Reuse of Heavy Metal from Industrial Effluent Water

Jiefu Wang
UCD school of civil engineering, University College Dublin, Dublin 4, Ireland
jiefu.wang@ucdconnect.ie
2807251415@qq.com

Abstract. Aimed to select an effective and green method for wastewater treatment and heavy metal recovery, we comprehensively analyze the most popular used methods and technologies in the lab and industry in this paper. On one hand, we study the contents and harm of various heavy metal ions in industrial wastewater especially electroplating wastewater, which can provide us an original criterial for choosing a general water treatment method. On the other hand, we elaborate almost all the current methods and technologies for heavy metal recycling and contrast their advantages and shortages. Finally, we draw a promising perspective for the development trend of this area, which help the actual industrial choice and points out the development direction in future.

1. INTRODUCTION
Currently, the problem of Heavy metal pollution attaches more and more attention since its widespread effects on terrestrial and marine wild life as the growth of modern industry. Generally, heavy metals toxic to living organisms in the form of cations due to their ability to bind to biomolecules such as proteins [1]. Recent studies indicated that heavy metal pollution played a major role in the poisoning and decline of various populations [2-3]. The aim of this study is to analyze the content and harm of common heavy metals and investigate the development of methods for water treatment and reuse of heavy metals from industrial effluent water.

Wastewater produced by any industry contains certain toxic and harmful pollutants, such as organic pollutants, inorganic pollutants and biological pollutants, among which the disposal and recovery of heavy metal pollutants are particularly important. Industrial wastewater usually contains various heavy metal elements such as Cr, Cd, Cu, Ni, Pb, As, and Zn [4]. It is generally believed that wastewater containing more than 5 grams of heavy metals per cubic centimeter is called heavy metal wastewater. Heavy metals are highly toxic. Once these waste waters flow into rivers, they will cause serious pollution to water resources. After entering the human body via the food chain, it will have a great impact on human health [5]. The relevant standards formulated for the discharge of industrial waste water in most countries stipulate the content of heavy metal elements in the waste water that is allowed to be discharged. Therefore, we summarized the regulations of the US Environmental Protection Agency on the content of heavy metals in drinking water, and the impact on the human body caused by various types of heavy metal intake in the Figure 1.

On one hand, in terms of several heavy metals in the Figure 1, we can evidently see that even extremely low-content of Cd, As and Hg will cause a great damage to our health, which results in the great demand and necessity of solving the problem of water treatment. On the other hand, some heavy metals such as Cu, Cr, Au, Ni and Zn are valuable for industrial production if we can recycle and reuse
the heavy metals from the industrial effluent water, which also means to turn waste to treasure. Therefore, it is very meaningful and worthwhile for us to attach enough attention to improving the technology of waste water treatment and solving this problem through a kind of green, cheap and easy-operation method.

At present, researchers have developed a variety of methods for the treatment of industrial wastewater, and the most commonly used methods are concluded as shown in Figure 2 [4]. The traditional methods include following typical divides: chemical precipitation method [8], adsorption method [9-11], ion exchange method [12], electrochemical method [13] and biodegradation method [14-15]. Besides, there are some recent developments and advanced water treatment technologies such as membrane technology [16], photocatalysis technology [17-18] and nanotechnology [19]. Through the analysis of the classical and novel methods, we can draw a clear map for each technology matched with their applied condition, which can provide useful suggestions for the industry and dig out the blank space for further exploration.

**Figure 1. US EPA regulations on the content of heavy metals in drinking water and the impact of various types of heavy metals on human body**

**Figure 2. Current industrial methods for wastewater treatment**

### 2. Conventional methods of recycling heavy metals in industrial wastewater

#### 2.1 Chemical precipitation method

Chemical precipitation method is one of the common methods for industrial wastewater treatment. It has the advantages of simple process, low investment, mature technology and high degree of automation. It is suitable for the treatment of heavy metal wastewater with high heavy metal content. It removes heavy metals from water by adding chemical reagents that can convert heavy metal salts in water into hardly soluble salts, which can be removed and recycled. For example, most of the heavy metal ions can be precipitated by adjusting the pH of the solution. The reaction mechanism is as shown in formula (1).

\[
M^{n+} + n\ (OH)^- \leftrightarrow M(OH)_n\downarrow \quad (1)
\]

Among them, lime (calcium hydroxide) is the most commonly used precipitant. Charerntanyarak [8]
uses calcium hydroxide to adjust the pH to 11 and reduces the Zn(II) and Cd(II) solubility in the effluent from 450 mg/L and 1085 mg/L to less than 5 mg/L. In the application of reagents, due to the small precipitate particles, it is usually necessary to add a co-precipitant to aid in sedimentation. For example, lime-polyacrylamide system is used to treat Mn2+ in pit waste water, and iron salt-lime system is used to treat Cr3+、Ni2+ and Pd2+ in waste water.

