



Removal of heavy metal ions: Chemical precipitation

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Abstract

In today's world, the heavy metal pollution has become one of the most serious environmental problems. Due to industrialization of today's generation, we have more waste products. These products are rich in heavy metal ions and require a special treatment because of their recalcitrance and persistence nature.

With growing industrialization, technologies have also grown in recent years. Thus, we have various methods for the treatment of waste products, mainly waste water for the removal of heavy metal. This paper reviews the latest technologies that have been used for the treatment of wastewater which is rich in heavy metals.

Some of the most common technologies include electrochemical methods, ion-exchange, coagulation–flocculation, chemical precipitation, adsorption and membrane filtration. About 156 published studies (1999–2023) are reviewed in this paper. From the literature survey articles, it's evident that ion-exchange, adsorption and membrane filtration are the most frequently studied and used methods for the treatment of heavy metal wastewater.

Keywords: Heavy metal ions, chelating agent, surfactant, polyvinylamine, chemical precipitation, ultrafiltration, polymer-enhanced ultrafiltration

Introduction

The term, heavy metals indicate the elements with high atomic weight which mainly includes the metallic elements from the atomic weight between 63.5 (Cu) and 200.6 (Hg).

These metal ions have specific gravity >5.0 (M.I. Ojovan, W.E. Lee, 2005) ^[1]. In developing and under-developing countries, metal industries like metal plating facilities, batteries, mining operations etc., mainly added heavy metal ions in the industrial waste water. The direct or indirect discharge of these waste in water bodies enhances the concentration of these heavy metals.

The industrial wastes always have inorganic and organic waste. Although organic waste is biodegradable and does not create a threat to the environment, inorganic waste like heavy metals are non-biodegradable therefore they accumulate in nature.

Detailed Study of Heavy Metal ions

Many of the heavy metal ions are toxic like Zn, Hg, Pb, Cr and Ni etc., their treatment must be an essential step of all industrial processes.

Galvanization is the main process in which zinc is used. Although it is a trace element in the human body and widely used in pigments of printing ink, plastics and cosmetics. It can interact with biomolecules like proteins. In the living organisms.

The recommended dietary allowances of zinc for men are 11mg/day and for women is 8mg/day (ATSRD, 2005). High level ingestion can disrupt many biological processes. (Oyaro *et al.*, 2007).

Another most important metal ion is copper that also plays an important role in animal metabolism. Again, excess of it is also lethal to human beings. (Paulino *et al.*, 2006).

Another transition element Nickel causes serious lung and kidney problems including gastrointestinal distress and pulmonary fibrosis at its ingestion more than its critical level. (Borba *et al.*, 2006).

Mercury acts as a neurotoxin and has the ability to damage the CNS even its high concentrations can impair the pulmonary and kidney function. (Namasivayam and Kadirvelu, 1999). We should not forget the mercury poisoning in Minamata Bay.

U.S. Environmental Protection Agency has even classified Cd as a probable human carcinogen.

After mercury, Pb is another heavy metal that can damage CNS and kidney. Other symptoms of excess of Pb are anemia, insomnia, headache, dizziness, irritability, weakness of muscles, hallucination and renal damages (Naseem and Tahir, 2001).

Chromium, an element of 3d-series with two most common oxidation states: Cr(III) and Cr(VI) also affects human physiology as it can accumulate in the food chain. (Khezami and Capart, 2005).

Overall we can summarise that nowadays heavy metals are main environmental pollutants due to their toxic effect.

Thus, they should be removed from the wastewater before discharging in the water bodies and these effective measurements have to be taken by industries.

Nowadays there are many advanced methods like chemical precipitation, ion-exchange, adsorption, membrane filtration, electrochemical treatment technologies, etc. that help us to remove these heavy metal ions.

This review article deals with the current and latest techniques for the removal of heavy metal ions from wastewater including their advantages and limitations in application are also evaluated.

Methods for the removal of Heavy metal ions:

1. Chemical precipitation

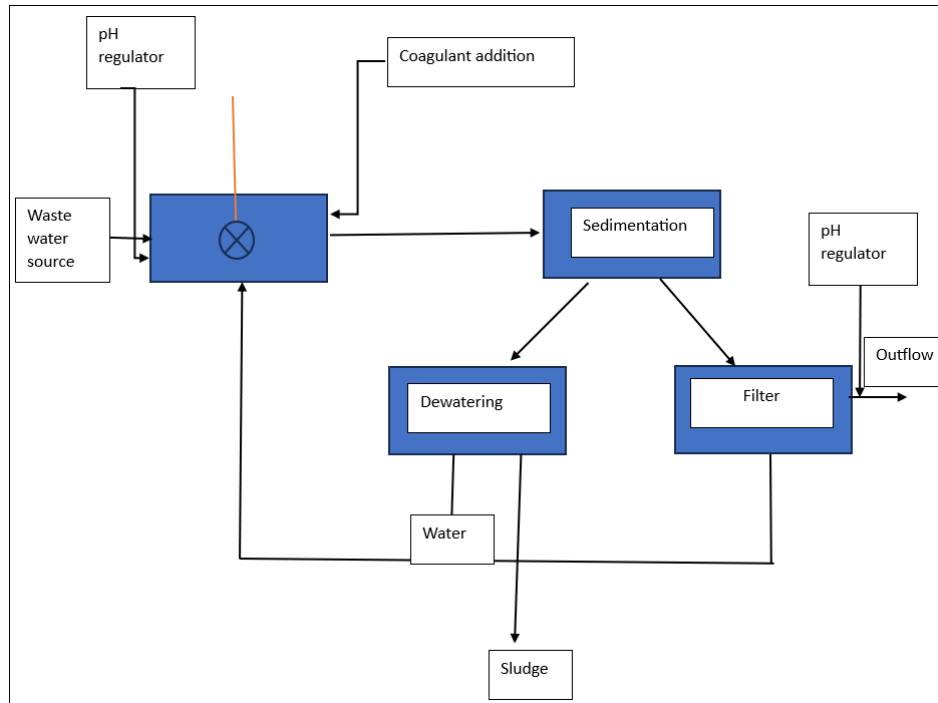
One of the most effective methods of the removal of heavy metal ions from the wastewater is (Renu; Madhu Agarwal; Kailash Singh, 2017) ^[2]. Other methods like Adsorption and

