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A review of treatment methods used to remove heavy metals from industrial wastewater

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Degree of Bachelor of Science in Environmental Engineering

BY

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Abstract

Heavy metals like arsenic, copper, cadmium, chromium, nickel, zinc, lead, and mercury are major pollutants of fresh water reservoirs because of their toxic, nonbiodegradable, and persistent nature. The industrial growth is the major source of heavy metals introducing such pollutants into different segments of the environment including air, water, soil, and biosphere. They may accumulate in the human body by means of the food chain. Methods for treating industrial wastewater containing heavy metals often involve technologies for reduction of toxicity in order to meet technology-based treatment standards. Was focused on the recently developed and newly applicable various treatment processes for the removal of heavy metals from industrial wastewater. Physico-chemical removal processes such as; adsorption on new adsorbents, ion exchange, membrane filtration, electrodialysis, reverse osmosis, ultrafiltration and photocatalysis . Their advantages and drawbacks were evaluated. Bioadsorption techniques are eco friendly best solutions for removing heavy metals from wastewater rather than physicchemical methods. But chemical methods are most suitable treatments for toxic inorganic compounds produced from various industries which cannot removed from any biological and physical techniques.

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Chapter 1

Introduction

Chapter One

1.1 INTRODUCTION

The environmental issues due to globalization and rapid industrialization are becoming more and more nuisance for human being. Therefore efficient and effective methods are needed especially for chemical industries. Heavy metals present in wastewater and industrial effluent is major concern of environmental pollution. Heavy metals are generally considered those whose density exceeds 5 g per cubic centimeter. Most of the elements falls into this category are highly water soluble, well-known toxics and carcinogenic agents. Heavy metals are considered to be the following elements: Copper, Silver, Zinc, Cadmium, Gold, Mercury, Lead, Chromium, Iron, Nickel, Tin, Arsenic, Selenium, Molybdenum, Cobalt, Manganese, and Aluminum. They represent serious threats to the human population and the fauna and flora of the receiving water bodies [Babel, S. and T.A. Kurniawan, Cr (VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan. *Chemosphere*, 2004. 54(7): p. 951-967]. They can be absorbed and accumulated in human body and caused serious health effects like cancer, organ damage, nervous system damage, and in extreme cases, death. Also it reduces growth and development. Industrial wastewater streams containing heavy metals are produced from different industries. Heavy metals such as cadmium, zinc, lead, chromium, nickel, copper, vanadium, platinum, silver, and titanium are generated in electroplating, electrolysis depositions, conversioncoating, and anodizing-cleaning, milling, and etching industries. Significant amount of heavy metals wastes like Tin, lead, and nickel result from printed circuit board (PCB) manufacturing. Wood processing industries where a chromated copper-arsenate wood treatment produces arsenic containing wastes; inorganic pigment manufacturing producing pigments contain chromium compounds and cadmium sulfide; petroleum refining generates conversion catalysts contaminated with nickel, vanadium, and chromium; and photographic operations producing film with high concentrations of silver and ferrocyanide. All of these generators produce a large quantity of wastewaters, residues, and sludge that can be categorized as hazardous wastes requiring extensive waste treatment [Sörme, L. and R. Lagerkvist, Sources of heavy metals in urban wastewater in Stockholm. *Science of the Total Environment*, 2002. 298(1): p. 131-145.]. As the low amounts of these metals are highly toxic, removal of heavy metals from wastewater has recently become the subject of considerable interest owing to strict legislations. Wastewater regulations were established to minimize human and environmental exposure to hazardous chemicals. These include limits on the types and concentration of heavy metals that may be present in the discharged wastewater. The Maximum Contaminated Level (MCL) standards, for those heavy metals, established by USEPA [Babel, S. and T.A. Kurniawan, Low-cost adsorbents for heavy metals uptake from contaminated water: a review. *Journal of hazardous materials*, 2003. 97(1): p. 219-243.] are summarized in Table 1. Therefore it is necessary to treat metal contaminated wastewater prior to its discharge to the environment. Heavy

metal removal from inorganic effluent can be achieved by conventional treatment processes. Removal of heavy metals from industrial wastewaters can be accomplished through various treatment options, including such unit operations as chemical precipitation, coagulation, complexation, activated carbon adsorption, ion exchange, solvent extraction, foam flotation, electrodeposition, cementation, and membrane operations. This paper describes these various treatment strategies and methodologies employed for heavy metal removal.

TABLE 1 The MCL standards for the most hazardous heavy metals (Babel and Kurniawan, 2003)

Heavy metal	Toxicities	MCL(mg/L)
Arsenic	Skin manifestations, visceral cancers, vascular disease	0.05
Cadmium	Kidney damage, renal disorder, human carcinogen	0.01
Chromium	Headache, diarrhea, nausea, vomiting, carcinogen	0.05
Copper	Liver damage, Wilson disease, insomnia	0.25
Nikel	Dermatitis, nausea, chronic asthma, coughing, human carcinogen	0.20
Zinc	Depression, lethargy, neurological signs and nervous system	0.80
Lead	Damage the fetal brain, diseases of the kidneys, circulatory system and nervous system	0.006
Mercury	Rheumatoid arthritis, and diseases of the kidneys, circulatory system and nervous system	0.00003

Chemical precipitations, conventional adsorption [Maity, H., et al., Protein hydrogen exchange mechanism: local fluctuations. *Protein science*, 2003. 12(1): p. 153-160. / amritphale, S., et al., Adsorption behavior of lead ions on pyrophyllite surface main group metal chemistry, 1999. 22(9): p. 557-566. / Chandra Sekhar, K., et al., Removal of heavy metals using a plant biomass with reference to environmental control. *International Journal of Mineral Processing*, 2003. 68(1): p. 37-45. / Prasad, B. and U. Pandey, Separation and preconcentration of copper and cadmium ions from multielemental solutions using *Nostoc muscorum*-based biosorbents. *World Journal of Microbiology and Biotechnology*, 2000. 16(8-9): p. 819-827. / Ho, Y.-S. and G.

McKay, Pseudo second order model for sorption processes. *Process Biochemistry*, 1999. 34(5): p. 451-465.], ion exchange [Vaca Mier, M., et al., Heavy metal removal with Mexican clinoptilolite: multi-component ionic exchange. *Water research*, 2001. 35(2): p. 373-378.], membrane separation methods [Reddad, Z., et al., Adsorption of several metal ions onto a low-cost biosorbent: kinetic and equilibrium studies. *Environmental science and technology*, 2002. 36(9): p. 2067-2073.] and electroremediation methods are used more commonly to treat industrial wastewater. Among these methods precipitation is most economical and hence widely used, but many industries still use chemical procedures for treatment of effluents due to economic factors [Zhou, W. and W. Zimmermann, Decolorization of industrial effluents containing reactive dyes by actinomycetes. *FEMS microbiology letters*, 1993. 107(2): p. 157-161. , Sergeev, V., et al., Groundwater protection against pollution by heavy metals at waste disposal sites. *Water Science and Technology*, 1996. 34(7): p. 383-387.]. However due to complexing agents in wastewater, efficiency of the precipitation process can drastically be decreased [Salim, M. and B. Shaikh, Distribution and availability of zinc in soil fractions to wheat on some alkaline calcareous soils. *Zeitschrift für Pflanzenernährung und Bodenkunde*, 1988. 151(6): p. 385-389.] and this creates incomplete processing and production of toxic sludge. Therefore numerous novel approaches have been studied to develop cost effective and more efficient heavy metal adsorption techniques [Eccles, H., Treatment of metal contaminated wastes: why select a biological process? *Trends in biotechnology*, 1999. 17(12): p. 462-465.]. Biosorption is considered as a user-friendly, effective purification and separation method for the removal of heavy metals from industrial wastewater with the advantages of specific affinity, low cost and simple design [AlAsheh, S., et al., Predictions of binary sorption isotherms for the sorption of heavy metals by pine bark using single isotherm data. *Chemosphere*, 2000. 41(5): p. 659-665. , Muhammad, S., M.T. Shah, and S. Khan, Health risk assessment of heavy metals and their source apportionment in drinking water of Kohistan region, northern Pakistan. *Microchemical Journal*, 2011. 98(2): p. 334-343.]. Therefore it has been widely used for treatment of wastewater. Sorption with sorbents made of agricultural or industrial by products are used widely to remove heavy metals from aqueous solution due to their abundant availability, low cost, and favorable physical, chemical and surface .

1.2 Statement of problem

As a result of different human activities, the world is facing serious threats of air, land, and water pollutions. Water pollution in particular, has raised severe environmental impacts. In addition to the shortage of resources of water due to drought and misuse, production of large volumes of wastewater has put a lot of pressure on humankind. There are different types of water contaminants. They are summarized in Figure 1. Among these pollutants, the inorganic pollutants are extremely harmful due to their high toxicity and non-biodegradability. Sources of inorganic pollutants Heavy metals, like mercury, lead, tin, cadmium, selenium, and Arsenic are introduced to the environment by different human activities and deposit slowly in the surrounding water and soil [*J Hazard Mat* 97: 219-243]. In many

Developing countries, little attention is paid to the environmental issues that the drainage of waste water into lakes and rivers is very common. The uncontrolled activities cause poisoning of fresh water resources which affects the entire ecosystem. The top six toxic pollutants are given in Table 2 whereas the major sources of



Figure 1 Different water Contaminants

The Top Six Toxic Threats:	Estimated Population at risk at Identified Sites*(million people)
1. Lead	10
2. Mercury	8.6
3. Chromium	7.3
4. Arsenic	3.7
5. Pesticides	3.4
6. Radionuclides	3.3

Table 2 the top six Toxic Threats

1.3 The objectives of the present work

The objectives of this present review work is summarized as below :-

- In this study, an overview of the physical, chemical and biological methods (Chemical Precipitation, adsorption, Coagulation and Flocculation , Membrane Filtration , Electro dialysi Flotation, Ion exchange, Electrochemical Treatments) for removing heavy metals from wastewater is presented .
- This paper also reviews a summary of heavy elements adequately and effects of some important heavy metals on human health, various sources it and need for the removal of heavy metals from water .
- considered the main objective of sewage treatment Purify wastewater without harming the public health and causing other nuisance . And gain energy, nutrients, water, and as well other valuable resources from wastewater during purification stepsand also Get rid of heavy metals existing a concentration higher than the permissible concentrations .

Chapter Two

Harmful effects of heavy metals

Chapter Two

2.1 Harmful effects of heavy metals

The heavy metals elements are accessed as toxic and harmful to the health of human beings and other living organisms even in low concentrations, due to the gradual bioaccumulation. The accumulation of these chemicals in the living organisms is greater than their release. The negative effects are appeared as these elements cannot biodegrade or easily break down (Hossain, 2013; Abas et al., 2013). Therefore, during the last years, an increasing attention has been focused on the separation, pre-concentration and /or determination of trace heavy metal ions in the environment.

2.1.1 Chromiumm _Cr_(VI)

Chromiumm is an oxidising agent, is carcino- genic in nature and is also harmful to plants and animals (Barnhart 1997). Exposure to chromium(VI) can cause cancer in the digestive tract and lungs, epigastric pain, nausea, severe diarrhoea, vomiting and haemorrhage liver damage,skin Irritation,ulcer,edema, and damage too circulatory and nerve tissue. Chromium often accumulates in aquatic life, adding to the danger of eating fish that may have been exposed to high levels of chromium, chromium is used in metal alloys and pigments for paints, cement, paper, rubber, and other materials .(Mohanty et al., 2005). Although chromium can access Many oxidation states, chromium(VI) and chromium(III) are the species that are mainly found in industrial effluents (Mohan and Pittman 2006). Chromium(VI) is more toxic than chromium(III) and is of more concern (Al-Othman et al. 2012). The specific sources of chromium are leather tanning, electroplating, nuclear power plants and textile industries

2.1 . 2 Copper cu(II) and cu(IV)

Copper is toxic and carcinogenic when it is ingested in large amounts and causes headache, vomiting, nausea, kidney failure, it can cause anemia, liver and kidney damage, and stomach and intestinal irritation. respiratory problems Kidneys,brain, skin ˆheart and abdominal pain, problems,accumulation in the Natural deposits, refining of nonferrous metal, pigment, printing ˆmetal refineries, smelting, mining and the photo- graphic (Ren et al. 2008; Hu et al. 2013; Lan et al. 2013) . Copper normally occurs in drinking water from copper pipes, as well as from additives designed to control algal growth and sources of copper include smelting, mining, electroplating, surface finishing, electric appliances, electrolysis and electrical components contaminant in food especially shellfish, liver, mushroom, nuts, chocolate, PCB designing, (Yin et al. 2012; Bilal et al. 2013; Lan et al. 2013).

2.1.3 Zinc

is essential for human health but large quantities of zinc can cause nausea, anemia, skin irritation, disruptions to protein metabolism, and arteriosclerosis(Oyaro et al.,

2007) . Zinc is also associated with metal fume fever, a flu-like illness resulting from occupational exposure to zinc or other metals(Oyaro et al., 2007) . Additionally, elevated zinc levels can harm natural ecosystems and reduce agricultural productivity by inhibiting the uptake of other essential nutrients by plants, and it can also cause damage through its tendency to bio-accumulate in aquatic and terrestrial animal life.(Oyaro et al., 2007). Source of zinc Galvanization process, wood preservatives, accelerators for rubber vulcanization, photographic paper, catalysts, textiles, pigments, fertilizers, steel production, ceramics and batteries (Parker 1980)

2.1.4 Arsenic

Arsenic can cause skin, lung, bladder and kidney cancer, muscular weakness, loss of appetite, nausea and Vomiting , diarrhea,black foot disease, (Mohan and Pittman 2007). source of pollution Ceramic, fertilizers, detergents, Metallurgical, dyes, glasswares,Pesticides industries(Mohan and Pittman 2007).

2.1.5 Antimony

Antimony is a metal used in the compound antimony trioxide, a flame retardant and It is considered suspected human carcinogen. Most antimony compounds do not bioaccumulate in aquatic life(Borba et al., 2006) . It can also be found in batteries, pigments, and ceramics and glass.Everyone is exposed to low levels of antimony in the environment. Acute (shortterm) exposure to Antimony by inhalation in humans results in effects on the skin and eyes. Respiratory effects, such as Inflammation of the lungs, chronic bronchitis, and chronic emphysema, Human Exposure to high levels of antimony for short periods of time causes nausea, vomiting, and diarrhea(Borba et al., 2006).

2.1.6 Cadmium

Cadmium derives its toxicological properties from its chemical similarity to zinc an essential micronutrient for plants, animals and humans. Cadmium is biopersistent and, once absorbed by an organism, remains resident for many years (over decades for humans) although it is eventually excreted. Cadmium as a human carcinogen and it is known to cause deleterious effects to health and bone demineralisation either through direct bone damage or as a result of renal dysfunction In long-term exposure is associated with renal dysfunction. High exposure can lead to obstructive lung disease and has been linked to lung cancer . (Fu and Wang 2011) major source of cadmium are corrosion of galvanised pipe, erosion of an essential element and is required for enzyme synthesis as well as tissue and bone development. In addition, the metal can be linked to increased blood pressure and effects on the myocardium in animals.

