

The Pennsylvania State University
The Graduate School

**ELECTROWINNING PROCESS FOR COPPER REMOVAL FROM WASTE BRINE
AND CRITICAL REVIEW**

A Thesis in
Environmental Pollution Control
by
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Abstract

Copper is one of the chemical elements that has been increasingly popular as civilization has advanced, particularly in the various sectors. However, copper, which is widely used in industrial applications, is also frequently found in high concentrations in wastewater. Several copper removal techniques have been utilized, and electrowinning process is commonly used to recover heavy metals by applying a voltage across electrodes immersed in a concentrated solution. Electrowinning procedure can be a way out of increasing copper concentrations in digested biosolids at the Pennsylvania State University Wastewater Treatment Plant in University Park.

This main objective is to verify whether electrowinning could be applied for copper removal from actual waste brine at Penn State University's Steam Plant. Also, identifying technical issues to be solved, is another goal for providing against long-term electrowinning operation at wastewater treatment. Multiple-case studies and removing dissolved copper from actual waste brine at Penn State University's Steam Plant was conducted. Before the research with actual waste brine, copper removal research was carried out in a 1000 L tank for 80 hours to find out whether the result is comparable to an experiment in a smaller tank. Copper had a 90% removal rate at 1 M brine after 80 hours in a large tank, as well as a small tank, indicating that wastewater sample from University can be treated with this process for copper removal.

After determining whether the data is comparable to that of a small-scale tank experiment, copper removal was conducted with a synthetic waste brine solution from Penn

State University's Steam Plant. Copper removal effects at a voltage at 3 V were around 74% reduction from 33.5 to 8.65 mg/L for 6 hours, whereas at 2 V and 2.5 V, just 30% removal was observed. More various voltages should be applied in copper removal from actual waste brine as well as operating long-term electrowinning at University Park Plant in follow-up study.

Table of Contents

List of Figures	vi
List of Tables.....	vii
Acknowledgements.....	viii
Chapter 1. Introduction	1
Chapter 2. Literature Review	3
2.1. Available Techniques of Copper Removal	3
2.1.1. Chemical Precipitation	3
2.1.2. Ion Exchange	4
2.1.3. Adsorption	5
2.1.4. Membrane-based	6
2.1.4.1. Ultrafiltration	6
2.1.4.2. Nanofiltration.....	8
2.1.4.3. Microfiltration.....	8
2.1.4.4. Reverse Osmosis.....	9
2.1.5. Electrodialysis	9
2.1.6 Coagulation and Flocculation.....	10
2.1.7. Electrochemical treatment	11
2.2. Electrowinning for Copper Removal	13
2.2.1. Non-PSU Studies.....	13
2.2.2. PSU Studies.....	18
2.2.3. Unresolved Studies	23
Chapter 3. Materials and Methods	26
3.1. PSU Copper source and samples	26
3.2. Electrowinning Devices	26
3.3. Operating Conditions	27
3.4. Synthetic Waste Brine Solution	28
3.5. Copper Removal from Wastewater.....	28
3.6. Chlorine Analysis.....	28
Chapter 4. Results and discussion.....	30
4.1. Copper Removal from Synthetic Waste Brine Solution	30
4.2. Copper Removal from Actual Waste Brine	33
Chapter 5. Conclusion.....	37
References.....	38

List of Figures

Figure 1. Effect of contact time as a function of copper recovery percentage.....	16
Figure 2. Effect of pH as a function of amount of copper deposited on stainless steel	17
Figure 3. The effect of Cu (II) concentration and cathode potential on the copper electrodeposition	18
Figure 4. The concentration of copper varies according to reaction time of electrowinning process with different flow rate	20
Figure 5. Maximum copper reduction of copper after applying electrowinning with different flow rates.....	20
Figure 6. Effect of Synthetic Brine Solution on Cu.....	21
Figure 7. A semi log plot of the course of copper electrowinning with four different salt concentration	22
Figure 8. Effects of Brine Concentration on Copper Removal and Chlorine Production. The concentration of sodium chloride was controlled at 1 M.....	25
Figure 9. Copper Electrowinning System.....	27
Figure 10. Copper Concentration at a 32.5 L tank.....	30
Figure 11. Copper Concentration at a 1000 L tank.....	32
Figure 12. Effect of actual waste brine on copper concentration as a function of time at specified voltage performances	34
Figure 13. Effect of actual waste brine on free and total chlorine concentration as a function of time	36

