and soil (Antoniadis et al. 2018).

Because of the elevated level of Cr (VI) solubility as well as mobility in aqueous solution, it can easily move into various living biota and causes numerous physiological disorders, for example, anemia, diarrhea, nausea, epigastric discomfort, circulatory shutdown, internal hemorrhaging, stomach damage, skin irritation, ulcers, vomiting, lung cancer, and kidney cancer (Jobby et al. 2018).

### *7.1.2 Copper and Its Oxidation States*

Copper (Cu) is the transition element which is placed in the fourth period and group IB of the periodic table (Wuana and Okieimen 2011). It has the atomic and mass number of 29 and 63.546, respectively. Globally, it is the third most used element and is twenty-fifth most abundant constituent of the earth (Karlin and Tyeklár 2012).

There are three main oxidation states of copper, metallic or solid copper having zero oxidation state, i.e., Cu (0), whereas cuprous Cu(I) and cupric Cu (II) ions are other two forms. The most important oxidation state of copper is Cu (II), which is coordinated with six water molecules and is usually encountered in water. Compounds of cupric are of green or blue color and commonly water-soluble. After entering into the environment, Cu (II) binds itself with the various organic and inorganic materials which are present in the water, soil, and sediments depending on the presence of various competing ions, pH, and oxidation-reduction potential of the environment.

## 7.2 Sources of Chromium and Copper

Chromium and copper enter into the environment from both natural and anthropogenic processes (Fig. 7.1). However, its concentration is low, when occurs naturally, and becomes high when released into the environment from industries.

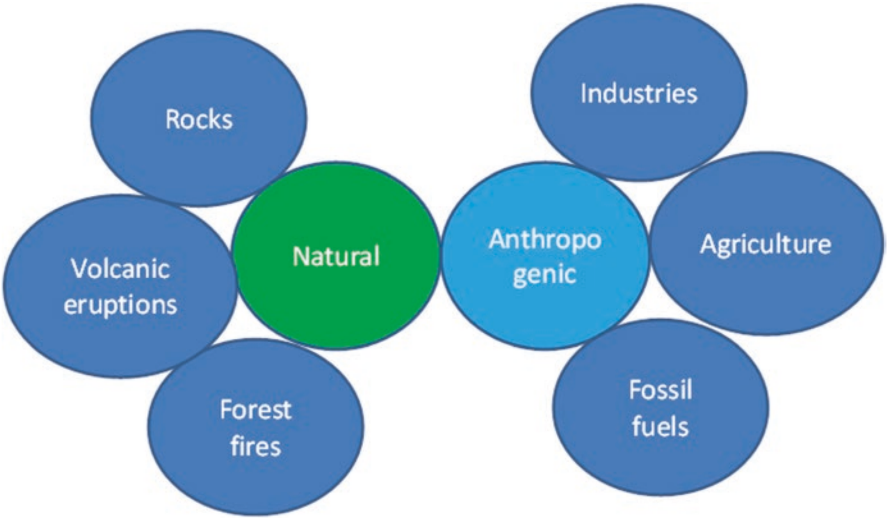

**Fig. 7.1** Different sources of chromium and copper

### *7.2.1 Natural Sources*

Chromium occurs naturally in different types of rocks, minerals, and ores and is released into the environment by its natural degradation, interaction, and reactions. It is the twenty-first largely available element in the rocks, having an average concentration of 100 mg/kg rock. Some examples of natural rocks having chromium are igneous rocks, sedimentary rocks, ultramafic rocks, and felsic rocks (granites). Chromite and a range of spinel-type minerals are a natural source of chromium (Kabata-Pendias and Mukherjee 2007).

Likewise, copper is a reddish-brown element which exists naturally in rocks, sediments, soil, air, and water. Out of total copper, which is present on earth, almost two-third is present in igneous (volcanic) while one-fourth in sedimentary rocks. It is also released through volcanic eruptions, windblown dust, forest fires, decaying of organic material, and sea spray.

### *7.2.2 Anthropogenic Sources*

Man-made activities are the major source of environmental contamination with chromium. Some major sources of chromium are brass, paper and pulp, automobile, fertilizer, steel, textile, metal finishing, chromite ore processing industry, magnetic tapes, wood protection, leather tanning, petroleum distillation, electrical equipment, etc. (Kabata-Pendias and Mukherjee 2007; Mohan and Pittman Jr 2006). These all sources produce a huge quantity of chromium-containing effluents which pollute both surface and groundwater resources. Although chromium can be derived from natural sources, a high amount of it is entering into the environment as a result of industrial activities, like electroplating and leather tanning (Blowes 2002). During chrome tanning process of hides, almost 40% of unused salts of chromium are released in the effluents (Chowdhury et al. 2016). Other important anthropogenic chromium sources are municipal wastes and resultant sludge of municipal waste. Industrial and residential sewage treatment plants also discharge a significant amount of chromium into water bodies. More or less, all chemical laboratories such as research, academic, and industrial releases significant chromium (both trivalent and hexavalent) amount into the environment (Testa et al. 2004).

Vehicles are another contributor of Cr emission into the environment (Ferretti et al. 1995). Incineration, coal, and wood combustion also release 50,000 tons per year of Cr worldwide (Merian 1984). A significant amount of Cr is present in fertilizers (Krüger et al. 2017). According to the International Agency for Research on Cancer (IARC), normally the cigarettes made in the US have 0.24–6.3 mg of Cr per kg. Higher levels of Cr have been found in areas near landfills and hazardous waste disposal sites. House dust and soil also contain Cr (VI) (Shankar and Venkateswarlu 2011).

Copper is also released through various anthropogenic sources, for instance, mining, fossil fuel combustion, solid waste, traffic emissions, and wastewater of various industries like chemicals, paints, fertilizer, fungicides, etc. (Ameh and Sayes 2019). Bulk of copper is mined each year because of its application in different processes, so copper mining itself is a cause of pollution as it involves different steps from mining to milling of copper and is therefore deteriorating the environment.

Another main source of copper release into the environment is through various agricultural practices. Copper in the form of copper sulfate has been known to be used as the first chemical against various plant diseases, whereas other hydroxides and oxychlorides of copper are also used as pesticides, herbicides, fungicide, nematicides, etc. (El-Hak and Mobarak 2019; Iwinski et al. 2017). Phosphate-based fertilizers also contain a large quantity of copper and are a key source of copper in soil. Copper is also used for wood preservation. In North America, greater than 79,000 tons of copper are used annually, which showed a 50% share of the wood preservation in the global market (Anjum et al. 2015). Because of the antimicrobial properties of copper, it also has wide applications in the field of medicines (Anjum et al. 2015).