2.1.7 Lead (Pb)

High levels of exposure may result in toxic biochemical effects in humans which in turn cause problems in the synthesis of haemoglobin, effects on the kidneys, gastrointestinal tract, joints and reproductive system, and acute or chronic damage to

the nervous system damage, liver and brain functions and central, anemia, Headache (Naseem and Tahir 2001). Lead poisoning, which is so severe as to cause evident illness, is now very rare indeed (Naseem and Tahir 2001). And lead can have small, subtle, subclinical effects, particularly on neuropsychological developments in children (Meena et al., 2005). Although most people receive the bulk of their lead intake from food, in specific populations other sources may be more important, such as water in areas with lead piping and plumbosolvent water, air near point of source emissions, soil, dust, paint flakes in old houses or contaminated land. Source of lead pollution Glass, lead paint, printing, Batteries Manufacturing industries (Meena et al., 2005).

2.1.8 Mercury

Mercury is a toxic substance which has no known function in human biochemistry or physiology and does not occur naturally in living organisms. Inorganic mercury poisoning is associated with tremors, gingivitis and/or minor psychological changes, together with spontaneous abortion and congenital malformation. It is a neurotoxin that can affect the central nervous system. If it is exceeded in concentration it can cause pulmonary, chest pain and dyspnoea and causes mental retardation, genetic defects, Teratogenic effects (Namasivayam and Kadirvelu 1999). The major natural source of mercury is the degassing of the Earth's crust, emissions from volcanoes and evaporation from natural bodies of water, Chlor alkali industry and battery industries, Paints, pulp and paper, oil refining, Rubber processing And fertilizer industries Batteries, Thermometers, Fluorescent light tubes and high Intensity street lamps, pesticides, cosmetics, pharmaceuticals industries (Liu and Huang, 2011).

2.1.9 Nickel

Is a human carcinogen in nature, Small amounts of Nickel are needed by the human body to produce red blood cells, however, in excessive amounts, can become mildly toxic. Short-term overexposure to nickel is not known to cause any health problems, but longterm exposure can cause decreased body weight, heart and liver damage, and skin irritation. And causes kidney and lung problems, gastrointestinal distress and pulmonary fibrosis, Acute poisoning of Ni (II) causes headache, dizziness, nausea vomiting, Chest pain, extreme weakness (Borba et al., 2006). Source of nickel are electroplating batteries, silver refineries, zinc base castin, metal finishing and forging, batteries manufacturing, mining Industries (Kadirvelu and Namasivayam, 2003).

2.1.10 Selenium (Se)

Selenium is a trace mineral, and is used in many industrial sectors, such as the electronic, paint, pharmaceutical, ink, rubber, and glass industries (Rayman M.P. Selenium and human health). Se is an essential trace element for living bodies, as it is necessary for cellular function. Short-term exposure to Se can cause nausea, vomiting, and diarrhea, while longterm exposure causes stomach pain and respiratory problems, including bronchitis and health problems such hair and fingernail loss, damage to kidney and liver tissue, damage to circulatory tissue, and more severe damage to the nervous system (Rayman M.P. Selenium and human health.). Selenium accumulates in living tissue, causing high selenium content in fish and other organisms (Rayman M.P. Selenium and human health.). Anthropogenic sources of selenium include coal burning, mining, and smelting of sulfide ores Precipitation.

2.1.11 Barium(Ba)

Barium is an abundant and natural material used for various industrial purposes, such as drilling mud, and the paint, brick making, ceramics, glass, and rubber industries. Shortterm exposure of Ba-based compounds can cause vomiting, abdominal pain, respiratory problems, fluctuations in blood pressure, and intense muscle pain, whereas long-term exposure can alter heart rate, cause paralysis, and sometimes even lead to death [Oskarsson and et al., 2008] . Barium can be present in landfill leachate, coal waste, corrosion inhibitors, de-icing products, and high-octane fuels.

2.1.12 Silver (Ag)

Silver is used in its metallic form, as well as in its complexed form. It is employed in jewelry, electronic industries, photographic films, and antimicrobial agents. Although Ag has antimicrobial properties, exposure to high levels of silver can cause argyria, skin irritation, throat irritation, respiratory problems, and skin rashes [Banu A.N., Kudesia N and et al., 2004]. Although Ag is absorbed and digested in the soft tissue,it can cause neurotoxic damage. Ag primary enters the human body through the genital tract and during inhaling, where it deposits in the lungs [panyala N. R and et al., 2008] . Source pollution of silver Smelting, mining and coal burning[panyala N. R and et al., 2008] .

2.2. Regulatory Limits of Heavy Metals

Although heavy metals are natural materials, technological activities have altered their cycles in environments. Due to this alternation in cycles, metals are consumed in different parts of the environment, which is leading to various harmful effects on living bodies. Among heavy metals, few metals are essential, such as Fe, Cu, Zn, and Mn for living bodies, but after a specific concentration, these metals have become toxic [pratish, Kumar A and et al., 2004]. On the other hand, heavy metals such as Pd and Hg are useful for human bodies, but have a detrimental effect on human health if they accumulate more over time. Essentially, human bodies are in contact with these metals during ingestion and breathing processes. The risk of exposure of these heavy metals to people is high, whether working or living near the industrial areas related to these metals and their corresponding compounds. In short, heavy metals are not harmful to human health until they exceed the limits of toxicity. The pathway in which heavy metals affect human bodies depends on the specific metals, but ultimately all metals produce reactive oxygen radicals, which leads to various diseases in living bodies. Thus, it is essential to establish a limit above which toxic elements were considered [pratish, Kumar A and et al., 2004]. Based on the toxicity, the regulatory limits of heavy metals set by the various well-known organizations are summarized in Table 3.

Sl.No.	Heavy Metals	Name of the Organization	Regulatory Limits
1	Silver (Ag)	EPA	Drinking water: not exceed 0.10 ppb
		Occupational Safety and Health Administration (OSHA)	0.01 mg/m³ in workplace air
2	Arsenic (As)	EPA	Drinking water: 0.01 parts per million (ppm)
		OSHA	10.0 µg/m³ in workplace
3	Barium (Ba)	EPA	Drinking water: 2.0 ppm
		OSHA	0.5 mg/m³ in workplace for soluble barium compounds
4	Cadmium (Cd)	EPA	Drinking water: 0.005 ppm
		OSHA	5.0 µg/m³ in workplace
		Food and Drug Administration (FDA)	Bottled drinking water: 5 parts per billion (ppb)
5		EPA	Drinking water: 1–2 ppb

6	Chromium (Cr)	EPA	Drinking water: 0.1 ppm
		OSHA	0.0005–1.0 mg/m ³ in workplace depending on the compounds
		FDA	Bottled drinking water: 1 ppm
7	Copper (Cu)	EPA	Drinking water: 1.5 mg/L
		World Health Organization (WHO)	2 mg/L
8	Iron (Fe)	EPA	Drinking water: 0.3 mg/L
		WHO	Drinking water: 0.1 mg/L
9	Mercury (Hg)	EPA	Drinking water: 2 ppb
		OSHA	0.1 mg/m ³ in workplace for organic Hg and 0.05 mg/m ³ in workplace for metallic Hg vapour

		FDA	1 part of methylmercury in a million parts of seafood
10	Manganese (Mn)	WHO	0.4 mg/L
		EPA	Drinking water: 0.05 mg/L
11	Nickel (Ni)	WHO	Drinking water: 70 µg/L
		EU (European Union)	Drinking water: 20 µg/L
12	Lead (Pb)	EPA	Drinking water: 15 ppb and 0.15 µg/m³ in air.
13	Selenium (Se)	EPA	Drinking water: 50 ppb
		OSHA	0.2 mg/m³ in workplace air

Table 3: Summary of regulatory limits of heavy metals

Chapter Three

**HEAVY METAL WASTEWATER
TREATMENT TECHNIQUES**

3.1 Introduction

A great increasing of wastewater amount containing harmful heavy metals for different living forms is continuously generated with the development of different industries. When the wastewater containing these pollutants inappropriately discharged or inefficiently treated, it becomes one of the critical environmental problems, since metals can accumulate in all the living organisms and they are not degradable. So that, it is necessary to adopt the wastewater treatment technologies to minimize the hazardous contaminants. Various techniques have been applied for treatment of heavy metals in wastewater include physicochemical remediation, phytoremediation and microbial remediation (Nsimba, 2012). Table(3.1) explains the description of the processes and their disadvantages.

Table (3.1): Remediation techniques used for the removal of heavy metals from wastewater.

Applied technique	Technique details	Disadvantages
Coagulationfloculation	<p>-Coagulation is the destabilization of colloidal particles by neutralizing the forces and forming the sediments through keep them apart.</p> <p>-Floculation includes adding polymers to bind the unstable flocs through forming the bridges between them for agglomeration (Zheng et al., 2011).</p>	Consumption of chemicals and increased volume generated of sludge (Fu and Wang, 2011).
Flotation	Separate heavy metals from a liquid media using bubble attachment in mineral processing. This process is classified into: dissolved air flotation(DAF) (Tessele et al., 1998; ion flotation (Polat and Erdogan, 2007) and flotation precipitation (Capponi et al., 2006).	High initial capital cost, high costs of operations and maintenance (Rubio et al., 2002).

Chemical precipitation	Adding chemicals to react with metal ions to convert them insoluble precipitates which are separated from the media by sedimentation or filtration(Ku and Jung, 2001; Oncel et al., 2013).	Generates large amount of sludge caused a problem of disposal and great difficulties for treated it (Fu and Wang, 2011).
Electrochemical	Using a cathode surface to plat-out of metal ions on it and the metal ions can be recovered in the elemental metal(Fu and Wang, 2011).	Expensive electricity supply, High initial capital investment and the pH sensitive (Fu and Wang, 2011).
Ion exchange	Metal ions were displaced from their solutions and were exchanged on the exchangeable resin by electrostatic forces (Fu and Wang, 2011; Nsimba, 2012).	Partial removal for certain ions, high cost (Nsimba, 2012), may cause many secondary pollution during the regeneration process by chemical reagents (Fu and Wang, 2011).
Ultrafiltration (UF)	Using pressure driven membranes (Fu and Wang, 2011).	Problem of disposal of large amount of sludge, low flow rate (Yahaya and Don, 2014).
Reverse osmosis (RO)	Using a semi-permeable membrane at a pressure more than osmotic pressure resulted by the dissolved solids, the water is forced to diffuse across the membrane from the lower concentration side to another with higher concentration (Nsimba,	Expensive (Yahaya 2014).

	2012)	
Electrodialysis	Separation of ions through charged semimembranes from one solution to another utilizing the electric field as the driving force. So, cations and anions can be separated by the electrical potential generated between two electrodes, as well as the formation of cells of concentrated and dilute salts are formed (Sadrzadeha et al., 2009; Yahaya and Don, 2014).	Clogging the membrane by formation of metal hydroxides (Yahaya and Don, 2014).
Nanofiltration	Using a semi-permeable membranes which have pore size between those of RO and UF. Utilizing the pressure-driving to sepatate metal ions (Coman et al., 2013).	It is complex process, affecting on the micro-hydrodynamic, events of interfacial are occurred at the nanopores and surface of membrane(Coman et al., 2013)
Phytoremediation	Using specified plants substantially or partially treatment of soil, sediment, sludge, surface and ground water, and wastewater(Yahaya and Don, 2014).	The process needs a long time for removing metal ions, the difficulty of plant regeneration (Yahaya and Don, 2014).

Solvent extraction	It is a suitable process to selectively extract metal ions from contaminated solutions (liquid-liquid extraction system) by mixing them with extraction agent as organic phase (Hoogerstraete et al., 2013)	Expensive (Hoogerstraete et al., 2013).
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Adsorption has a strong attention as an effective and economic method for removal of heavy metals from wastewater. This process offers flexibility in design and operation and it produces treated effluent with high quality. In some times, the adsorption is reversible as adsorbents can be regenerated using proper desorption process (Fu and Wang, 2011).

3.2 Heavy Metal Removal Methods

There are many ways, the most prominent of which are :-

3.2.1 Physical Methods

Following methods have been used by various researchers for removal of heavy metals. Physical separation techniques are primarily applicable to particulate forms of metals, discrete particles or metalbearing particles [Dermont, G., et al., Metal contaminated soils: remediation practices and treatment technologies. Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management, 2008. 12(3): p. 188-209.]. Physical separation consists of mechanical screening, hydrodynamic classification, gravity concentration, flotation, magnetic separation, electrostatic separation, and attrition scrubbing [Dermont, G., et al., Metal contaminated soils: remediation practices and treatment technologies. Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management, 2008. 12(3): p. 188-209.]. The efficiency of physical separation depends on various soil characteristics such as particle size distribution, particulate shape, clay content, moisture content, humic content, heterogeneity of soil matrix, density between soil matrix and metal contaminants, magnetic properties, and hydrophobic properties of particle surface [Smith, L., Contaminants and remedial options at selected metal-contaminated sites. Technical resource report, 1995, Battelle, Columbus, OH (United States). , Williford, C., R.M. Bricka, and I. Iskandar, Physical separation of metal contaminated soils2000: CRC Press LLC, Boca Raton.].

3.2.2 Chemical Methods

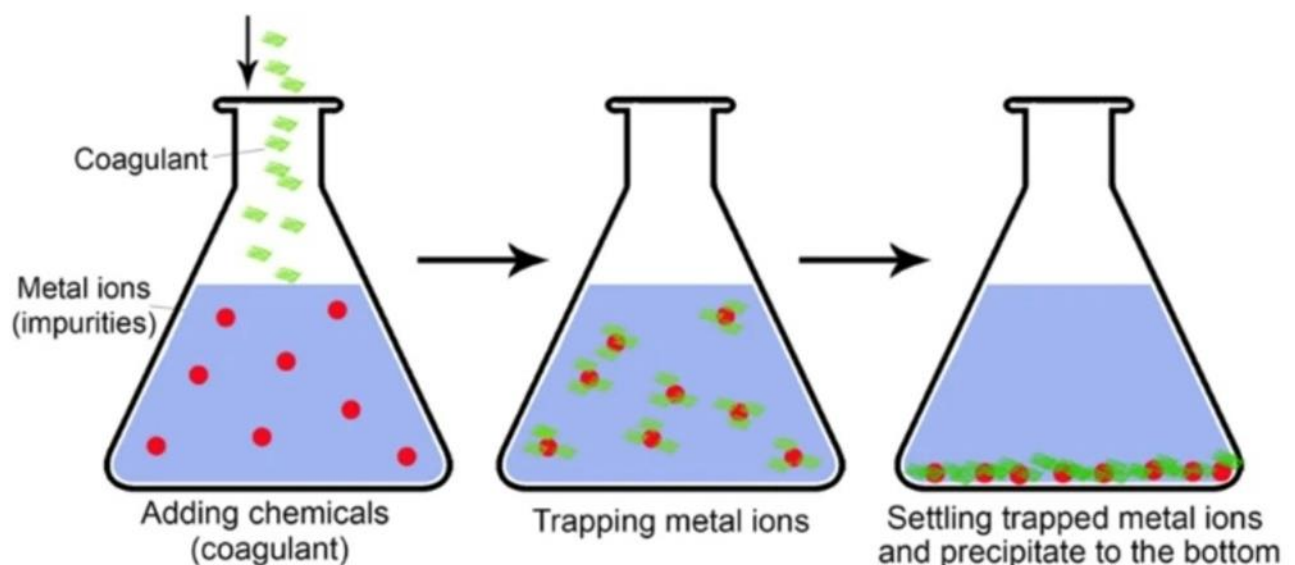
The conventional chemical processes for removing heavy metals from wastewater include many processes such as chemical precipitation, flotation, adsorption, ion

exchange, and electrochemical deposition. Factors that may limit the applicability and effectiveness of the chemical process are high content of clay/silt, humic, calcite, Fe & Ca, heavy metals, anions, or high buffering capacity [Fu, F. and Q. Wang, Removal of heavy metal ions from wastewaters: a review. Journal of Environmental Management, 2011. 92(3): p. 407-418.].