List of Tables

Table 1. Available Techniques for Copper Removal.....	13
Table 2. Estimated Current Efficiency.....	23
Table 3. Hourly Copper Removal at a 32.5 tank	31
Table 4. Hourly Copper Removal at a 1000 L tank	33

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Chapter 1

Introduction

Copper is one of the most important elements and is considered as one of the most widely used metals in various industrial and agricultural practices. It is also one of the earliest metals that was collected and utilized and has contributed to an important role in society's survival and improvement since the early days of civilization (Ab Hamid, 2022). Copper is currently utilized in the construction of structures, the generation and transmission of energy, the manufacture of electrical products, the manufacture of industrial machinery, and the manufacture of transportation vehicles. Heavy metals, on the other hand, are non-biodegradable, toxic, and easily accumulated in living creatures in general, and in people in small amounts. Due to the high concentration, it can lead to severe problems such as cancer in the body, impair the neurological system, and induce kidney failures, and can be fatal. As a result, it is critical to employ as simple and effective heavy metal treatment and removal methods as possible. It is vital to remove copper from water resources before it is discharged into the environment. Thus, electrowinning process as well as the available techniques such as adsorption, cementation, membrane filtration, electrodialysis, and photocatalysis have been developed over the years for the removal of copper ions from industrial wastewater.

The Pennsylvania State University Wastewater Treatment Plant at University Park is experiencing elevated levels of copper in digested biosolids. The source of copper in the Wastewater Treatment Plant at University Park biosolid was found in the polisher softener's waste brine that collects condensate from the University steam operation. The copper entering the treatment facility was discovered to be the result of typical corrosion of copper pipes and

fixtures in the water distribution system. The Limit of copper concentration is regulated at 1,500 mg/kg, dry weight under the Pollutant Limits for the land Application of Sewage Sludge (USEPA, 1994). The current levels range from between 1,000 and 1,600 mg/L, and 50% copper removal would be the goal. An alternative to land application is to dispose biosolids to a landfill which not only incurs an additional annual cost of \$100,000, but also limits resource recycling. For this reason, Goldbug® has been used for the PSU study about removal of dissolved copper ions in the synthetic waste brine solution. The overarching aim of this research was to verify whether electrowinning could be applied for removing dissolved copper from actual waste brine at Penn State University's Steam Plant. Also, it should be identified whether there are technical issues to be solved for providing against long-term electrowinning operation at wastewater treatment.

Chapter 2

Literature Review

2.1 Available Techniques of Copper Removal

2.1.1 Chemical Precipitation

Chemical precipitation is an efficient method that is commonly utilized in industry. It is relatively simple and inexpensive to operate. Chemicals react with heavy metal ions to generate precipitates during the precipitation process. Sedimentation or filtering techniques can separate these insoluble precipitates from the water. Finally, the treated water can be reused or released properly. Hydroxide and sulfide precipitation are two common chemical precipitation reactions. The most common chemical precipitation process is hydroxylation. This approach is relatively inexpensive, and pH regulation is also relatively simple. The various metal hydroxides are minimized when the pH range is 8.0-11.0 (Agarwal, 2015). Metal hydroxides can be removed using flocculation and sedimentation. When employing chemical precipitation techniques, there are some restrictions to copper removal. The chemical precipitation method often introduces a large number of inorganic ions into the wastewater, leading to high salinity when removing copper due to the need to add additional agents or adjust the pH value, leading to an extreme pH environment, which makes it difficult to achieve environmentally friendly effluent quality (Liu and Wang, 2023).