2.2 Adsorption method
When a fluid comes into contact with a porous solid, a component or components of the fluid accumulate at the solid surface, wherein this phenomenon is known as adsorption. According to the different adsorption process, the common adsorptions can be divided into two types: physical adsorption and chemical adsorption. Most of the adsorption processes often contain the simultaneous existence of two adsorption processes. The use of adsorption as a treatment method for heavy metal wastewater has the advantages of simple manufacturing process, easy operation, wide applicability, etc. At the same time, the heavy metal recovery can be realized by the desorption and concentration process, which makes the whole process extremely convenient for large-scale use.

In a broad sense, all substances have an adsorption effect, but the actual selection of adsorbents should also consider several requirements: strong adsorption capacity, low equilibrium solubility, good selection, easy desorption and good stability. The commonly used adsorbent and its adsorption capacity for different heavy metal ions are summarized and analyzed in Figure 3 [9]. In practice, the pH of the solution, the type of electrolyte in the solution, and the reaction temperature may all affect the performance of the adsorption. Srivastava [10] used nano-alumina powder as adsorbent to treat nickel-containing wastewater. It was found that nickel removal was affected by the initial content of Ni2+, stirring speed, and contact time. Krishnie [11] et al. used pine sawdust as an adsorbent to treat nickel-containing wastewater, and had higher adsorption capacity at low doses of adsorbent, higher pH and higher initial content. These examples provide us with a fact that different adsorbents match with different heavy metals and there is a large imagination space for us to turn waste to treasure through choosing rational and cheap adsorbents.

Figure 3. Typical sorbents and their adsorption capacity for different heavy metal ions

2.3 Ion exchange method
The ion exchange method refers to use the ions in the solid ion exchanger to exchange with the metal ions in the wastewater to achieve the purpose of recycling or removing heavy metal ions in the wastewater. The basic reaction mechanism of this process is shown in equation (2).

\[ nR\text{SO}_3^- - H^+ + M^{n+} \leftrightarrow nR\text{SO}_3^- - M^{n+} + nH^+ \]  

Wherein, \( R\text{SO}_3^- - H^+ \) and \( M^{n+} \) represent the ion exchange resins with anionic functional groups, and the metal cations, respectively. For example, we can use the cation exchangers containing sulfonic acid groups to remove Ni\(^{2+}\) in water. And when the concentration of Ni\(^{2+}\) in waste water reaches to 200-400 mg/L, the treatment effect is particularly prominent and the removed Ni\(^{2+}\) can also be recycled and reused [12]. In a word, the ion exchange method is often suitable for the deep treatment of the waste water with high water content and low heavy metal content, which can effectively remove
the low-content heavy metal but relatively long processing time.

2.4 Electrochemical method
Conventional electrochemical wastewater treatment methods include electrocoagulation, electrosorption, electroreduction and electrodialysis. The electrochemical method has the advantages of high efficiency, easy control, low chemical consumption, and good effect, but the method has high equipment cost and large energy consumption which limits its large-scale use. However, the recent development of fuel cell technology provides a new approach for the electrochemical treatment of industrial wastewater. It has the advantages of high efficiency, low pollution, and wide source of raw material, etc. The redox reaction occurs at the electrode and reduces the heavy metal ions in the cathode wastewater to metal. For example, BaBH₄-Ni(II) fuel cells are used in the work of Zhang et al.[13]. The removal rate of Ni is 54.8%. It might be another promising method for industrial application once we solve the problem of energy consumption.