3.2.2.1 Chemical Precipitation

Chemical precipitation is one of the most widely used for heavy metal removal from inorganic effluent in industry due to its simple operation [Ku, Y. and I.-L. Jung, Photocatalytic reduction of Cr (VI) in aqueous solutions by UV irradiation with the presence of titanium dioxide. Water Research, 2001. 35(1): p. 135-142.]. These conventional chemical precipitation processes produce insoluble precipitates of heavy metals as hydroxide, sulfide, carbonate and phosphate. The mechanism of this process is based on to produce insoluble metal precipitation by reacting dissolved metals in the solution and precipitant. In the precipitation process very fine particles are generated and chemical precipitants, coagulants, and flocculation processes are used to increase their particle size to remove them as sludge [Fu, F. and Q. Wang, Removal of heavy metal ions from wastewaters: a review. Journal of Environmental Management, 2011. 92(3): p. 407-418. , Ku, Y. and I.-L. Jung, Photocatalytic reduction of Cr (VI) in aqueous solutions by UV irradiation with the presence of titanium dioxide. Water Research, 2001. 35(1): p. 135-142.]. Once the metals precipitate and form solids, they can easily be removed, and low metal concentrations, can be discharged. Removal percentage of metal ions in the solution may be improved to optimum by changing major parameters such as pH, temperature initial concentration, charge of the ions etc.

The most commonly used precipitation technique is hydroxide treatment due to its relative simplicity, low cost of precipitant (lime), and ease of automatic pH control .



(Fig1): A simple schematic of the chemical precipitation process.

The coagulant is added to wastewater and stirred to trapping metal ions that settle and

precipitate to the bottom of the container.

3.2.2.2 Coagulation and Flocculation

The coagulation-flocculation mechanism is based on zeta potential (ζ) measurement as the criteria to define the electrostatic interaction between pollutants and coagulant/flocculant agents [López-Maldonado, E., et al., Coagulation flocculation mechanisms in wastewater treatment plants through zeta potential measurements. *Journal of hazardous materials*, 2014. 279: p. 1-10.]. Coagulation process is reduced the net surface charge of the colloidal particles to stabilize by electrostatic repulsion process [Benefield, L.D., J.F. Judkins, and B.L. Weand, *Process chemistry for water and wastewater treatment* 1982: Prentice Hall Inc.]. Flocculation process continually increases the particle size to discrete particles through additional collisions and interaction with inorganic polymers formed by the organic polymers added [Tripathy, T. and B.R. De, *Flocculation: a new way to treat the waste water*. 2006.]. Once discrete particles are flocculated into larger particles, they can be removed or separated by filtration, straining or floatation. Production of sludge, application of chemicals and transfer of toxic compounds into solid phase are main drawbacks of this process .

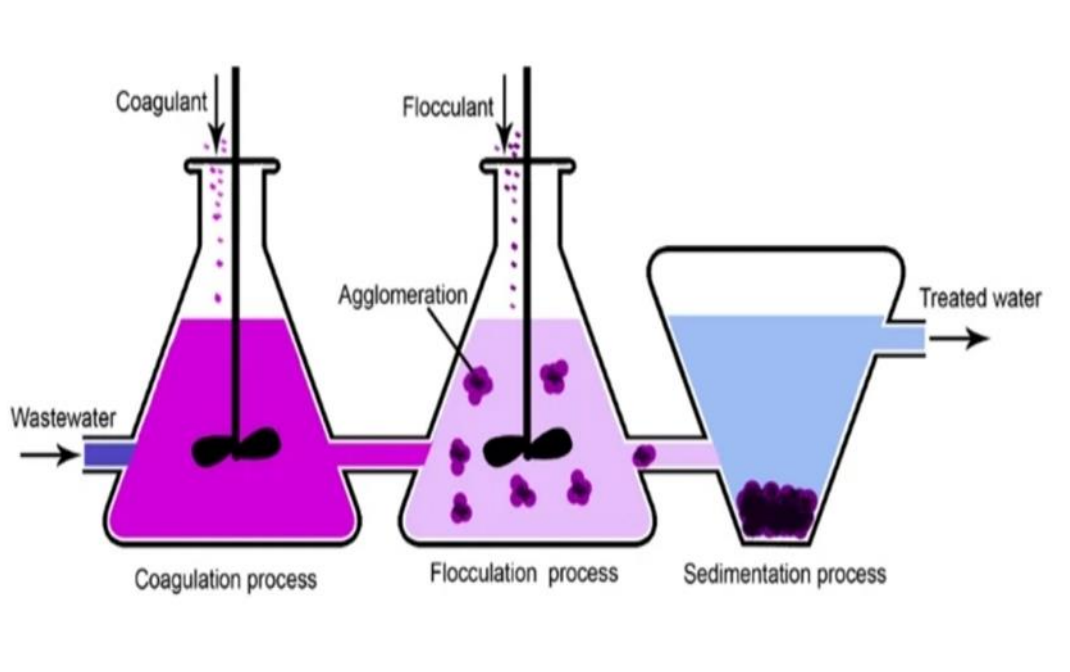


Figure (2) An illustrative schematic of the coagulation-flocculation treatment process.

Coagulation and flocculation could be either two sequential processes or one process. The sedimentation process could be replaced with filtration or another method.

3.2.2.3 Electrochemical Treatments

Electrolysis: Electrolytic recovery is one technology used to remove metals from wastewater streams. This process uses electricity to pass a current through an aqueous metal-bearing solution containing a cathode plate and an insoluble anode. Electricity can be generated by movements of electrons from one element to another. Electrochemical process to treat wastewater containing heavy metals is to precipitate the heavy metals in a weak acidic or neutralized catholyte as hydroxides. Electrochemical treatments of wastewater involve electro deposition, electrocoagulation, electro-flotation and electro oxidation [Shim, H.Y., et al., Application of Electrocoagulation and Electrolysis on the Precipitation of Heavy Metals and Particulate Solids in Washwater from the Soil Washing. *Journal of Agricultural Chemistry and Environment*, 2014. 3(04): p. 130.]. Electrodestabilization of colloids is called coagulation and precipitation by hydroxide formation to acceptable levels. It is the most common heavy metal precipitation method forming coagulants by electrolytic oxidation and destabilizing contaminants to form flocs [Mollah, M.Y.A., et al., Electrocoagulation (EC)—science and applications. *Journal of hazardous materials*, 2001. 84(1): p. 29-41.]. The electrocoagulation process the coagulant is generated in situ by electrolytic oxidation of an appropriate anode material. In this process, charged ionic metal species are removed from wastewater by allowing it to react with anion in the effluent. This process is characterized by reduced sludge production, no requirement for chemical use, and ease of operation. However, chemical precipitation requires a large amount of chemicals to reduce metals to an acceptable level for discharge. Other drawbacks are huge sludge production, slow metal precipitation, poor settling, the aggregation of metal precipitates, and the longterm environmental impacts of sludge disposal [Aziz, H.A., M.N. Adlan, and K.S. Ariffin, Heavy metals (Cd, Pb, Zn, Ni, Cu and Cr (III)) removal from water in Malaysia: Post treatment by high quality limestone. *Bioresource Technology*, 2008.

99(6): p. 1578-1583.]. It changes the aqueous pollution problem to a solid waste disposal problem without recovering the metal .

3.2.2.4 Ion Exchange

Ion exchange can attract soluble ions from the liquid phase to the solid phase, which is the most widely used method in water treatment industry. As a cost-effective method, ion exchange process normally involves low-cost materials and convenient operations, and it has been proved to be very effective for removing heavy metals from aqueous solutions, particular for treating water with low concentration of heavy metals [Dizge, N., B. Keskinler, and H. Barlas, Sorption of Ni (II) ions from aqueous solution by

Lewatit cation-exchange resin. *Journal of hazardous materials*, 2009. 167(1): p. 915-926. , Hamdaoui, O., Removal of copper (II) from aqueous phase by Purolite C100MB cation exchange resin in fixed bed columns: Modeling. *Journal of hazardous materials*, 2009. 161(2): p. 737-746.]. In this process cations or anions containing special ion exchanger is used to remove metal ions in the solution. Commonly used ion exchangers are synthetic organic ion exchange resins. It can be

used only low concentrated metal solution and this method is highly sensitive with the pH of the aqueous phase. Ion exchange resins are water-insoluble solid substances which can absorb positively or negatively charged ions from an electrolyte solution and release other ions with the same charges into the solution in an equivalent amount. The positively charged ions in cationic resins such as hydrogen and sodium ions are exchanged with positively charged ions, such as nickel, copper and zinc ions, in the solutions. Similarly, the negative ions in the resins such as hydroxyl and chloride ions can be replaced by the negatively charged ions such as chromate, sulfate, nitrate, cyanide and dissolved organic carbon (DOC) .

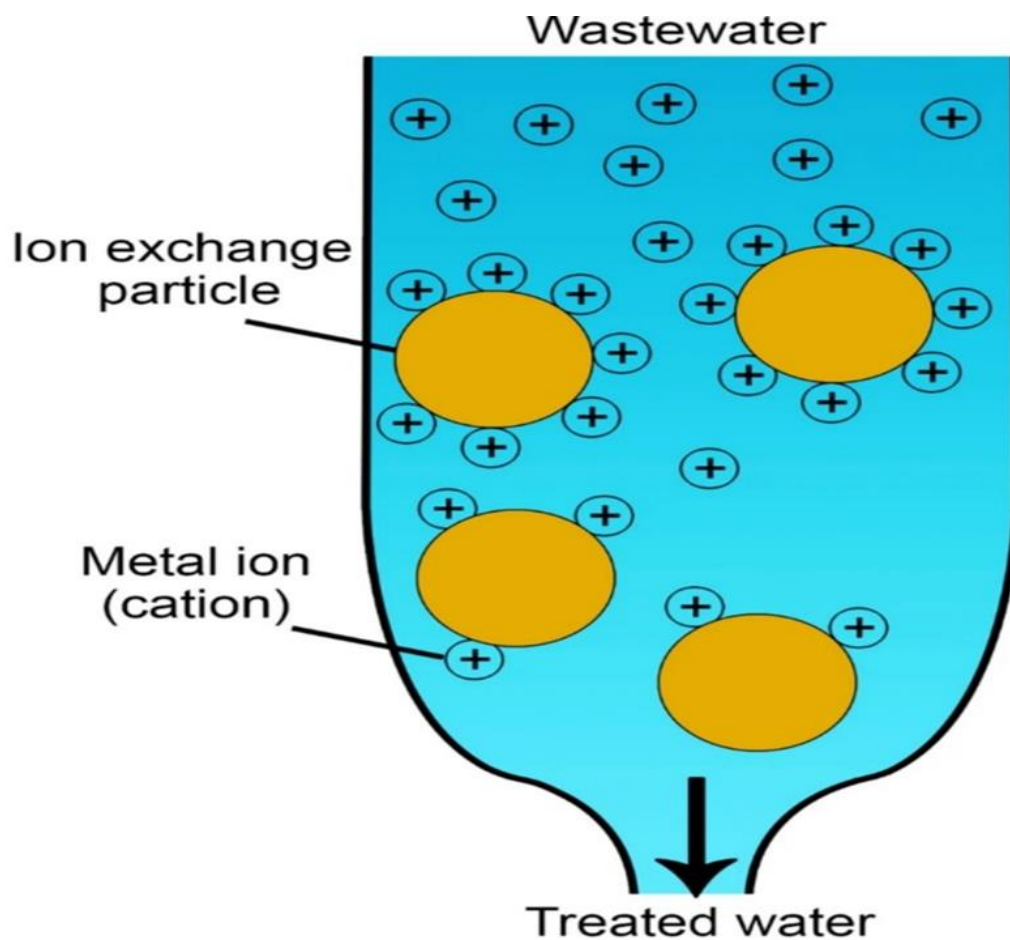


Figure (3) A diagram of Ionic exchange The metal ions (cations) of wastewater occurs in the position of these in the ion exchange particles such(H and Na) anion could also be removed by tis method.

3.2.25 Membrane Filtration

Membrane filtration has received considerable attention for the treatment of inorganic effluent. It is capable of removing suspended solid, organic compounds and inorganic contaminants such as heavy metals. Depending on the size of the particle that can be retained, various types of membrane filtration such as ultrafiltration, nanofiltration and reverse osmosis can be employed for heavy metal removal from wastewater.

3.2.2.5.1 Ultrafiltration(UF): Utilizes membrane to separate heavy metals, macromolecules and suspended solids from inorganic solution on the basis of the pore size (5–20 nm) and molecular weight of the separating compounds (1000–100,000 Da) [Vigneswaran, R., et al., Cerebral palsy and placental infection: a case-cohort study. *BMC pregnancy and childbirth*, 2004. 4(1): p. 1.]. UF presents some advantages such as lower driving force and a smaller space requirement due to its high packing density. Polymer-supported ultrafiltration (PSU) technique adds water soluble polymeric ligands to bind metal ions and form macromolecular complexes by producing a free targeted metal ions effluent [Rether, A. and M. Schuster, Selective separation and recovery of heavy metal ions using water-soluble N-benzoylthiourea modified PAMAM polymers. *Reactive and Functional Polymers*, 2003. 57(1): p. 13–21.]. Advantages of the PSU technology are the low-energy requirements involved in ultrafiltration, the very fast reaction kinetics and higher selectivity of separation of selective bonding agents in aqueous solution. Another similar technique, complexation–ultrafiltration, proves to be a promising alternative to technologies based on precipitation and ion exchange. The use of water-soluble metal-binding polymers in combination with ultrafiltration (UF) is a hybrid approach to concentrate selectively and to recover heavy metals in the solution. In the complexation – UF process cationic forms of heavy metals are first complexed by a macro-ligand in order to increase their molecular weight with a size larger than the pores of the selected membrane [Petrov, S. and V. Nenov, Removal and recovery of copper from wastewater by a complexation ultrafiltration process. *Desalination*, 2004. 162: p. 201209. , Trivunac, K. and S. Stevanovic, Removal of heavy metal ions from water by complexation-assisted ultrafiltration. *Chemosphere*, 2006. 64(3): p. 486–491.]. The advantages of complexation–filtration process are the high separation selectivity due to the use of a selective binding and low-energy requirements involved in these processes. Water-soluble polymeric ligands have shown to be powerful substances to remove trace metals from aqueous solutions and industrial wastewater through membrane processes.

