



## MINIMIZATION OF INDUSTRIAL WASTE WATER CONTAINING HEAVY METALS ON ENVIRONMENT

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### Abstract

*Green chemical science recognizes the concept of developing innovative environmentally benign technologies to protect human health and ecosystems. In order to explore this concept for minimizing industrial waste and for reducing the environmental impact of hazardous chemicals (heavy metals). Innovative processes for treating industrial wastewater containing heavy metals often involve technologies for reduction of toxicity in order to meet technology-based treatment standards. This article reviews the recent developments and technical applicability of various treatments for the removal of heavy metals from industrial wastewater. A particular focus is given to innovative physico-chemical removal processes such as, adsorption on new adsorbents, membrane filtration, electrodialysis, and photocatalysis. Their advantages and limitations in application are evaluated. It is evident from survey that new adsorbents and membrane filtration are the most frequently studied and widely applied for the treatment of metal-contaminated wastewater. However, in the near future, the most promising methods to treat such complex systems will be the photo catalytic ones which consume cheap photons from the UV-near visible region. They induce both degradation of organic pollutants and recovery of metals in one-pot systems. . In general, the technical applicability, plant simplicity and cost-effectiveness are the key factors in selecting the most suitable treatment for inorganic effluent.*

**Keywords:** Heavy metals, Industrial wastewater treatment, Removal, Innovative techniques.

### Introduction

Due to the discharge of large amounts of metal-contaminated wastewater, industries bearing heavy metals, such as Cd, Cr, Cu, Ni, As, Pb, Mo and Zn, are the most hazardous among the chemical-intensive industries. Because of their high solubility in the aquatic environments, heavy metals can be absorbed by living organisms. Once they enter the food chain, large concentrations of heavy metals may accumulate in the human body. If the metals are ingested beyond the permitted concentration, they can cause serious health disorders (Babel and Kurniawan, 2004). Therefore, it is necessary to treat metal-contaminated wastewater prior to its discharge to the environment. Heavy metal removal from inorganic

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effluent can be achieved by conventional treatment processes such as chemical precipitation, ion exchange, and electrochemical removal. These processes have significant disadvantages, which are, for instance, incomplete removal, high-energy requirements, and production of toxic sludge. Recently, numerous approaches have been studied for the development of cheaper and more effective technologies, both to decrease the amount of wastewater produced and to improve the quality of the treated effluent. Adsorption has become one of the alternative treatments, in recent years, the search for low-cost adsorbents that have metal-binding capacities has intensified. The adsorbents may be of mineral, organic or biological origin, zeolites, industrial by-products, agricultural wastes, biomass, and polymeric materials (Kurniawan et al, 2004). Membrane separation has been increasingly used recently for the treatment of inorganic effluent due to its convenient operation. There are different types of membrane filtration such as ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) (Kurniawan et al, 2006). Electrotreatments such as electrodialysis has also contributed to environmental protection. Photocatalytic process is an innovative and promising technique for efficient destruction of pollutants in water (Skubal et al, 2004). Although many techniques can be employed for the treatment of inorganic effluent, the ideal treatment should be not only suitable, appropriate and applicable to the local conditions, but also able to meet the maximum contaminant level (MCL) standards established. This article presents an overview of various innovative physico-chemical treatments for removal of heavy metals from industrial wastewater.

### **Heavy metals in industrial waste water and toxicity**

Heavy metals are generally considered to be those whose density exceeds 5 g per cubic centimeter. A large number of elements fall into this category, but the ones listed in table -1 are those of relevance in the environmental context. Arsenic is usually regarded as a hazardous heavy metal even though it is actually a semi-metal. Heavy metals cause serious health effects, including reduced growth and development, cancer, organ damage, nervous system damage, and in extreme cases, death. Exposure to some metals, such as mercury and lead, may also cause development of autoimmunity, in which a person's immune system attacks its own cells. This can lead to joint diseases such as rheumatoid arthritis, and diseases of the kidneys, circulatory system, nervous system, and damaging of the fetal brain. At higher doses, heavy metals can cause irreversible brain damage. . Wastewater regulations were established to minimize human and environmental exposure to hazardous chemicals. This includes limits on the types and concentration of heavy metals that may be present in the discharged wastewater. The MCL standards, for those heavy metals, established by USEPA (Babal and Kurniawan, 2003) are summarized in table- 1.

