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Chapter 7

Determination of Trace Metals in Waste Water and Their Removal Processes

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Additional information is available at the end of the chapter

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1. Introduction

Since the second part of 20th century, there has been growing concern over the diverse effects of heavy metals on humans and aquatic ecosystems. Environmental impact of heavy metals was earlier mostly attributed to industrial sources. In recent years, metal production emissions have decreased in many countries due to strict legislation, improved cleaning/purification technology and altered industrial activities. Today and in the future, dissipate losses from consumption of various metal containing goods are of most concern. Therefore, regulations for heavy metal containing waste disposal have been tightened [1].

A significant part of the anthropogenic emissions of heavy metals ends up in wastewater. Major industrial sources include surface treatment processes with elements such as Cd, Pb, Mn, Cu, Zn, Cr, Hg, As, Fe and Ni, as well as industrial products that, at the end of their life, are discharged in wastes. Major urban inputs to sewage water include household effluents, drainage water, business effluents (e.g. car washes, dental uses, other enterprises, etc.), atmospheric deposition, and traffic related emissions (vehicle exhaust, brake linings, tires, asphalt wear, gasoline/oil leakage, etc.) transported with storm water into the sewerage system. For most applications of heavy metals, the applications are estimated to be the same in nearly all countries, but the consumption pattern may be different. For some applications which during the last decade has been phased out in some countries, there may, however, today be significant differences in uses [2-4].

Most common sources of heavy metals to waste and/or waste water are [1]; (i) Mining and extraction; by mining and extraction a part of the heavy metals will end up in tailings and other waste products. A significant part of the turn over of the four heavy metals with mining waste actually concerns the presence of the heavy metals in waste from extraction of other metals like zinc, copper and nickel. It should, however, be kept in mind that mining waste is generated in-

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dependent of the subsequent application of the heavy metal. (ii) Primary smelting and processing; a minor part of the heavy metals will end up in waste from the further processing of the metals. (iii) Use phase; a small part of the heavy metals may be lost from the products during use by corrosion and wear. The lost material may be discharged to the environment or end up in solid waste either as dust or indirectly via sewage sludge. (iv) Waste disposal; the main part of the heavy metals will still be present when the discarded products are disposed off. The heavy metals will either be collected for recycling or disposed of to municipal solid waste incinerators (MSWI) or landfills or liquid waste. A minor part will be disposed of as chemical waste and recycled or landfilled via chemical waste treatment. (v) vulconic erruptions. (vi) fossil fuel combustion. (vii) agriculture (viii) erosions (ix) metallurgical industries. Actually metal pollutants are neither generated nor compleletely eliminated; they are only transferred from one source to another. Their chemical forms may be changed or they are collected and immobilized not to reach the human, animals or plants.

The term *heavy metal* has never been defined by any authoritative body such as The International Union of Pure and Applied Chemistry (IUPAC). It has been given such a wide range of meanings by different authors that it is effectively meaningless. No relationship can be found between density (specific gravity) and any of the various physicochemical concepts that have been used to define "heavy metals" and the toxicity or ecotoxicity attributed to *heavy metals*. The term bioavailability is more appropriate to define the potential toxicity of metallic elements and their compounds. Bioavailability depends on biological parameters as well as the physicochemical properties of metallic elements, their ions, and compounds. These in turn depend upon the atomic structure of the metallic elements. Thus, any classification of the metallic elements to be used in scientifically based legislation must itself be based on the periodic table or some subdivision of it. In conclusion, heavy metals commonly used in industry and generically toxic to animals and to aerobic and anaerobic processes, but all of them are not dense nor entirely metallic. Includes As, Cd, Cr, Cu, Pb, Hg, Ni, Se, Zn. All of them pose a number of undesired properties that affect humans and the environment [5].

Effluents from textile, leather, tannery, electroplating, galvanizing, pigment and dyes, metallurgical and paint industries and other metal processing and refining operations at small and large-scale sector contain considerable amounts of toxic metal ions [4]. The toxic metals and their ions are not only potential human health hazards but also to another life forms. Toxic metal ions cause physical discomfort and sometimes life-threatening illness including irreversible damage to vital body system [6]. From the eco-toxicological point of view, the most dangerous metals are mercury, lead, cadmium and chromium(VI). In many instances, the effect of heavy metals on human is not well understood. Metal ions in the environment bioaccumulate and are biomagnified along the food chain. Therefore, their toxic effect is more pronounced in animals at higher trophic levels. Mine tailing and effluents from non-ferrous metals industry are the major sources of heavy metals in the environment. Among commonly used heavy metals, Cr(III), Cu, Zn, Ni and V are comparatively less toxic then Fe and Al. Cu is mainly employed in electric goods industry and brass production. Major applications for Zn are galvanization and production of alloys. Cadmium has a half-life of 10–30 years and its accumulation in human body affects kidney, bone and also causes cancer and its use is increasing in industrial applica-

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tions such as electroplating and making pigments and batteries. Chromium compounds are nephrotoxic and carcinogenic in nature. As a result of increasing awareness about the toxicity of Hg and Pb, their large-scale use by various industries has been either curtailed or eliminated. An effluent treatment facility within the industry discharging heavy metals contaminated effluent will be more efficient than treating large volumes of mixed wastewater in a general sewage treatment plant. Thus it is beneficial to devise separate treatment procedures for scavenging heavy metals from the industrial wastewater [4,6,7].

The analysis of wastewater for trace and heavy metal contamination is an important step in ensuring human and environmental health. Wastewater is regulated differently in different countries, but the goal is to minimize the pollution introduced into natural waterways. In recent years, metal production emissions have decreased in many countries due to heavy legislation, improved production and cleaning technology. A variety of inorganic techniques can be used to measure trace elements in waste water including flame atomic absorption spectrometry (FAAS) and graphite furnace (or electrothermal) atomic absorption spectrometry (GFAAS or ETAAS), inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). Depending upon the number of elements to be determined, expected concentration range of analytes and the number of samples to be run, the most suitable technique for business requirements can be chosen.

Several industrial wastewater streams may contain heavy metals such as Sb, Cr, Cu, Pb, Zn, Co, Ni, etc. The toxic metals, existing in high or even in low concentrations, must be effectively treated/removed from the wastewaters. Among the various treatment methods applied to remove heavy or trace metals, chemical precipitation process has been the most common technology. The conventional heavy metal removal process has some inherent shortcomings such as requiring a large area of land, a sludge dewatering facility, skillful operators and multiple basin configuration. In recent years, some new processes such as biosorption, neutralization, precipitation, ion exchange, adsorption etc. have been developed and extensively used for the heavy metal removal from wastewater.

In this chapter the novel and common methods for the determination of trace heavy metals in waste water and their removal processes are explained.

