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Problems of Trace Elements in Water and Wastewater Treatment

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5.1 Drinking Water

5.1.1 Sources

Fresh water only represents approximately 3% of all water resources on earth, and its amount is estimated at 35 million m³. Rivers, lakes, and shallow groundwater make up a mere 0.4% of the total volume of freshwater on the planet, with the rest being stored in the form of glaciers and snow cover in Antarctica and the Arctic or exists as groundwater. Access to drinking water in many countries is limited. Guidelines for the purity of drinking water are provided by European Union and government organizations. Criteria for drinking water quality are based on a few water quality variables such as microbiological and biological indicators, physical properties, organics, inorganics, and trace element concentrations.

5.1.2 Regulations

The World Health Organization (WHO) has proclaimed that “All people, whatever their stage of development and their social and economic conditions have the right to have access to an adequate supply of safe drinking water.” [1]. The EU standards for water quality are derived from WHO Guidelines for Drinking Water Quality. The EU Drinking Water Directive (98/83/EC, November 3, 1998, on the quality of water intended for human consumption) is a seminal document for European countries in this respect. It is reviewed every five years by the European Commission, which brings it in line with WHO guidelines. In 2015 the Polish minister of health published a decree (2), whose contents correspond to EU recommendations. In the US, the Environmental Protection Agency issued the Safe Drinking Water Act which establishes the water purity requirements for all states.

Safe drinking-water as defined by WHO *Guidelines for Drinking-water Quality* does not represent any significant risk to health over a lifetime of consumption, including different sensitivities that may occur between life stages.

Quality criteria recommended for water and wastewater are shown in Table 5.1. The WHO determines which substances can be present in drinking water and sets the level of a contaminant below which there is no known or expected risk to health. Not all countries follow these recommendations.

Table 5.1 demonstrates the limit values for inorganic elements in potable water according to agencies and regulations from different countries. Some of the values (Table 5.1, shaded cells) are higher than those recommended by WHO.

It is remarkable that the European Union allows a barium (Ba) value which is almost three times higher than the one established by WHO. Another value that is higher than the one recommended by WHO is the value of Ba set by the United States Environmental Protection Agency (EPA), which is almost three times higher. This contaminant derives from drilling wastes, discharges from metal refineries, and from erosion of natural deposits.

The values of lead (Pb) in Argentina and Chile are five times higher than the value recommended by WHO, which may be put down to the fact that the sewage systems in some South American countries are made of Pb instead of PVC. In Mexico the limit value of arsenic (As) is higher than that recommended by WHO. In 2012, WHO published an article explaining that long-term exposure to inorganic As can produce, among other effects, skin lesions and skin cancer. Since then, developed countries have changed their regulations, but the problem of high As concentrations in water, especially in cities, remains unsolved.

5.2 Wastewater

5.2.1 Sources

Although there are several trace elements that are present in water and wastewater (Table 5.2), aluminum (Al), cobalt (Co), fluorine (F), iron (Fe), lithium (Li), manganese (Mn), molybdenum (Mo), selenium (Se), and tin (Sn) are the most common trace elements in drinking water and municipal wastewater. This list does not include a special group of trace elements – heavy metals such as arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), and zinc (Zn), which have been proved to pose a threat to health due to accumulation in plants. Various sources of the dissolved components in water and wastewater can generally be divided into those of natural and those anthropogenic origin.

Natural sources are primarily headwaters, erosion of trace element-bearing mineral deposits and a result of volcanic rocks weathering and as well as erosion of tungsten-bearing mineral deposits [9].

The major *anthropogenic sources* are mining, smelting, industrial processing of ores and metals, coal combustion, as well as chemical and electronic industries. According to Geng and co-workers [10] mine drainage and agricultural activities are the major upstream sources, whereas industrial activities and sea tides are the major downstream sources. Some of the anthropogenic sources are characterized in detail below.

Table 5.1 A comparison of limit values in potable water.

