

Precious Metals Recovery from Electroplating Wastewater: A Review

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Abstract. Metal bearing electroplating wastewater posts great health and environmental concerns, but could also provide opportunities for precious and valuable metal recovery, which can make the treatment process more cost-effective and sustainable. Current conventional electroplating wastewater treatment and metal recovery methods include chemical precipitation, coagulation and flocculation, ion exchange, membrane filtration, adsorption, electrochemical treatment and photocatalysis. However, these physico-chemical methods have several disadvantages such as high initial capital cost, high operational cost due to expensive chemical reagents and electricity supply, generation of metal complexes sludge which requires further treatment, ineffective in diluted and/or concentrated wastewater, low precious metal selectivity, and slow recovery process. On the other hand, metal bio-reduction assisted by bioactive phytochemical compounds extracted from plants and plant parts is a new found technology explored by several researchers in recent years aiming to recover precious and valuable metals from secondary sources mainly industrial wastewater by utilizing low-cost and eco-friendly biomaterials as reagents. Extract of plants contains polyphenolic compounds which have great antioxidant properties and reducing capacities, able to reduce metal ions into zerovalent metal atoms and stabilize the metal particles formed. This green bio-recovery method has a value added in their end products since the metals are recovered in nano-sized particles which are more valuable and have high commercial demand in other fields ranging from electrochemistry to medicine.

1. Introduction

Electroplating is the application of a metal coating onto a metallic or other conducting surfaces by an electrochemical process [1]. In typical electroplating industries, large amount of wastewater are generated from rinsed water of the electroplated parts [2] which equivalent to 20% of the chemicals used in the metal salts plating baths [3]. This wastewater contains high amount of metal ions which exceeds the industrial effluent discharge limits stated by the Department of Environment and hence must be treated before being discharged due to their high toxicity [4]. However, in certain electroplating industries especially involving precious metals such as silver, gold and platinum, the wastewater contains adequate amounts of precious and valuable metals. Hence, a suitable wastewater treatment is required not only to remove the heavy metals but also to recover those precious and valuable metals for both growing economics and environmental concerns. Recently, several conventional wastewater treatment methods have been applied in electroplating industries.



2. Conventional wastewater treatments and metal recovery methods

Currently used wastewater treatments and metal recovery methods in electroplating industries are chemical precipitation, coagulation and flocculation, ion exchange, membrane filtration, adsorption, electrochemical treatment and photocatalysis [5]–[9].

2.1. Chemical precipitation

Chemical precipitation is a process to form insoluble metal precipitates by reacting precipitant agent of hydroxides or sulfides with the dissolved metal ions [6]. This technique is the most widely used treatment methods in current electroplating industries [10], [11] which employed pH adjustment to basic conditions to reduce the metal ions solubility in the wastewater. Although sulfide precipitation could achieve high metal removal and are not amphoteric [7], but hydroxide precipitation are more preferable due to the precipitant agents (lime and limestone) availability and low-cost in most countries [12]. The metal precipitates formed are recovered using a solid separation process such as coagulation and/or sedimentation or filtration [8] and the precious metals are purified by chemical extraction process [13]. Advantages of chemical precipitation method are simple operation and low capital cost due to their availability and low-cost precipitant agents, while the disadvantages are it generate excessive amount of sludge that requires further treatment in order to recover metals, slow metal precipitation, poor settling, the aggregation of metal precipitates, and the long-term environmental impacts of sludge disposal [6]–[9].

2.2. Coagulation and flocculation

Coagulation is the destabilization of colloidal particles by neutralizing the repulsive forces that keep them apart using a coagulant [6] of ferric or alum salts [7]. On the other hand, flocculation is the action of flocculants polymer to form bridges and bind the unstable particles to form larger particles or bulky floccules [6]. The bulky metal floccules can subsequently be recovered by sedimentation or filtration [7]. However, in electroplating industries, amphoteric polyelectrolyte coagulant/flocculant such as polydiallyldimethylammonium chloride (polyDADMAC) [14], polyethyleneimine-sodium xanthogenate (PEX) [15], and mercaptoacetyl polyethyleneimine (MAPEI) [16] were commercially used to remove or recover soluble metal ions from the wastewater effectively based on their chelating ability. The advantages of coagulation–flocculation method are shorter time to settle out suspended solids, improved sludge settling, dewatering characteristics, bacterial inactivation capability and sludge stability while the disadvantages are high operational cost due to chemical consumption and treatment of the sludge generated to recover metals [6], [7], [9].

