

## Removal of Heavy Metal from Wastewater: A Review of Current Treatment Processes

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### ABSTRACT

Currently Heavy metal contamination has become one of the most serious environmental threat. The treatment of heavy metals is of special anxiety due to their recalcitrance and persistence in the environment. In recent years, multiple methods for heavy metal exclusion from wastewater have been comprehensively developed. This paper reviews the existing procedures that have been used to treat heavy metal wastewater and evaluates these techniques. These technologies include membrane filtration, ion-exchange, electroless nickel plating, rinse water treatment and Sayong ball chemical method. About 62 published studies (1972-2015) are reviewed in this paper. It is marked from the literature survey articles that ion-exchange and membrane filtration are the most frequently studied for the treatment of heavy metal wastewater.

### Keywords:

Heavy Metals, Waste processing,  
Environmental, Ecology, Water  
Treatment

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## 1. Introduction

This paper review different techniques for filtration and water treatment. Industrial wastewaters like electroplating or acid mine wastewaters contain various kinds of toxic substances such as cyanides, alkaline cleaning agents, degreasing solvents, oil, fat and metals. Most of the metals such as copper, nickel, chromium, silver and zinc are harmful when they are discharged without treatment[1]. The pollution of heavy metals has gained worldwide attention due to their toxicity, difficult degradation, and accumulation in the living organisms[2]. This matter has been officially discussed for the first time by the world leaders in Stockholm Declaration during the United Nation Conference[3]. Malaysia was one of the countries which signed the Stockholm Declaration, hence the establishment of Malaysia Environmental Quality Act in 1974[4]. Amendments to this Act were made according to the current issues and the last amendment was made in 2009. As Malaysia has enjoyed one of the least polluted urban environments in Asia. The goal of achieving industrial country status by the year 2020 and the associated rapid economic growth have started to impose costs in terms of industrial pollution and the degradation of urban environment[5].

The industrial activities involving chemicals and heavy metals become a great concern in wastewater discharge activity to the environment. Heavy metals such as cadmium, lead, zinc, nickel, copper and chromium (III) or their compounds have been used extensively by various metal-finishing, mining and chemical industries [6,7]. This has led to a sharp increase in the contamination of water.

Because of their toxicity, the presence of any of these metals in excessive quantities will interfere with many beneficial uses of the water[6]. Heavy metals are chemical components with a specific gravity which minimum 5 times the water specific gravity[8]. There is permissible limit for heavy metals to exist in water as stated in Malaysia Environmental Quality Act, 1974 as shown in Table 1.

**Table 1**

Acceptable conditions for discharge of industrial effluent for mixed effluent of standards A and B  
**ACCEPTABLE CONDITIONS FOR DISCHARGE OF INDUSTRIAL EFFLUENT FOR MIXED EFFLUENT OF STANDARDS A AND B**

Parameter		Unit	Standard	
(1)	(2)	(3)	A *	B **
(i) Temperature	°C	40		40
(ii) pH Value	-	6.0-9.0		5.5-9.0
(iii) BOD <sub>5</sub> at 20°C	mg/L	20		40
(iv) Suspended Solids	mg/L	50		100
(v) Mercury	mg/L	0.005		0.05
(vi) Cadmium	mg/L	0.01		0.02
(vii) Chromium, Hexavalent	mg/L	0.05		0.05
(viii) Chromium, Trivalent	mg/L	0.20		1.0
(ix) Arsenic	mg/L	0.05		0.10
(x) Cyanide	mg/L	0.05		0.10
(xi) Lead	mg/L	0.10		0.5
(xii) Copper	mg/L	0.20		1.0
(xiii) Manganese	mg/L	0.20		1.0
(xiv) Nickel	mg/L	0.20		1.0
(xv) Tin	mg/L	0.20		1.0
(xvi) Zinc	mg/L	2.0		2.0
(xvii) Boron	mg/L	1.0		4.0
(xviii) Iron (Fe)	mg/L	1.0		5.0
(xix) Silver	mg/L	0.1		1.0
(xx) Aluminium	mg/L	10		15
(xxi) Selenium	mg/L	0.02		0.5
(xxii) Barium	mg/L	1.0		2.0
(xxiii) Fluoride	mg/L	2.0		5.0
(xxiv) Formaldehyde	mg/L	1.0		2.0
(xxv) Phenol	mg/L	0.001		1.0
(xxvi) Free Chlorine	mg/L	1.0		2.0
(xxvii) Sulphide	mg/L	0.50		0.50
(xxviii) Oil and Grease	mg/L	1.0		10
(xxix) Ammoniacal Nitrogen	mg/L	10		20
(xxx) Colour	ADMI*	100		200

ADMI- American Dye Manufactures Institute

**Note** : \*A: Discharge upstream of water supply sources

\*\*B: Discharge downstream of water supply sources

There is a raising alarm for the heavy metals in wastewater existence and contamination generated from industries such as plating. Elements such as silver, chromium, copper, lead, zinc, and mercury exhibit human toxicity at even low concentrations[9,10]. Excess amount of heavy metals will be harmful to the human body, aquatic life and environment[11]. Research shows that human body with excess heavy metals can cause health hazard[12]. Table 2. Shows the acute and chronic effect of heavy metals to human.