## 7.3 Environmental Effects of Chromium and Copper

Environmental pollution due to Cr (VI) is attaining more attention as it is present globally with elevated levels in water and soil due to both natural and anthropogenic sources (Ashraf et al. 2017; Brasili et al. 2020). These comprise mining, dyeing, incineration, fertilizers, wood, and paper processing which results in elevation of Cr (VI) in water and soil (Jones et al. 2019; Yang et al. 2020).

Chromium has been reported globally above the permissible limit in water and soil of different countries like Pakistan, China, and India (Bhattacharya et al. 2019; Raza et al. 2017). A number of tanneries (both registered and unregistered) in Pakistan are releasing chromium in their effluent, which ultimately contaminates the environment. Drinking water pollution with a high chromium concentration of 5.50 mg $L^{-1}$ has also been noticed in Sahiwal, Pakistan (Zahir et al. 2015). Increase in chromium concentration in the soil results in the appearance of genetic modification in the plants. Acidification of soil can also affect the utilization of chromium by plants (Hayat et al. 2012). Plant physiology is also affected by Cr (VI), along with reduction in plant growth, chorosis, and necrosis (Haroon et al. 2020). Literature showed that numerous medicinal plants which are grown near industries have accumulated various heavy metals like chromium and copper (Bolan et al. 2017; Kohzadi et al. 2019). Even though Cr (III) is a vital nutrient for humans' metabolism, if its concentration increases from 150 mg $L^{-1}$, it is harmful for the plant physiology (Haroon et al. 2016).

In Mexico (Sonora), almost 43% of drinking water from different sources (storage tanks and wells) showed higher amount of Cd, Cu, As, and Pb (Organization 2018). Elevated levels of Cu, Cd, and Pb have been reported in the drinking water of 10 different cities of Saudi Arabia which is ascribed with Kuwaiti and the Gulf War oil fires (Chowdhury et al. 2016). Another report of ten years in rural regions of India indicated the high values (above WHO values) for As, Cr, Mn, Pb, Zn, and Ni in groundwater, which was associated with the pharmaceutical, pesticide, paint, and fertilizer industries (Bajwa et al. 2017; Chowdhury et al. 2016). Wastewater from industries pollutes the nearby water bodies. Coal combustion in industries is the key source of air pollution, as coal contains trace amounts of chromium, while dumping of resultant chromium-containing solid waste will result in elevated concentration of chromium in air and soil, respectively. In contrast, globally, the release of chromium in soil, water, and air is 896, 142, and 30 thousand metric tons per year, respectively (Mohan and Pittman Jr 2006).

Copper is a vital micronutrient for different biotic components of the environment (Zitoun 2019), but a high level of copper can also result in environmental pollution. It is known as a priority pollutant as reported by US-EPA and is normally present in various water bodies (Sruthi et al. 2018). Copper speciation in the water bodies is actually responsible for the toxicity of copper (Tait et al. 2018). Cu has attained great consideration because of its dual effect towards plants, i.e., at optimum amount, it is essential, whereas it becomes toxic at higher concentrations (Ameh and Sayes 2019). Copper is among the eight important micronutrients which are needed for the growth of plants (Nazir et al. 2019) and is also linked with several physiological as well as biochemical processes (Garcia et al. 2014). Copper is a part of the structures of various regulatory proteins (enzymes) and helps in protein synthesis, respiration of mitochondria, metabolism of cell wall, photosynthetic electron transport, oxidative stress response, and hormone signaling (Nazir et al. 2019; Zhang et al. 2019). Plastocyanin (an electron carrier proteins) also contains a large amount (50%) of the copper inside the plastids (Zhang et al. 2019). Copper has the ability to easily gain and lose electrons; therefore, it acts as a cofactor in various enzymes like laccase, polyphenol oxidase, and amino oxidase and plays an important role of antioxidants under conditions of stress (Nazir et al. 2019; Zhang et al. 2019).

On the other hand, exposure to excess copper by the plants will affect various bio-physiochemical processes (Ameh and Sayes 2019; Jaime-Pérez et al. 2019) and will result in oxidative stress along with alterations in RNA and DNA (Ameh and Sayes 2019; Jaime-Pérez et al. 2019). 20–30 mg $kg^{-1}$ is the toxic range of copper for plants (Marschner 2011). Excess uptake of Cu can affect photosynthesis, enzymatic activity, respiration, and growth of plant (Lillo et al. 2019; Zhang et al. 2019). Various visual symptoms of excess copper content in plants are chlorosis, nutrient deficiency, necrosis, reduced growth of shoots and roots, and even death in severe toxic conditions (Zhang et al. 2019).

In the soil of the USA, the threshold limit of copper for crops plantation is 100 mg $kg^{-1}$ (Kabata-Pendias 2010). As copper has high density, so its mobility in soil is less and it mostly accumulates in topsoil (Araújo et al. 2019; Ju et al. 2019). About 80% of copper is present in soil as sulfides and oxides, which are not soluble and have low phytoavailability (Mihaljevič et al. 2019). However, some Cu (20%) is present as carbonates and hydroxyl compounds in soil and is mostly available to the plants in this form. Copper in $Cu^{2+}$ form is generally absorbed by plants because of its strong binding ability with organic materials than other species of copper (Ogunkunle et al. 2019). The presence of a higher amount of copper in soil reduces crop production and ultimately threatens the health of humans (Rizwan et al. 2016). Another source of environmental pollution is the release of inorganic Cu into the atmosphere in the form of particulate matter, mist, and dust particles (Fang et al. 2011). High concentration of copper has been found in the river (Nyam-wamba) near the copper mine of Kilembe, Western Uganda. Another study showed a high copper level of 15.01 mg/L in both ground and surface water at 33 places, which are located near mines of copper at Malanjhkhand in India. Cu's highest concentration, i.e., 2.8 mg/L, was reported in well water of Pothi Bala (AJ&K) (Javaid et al. 2008). The permissible Cu concentration in the case of soil on which application of sewage sludge is carried out is 50–140 mg/kg as per European Standards (Radojevic and Bashkin 2006). Different regions of Pakistan revealed the copper range of <6–412 mg/kg in both dust and soil, whereas the highest content of copper was reported in contaminated soil of the Kohistan region (Muhammad et al. 2011). The industrial area of Islamabad (Pakistan) also showed elevated copper concentration level, from 8.88 to 357.40 mg/kg (Malik et al. 2010). A high concentration of copper was found in the sediments of Malir River (Karachi, Pakistan), i.e., 272 mg/kg, and River Ravi (Punjab, Pakistan), i.e., 159.79 mg/kg (Abdul et al. 2009; Siddique et al. 2009). Elevated range of copper (09–75 mg/kg) was reported in different vegetables grown in Gillgit (Northern Pakistan) (Khan et al. 2010). The mentioned values here are alarming as the allowable intake value for copper is 10 mg per day. The maximum amount of Cu reported in Chile, Hong Kong, India, Nigeria, and the USA was 1.2 mg/L, 4.6 mg/L, 1.9 mg/L (Xu et al. 2006), 0.01 mg/L (Olalekan et al. 2018), and 4.8 mg/L, respectively (Zahoorullah and Zai 2003).