**TABLE-1: The MCL standards for the most hazardous heavy metals**

Heavy metal	Toxicities	MCL(mg/L)
Arsenic	Skin manifestations, visceral cancers, vascular disease	0.050
Cadmium	Kidney damage, renal disorder, human carcinogen	0.01
Chromium	Headache, diarrhea, nausea, vomiting, carcinogenic	0.05
Copper	Liver damage, Wilson disease, insomnia	0.25
Nickel	Dermatitis, nausea, chronic asthma, coughing, human carcinogen	0.20
Zinc	Depression, lethargy, neurological signs and increased thirst	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

Industrial wastewater streams containing heavy metals are produced from different industries. Electroplating, petrochemical, paper and pulp, fertilizer and metal surface treatment processes generate significant quantities of wastewaters containing heavy metals (such as cadmium, zinc, lead, chromium, nickel, copper, vanadium, platinum, silver, and titanium) from a variety of applications. These include electroplating, electroless depositions, conversion-coating, anodizing-cleaning, milling, and etching. Another significant source of heavy metals wastes result from printed circuit board (PCB) manufacturing. Tin, lead, and nickel solder plates are the most widely used resistant over plates. Other sources for the metal wastes include; the wood processing industry where a chromated copper-arsenate wood treatment produces arsenic-containing wastes, inorganic pigment manufacturing producing pigments that contain chromium compounds and cadmium sulfide, petroleum refining which 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 sludges that can be categorized as hazardous wastes on environment

## **Techniques for treating industrial waste water**

### **1. Conventional processes for removal of heavy metal (chemical precipitation)**

The conventional processes for removing heavy metals from wastewater include many processes such as chemical precipitation, flotation, adsorption, ion exchange, and electrochemical deposition. Chemical precipitation is the most widely used for heavy metal removal from inorganic effluent. Lime and limestone are the most commonly employed precipitant agents due to their availability and low-cost in most countries. Other advantages of using lime precipitation include the simplicity of the process, inexpensive equipment requirement, and convenient and safe operations. However, chemical precipitation requires a large amount of chemicals to reduce metals to an acceptable level for discharge. Other drawbacks are its excessive sludge production that requires further treatment, slow metal precipitation, poor settling, and the aggregation of metal precipitates, and the long-term environmental impacts of sludge disposal (Aziz et al, 2008). Ion exchange is another method used successfully in the industry for the removal of heavy metals from effluent. An ion exchange is a solid capable of exchanging either cations or anions from the surrounding materials. Commonly used matrices for ion exchange are synthetic organic ion exchange resins.. This process uses electricity to pass a current through an aqueous metal-bearing solution containing a cathode plate and an insoluble anode. Positively charged metallic ions cling to the negatively charged cathodes leaving behind a metal deposit that is strippable and recoverable. A noticeable disadvantage was that corrosion could become a significant limiting factor, where electrodes would frequently have to be replaced.

### **2. Adsorption on new adsorbents**

Sorption actually describes a group of processes, which includes adsorption and precipitation reactions. Recently, adsorption has become one of the alternative treatment techniques for wastewater laden with heavy metals. Basically, adsorption is a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid, and becomes bound by physical and chemical interactions. Low-cost adsorbents, derived from agricultural waste, industrial by-product, natural material, or modified biopolymers, have been recently developed and applied for the removal of heavy metals from metal-contaminated wastewater. In general, there are three main steps involved in pollutant sorption onto solid sorbent: (1) the transport of the pollutant from the bulk solution to the sorbent surface (2) adsorption on the particle surface and (3) transport within the sorbent particle. Technical applicability and cost-effectiveness are the key factors that play major roles in the selection of the most suitable adsorbent to treat inorganic effluent.

#### **(a) Adsorption on modified natural materials**

Natural zeolites gained a significant interest, mainly due to their valuable properties as ion exchange capability. Among the most frequently studied natural zeolites, clinoptilolite was shown to

have high selectivity for certain heavy metal ions such as Pb(II), Cd(II), Zn(II), and Cu(II). It was demonstrated that the cation-exchange capability of clinoptilolite depends on the pre-treatment method and that conditioning improves its ion exchange ability and removal efficiency. (Aklil et al,2004). Table -2 presents the highest reported metal adsorption capacities of low-cost adsorbents from various modified natural materials.