**Table 2**

Acute and chronic effect of heavy metals to human [9,12-18]

Metal	Acute	Chronic
Copper	Blue vomitus, GI irritation/ hemorrhage, hemolysis, metal fume fever (MFF) - inhaled	vineyard sprayer's lung (inhaled); Wilson disease (hepatic and basal ganglia degeneration)
Iron	Vomiting, GI hemorrhage, cardiac depression, metabolic acidosis	Hepatic cirrhosis
Lead	nausea, vomiting, encephalopathy (headache, seizures, ataxia, obtundation)	encephalopathy, anemia, abdominal pain, nephropathy, foot-drop/wrist-drop
Manganese	Metal fume fever (MFF) - inhaled	Parkinson-like syndrome, respiratory, neuropsychiatric
Nickel	Skin problem or rashes; nickel carbonyl: myocarditis, acute lung injury (ALI), encephalopathy	Occupational (inhaled): pulmonary fibrosis, reduced sperm count, nasopharyngeal tumors

As shown in Table 2, nickel can cause acute and chronic toxicity effect to human. Dermatitis (rash) is an acute effect of nickel to human health[12]. Meanwhile, nickel carbonyl can cause myocarditis; inflammation of the heart muscle, Acute Lung Injury (ALI) and encephalopathy; disease of the brain[8,19].

Chronic toxicity effects usually happen to people who are exposed to nickel frequently especially in industrial occupational sector. When the workers inhale nickel for a long period of time; months or years, it can cause chronic toxicity effects like pulmonary fibrosis, reduced sperm count for men and nasopharyngeal tumors.

Plants have the ability to accumulate heavy metals from many environments [20-23]. Metal uptake is most probable when plants grow in soils with naturally high metal concentrations or in soils enriched with metals from anthropogenic sources, such as smelting, fungicides, electroplating, mine waste, and sewage/sludge[24-27]. Metal uptake by plants may pose risks to human health when garden vegetables are cultivated on or near mine tailings/wastes[22,28]. This would pose concerns, as lead, cadmium, arsenic, and other heavy metals accumulate in the leaves and roots of vegetable plants [25,26,29]. Metal accumulation depends on plant species, chemical species, and soil condition [30-33].

However, most of these methods require high operational and maintenance costs, and generate toxic sludge[2,34]. In recent years, bio-electrochemical systems (BESs) have attracted considerable attention for their innovative features and environmental benefits[35].

Ion exchange technique is a popular method used in the industry but it involves chemicals resin and is very expensive. Promising wastewater treatment techniques are important to filter the effluent before it can be discharged to the water stream. The objective of this paper is to find the most common treatment process for heavy metal removal from wastewater. It is hope that a green technology could be an alternative method to treat and manage water pollution issue.

## 2. Water Treatment

The pollution of heavy metals has gained worldwide attention due to their toxicity, difficult degradation, and accumulation in the living organisms[2]. The treatment of aqueous or oily effluents is one of the most serious environmental issues faced by the minerals and metallurgy industries[36]. Water treatment is the process of removing contaminants from wastewater, primarily from household and industrial wastes. It includes physical, chemical, and biological processes to remove these contaminants and produce environmentally safe treated wastewater (or treated effluent). A

by-product of water treatment is usually a semi-solid waste or slurry, called sewage sludge that has to undergo further treatment before being suitable for disposal or land application.

## 2.1 Membrane Technology

Membrane science has taken its place among the most important topics of research in the world today, with sales of membrane systems topping US\$ 1 billion annually[37]. Membrane technology has become increasingly attractive for treating and recycling wastewater in the plating industry because of its high efficiency, ease of operation and low cost [38,39]. Membrane separation technology and its applications have been rapidly developed in recent years[40]. The use of membranes for wastewater treatment and removal of heavy metals recovery have attracted considerable attention in many industries. The membrane process can be divided into three categories:

- (i) High pressure reverse osmosis,
- (ii) Low pressure reverse osmosis, and
- (iii) Ultrafiltration (very low pressure).