2. Toxicity effects of some heavy metals in the wastewater [1,3,5]

All heavy metals are effected to human and environment by different ways. For example; lead in the environment is mainly particulate bound with relatively low mobility and bioavailability. Lead does, in general, not bioaccumulate and there is no increase in concentration of the metal in food chains. Lead is not essential for plant or animal life. Of particular concern for the general population is the effect of lead on the central nervous system. Lead has been shown to have effects on haemoglobin synthesis and anaemia has been observed in children at lead blood levels above 40 μg/dl. Lead is known to cause kidney damage. Some of the effects are reversible, whereas chronic exposure to high lead levels may result in continued decreased kidney function and possible renal failure. The evidence for carcinogenici-

ty of lead and several inorganic lead compounds in humans is inadequate. Classification of The International Agency for Research on Cancer (IARC) is class 2B which is the agent (mixture) is possibly carcinogenic to humans. The exposure circumstance entails exposures that are possibly carcinogenic to humans. In the environment, lead binds strongly to particles, such as soil, sediment and sewage sludge. Because of the low solubility of most of its salts, lead tends to precipitate out of complex solutions. It does not bioaccumulate in most organisms, but can accumulate in biota feeding primarily on particles, e.g. mussels and worms. These organisms often possess special metal binding proteins that removes the metals from general distribution in their organism. Like in humans, lead may accumulate in the bones. One of the most important factors influencing the aquatic toxicity of lead is the free ionic concentration and the availability of lead to organisms. Lead is unlikely to affect aquatic plants at levels that might be found in the general environment.

Mercury is a peculiar metal. Most conspicuous is its fluidity at room temperature, but more important for the possible exposure of man and the environment to mercury are two other properties:

1. Under reducing conditions in the environment, ionic mercury changes to the uncharged elemental mercury which is volatile and may be transported over long distances by air.

2. Mercury may be chemically or biologically transformed to methylmercury and dimethylmercury, of which the former is bioaccumulative and the latter is also volatile and may be transported over long distances. Mercury is not essential for plant or animal life. The organic forms of mercury are generally more toxic to aquatic organisms than the inorganic forms. Aquatic plants are affected by mercury in the water at concentrations approaching 1 mg/litre for inorganic mercury, but at much lower concentrations of organic mercury.

Cadmium and cadmium compounds are, compared to other heavy metals, relatively water soluble. They are therefore also more mobile in e.g. soil, generally more bioavailable and tends to bioaccumulate. Cadmium is not essential for plant or animal life. Cadmium is readily accumulated by many organisms, particularly by microorganisms and molluscs where the bioconcentration factors are in the order of thousands. In aquatic systems, cadmium is most readily absorbed by organisms directly from the water in its free ionic form Cd (II). The acute toxicity of cadmium to aquatic organisms is variable, even between closely related species, and is related to the free ionic concentration of the metal. Cadmium interacts with the calcium metabolism of animals. In fish it causes lack of calcium (hypocalcaemia), probably by inhibiting calcium uptake from the water. Effects of long-term exposure can include larval mortality and temporary reduction in growth.

Chromium occurs in a number of oxidation states, but Cr(III) (trivalent chromium) and Cr(IV) (hexavalent chromium) are of main biological relevance. There is a great difference between Cr(III) and Cr(VI) with respect to toxicological and environmental properties, and they must always be considered separately. Chromium is similar to lead typically found bound to particles. Chromium is in general not bioaccumulated and there is no increase in concentration of the metal in food chains. Contrary to the three other mentioned heavy metals, Cr(III) is an essential nutrient for man in amounts of 50 - 200 μg/day. Chromium is nec-

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essary for the metabolism of insulin. It is also essential for animals, whereas it is not known whether it is an essential nutrient for plants, but all plants contain the element. In general, Cr(III) is considerably less toxic than Cr(VI). Cr(VI) has been demonstrated to have a number of adverse effects ranging from causing irritation to cancer. Hexavalent chromium is in general more toxic to organisms in the environment that the trivalent chromium. Almost all the hexavalent chromium in the environment is a result of human activities. Chromium can make fish more susceptible to infection; high concentrations can damage and/or accumulate in various fish tissues and in invertebrates such as snails and worms. Reproduction of the water flea Daphnia was affected by exposure to 0.01 mg hexavalent chromium/litre. Hexavalent chromium is accumulated by aquatic species by passive diffusion. In general, invertebrate species, such as polychaete worms, insects, and crustaceans are more sensitive to the toxic effects of chromium than vertebrates such as some fish. The lethal chromium level for several aquatic and terrestrial invertebrates has been reported to be 0.05 mg/litre.

Copper can be found in many wastewater sources including, printed circuit board manufacturing, electronics plating, plating, wire drawing, copper polishing, paint manufacturing, wood preservatives and printing operations. Typical concentrations vary from several thousand mg/l from plating bath waste to less than 1 ppm from copper cleaning operations. Copper can be found in many kinds of food, in drinking water and in air. Because of that we absorb eminent quantities of copper each day by eating, drinking and breathing. The absorption of copper is necessary, because copper is a trace element that is essential for human health. Although humans can handle proportionally large concentrations of copper, too much copper can still cause eminent health problems. When copper ends up in soil it strongly attaches to organic matter and minerals. As a result it does not travel very far after release and it hardly ever enters groundwater. In surface water copper can travel great distances, either suspended on sludge particles or as free ions [8].

Nickel is a naturally occurring element widely used in many industrial applications for the shipbuilding, automobile, electrical, oil, food and chemical industries. Although it is not harmful in low quantities, nickel is toxic to humans and animals when in high concentrations. Nickel can be present in wastewater as a result of human activities. Sources of nickel in wastewater include ship cruise effluents, industrial applications and the chemical industry [9].

Arsenic is found in wastewater from electronic manufactures making gallium arsenide wafers and electronic devices. It also can be found in silicon semiconductor operations that use high dose arsenic implants. Other sources of arsenic are ground water in agricultural areas where arsenic was once used as an insecticide. Most environmental arsenic problems are the result of mobilization under natural conditions. However, mining activities, combustion of fossil fuels, use of arsenic pesticides, herbicides, and crop desiccants and use of arsenic additives to livestock feed create additional impacts. Arsenic exists in the −3, 0, +3 and +5 oxidation states. Each of them have diffrenet toxic effect both human and environment.

Actually all chemicals, including even essential elements, drugs and in fact water, are toxic above (and below) their limiting values. However, some elements such as arsenic lead, cadmium, mercury, described as toxic, are known to be toxic for living beings at any concentration and they are not asked to be taken in to the body even in ultratrace levels.

3. Determination Techniques of Heavy Metals in Waste Water Samples

In order to determine the heavy trace metals, there are many inorganic techniques such as FAAS, ETAAS, ICP-OES, ICP-MS as well as anodic stripping and recently laser induced breakdown spectroscopy (LIBS). Each technique has its own advantages and disadvantages which will be discussed in this chapter.

Actually all the steps of an analysis, namely (i) representative sampling, (ii) to prevent analyte loss e.g. its sorption on vessel wall, (iii) contamination from the environment, wares, chemicals added to the sample, (iv) transfer the sample to the lab, (v) treatment of sample prior to analysis (leaching, extraction, preconcentration/separation of the analytes, (vi) choose of the method considering its limitations, (vii) calibration of the vessels, instrument etc, (viii) preparation of sample, all solutions, standards correctly and appropriately, (ix) to test the accuracy of the method using Certified Reference Materials (CRM), (x) evaluation of results statistically and reporting are all the rings of a chain. Each step is important and potential source of error if not applied conveniently. The weakest ring of the chain limits the accuracy and quality of the results. If it is broken, the analysis collapses. Therefore, all the steps of an analysis should be performed with caution. A problem or error even in one of those steps causes the result to be wrong. As in all analyses, sample preparation step is the most important one which should be completed quickly, easy and safely. Waste water samples may contain particulates or organic materials which may require pretreatment before spectrometric analysis. In order to analyze total metal content of a sample, concentration of metals inorganically and organically bound, dissolved or particulated materials should be found.