## 7.4 Health Effects of Chromium and Copper

On the basis of time of exposure, toxicity can be defined as acute and chronic. Acute toxicity is displayed within a short time due to the short-term single exposure of a few minutes or several days with the toxic substance like heavy metals and is used to indicate a hazardous event or toxic properties of a substance. However, chronic or toxic effects (toxicity) are defined as sub-lethal effects due to the prolonged exposure generally to a small quantity of toxic substances.

Public health concerns in the case of chromium are mainly related to the Cr (VI), due to its toxic properties on animals, microorganisms, plants, and humans (Alemayehu et al. 2011). The human health risks depend on dosage, exposure level, and time duration of Cr (VI). Chromium enters into the body of living organisms through either food or water, whereas acute and chronic effects include neurological, cardiovascular, renal, hematological, gastrointestinal, hepatic, and even death. A long-term and continuative exposure, i.e., occupational exposure, to even low amount of chromium, can affect the blood, skin, immune, and respiratory system (Zhang et al. 2014). Nonoccupational exposure includes cigarette smoke, contaminated water, air, and food (Shankar and Venkateswarlu 2011). Workers in a German chrome ore industry developed lung cancer. Numerous studies also confirmed elevated level of cancers (lung and nose) in people exposed to different Cr processing industries (Shankar and Venkateswarlu 2011).

The genotoxicity effect of chromium at cell level results in the damage of DNA, oxidative stress, and development of the tumor (Wise et al. 2019). According to USEPA (United States Environmental Protection Agency), Cr(VI) is listed among seventeen hazardous metalloids and metals that are risky to the health of humans. Moreover, exposure to Cr (VI) by other living things like animals and plants also results in severe health issues in them (Jobby et al. 2018).

In order to protect environmental health, the recommended maximum permissible limit of Cr is 64 mg per kg (Shahid et al. 2017). Literature revealed the elevated levels of various heavy metals including Cr in the blood of welders who are occupationally exposed to the fumes of welding and also displayed more oxidative stress than control group (Mahmood et al. 2015). Similarly, welders working in the stainless steel industry are exposed to the Cr (VI) and have high risk of pharynx and larynx cancer (Gustavsson et al. 1998). Another study in Lahore, Pakistan, reported higher amount of Cr, Pb, and Cd in cancer and diabetic patients (Shafique et al. 2011).

Cr analysis in groundwater catchment of Luan River (China) indicated 2.074 hazard value for people living in the surroundings of the study area, which is greater than the permissible value (1) and $3.99 \times 10^{-5}$ was the average carcinogenic risk value for studied metal of Cr (Liu and Ma 2020). Literature revealed the highest cancer risks ($6.54 \times 10^{-3}$) probability in public of Khorramabad, Iran, through drinking water contaminated with chromium (Mohammadi et al. 2019b). Cr (VI) was also reported in the ground (1.35 mg $L^{-1}$) and surface water (0.027–2.48 mg $L^{-1}$) of India in Odisha state of the Sukinda area. The cancer risk due to Cr contaminated water in children and adults was $1.05 \times 10^{-3}$ and $1.21 \times 10^{-3}$, respectively, while the oral hazard index was 1.64 and 1.90 times higher in children and adults, respectively (Naz et al. 2016). Generally, chromium does not accumulate in the body of fish, but when a large amount of chromium enters into surface water it can affect fish gills. In the case of animals, chromium can weaken the immune system and cause respiratory difficulties, genetic disorders, infertility, and development of tumors. Chronic exposure of chromium in humans can result in skin lesions and causes various respiratory diseases even cancer of broncho pulmonary (Ahmad et al. 2012).

Copper is an important element for living organisms, but in excess amount it has many negative effects on plants, animals, and humans (Zhou et al. 2018). Daily intake of copper occurs through diet, i.e., 75% and 25% through food and drinking water, respectively (Brewer 2015). Copper is mainly present as organic cuprous ($Cu^+$) form in solid food (Ceko et al. 2014) and as inorganic cupric ($Cu^{2+}$) form in drinking water. The $Cu^{2+}$ is toxic and carcinogenic when used in excess amount through ingestion. The excessive consumption of $Cu^{2+}$ will result in its liver deposition following vomiting, abdominal pain, headache, liver failure, etc. (Akar et al. 2009).

The average intake of Cu from drinking water is in the range of 0.1–1 mg per day. The permissible limit of $Cu^{2+}$ for industrial effluent is 1.3 mg/L by US, EPA (Shawabkeh et al. 2004), whereas for drinking water the allowable limit of $Cu^{2+}$ is 1.5 mg/L as recommended by WHO (Organization 2018). The acute effects of copper intake in humans include various gastrointestinal symptoms, for example, abdominal pain and nausea (Taylor et al. 2020). The RfD (oral) value of 0.04 mg Cu/kg/day is protective for children and adults of any acute or chronic toxicity (Taylor et al. 2020). It is reported that excess amount of copper in drinking water has caused pink disease (toxic syndrome) in infants (Thornton 1983). However, another disease (chronic) due to the excess use of copper is hepatolenticular degeneration, also known as Wilson's disease, which damages various body organs of a person and will result in death (santé et al. 2004).

Another occupational hazard of copper intake through aerosol is the vineyard sprayer's lung disease (Todd et al. 1934). Exposure to a large amount of copper for a long time will result in a high percentage of copper in tissues and serum, which affects the immune system and leads to oxidative stress (Turnlund et al. 2004). If excess of copper is present in freshwater bodies, then it will impair the osmoregulatory mechanism of aquatic organisms (Lee et al. 2010).

Copper piping network is mostly used in homes and public supply of drinking water which is the main source of copper exposure to people (Uauy et al. 2008). Cases of liver cirrhosis were reported in various regions of India in some young children, when they used milk which was stored in the copper containers (Nayak and Chitale 2013; Uauy et al. 2008).