2.3. Ion exchange

In ion exchange, the ion exchanger (resin) exchanges its cations with the metal ions in the wastewater without any structural change of the resin [6]. The metal is then recovered by elution with suitable reagents after separating the loaded resin from the wastewater. Common cation exchangers are strongly acidic resins with sulfonic acid groups ($-\text{SO}_3\text{H}$) and weakly acid resins with carboxylic acid groups ($-\text{COOH}$) [7] where hydrogen ions in the groups serve as exchangeable ions with the metal cations in the wastewater. Instead of natural resins such as Clinoptilolite [17], synthetic resins such as Amberlite [18] and Purolite [19] were frequently used in electroplating industries since it is more effective and inexpensive [20]. The advantages of ion exchange method are no sludge generation, high treatment capacity, high removal efficiency in which certain resins ligands can selectively bond with certain metal cations and fast kinetics, while the disadvantages are required a pre-treatment systems for secondary effluent, not suitable for all types of metals and high capital and operational costs [6], [7], [21].

2.4. Membrane filtration

Membrane filtration is a method that separates particles in a fluid by applying a pressure onto the fluid to pass across a porous membrane or filter [6]. Membrane filtration generally divided into three types which are ultrafiltration, nanofiltration and reverse osmosis, depending on the size of the particle that can be retained [6], [8], [22]. Ultrafiltration 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) to allow the passage of water

and low-molecular weight solutes, while retaining the larger sized macromolecules [6], [8], [23]. Nanofiltration involves mechanism of steric (sieving) and electrical (Donnan) effects [24]. A Donnan potential is created between the charged anions in the nanofiltration membrane and the co-ions in the effluent to reject the latter [6]. The significance of this membrane lies in its small pore and membrane surface charge [9], which allows charged solutes smaller than the membrane pores to be rejected along with the bigger neutral solutes and salts. Reverse osmosis is a pressure-driven membrane process in which water can pass through the semi-permeable membrane (pore size down to 10^{-4} μm) [25] and retained the heavy metal inside [6], [7]. In reverse osmosis, cationic compounds were separated from water by exerting a greater hydrostatic pressure than the osmotic pressure of the feeding solution [6]. The advantages of membrane filtration method are small space requirement, low pressure, high selectivity and separation efficiency while the disadvantages are high operational cost due to membrane fouling, high capital cost of membrane sheets, and low permeate flux [6]–[8], [22].

2.5. Adsorption

Adsorption is a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid (adsorbents), and becomes bound by physical and/or chemical interactions [6]. Generally, the mechanisms involved in adsorption of metal ions onto a solid adsorbent are: (1) the transport of the metal ions from the bulk solution/wastewater to the adsorbent surface; (2) adsorption on the particle surface; and (3) transport within the adsorbent particles [8]. Widely used adsorbent types to recover metal from electroplating wastewater are activated carbons [26], carbon nanotubes (CNTs) [27], low-cost adsorbents [28] such as agricultural wastes [29] and industrial by-products [30], bioadsorbents [31] and modified biopolymers derived from chitosan [32]. The advantages of adsorption method are low-cost adsorbent, easy operating conditions, wide pH range and high metal-binding capacities while the disadvantages are low selectivity and recovery efficiency, and production of waste products [7]–[9], [33].

2.6. Electrochemical treatment

Electrochemical treatment is a method that involve plating-out of metal ions on a cathode surface using an electric current [7]. Currently applied electrochemical treatment methods in electroplating industries are electrocoagulation, electrodeposition and electrodialysis [9]. Electrocoagulation involves the generation of coagulants in situ [7] by dissolving electrically either aluminium or iron ions from aluminium [34] or iron [35] electrodes. The coagulants ions are generated at the anode, and hydrogen gas is released from the cathode to help float the flocculated particles out of the water [7]. Electrodeposition or electrowinning is an electrolytic process that involves redox (reduction–oxidation) reaction where the positively charged metal ions (cations) are reduced and deposited at the cathode while the negatively charged ions (anions) are oxidize at the anode [6]. Electrodeposition is a clean technology with no presence of the permanent residues for the recovery of metals [9]. Electrodialysis is a membrane separation in which ionized species in the solution are passed through an ion exchange membrane by applying an electric potential [6]. 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 [8]. Electrodialysis generates two new solutions: one concentrated on ions and another consisting of almost pure water which are able to be reused back in the plating process [36]. The advantages of electrochemical treatment method are rapid and well controlled process, low chemical requirement, high selectivity, and no sludge generation while the disadvantages are high initial capital cost, and high operational cost due to energy consumption and expensive electricity supply [6]–[9].

2.7. Photocatalysis

Photocatalysis is a method that couples low-energy ultraviolet light with semiconductor catalyst particles to reduce metal ions contain in an electrolyte by the photogenerated electrons [37]. When semiconductor particles are illuminated by ultraviolet light with energy greater than the bandgap energy of the photocatalyst, electron/hole pairs are generated within the catalyst particles [37]. In photocatalytic oxidation, the electron/hole recombination are suppressed by the electron scavenger to allow the photogenerated holes undergo anodic reactions, while in photocatalytic reduction, the hole

scavenger is adopted and the photogenerated electrons are allowed to undergo cathodic reactions [8], [37], [38]. Commonly used semiconductor photocatalysts are TiO_2 , ZnO , CeO_2 , CdS and ZnS which derived from chalcogenides compounds [38]. The metals are deposited onto the surface of the photocatalyst and later can be extracted from the slurry by mechanical and/or chemical means. The advantages of photocatalysis method are simultaneous metal recovery and organic pollutant removal, generate less harmful by-products while the disadvantages are high capital cost of the photocatalysts, long duration time and limited applications [8], [37].