As stated in Standard Methods, samples which are colorless and transparent, having a turbidity of <1 NTU (Nephelometric Turbidity Unit), no odor and single phase may be analyzed directly or, if necessary, after enrichment by atomic absorption spectrometry (flame or electro thermal vaporization) or inductively coupled plasma spectrometry (atomic emission or mass spectrometry) for metals without digestion. For further verification or if changes in existing matrices are encountered, comparison of digested and undigested samples should be done [10].

If samples have particulates and only the dissolved metals will be analyzed, filtration of sample and analyzing of filtrate will be enough. To be on the safe side, if particulates involved, convenient digestion procedures are suggested. Since different filtration procedures produce different blank values, it is always suggested to study with a blank solution. If only the metal contents of particulates are asked to be determined, then the sample is filtered and the filter is digested and analyzed.

In order to reduce interferences, organic matrix of the sample should be destroyed by digestion as well as metal containing compounds are decomposed to obtain free metal ions which can be determined by atomic absorption spectrometry (AAS) or inductively coupled plasma (ICP) more conveniently. The procedures for destroying organic material and dissolving heavy metals fall into three groups; wet digestion by acid mixtures prior to elemental analysis, dry ashing, followed by acid dissolution of the ash and microwave assisted digestion

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[11]. In Standard Methods if metal concentration is around 10-100, it is advised to digest 10 mL of sample. For less metal concentrations, sample volume could be around 100 mL for subsequent enrichment [10]. For most digestion procedures, nitric acid is used which is an acceptable matrix for both flame and electrothermal atomic absorption and ICP-MS [12]. For nitric acid digestion, 100 mL of sample is heated in a beaker with 5 mL concentrated nitric acid. Boiling should be prevented and addition of acid should be repeated til a light colored, clear solution is obtained [10]. Sometimes, if the samples involve readily oxidasable organic matters, mixtures of HNO_3- H_2SO_4 or HNO_3- HCl may be used. Samples with high organic contents, mixtures of HNO_3- $HClO_4$ or HNO_3-H_2O_2 or HNO_3-$HClO_4$-HF can be used. The latter is especially important for the dissolution of particulate matter. For samples which have high organic content, dry ashing may be favored. Wet digestion systems are performed either with a reflux or in a beaker on a laboratory hot plate. These methods are temperature limited because of the risk of contaminants from the air, laboratory equipment etc. Also there may be lost of volatile elements (As, Cd, Pb, Se, Zn and Hg etc.). Temperature limitation can be overcome by closed pressure vessels, i.e. microwave digestion. Closed systems allow high pressures above atmosphere to be used. This allows boiling at higher temperatures and often leads to complete dissolution of most samples [13]. In the American Society for Testing and Materials (ASTM) Standards (D1971-11) 'Standard practices for digestion of water samples for determination of metals by FAAS, ETAAS, ICP-OES or ICP-MS' for waste water samples it is advised to use, 100 volume of sample: 5 volume HCl: 1 volume HNO_3 is put to microwave digestion vessels for 30 minutes at 121ºC and 15 psig [14]. A comparision of digestion techniques is given in Table 1.

	Wet Ashing	**Microwave Digestion**
Time Consumption	Slow	Rapid
Temperature	Low	High
Pressure	Atmospheric	Above Atmospheric
Operator Skills	High	Moderate
Safety	Corrosive-explosive reagents	Corrosive-explosive reagents
Operating Cost	Low	High
Environmental Effect	High	Low
Analyte Loss&Contamination	High	Low

Table 1. Comparision of Digestion Techniques.

After choosing the effective sample preparation step, most useful techniques were explained below, like atomic absorption spectrometry (AAS), inductively coupled plasma optical emission spectrometry (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS), laser induced breakdown spectroscopy (LIBS) and anodic stripping.

3.1. Atomic Absorption Spectrometry

Atomic Absorption Spectrometry (AAS) is an analytical method for quantification of over 70 different elements in solution or directly in solid samples. Procedure depends on atomization of elements by different atomization techniques like flame (FAAS), electrothermal (ETAAS), hydride or cold vapor. Each atomization technique has its advantages and limitations or drawbacks. A comparision of several AAS techniques is given in Table 2.

Two types of flame are used in FAAS: (i) air/acetylene flame, (ii) nitrous oxide/acetylene flame. Flame type depends on thermal stability of the analyte and its possible compounds formed with flame concomitants. Temperature formed in air-acetylene flame is around 2300°C whereas acetylene-nitrous oxide (dinitrogen oxide) flame is around 3000°C [15]. Generally with air/acetylene flame antimony, bismuth, cadmium, calcium, cesium, chromium, cobalt, copper, gold, itidium, iron, lead, lithium, magnesium, manganese, nickel, palladium, platinium, potassium, rhodium, ruthenium, silver, sodium, strontium, thallium, tin and zinc can be determined. On the other hand for refractory elements such as aluminium, barium, molybdenum, osmium, rhenium, silicon, thorium, titanium and vanadium, nitrous oxide/acetylene flame should be used [10]. But some elements like vanadium, zirconium, molibdenium and boron has lower sensitivity in the determination by FAAS because the temperature is insufficient to break down compounds of these elements. Samples should be in solution form, or digested to be detected by FAAS. Typical detection limits are around ppm range and sample analysis took 10-15 seconds per element [16]. The block diagrame of FAAS and GFAAS is depicted in Figure 1. Generally, hollow cathode lamps as source, flame or graphite furnace as an atomizer, grating as a wavelength selector and photomultiplier as a detector are used.

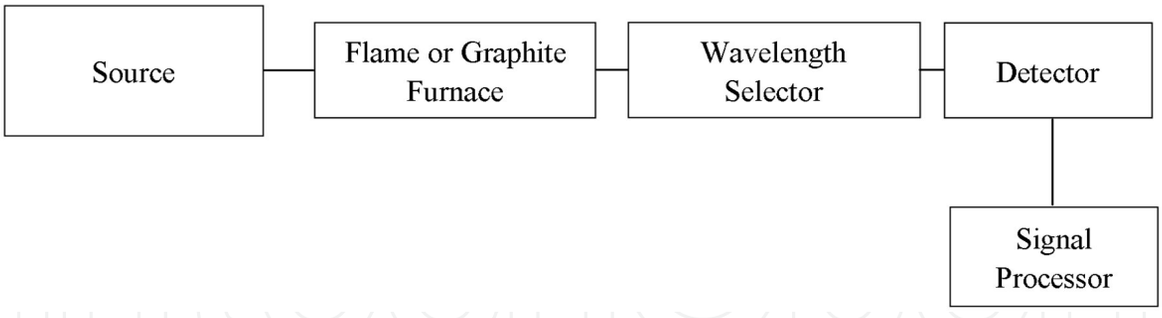


Figure 1. Block Diagram for FAAS and GFAAS.

Mahmoud et al. determined Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb by FAAS after enrichment with chemically modified silica gel N-(1-carboxy-6-hydroxy) benzylidenepropylamine (SiG-CHBPA) [16]. Afkhami et al. determined Cd in water samples after cloud point extraction in Triton X-114 without adding chelating agents [18]. Mohamed et al. determined chromium species based on the catalytic effect of Cr(III) and/or Cr(VI) on the oxidation of 2-amino-5-methylphenol (AMP) with H_2O_2 by FAAS [19]. Mahmoud et al. pre-concentrated Pb(II) by newly modified three alumina–physically loaded-dithizone adsorbents then determined by FAAS [20]. Cassella et al. prepared a minicolumn packed with a styrene-divinylbenzene resin func-

tionalized with (S)-2-[hydroxy-bis-(4-vinyl-phenyl)-methyl]- pyrrolidine-1-carboxylic acid ethyl ester to determine Cu in water samples [21]. Carletto et al. used 8-hydroxyquinoline-chitosan chelating resin in an automated on-line preconcentration system for determination of Zn(II) by FAAS [22]. Gunduz et al. preconcentrated Cu and Cd using TiO_2 core-Au shell nanoparticles modified with 11-mercaptoundecanoic acid and analysed their slurry [23].