## 7.5 Treatment Methods for Hexavalent Chromium and Copper Removal

### *7.5.1 Physicochemical Methods*

#### 7.5.1.1 Adsorption of Chromium and Copper

Adsorption is considered an effective method for the removal of heavy metals. It is an economical method capable of removing heavy metals at very low concentration (Ali 2012). During adsorption, soluble gases and liquids attach onto the surface of adsorbents. The adsorbents used for the removal of heavy metals include activated carbon (Sountharajah et al. 2015), fly ash (Weng and Huang 2004), modified chitosan (Justi et al. 2005), landfill clay (Ghorbel-Abid and Trabelsi-Ayadi 2015), peat (Ho and McKay 1999), and manganese oxides (Kim et al. 2013).

Adsorption can be divided into two main types, i.e., physisorption and chemisorption. In physisorption, van der Waals force is responsible for the attachment of pollutant and adsorbent. On the other hand, chemisorption occurs as a result of chemical bonding between adsorbent and adsorbate. Adsorption capacity of the adsorbents depends upon the characteristic of adsorbent surface. For example, surface charge, surface area, and functional groups on the adsorbent can have different removal efficiencies for different pollutants.

Several studies have been focusing on the removal of hexavalent chromium using natural (Enniya et al. 2018), synthetic (Huang et al. 2015), waste (Valentín-Reyes et al. 2019), and composite materials (Geng et al. 2019; Vakili et al. 2018). A wide variety of adsorbents can be used for the treatment, such as activated carbon (Valentín-Reyes et al. 2019), carbon nanotubes (Huang et al. 2015), chitosan (Vakili et al. 2018), graphene oxide (Geng et al. 2019), apple peels, etc. (Enniya et al. 2018). Recent studies on chromium removal are shown in Table 7.1.

The Fourier Transform Infrared (FTIR) results before and after Cr (VI) adsorption suggest that band stretching of C = O, C-O-C, C = C, and C≡C groups was involved for the binding of Cr (VI) (Enniya et al. 2018). The nitrate, amine, and amide groups can also be involved in the binding process (Geng et al. 2019). Other mechanisms involved chelation, electrostatic interaction, and reduction (Geng et al. 2019; Vakili et al. 2018). Several studies focused on the reduction of Cr (VI) to Cr (III) besides adsorption, as 50% reduction was observed on modified activated carbon (Valentín-Reyes et al. 2019).

Several factors might affect the removal efficiency of the Cr (VI). Mostly, the highest adsorption occurs at acidic pH 2.0 (Enniya et al. 2018; Geng et al. 2019; Haroon et al. 2017; Vakili et al. 2018), with adsorption capacity ranging from 39 to 436.2 mg/g. It fits best with Freundlish isotherm, follows pseudo-second-order kinetics, and is spontaneous and endothermic reaction (Enniya et al. 2018; Huang et al. 2015). The Langmuir isotherm is also reported (Huang et al. 2015), while Geng et al. reported that Cr (VI) adsorption initially followed pseudo-second-order and at the end it became multistep influence (Geng et al. 2019). This suggests that Cr (VI) adsorption is highly dependent on the type of adsorbent used.

**Table 7.1** Technologies used for chromium removal

| S. no. | Method | Types | Mechanism | Removal effficiency (%) | Adsorption capacity (mg $g^{-1}$) | Medium | References |
|---|---|---|---|---|---|---|---|
| 01 | Adsorption | Activated carbon, graphene oxide, apple peel, | Chelation, reduction, binding with acid components, etc. | 99 | 39–436 | Aqueous | Enniya et al. (2018), Geng et al. (2019), Huang et al. (2015), Vakili et al. (2018), and Valentín-Reyes et al. (2019) |
| 02 | Electrocoagulation | Use of iron, aluminum, copper as electrodes. | Charge neutralization, aggregate formation, and reduction to Cr (III) | 88–100 | – | Aqueous | Arroyo et al. (2009), Khan et al. (2019), Mahmad et al. (2016), Pan et al. (2017), and Pikna et al. (2020) |
| 03 | Membrane filtration | Microfiltration | Cr (VI) aggregation by micelle, coagulation, etc. and size-based separation. | 99.6 | – | Aqueous | Doke and Yadav (2014), Liu et al. (2020), Vasanth et al. (2012), and Visvanathan et al. (1989) |
| | | Ultrafiltration | Cr (VI) size enhancement and size-based separation. | 90–100 | – | Aqueous | Aliane et al. (2001), Aroua et al. (2007), Ghosh and Bhattacharya (2006), and Muthumareeswaran et al. (2017) |
| | | Nanofiltration | Selective removal of divalent and larger ions and particles. | 80–99.8 | – | Aqueous | Mnif et al. (2017), Wei et al. (2019), and Zolfaghari and Kargar (2019) |
| | | Reverse Osmosis | Selective rejection of monovalent and larger ions. | 99 | – | Aqueous | Gaikwad and Balomajumder (2017) and Piedra et al. (2015) |
| 04 | Ion exchange | Anion exchange | Adsorption or binding with functional groups on ion exchange resins. | 97–100 | 236–277 | Aqueous | El-Mehalmey et al. (2018), Meshram et al. (2018), Rapti et al. (2016), and Xie et al. (2019) |
| 05 | Bioremediation | Fungi | Reduction of Cr (VI) to Cr (III) and bioaccumulation. | 89–99.4 | 2.12–4.9 | Aqueous | bibi et al. (2018) and Kumar and Dwivedi (2019a, b) |
| | | Bacteria | Reduction using chromate reductase enzyme. | 92–100 | – | Aqueous | Baldiris et al. (2018), Hossan et al. (2020), Tariq et al. (2019), and Tharannum (2020) |

Different studies on copper removal are shown in Table 7.2. In a study, chitosan was modified with ethylenediaminetetra-acetic acid (CS-EDTA) and was used for copper removal from aqueous solution. The adsorption capacity of CS-EDTA was also compared with chitin and chitosan. The adsorption capacity of CS-EDTA for copper was maximum, i.e., 58. 67 and 110 mg $g^{-1}$. The adsorption kinetics was best fit to pseudo-second-order (Labidi et al. 2016). In another study, sulfur microparticles were synthesized by using facile method. These microparticles were used for the removal of copper from aqueous solution of ethanol. Sigmoidal kinetic mode best explained the adsorption process. Sulfur microparticles caused physical adsorption (Xie et al. 2017). Batool et al. (2017) removed copper from water using low-cost farmyard and poultry manure-derived biochars. Both types of biochars efficiently removed copper from water. The adsorption capacity of farmyard-based biochar was maximum (44.50 mg/g). Chemisorption was observed during that study (Batool et al. 2017). Anbinder et al. 2019, studied the structural mechanism involved in the adsorption of copper. The interaction between copper and chitosan matices was through $NH_2$ groups in a pendant fashion. In the case of chromium, the adsorption was due to azanide and OH functional groups (Anbinder et al. 2019). Dong et al. (2019) recently removed copper ions from aqueous solution by using modified wheat straw. The wheat straw was modified with polyethylenimine (PEI) by using epichlorohydrin (ECH) as grafting agent. The mechanism behind this adsorption was coordination. The adsorption capacity of modified wheat straw was 48.6 mg/g. The copper adsorbed wheat straw was also regenerated by using 0.1 molar HCl solution (Dong et al. 2019).