Contaminant (µg/L)	WHO ^a	Argentina ^b	Chile ^c	Colombia ^d	Mexico ^e	Peru ^f	EPA ^g	EU ^h	Spain ⁱ
Aluminum (Al)	200	200	—	200	200	200	—	200	200
Antimony (Sb)	5	20	—	20	—	20	6	5	5
Arsenic (As)	10	10	10	10	25	10	10	10	10
Barium (Ba)	700	—	1000	700	700	700	2000	100	—
Bohrium (Bh)	300	500	—	300	—	1500	—	1000	1000
Cadmium (Cd)	3	5	10	3	5	3	5	5	5
Calcium (Ca)	—	—	—	60000	—	—	—	100000	—
Chromium (Cr)	50	50	50	50	50	50	100	50	50
Copper (Cu)	2000	1000	2000	1000	2000	2000	1300	2000	2000
Iron (Fe)	300	300	300	300	300	300	300	200	200
Lead (Pb)	10	50	50	10	25	10	15	10	10
Manganese (Mn)	500	100	100	100	150	500	50	50	—
Mercury (Hg)	1	1	1	1	1	1	2	1	—
Molybdenum (Mo)	70	—	—	70	—	70	—	—	—
Nickel (Ni)	20	20	—	20	—	20	—	20	20
Selenium (Se)	10	10	10	10	50	10	50	10	10
Zinc (Zn)	3000	5000	3000	5000	5000	3000	5000	5000	—

a Guidelines for drinking-water quality.

b Directive 2126/71.

c Norma Chilena Oficial 409/1.Of. 2005.

d Procedural resolution 2115 of 2007, Directive 1575/2007.

e Modification in 2000 of NOM-127-SSA1-1994.

f Regulation of the Quality of Water for Human Consumption DS N° 031-2010-SA.

g United States Environmental Protection Agency,

h Directive 98/83/CE,

i Royal Decree 140/2003.

Table 5.2 Anthropogenic sources of trace elements in water and wastewater.

Element	Anthropogenic source
Aluminum (Al)	Mining and processing, food additives, kitchenware, coagulants
Antimony (Sb)	Batteries, accumulators, paints
Arsenic (As)	Glass, ceramics, textiles, paints, agricultural chemicals (pesticides), batteries, accumulators
Barium (Ba)	Mining, refining and processing, coal combustion, plastics, coatings, ceramics, glass, electronics, cosmetics
Boron (B)	Coal and fossil fuels combustion, copper smelters, chemical industry, mining, chemical fertilizers [3]
Cadmium (Cd)	Plating, tanning, mining, smelting and industrial processing of ores and metals, coal combustion, batteries, accumulators, plastics, paints [4]
Chromium (Cr)	Coal combustion, batteries, accumulators, plastics, paints [4]
Cobalt (Co)	Coal combustion
Copper (Cu)	Mining, smelting and industrial processing of ores and metals, batteries, accumulators, paints [4]
Fluorine (F)	Phosphate fertilizer plants, aluminum smelters, plants producing fluoride chemicals, ceramics and glass [5]
Iron (Fe)	Corroded pipes, mining and processing
Lead (Pb)	Battery, accumulators, paints, gasolines, mining, smelting and industrial processing of ores and metals, plastics, paints [4]
Lithium (Li)	Batteries, accumulators
Manganese (Mn)	Coal combustion
Mercury (Hg)	Coal combustion, batteries, accumulators, paints, dental amalgam
Molybdenum (Mo)	Aluminum etching [6]
Nickel (Ni)	Mining, smelting and industrial processing of ores and metals, coal combustion, pipes and containers [4, 7]
Selenium (Se)	Coal and fossil fuels combustion, phosphate fertilizers, vulcanized rubber
Silver (Ag)	Spent fixer solutions used in photographic processing of film and development of x-rays, mining and processing [8]
Tin (Sn)	Mining, smelting and industrial processing of ores and metals
Zinc (Zn)	Mining, smelting and industrial processing of ores and metals, coal combustion, batteries, accumulators, plastics, paints [4]

A significant part of the anthropogenic emissions of trace elements ends up in wastewater. Anthropogenic sources are of industrial and urban origins. The former includes surface treatment processes, coal combustion, as well as smelting and mining processes, while the latter includes household effluents, agricultural activities, drainage water, business effluents, atmospheric deposition, and traffic related emissions such as vehicle exhaust, brake linings, tires, asphalt wear, and gasoline/oil leakage [11].

Water quality undergoes a change during the transport from the treatment plant to the consumer's tap. The water delivery system consists of a pipe network made from various materials; cement, galvanized iron, stainless steel, copper, and plastics.