3.2.2.5.2 Reverse osmosis (Ro) :is a separation process that uses pressure to force a solution through a membrane that retains the solute on one side and allows the pure solvent to pass to the other side. The membrane here is semipermeable, meaning it allows the passage of solvent but not for metals. The membranes used for reverse osmosis have a dense barrier layer in the polymer matrix where most separation occurs. Reverse osmosis can remove many types of molecules and ions from solutions, including bacteria, and is used in both industrial processes. Reverse osmosis involves a diffusive mechanism, so that separation efficiency is dependent on solute concentration, pressure, and water flux rate [Crittenden, J.C., et al.,

Understanding and Improving Process Performance of Advanced Oxidation Processes (AOPs)].

3.2.2.5.3 Electrodesialysis (ED) is a membrane separation in which ionized species in the solution are passed through an ion exchange membrane by applying an electric potential. The membranes are thin sheets of plastic materials with either anionic or cationic characteristics. When a solution containing ionic species passes through the cell compartments, the anions migrate toward the anode and the cations toward the cathode, crossing the anion exchange and cation-exchange membranes [CHEN, L. and Q. CHEN, Industrial application of UF membrane in the pretreatment for RO system [J]. Membrane Science and Technology, 2003. 4: p. 009.]. A noticeable disadvantage is membranes replacement and the corrosion process [Kurniawan, T.A., et al., Physico-chemical treatment techniques for wastewater laden with heavy metals. Chemical engineering journal, 2006. 118(1): p. 83-98.]. Using membranes with higher ion exchange capacity resulted in better cell performance. Effects of flow rate, temperature and voltage at different concentrations using two types of commercial membranes, using a laboratory ED cell, on lead removal were studied [Mohammadi, B. and O. Pironneau, Shape optimization in fluid mechanics. Annu. Rev. Fluid Mech., 2004. 36: p. 255-279.]. Results show that increasing voltage and temperature improved cell performance and separation percentage decreased with an increasing flow rate. This offers advantages for the treatment of highly concentrated wastewater laden with heavy metals to recovery undesirable impurities from water .

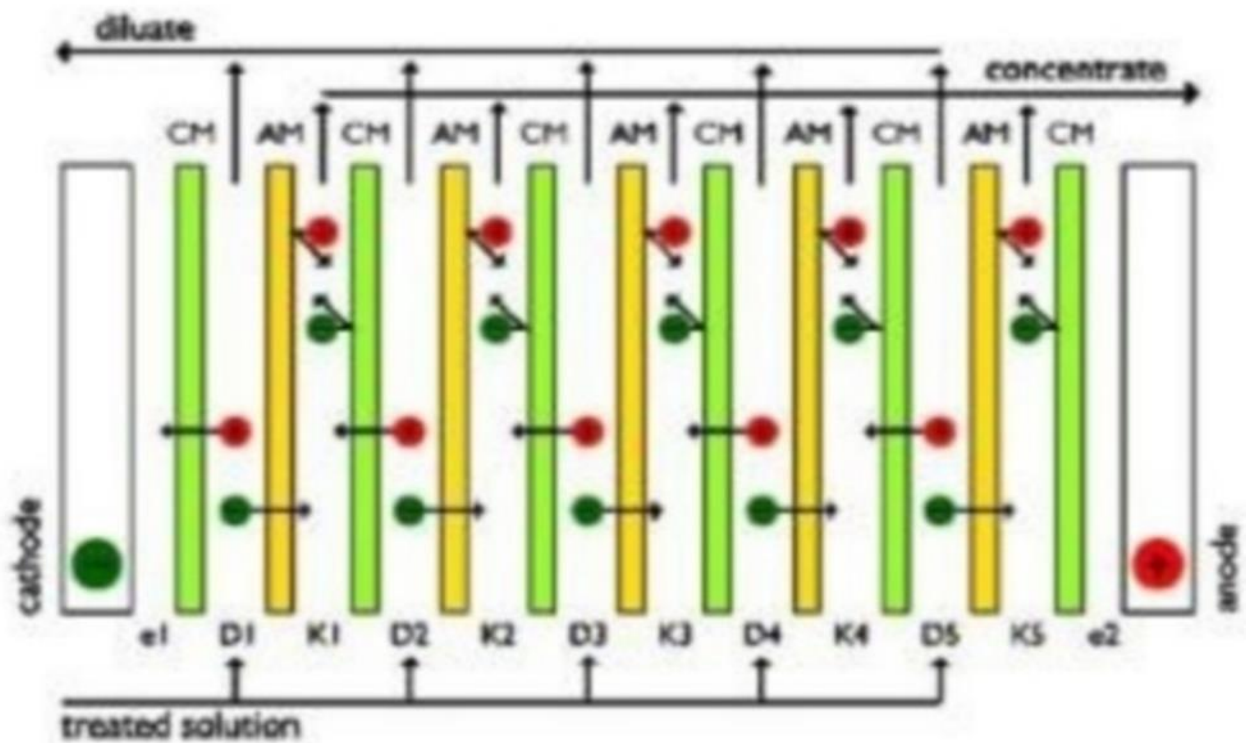


Figure 4 Electrodesialysis principles (Chen, 2004) CM – cation exchange Membrane, D-dialute chamber, e1 and e2-electrode chambers, AM-anion Exchange membrane and K-concentrate chamber.

3.2.2.5.4 Nanofiltration (NF): membranes are a relatively new class of membranes which have properties in between those of ultrafiltration (UF) membranes and reverse-osmosis (RO) ones. Their separation mechanisms involve both steric (sieving) effects and electrical (Donnan) effects. The significance of this membrane, besides having small pores is the membrane's surface charges, which allows charged solutes that are smaller than the membrane pores to be rejected along with bigger neutral solutes and salts. Furthermore it is capable of rejecting multivalent ions effectively, and on the other hand lets the monovalent ions pass through. These are the characteristics that make the nanofiltration membrane a potential process to reject heavy metal ions, which in general are multivalent ions

3.2.2.6 Adsorption

Many physical, chemical and biological operations take place at the boundary between two phases, while others occur at that interface. Adsorption is referred to the change in concentration of a given solute at the interface as compared to the neighboring phases. This process can be considered in the following systems according to the phases in contact: solid-liquid, liquid-gas and solid-gas. The development of adsorption process as a large-scale in industrial wastewater treatment is mainly based on the solid-liquid (Parfitt and Rochester, 1983; Ottawil et al., 1983) and the solid-gas (Yang, 1997) interfaces, but in different laboratory investigations, all types of interfaces are used (Do, 2000). Adsorption phenomena was earlier observed for gases by Scheels in 1773 (Scheele, 1773). This observation was continued by Lowitz in 1785 for solutions as cited in (Dabrowski, 2001). Adsorption on a solid surface can be defined as a mass transfer process by which the substance is transferred from the liquid phase and accumulated at the solid surface and bonded by physical and/or chemical reactions. The substance adsorbed on the solid surface is the adsorbate and the adsorbing material is named the adsorbent. Plenty of materials are applied as adsorbent to attach great variety of pollutants. Generally, functional groups and/or porous surface are needed to ensure the efficiency of this process. There are different driving forces involved in the adsorption process to be considered as (Bellmann, 2008) :-

- Ion pairing :- when electrostatic interactions between ions with different charges are take place .
- Ion exchange :- when the counter ions of the double layer are replaced by adsorbate ions with the same charge .
- Adsorption by polarization of π -electrons :- when interaction between positive charges at the surface of aromatic molecule groups and adsorbent .
- Acid-base interaction :- including the formation of hydrogen-bond between adsorbate and adsorbent .
- Adsorption resulted by dispersive forces .
- Hydrophobic bonding :- this type of force occur when there are attractive interaction between hydrophobic species of adsorbate molecules and adsorbent surface.

3.2.2.6.1 Types of adsorption

Adsorption can be divided into two main types depending on the type of attraction forces between adsorbate and adsorbent: physical and chemical adsorption (Fomkin, 2009; Sharma, 2013; Patel, 2017).

Physical adsorption or physisorption: When the interaction between the adsorbent surface and adsorbed molecules has a physical nature as the force of attractions are van der Waals forces, as they are weak, the process results are reversible and it is not specific with respect to adsorbent. Physical adsorption takes place with formation of multilayer of adsorbate on adsorbent. The energy of intermolecular forces and interatomic interactions is ranging between 10-20 KJ/mol. Physisorption prevails at low temperature, and energy of activation is 5-10 KJ/mol. It has low enthalpy (ΔH_o) of adsorption with value of 20-40 KJ/mol and it takes place at low temperature. It is an exothermic process and the physisorption decreases when the temperature increases. In highly porous material, the mechanism of hydrogen storage on the surface is shown in Figure (2.1). There is no chemical reaction between the accumulated hydrogen molecules and the porous material surface (Schlapbach, 2009).

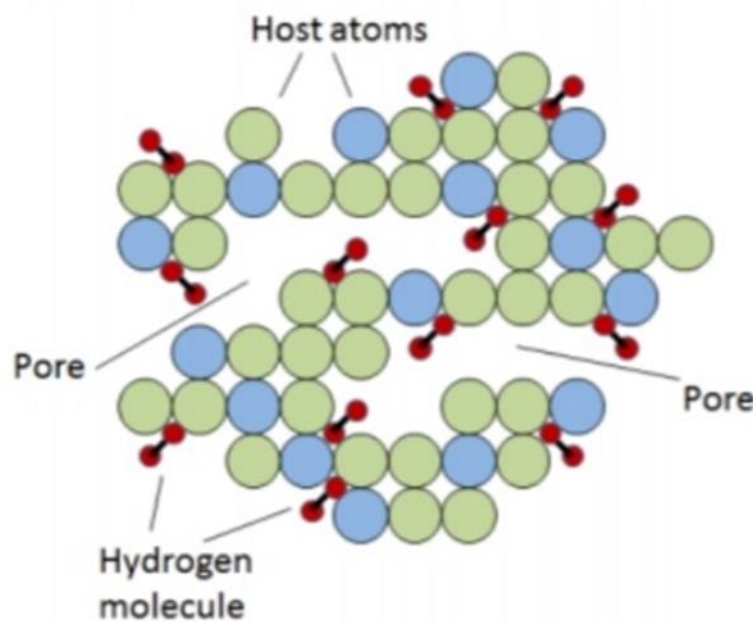


Fig. (5): Hydrogen storage mechanism including physisorption (Schlapbach, 2009).

Chemical adsorption or chemisorption: This type refers to ion exchange, coordination and chelation, complexation (Liu, 2014). The most valuable parameters for this type are the specific surface area of phases, types and number of active sites, and stability of active sites. The chemical adsorption takes place when the force of attraction existing between adsorbate and adsorbent are chemical forces or chemical bond with formation of unilayer of adsorbate on adsorbent. Chemisorption is irreversible. The main advantages of this type are high selectivity of removal and the ability to remove small concentration of pollutant. Chemisorption increases with increase of temperature where energy of activation is between 10-100 KJ/mol. It has high enthalpy of adsorption (ΔH_o) and takes place at all temperature and it is highly

specific with respect to adsorbent i.e. occurs only if there is some possibility of chemical bonding between adsorbate and adsorbent.

The mechanism of hydrogen storage onto certain pollutant like metals in chemisorption is shown by Figure (2.2a), when hydrogen molecules attached on the material surface, then, the molecules split into separate atoms. These atoms distribute randomly through structure of material (Figure 2. 2b). The hydrogen compounds and ordinary arranged. To form ionic, metallic bonds or covalent with the metal atoms (Figure 2.2c) (Schlapbach, 2009).

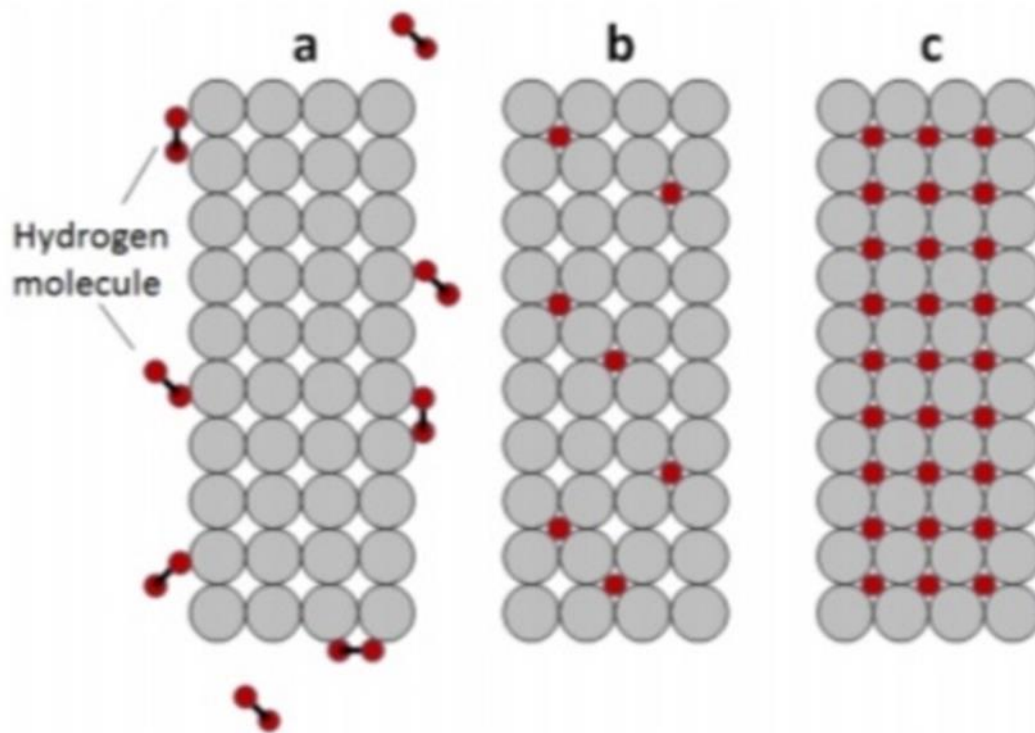
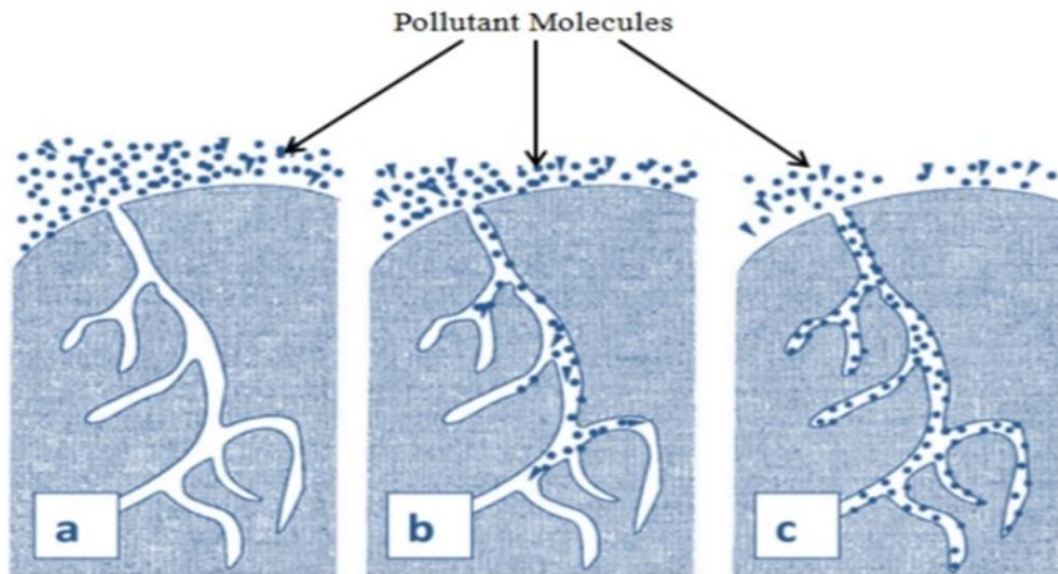


Fig. (6): Hydrogen storage mechanism including chemisorption (Schlapbach, 2009). At favorable conditions, both types of adsorption can take place alternately or simultaneously.