**TABLE- 2. Adsorption capacities of modified natural materials for heavy metals.**

Absorbent	Absorption capacity (MG/G)					
	Pb <sup>2+</sup>	Cd <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Cr <sup>6+</sup>	Ni <sup>2+</sup>
<b>Zeolite clinoptilolite</b>	<b>1.6</b>	<b>2.4</b>	<b>0.5</b>	<b>1.64</b>	-	<b>0.48</b>
Modified zeolite, MMZ	<b>123</b>	-	-	-	-	<b>8</b>
HCl-treated clay	-	-	<b>63.2</b>	<b>83.3</b>	-	-
Clay/poly(methoxyethyl)acrylamide	81.02	-	20.6	29.8	-	80.9
Calcined phosphate	155.0	-	-	-	-	-
Activated phosphate	4	-	-	-	-	-
Zirconium phosphate	398	-	-	-	-	-

### (b) Adsorption on modified agriculture and biological wastes (bio-sorption)

Recently, a great deal of interest in the research for the removal of heavy metals from industrial effluent has been focused on the use of agricultural by-products as adsorbents. The use of agricultural by-products in bioremediation of heavy metal ions is known as bio-sorption. This utilizes inactive (non-living) microbial biomass to bind and concentrate heavy metals from waste streams by purely physico-chemical pathways (mainly chelation and adsorption) of uptake.. Table -3 shows the adsorption capacities of different biosorbents.

**TABLE- 3. Adsorption capacities of some agricultural and biological wastes for heavy metals.**

Adsorbent	Adsorption capacity (mg/g)				
	Pb <sup>2+</sup>	Cd <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Cr <sup>6+</sup>
Maize cobe and husk	456	493.7	495.9	-	-
Coconut shell charcoal	-	-	-	-	3.65
Pecan shells activated carbon	-	-	13.9	31.7	-
Rice husk	2.0	-	-	-	0.79
Modified rice hull	-	-	-	-	23.4
<i>Spirogyra</i> (green alga)	-	-	-	133	-
Ecklonia maxima – marine alga	235	-	-	90	-
<i>Ulva lactuca</i>	-	-	-	-	112.3
<i>Oedogonium</i> species	145	-	-	-	-
<i>Nostoc</i> species	93.5	-	-	-	-
<i>Bacillus</i> – bacterial biomass	467	85.3	418	381	39.9

### 3. Membrane filtration

Membrane filtration has received considerable attention for the treatment of inorganic effluent, since it is capable of removing not only suspended solid and organic compounds, but also 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. Ultrafiltration (UF) utilizes permeable 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). These unique specialties enable UF to allow the passage of water and low-molecular weight solutes, while retaining the macromolecules, which have a size larger than the pore size of the membrane. A new integrated process combining adsorption, membrane separation and flotation developed for the selective separation of heavy metals from wastewater. The process was divided into the following three stages: firstly, heavy metal bonding (adsorption) by a bonding agent, secondly, wastewater filtration to separate the loaded bonding agent by two variants: cross flow microfiltration for low-contaminated wastewater or a hybrid process combining flotation and submerged microfiltration for highly contaminated wastewater and thirdly, bonding agent regeneration). Bloocher et al. (2003).

### 4. Electrodialysis

Electrodialysis (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, 2004). Some interesting results were reported by Tzanetakis et al. (2003), who evaluated the performance of the ion exchange membranes for the electrodialysis of Ni (II) and Co (II) ions from a synthetic solution. 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 et al.,2004).

ED process modeled based on basic electrochemistry rules and copper ion separation experimental data. The experiments were performed for zinc, lead and chromium ions. It was found that performance of an ED cell is almost independent on the type of ions and only depends on the operating conditions and the cell structure. In spite of its limitation, ED offers advantages for the treatment of wastewater laden with heavy metals such as the ability to produce a highly concentrated stream for recovery and the rejection of undesirable impurities from water. Moreover, valuable metals such as Cr and Cu can be recovered. Since ED is a membrane process, it requires clean feed, careful operation, periodic maintenance to prevent any stack damages.