The urban distribution system of the pipe network releases numerous contaminants to drinking water, especially trace elements. For many years Cu was the most popular material for piping all over the world. The release of corrosion products, especially copper ions (episodes called “blue water”) resulting from microbiological activity has been observed [12]. Copper corrosion in drinking water piping systems is related to redox reactions, chemical processes, and microbiologically influenced corrosion [13]. Galvanized steel pipes result in Pb release to drinking water [14]. Plumbing materials causing plumbosolvency and galvanized iron pipes containing zinc coating with lead impurities are the major source of Pb in drinking water [15]. Polymeric pipes, including polypropylene (PP), polyethylene (PE) and polyvinyl chloride (PVC), were used instead of lead pipes. Stabilizers which are components of PVC pipes are composed of heavy metal salts (Pb, Cd) [16]. Egyptian researchers [15] used polyvinyl chloride, polypropylene, and galvanized iron pipes to check Pb and Fe release during work under varying parameters of flow (stagnation time, water quality parameters). They observed a high Pb and Fe release, especially at low pH values. Zhang and Lin [17] also confirmed a release of Pb compounds (used as the stabilizer in uPVC pipes) to drinking water. The influence of temperature on the Pb corrosion products’ release to potable water was examined by Masters *et al.* [18]. Chojnacka *et al.* [19] investigated the composition of potable water from various pipes and analyzed the mineral content of human hair of people who drank the water. Both analyses confirmed that trace elements such as: Ni, Ti, Al, Hg, Sn, Mo, Li, Ag, Cu, Sr, and B were released from plastic; Zr, and Zn from steel, and: Ag, Cu, Si, and As from copper pipes.

5.2.1.1 Wastewater Treatment Plant and Sewage Sludge

Trace elements are present in both industrial and municipal wastewater. Trace elements in municipal wastewater are derived from chemicals used for treatment and sludge conditioning processes. For example, Al-based coagulants such as aluminum sulfate or polyaluminum chloride are commonly used in drinking water treatment to enhance the removal of particulate, colloidal, and dissolved substances by coagulation processes [20]. The application of Al as a coagulant for drinking water treatment may increase Al concentrations in the treated water. Ferric chloride applied as a precipitating agent is another compound commonly used in the treatment of wastewater solids.

Heavy metals in sewage are mostly associated with suspended solids and enrich sludge during the treatment process in a wastewater treatment plant [21].

One of the key challenges for wastewater treatment plants is appropriate sludge management. Sewage sludge contains valuable nutrients such as nitrogen, phosphorus, organic matter, and essential trace elements that improve soil structure and properties and can therefore be used as effective organic fertilizers [22]. However, sludge that accumulates valuable biological compounds also tends to attract toxic compounds and ions (e.g., heavy metals).

5.2.2 Composition and Characteristics of Wastewaters

Industrial wastewater varies markedly depending on its source. Usually it is a multi-component mixture consisting of many species in all three basic physical states, suspended, or dissolved in water.

Chemical elements like Cu, Ni, Cr, Pb, and Hg, which are considered trace in terms of their appearance in the environment and drinking water, tend to have much higher concentrations in industrial wastewater, easily reaching levels way above 100 ppm. Moreover, those elements are usually considered valuable and the main reason for water treatment is not purification, but rather reclamation of valuable species. This is one of the many reasons why industrial wastewater treatment requires a completely different approach compared to municipal water treatment. Furthermore, high toxicity and extreme pH, which are typical for industrial wastewater, may have a negative impact on the viability of microorganisms and the longevity of the equipment used in municipal water treatment. That is the reason why internal water treatment facilities are accommodated inside industrial plants. The purpose is to retrieve valuable trace elements and purify wastewater so it can be safely transferred to the municipal water treatment plant or discharged to the environment without further management.

Mining activities such as the extraction and processing of metals can also release trace elements to the environment. Metal mining and smelting are regarded as major sources of heavy metals in wastewater [23]. Sulfidic mining waste is among the biggest contributors to environmental contamination by trace elements. The contact of metal sulfides with water and atmospheric oxygen leads to oxidation processes and production of acidic leachate containing heavy metals. Acid mine drainage water (AMDW) with a pH of about 2 and containing several heavy metal ions is a significant environmental problem caused by the mining industry around the world [24], since AMDW may cause the extinction of aquatic life.

Mineral processing wastewater is usually alkaline with a pH ranging from 11–13 and contains different concentrations of trace elements such as Pb, Zn, Cu, Fe, and As ranging from a few ppb up to >20 ppm, depending on specific wastewater sources and processing methods. Usually this kind of wastewater is additionally contaminated with acidic ions such as Cl^- , F^- , CNO^- , SNO^- , CN^- , SO_3^{2-} , and SO_4^{2-} . In the case of mineral processing, specific concentrations of wastewater can vary significantly even within one processing plant, due to variations in the composition of mineral ore [25].