3.2.2.6.2 Adsorption mechanism

The mechanism of adsorption onto solid adsorbent is divided into three steps: (i) the transport of the adsorbate from the bulk solution to the surface of adsorbent; (ii) migration into pores of adsorbent; (iii) monolayer build-up of adsorbate (Figure 2.3ac).

In step (1), the adsorbate diffuse on the adsorbent surface by intermolecular forces between adsorbent and adsorbate. By second step, the migration of adsorbate into pores of adsorbent is takes place. Finally, the particles of adsorbate are distributed on the surface of adsorbent, filled up the volume of pores, finally the adsorbate are formed the monolayer of reacted molecules, atoms and ions to the active sites (Mckay, 1996;Iakovleva and Sillanpaa, 2013).



. (7): Schematic explanation of three steps of adsorption mechanism: (a) Diffusion step of adsorbate towards adsorbent surface (b) migration Through the adsorbent pores © building the monolayer of Adsorbate onto adsorbent (Repo, 2011).

3.2.3 Biological Methods

Biological removal of heavy metals in wastewater involves the use of biological techniques for the elimination of pollutants from wastewater. In this processes microorganisms play a role of settling solids in the solution. Activated sludge, trickling filters, stabilization ponds are widely used for treating wastewater. Activated sludge is the most common option uses microorganisms in the treatment process to break down organic material with aeration and agitation, and then allows solids to settle out. Bacteria containing “activated sludge” is continually recirculated back to the aeration basin to increase the rate of organic decomposition. Most of the research on heavy metals removal in biological systems has been directed towards the suspended growth activated sludge process. Trickling Filters which consist beds of coarse media (often stones or plastic) help to grow microorganisms. Wastewater is sprayed into the air (aeration), then allowed to trickle through the media and microorganisms break down organic materials in the wastewater. Trickling filters drain at the bottom and the wastewater is collected and then undergoes sedimentation. Stabilization ponds or lagoons are slow, cheap, and relatively inefficient, biological method that can be used for various types of wastewater. They rely on the interaction of sunlight, algae, microorganisms, and oxygen.

Chapter Four

**Literature reviews on
heavy metals**

Chapter Four

1.4 Arsenic

1.4.1 Environmental Occurrence, Industrial Production and Use Arsenic is a ubiquitous element that is detected at low concentrations in virtually all environmental matrices(Georgia: Center for Disease Control, Atlanta; 2000) . The major inorganic forms of arsenic include the trivalent arsenite and the pentavalent arsenate. The organic forms are the methylated metabolites – monomethylarsonic acid (MMA), dimethylarsinic acid (DMA) and trimethylarsine oxide. Environmental pollution by arsenic occurs as a result of natural phenomena such as volcanic eruptions and soil erosion, and anthropogenic activities (Georgia: Center for Disease Control, Atlanta; 2000) . Several arsenic-containing compounds are produced industrially, and have been used to manufacture products with agricultural applications such as insecticides, herbicides, fungicides, algicides, sheep dips, wood preservatives, and dye-stuffs. They have also been used in veterinary medicine for the eradication of tapeworms in sheep and cattle . (Tchounwou PB et al) Arsenic compounds have also been used in the medical field for at least a century in the treatment of syphilis, yaws, amoebic dysentery, and trypanosomiasis(Tchounwou PB et al and Centeno JA) . Arsenic-based drugs are still used in treating certain tropical diseases such as African sleeping sickness and amoebic dysentery, and in veterinary medicine to treat parasitic diseases, including filariasis in dogs and black head in turkeys and chickens(Centeno JA et al) . Recently, arsenic trioxide has been approved by the Food and Drug Administration as an anticancer agent in the treatment of acute promyelocytic leukemia (Rousselot P and Laboume S) . Its therapeutic action has been attributed to the induction of programmed cell death (apoptosis) in leukemia cells (Yedjou GC et al) .

1.4.2 Potential for Human Exposure

It is estimated that several million people are exposed to arsenic chronically throughout the world, Exposure to arsenic occurs via the oral route (ingestion), inhalation, dermal contact, and the parenteral route to some extent(Tchounwou PB and Wilson B et al) . Diet, for most individuals, is the largest source of exposure, with an average intake of about 50 µg per day. Intake from air, water and soil are usually much smaller, but exposure from these media may become significant in areas of arsenic contamination. Workers who produce or use arsenic compounds in such occupations as vineyards, ceramics, glassmaking, smelting, refining of metallic ores, pesticide manufacturing and application, wood preservation, semiconductor manufacturing can be exposed to substantially higher levels of arsenic . Arsenic has also been identified at 781 sites of the 1,300 hazardous waste sites that have been proposed by the U.S. EPA for inclusion on the national priority list (Georgia: Center for Disease Control, Atlanta; 2000) . Human exposure at these sites may occur by a variety of pathways, including inhalation of dusts in air, ingestion of contaminated water or soil, or through the food chain (Tchounwou PB) . Contamination with high levels of arsenic is of concern because arsenic can cause a number of human health

effects. Several epidemiological studies have reported a strong association between arsenic exposure and increased risks of both carcinogenic and systemic health effects (Tchounwou PB and Patlolla AK). Exposed to high concentrations of arsenic in their drinking water and are displaying various clinico-pathological conditions including cardiovascular and peripheral vascular disease, developmental anomalies, neurologic and neurobehavioural disorders, diabetes, hearing loss, portal fibrosis, hematologic disorders (anemia, leukopenia and eosinophilia) and carcinoma (Tchounwou PB and Centeno JA). Arsenic exposure affects virtually all organ systems including the cardiovascular, dermatologic, nervous, hepatobiliary, renal, gastro-intestinal, and respiratory systems (Tchounwou PB et al). Research has also pointed to significantly higher standardized mortality rates for cancers of the bladder, kidney, skin, and liver in many areas of arsenic pollution. The severity of adverse health effects is related to the chemical form of arsenic, and is also time- and dose-dependent [Tchounwou PB and Wilson BA]. Although the evidence of carcinogenicity of arsenic in humans seems strong, the mechanism by which it produces tumors in humans is not completely understood [Chappell W, Beck B and Brown K].

1.4.3 Mechanisms of Toxicity and Carcinogenicity

Analyzing the toxic effects of arsenic is complicated because the toxicity is highly influenced by its oxidation state and solubility, as well as many other intrinsic and extrinsic factors (Centeno JA et al). Several studies have indicated that the toxicity of arsenic depends on the exposure dose, frequency and duration, the biological species, age, and gender, as well as on individual susceptibilities, genetic and nutritional factors (Abernathy CO and Liu YP). Most cases of human toxicity from arsenic have been associated with exposure to inorganic arsenic. Inorganic trivalent arsenite (As^{III}) is 2–10 times more toxic than pentavalent arsenate (As^{V}) (Goyer RA. et al). One of the mechanisms by which arsenic exerts its toxic effect is through impairment of cellular respiration by the inhibition of various mitochondrial enzymes, and the uncoupling of oxidative phosphorylation (Wang Z and Rossman). and it has been reported that arsenic trioxide induces DNA damage in human lymphocytes and also in mice leukocytes (Saleha Banu B). Arsenic compounds have also been shown to induce gene amplification, arrest cells in mitosis, inhibit DNA repair, and induce expression of the c-fos gene and the oxidative stress protein heme oxygenase in mammalian cells (Saleha Banu B et al). They have been implicated as promoters and comutagens for a variety of toxic agents (Barrett JC and Lamb PW). Recent studies in our laboratory have demonstrated that arsenic trioxide is cytotoxic and able to transcriptionally induce a significant number of stress genes and related proteins in human liver carcinoma cells (Tchounwou PB et al). Epidemiological investigations have indicated that long-term arsenic exposure results in promotion of carcinogenesis. Several hypotheses have been proposed to describe the mechanism of arsenic-induced carcinogenesis. Zhao et al. Arsenic trioxide is a tumor specific agent capable of inducing apoptosis selectively in acute promyelocytic leukemia cells. Several recent studies have shown that arsenic can induce apoptosis through alterations in other cell signaling pathways (Seol JG, Park WH and et al). In addition to acute promyelocytic leukemia, arsenic is thought to have therapeutic potential for

myeloma (Deaglio S et al). In summary, numerous cancer chemotherapy studies in cell cultures and in patients with acute promyelocytic leukemia demonstrate that arsenic trioxide administration can lead to cell-cycle arrest and apoptosis in malignant cells. A recent review discusses nine different possible modes of action of arsenic carcinogenesis: induced chromosomal abnormalities, oxidative stress, altered DNA repair, altered DNA methylation patterns, altered growth factors, enhanced cell proliferation, promotion/progression, suppression of p53, and gene amplification (Miller WH et al) . Presently, three modes (chromosomal abnormality, oxidative stress, and altered growth factors) of arsenic carcinogenesis have shown a degree of positive evidence, both in experimental systems (animal and human cells) and in human tissues. The remaining possible modes of carcinogenic action (progression of carcinogenesis, altered DNA repair, p53 suppression, altered DNA methylation patterns and gene amplification) do not have as much evidence, particularly from in vivo studies with laboratory animals, in vitro studies with cultured human cells, or human data from case or population studies. Thus, the mode-of-action studies suggest that arsenic might be acting as a cocarcinogen, a promoter, or a progressor of carcinogenesis.

2.4 Chromium

2.4.1 Environmental Occurrence, Industrial Production and Use Chromium (Cr) is a naturally occurring element present in the earth's crust, with oxidation states (or valence states) ranging from chromium (II) to chromium (VI) [Jacobs JA, Testa SM and et al]. Chromium compounds are stable in the trivalent . [Cr(III)] form and occur in nature in this state in ores, such as ferrochromite. The hexavalent [Cr(VI)] form is the secondmost stable state (Patlolla A, Barnes C and et al) .Elemental chromium [Cr(0)] does not occur naturally. Chromium enters into various environmental matrices (air, water, and soil) from a wide variety of natural and anthropogenic sources with the largest release coming from industrial establishments. Industries with the largest contribution to chromium release include metal processing, tannery facilities, chromate production, stainless steel welding, and ferrochrome and chrome pigment production. The increase in the environmental concentrations of chromium has been linked to air and wastewater release of chromium, mainly from metallurgical, refractory, and chemical industries. Chromium released into the environment from anthropogenic activity occurs mainly in the hexavalent form [Cr(VI)] (Agency for Toxic Substances and Disease Registry (ATSDR) Toxicological Profile for Chromium) . Hexavalent chromium [Cr(VI)] is a toxic industrial pollutant that is classified as human carcinogen by several regulatory and non-regulatory agencies [Agency for Toxic Substances and Disease Registry (ATSDR) Toxicological Profile for Chromium]. The health hazard associated with exposure to chromium depends on its oxidation state, ranging from the low toxicity of the metal form to the high toxicity of the hexavalent form. All Cr(VI)containing compounds were once thought to be man-made, with only Cr(III) naturally ubiquitous in air, water, soil and biological materials. Recently, however, naturally occurring Cr(VI) has been found in ground and surface waters at values exceeding the World Health Organization limit for drinking water of 50 µg of Cr(VI) per liter (Velma V, and et

al). Chromium is widely used in numerous industrial processes and as a result, is a contaminant of many environmental systems (Cohen MD and et al) . Commercially chromium compounds are used in industrial welding, chrome plating, dyes and pigments, leather tanning and wood preservation. Chromium is also used as anticorrosive in cooking systems and boilers(Norseth T and et al) .

2.4.2 Potential for Human Exposure

It is estimated that more than 300,000 workers are exposed annually to chromium and chromium-containing compounds in the workplace. In humans and animals, [Cr(III)] is an essential nutrient that plays a role in glucose, fat and protein metabolism by potentiating the action of insulin(Goyer RA. Ana et al) . However, occupational exposure has been a major concern because of the high risk of Cr-induced diseases in industrial workers occupationally exposed to Cr(VI)(Guertin J and et al). Also, the general human population and some wildlife may also be at risk. It is estimated that 33 tons of total Cr are released annually into the environment(Agency for Toxic Substances and Disease Registry (ATSDR) Toxicological Profile for Chromium). Non-occupational exposure occurs via ingestion of chromium containing food and water whereas occupational exposure occurs via inhalation(Langård S, Vigander T and et al) . even though the principal route of human exposure to chromium is through inhalation, and the lung is the primary target organ, significant human exposure to chromium has also been reported to take place through the skin(Shelnutt SR and et al) .For example, the widespread incidence of dermatitis noticed among construction workers is attributed to their exposure to chromium present in cement(Shelnutt SR and et al) . Occupational and environmental exposure to Cr(VI)containing compounds is known to cause multiorgan toxicity such as renal damage, allergy and asthma, and cancer of the respiratory tract in humans(Goyer RA and et al). Breathing high levels of chromium (VI) can cause irritation to the lining of the nose, and nose ulcers. The main health problems seen in animals following ingestion of chromium (VI) compounds are irritation and ulcers in the stomach and small intestine, anemia, sperm damage and male reproductive system damage. Chromium (III) compounds are much less toxic and do not appear to cause these problems. Some individuals are extremely sensitive to chromium(VI) or chromium(III), allergic reactions consisting of severe redness and swelling of the skin have been noted. An increase in stomach tumors was observed in humans and animals exposed to chromium(VI) in drinking water. Accidental or intentional ingestion of extremely high doses of chromium (VI) compounds by humans has resulted in severe respiratory, cardiovascular, gastrointestinal, hematological, hepatic, renal, and neurological effects as part of the sequelae leading to death or in patients who survived because of medical treatment(Atlanta, GA: Public Health Service; 2008. Toxicological Profile for Chromium.) . Although the evidence of carcinogenicity of chromium in humans and terrestrial mammals seems strong, the mechanism by which it causes cancer is not completely understood (Chen TL, and et al) .