ETAAS is basically same as FAAS; the only difference is flame is replaced by graphite tube which can be heated up to 3000 °C for atomization. Since sample is atomized in a much smaller volume the atoms density will be higher, its detection limit is much more than FAAS, around ppb range. Graphite furnace program typically consists of four stages; drying for evaporation of solvent; pyrolysis for removal of matrix constituents; atomization for generation of free gaseous atoms of the analyte; cleaning for removal of residuals in high temperature. Generally samples are liquids, but there are some commercial solid sampling instruments also. Analyze took 3-4 minutes per element. 50 and more elements can be analyzed by GFAAS [15].

Burguera et al. determined of beryllium in natural and waste waters using on-line flow-injection preconcentration by precipitation dissolution for electrothermal atomic absorption spectrometry. They used a precipitation method quantitatively with NH_4OH-NH_4Cl and collected in a knotted tube of Tygon without using a filter then the precipitate was dissolved with nitric acid injected to graphite furnace [24]. Baysal et al. accomplished to preconcentrate Pb by cobalt/pyrrolidine dithiocarbamate complex ($Co(PDC)_2$). For this purpose, at first, lead was coprecipitated with cobalt/pyrrolidine dithiocarbamate complex formed using ammonium pyrrolidine dithiocarbamate (APDC) as a chelating agent and cobalt as a carrier element. The supernatant was then separated and the slurry of the precipitate prepared in Triton X-100 was directly analyzed [25].

Hydride generation atomic absorption spectrometry is a technique for some metalloid elements such as arsenic, antimony, selenium as well as tin, bismuth and lead which are introduced to instrument in gas phase. Hydride is generated mostly by adding sodium borohydride to the sample in acidic media in a generator chamber. The volatile hydride of the analyte generated is transferred to the atomizer by inert gas where it is atomized. The oxidation state of the metaloid is very improtant so before introducing to the hydride system, specific metalloid oxidation state should be produced. This method lowers limit of detection (LOD) 10-100 times [15,27]

Coelho et al, presented a simple procedure was developed for the direct determination of As(III) and As(V) in water samples by flow injection hydride generation atomic absorption spectrometry (FI–HG–AAS), without pre-reduction of As(V) [24]. Cabon and Madec determined antimony in sea water samples by continuous flow injection hydride generation atomic absorption spectrometry. After continuous flow injection hydride generation and collection onto a graphite tube coated with iridium, antimony was determined by graphite furnace atomic absorption spectrometry [28]. Yersel et al. developed a seperation method with a synthetic zeolite (mordenite) was developed in order to eliminate the gas phase interference of Sb(III) on As(III) during quartz furnace hydride generation atomic absorption spectrometric determination [29]. Anthemidis et al. determined arsenic (III) and total arsenic in water by using an on-line sequential insertion system and hydride generation atomic ab-

sorption spectrometry [31]. Erdogan et al. determined inorganic arsenic species by hydride generation atomic absorption spectrometry in water samples after preconcentration/separation on nano ZrO_2/B_2O_3 by solid phase extraction [31]. Korkmaz et al. developed a novel silica trap for lead determination by hydride generation atomic absorption spectrometry. The device consists of a 7.0cm silica tubing which is externally heated to a desired temperature. The lead hydride vapor is generated by a conventional hydride-generation flow system. The trap is placed between the gas–liquid separator and silica T-tube; the device traps analyte species at 500 °C and releases them when heated further to 750 °C. The presence of hydrogen gas is required for revolatilization; O_2 gas must also be present [32].

Cold vapour atomization technique is used for the determination of mercury which is the only element to have enough vapour pressure at room temperature. Method is based on converting mercury into Hg^{+2}, followed by reduction of Hg^{+2} with tin(II)chloride or borohydride. Then produced elementel mercury swept into a long-pass absorption tube along with an inert gas. Absorbance of this gas at 253.7 nm determines the concentration. Detection limit is around ppb range. Beside to inorganic mercury compounds, organic mercury compounds are problematic as they cannot be reduced to the element by sodium tetrahydroborate, and particularly not by stannous chloride. So it is advised to apply an appropriate digestion methode prior to the actual determination [15].

Kagaya et al. managed to determine organic mercury, including methylmercury and phenylmercury, as well as inorganic mercury by cold vapor atomic absorption spectrometry (CV-AAS) by adding sodium hypochloride solution [33]. Pourreza and Ghanemi developed a novel solid phase extraction for the determination of mercury. The Hg(II) ions were retained on a mini-column packed with agar powder modified with 2-mercaptobenzimidazole. The retained Hg(II) ions were eluted and analysed by CV-AAS [34]. Sahan and Sahin developed for on-line solid phase preconcentration and cold vapour atomic absorption spectrometric determination of Cd(II) in aqueous samples. Lewatit Monoplus TP207 iminodiacetate chelating resin was used for the separation and preconcentration of Cd(II) ions at pH 4.0 [35].

However, qualitative analysis cannot be made by AAS because a specific hollow cathode lamp (HCL) is used for each element. Therefore, elements should be determined one by one which make a qualitative analysis almost impossible. In addition, non-metals cannot be determined because their atomic absorption wavelengths are in far UV range which is not suitable for analysis due to absorption of air components.

Since 2004, new generation high resolution continuum source atomic absorption spectrometer (HR-CS-AAS) which is equipped with high intensity xenon short-arc lamp, high resolution double monochromator, CCD detector are produced. The continuous source lamp emits radiation of intensity at least an order of magnitude above that of a typical hollow cathode lamp (HCL) over the entire wavelength range from 190 nm to 900 nm. With these instruments, aside from the analysis line, the spectral environment is also recorded simultaneously, which shows noises and interferences effecting analysis. Improved simultaneous background correction and capabilities to correct spectral interferences, increase the accuracy of analytical results. With high resolution detector, interferences are minimized through optimum line separation. With these instruments, not only metals and non-metals e.g. F, Cl, Br, I, S, P can be determined

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by their hyperfine structured diatomic molecular absorbances. There are various papers for fluoride determination by GaF [36], SrF [37], AlF [38], CaF [39], chloride by AlCl [40], InCl [41], bromide by AlBr [42], CaBr [43], sulfur by CS [44], phosphorus by PO [45].

	FAAS	GFAAS	Hydride Generation AAS	Cold Vapour AAS
Elements	68	50	As, Se, Sb, Bi, Pb, Sn	Hg
Limit of Detection	+	++++	++++	++++
Precision	++++	+	+	+
Interferences	+++	+	++++	++++
Analysis Time	++++	+	++	++
Sample Preparation	+++	+++	++	++
Operation Skills	+++	++	++	++
Operation Costs	++++	++	++	++

+Bad, ++:Moderate, +++:Good, ++++:Very Good

Table 2. Comparision of AAS techniques.