#### 7.5.1.2 Electrocoagulation-Based Chromium and Copper Removal

Electrocoagulation (EC) is the electrochemical process which generates metal ions. These metal ions destabilize the pollutants by neutralizing the electric charge on them. The charged metal ions with the oppositely charged pollutants form flocs. EC process is very effective for the removal of pollutants. This process produces little amount of sludge, there is no chemical requirements, and its operation is simple (Rajeshwar and Ibanez 1997).

Electrochemical process mechanism in an aqueous solution is very complex (Lin et al. 1998). There are three most commonly involved mechanisms during the electrochemical process, i.e., electrocoagulation (EC), electrooxidation (EO), and electroflotation (EF). EC process results in the destabilization of pollutants by the production of electric current. During the EC process, metals and metal hydroxide cations are used. EO process breaks down organic pollutants into carbon dioxide, water, and other oxides by oxidation. EF, on the other hand, produces hydrogen and oxygen gas bubbles which carry the pollutants to the surface. Other possible mechanisms during electrocoagulation are sorption and coagulation (Malkin 2003).

The electrocoagulation is a simple electrochemical process relying on the flow of current through electrodes (usually Iron or Aluminum) which dissociates in the solution to neutralize the Cr(VI). Compared to aluminum anodes, the iron anodes

**Table 7.2** Technologies used for copper removal

| Method | Types | Mechanism | Removal efficiency (%) | Adsorption capacity (mg $g^{-1}$) | Medium | References |
|---|---|---|---|---|---|---|
| Adsorption | Chitosan- ethylenediaminetetra-acetic acid (CS-EDTA) | Pseudo-second-order | – | 58. 67 and 110 | Aqueous | Labidi et al. (2016) |
| | Sulfur microparticles | Mass transfer, coordination and physical adsorption | – | – | Ethanol-aqueous solution | Xie et al. (2017) |
| | Farmyard and poultry manure-based biochars | Multilayer sorption, chemical interaction | – | 44.50 | Water | Batool et al. (2017) |
| | Chitosan matrix | Amino groups in a pendant fashion | – | – | Aqueous | Anbinder et al. (2019) |
| | Wheat straw (WS) was modified by polyethylenimine (PEI) | Coordination | – | 48.6 | Aqueous | Dong et al. (2019) |
| Electrocoagulation | Mucilage of Opuntia ficus indica (OFI) | Electrochemical production of metal ions and buoyant gas bubbles | 100 | – | Water | Adjeroud et al. (2018) |
| | New cell design | Electrochemical production of metal ions | 98 | – | Copper plating plant Effluents | Kilany et al. (2020) |
| | Electro-Fenton and electrocoagulation | Oxidation, electrochemical production of metal ions | – | – | Wastewater | Guan et al. (2018) |
| | Photovoltaic Electrocoagulation | Electrochemical production of metal ions | 99.01 | – | Aqueous solution | Thanh et al. (2019) |

| Method | Types | Mechanism | Removal efficiency (%) | Adsorption capacity (mg $g^{-1}$) | Medium | References |
|---|---|---|---|---|---|---|
| Ion exchange | Polymeric submicron ion exchange resins | Solid phase ions shared with equal ion numbers from contaminated water | 46 | – | River water | Murray and Örmeci (2019) |
| | Amberlite IRC-86 | Solid phase ions shared with equal ion numbers from contaminated water | 78.9 | – | Bioleached wastewater | Choi et al. (2020) |
| | Chelating resins | Solid phase ions shared with equal ion numbers from contaminated water | – | 167 | Synthetic effluents | Edebali and Pehlivan (2016) |
| | Phosphorylated fullerene/ sulfonated polyvinyl alcohol (PFSP) cation exchange membrane | Solid phase ions shared with equal ion numbers from contaminated water | 73.2 | 1.67 | Wastewater | Rikame et al. (2017) |
| | Hydrophilic nanoporous ion exchange barrier membrane, | Stripping | 100 | – | Aqueous solution | Song et al. (2018) |

(continued)

**Table 7.2** (continued)

| Method | Types | Mechanism | Removal efficiency (%) | Adsorption capacity (mg $g^{-1}$) | Medium | References |
|---|---|---|---|---|---|---|
| Membrane filtration | PEI-based nanofiltration membranes | The membrane structure acts as a selective barrier that allows movement of molecules to pass through with the help of a driving force producing large residual volumes | 86 | – | Wastewater | Bandehali et al. (2019) |
| | Reusable novel membranes | Bacterial cellulose (BC) nanofibril network as a template and chitosan (Ch) as the active phase | 50 | – | Wastewaters | Urbina et al. (2018) |
| | Modified cellulose acetate ultrafiltration membranes | Increases the available sites in the modified membranes | 99.1 | – | Synthetic wastewater | Kanagaraj et al. (2020) |
| | Novel membranes based on polyethersulfone (PES) | Increases the available sites in the nanocomposite membranes | 90 | – | Water | Rafieian et al. (2019) |
| | Electrospun nanofiber membrane | Pseudo-second-order, Langmuir-type adsorption | – | 120.77 | Industrial wastewater | Chen et al. (2018) |

| Method | Types | Mechanism | Removal efficiency (%) | Adsorption capacity (mg $g^{-1}$) | Medium | References |
|---|---|---|---|---|---|---|
| Bioremediation | *Myriophyllum aquaticum* | Metabolism by the plants and biodegradation by rhizosphere microorganisms | – | – | Wastewater | Guo et al. (2020) |
| | Aquatic plant species | Metabolism by the plants | – | 63.1 mg/kg | Synthetic wastewater | Lu et al. (2018) |
| | *Pistia stratiotes* | First-order elimination kinetics | 96.38 | – | Surface and distilled water | Tang et al. (2020) |
| | *Limnocharis flava* | 1st order, Rate Law model | 39.9 | – | Distilled, mineral, and surface water | Alikasturi et al. (2019) |
| | *Pseudomonas stutzeri* LA3 | Breaking complex pollutants into simpler form | 50 | – | LB broth | Palanivel et al. (2020) |
| | *Escherichia coli* | Adsorption | 91.5 | – | Aqueous solutions | Wang et al. (2019) |

are preferred due to their higher removal efficiency and affinity for Cr(VI) (Pikna et al. 2020). This is an efficient method for recovering Cr(VI) in solid form. The method has been applied on several types of wastewaters and aqueous media such as leachate (Arroyo et al. 2009; Mahmad et al. 2016).