Coal combustion is the second of the biggest source of trace element contamination in the environment: at the same time coal is the most abundant fossil fuel used throughout the world for electricity production. Modern coal-fired boilers are usually equipped with a wet flue gas desulfurization (FGD) system, where some trace elements leave with FGD solid residue (gypsum), while the greater portion is distributed in the form of dissolved species in the supernatant water in the process of coal combustion. The distribution of trace elements between sludge and wastewater depends on operating parameters, especially pH [26]. Due to the fact that FGD water may contain several hazardous trace elements, it is crucial to remove those elements before the supernatant is discharged into the environment [27]. Trace elements associated with coal combustion depend on the type of coal utilized in the process. Ohki *et al.* [27] analyzed the contents of trace elements in various FGD water samples. They revealed the presence of Co, Cu, Hg, Mn, Ni, Se, and Zn in most of them, while the highest contribution was of B with a total concentration ranging from 1.4–51 mg/L.

Electronic waste (e-waste) produced by the electronics industry is a heterogeneous material made of metal, plastics, glass, and ceramics and includes several toxic compounds such as a broad range of toxic metals (Cu, Pb, Sn, Ni, Fe, Al, Cd, Be, and Pd) [28]. Printed circuit boards are a major component of e-wastes. However, other electronic

devices such as refrigerators, air conditioners, and consumer electronic appliances such as computers which have been discarded by their users are also regarded as electronic waste [29]. The printed circuit boards industry requires chemical-intensive manufacturing processes, which lead to the production of large quantities of electronic wastewater. The regulated pollutants most often detected in electronic wastewater are Cu, Pb, Ni, and Ag; however, other metals are also found in wastewater, including Ba, Be, Cr, Co, Au, and Zn [28]. Apart from the common metals such as Fe, Cu, Al, and Ni, e-waste also contains traces of precious and rare elements, like Au, Ag, Pt, Pd, Cd, Se, As, Co, Te, Ta, Ru, Ge, Ga, Rh, Sn, Pb, and Bi [27].

Wastewater from *battery production* is contaminated with various trace elements, but most importantly Pb (up to 5 ppm) [31]. It can also contain a number of other contaminants like Fe, Al, Ca (up to 100 ppm), Cu, and Mn (up to 20 ppm). This type of wastewater is usually highly acidic with a pH varying between 2 and 4. Battery industry wastewater is usually clear with low concentrations of organic pollutants with TOC (Total Organic Carbon) concentration rarely exceeding 20 ppm.

Pesticides and fertilizers, their production and application, are the most likely sources of groundwater contamination with trace elements such as boron, As, F, and Se [32]. Excessive use of soil conditioners leads to migration of pollutants to groundwater and in turn water deterioration. For example, Giambastiani and co-workers [33] analyzed groundwater samples collected from an unconfined shallow aquifer (from the field site in Northern Italy) for trace element concentrations. The groundwater composition showed values of Fe, Mn, Al, As, and Hg above the recommended international and national guideline values (Italian and European normative limits for drinking water, the US EPA, and WHO guidelines).

The *tannery industry* produces much more complex wastewater. The mixture is slightly alkali (pH 7.4–8.5), contains high concentrations of suspended solids (up to 4 g/L) and dissolved solids of both organic and inorganic origin (up to 50 g/L). The main trace element present in tannery wastewater is Cr whose concentration, depending on the technology used in the specific plant, varies from 4 ppm up to >100 ppm.

The *paper industry* is usually considered as one which has the highest share of wastewater production. Production of one ton of paper can consume up to 1000 tonnes of water, producing a very complex waste [34]. Paper industry wastewater is usually neutral or slightly alkali (pH 7.0–7.5) with moderate concentrations of suspended solids (300–600 ppm) and moderate oxygen demand. This type of waste contains high concentrations of sodium (Na) (200–400 ppm), potassium (K) (5–10 ppm), and magnesium (Mg) (10–40 ppm), however, the most important contaminant is Ca with concentrations oscillating between 200 and 300 ppm [35, 36].

5.3 Water Treatment

5.3.1 Drinking Water

The reverse osmosis filtration system is the most popular method of tap water purification. It is an easy way to remove all the unwanted trace elements from drinking water. Unfortunately, the reverse osmosis system also removes important microelements from water (e.g., Mg, Ca, K, Na) causing lack of minerals and, according to WHO, water

produced by reverse osmosis is not suitable for long-term human consumption. To improve water filtered by reverse osmosis, we need to remineralize it with mineral filters [37]. Such mineralized water has perfectly balanced proportions of necessary microelements that have a major impact on the physiology of human bodies.