3.2. Inductively Coupled Plasma Optical Emission Spectrometry

Inductively coupled plasma-optical (or atomic) emission spectrometry (ICP-OES or ICP-AES) is an analytical technique used for determination of trace metals. This is a multi-element technique which uses a plasma source to excite the atoms in samples. These excited atoms emit light of a characteristic wavelength, and a dedector measures the intensity of the emitted light, which is related with the concentration. Samples are heated through 10000 ºC to atomize effectively which is an important advantage for ICP technique. Another advantage is multi element analysis. With ICP technique, 60 elements can be analysed in single sample run less than a minute simultaneously, or in a few minutes sequentially. Besides instrument is only optimized for one time for e set of metal analysis. High operating temperature lowers the interferences. Determinations can be accomplised in wide lineer range and refractory elements can be determined at low concentrations (B, P, W, Zr, U). On the other hand consumption of inert gas is very much higher than AAS techniques which cause high operating costs.

ICP instruments can be 'axial' and 'radial' according to their plasma configuration. In radial configuration, the plasma source is viewed from the side. Emissions from axial plasma are viewed from horizontally along its length, which reduces background signals resulting in lower detection limits. Some instruments have both viewing modes [46]. The block diagrame of ICP-OES is depicted in Figure 2. Generally, radio frequency (RF) powered torch as a source, polychromators as a wavelength selector, photomultiplier (PMT) or charge capacitive discharged arrays (CCD) as a dedectors are used.

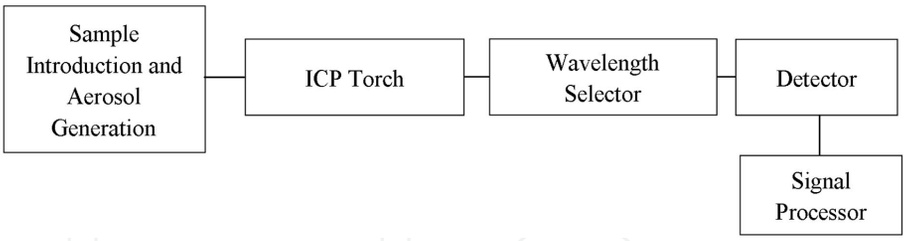


Figure 2. Block Diagram of ICP-OES.

Enrichment/separation procedures have been applied prior to ICP analyses as well. Atanassove et al. used sodium diethyldithiocarbamate to co-precipitate for the pre-concentration of Se, Cu, Pb, Zn, Fe, Co, Ni, Mn, Cr and Cd to detect by ICP-AES [47]. Zougagh et al. determined Cd in water ICP-AES with on-line adsorption preconcentration using DPTH-gel and TS-gel microcolumns [48]. Zogagh et al. developed a simple, sensitive, low-cost and rapid, flow injection system for the on-line preconcentration of lead by sorption on a microcolumn packed with silica gel funtionalized with methylthiosalicylate (TS-gel) then the metal is directly retained on the sorbent column and subsequently then eluted from it by EDTA and elution determined by ICP-AES [49].

3.3. Inductively Coupled Plasma Mass Spectrometry

Inductively coupled plasma mass spectrometry (ICP-MS) is a multi-element technique which uses plasma source to atomize the sample, and then ions are detected by mass spectrometer. Mass spectrometer separate ions according to their mass to charge ratio. This technique has excellent detection limits, in ppt (part per thousand) range. Samples generally introduced as an aerosol, liquid or solid. Solid samples are dissolved prior to analysis or by a laser solid samples are converted directly to aerosol. All elements can analyze in a minute, simultaneously. But it needs high skilled operator, because method development is moderately difficult from other techniques. There are various types of ICP-MS instruments; HR-ICP-MS (high resolution inductively coupled plasma mass spectrometry and MC-ICP-MS (multi collector inductively coupled plasma mass spectrometry). HR-ICP-MS, has both magnetic sector and electric sector to separate and focus ions. By these instruments eliminatenation or reduction of the effect of interferences due to mass overlap is accomplished but operation cost, time and complexity will increase. MC-ICP-MS, are designed to perform high-precision isotope ratio analysis. They have multiple detectors to collect every isotope of a single element but the major disadvantage of system is that all the isotopes should be in a narrow mass range which eliminates these instruments from routine analysis [46]. The block diagrame of ICP-MS is depicted in Figure 3. The main difference from ICP-OES is that quadropole mass spectrometers are used instead of wavelength selectors to detect the analytes.

Krishna et al. used moss (Funaria hygrometrica), immobilized in a polysilicate matrix as substrate for speciation of Cr(III) and Cr(VI) in various water samples and determined by ICP-MS and FAAS [41]. Hu et al. simultaneously separated and speciated inorganic As(III)/As(V) and Cr(III)/Cr(VI) in natural waters by capillary microextraction with mesoporous Al_2O_3 before de-

termination with ICP-MS [51]. Chen et al. speciated of chromium in waste water using ion chromatography coupled inductively coupled plasma mass spectrometry [52].

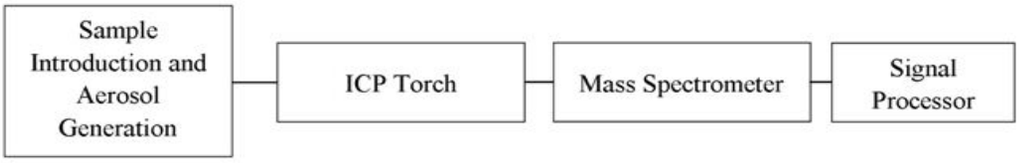


Figure 3. Block diagram of ICP-MS instrument.

Both ICP-OES and ICP-MS are not free of interferences. ICP-OES suffers from spectral interferences due to wavelength overlap of different elements. Similarly, in ICP-MS, the combination of different elements forms diatomic molecules which give the same (or indistinguishable) signal as that the analyte. In Table 3, a comparision of AAS and ICP techniques is given.

	FAAS	GFAAS	ICP-OES	ICP-MS
Analysis Time	++	+	+++	+++
Cost of Instrument	+++	++	++	+
Solid Sample Analysis	-	+++	-	-
Operating Cost	+	++	++	++
LOD	+	++	++	+++
Lineer Range	+	+	+++	+++
Precision	+++	+	++	++

-: Cannot Accomplished, +: Bad, ++: Medium, +++: Good

Table 3. Comparision of AAS and ICP Techniques.

3.4. Laser Induced Breakdown Spectroscopy (LIBS)

Laser Induced Breakdown Spectroscopy (LIBS) is a type of atomic emission spectroscopy which uses a highly energetic laser pulse as the excitation source. It is based on analysing of atomic emission lines close to the surface of sample generated by laser pulse where the very high field intensity initiates an avalenche ionisation of the sample elements, giving rise to the breakdown effect. Spectral and time-resolved analysis of this emission are suitable to identify atomic species originally present at the sample surface [53]. It can determine various metals but only limitation is the power of laser, sensitivity and wavelength range of the spectrometer. Generally this technique is used for solid samples because there are many accurate methods for liquid samples which does not require preparatory steps. Addition to

this, using LIBS for liquid samples may cause many problems due to the complex laser-plasma generation mechanisms in liquids [54]. Also splashing, waves, bubbles and aerosols caused by the shockwave accompanying the plasma formation effects precision and analytical performance. In order to overcome these problems, there are various procedures for liquid samples like analysing the surface of a static liquid body, the surface of a vertical flow of a liquid, the surface of a vertical flow of a liquid or of infalling droplets, the bulk of a liquid or dried sample of the liquid deposited on a solid substrate [55]. Though the results obtained were satisfactory, but it is obvious that such experimental tricks contradict with one of the most attractive advantages of LIBS, namely working on an unprepared sample, which facilitate in-situ and real-time measurements [56]. The block diagrame of LIBS is depicted in Figure 4. Laser generates spark and plasma light is collected by a fiber optic and directed into a spectrograph. A sample output spectrum can be seen from figure 4.