The mechanism of electrocoagulation depends on the generation of coagulant from the anodes due to oxidation, destabilizing contaminants, breaking of emulsions, particulate suspension, and forming flocks by aggregating destabilized phases (Arroyo et al. 2009). The iron (II) gets oxidized into iron (III) besides Cr (VI) into Cr (III) and forms oxides of iron with chromium (Pan et al. 2017). Usually, Cr (VI) can be recovered as precipitates in the EC process in the form of oxides of iron and Cr (VI) with 20% Cr by weight. The solid precipitates are mainly chromite ($FeCr_2O_4$) or their hydroxides or $Cr_2O_3$, $Fe2O_3$, $FeCr_2O_4$ mixtures (Arroyo et al. 2009; Pikna et al. 2020).

The parameters affecting the EC process are pH, current, and electrolyte concentration. Pikna et al. (2020) optimized Cr (VI) recovery from four steel slag leachates in 140–430 min, pH 6.0, and 0.1–0.5 A to completely remove 1 g/L of Cr (VI) (Pikna et al. 2020). Khan et al. reported a 100% removal efficiency at 1.48 A current, pH 3.0, and process time of 21.47 min (Khan et al. 2019). The iron-based anodes have superior removal efficiency at pH 7.0, while aluminum electrode is active at acidic pH (3.0) with comparatively lower removal efficiencies (Mahmad et al. 2016).

The cost effectiveness of this process should be considered as it is an energy-consuming process. The pH and electrolyte concentrations are very important in energy efficiency of EC process as pH 6.0 is efficient and higher pH (8.0) can consume more current. In contrast, low electrolytes (1000 mg/L NaCl) consume more current compared to higher electrolytes (50,000 mg/L NaCl) (Pikna et al. 2020). The energy consumed per gram Cr (VI) removed is 12.97–Watt/hour during an EC process (Khan et al. 2019).

Electrocoagulation-electroflotation (EC-EF) process was used for the removal of copper from water by using *Opuntia ficus indica* (OFI) plant mucilage. The OFI mucilage removed copper completely. Mucilage also increased the sludge settling rate. OFI mucilage which is found to be an active natural coagulant can be used for copper removal instead of chemical coagulants (Adjeroud et al. 2018). Kilany et al. 2020, developed a new electrocoagulation reactor. In a new design, a helical tube anode was placed between two (vertical cylindrical screen) cathodes. The new reactor was used for both oil and Cu removal from electroplating plant effluent. Under optimum conditions, copper and oil removal was 98% and 85%, respectively (Kilany et al. 2020). Guan et al. (2018) designed electrochemical reactor for Cu-EDTA degradation. In electrochemical reactor electro-Fenton and electrocoagulation process were used. During Electro-Fenton process, •OH radicals were generated which were responsible for Cu-EDTA destruction which releases copper ions. These copper ions were removed by using the electrocoagulation process (Guan et al. 2018). A solar photovoltaic cell (PV) was used as renewable energy source for the electrocoagulation process. This process was highly efficient for copper removal

(99.01%) and energy saving (1.039 kWh/m$^3$). The use of PV system with electrocoagulation process can make it a sustainable process (Thanh et al. 2019).

#### 7.5.1.3 Membrane Filtration-Based Chromium and Copper Removal

Membrane filtration technologies are broadly divided into five major processes, i.e., microfiltration (MF), nanofiltration (NF), ultrafiltration (UF), reverse osmosis (RO), and electrodialysis (ED). The major difference in these technologies includes pore size, permeability, and operating pressure (Murthy and Chaudhari 2009). The main advantages of membrane technologies include high efficiency, complete removal of pollutants, and sometimes they consume less energy than thconventional methods (Farno et al. 2014; Marjani et al. 2012; Rezakazemi et al. 2013a; Rezakazemi et al. 2015). Due to the above-mentioned advantages, this technology was used for the removal of heavy metals from different industries wastewater (Baheri et al. 2015; Rezakazemi et al. 2012, 2013b).

Due to the simple separation mechanism of membrane technologies, they are widely used for treatment of water and wastewater (Murthy and Chaudhari 2009; Padaki et al. 2015). This separation mechanism is same for almost all membrane processes with minor exceptions. The rejection of pollutants is due to higher transmembrane pressure (Sutherland 2008). The separation of pollutants takes place with the help of semipermeable membrane. This semipermeable membrane blocks the passage of pollutants through the membrane (Sutherland 2008; Van der Bruggen and Vandecasteele 2003).

Microfiltration and ultrafiltration cannot remove dissolved Cr (VI) due to larger pore size. The removal can be enhanced by prefiltration aggregation of the Cr (VI) by various means. A surfactant-based separation process utilized the use of cetylpyridinium chloride (CPC) to create Cr (VI) micelle that further passed through titanium-based microfiltration membrane with 99% removal (Doke and Yadav 2014). Precipitating Cr (VI) into hydroxides with electric field across the microfiltration membrane reduced the membrane fouling besides removing Cr (VI) (Visvanathan et al. 1989). Similarly, biomass-assisted ceramic membrane microfiltration using baker's yeast removed 94% of 100 mg-Cr (VI)/L (Vasanth et al. 2012). A composite polyacrylonitrile electrospun membrane was effectively removing Cr (VI) and Cd (II) with nanoparticles having 90% regeneration ability (Liu et al. 2020).

A similar method can be applied for Cr (VI) removal by ultrafiltration. The polymer-enhanced ultrafiltration using chitosan, polyethyleneimine, and pectin was used to remove 100% Cr (VI) (Aroua et al. 2007). A micelle-enhanced ultrafiltration using cetyl pyridinium chloride (CPC) as surfactant was good for low concentration feed, but pressure started increasing when the concentration was increased upto 50 mM (Ghosh and Bhattacharya 2006). An indigenously prepared hydrolyzed polyacrylonitrile membrane effectively rejected 90% of $\leq$25 mg Cr (VI)/L at neutral pH in drinking water (Muthumareeswaran et al. 2017). Water-soluble macroligand formed complexation with Cr (VI) before ultrafiltration to achieve 95% removal efficiency (Aliane et al. 2001).