5.3.2 Wastewater Treatment

5.3.2.1 Biological Methods

Industrial wastewater differs significantly from municipal wastewater and requires a different approach. Methods which are commonly used in treatment need to be adjusted for elevated heavy metal concentrations, extreme pH, and high toxicity of industrial wastewater. In many cases even the best adjustment of those methods is insufficient and there is a need to incorporate new methods designed specifically to remove a specific element or group of elements down to concentrations which are acceptable for discharge to the environment or a municipal water treatment plant.

General methods are the most important in industrial water treatment because they bring about the reduction of concentrations of all or at least most of the contaminants. The most common method used in both municipal and industrial water treatment are biological methods of treatment, either aerobic or anaerobic. Both processes are used mainly in the treatment of organic contaminants, although they can be used in the treatment of organic–inorganic systems as well. This method makes use of microorganisms such as bacteria, fungi, and plants that are responsible for the removal of contaminating species. There are four basic mechanisms of purification by means of biological methods: metabolic oxidation, metabolic reduction, bioaccumulation, and biosorption, with oxidation being restricted only to aerobic, while metabolic reduction restricted to anaerobic treatment. Bioaccumulation is a process which utilizes living organisms which by means of metabolic digestion remove toxic components from the solution. The nature of this process is biological whereas biosorption is physicochemical where separated species are bound to the surface of selective biomass. In other words bioaccumulation requires living organisms, while biosorption can utilize inanimate biomass, for example, bagasse, seeds, and eggshells. The greatest advantage of biological processes is cost-effectiveness. Microorganisms selected for water treatment purposes usually feed solely on the sewage, and require little to none additional nutrients. Biosorption is cost-effective as well. Sorbents used in water treatment are, in the majority of cases, by-products or wastes from other industries and can be acquired at affordable prices. The main drawback of those processes is sludge/biosorbent management. Heavy metal-enriched sludge/biosorbent is usually toxic and needs to be either stored in landfill or burned. However, the high humidity of the solid phase makes the drying and combustion very expensive. An alternative solution, in cases where the biosorbent is rich in micro and macroelements, is to use it as a fodder additive. Toxicity is another important issue related with microorganism-based trace element removal. Many heavy metals, especially at high concentrations, are deadly to even the most resistant species of bacteria, algae, and fungi. Therefore, in many cases of highly contaminated industrial wastewater, biological treatment would be impractical or even impossible.

Trabelesi *et al.* [38] described a two-stage process for treatment of leachate from landfill of municipal solid waste. This leachate is rich in various heavy metals such as Ni, Pb, Fe, and Cr with concentrations ranging from 0.3–7.4 mg/L, depending on trace

element content. The two-stage process described in the article consisted of anaerobic reduction followed by aerobic oxidation, each of the steps resulting in a decrease in total heavy metal concentrations. In the first stage, anaerobic reduction, microorganisms endemic to the landfill and present in the leachate transformed Ni, Pb, and Fe into insoluble forms, effectively decreasing concentrations of the heavy metals from 0.3 to 0.15 mg/L, from 0.48 to 0.36 mg/L and from 7.4 to 2.98 mg/L for Ni, Pb, and Fe respectively. The second stage used 25 species of inoculated pre-selected microorganisms that were used for heavy metal separation by aerobic oxidation. This second stage allowed for a further removal of the mentioned heavy Pb, resulting in the final concentrations dropping below detection levels. Similarly, the aerobic process further reduced Fe concentrations from 2.98 mg/L, after anaerobic process, to the final 1.09 mg/L. Finally, the second stage of the method allowed for reducing Cr concentrations from 2.15 to 1.04 mg/L.

Witek-Krowiak *et al.* [39] presented experimental results of Cr(III) ion removal from a water solution by means of biosorption on soybean meal. The authors used the optimization technique based on response surface methodology, and determined that in the optimal conditions (temperature, biosorbent dosage, and initial metal ion concentration), the maximum Cr uptake is equal to 61.07 mg of Cr(III) per gram of biosorbent. Moreover, subsequent kinetic studies proved that it is possible to greatly reduce Cr concentrations by means of biosorption, proving this method as a viable alternative in industrial wastewater treatment.

Podder and Majumder [40] examined the process of As removal from wastewater by simultaneous accumulation and biosorption with the use of immobilized *Corynebacterium glutamicum*. This microorganism showed great affinity toward As ions resulting in maximum uptakes of 1738 mg/g for As(III) ions and 2843 mg/g for AS(V) ions, yielding the final removal of up to >90% in a single step process.