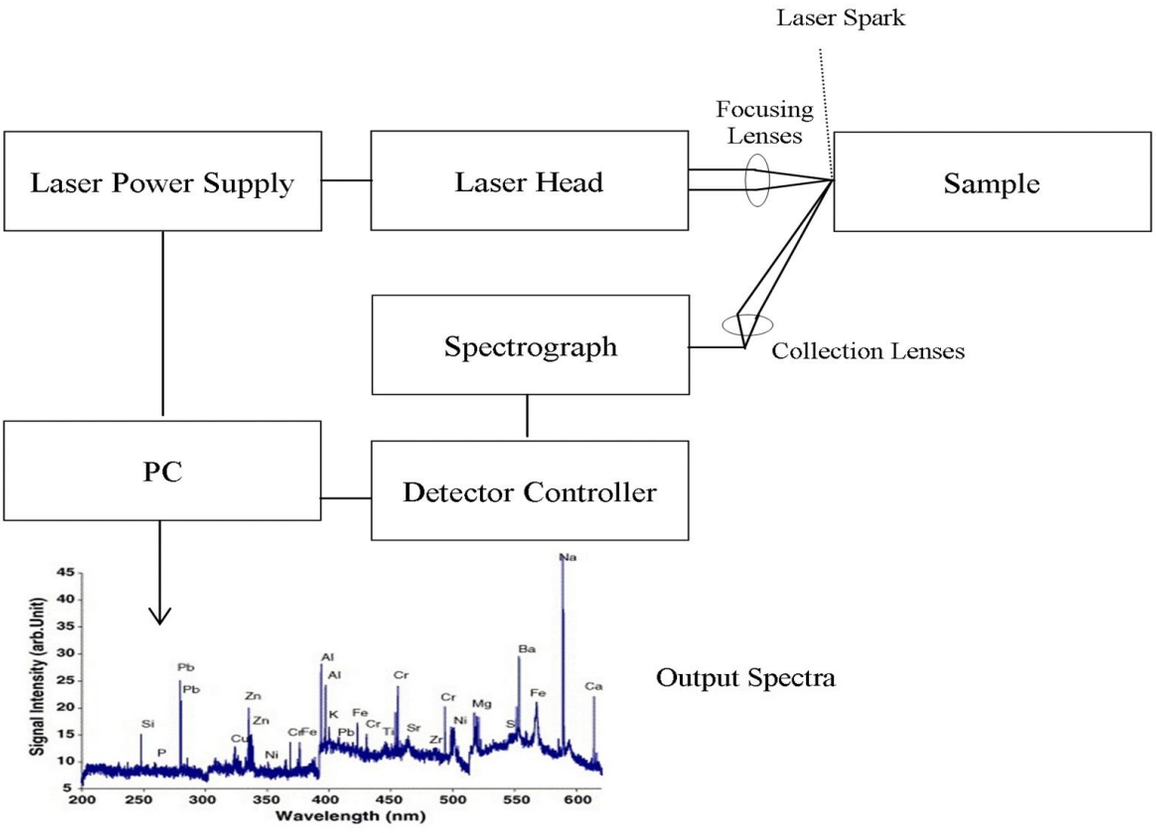


Figure 4. Scheme of an LIBS instrument (Spectra from Reference 48).

Gondal and Hussain, accomplished to determine many toxic trace elements in paint manufacturing plant waste water by LIBS. The results of LIBS method showed accuracy with the results found by ICP in the range of 0.03-0.6 %, which shows that this method can easily be used for trace element analysis [57]. Rai and Rai have also determined Cr in waste water collected from Cr-electroplating industry [58].

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3.5. Anodic Stripping Voltammetry (ASV)

Anodic Stripping Voltammetry (ASV) is an analytical technique that specifically detects heavy metals in various matrices. Its sensitivity is 10 to 100 times more than ETAAS for some metals. Since its limit of detection is low, it may not require any preconcentration step. It also allows determining 4 to 6 metals simultaneously with inexpensive instrumentation. ASV technique consists of three steps. First step is electroplating of certain metals in solution onto an electrode which concentrates the metal. Second, stirring is stopped and then finally metals on the electrode are stripped off which generates a current that can be measured. This current is characteristic for each metal and by its magnitude quantification can be done. The stripping step can be either linear, staircase, square wave, or pulse [59].

Sonthalia et al. used anodic stripping for determination of various metals (Ag, Cu, Pb, Cd and Zn) in several waste water samples. Boron-doped diamond thin film is used [60]. McGaw and Swain compared the performance of boron-doped diamond (BDD) with Hg-coated glassy carbon (Hg-GC) electrode for the anodic stripping voltammetry (ASV) for determination of heavy metal ions (Zn^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+}, Ag^{+}). Generally Hg has been used as the electrode for ASV but there is an ongoing search for alternate electrodes and diamond is one of these. Produced BDD showed comparable results with Hg electrodes [61]. Bernalte et al. determined mercury by screen-printed gold electrodes with anodic stripping voltammetry [62]. Mousavi et al. developed a sensitive and selective method for the determination of lead (II) with a 1,4-bis(prop-2-enyloxy)-9,10-anthraquinone (AQ) modified carbon paste electrode [63]. Kong et al. produced a method for the simultaneous determination of cadmium (II) and copper (II) during the adsorption process onto Pseudomonas aeruginosa was developed. The concentration of the free metal ions was successfully detected by square wave anodic stripping voltammetry (SWASV) on the mercaptoethane sulfonate (MES) modified gold electrode, while the P. aeruginosa was efficiently avoided approaching to the electrode surface by the MES monolayer [64]. Giacomino et al. investigated parameters affecting the determination of mercury by anodic stripping voltammetry using a gold electrode. Potential wave forms (linear sweep, differential pulse, square wave), potential scan parameters, deposition time, deposition potential and surface cleaning procedures were examined for their effect on the mercury peak shape and intensity and five supporting electrolytes were tested. The best responses were obtained with square wave potential wave form and diluted HCl as supporting electrolyte [65].

The literature is full of papers on the application of various methods for the determination of metals in waste water. Innumerous procedures, preconcentration/separation techniques, digestion techniques for several samples have been proposed.

4. Removal of heavy metals from waste water

Cadmium, zinc, copper, nickel, lead, mercury and chromium are often detected in industrial wastewaters, which originate from metal plating, mining activities, smelting, battery manufacture, tanneries, petroleum refining, paint manufacture, pesticides, pigment manufacture,

printing and photographic industries, etc. The toxic metals, probably existing in high concentrations (even up to 500 mg/L), must be effectively treated/removed from the wastewaters. If the wastewaters were discharged directly into natural waters, it will constitute a great risk for the aquatic ecosystem, whilst the direct discharge into the sewerage system may affect negatively the subsequent biological wastewater treatment [66].

In recent years, the removal of toxic heavy metal ions from sewage, industrial and mining waste effluents has been widely studied. Their presence in streams and lakes has been responsible for several types of health problems in animals, plants and human beings. Among the many methods available to reduce heavy metal concentration from wastewater, the most common ones are chemical precipitation, ion-exchange, adsorption, coagulation, cementation, electro-dialysis, electro-winning, electro-coagulation and reverse osmosis (See in Figure 5) [4, 67-70].