The process involves flowing the solution under pressure through an appropriate porous membrane and extracting permeate or clean water flow of the membrane at atmospheric pressure. There are many types of membrane filtration techniques including reverse osmosis (RO), microfiltration (MF), Nano-filtration (NF) and ultrafiltration (UF) as shown in Figure1.

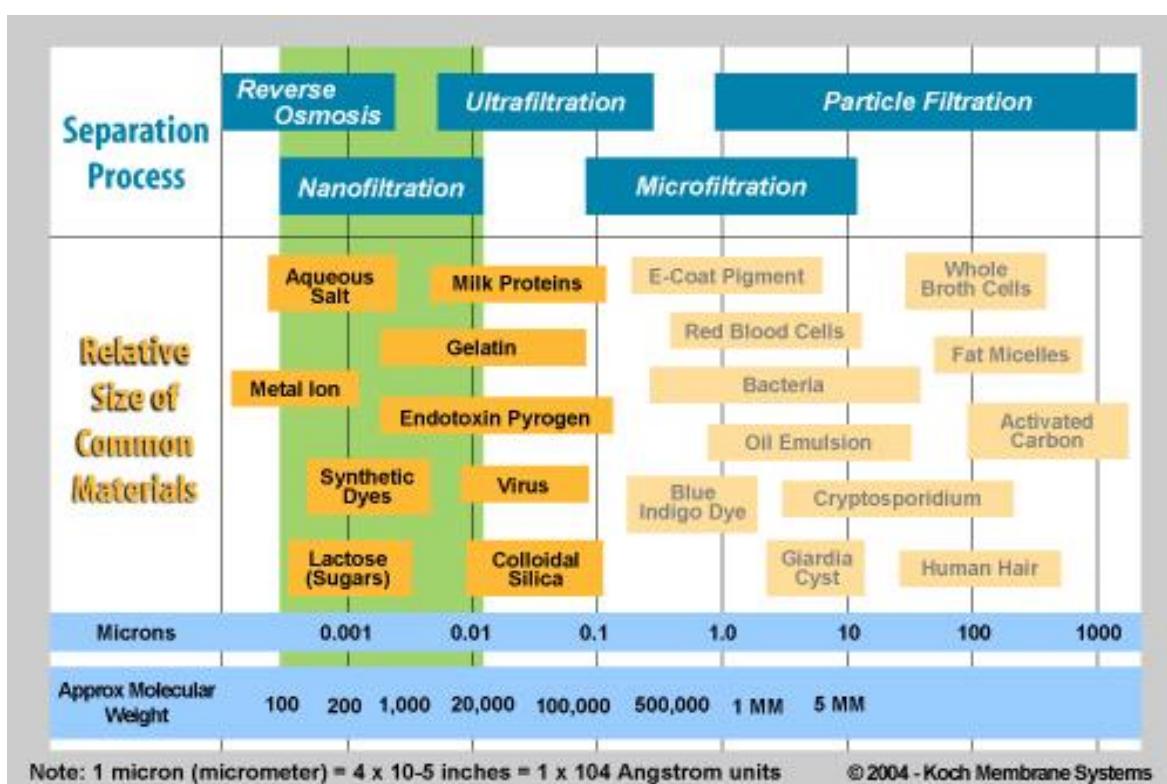


Fig. 1. Separation process and its potential to filter common materials

For membrane filtration treatment aimed to remove heavy metals, NF and RO is the separation process needed. These two processes can filter particle lower than  $0.001\mu\text{m}$ . NF membrane's technology applies pressure to discrete soluble ions from water through a semi permeable membrane. Nano filtration (NF) is the transitional process between UF and RO. NF is a favorable

technology for the elimination of heavy metal ions such as nickel[41], chromium, copper and arsenic from wastewater [42-44] .Most NF membranes are composite materials supported by polymer substrate and created in a spiral design which the prime model is presently used for industrial purposes. Figure 2 shows an example of NF system.



**Fig. 2.** Nano-filtration ion exchange system for industrial application

## 2.2 Ion Exchange Process

During the last 50 years, ion exchange membranes have evolved from a laboratory tool to industrial products with significant technical and commercial impact[45]. Ion-exchange processes have been widely used to remove heavy metals from wastewater due to their many advantages, such as high treatment capacity, high removal efficiency and fast kinetics[46]. The ion exchange process is an operative medium in eradicating heavy metals from wastewaters by a reversible chemical reaction, accomplished by the ions exchange in the resin. Various resins can be used with many heavy metals for any specific purpose. Synthetic organic resins are widely used due to their abilities of being manufactured for particular applications. Inorganic gels have also been investigated for the removal of heavy metals because of their stability under more drastic physical conditions[47]. Many researchers have established that zeolites exhibit good cat-ion-exchange capacities for heavy metal ions under different experimental conditions [42,48,49].The disadvantages of ion exchange process are not all ion exchange resin is suitable for metal removal and the process needs high capital cost.