Nanofiltration is highly suited for the divalent ion removal from water. Zolfaghari and Kargar (2019), optimized the membrane filtration containing microfiltration and nanofiltration as: pH 10.0, pressure: 0.1 MPa pressure, 0.1 mg-Cr (VI)/L, and 500 mg-sulfate/L to achieve 99.8% removal (Zolfaghari and Kargar 2019). Nanofiltration membrane with enhanced negative charges showed comparatively better Cr (VI) and sulfate rejection (80%) at pH 7 than the positively charged membrane at similar permeance of 11.5 L $m^{-2}$ $h^{-1}$ $bar^{-1}$ (Wei et al. 2019). Similarly, 99.7% Cr (VI) rejection was obtained using commercial nanofiltration membrane on shock absorber manufacturing wastewater (Mnif et al. 2017).

Reverse osmosis (RO) membrane selectively removes monovalent ions and utilizes the semipermeable membrane that only allows water molecules to pass under high pressure. A near 100% removal efficiency of 228 mgCr(VI)/L was reported with a polyamide reverse osmosis membrane with 30 bar pressure, 29% flux, and 95% water recovery (Piedra et al. 2015). The flat sheet polyamide RO membrane simultaneously rejected 99.7% of 5 mg/L fluoride and Cr (VI) with at 16 bar pressure and pH 8.0 (Gaikwad and Balomajumder 2017).

Bandehali et al. (2019) removed lead and copper from wastewater using modified PEI-based nanofiltration membrane. The water flux of modified membrane was higher than the PEI membrane. The lead and copper rejection of modified membrane was 85 and 86%, respectively. The lead and copper removal of this membrane was better than other membranes reported in the literature (Bandehali et al. 2019). A novel membrane using *in situ* and *ex situ* route was developed by Urbina et al. (2018) for the removal of copper from wastewater. Bacterial cellulose and chitosan were the main components of these novel membranes. The highest removal of copper was achieved with the membranes synthesiszed by using *in situ* biosynthesis. These novel membranes are easy to clean and can also be reused (Urbina et al. 2018). Recently Kanagaraj et al. 2020, used phase inversion technique for the development of a modified cellulose acetate (CA) membrane for the removal of humic acid and copper. The maximum humic acid and copper rejection was 98.5 and 99.1%, respectively. The newly developed membrane also had higher flux rate and hydrophilicity. The modified CA membrane also had better anti-fouling property (Kanagaraj et al. 2020). In a novel membrane, polyethersulfone (PES) and amine-functionalized cellulose nanocrystals (CNC) were used for Cu and dye removal from water. The surface of CNC was further modified with the help of triethoxysilane. The modified membrane was able to enhance the removal of copper and dye to 90 and 99%, respectively. The modified membrane had been found as simple and highly efficient technique for pollutants' removal (Rafieian et al. 2019). Chen et al. (2018) removed copper from wastewater by using electrospun nanofiber membrane. The maximum adsorption capacity of this membrane for copper was 120.77 mg/g. The membrane was able to prevent adsorbents' loss and aggregation. The mechanism behind copper removal followed Langmuir-type adsorption (Chen et al. 2018).

#### 7.5.1.4 Ion Exchange-Based Chromium and Copper Removal

Ion exchange results in the interchange of ions between liquid and solid phases (Kurniawan et al. 2006). During the ion exchange process, resins remove ions from electrolytic solution and replace other ions of the same concentration. There is no structural change of resins (Rengaraj et al. 2001; Vigneswaran et al. 2005). There is also recovery of heavy metals from inorganic compounds existing in the wastewater (Daṃbrowski et al. 2004). Ion exchange is an economical and efficient process for the removal of heavy metals. There is less generation of sludge during this process (Chiarle et al. 2000; Lacour et al. 2001; Lin et al. 2000; Rengaraj et al. 2001).

Ion exchange takes place in three stages. At first, there is physical adsorption followed by formation of complex between heavy metal ions and oppositely charged ions; at the end, there is hydration on the surface of adsorbents (Ferreira et al. 1999). There is reversible exchange of ions between solid and liquid phases. During the ion exchange process, strong acidic cations can effectively remove heavy metals (Kang et al. 2004).

Strong base anion exchange is an effective way to remove aqueous Cr (VI). This technology utilizes a filter bed filled with polymeric resins with functionalized surfaces (quaternary amines) (Gorman et al. 2016). These resins when completely exhausted with the pollutants can be regenerated using 4 Molar acid (Rapti et al. 2016), 15% base (Meshram et al. 2018), or 15% sodium chloride solution (Subramonian and Clifford 1988) and efficiently removes monovalent and more selectively divalent anions (Subramonian and Clifford 1988).

A novel composite metal organic framework silica gel has been reported to uptake 277 mgCr(VI)/g even in the presence of competitive ions (El-Mehalmey et al. 2018). A protonated amine-functionalized metal organic framework in a column has been reported to remove over 1000 mgCr(VI)/L at pH 3.0 and very low concentrations of 6 ppm to 47 ppb which is difficult to remove by precipitation method (Rapti et al. 2016). Hypercrosslinked imidazolium-based polyionic liquids were reported to effectively adsorb 236 mgCr(VI)/L with 84% adsorption sites as anionic exchange resin at a broad pH range (Xie et al. 2019). Similarly, a strong base anion exchange membrane (Amberlite IRA400 and IRA900) was able to achieve over 97% Cr (VI) removal of 50 ppm from aqueous solutions and real wastewater (Meshram et al. 2018).

The limitation of this technology is the generation of spent brine containing Cr (VI). Chen et al., adapted a photochemical technique with carbon-centered radicals to reduce Cr (VI) into Cr(III) precipitates in the spent brine containing Cr(VI). Acidic pH enhanced the reduction and presence of chlorides decreased the removal efficiency (Chen and Liu 2020).