## 5. Photocatalysis

In the recent years, photocatalytic process in aqueous suspension of semiconductor has received considerable attention in view of solar energy conversion. This photocatalytic process was achieved for rapid and efficient destruction of environmental pollutants. Upon illumination of semiconductor–electrolyte interface with light energy greater than the semiconductor band gap, electron–hole pairs ( $e^-/h^+$ ) are formed in the conduction and the valence band of the semiconductor, respectively (Herrmann, 1999). These charge carriers, which migrate to the semiconductor surface, are capable of reducing or oxidizing species in solution having suitable redox potential. Various semiconductors have been used.  $TiO_2$ ,  $ZnO$ ,  $CeO_2$ ,  $CdS$ ,  $ZnS$ , etc. As generally observed, the best photocatalytic performances with maximum quantum yields are always obtained with titanium dioxide. The mechanism of photocatalysis over titanium dioxide particle was reported (Zhang and Itoh, 2006). The generated electron–hole pairs must be trapped in order to avoid recombination. The hydroxyl ions ( $OH^-$ ) are the likely traps for holes, leading to the formation of hydroxyl radicals which are strong oxidant agents, while the traps for electrons are adsorbed oxygen species, leading to the formation of superoxide species ( $O_2^-$ ) which are unstable, reactive and may evolve in several ways.

### Evaluation of heavy metals removal processes

In general, physico-chemical treatments offer various advantages such as their rapid process, ease of operation and control, flexibility to change of temperature. Unlike in biological system, physico-chemical treatment can accommodate variable input loads and flow such as seasonal flows and complex discharge. Whenever it is required, chemical plants can be modified. In addition, the treatment system requires a lower space and installation cost. Their benefits, however, are outweighed by a number of drawbacks such as their high operational costs due to the chemicals used, high-energy consumption and handling costs for sludge disposal. However, with reduced chemical costs (such as utilizing of low-cost adsorbents) and a feasible sludge disposal, physico-chemical treatments have been found as one of the most suitable treatments for inorganic effluent.

In wastewater systems containing heavy metals with other organic pollutants, the presence of one species usually impedes the removal of the other. For instance, hydrometallurgy, a classical process to recover metals, is inhibited by the presence of organic compounds and a pre-treatment step, to remove or destroy organics, is generally required, pyrometallurgy which is able to decontaminate systems from organic pollutants and recover metals suffers from lack of controllability, demanding extremely high temperatures. The most promising methods to treat such complex systems are the photocatalytic ones which consume cheap photons from the UV-near visible region. These photo catalysts serve as electron relays, from the organic substrates to metal ions. Thus, they induce both degradation of organic

pollutants and recovery of metals in one-pot systems, operable at traces of the target compounds. Table - 4 summarizes the main advantages and disadvantages of the various physico-chemical treatments presented in this study.

**TABLE- 4: The main advantages and disadvantages of the various physico-chemical methods for treatment of heavy metal in wastewater.**

Treatment method	Advantages	Disadvantages
Chemical precipitation	Low capital cost, simple operation	Sludge generation, extra operational cost for sludge disposal
Adsorption with new adsorbents	Low-cost, easy operating conditions, having wide pH range, high metal-binding capacities	Low selectivity, production of waste products
Membrane filtration	Small space requirement, low pressure, high separation selectivity	High operational cost due to membrane fouling
Electrodialysis	High separation selectivity	High operational cost
Photocatalysis	Removal of metals and organic pollutant simultaneously, less harmful by-products	Long duration time, limited applications

## Conclusions

Over the past two decades, environmental regulations have become more stringent, requiring an improved quality of treated effluent. In recent years, a wide range of treatment technologies such as chemical precipitation, adsorption, membrane filtration, electrodialysis, and photocatalysis, have been developed for heavy metal removal from contaminated wastewater. It is evident from the literature survey that: lime precipitation has been found as one of the most effective conventional means to treat inorganic effluent with a metal concentration higher than 1000 mg/L new adsorbents and membrane filtration are the most frequently studied and widely applied for the treatment of the heavy metal-contaminated wastewater; photocatalysis is a promising innovative technique for a clean and efficient treatment. Although many techniques can be employed for the treatment of wastewater laden with heavy metals, it is important to note that the selection of the most suitable treatment for metal-contaminated wastewater depends on some basic parameters such as pH, initial metal concentration, the overall treatment performance compared to other technologies, environmental impact as well as economics parameter such as the capital investment and operational costs. Finally, technical applicability, plant



simplicity and cost-effectiveness are the key factors that play major roles in the selection of the most suitable treatment system for inorganic effluent. All the factors mentioned above should be taken into consideration in selecting the most effective and inexpensive treatment in order to protect the environment.

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