Wastewater from industrial, municipal, and agricultural activities has different levels of trace elements, and varies considerably with the nature of its origin. Trace elements can influence the biological treatment process in wastewater treatment plants, causing metabolism inhibition of microorganisms in activated sludge and thus decreasing the efficiency of wastewater purification. The toxicity of heavy metals depends on two factors; speciation of metals and their concentration.

Research conducted with unacclimatized and acclimatized biomass showed that the presence of Cr(VI) inhibited the growth of unacclimatized activated sludge, thus decreasing the maximum specific growth rate. In the case of acclimatized biomass, Cr(VI) causes a greater decrease in bacterial growth [41]. You *et al.* [42] checked the effect of heavy metals (Pb, Ni, Cd) on the nitrification mechanisms of activated sludge taken from a sequencing batch reactor (SBR) and anaerobic–anoxic–oxic (A2O) processes. They didn't observe the synergistic effect when more than one heavy metal was added to the sludge.

5.3.2.2 Precipitation

Precipitation is a process in which a species soluble in water crystallizes, so it can be separated with the use of mechanical separation like filtration and sedimentation. A necessary condition for crystallization is for separated species to have concentrations exceeding the saturation concentration. This can be achieved in various ways. Solvent evaporation is the simplest method, however, in the case of aqueous solutions it has

drawbacks which are high evaporation heat and high boiling point of water. Alternatively, species can be crystallized by alteration into a less soluble form, either by redox reaction, pH adjustment, or by the creation of coordination complexes.

De Luna *et al.* [43] described Pb(II) crystallization in the fluidized-bed reactor for Pb removal from aqueous solutions. In this process Pb(II) ions are contacted with anhydrous Na_2CO_3 . In effect, Pb^{2+} ions react with carbonate ions, creating a practically insoluble lead carbonate. Under the optimal pH 8–9 conditions of a carbonate:lead molar ratio of 3:1 and 1.85 g/L of initial crystal seed concentration, this process offers an >99% Pb removal efficiency and ~100% Pb conversion ratio.

Ayati and Madsen [44] described heavy metal removal with precipitation by means of the reaction with phosphate ions. The experimenters examined the precipitation of three different heavy metals: Cd, Pb, and Cu. Experiments were conducted for binary water-heavy metal model solutions and in the presence of calcium ions. It has been observed, that although the presence of calcium increases the amount of phosphoric acid necessary to precipitate heavy metals, the solubility of Ca-heavy metal crystals is lower than that of pure heavy metal phosphates; therefore, the presence of metallic additives can be beneficial for overall selectivity of the process.

Scientists from the University of Kentucky [45] have developed a method for heavy metal removal from acid mine drainage, based on complexing precipitation. Dialkali salt of 1,3-benzenediamidoethanethiol ($\text{Na}_2(\text{BDET})$) was used to purify Pikeville Mine drainage, which contained numerous harmful trace elements, for example, Fe, Mn, As, antimony (Sb), and strontium (Sr). BDET treatment resulted in a significant reduction of trace element concentrations in the leachate. Iron concentrations dropped from the initial value of 193 ppm to the value below the detection limit of the ICP procedure (<0.009 ppm). The initial concentration of Mn, 4.65 ppm, dropped by more than 97%, while the reduction of other examined elements oscillated around 40–60%.

Suzuki *et al.* [46] described the method of swine wastewater treatment by means of crystallization. Swine husbandry produces wastewater rich in phosphoric anions, Mg, ammonia, and Ca. Due to sewage aeration, CO_2 is removed from the solution resulting in pH elevation and crystallization of struvite ($\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$) and hydroxyapatite (HAP). The examined method provided a great improvement to the water treatment process in multiple areas. Phosphorus and Ca removal in the controlled environment of a crystallizer reduces scaling of the installation, while struvite, the main product of crystallization, is a valuable source of phosphorus commonly used as fertilizer. Therefore, the obtained precipitate can be sold, effectively reducing costs of water treatment.