Another efficient method for dealing with hazardous heavy metal ions is sulfide precipitation. The key benefits of employing sulfides are that metal sulfide precipitates have lower solubility than hydroxide precipitates and are not amphoteric (Estay and Barros, 2021). As compared to hydroxide precipitation, the sulfide precipitation procedure can accomplish a

higher degree of metal removal over a wider pH range. There is also a limit to this procedure since metal sulfide precipitation produces colloidal precipitates that are difficult to separate using filtration or settling methods. When paired with other approaches, chemical precipitation has proven effective. González-Munoz et al. (2006) discovered sulfide precipitation as a method for reusing and recovering heavy metal ions, with nanofiltration as a secondary step. The results showed that sulfide precipitation successfully reduced the metal content, and nanofiltration produced solutions that could be directly reused in the plant.

2.1.2 Ion Exchange

Ion exchange has numerous benefits, including high removal efficiency, quick kinetics, and treatment capacity (Kang et al. 2004). The ability of ion exchange resin to exchange its cations with metal ions contained in wastewater is remarkable. This capability is shared by both synthetic and natural solid resins. Strongly acidic and slightly acidic resins are the most common cation exchangers. The hydrogen ions in strongly acidic resins with sulfonic acid groups (-SO₃H) and weakly acidic resins with carboxylic acid groups (-COOH) can function as exchangeable ions with metal cations. Several variables influence heavy metal ion uptake by ion-exchange resins, including starting metal concentration, temperature, pH, and contact time (Gode and Pehlivan, 2006). Ionic charge also is essential because ion exchange resin with a greater ionic charge adsorbs faster. Natural zeolites and naturally occurring silicate minerals, in addition to manufactured resins, have been widely employed for heavy metal removal from aqueous solutions due to their availability and inexpensive cost. Zeolites are currently scarce in comparison to synthetic resins. Zeolites are only used on a laboratory scale. There is still a lot of work to be done before zeolites can be used on a large scale.

2.1.3 Adsorption

Adsorption is now acknowledged as a viable and cost-effective approach for heavy metal wastewater treatment. The adsorption process is versatile in terms of design and operation, and it produces high-quality treated effluent in many circumstances. Another advantage of adsorption is that it is reversible. Adsorbents are classified into four types: activated carbon adsorbents, carbon nanotube adsorbents, low-cost adsorbents, and bio-adsorbents. The utility of activated carbon adsorbents stems primarily from their large micropore volumes and resulting high surface area. Carbon nanotubes are a relatively novel adsorbent that has shown remarkable potential for removing heavy metal ions. In the instance of Li et al. (2010), CNTs immobilized by calcium alginate were utilized as adsorbents to remove copper ions, with maximal copper sorption capacities of 67.7 mg/g when pH = 5 and temperature = 25°C. Although activated carbon has traditionally been the most popular adsorbent, its exorbitant cost has led more and more researchers to explore for less expensive and more widely accessible adsorbents that remove heavy metals. Agricultural waste, industrial byproducts, and natural substances were all discovered by the researchers to be useful as adsorbents. However, disposal of such adsorbents after the adsorption process is a big challenge to avoid environmental risks (Qasem and Mohammed, 2021).

Copper can be removed from aqueous solution by brine sediments, according to Agouborde and Navia (2009). Using a 1/40 adsorbent/solution ratio, the maximum adsorption capacity for copper was found to be 4.69, 2.31, and 4.33 mg/g. According to Apiratikul and Pavasant (2008), typical biosorbents can be produced from three sources: First, there is non-living biomass, such as bark, lignin, shrimp, krill, squid, crab shell, and so on. Another example is algal biomass, which is seen as a possible substrate for biofuel production. The

other one is microbiological biomass, which includes bacteria, fungus, and yeast. Algae has been identified as a renewable natural biomass by certain researchers. The extensive availability, low cost, high metal sorption capacity, and generally consistent quality are only a few of the benefits of using algae as a biosorbent.

2.1.4 Membrane based

Membrane technology has a compact system, and can be employed on large scales (Harharah and Abdalla, 2022). It can be defined as the microbiological analyzing of water by making a special filter to trap the microorganisms. This is categorized by the pore size of the membrane, and can be demonstrated as ultra-, nano-, and microfiltration. Also, this separation is used in purifying macromolecular solutions. However, membrane fouling is one of the main drawbacks encountered during the practical application. This disadvantage affects the operating flux and the life of membranes (Gul and Hruza, 2021).