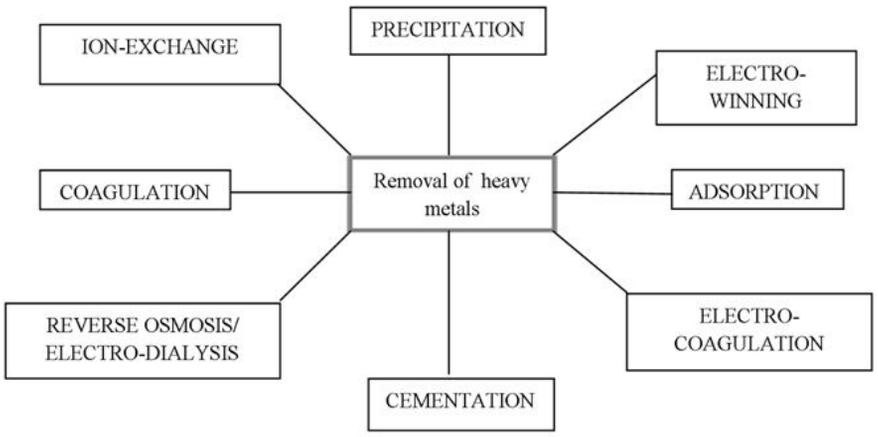


Figure 5. Some conventional methods for the removal of heavy metals.

Some conventional methods are explained below [4, 71-76];

1. Precipitation is the most common method for removing toxic heavy metals up to parts per million (ppm) levels from water. Since some metal salts are insoluble in water and which get precipitated when correct anion is added. Although the process is cost effective its efficiency is affected by low pH and the presence of other salts (ions). The process requires addition of other chemicals, which finally leads to the generation of a high water content sludge, the disposal of which is cost intensive. Precipitation with lime, bisulphide or ion exchange lacks the specificity and is ineffective in removal of the metal ions at low concentration.

2. Ion exchange is another method used successfully in the industry for the removal of heavy metals from effluents. Though it is relatively expensive as compared to the other methods, it has the ability to achieve ppb levels of clean up while handling a relatively large volume. An ion exchanger is a solid capable of exchanging either cations or anions from the sur-

rounding materials. Commonly used matrices for ion exchange are synthetic organic ion exchange resins. The disadvantage of this method is that it cannot handle concentrated metal solution as the matrix gets easily fouled by organics and other solids in the wastewater. Moreover ion exchange is nonselective and is highly sensitive to pH of the solution.

3. Electro-winning is widely used in the mining and metallurgical industrial operations for heap leaching and acid mine drainage. It is also used in the metal transformation and electronics and electrical industries for removal and recovery of metals. Metals like Ag, Au, Cd, Co, Cr, Ni, Pb, Sn and Zn present in the effluents can be recovered by electro-deposition using insoluble anodes.

4. Electro-coagulation is an electrochemical approach, which uses an electrical current to remove metals from solution. Electro-coagulation system is also effective in removing suspended solids, dissolved metals, tannins and dyes. The contaminants presents in wastewater are maintained in solution by electrical charges. When these ions and other charged particles are neutralized with ions of opposite electrical charges provided by electrocoagulation system, they become destabilized and precipitate in a stable form.

5. Cementation is a type of another precipitation method implying an electrochemical mechanism in which a metal having a higher oxidation potential passes into solution e.g. oxidation of metallic iron, Fe(0) to ferrous Fe(II) to replace a metal having a lower oxidation potential. Copper is most frequently separated by cementation along with noble metals such as Ag, Au and Pb as well as As, Cd, Ga, Pb, Sb and Sn can be recovered in this manner.

6. Reverse osmosis and electro-dialysis involves the use of semi-permeable membranes for the recovery of metal ions from dilute wastewater. In electro-dialysis, selective membranes (alternation of cation and anion membranes) are fitted between the electrodes in electrolytic cells, and under continuous electrical current the associated.

Most of these methods suffer from some drawbacks such as high capital and operational costs and problem of disposal of residual metal sludge. Ionexchange is feasible when an exchanger has a high selectively for the metal to be removed and the concentrations of competing ions are low. The metal may then be recovered by incinerating the metal-saturated resin and the cost of such a process naturally limits its application to only the more valuable metals. In many cases, however, the heavy metals are not valuable enough to warrant the use of special selective exchangers/resins from an economic point of view. Cost efective alternative technologies or sorbents for treatment of metals contaminated waste streams are needed. Natural materials that are available in large quantities, or certain waste products from industrial or agricultural operations, may have potential as inexpensive sorbents. Due to their low cost, after these materials have been expended, they can be disposed of without expensive regeneration. Cost is an important parameter for comparing the sorbent materials. However, cost information is seldom reported, and the expense of individual sorbents varies depending on the degree of processing required and local availability. In general, a sorbent can be assumed as ‘low cost'' if it requires little processing, is abundant in nature, or is a by-product or waste material from another in-

dustry. Of course improved sorption capacity may compensate the cost of additional processing. This has encouraged research into using low-cost adsorbent materials to purify water contaminated with metals. Another major disadvantage with conventional treatment technologies is the production of toxic chemical sludge and its disposal/treatment is not eco-friendly. Therefore, removal of toxic heavy metals to an environmentally safe level in a cost effective and environment friendly manner assumes great importance.

In light of the above, biological materials and some adsorption materials have emerged as an economic and eco-friendly option. Adsorption is one the physico-chemical treatment processes found to be effective in removing heavy metals from aqueous solutions. According to literature, an adsorbent (sorbent) can be considered as cheap or low-cost if it is abundant in nature, requires little processing and is a byproduct of waste material from waste industry [66-68, 76-78].

Of course improved sorption capacity may compensate the cost of additional processing. Some of the reported low-cost sorbents such as bark/tannin-rich materials, lignin, chitin/chitosan, dead biomass, seaweed/algae/alginate, xanthate, zeolite, clay, fly ash, peat moss, bone gelatin beads, leaf mould, moss, iron-oxide-coated sand, modified wool and modified cotton. Important parameters for the sorbent effectiveness are effected by pH, metal concentration, ligand concentration, competing ions, and particle size [4, 66-68].

Another type of sorbent is plant waste [68]. Plant wastes are inexpensive as they have no or very low economic value. Most of the adsorption studies have been focused on untreated plant wastes such as papaya wood, maize leaf, teak leaf powder, lalang (Imperata cylindrica) leaf powder, rubber (Hevea brasiliensis) leaf powder, Coriandrum sativum, peanut hull pellets, sago waste, saltbush (Atriplex canescens) leaves, tree fern, rice husk ash and neem bark, grape stalk wastes, etc. Some of the advantages of using plant wastes for wastewater treatment include simple technique, requires little processing, good adsorption capacity, selective adsorption of heavy metal ions, low cost, free availability and easy regeneration. However, the application of untreated plant wastes as adsorbents can also bring several problems such as low adsorption capacity, high chemical oxygen demand (COD) and biological chemical demand (BOD) as well as total organic carbon (TOC) due to release of soluble organic compounds contained in the plant materials. The increase of the COD, BOD and TOC can cause depletion of oxygen content in water and can threaten the aquatic life. Therefore, plant wastes need to be modified or treated before being applied for the decontamination of heavy metals. A comparison of adsorption efficiency between chemically modified and unmodified adsorbents was also reported in literature [67].