5.3.2.3 Adsorption

Another traditional water-treatment process which has been found to be useful in the retrieval of trace elements from industrial waste streams is adsorption in which wastewater is contacted with the surface of an adsorbent where separated species are selectively bound to the surface via physical or chemical interactions. In order for this method to be applicable and cost-efficient, the adsorbent needs to have several properties. First, it needs to have an affinity toward species which are meant to be separated, so the process is reversible. Second, in order to minimize the volume of the adsorption apparatus, the adsorbent should have a large specific area. Third, it should have sufficient mechanical properties that will prevent it from being damaged in the adsorber. Fourth, the last requirement, depends on the specific process and can be divided into

two cases. In the first case, the adsorbate is valuable, and it is beneficial to reclaim it after adsorption, for example, Cu and Cr. Here the adsorption process should be reversible, and the mechanical and physicochemical properties of adsorbent should ensure its longevity. The other case is when the adsorbate, for example, As and Hg, is unwanted and needs to be permanently removed from the environment. Here adsorption should be highly irreversible, and the adsorbent should be cheap and easily accessible. In this case a heavy-metal enriched adsorbent is usually used as cheap construction material utilized to construct a road foundation or to fill exploited mine shafts [47].

The most common adsorbent used in trace element removal is activated carbon (AC). Due to constant progress in the implementation of environment-friendly technologies the demand for AC is increasing. Simultaneously, a reduction in the use of coal-based technologies decreases the coal-based AC supply. This creates a need for improvement in adsorption either by a better use of available activated carbon or by the application of alternative adsorbents.

Ahn *et al.* [48] presented a study on Cd removal from wastewater with the use of virgin and modified AC. They treated the surface of AC with three different surfactants: sodium dodecyl sulfate (SDS), sodium dodecyl benzene sulfonate (SDBS), and dioctyl sulfosuccinate sodium (DSS). The idea was to change the physicochemical properties of the AC surface and increase the number of active sites for Cd adsorption. In effect the maximum uptake of activated carbon increased from 0.016 mmol/g to 0.198 mmol/g.

Alternatively, many researchers, for example, Tofighy and Mohammadi [49] looked for alternatives which can replace AC. The mentioned group described the treatment of model industrial wastewater containing high concentrations of Pb, Cu, Cd, Zn, and Co with the use of adsorption on the surface of carbon nanotubes. Carbon nanotubes are a novel nanomaterial which due to very small dimensions have two very important properties in terms of adsorption application: unusual surface properties and a very large specific area. Both traits make carbon nanotubes a promising alternative for AC. In the study the application of nanotube adsorption uptakes varied, depending on the examined trace element, from 5–25 mg/g, giving the best results for Pb and Cd, and slightly worse for Zn, Co, and Cu.

Low-cost inorganic adsorbents of mineral or industrial origin are an alternative to expensive carbon-based adsorbents. The fly ash by-product of coal-fired power plants is an interesting example of this type of adsorbent. It is a heterogeneous material composed of numerous substances, mainly mineral oxides, for example, silicon dioxide, aluminum oxides, and iron oxides. Wang *et al.* [50] present a study on adsorption of As on NaOH-modified fly ash. In this study, fly ash had been contacted with model wastewater in a ratio of 1:10 S:L. Arsenic concentrations ranged between 1 and 10 mg/L. With the optimal pH range of 3–7, this adsorbent provided <95% As removal. Other low-cost alternatives for carbon-based adsorbents are sewage sludge ash, zeolites, recycled alum sludge, Mn oxides kaolinite, and resins [49].

5.3.2.4 Ion Exchange

Ion exchange is similar to adsorption in that separated species are accumulated on the surface of the acceptor phase. Yet, the said process possesses a set of distinguishing traits and is almost always regarded separately. Whereas adsorption is a process which uses a cheap adsorbent for separation of numerous impurities, it provides very little to no control over selectivity: ion exchange utilizes a sophisticated, frequently specially

designed adsorbent with a high affinity toward one group of ions, a narrow class of ion(s), or even toward one specific ion type. Moreover, due to high costs of ion exchanger manufacturing, this process is always designed to be reversible, allowing for prolonged use of one sorbent batch as well as for sorbate reclamation for further processing. This method is best used when water contaminants are of great value or when high selectivity is required. Among the biggest disadvantages of this process are its periodic nature, which complicates design and operation, a high investment cost in comparison with other water treatment processes, and high pretreatment requirements.

Ion exchangers are usually functionalized polymeric resins or mineral structures, like montmorillonite and zeolite. Separation is based on the process in which ions of the electrolyte are transported from the liquid phase and interchanged on the surface of an ion exchanger with other ions maintaining the electrolytic balance. Sorbed ions can be retrieved by elution with suitable agents, which alter the dissociation equilibrium through changes of pH or ionic strength.