2.1.4.1. Ultrafiltration

Ultrafiltration is a variety of membrane filtration in which forces such as pressure or concentration gradients lead to a separation through a semipermeable membrane. Suspended solids and solutes of high molecular weight are retained in the so-called retentate, while water and low molecular weight solutes pass through the membrane in the permeate. This separation process is used in industry and research for purifying and concentrating macromolecular solutions, ranging from 10³ to 10⁶ Da, especially protein solutions (Guo and Li, 2023).

The bonding of ultrafiltration with surfactant results in micellar enhanced ultrafiltration. Due to its high flux and great selectivity, it consumes little energy, is highly efficient at removing waste, and requires little space. When heavy metal concentrations are minimal, micellar enhanced ultrafiltration is best suited for wastewater treatment. A surfactant is combined with wastewater at a concentration greater than the critical micellar concentration in micellar enhanced ultrafiltration. Surfactant monomers combine and enhance the formation of certain micelles in the solution above critical micellar concentration. A hydrophilic head and a hydrophobic tail make up the surfactant. The greatest retentions are typically attained by surfactants, whose electric charge is the opposite of that of the metal ions. Polyelectrolytes, cationic surfactants, and anionic surfactants, such as sodium dodecyl sulfate, are utilized to effectively remove heavy metals in this respect. Several parameters influence the performance of micellar enhanced ultrafiltration, including the added solutes, surfactant type, operation circumstances, and membrane type.

The combination of ultrafiltration and binding polymers results in polymer enhanced ultrafiltration. The polymer enhanced ultrafiltration technique inhibits and removes polymer-bonded metal ions while allowing water and simple components to pass through the membrane pores. Polymer enhanced ultrafiltration demonstrates excellent polymer bonding, extraction, the ability to recover and reuse complexation polymer of retentate, minimal energy requirements, and low-cost operation. The fundamental issue in developing this technology remains the selection of acceptable water-soluble polymer macro-ligands.

2.1.4.2. Nanofiltration

Nanofiltration is used to concentrate constituents whose molecular weight is >1000 Da and remove solutes whose size of $0.0005\text{--}0.007\ \mu\text{m}$ with molecular weights >200 Da. Thus, the operating range of NF is between UF and reverse osmosis processes. The nanofiltration membranes are composed of polymer composites of multiple-layer thin-film of negatively charged chemical groups. Anti-fouling nanofiltration membranes containing CeO₂/Ce₇O₁₂ and PES were synthesized through phase inversion and used to extract Fe³⁺, Al³⁺, Co²⁺, Cd²⁺, Cu²⁺, and humic acid from wastewater and reached extraction efficiency between 94 and 98%. Most advanced nanofiltration membranes are prepared by interfacial polymerization to form a polyamide separation layer on a porous support (Liu and Chen, 2022). The focus of nanofiltration membrane utilization for copper removal from wastewater still needs diversification (Nompumelelo and Edward, 2023).

2.1.4.3. Microfiltration

Microfiltration is a low pressure-driven membrane technique that separates microorganisms and suspended particles from the process liquid while removing all bacteria. Microfiltration is commonly employed for commercial reasons in the pharmaceutical and biological sectors, particularly for turbidity reduction, removal of suspended particles, giardia, and cryptosporidium. The microfiltration system, on the other hand, has applications in particle removal from rinse water in the semiconductor sector, sterilization of beer and wine, clarification of various juices and cider, and wastewater treatment. Because of its limited removal capacity, the use of microfiltration in heavy metal removal has received insufficient attention. It has, however, been employed by altering the membrane or by

chemically pre-treating the feed solution. The microfiltration process comes in two major configurations, depending on the mode of application: crossflow and dead-end.