Polymeric submicron ion exchange resins (SMR) were used for the removal of copper, nickel, and zinc from water. The copper removal from river water was 46%, while in wastewater copper removal was 38% (Murray and Örmeci 2019). Choi et al. 2020, removed copper from bioleached wastewater by using Amberlite IRC-86 ion exchange resin. The copper removal was pH-dependent. The maximum Cu removal was 78.9% at pH value of 5. Two-step sequential process was more effective in copper removal (Choi et al. 2020). Bispicolylamine and iminodiacetate were used as chelating resins for copper removal from water. These chelating resins required a short contact time for copper removal. These resins were reusable without a major reduction in their removal capacity (Edebali and Pehlivan 2016). Rikame et al. (2017) developed phosphorylated fullerene/sulfonated polyvinyl alcohol (PFSP) cation exchange membrane capable of not only removing copper from wastewater but also produced electricity. The cationic membrane was used in microbial fuel cell (MFC). The ion exchange capacity of the membrane was 1.67 meq/g. PFSP cation exchange membrane removed 73.2% copper from wastewater. Copper removal efficiency and electricity generation of PFSP cation exchange membrane were better than Ultrex membrane (Rikame et al. 2017). In another study, Song et al. (2018) removed copper and nickel from aqueous solution using hydrophilic nanoporous ion exchange barrier membrane. The membrane was highly selective for copper and nickel removal. Higher copper flux was observed during the separation. Stripping was the major mechanism behind copper removal. The membrane showed high stability in organic extract (Song et al. 2018).

### *7.5.2 Bioremediation-Based Chromium and Copper Removal*

Bioremediation is the removal of pollutants with the help of microorganisms. These pollutants act as food and energy source for the microorganisms (Azubuike et al. 2016). The microorganisms break down complex and toxic pollutants into a simple and less toxic form (Ayangbenro and Babalola 2017). Microorganisms are grown in a polluted environment so that they can produce enzymes and metabolites. These metabolites are capable of breaking complex pollutants into a simpler form. During the breakdown of pollutants, energy is also released which is used by the microorganisms for their own growth (Azubuike et al. 2016). Microorganisms capable of heavy metal transformation can be isolated from both aerobic and anaerobic conditions. Mostly, aerobic microorganisms are used for bioremediation (Azubuike et al. 2016). Phytoremediation, on the other hand, is removal of pollutants with the help of plants. This technique is widely used in constructed wetlands and oil spills. It is also called green technology due to its environment friendliness, cost-effectiveness, and efficiency (Ali et al. 2013). Several mechanisms can be involved during the phytoremediation process. The major six mechanisms involved during phytoremediation are phytofiltration, phytovolatilation, phytostabilization, phytoextraction, rhizodegradation, and phytodegradation (Ali et al. 2013).

The removal or conversion of pollutants by living forms is one of the cost-effective and easy methods. Several fungal species have been reported to tolerate and reduce Cr (VI). A 1000 mgCr(VI)/L and many other heavy metal tolerating *Trichoderma lixii* was able to reduce Cr(VI) into Cr(III) under various environmental stresses (pH, temperature, tannary wastewater, etc.) by 99.4% (Kumar and Dwivedi 2019b). *Aspergillus flavus* tolerating 800 mgCr(VI)/L was also reported to reduce 89% Cr(VI) into Cr(III) (Kumar and Dwivedi 2019a). Fungi isolated from contaminated soil showed promising results of intracellular (Rhizopus sp.) and extracellular (*Aspergillus fumigatum* and *Penicilium radicum*) reduction of Cr (VI) with 95% removal efficiency in addition to the safe production of Lactuca sativa L crop by acting as in situ biofertilizer (bibi et al. 2018).

A bacterial strain *Staphylococcus aureus* could tolerate 22 mM Cr (VI) and removed 99% of 100 mgCr(VI)/L in 24h (Tariq et al. 2019). A range of Cr (VI) stress (10–500 mg/L) on *Stenotrophomonas maltophilia* with 92–100% removal efficiency at 37$^o$C and pH 7.0. The higher ability of this strain might be associated with the chromate reductase gene *ChrR* and soluble fraction of the cell (Baldiris et al. 2018). An attempt to improve strain of *Bacillus amyloliquifaciens* by physical (UV irradiation) and chemical mutagens (acrylamide, ethidium bromide, and ethyl methane sulphonate) improved the removal efficiency of wild type (74%) to a higher level of 83% and 96% by UV irradiation and acrylamide, respectively (Tharannum 2020). Another strain of *Klebsiella* sp. also reduced 95% Cr (VI) in Luria-Bertani broth and only 63% in real tannery wastewater. This suggests that any bioremediation method utilized should be checked in real or natural conditions as well (Hossan et al. 2020).

Guo et al. (2020) recently used *Myriophyllum aquaticum* for the removal of tetracycline and copper from wastewater. *M. aquaticum* effectively removed both pollutants. In the presence of low copper concentration, tetracycline removal was higher. The role of *M. aquaticum* in the removal of tetracyclines was major as compared to the microbial biofilms (Guo et al. 2020). Eight aquatic plants were used for the removal of copper from wastewater. The copper removal was maximum in the presence of *Eichhornia crassipes* and *Pistia stratiotes*. Copper was mostly accumulated in the roots and shoots of these aquatic plants. Copper removal was affected by the presence of lignin contents in the aquatic plants. The higher the concentration of lignin in plants, the greater was the copper removal (Lu et al. 2018). Tang et al. (2020) used *Pistia stratiotes* for copper removal from distilled and surface water. *Pistia stratiotes* effectively removed copper from both distilled and surface water. The maximum removal efficiency for copper was achieved in surface water (96.38%). First-order elimination kinetics was dominant during copper removal from both types of water. The species got the ability to remove copper from both nutrient-rich and nutrient-deficient wastewater (Tang et al. 2020). Alikasturi et al. (2019) removed copper from surface, mineral, and distilled water by using *Limnocharis flava*. Maximum copper removal efficency was achieved in distilled water, i.e., 39.9%. First-order rate law model best fit the absorption process (Alikasturi et al. 2019). Palanivel et al. (2020) used *Pseudomonas stutzeri* LA3 for copper removal. The maximum copper removal efficiency was 50%. Copper removal was by adsorption and absorption process. Bacterial cell structure was also altered due to copper absorption. (Palanivel et al. 2020). Genetically engineered *Escherichia coli* cell were used by Wang et al. (2019) for copper removal from aqueous solution. The plasmid of E. coli was modified by adding a copper sensor and copper adsorbent in the plasmid. The modification enhanced the copper removal efficency of E. coli. The maximum copper adsorption was 91.5% (Wang et al. 2019).

## 7.6 Conclusion

Among the various oxidation states of chromium and copper, Cr (VI) and Cu (II) are the most toxic forms, and when they enters into the environment, they have negative effects on the environment (air, water, soil) as well as on the health of all living organisms. There are different methods which can be used for the treatment of both chromium and copper, like adsorption, ion exchange, membrane filtration, electrocoagulation, and bioremediation. Based on the current study, it is concluded that both adsorption and bioremediation are economical and efficient solutions for the treatment of chromium- and copper-contaminated water.

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