2.4.3 Mechanisms of Toxicity and Carcinogenicity

Major factors governing the toxicity of chromium compounds are oxidation state and

solubility. Cr(VI) compounds, which are powerful oxidizing agents and thus tend to be irritating and corrosive, appear to be much more toxic systemically than Cr(III) compounds, given similar amount and solubility [Connett PH and et al]. Although the mechanisms of biological interaction are uncertain, the variation in toxicity may be related to the ease with which Cr(VI) can pass through cell membranes and its subsequent intracellular reduction to reactive intermediates. Since Cr(III) is poorly absorbed by any route, the toxicity of chromium is mainly attributable to the Cr(VI) form. It can be absorbed by the lung and gastrointestinal tract, and even to a certain extent by intact skin. The reduction of Cr(VI) is considered as being a detoxification process when it occurs at a distance from the target site for toxic or genotoxic effect while reduction of Cr(VI) may serve to activate chromium toxicity if it takes place in or near the cell nucleus of target organs(Dayan AD and Paine AJ) . If Cr(VI) is reduced to Cr(III) extracellularly, this form of the metal is not readily transported into cells and so toxicity is not observed. The balance that exists between extracellular Cr(VI) and intracellular Cr(III) is what ultimately dictates the amount and rate at which Cr(VI) can enter cells and impart its toxic effects(Cohen MD, Kargacin B and Klein CB) . Studies with animal models have also reported many harmful effects of Cr (VI) on mammals. Adverse health effects induced by Cr (VI) have also been reported in humans. Epidemiological investigations have reported respiratory cancers in workers occupationally exposed to Cr (VI)containing compounds(Costa M and et al). DNA strand breaks in peripheral lymphocytes and lipid peroxidation products in urine observed in chromium-exposed workers also support the evidence of Cr (VI)induced toxicity to humans (Gambelunghe A and et al) .Oxidative damage is considered to be the underlying cause of these genotoxic effects including chromosomal abnormalities (Wise JP and et al) , and DNA strand breaks(Xie H, Wise SS and et al) .Nevertheless, recent studies indicate a biological relevance of non-oxidative mechanisms in Cr(VI) carcinogenesis(Zhitkovich A, and et al) .Carcinogenicity appears to be associated with the inhalation of the less soluble/insoluble Cr(VI) compounds) Katz SA and Salem H) . Epidemiological evidence strongly points to Cr(VI) as the agent in carcinogenesis. Solubility and other characteristics of chromium, such as size, crystal modification, surface charge, and the ability to be phagocytized might be important in determining cancer risk (Norseth T and et al) .Studies in our laboratory have indicated that chromium (VI) is cytotoxic and able to induce DNA damaging effects such as chromosomal abnormalities(Patlolla AK and et al) . Recently, our laboratory has also demonstrated that chromium (VI) induces biochemical, genotoxic and histopathologic effects in liver and kidney of goldfish, carassius auratus(Velma V, and et al) .a metal cannot be classified as carcinogenic per se since its different compounds may have different potencies. Because of the multiple chemical exposure in industrial establishments, it is difficult from an epidemiological standpoint to relate the carcinogenic effect to a single compound. Thus, the carcinogenic risk must often be related to a process or to a group of metal compounds rather than to a single substance. Differences in carcinogenic potential are related not only to different chemical forms of the same metal but also to the particle size of the inhaled aerosol and to physical characteristics of the particle such as surface charge and crystal modification(Norseth T and et al) .

3.4. Lead

3.4.1 Environmental Occurrence, Industrial Production and Use Lead is a naturally occurring bluish-gray metal present in small amounts in the earth's crust. Although lead occurs naturally in the environment, anthropogenic activities such as fossil fuels burning, mining, and manufacturing contribute to the release of high concentrations. Lead has many different industrial, agricultural and domestic applications. It is currently used in the production of lead-acid batteries, ammunitions, metal products (solder and pipes), and devices to shield X-rays (Gabby PN and Reston, VA) . In recent years, the industrial use of lead has been significantly reduced from paints and ceramic products, caulking, and pipe solder [Centers for Disease control (CDC) Preventing Lead Poisoning in Young children]. Today, the largest source of lead poisoning in children comes from dust and chips from deteriorating lead paint on interior surfaces [Lanphear BP and et al].

3.4.2 Potential for Human Exposure

Exposure to lead occurs mainly via inhalation of lead-contaminated dust particles or aerosols, and ingestion of lead-contaminated food, water, and paints [Department of Health and Human Services; 1992.]. Adults absorb 35 to 50% of lead through drinking water and the absorption rate for children may be greater than 50%. Lead absorption is influenced by factors such as age and physiological status. In the human body, the greatest percentage of lead is taken into the kidney, followed by the liver and the other soft tissues such as heart and brain, however, the lead in the skeleton represents the major body fraction [Flora SJS, Flora GJS and Saxena G]. The nervous system is the most vulnerable target of lead poisoning. Headache, poor attention span, irritability, loss of memory and dullness are the early symptoms of the effects of lead exposure on the central nervous system (Department of Health and Human Services; 1999. Toxicological Profile for Lead) . Since the late 1970's, lead exposure has decreased significantly as a result of multiple efforts including the elimination of lead in gasoline, and the reduction of lead levels in residential paints, food and drink cans, and plumbing systems (Pirkle JL, and et al) . Lead is the most systemic toxicant that affects several organs in the body including the kidneys, liver, central nervous system, hematopoietic system, endocrine system, and reproductive system (Department of Health and Human Services; 1999) . Lead exposure usually results from lead in deteriorating household paints, lead in the work place, lead in crystals and ceramic containers that leaches into water and food, lead use in hobbies, and lead use in some traditional medicines and cosmetics (Department of Health and Human Services; 1999) .

3.4.3 Molecular Mechanisms of Toxicity and Carcinogenicity There are many published studies that have documented the adverse effects of lead in children and the adult population. In children, these studies have shown an association between blood level poisoning and diminished intelligence, lower intelligence quotient-IQ, delayed or impaired neurobehavioral development, decreased hearing acuity, speech and language handicaps, growth retardation, poor attention span, and anti social and diligent behaviors (Kaul B and et al) . In the adult population, reproductive effects, such as

decreased sperm count in men and spontaneous abortions in women have been associated with high lead exposure (Apostoli P and Kiss P). Acute exposure to lead induces brain damage, kidney damage, and gastrointestinal diseases, while chronic exposure may cause adverse effects on the blood, central nervous system, blood pressure, kidneys, and vitamin D metabolism (Department of Health and Human Services; 1999). One of the major mechanisms by which lead exerts its toxic effect is through biochemical processes that include lead's ability to inhibit or mimic the actions of calcium and to interact with proteins [Department of Health and Human Services; 1999].

4.4 Mercury

4.4.1 Environmental Occurrence, Industrial Production and Use Mercury is a heavy metal belonging to the transition element series of the periodic table. It is unique in that it exists or is found in nature in three forms (elemental, inorganic, and organic), with each having its own profile of toxicity (Clarkson TW and et al). At room temperature elemental mercury exists as a liquid which has a high vapor pressure and is released into the environment as mercury vapor. Mercury also exists as a cation with oxidation states of +1 (mercurous) or +2 (mercuric) (Guzzi G and et al). Methylmercury is the most frequently encountered compound of the organic form found in the environment, and is formed as a result of the methylation of inorganic (mercuric) forms of mercury by microorganisms found in soil and water [Dopp E, Hartmann LM and et al]. Mercury is a widespread environmental toxicant and pollutant which induces severe alterations in the body tissues and causes a wide range of adverse health effects (Sarkar BA and et al). Both humans and animals are exposed to various chemical forms of mercury in the environment. These include elemental mercury vapor (Hg_0), inorganic mercurous (Hg^{+1}), mercuric (Hg^{+2}), and the organic mercury compounds [Zahir A, and et al]. Because mercury is ubiquitous in the environment, humans, plants and animals are all unable to avoid exposure to some form of mercury [Holmes P, Hames KAF and et al]. Mercury is utilized in the electrical industry (switches, thermostats, batteries), dentistry (dental amalgams), and numerous industrial processes including the production of caustic soda, in nuclear reactors, as antifungal agents for wood processing, as a solvent for reactive and precious metal, and as a preservative of pharmaceutical products [Tchounwou PB, Ayensu WK, and et al]. The industrial demand for mercury peaked in 1964 and began to sharply decline between 1980 and 1994 as a result of federal bans on mercury additives in paints, pesticides, and the reduction of its use in batteries [Environmental Protection Agency].

4.4.2 Potential for Human Exposure

Humans are exposed to all forms of mercury through accidents, environmental pollution, food contamination, dental care, preventive medical practices, industrial and agricultural operations, and occupational operations [Sarkar BA. And et al]. The major sources of chronic, low level mercury exposure are dental amalgams and fish consumption. Mercury enters water as a natural process of off-gassing from the earth's crust and also through industrial pollution [Dopp E, Hartmann LM and et al]. The two most highly absorbed species are elemental mercury (Hg_0) and methyl

mercury (MeHg). Dental amalgams contain over 50% elemental mercury [Zahir A, Rizwi SJ and et al]. The elemental vapor is highly lipophilic and is effectively absorbed through the lungs and tissues lining the mouth. Gastrointestinal tract . All forms of mercury are toxic and their effects include gastrointestinal toxicity, neurotoxicity, and nephrotoxicity [Tchounwou PB, and et al].

4.4.3 Molecular Mechanisms of Mercury Toxicity Carcinogenicity The molecular mechanisms of toxicity of mercury are based on its chemical activity and biological features which suggest that oxidative stress is involved in its toxicity (Valko M, and et al) .Metal-induced carcinogenicity has been a research subject of great public health interest. Generally, carcinogenesis is considered to have three stages including initiation, promotion, and progression and metastasis. Although mutations of DNA, which can activate oncogenesis or inhibit tumor suppression, were traditionally thought to be crucial factors for the initiation of carcinogenesis, recent studies have demonstrated that other molecular events such as transcription activation, signal transduction, oncogene , and recombination, also constitute significant contributing factors (Leaner VD and et al) .Studies have shown that mercury and other toxic metals effect cellular organelles and adversely affect their biologic functions (Leaner VD and et al) . Accumulating evidence also suggests that ROS play a major role in the mediation of metalinduced cellular responses and carcinogenesis (Magos L and Clarkson TW) .The connection between mercury exposure and carcinogenesis is very controversial. While some studies have confirmed its genotoxic potential, others have not shown an association between mercury exposure and genotoxic damage (Valko M, Izakovic M and et al) . In studies implicating mercury as a genotoxic agent, oxidative stress has been described has the molecular mechanism of toxicity (Valko M, Rhodes CJ and et al) .

5.4 Cadmium

5.4.1 Environmental Occurrence, Industrial Production and Use Cadmium is a heavy metal of considerable environmental and occupational concern. It is widely distributed in the earth's crust at an average concentration of about 0.1 mg/kg. The highest level of cadmium compounds in the environment is accumulated in sedimentary rocks, and marine phosphates contain about 15 mg cadmium/kg (Geneva, Switzerland: World Health Organization; 1987) . Cadmium is frequently used in various industrial activities. The major industrial applications of cadmium include the production of alloys, pigments, and batteries [Wilson et al]. Although the use of cadmium in batteries has shown considerable growth in recent years, its commercial use has declined in developed countries in response to environmental concerns.

5.4.2 Potential for Human Exposure

The main routes of exposure to cadmium are via inhalation or cigarette smoke, and ingestion of food. Skin absorption is rare. Human exposure to cadmium is possible

through a number of several sources including employment in primary metal industries, eating contaminated food, smoking cigarettes, and working in cadmium-contaminated work places, with smoking being a major contributor [Lyon, France: 1993.]. Other sources of cadmium include emissions from industrial activities, including mining, smelting, and manufacturing of batteries, pigments, stabilizers, and alloys [Agency for Toxic Substances and Disease Registry]. Cadmium is also present in trace amounts in certain foods such as leafy vegetables, potatoes, grains and seeds, liver and kidney, and crustaceans and mollusks [Satarug S et al]. In addition, foodstuffs that are rich in cadmium can greatly increase the cadmium concentration in human bodies. Examples are liver mushrooms, shellfish, mussels, cocoa powder and dried seaweed. An important distribution route is the circulatory system whereas blood vessels are considered to be main stream organs of cadmium toxicity. Chronic inhalation exposure to cadmium particulates is generally associated with changes in pulmonary function Exposure to cadmium is commonly determined by measuring cadmium levels in blood or urine (Jarup L, et al) .

5.4.3Molecular Mechanisms of Toxicity and Carcinogenicity Cadmium is a severe pulmonary and gastrointestinal irritant, which can be fatal if inhaled or ingested. After acute ingestion, symptoms such as abdominal pain, burning sensation, nausea, vomiting, salivation, muscle cramps, vertigo, shock, loss of consciousness and convulsions usually appear within 15 to 30 min [Baselt RC, et al]. Acute cadmium ingestion can also cause gastrointestinal tract erosion, pulmonary, hepatic or renal injury and coma, depending on the route of poisoning [Baselt RC, et al]. Chronic exposure to cadmium has a depressive effect on levels of norepinephrine, serotonin, and acetylcholine [Singhal RL, et al]. Rodent studies have shown that chronic inhalation of cadmium causes pulmonary adenocarcinomas (Waalkes MP, et al) It can also cause prostatic proliferative lesions including adenocarcinomas, after systemic or direct exposure [Waalkes MP, et al].Although the mechanisms of cadmium toxicity are poorly understood, it has been speculated that cadmium causes damage to cells primarily through the generation of ROS [Free Radic Biol Med. 1995;18:321–336]. which causes single-strand DNA damage and disrupts the synthesis of nucleic acids and proteins [Mitra RS.,et al].Thus, the lung is the most definitively established site of human carcinogenesis from cadmium exposure. Other target tissues of cadmium carcinogenesis in animals include injection sites, adrenals, testes, and the hemopoietic system [Lyon, France: 1993]. In some studies, occupational or environmental cadmium exposure has also been associated with development of cancers of the prostate, kidney, liver, hematopoietic system and stomach (Waalkes MP, Misra R et al).

Chapter Five

**Conclusions and
Recommendations for future
work**

Chapter Five

5.1 Conclusions

Heavy metal pollution is one of the most dangerous situations being faced today and most important environmental problems throughout the world. They are harmful even in trace concentrations and are not biodegradable and thus accumulate in the ecosystem. Heavy metals have been classified into two types as essential and non-essential. Essential heavy metals are less toxic at low concentrations and they act as coenzyme in biological processes. Non-essential heavy metals are highly toxic even at very low concentrations, they are non-biodegradable. Many of them are carcinogenic, cause birth defects and are extremely fatal. Hence, it is necessary to remove these toxic metals from wastewater before it is discharged into open waters. Adsorption is one such technique that caters not only to the remediation of heavy metal from wastewater, it is also eco-friendly with a low footprint. Adsorption is also an economical method which has certain advantages over conventional methods such as they minimise chemical and Biological sludge, high efficiency, low cost, regeneration of adsorbents and possibility of Metal recovery. Adsorption is based on bio-sorption mechanism. The efficiency of adsorbents depends on type of adsorbents for the removal of heavy metals. Adsorbents like activated are widely used, but it is restricted due to its high cost. So, it is necessary to look for options that are sustainable and aim at remediating the larger prospect of the problem. Low-cost adsorbents like agricultural wastes, industrial wastes and biochar aid not only in removal of heavy metals but are also cheap methods. Their raw material is easily available and these adsorbents can be easily manufactured. So, it is a green technology that greatly enhances the process of wastewater treatment. Further research into developing more low-cost adsorbents can help in further remedial of heavy metals.