2.1.4.4. Reverse Osmosis

The reverse osmosis technology can not only remove the salts and other substances in the ion state, can also remove suspended solids, organic matter, colloids, bacteria and viruses, only water can go through reverse osmosis membrane, so as to ensure the water from being polluted (Jiang et al. 2018). Reverse osmosis with pore size of less than 1 nm and high water pressure filters out all types of pathogens and waterborne impurities (Loo et al. 2012). Reverse osmosis (RO) membranes are considered the most effective process for copper removal due to their higher degree of purification and high rejection level of contaminants (Harharah and Abdalla, 2022). Additionally, reverse osmosis systems, which are self-cleaning and self-contained, also require relatively minimal maintenance. Modern reverse osmosis membrane systems use electricity and high-pressure water instead of chemicals. Reverse osmosis systems can be transportable and powered by being connected with photovoltaic systems or mounted on vehicles. They can securely dispose of the wastewater they treat or reuse and recycle it back into manufacturing. However, a high volume of salty wastewater could be generated, and it can cause an adverse impact on the environment due to its high salinity (Panagopoulos and Haralambous, 2019).

2.1.5. Electrodialysis

A membrane technique known as electrodialysis uses an electric field as the driving force to separate ions that are transferred via charged membranes from one solution to

another. Anion-exchange and cation-exchange membranes are the two main types of ion-exchange membranes that are used in the majority of electro dialysis procedures. Cifuentes et al. (2009) investigated the efficacy of electro dialysis in the separation of Cu and recovery of water from copper solutions. The removal of Cu from the working solution via electro dialysis was demonstrated to be extremely successful. The main advantages are no osmotic pressure, environmentally friendly, no additional chemicals and ion exchange membranes have long useful life. But electro dialysis has various limitations. A major disadvantage of electro dialysis system is membrane fouling because it reduces the limiting current (Oztekin and Altin, 2016).

2.1.6. Coagulation and flocculation

In a traditional water treatment plant, sedimentation and filtration are always carried out after coagulation and flocculation. Coagulation is the destabilization of colloids by neutralizing the forces that keep them parted (Qasem and Mohammed, 2021). Aluminum and ferric chloride are extensively utilized in the conventional wastewater treatment procedure. El Samrani et al. (2008) discovered that using two commercial coagulants, ferric chloride and poly aluminum chloride (PACl), to coagulate combined sewer overflow may successfully remove heavy metals from wastewater. Flocculation is the process in which polymers create connections between flocs and bind the small particles into big ones so that they may be filtered out. Heredia and Martin (2009) announced the development of a novel commercial tannin-based flocculant to remove Zn^{2+} , Ni^{2+} , and Cu^{2+} from wastewater using a coagulation-flocculation method as existing flocculants are not particularly effective at doing so. Some of the studies conducted on coagulation-flocculation for heavy metal removal from different wastewater sources. The typical heavy metals removed by this method include Cu^{2+} (Qasem

and Mohammed, 2021). Owing to its easy operation, relatively simple design, and low energy consumption, coagulation–flocculation has been successfully employed in different types of industries. However, the production of sludge as a secondary pollutant from the coagulation–flocculation process was one of the challenges faced in treatment facilities (Teh and Budiman, 2016).

2.1.7. Electrochemical treatment

Electrochemical methods recover metals in their elemental metal state by plating out metal ions on a cathode surface (Fu and Wang, 2011). Electrochemical waste water solutions were not widely used a few decades ago because of high capital costs and expensive electrical supply. However, due to strict environmental regulations, electrochemical technologies are becoming increasingly commonly used. Several research investigated electrocoagulation, electroflotation, and electrodeposition. Jack et al. (2014) investigated the performance of an Electrocoagulation system for copper removal. Their preliminary laboratory study revealed that copper levels in settlings might be lowered by up to 95%. When this system was scaled up, it achieved a copper reduction of 88% at 34 W h/m' and a removal of 96% at 112 W.