2.5 Biological methods
The biological wastewater treatment method is a new type of technology, which mainly removes and recycles the heavy metal ions in the wastewater through the adsorption or conversion function of certain specific organisms. Recently, Sheoran et al.[14]. used a bioreactor to treat industrial waste water containing nickel and organic matter. Under a low pH, the removal rate of nickel could reach 99.7%. And Lesage’s group[15] tried to treat the industrial wastewater containing cobalt, nickel and zinc with foliar seaweed. The maximum adsorption of zinc is 2.3, 3.0, and 6.8 mg/L, respectively.

The use of biological treatment of heavy metals in wastewater has some advantages such as simple operation, strong adaptability, and no secondary pollution, but there are also some deficiencies, such as the removal efficiency easily effected by the environment, longer processing cycles, inability to handle high levels of heavy metal wastewater, etc., which also limited its application to a certain extent. However, the biological method is still a promising field where we should seek for more stable and effective bioreactor and organisms.

3. The development of novel water treatment technologies

3.1 membrane filtration
The membrane filtration process is a technology developed in the late 1970s, with a distinct aim to obtain a membrane with good performance. The membrane filtration has higher separation efficiency, less pollution, and lower energy consumption than traditional treatment technologies. The common membrane mainly used in membrane filtration technology includes: reverse osmosis (RO), ultrafiltration (UF), nanofiltration (NF) and so on.

Taking RO as an example, the RO method uses a membrane separation and filtration technology driven by the force from osmotic pressure differential. The membrane has sub-nanometer pores and operates under hydraulic pressure. Both monovalent and multivalent ions can be removed by RO membrane filtration. Recently, Malamis[16] performed the use of metal-enhanced RO systems which has achieved a 98.4% removal rate of heavy metal wastewater, greatly improving the efficiency of wastewater treatment. Compared with its advantages in separation efficiency and energy consumption, the repeated use and stable performance of membrane materials however become a big challenge in this field, which means the cost may grow up due to the periodical exchange of membrane at present.

3.2 Photocatalysis Process
Photocatalytic water treatment processes, especially the advanced oxidation processes (AOPs) are recently developed water treatment technologies[17]. The method is simple in design, low in cost and high in efficiency. At the same time, the catalyst used is non-toxic and will not cause secondary pollution. The general mechanism of photocatalytic process can be expressed by formula (3)-(5).

\[
SC + hv \rightarrow e^- + h^+ \quad (3)
\]
The semiconductor catalyst produces the separation of electrons and hole pairs under light conditions. The heavy metal adsorbed on the surface of the catalyst performs the following photocatalytic reactions, produces metal crystallites and turns to precipitates, which can be finally recycled and reused.

\[ M^{n+} + e^- \rightarrow M \quad (4) \]
\[ D + h^+ \rightarrow D^+ \quad (5) \]

Currently used semiconductor catalysts\(^{[18]}\) mainly include TiO\(_2\), ZnO, WO\(_2\), CdS, ZnS, WS\(_2\), etc., of which titanium dioxide is the most commonly used material since its high photocatalytic efficiency and easy preparation.

### 3.3 Nanotechnology

Over the past two decades, nanotechnology has become a hot area of material science. Compared with conventional materials, nanomaterials have following advantages such as extremely high specific surface area, short ion diffusion path, good dispersion, which are widely used in the treatment of wastewaters containing various heavy metal. At present, the two main technologies studied are in-situ treatment and off-site treatment. In-situ treatment refers to the direct addition of nanomaterials to waste water, while non-in-situ technology first transfers waste water to a suitable site and then performs a unified treatment.

Nanomaterials for wastewater treatment are generally adsorptive, reactive or magnetic, including the metal organic covalent compound (MOF) with a nanoporous structure, the adsorbed nanomagnetic oxide (NMO), the mixed magnetic nanoparticle (MNP) and so on. Among them, the MOF material has a relatively high specific surface area, an extremely high adsorption capacity, low toxicity and cheap price, which results in its widespread application in industrial treatment. Recently, Yan Huanga\(^{[19]}\) et al. used ZIF-8 and ZIF-67 porous adsorbents to remove more than 99.4% of Pb\(^{2+}\) and 97.4% of Cu\(^{2+}\) from wastewater, and it only takes tens of minutes to achieve equilibrium adsorption, which proved the great potential of MOF material applied in mature industrial wastewater treatment.