Ion exchange has been proven successful in the separation of different heavy metal ions from various solutions. Feng *et al.* [51] described a two-stage method for the treatment of acid mine water consisting of $\text{Ca}(\text{OH})_2$ precipitation and resin ion exchange. Highly acidic wastewater (pH 1.65) containing 2.9% of suspended solids and 1.31% of dissolved salts, contained numerous heavy metals and trace elements, for example, Al (249 ppm), Ca (300 ppm), K (558 ppm), Mn (113 ppm), Mg (359 ppm), Cl (954 ppm), and Br (280 ppm). At first, the acid mine water was treated with slaked lime and H_2O_2 as an oxidant. This procedure resulted in a significant drop in cation concentrations. However, even though concentration of almost every single cation dropped to below the 1.0 ppm level, the targeted discharge standards of Dallas and Day were not achieved. Therefore, an additional step of ion exchange was incorporated in order to improve the process and polish the product. Pre-treated water was mixed with the IR120H resin in order to remove high amounts of Ca^{2+} cations and residuals of other metallic anions.

Lin and Kiang [52] investigated the application of polymeric ion exchangers for the retrieval of chromic acid (H_2CrO_4) from the wastewater produced in industries like plating, leather tanning, and electronic stripping of Cu. By application of strong base anionic and strong acid cationic ion exchangers, researchers were able to design a process of a continuous almost 100% acid recovery.

5.3.2.5 Membrane Processes

Membrane processes are a wide group of separation methods which incorporate a semi-permeable layer as a boundary between two phases. This semi-permeable layer, depending on the exact mechanism of the membrane process, is either just an interface or directly participates in the separation. From the point of view of industrial wastewater treatment, three membrane processes are of the most significance: ultrafiltration, nanofiltration, and reverse osmosis. The first two are similar to traditional filtration in that the membrane is a porous layer, and some particles and molecules are able to pass through pores while others are not. The main difference between these processes is the size of pores. In ultrafiltration pores are in the range of 0.002–0.1 μm and whether a particle or molecule is able to pass through a pore is mainly a matter of size comparison. In nanofiltration, pores are smaller, which is why nano-world interactions take place. The third of the mentioned membrane processes is slightly different in principle from the previous two. Reverse osmosis uses a polymeric membrane with a dense active

layer. Small water molecules can easily fit in the free volumes between polymer chains, while larger molecules of suspended solids are unable to penetrate. Therefore, by applying pressure on the feed side, water molecules can be pushed through the membrane, while the impurities are unable to permeate.

Among the greatest advantages of membrane separation techniques is the simplicity of design, ease of scale-up, and very good selectivity. On the other hand, membrane processes tend to be expensive due to high installation costs and extensive pre-treatment requirements. Therefore, membrane processes tend to be used only in a limited number of applications where the quality of the final product is especially important, and the selectivity is a key factor when it comes to separation method selection.

Heavy metal ions have diameters far too small in order to be successfully separated with solely ultrafiltration (UF). A possible solution is to use a two-step hybrid process in which the main target of the first step is to bind heavy metal ions in a way that its agglomerates are bigger than the pore diameter of the UF membrane. Precipitation, adsorption, complexing, microencapsulation, and so on, are among possible solutions to this problem. One such application has been described in a research paper by Alpatova *et al.* [53], in which UF is aided by heavy metal complexing with humic acid. Researchers investigated the separation of four different heavy metals: Bp(II), Cu(II), Ni(I,I) and Co(II), with heavy metal concentrations ranging from 5–30 ppm. The addition of humic acid and pH adjustment increased heavy metal rejection from below 10% up to almost 90%.

Nanofiltration, due to smaller pore diameters, is more suitable for trace element separation than previously described UF. Ahn *et al.* [54] described the treatment of electroplating rinse water rich in Ni ions. Solutions containing from 0.5–15 mM of NiSO₄ and NiCl₂ were separated with the NTR-7250 nanofiltration membrane with an applied pressure of ~0.3 MPa. The percentage rejection for NiCl₂ salts ranged between 70% and 85%, depending on salt concentrations, whereas for NiSO₄ a constant rejection of 94% was achieved independently on concentration.

Of the three mentioned membrane processes, which are applicable in trace element separation, reverse osmosis offers the best selectivity. Benito and Ruíz [55] applied reverse osmosis in the process of metal finishing wastewater treatment. Real industry wastewater has been examined, containing various impurities (Ca, Cr, Cu, Fe, Ni, Sn, Zn, Na, F) with a total dissolved solids concentration ranging from 338 ppm up to 1954 ppm. Wastewater was treated with the ACMTM reverse osmosis membrane, giving an average salt rejection of a minimum 97% with an average of 99% and water purification efficiency of 95%.

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