Solid and liquid are separated using the electroflotation technique. Tiny hydrogen and oxygen gas bubbles produced by water electrolysis lift pollutants to the surface of a body of water (Fu and Wang, 2011). The mechanism of electroflotation is mainly based on carrying out water electrolysis on insoluble electrodes, while the flotation effect is introduced to facilitate the treatment process (Sillanpää and Shestakova, 2017). Heavy metals can be

removed from industrial waste water using electroflotation. However, the removal efficiency of the EF process toward heavy metal is limited due to low O₂ evolution overpotentials (Fu and Wang, 2011). Belkacem et al. (2008) investigated the use of aluminum electrodes in the electroflotation approach for wastewater purification. Their research demonstrated that 99% of the metal was removed. Electrodeposition has been widely used to recover metals from wastewater. It is a clean process that leaves no permanent residues after removing heavy metals from wastewater. Because it is a two stepped process during which particles are destabilized at first by neutralizing the forces that keep them apart and subsequently the destabilized neutral particles are aggregated in a second step (Beulah, 2022). Chang et al. (2009) recovered copper from EDTA-copper wastewater using electrodeposition and ultrasonic. They studied whether the approach could efficiently remove copper, and the copper removal rate was 95.6%. Electrodeposition is a process that can achieve good reduction while also producing less sludge. Rahimi et al. (2018) created a thermally regenerating ammonia battery (TRAB) to extract copper from water while also producing energy. When the starting copper concentration was 0.05M, the percentage of copper elimination reduced from 51% (C_i =0.01M) to 2%. (J-0.002M)

Table 1. Available Techniques for Copper Removal

	Advantages	Disadvantages
Chemical Precipitation	- Simple and inexpensive to operate	- Leading to an extreme pH environment
Ion Exchange	- High removal efficiency - Quick kinetics	- Used on a laboratory scale, especially zeolite
Adsorption	- Viable and cost-effective - Reversible	- Disposal of such adsorbents
Membrane Filtration	- Compact system - Employed on large scales	- Membrane fouling
Reverse Osmosis	- High degree of purification - High rejection level of contaminate	- High volume of brine produced
Electrodialysis	- No osmotic pressure - Environmentally friendly	- Membrane Fouling
Coagulation & Flocculation	- Easy operation - Low energy consumption	- The production of sludge as a secondary pollutant
Electrochemical treatment	- Suitable for strict environmental regulations	- High capital costs

2.2. Electrowinning for Copper Removal

2.2.1 Non-PSU studies

Electrowinning, also called electroextraction, is the electrodeposition of metals from their ores that have been put in solution via a process commonly referred to as leaching (Yu, 2015). This process is commonly used to recover metals such as copper, zinc, nickel, and

cobalt by applying a voltage across electrodes immersed in a concentrated solution. Electrowinning utilizes electroplating on a large scale and are important techniques for the economical and straightforward purification of non-ferrous metals. The main processes occurring on the electrode are the charging-up of the double electric layer, charge transfer in the electrochemical reaction, and diffusion (Cesiulis, 2023). A current is transmitted from an anode through an aqueous solution containing the metal, and the metal is removed and deposited onto the cathode in the traditional electrowinning process. Sulfur dioxide electrooxidation relies heavily on anode material on copper electrowinning from sulfate electrolyte in the presence of sulfuric acid (Naik and Das, 2000). Comparing the various anodes, they found that the graphite anode performed the best. For the purpose of electrowinning copper from a diluted cyanide solution, Lu et al. (2002) developed a membrane cell with a graphite cathode. According to Lu et al., copper current deposition effectiveness increases with surface area but declines as cyanide and copper mole ratios rise.

Electrowinning was used by Gorgievski et al. (2009) to recover copper from acid mine drainage, which contains a minor amount of ferrous/ferric ions. By using the direct electrowinning process, copper may be effectively extracted from acid mine drainage, and a removal rate of above 92% can be attained, according to Gorgievski et al. For cathode use, porous copper sheets and carbon felt are both suitable options. As a result of oxygen evolution in the anode reaction, which raises the acid content and lowers cell voltage, the pH value decreases. EMEW electrowinning, for enhancing mass transfer and allowing for improvements in efficiency, was developed by EMEW clean technologies in Australia (Gower, 2020). The electrolyte is circulated at a very high flow rate past the anode and cathode in EMEW electrowinning process, similar to a cyclone. This approach considerably