### 4. Conclusion

With the development of society, the demand for wastewater treatment and heavy metal recovery has greatly increased. But the contradiction between environmental pollution and the dependence of electricity is growing at the same time. It is necessary for us to figure out a rational method of recycling heavy metals from industrial wastewater. Through the analysis of the classical and novel methods, we draw a clear map for each technology matched with their applied condition in this paper, which can provide useful suggestions for the industry. And there remains a large research space for turning waste to treasure.

### Reference

[1] Shakya M, Sharma P, Meryem S S, et al. Heavy Metal Removal from Industrial Wastewater Using Fungi: Uptake Mechanism and Biochemical Aspects\([J]\). Journal of Environmental Engineering, 2015, 2015.
[2] Yuan C, Weng C H. Electrokinetic enhancement removal of heavy metals from industrial wastewater sludge\([J]\). Chemosphere, 2006, 65(1):88-96.
[3] Barakat M A. New trends in removing heavy metals from industrial wastewater\([J]\). Arabian Journal of Chemistry, 2011, 4(4):361-377.
[4] Dabrowski A, Hubicki Z, Podkościelny P, et al. Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method\([J]\). Chemosphere, 2004, 56(2):91-106.
[5] Azimi A, Azari A, Rezakazemi M, et al. Removal of Heavy Metals from Industrial Wastewaters: A Review\([J]\). Chembioeng Reviews, 2017, 4(1):37-59.
[6] Table of Regulated Drinking Water Contaminants, Environmental Protection Agency (EPA), Washington 1980. www.epa.gov/ground-water-and-drinking-water/table-regulateddrinking-water-contaminants

[7] Barakat M A. New trends in removing heavy metals from industrial wastewater[J]. Arabian Journal of Chemistry, 2011, 4(4):361-377.

[8] Charerntanyarak L. Heavy metals removal by chemical coagulation and precipitation[J]. Water Science & Technology, 1999, 39(10–11):135-138.

[9] Renjie Li, Adsorptive Removal of Hg(II), Cr(VI) and Pb(II) Ions from Aqueous Solutions Using Nitrogen-Containing Conductive Polymer Composites[D]. Dalian University of Technology, 2016.

[10] Srivastava V, Weng C H, Singh V K, et al. Adsorption of Nickel Ions from Aqueous Solutions by Nano Alumina: Kinetic, Mass Transfer, and Equilibrium Studies[J]. Journal of Chemical & Engineering Data, 2011, 56(4):1414-1422.

[11] Krishnie M. Removal of nickel from wastewater using an agricultural adsorbent[J]. Water SA, 2011, 11(1):41-46

[12] Ismail I, Soliman A, Abdel-Monem N, et al. Nickel removal from electroplating waste water using stand-alone and electrically assisted ion exchange processes[J]. International Journal of Environmental Science & Technology, 2014, 11(1):199-206.

[13] Zhang H, Xu W, Wu Z, et al. Removal of Cr(VI) with Cogeneration of Electricity by an Alkaline Fuel Cell Reactor[J]. Journal of Physical Chemistry C, 2013, 117(28):14479–14484.

[14] Sheoran V, Chaudhary R, Tholia N K. Treatment of industrial waste- water by organic wastes[J]. Journal of Scientific & Industrial Research, 2013, 72:255-260.

[15] Lesage E, Mundia C, Rousseau D P L, et al. Sorption of Co, Cu, Ni and Zn from industrial effluents by the submerged aquatic macrophyte Myriophyllum spicatum L.[J]. Ecological Engineering, 2007, 30(4):320-325.

[16] Mohan S, Fields P G. Assessment of metal removal, biomass activity and RO concentrate treatment in an MBR–RO system[J]. Journal of Hazardous Materials, 2012, 209-210(1):1-8.

[17] Sadyrbaeva T Z. Removal of chromium(VI) from aqueous solutions using a novel hybrid liquid membrane—electrodialysis process[J]. Chemical Engineering & Processing Process Intensification, 2016, 99:183-191.

[18] Herrmann J M. Heterogeneous photocatalysis: state of the art and present applications In honor of Pr. R.L. Burwell Jr. (1912–2003), Former Head of Ipatieff Laboratories, Northwestern University, Evanston (Ill)[J]. Topics in Catalysis, 2005, 34(1-4):49-65.

[19] Huang Y, Zeng X, Guo L, et al. Heavy metal ion removal of wastewater by zeolite-imidazolate frameworks[J]. Separation & Purification Technology, 2017.