Ion exchange are also quite effective but the chemical precipitation is relatively simple and inexpensive with more accurate results.

The process of chemical precipitation involves the wastewater containing heavy metal ions with appropriate reagent which further form precipitate that is allowed to settle at the bottom to be decanted.

This precipitate contains a good amount of heavy metal ions

and left behind water free from metal ions. (US Environmental Protection Agency (US EPA) 2000, Fu and Wang 2011) [7]. Many Sulfur-containing precipitation agents such as potassium/sodium thiocarbonate (STC) and 2,4,6-trimercaptotiazine (TMT) are used for this purpose. Major disadvantages of use of Sulphur-containing precipitation agents' emission of H₂S gas, low solubility of metal sulphide and sensitive process.



2. Chelating precipitation

In the Chelating precipitation we mainly use certain complexing agents like EDTA. At the same time, these chelating complexing agents have many environmental problems (Fu *et al.*, 2012).

Therefore along with heavy metal ions, these chelating agents have to be removed. The method used for this is mainly the Fenton-chemical precipitation process in which soluble iron cation reacts with H₂O₂ whereas some other metal ions like Ni (II) must be removed by some general

Conventional methods. With the use of EDTA, Ni(II) concentration even reduced from 50 mg/l to 3.6 mg/l in Fenton reaction Fu *et al.* (2009).

In the advanced Fenton-chemical precipitation process for wastewater containing chelated heavy metal, the author has used zero valent metal ions as they have low toxicity and cost.

Comparison of this work with their previous work concluded as below:

Heavy Metal	Initial metal concentration	Precipitant	Optimum pH	Removal efficiency
Nickel	50 ppm	Alkali	2.52	97.4%
Nickel	50 ppm	Alkali	10.9	92%
Nickel	100 mM	Iron (II) Sulphate	3.01	99%
Copper, Zinc, Chromium, Lead	100 ppm	Lime	8-10	99.6%
Copper, Chromium	48.5 ppm	Slaked Lime & Sodium hydroxide	8.6- 11.9	98.3%
Copper, Cadmium	50 ppm	Thiol legend (Pyridine based)	4.5	99.9%
Zinc	200 ppm	Sulfate reducing bacteria	6.9	-
Cd, Cu, Pb, Ni, Zn		Sodium decanoate	4-7	>91%

Fu *et al.* (2012)

3. Ultrafiltration method

Ultrafiltration (UF) and Polymer-Enhanced Ultrafiltration (PEUF) are other most important methods for the removal of heavy metal ions from wastewater. Landaburu-Aguirre *et al.* (2010) [9] removed approx 98% Cd and Zn with the use of Micellar-Enhanced Ultrafiltration method (MEUF).

Polyethyleneimine is used to remove copper by Camarillo *et al* (2012) and use of sulfonated PVA is found more efficient over non-sulfonated PVA for the removal of copper ions. Use of synthetic surfactants causes leakage issue so biodegradable surfactants are always prefer in UF methods (Hung *et al.*, 2015) [4].

UF methods	Complexing agent	Heavy metal ions	optimum pH
MEUF	SDS, TX114	Cu, Ni	11(9)
MEUF	SDS	Cd, Zn	-(10)

PEUF	PVA (polyvinylamine)	Hg	-(11)
PEUF	PVA and sulfonated PVA	Co	5.9 - 6.5(12)

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Results with other precipitating agents

Some other precipitating agents which are widely used for the chemical precipitation are Lime - calcium oxide, CaO, Ferrous sulphate, Fe(SO₄)₃, Alum or filter alum, Al₂(SO₄)₃·14H₂O, Ferric chloride, FeCl₃ and certain Polymer (US Environmental Protection Agency (US EPA) 2000)

In the precipitation method of metal hydroxides, the alkaline medium decreases the solubility of metal hydroxides and leads to the formation of metal hydroxide precipitate. (Wang *et al.* 2004)^[4].

In the chemical precipitation, the formation of metal hydroxide is a simple method with low implementation cost. Although it involves the formation of large volume of sludge which has quite low density so very difficult to dewater. (Menezes *et al.* 2010)^[6]

In case of amphoteric metal hydroxides, use of certain pH with complexing agents can control the precipitation of other metal ions. (Fu and Wang 2011)^[7].

Remarks on Chemical Precipitation Method

Chemical precipitation also does not give good results with low concentration of metal ions. With all the advantages and limitations, chemical precipitation is a much more adaptable method by most of the industries due to low cost and effective results.

Conclusions

Today, removal of hazardous heavy metal pollution from wastewater cannot be a choice for any industry but it is an essential step which should be followed by all industries to protect our environment for the future purpose. To meet this demand of environment regulation, we have a large number of efficient methods and chemical precipitation with the use of various precipitating agents is one of them. It is evident from the literature survey of 156 articles that ion-exchange, adsorption and membrane.

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