improves copper ion mass transfer and removal efficiency. Electrowinning technique called Vortex was created in 1992 by EMEW Clean Technologies in Australia. In conventional electrowinning, anode and cathode are immersed at low flow rates or left stationary in an electrolyte solution. Following a reaction, the metal ions diffused onto the cathode. This method dramatically increases copper ion mass transfer and raises the effectiveness of copper removal. EMEW electrowinning cells are designed in the same way as ordinary electrowinning cells. The electrolyte would produce a cyclone flow because of the EMEW cell's extremely high flow rate. The EMEW electrowinning cell has a cylindrical construction, and a stainless steel sheet is put into the cell's body to act as the cathode. From the cell's bottom, the electrolyte is poured into the system. Metal will plate on the cathode when the anode and cathode are powered.

Unlike other methods for heavy metal removal, electrowinning is a clean single-step method that produces no secondary waste and which can be directly applied to produce high quality metal deposits from solutions without requiring additional chemicals. (Hannula and Khalid, 2019). A divided cell design avoids this problem at the expense of higher system resistance and therefore higher energy consumption, whereas both oxidation and reduction reactions occur in the same chamber with the possibility of desired reaction products being re-oxidized or re-reduced on the counter electrode in an undivided cell (Zuo and Garcia-Segura, 2023). Smara et al. (2005) performed an experiment with an initial Cu^{2+} concentration in the receiver of 200 mg/L, the other experimental conditions being 40 mg/L and $0.09 \text{ dm}^3 \text{ h}^{-1}$ for the feed solution and 2 A m^{-2} for the current density. The experimental result was approximately 1.5 mg/L at the feed compartment's outflow. This dramatic reduction demonstrates that high copper levels can be reached at lower concentration without

reducing the effectiveness of the electrowinning process.

Removal of copper ions using electrowinning process has also been applied at acidic solution as well as brine solution. The electrodeposition of copper from synthesized and real dilute leaching solution was studied. Contact time or reaction time being an important factor influences copper recovery efficiency in the electrowinning process (Subramanya, 2021). Experiments were carried out in monopolar batch studies for varied contact times of 15 minutes, 30 minutes, 45 minutes, 60 minutes, and 120 minutes at 2 V at 510 rpm. Copper rate of recovery was slow at the initial stage. As the reaction time increases rate of copper recovery efficiency also increases (Chen et al., 2013). The copper recovery percentage was determined to be 32.62% at 2 V for 120 minutes. Figure 1 depicts the effect of contact time on copper recovery percentage for 2 V at 510 rpm.

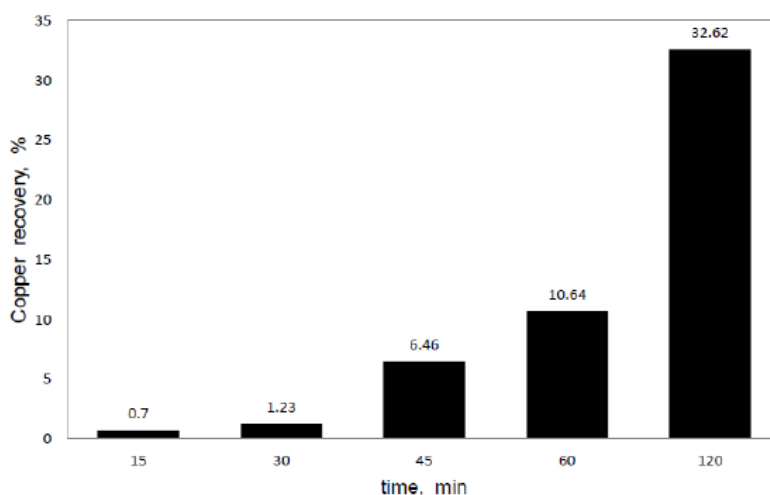


Figure 1. Effect of contact time as a function of copper recovery percentage (Subramanya, 2021)

It has been established by previous researches that the influent pH is an important operating factor influencing the performance of electro deposition process. Experiments were carried out at pH levels of 0.93, 1.06, 2.42, and 4.25 to investigate its influence. Because the obtained wastewater was acidic, the pH was corrected using 0.1 N sodium hydroxide to achieve the necessary pH for the experiment. The Figure 2 shows amount of copper deposited on the cathode. Although the quantity of copper deposition grew when the pH was raised more, it was not cost effective since the amount of sodium hydroxide consumed rose as the pH was raised. It should also be mentioned that prior studies that shown maximal clearance had pH values ranging from 6 to 8.