In a conclusion, a wide range of low-cost adsorbents obtained from naturel and chemical sorbent or chemically modified plant wastes has been studied and most studies were focused on the removal of heavy metal ions such as Cd, Cu, Pb, Zn, Ni and Cr(VI) ions. The most common chemicals used for treatment of plant wastes are acids and bases. Chemically modified plant wastes vary greatly in their ability to adsorb heavy metal ions from solution. Chemical modification in general improved the adsorption capacity of adsorbents probably due to higher number of active binding sites after modification, better ion-exchange properties and formation of new functional groups that favours metal up-

take. Although chemically modified plant wastes can enhance the adsorption of heavy metal ions, the cost of chemicals used and methods of modification also have to be taken into consideration in order to produce 'low-cost' adsorbents.

Another option is using biological materials [4, 66-68, 76, 77]. Biomaterials of microbial and plant origin interact effectively with heavy metals. Metabolically inactive dead biomass due to their unique chemical composition sequesters metal ions and metal complexes from solution, which obviates the necessity to maintain special growth-supporting conditions. Metal-sorption by various types of biomaterials can find enormous applications for removing metals from solution and their recovery. Rather than searching thousands of microbial species for particular metal sequestering features, it is beneficial to look for biomasses that are readily available in large quantities to support potential demand. While choosing biomaterial for metal sorption, its origin is a major factor to be taken into account, which can come from (a) microorganisms as a by-product of fermentation industry, (b) organisms naturally available in large quantities in nature and (c) organisms cultivated or propagated for biosorption purposes using inexpensive media. Different non-living biomass types have been used to adsorb heavy metal ions from the environment. Seaweed, mold, bacteria, crab shells and yeast are among the different kinds of biomass, which have been tested for metal biosorption or removal. Advantages and disadvantages of biosorption by non-living biomass are as follows [67, 75-77]:

Advantages of biosorption;

1. Growth-independent, non-living biomass is not subject to toxicity limitation of cells. No requirement of costly nutrients required for the growth of cells in feed solutions. Therefore, the problems of disposal of surplus nutrients or metabolic products are not present.
2. Biomass can be procured from the existing fermentation industries, which is essentially a waste after fermentation.
3. The process is not governed by the physiological constraint of living microbial cells.
4. Because of non-living biomass behave as an ion exchanger; the process is very rapid and takes place between few minutes to few hours. Metal loading on biomass is often very high, leading to very efficient metal uptake.
5. Because cells are non-living, processing conditions are not restricted to those conducive for the growth of cells. In other words, a wider range of operating conditions such as pH, temperature and metal concentration is possible. No aseptic conditions are required for this process.
6. Metal can be desorbed readily and then recovered if the value and amount of metal recovered are significant and if the biomass is plentiful, metal-loaded biomass can be incinerated, thereby eliminating further treatment.

Disadvantages of biosorption;

1. Early saturation can be problem i.e. when metal interactive sites are occupied, metal desorption is necessary prior to further use, irrespective of the metal value.

2. The potential for biological process improvement (e.g. through genetic engineering of cells) is limited because cells are not metabolizing. Because production of the adsorptive agent occurs during pre-growth, there is no biological control over characteristic of biosorbent. This will be particularly true if waste biomass from a fermentation unit is being utilized.
3. There is no potential for biologically altering the metal valency state. For example less soluble forms or even for degradation of organometallic complexes.

Metabolic independent processes can mediate the biological uptake of heavy metal cations. Biosorption offers an economically feasible technology for efficient removal and recovery of metal(s) from aqueous solution. The process of biosorption has many attractive features including the selective removal of metals over a broad range of pH and temperature, its rapid kinetics of adsorption and desorption and low capital and operation cost. Biosorbent can easily be produced using inexpensive growth media or obtained as a by-product from industry. It is desirable to develop biosorbents with a wide range of metal affinities that can remove a variety of metal cations. These will be particularly useful for industrial effluents, which carry more than one type of metals. Alternatively a mixture of non-living biomass consisting of more than one type of microorganisms can be employed as biosorbents. Bacterial biomass, algal biomass, fungal biomass were applied to removal of metals in the waste waters. The use of immobilized biomass rather than native biomass has been recommended for large-scale application but various immobilization techniques have yet to be thoroughly investigated for ease, efficency and cost effectivity [67, 77].

Biosorption processes are applicable to effluents containing low concentrations of heavy metals for an extended period. This aspect makes it even more attractive for treatment of dilute effluent that originates either from an industrial plant or from the primary wastewater treatment facility. Thus biomass-based technologies need not necessarily replace the conventional treatment routes but may complement them. At present, information on different biosorbent materials is inadequate to accurately define the parameters for process scale up and design perfection including reliability and economic feasibility. To provide an economically viable treatment, the appropriate choice of biomass and proper operational conditions has to be identified. To predict the difference between the uptake capacities of the biomass, the experimental results should be tested against an adsorption model. The development of a packed bed or fluidized-bed biosorption model would be helpful for evaluating industrial-scale biosorption column performance, based on laboratory scale experiments and to understand the basic mechanism involved in order to develop better and effective biosorbent.

5. Conclusion

An unfortunate consequence of industrialization and industrial production is the generation and release of toxic waste products which are polluting our environment. Many trace and heavy metals (Cd, Pb, Mn, Cu, Zn, Cr, Fe and Ni) and their compounds have been found that are toxic. Many of them are used in several industrial activities including metallurgy,

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tanneries, petroleum refining, electroplating, textiles and in pigments. Their presence in environment has been responsible for several types of health problems in animals, plants and human beings. If the wastewaters were discharged directly into natural waters, it will constitute a great risk for the aquatic ecosystem, whilst the direct discharge into the sewerage system may affect negatively.

The analysis of wastewater for trace and heavy metal contamination is an important step in ensuring human and environmental health. Wastewater is regulated differently in different countries, but the goal is to minimize the pollution introduced into natural waterways. In recent years, metal production emissions have decreased in many countries due to legislation, improved cleaning technology and altered industrial activities. Today and in the future, dissipate losses from consumption of various metal containing goods are of most concern. Therefore, wastewater may need to be measured for a variety of metals at different concentrations, in different wastewater matrices. A variety of inorganic techniques can be used to measure trace elements in waste water including atomic absorption spectrometry (AAS), inductively coupled plasma optical emission spectrometry (ICP-OES) and ICP mass spectrometry (ICP-MS). Depending upon the number of elements that need to be determined and the number of samples that need to be run, the most suitable technique for business requirements can be chosen.

Several industrial wastewater streams may contain heavy metals such as Cd, Sb, Cr, Cu, Pb, Zn, Co, Ni, etc. The toxic metals, probably existing in high or even in low concentrations, must be effectively treated/removed from the wastewaters. The various treatment methods employed to remove heavy or trace metals, adsorption and chemical precipitation process is the most common treatment technology. The conventional heavy metal removal process has some inherent shortcomings such as requiring a large area of land, a sludge dewatering facility, skillful operators and multiple basin configuration. In recent years, some new processes have been developed for the heavy metal removal from wastewater, like biosorption, neutralization, precipitation, ion exchange etc. The use of al these techniques for removal of the heavy metals offers several advantages and limitations compared to each other. The important parameters for the selection of removal technique of heavy metal from waste water are waste type, the growth of the wastewater field, cheap or low-cost removal material, operational costs and problem of disposal of residual metal sludge. The significance of developing new treatment/removal methods for heavy metal from waste or waste water samples has been widely recognized especially in the fields of environmental sciences.

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