Removal of heavy metals from wastewater by chemical precipitation is simple and inexpensive. It has disadvantage such as production of sludge. This method is useful for the case when concentration of heavy metals is high and for low heavy metal concentration it is not effective. Further, Membrane Filtration process produces less solid waste and it consumes less chemical and has high efficiency, one of

the disadvantages is that they have low flow rates. In coagulation Flocculation method this method has advantage of sludge settling and dewatering and its Disadvantages are it has high cost and large consumption of chemicals. Ion exchange Method has advantages that there is no change in pH wastewater.

5.2 Recommendations for future works

This comprehensive review analysis also revealed the gap that still exists in our understanding and applicability and therefore more work is necessary:

1. to predict the performance of processes for heavy metal removal from wastewater

under wide range of operating condition. To do more work on heavy metal adsorption from wastewater.

2.research should be conducted using real wastewater for treating Different contaminants.

3.More research on introducing cost- effective materials and methods for heavy metal removal from wastewater carried out.

4.Future studies should also Focus on the pilot-scale process. The best techniques to achieve efficient metals recovery with less environmental impact and low cost are still under development.

Chapter Six

References

References

- 1. Al-Asheh, S., et al., Predictions of binary sorption isotherms for the sorption of heavy metals by pine bark using single isotherm Data. *Chemosphere*, 2000. 41(5): p. 659-665.
- Alinnor, I., Adsorption of heavy metal ions from aqueous solution by fly ash. *Fuel*, 2007 86(5): p. 853-857.
- A. O. Olaniran, A. Balgobind, and B. Pillay, "Bioavailability Of heavy metals in soil: Impact on microbial biodegradation Of organic compounds and possible improvement strategies," *International Journal of Molecular Sciences*, vol. 14, no. 5, pp. 10197–10228, 2013.
- 4. Amritphale, S., et al., Adsorption behavior of Lead ions on pyrophyllite surface. *Main group Metal chemistry*, 1999. 22(9): p. 557566.
- Aziz, H.A., M.N. Adlan, and K.S. Ariffin, Heavy metals (Cd, Pb, Zn, Ni, Cu and Cr (III)) Removal from water in Malaysia: Post Treatment by high quality limestone. *Bioresource Technology*, 2008. 99(6): p. 1578-1583.
- B. A. M. Bandowe, M. Bigalke, L. Boamah, E. Nyarko, F. K. Saalia, and W. Wilcke, "Polycyclic aromatic compounds (PAHs And oxygenated PAHs) and trace metals in fish species from Ghana (West Africa): Bioaccumulation and health risk assess-Ment," *Environment International*, vol. 65, pp. 135–146, 2014.
- Babel, S. and T.A. Kurniawan, Cr (VI) removal From synthetic wastewater using coconut shell Charcoal and commercial activated carbon Modified with oxidizing agents and/or Chitosan. *Chemosphere*, 2004. 54(7): p. 951- 967.
- Barkay, "Application of a mer-lux biosensor for estimating bioavailable Mercury in soil," *Soil Biology & Biochemistry*, vol. 32, no. 5, pp. 639–646, 2000.
- Babel, S. and T.A. Kurniawan, Low-cost Adsorbents for heavy metals uptake from Contaminated water: a review. *Journal of Hazardous materials*, 2003. 97(1): p. 219-243.
- Benefield, L.D., J.F. Judkins, and B.L. Weand, *Process chemistry for water and wastewater Treatment* 1982: Prentice Hall Inc.
- Barakat, M., Adsorption behavior of copper And cyanide ions at TiO₂–solution interface. *Journal of Colloid and Interface Science*, 2005. 291(2): p. 345-352.
- Bansode, R., et al., Adsorption of metal ions By pecan shellbased granular activated Carbons. *Bioresource Technology*, 2003. 89(2): p. 115-119.
- Baselt RC, Cravey RH. *Disposition of Toxic Drugs and Chemicals in Man*. 4th Edn. Chicago, IL: Year Book Medical Publishers; 1995. Pp. 105–107. [Google Scholar].
- C. Cervantes, J. Campos-García, S. Devars et al., "Interactions Of chromium with microorganisms and plants," *FEMS Microbi- Ology Reviews*, vol. 25, no. 3, pp. 335–347, 2001.
- Chandra Sekhar, K., et al., Removal of heavy Metals using a plant biomass with reference To environmental control. *International Journal Of Mineral*

Processing, 2003. 68(1): p. 37-45.

- Crini, G., Recent developments in Polysaccharide-based materials used as Adsorbents in wastewater treatment. *Progress In polymer science*, 2005. 30(1): p. 38-70.
- Crittenden, J.C., et al., Understanding and Improving Process Performance of Advanced Oxidation Processes (AOPs).
 - Centeno JA, Tchounwou PB, Patlolla AK, Mullick FG, Murakat L, Meza E, Gibb H, Longfellow D, Yedjou CG.
- Centeno JA, Gray MA, Mullick FG, Tchounwou PB, Tseng C. Arsenic in drinking water and health issues. In: Moore TA, Black A, Centeno JA, Harding JS, Trumm DA, editors. *Metal Contaminants in New Zealand*. New Zealand: Resolutionz Press; 2005. Pp. 195–219. [Google Scholar]
- Clarkson TW, Magos L, Myers GJ. The toxicology of mercury-current exposures and clinical manifestations. *New Engl J Med*. 2003;349:1731–1737. [PubMed] [Google Scholar]
- Connett PH, Wetterhahn KE. Metabolism of carcinogenic chromate by cellular constituents. *Struct Bonding*. 1983;54:93–24. [Google Scholar]
- Chappell W, Beck B, Brown K, North D, Thornton I, Chaney R, Cothorn R, Cothorn CR, North DW, Irgolic K, Thornton I, Tsongas T. Inorganic arsenic: A need and an opportunity to improve risk assessment. *Environ Health Perspect*.
- D. Osman and J. S. Cavet, “Copper Homeostasis in Bacteria,” *Advances in Applied Microbiology*, vol. 65, pp. 217–247, 2008.
- Dizge, N., B. Keskinler, and H. Barlas, Sorption of Ni (II) ions from aqueous solution By Lewatit cation-exchange resin. *Journal of Hazardous materials*, 2009. 167(1): p. 915- 926.
- Dopp E, Hartmann LM, Florea AM, Rettenmier AW, Hirner AV. Environmental distribution, analysis, and toxicity of organometal (loid) compounds. *Crit Rev Toxicol*. 2004;34:301–333. [PubMed] [Google Scholar]
- Dermont, G., et al., Metal-contaminated soils: Remediation practices and treatment Technologies. *Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management*, 2008. 12(3): p. 188-209.
- Dayan AD, Paine AJ. Mechanisms of chromium toxicity, carcinogenicity and allergenicity: review of the literature from 1985 to 2000. *Hum Exp Toxicol*. 2001;20(9):439–451. [PubMed] [Google Scholar]
- Deliyanni, E., E. Peleka, and K. Matis, Removal of zinc ion from water by sorption Onto iron-based nanoadsorbent. *Journal of Hazardous materials*, 2007. 141(1): p. 176
- Deaglio S, Canella D, Baj G, Arnulfo A, Waxman S, Malavasi F. Evidence of an immunologic mechanism behind the therapeutic effects of arsenic trioxide on myeloma cells. *Leuk Res*. 2001;25(3):237–239. [PubMed] [Google Scholar].
- Eccles, H., Treatment of metal-contaminated Wastes: why select a biological process *Trends in biotechnology*, 1999. 17(12): p. 462-465.
- Environmental pathology and health effects of arsenic poisoning: a critical

review. In: Naidu R, Smith E, Smith J, Bhattacharya P, editors.

- Fu, F. and Q. Wang, Removal of heavy metal Ions from wastewaters: a review. *Journal of Environmental Management*, 2011. 92(3): p. 407-418.
- Flora SJS, Flora GJS, Saxena G. Environmental occurrence, health effects and management of lead poisoning. In: Cascas SB, Sordo J, editors. *Lead: Chemistry, Analytical Aspects, Environmental Impacts and Health Effects*. Netherlands: Elsevier Publication; 2006. Pp. 158–228. [Google Scholar]
- Gomez-Serrano, V., et al., Adsorption of Mercury, cadmium and lead from aqueous Solution on heat-treated and sulphurized Activated carbon. *Water Research*, 1998. 32(1): p. 1-4.
- Gupta, V.K., M. Gupta, and S. Sharma, Process development for the removal of lead and chromium from aqueous solutions using red mud—an aluminium industry waste. *Water Research*, 2001. 35(5): p. 1125-1134.
- Gupta, V.K., A. Rastogi, and A. Nayak, Adsorption studies on the removal of Hexavalent chromium from aqueous solution Using a low cost fertilizer industry waste Material. *Journal of Colloid and Interface Science*, 2010. 342(1): p. 135-141.
- Ghosh, U.C., et al., Studies on Management Of Chromium (VI)–Contaminated Industrial Waste Effluent using Hydrous Titanium Oxide (HTO). *Water, Air, and Soil Pollution*, 2003.143(1-4): p. 245256.
- Goyer RA. Toxic effects of metals. In: Klaassen CD, editor. *Cassarett and Doull’s Toxicology: The Basic Science of Poisons*. New York: McGraw-Hill Publisher; 2001. Pp. 811–867. [Google Scholar].
- Guzzi G, LaPorta CAM. Molecular mechanisms triggered by mercury. *Toxicol*. 2008;244:1–12. [PubMed] [Google Scholar]
- Gabby PN. Lead: in *Mineral Commodity Summaries*. Reston, VA: U.S. Geological Survey; 2006. Available at http://minerals.usgs.gov/minerals/pubs/commodity/lead/lead_mcs05.pdf. [Google Scholar].
- Gambelunghe A, Piccinini R, Ambrogi M, Villarini M, Moretti M, Marchetti C, Abbritti G, Muzi G. Primary DNA damage in chrome-plating workers. *Toxicology*. 2003;188(2–3):187–195. [PubMed] [Google Scholar]
- Guertin J. Toxicity and health effects of chromium (all oxidation states) In: Guertin J, Jacobs JA, Avakian CP, editors. *Chromium (VI) Handbook*. Boca Raton, FL: CRC Press; 2005. Pp. 216–234. [Google Scholar]
- Ho, Y.-S. and G. McKay, Pseudo-second Order model for sorption processes. *Process Biochemistry*, 1999. 34(5): p. 451-465
- Hamdaoui, O., Removal of copper (II) from Aqueous phase by Purolite C100-MB cation Exchange resin in fixed bed columns: Modeling. *Journal of hazardous materials*, 2009. 161(2): p. 737-746.
- Holmes P, Hames KAF, Levy LS. Is low-level mercury exposure of concern to human health? *Sci Total Environ*. 2009;408:171–182. [PubMed] [Google Scholar]
- International Agency for Research on Cancer (IARC) Monographs – Cadmium. Lyon, France: 1993. [Google Scholar]

- J. Giner-Lamia, L. L´opez-Maury, F. J. Florencio, and P. J.
- Janssen, “Global transcriptional profiles of the copper responses in the *Cyanobacterium synechocystis* sp. PCC 6803,” *PloS ONE*, vol.9, no. 9, p. e108912, 2014.
- Jacobs JA, Testa SM. Overview of chromium(VI) in the environment: background and history. In: Guertin J, Jacobs JA, Avakian CP, editors. *Chromium (VI) Handbook*. Boca Raton, FL: CRC Press; 2005. Pp. 1–22. [Google Scholar]
- Jarup L, Berglund M, Elinder CG, et al. Health effects of cadmium exposure—a review of the literature and a risk estimate [published erratum appears in *Scand J Work Environ Health* 1998 Jun; 24(3):240] *Scand J Work Environ Health*. 1998;24(1):1. [PubMed] [Google Scholar]
- Kurniawan, T.A., et al., Physico–chemical Treatment techniques for wastewater laden With heavy metals. *Chemical engineering Journal*, 2006. 118(1): p. 83-98.
- Ku, Y. and I.-L. Jung, Photocatalytic reduction Of Cr (VI) in aqueous solutions by UV Irradiation with the presence of titanium Dioxide. *Water Research*, 2001. 35(1): p. 135-142.
- Kaul B, Sandhu RS, Depratt C, Reyes F. Follow-up screening of lead-poisoned children near an auto battery recycling plant, Haina, Dominican Republic. *Environ Health Perspect*. 1999;107(11):917–920. [PMC free article] [PubMed] [Google Scholar]
- Katz SA, Salem H. The toxicology of chromium with respect to its chemical speciation: a review. *J Appl Toxicol*. 1993;13(3):217–224. [PubMed] [Google Scholar]
- L. D. Rasmussen, S. J. Sørensen, R. R. Turner, and T.
- López-Maldonado, E., et al., Coagulation–Flocculation mechanisms in wastewater Treatment plants through zeta potential.
- Lanphear BP, Matte TD, Rogers J, et al. The contribution of lead-contaminated house dust and residential soil to children's blood lead levels. A pooled analysis of 12 epidemiologic studies. *Environ Res*. 1998;79:51–68. [PubMed] [Google Scholar]
- Lakatos, T., Jensen et al. 2002.
- Leaner VD, Donniger H, Birrer MJ. Transcription Factors as Targets for Cancer Therapy: AP-1 a Potential Therapeutic Target. *Curr Cancer Therap Rev*. 2007;3:1–6. [Google Scholar]
- Langård S, Vigander T. Occurrence of lung cancer in workers producing chromium pigments. *Br J Ind Med*. 1983;40(1):71–74. [PMC free article] [PubMed] [Google Scholar]
- Liu, K., et al., Step-growth polymerization of Inorganic nanoparticles. *Science*, 2010.
- M. Bissen and F. H. Frimmel, “Arsenic—a review. Part I: occurrence, toxicity, speciation, mobility,” *Acta Hydrochimica et Hydrobiologica*, vol. 31, no. 1, pp. 9–18, 2003.
- Moustafa, M. and G. Idris, Biological removal Of heavy metals from wastewater. *Alexandria Engineering Journal*, 2003. 42(6): p. 767-771.
- Mane, P., et al., Bioadsorption of selenium by Pretreated algal biomass. *Adv*.

Appl. Sci. Res, 2011. 2(2): p. 202-207.