3. New alternative metal recovery method

It has long been recognized that naturally occurring phytochemicals in plants and plant parts have great antioxidant properties and reducing capacities [39]. These phenolic compounds have the abilities to act as both reducing and capping agents [40], able to reduce metallic ions into zerovalent metal atoms and stabilize the metal particles formed [41]–[43].

3.1. Bio-recovery mechanisms

The phenolic compounds extracted from plants possess hydroxyl ($-\text{OH}$) and carboxyl ($-\text{COOH}$) groups which give their significant ability to scavenge free radicals, chelate metal ions and donate hydrogen atoms or electrons [44], [45]. According to Moran *et al.* [46] this general metal chelating ability of phenolic compounds is probably related to the high nucleophilic character of the aromatic rings rather than to specific chelating groups within the molecule. According to Makarov *et al.* [47], the mechanisms of metal bio-recovery assisted by plant extracts consists of three main phases: (1) the activation phase which the reduction of metal ions occur; (2) the growth phase which the adjacent metal atoms spontaneously coalesce into larger particles (Ostwald ripening), which is accompanied by an increase in the thermodynamic stability of particles; and (3) the process termination phase by capping the metal particles formed (Figure 1). During the activation phase, the phenolic compounds liberates reactive hydrogen ions through the hydroxyl groups and get oxidized to α,β -unsaturated carbonyl groups (Figure 2) [48], and simultaneously reduce the metal ions [49]. On the other hand, the negatively charged oxygen in the hydroxyl groups of polysaccharides will interact with the positively charged metal particle surfaces via electrostatic interactions and binds due to the presence of van der waals forces [50], [51]. During time, the metal particle will be fully capped and stabilized in the solution.

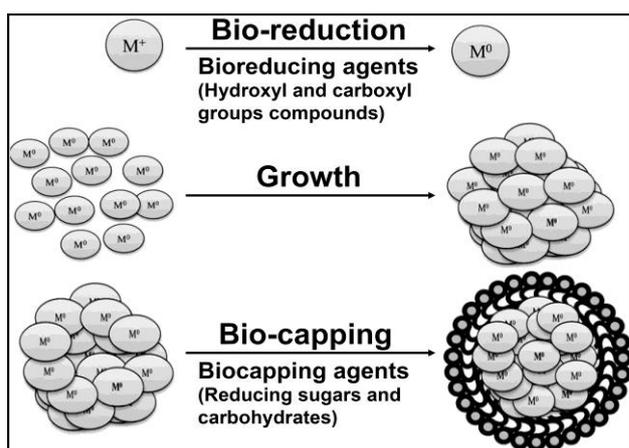


Figure 1. Mechanisms of metal bio-recovery [41].

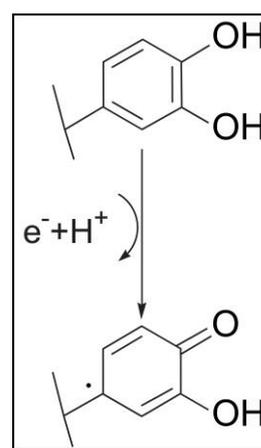


Figure 2. Hydroxyl oxidation [48].

3.2. Feasibility studies

Gatew and Mersha [52] use *Moringa stenopetala* seed powder extract to remove chromium from tannery wastewater which results 99.86% of chromium removal. Besides that, Azimi *et al.* [53] study chromium removal from tannery wastewater using acorn extract of *Quercus branti* and found 95.62% chromium removal efficiency. These results proved that the metal bio-reduction method assisted by plant extracts is very effective to remove and recover metals from wastewater. Several studies have reported that oil palm (*Elaeis guineensis*) leaves extracts are rich in phenolic compounds such as

flavonoids and phenolic acids [54], [55], and showed great antioxidant activities [56], [57]. This antioxidative properties of palm leaves extract have been utilize by Azmi *et al.* [58] to successfully recover silver from simulated silver electroplating wastewater and in nano-sized silver nanoparticles.

4. Conclusions

To conclude, conventional physico-chemical methods have their own advantages and disadvantages in recovering those precious metals from electroplating wastewater. However, the wastewater characteristics and the metals concentration level were the two main factors that influence the recovery effectiveness. We propose this new potential bio-recovery method which utilizing eco-friendly biomaterials, palm leaves extract, to recover precious metal from electroplating wastewater and could successfully obtain the recovered metals in nano-sized metallic particles.

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