## 2.3 Electro Less Nickel Plating

Advanced membrane technology has been increasingly attractive for wastewater treatment in metal electroplating industry [39,50-56] . The spent rinses from a typical nickel-plating operation can be generally classified as a solvent, alkaline, acidic, plating or final rinse. Electro less nickel (EN) plating is the most essential catalytic plating process which produces even deposits. The benefits of EN process are easy creation of a constant and even coating on the substrate surface with compound shape and ability of depositing on either conductive or nonconductive areas. EN plating has a unique chemical and mechanical properties namely uniformity, great corrosion resistance, wear and abrasion resistance, solder ability, and high hardness[57].

Both chemical and physical properties of an EN coating rely on its structure, formulation and operating conditions of the EN plating bath. Heavy metal exposure occurs significantly by



occupational exposure[9]. In order to operate the bath regularly, a safe standard operating procedure and maintenance practice is required.

#### *2.4 Rinse Water Treatment in Electroless Nickel Plating Process*

In EN plating process, the plating bath must be disposed only after a certain number of turnovers. Nevertheless, rinse water is a source of waste from electro less finishing processes use to remove any residual solution from the finished parts. The rinse water contains metallic contaminants and other bath constituents found in the electro less bath solution which requires treatment. It is very important to ensure that EN plating bath is maintained and operated at optimum conditions according to the manufacturer's recommendations.

A large number of processes have been developed to remove heavy metals from EN wastewater discharges. Some of these processes include chemical precipitation, coagulation/flocculation, ion exchange, cementation, biological operations, filtration, and membrane processes [10,58].

The effluent from real spent final rinse water from an electro less plating industry which uses ion exchange technique to treat their wastewater will be used in this research. Parameter from fifth schedule in EQA 1974 (heavy metals concentration) will be examined in the wastewater. The treated wastewater from the industrial partner will be used as reference for the treated wastewater obtained using the developed SBC membranes.

#### *2.5 Sayong Ball Clay (SBC)*

Clay is a natural material which usually found abundantly in the environment. Past research has proved that it could enhance its potential for human activities. Clay can appear in various colors; from white to dull gray or brown to a deep orange-red depending on the soil content. Clays are plastic due to their water content and become stiff, fragile and non-plastic upon drying or firing. Figure 3 shows the photo of raw SBC.



**Fig. 3.** Raw Sayong Ball Clay (SBC)

SBC is a type of clay which is a kaolinitic sedimentary clay that commonly consist of 20-80% kaolinite, 10-25% mica and 6-65% quartz[59-61]. Ball clay is also referred as a secondary clay; it has been transported away by natural watercourses from area or geology in which it was generated. Clay taken at different place will show several of chemical composition.

Ball clays act as a vital element in ceramic manufacturing while fired Kaolin (China clay) produces a pure white color, brittle stiff but weak when used alone. To make it workable, mixed it with ball clay to produce raw material. As a result of their sedimentary origin, raw ball clays have many colors, hence valuable in the ceramics industry for its white-firing properties, classified by the iron levels and fluxing oxides within the clay.

Sayong ball clay membrane can be fabricated without the assistance of high-tech sophisticated machineries and complicated production methods make the filters particularly attractive as a point-of-use treatment[62]. It gives improvement in water quality with the lowest suspended solid (192 mg/L), lowest COD (4 mg/L) and most colorless (1.1 Gardner units) filtered wastewater as compared to others.

### 3. Conclusion

Contamination of lethal heavy metal in wastewater is one of the utmost significant environmental issues around the globe. To meet the increased more and more rigid environmental regulations, an extensive assortment of process technologies such as membrane filtration, ion-exchange, electro less plating, rinse water treatment electro less plating and Sayong ball clay membrane filtration, have been established for removal of heavy metal from wastewater. It is evident from the literature assessment that ion-exchange and membrane filtration are the most commonly studied for the treatment of heavy metal wastewater. Ion-exchange processes have been widely used to remove metals from wastewater. Membrane filtration technology can remove heavy metal ions with high efficiency.

Ion exchange membrane processes evidently appear to be flexible and proficient of resolving quite diverse issues. Future developments in the area will come from those developers or users that will look at these technologies as tools to cope with their specific treatment requirements. But it should be emphasized that, for any purpose, preparation of ion exchange membranes or materials is the most crucial. To satisfy with a specific requirement, one had to choose a "proper" membrane from the "sea of membranes", optimize the operational condition and then design the process[45].

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