- Mitra RS. Protein synthesis in *Escherichia coli* during recovery from exposure to low levels of Cd²⁺ Appl Environ Microbiol. 1984;47:1012–1016. [PMC free article] [PubMed] [Google Scholar]
- Mohammadi, B. and O. Pironneau, Shape Optimization in fluid mechanics. Annu. Rev. Fluid Mech., 2004. 36: p. 255-279.
- Mollah, M.Y.A., et al., Electrocoagulation (EC)—science and applications. Journal of Hazardous materials, 2001. 84(1): p. 29-41.
- Maity, H., et al., Protein hydrogen exchange Mechanism: local fluctuations. Protein Science, 2003. 12(1): p. 153-160.
- M. O. Fashola, V. M. Ngole-Jeme, and O. O. Babalola, “Heavy Metal pollution from gold mines: Environmental effects and Bacterial strategies for resistance,” International Journal of Environmental Research and Public Health, vol. 13, no. 11, p. 1047, 2016.
- Magos L, Clarkson TW. Overview of the clinical toxicity of mercury. Ann Clin Biochem. 2006;43:257–268. [PubMed] [Google Scholar]
- National Research Council Canada (NRCC) Effects of Arsenic in the Environment. National Research Council of Canada; 1978. Pp. 1–349. [Google Scholar].
- National Research Council. Arsenic in Drinking Water. 2001 Update. 2001 On line at: <http://www.nap.edu/books/0309076293/html/>.
- Norseth T. The carcinogenicity of chromium. Environ Health Perspect. 1981;40:121–130. [PMC free article] [PubMed] [Google Scholar]
- Oskarsson A. Handbook on the Toxicology of Metals. Elsevier; Amsterdam, The Netherlands: 2015. Barium; pp. 625–634. [Google Scholar] [Ref list]
- P. T. Gauthier, W. P. Norwood, E. E. Prepas, and G. G. Pyle, “Metal/PAH mixtures in the aquatic environment: A review of Cotoxic mechanisms leading to more-than-additive outcomes,” Aquatic Toxicology, vol. 154, pp. 253–269, 2014.
- Pratish A., Kumar A., Hu Z. Adverse effect of heavy metals (As, Pb, Hg, and Cr) on health and their bioremediation strategies: A review. Int. Microbiol. 2018;21:97–106. Doi: 10.1007/s10123-018-0012-3. [PubMed] [CrossRef] [Google Scholar] [Ref list]
- Panyala N.R., Peña-Méndez E.M., Havel J. Silver or silver nanoparticles: A hazardous threat to the environment and human health? J. Appl. Biomed. 2008;6:117–129. Doi: 10.32725/jab.2008.015. [CrossRef] [Google Scholar] [Ref list]
- Patlolla AK, Armstrong N, Tchounwou PB. Cytogenetic evaluation of potassium dichromate toxicity in bone marrow cells of Sprague-Dawley rats. Metal Ions Biol Med. 2008;10:353–358. [Google Scholar]
- Prasad, B. and U. Pandey, Separation and Preconcentration of copper and cadmium ions From multielemental solutions using *Nostoc Muscorum*-based biosorbents. World Journal Of Microbiology and Biotechnology, 2000. 16(8-9): p. 819-827.
- Patlolla A, Barnes C, Yedjou C, Velma V, Tchounwou PB. Oxidative stress, DNA damage and antioxidant enzyme activity induced by hexavalent chromium in Sprague Dawley rats. Environ Toxicol. 2009;24(1):66–73. [PMC free article]

[PubMed] [Google Scholar].

- Paschal DC, Burt V, Caudill SP, Gunter EW, Pirkle JL, Sampson EJ, et al. Exposure of the U.S. population aged 6 years and older to cadmium: 1988–1994. *Arch Environ Contam Toxicol.* 2000;38:377–383. [PubMed] [Google Scholar]
- Reddad, Z., et al., Adsorption of several metal ions onto a low-cost biosorbent: kinetic and equilibrium studies. *Environmental science & Technology*, 2002. 36(9): p. 2067-2073.
- Rether, A. and M. Schuster, Selective Separation and recovery of heavy metal ions Using water-soluble N-benzoylthiourea Modified PAMAM polymers. *Reactive and Functional Polymers*, 2003. 57(1): p. 1321 .
- Rousselot P, Laboume S, Marolleau JP, Larghero T, Noguera ML, Brouet JC, Femand JP. Arsenic trioxide and melarsoprol induce apoptosis in plasma cell lines and in plasma cells from myeloma patients. *Cancer Res.* 1999;59:1041–1048. [PubMed] [Google Scholar]
- Rayman M.P. Selenium and human health. *Lancet.* 2012;379:1256–1268. Doi: 10.1016/S0140-6736(11)61452-9. [PubMed] [CrossRef] [Google Scholar] [Ref list]
- S. C. Booth, A. M. Weljie, and R. J. Turner, “Metabolomics Reveals differences of metal toxicity in cultures of *Pseudomonas Pseudoalcaligenes* KF707 grown on different carbon sources,” *Frontiers in Microbiology*, vol. 6, p. 827, 2015.
- S. Chen, H. Yin, J. Ye et al., “Influence of co-existed benzo[a]pyrene and copper on the cellular characteristics of *Stenotrophomonas maltophilia* during biodegradation and transformation,” *Bioresource Technology*, vol. 158, pp. 181–187, 2014.
- Sörme, L. and R. Lagerkvist, Sources of Heavy metals in urban wastewater in Stockholm. *Science of the Total Environment*, 2002. 298(1): p. 131-145.
- Sergeev, V., et al., Groundwater protection Against pollution by heavy metals at waste Disposal sites. *Water Science and Technology*, 1996. 34(7): p. 383-387.
- Sarkar BA. Mercury in the environment: Effects on health and reproduction. *Rev Environ Health.* 2005;20:39–56. [PubMed] [Google Scholar]
- Shelnutt SR, Goad P, Belsito DV. Dermatological toxicity of hexavalent chromium. *Crit. Rev Toxicol.* 2007;37:375–387. [PubMed] [Google Scholar]
- Salim, M. and B. Shaikh, Distribution and Availability of zinc in soil fractions to wheat on Some alkaline calcareous soils. *Zeitschrift für Pflanzenernährung und Bodenkunde*, 1988. 151(6): p. 385-389.
- .. Sawalha, M.F., et al., Sorption of hazardous Metals from single and multi-element Solutions by saltbush biomass in batch and Continuous mode: Interference of calcium and Magnesium in batch mode. *Journal of Environmental management*, 2009. 90(2): p. 1213-1218.
- Smith, L., Contaminants and remedial options At selected metalcontaminated sites. Technical resource report, 1995, Battelle, Columbus, OH (United States).
- Sharma, A.K., Experimental study on 75kW th Downdraft (biomass) gasifier system. *Renewable Energy*, 2009. 34(7): p. 1726-1733.
- Shim, H.Y., et al., Application of Electrocoagulation and

Electrolysis on the

Precipitation of Heavy Metals and Particulate Solids in Washwater from the Soil Washing. *Journal of Agricultural Chemistry and Environment*, 2014. 3(04): p. 130.

Seol JG, Park WH, Kim ES, Jung CW, Hyun JM, Kim BK, Lee YY. Effect of arsenic trioxide on cell cycle arrest in head and neck cancer cell-line PCI-1. *Biochem Biophys Res Commun*. 1999;265(2):400–404. [PubMed] [Google Scholar]

Satarug S, Baker JR, Urbenjapol S, Haswell-Elkins M, Reilly PE, Williams DJ, et al. A global perspective on cadmium pollution and toxicity in non-occupationally exposed population. *Toxicol Lett*. 2003;137:65–83. [PubMed] [Google Scholar]

Stohs Bagchi. Oxidative mechanisms in the toxicity of metal ions. *Free Radic Biol Med*. 1995;18:321–336. [PubMed] [Google Scholar]

Singhal RL, Merali Z, Hrdina PD. Aspects of the biochemical toxicology of cadmium. *Fed Proc*. 1976;35(1):75–80. [PubMed] [Google Scholar]

- Trivunac, K. and S. Stevanovic, Removal of Heavy metal ions from water by complexation-Assisted ultrafiltration. *Chemosphere*, 2006. 64(3): p. 486-491.

- Tripathy, T. and B.R. De, Flocculation: a new Way to treat the waste water. 2006.

- Tang, D.-S., et al., Extraction and purification Of solanesol from tobacco □I). Extraction and Silica gel column chromatography separation Of solanesol. *Separation and purification Technology*, 2007. 56(3): p. 291295.

- Tchounwou PB, Yedjou CG, Dorsey WC. Arsenic trioxide – induced transcriptional activation and expression of stress genes in human liver carcinoma cells (HepG2) *Cell Mol Biol*. 2003;49:1071–1079. [PubMed] [Google Scholar]

- Tchounwou PB, Wilson B, Ishaque A. Important considerations in the development of public health advisories for arsenic and arsenic-containing compounds in drinking water. *Rev Environ Health*. 1999;14(4):211–229. [PubMed] [Google Scholar].

- Tchounwou PB, Centeno JA. Toxicologic pathology. In: Gad SC, editor. *Handbook of Pre-Clinical Development*. New York. NY: John Wiley & Sons; 2008. Pp. 551–580. [Google Scholar].

- Tchounwou PB, Patlolla AK, Centeno JA. Carcinogenic and systemic health effects associated with arsenic exposure-a critical review. *Toxicol Pathol*. 2003;31(6):575–588. [PubMed] [Google Scholar].

- Tchounwou PB, Wilson BA, Abdelgnani AA, Ishaque AB, Patlolla AK. Differential cytotoxicity and gene expression in human liver carcinoma (HepG2) cells exposed to arsenic trioxide and monosodium acid methanearsonate (MSMA) *Intl J Mol Sci*. 2002;3:1117–1132. [Google Scholar].

- U. Hildebrandt, M. Regvar, and H. Bothe, “Arbuscular mycor-Rhiza and heavy metal tolerance,” *Phytochemistry*, vol. 68, no. 1, pp. 139–146, 2007.

- Yedjou GC, Moore P, Tchounwou PB. Dose and time dependent response of human leukemia (HL-60) cells to arsenic trioxide. *Intl J Environ Res Public Health*. 2006;3(2):136–140. [PMC free article] [PubMed] [Google Scholar]

- Vigneswaran, R., et al., Cerebral palsy and Placental infection: a case-cohort

study. *BMC Pregnancy and childbirth*, 2004. 4(1): p. 1.

- Valko M, Izakovic M, Mazur M, Rhodes CJ, Tesler J. Role of oxygen radicals in DNA damage and cancer incidence. *Mol Cell Biochem*. 2004;266:79–110. [PubMed] [Google Scholar]
- Valko M, Morris H, Cronin MTD. Metals, Toxicity, and oxidative Stress. *Curr Medici Chem*. 2005;12:1161–1208. [PubMed] [Google Scholar].
- Vaca Mier, M., et al., Heavy metal removal With Mexican clinoptilolite:: multi-component Ionic exchange. *Water research*, 2001.35(2): p. 373-378
- 36Velma V, Vutukuru SS, Tchounwou PB. Ecotoxicology of hexavalent chromium in freshwater fish: a critical review. *Rev Environ Health*. 2009;24(2):129–145. [PMC free article] [PubMed] [Google Scholar]
- Wu, J., et al., Cr (VI) removal from aqueous Solution by dried activated sludge biomass.*Journal of hazardous materials*, 2010. 176(1): p. 697-703.
- Williford, C., R.M. Bricka, and I. Iskandar, Physical separation of metal-contaminated Soils2000: CRC Press LLC, Boca Raton.
- Wilson DN Association Cadmium. Cadmium – market trends and influences; London. Cadmium 87 Proceedings of the 6th International Cadmium Conference; 1988. Pp. 9–16. [Google Scholar]
- Waalkes MP, Berthan G, editors. Handbook on Metal-Ligand Interactions of Biological Fluids. Vol. 2. New York: Marcel Dekker; 1995. Pp. 471–482. [Google Scholar]
- Wise SS, Holmes AL, Ketterer ME, Hartsock WJ, Fomchenko E, Katsifis SP, Thompson WD, Wise JP. Chromium is the proximate clastogenic species for lead chromate-induced clastogenicity in human bronchial cells. *Mutat Res*. 2004;560:79–89. [PubMed] [Google Scholar]
- Wise JP, Wise SS, Little JE. The cytotoxicity and genotoxicity of particulate and soluble hexavalent chromium in human lung cells. *Mutat Res*. 2002;517:221–229. [PubMed] [Google Scholar]
- Waalkes MP, Misra RR, Chang LW, editors. Toxicology of Metals. Boca Raton, FL: CRC Press; 1996. Pp. 231–244. [Google Scholar]
- Yedjou GC, Tchounwou PB. In vitro cytotoxic and genotoxic effects of arsenic trioxide on human leukemia cells using the MTT and alkaline single cell gel electrophoresis (comet) assays. *Mol Cell Biochem*. 2007;301:123–130. [PMC free article] [PubMed] [Google Scholar]
- Xie H, Wise SS, Holmes AL, Xu B, Wakeman T, Pelsue SC, Singh NP, Wise JP. Carcinogenic lead chromate induces DNA double-strand breaks in human lung cells. *Mutat Res*. 2005;586:160–172. [PMC free article] [PubMed] [Google Scholar].
- Zhou, W. and W. Zimmermann, Decolorization of industrial effluents Containing reactive dyes by actinomycetes.*FEMS microbiology letters*, 1993. 107(2): p. 157-161.

- Zahir A, Rizwi SJ, Haq SK, Khan RH. Low dose mercury toxicity and human health. *Environ Toxicol Pharmacol.* 2005;20:351–360. [PubMed] [Google Scholar]
- Zhitkovich A, Song Y, Quievryn G, Voitkun V. Non-oxidative mechanisms are responsible for the induction of mutagenesis by reduction of Cr(VI) with cysteine: role of ternary DNA adducts in Cr(III)-dependent mutagenesis. *Biochem.* 2001;40(2):549–60

الخلاصه:

تعد المعادن الثقيلة مثل الزرنيخ والنحاس والكاديوم والكروم والنيكل والزنك والرصاص والزرنيق من الملوثات الرئيسية لخزانات المياه العذبة بسبب طبيعتها السامة وغير القابلة للتحلل والثبات. النمو الصناعي هو المصدر الرئيسي للمعادن الثقيلة التي تدخل مثل هذه الملوثات في قطاعات مختلفة من البيئة بما في ذلك الهواء والماء والتربة والمحيط الحيوي. قد تتراكم في جسم الإنسان عن طريق السلسلة الغذائية. غالبًا ما تتضمن طرق معالجة مياه الصرف الصناعية المحتوية على معادن ثقيلة تقنيات لتقليل السمية من أجل تلبية معايير المعالجة القائمة على التكنولوجيا. تم التركيز على عمليات المعالجة المختلفة المطورة حديثًا والقابلة للتطبيق حديثًا لإزالة المعادن الثقيلة من مياه الصرف الصناعي. عمليات الإزالة الفيزيائية والكيميائية مثل؛ الامتزاز على الممتزات الجديدة، التبادل الأيوني، الترشيح الغشائي، التحلل الكهربائي، التناضح العكسي، الترشيح الفائق والتحفيز الضوئي. تم تقييم مزاياها وعيوبها. تعد تقنيات الامتصاص الحيوي أفضل الحلول الصديقة للبيئة لإزالة المعادن الثقيلة من مياه الصرف الصحي بدلاً من الطرق الفيزيائية والكيميائية. لكن الطرق الكيميائية هي أنسب العلاجات للمركبات غير العضوية السامة المنتجة من الصناعات المختلفة والتي لا يمكن إزالتها من أي تقنيات بيولوجية وفيزيائية.

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مراجعة طرق المعالجة المستخدمة لإزالة المعادن الثقيلة من مياه الصرف الصناعي

مشروع

مقدم الى كلية الهندسة في جامعة بابل كجزء
من متطلبات نيل درجة البكالوريوس علوم في
الهندسة البيئية

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