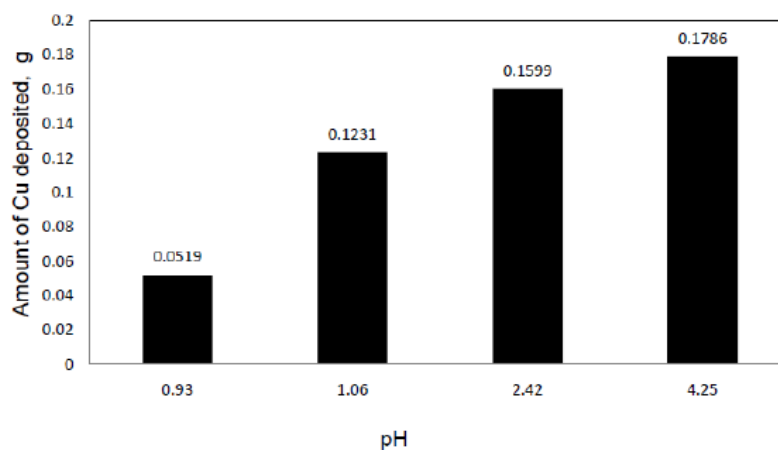


Figure 2. Effect of pH as a function of amount of copper deposited on stainless steel (Subramanya, 2021)

The influence of initial copper concentration on copper electrodeposition at different potentials is seen in Figure 3. Increasing copper concentration and potential has a favorable influence on copper recovery, according to the findings. This may be explained as increasing the copper ion concentration in the electrolyte solution feeds an appropriate and stable value

of copper to the cathode surface, which enhances the rate of deposition and hence the efficiency as well as other metrics. Also, increasing the copper concentration slightly increases the diffusivity of cupric ions although at higher concentrations, the diffusion coefficient of cupric ions decreases (Moats and Hiskey, 2000). The findings from acidic solution verify that electrowinning is deeply related to contact time and cathode potential on the copper electrodeposition, while partially affected by pH.

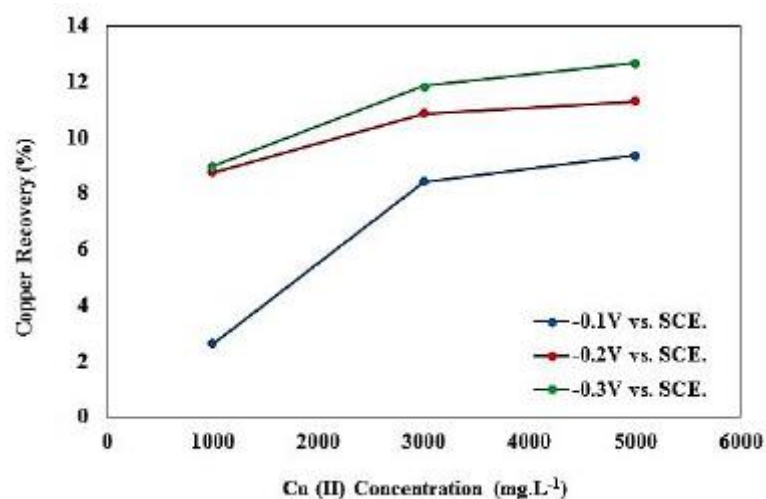


Figure 3. The effect of Cu (II) concentration and cathode potential on the copper electrodeposition (Sadrabadi et al., 2022)

2.2.2. PSU Studies

Copper levels in digested biosolids are increased at the Pennsylvania State University Wastewater Treatment Plant in University Park. The ultimate goal of wastewater biosolids land application is to achieve 50% copper removal in order to reduce landfill costs. The salt concentration had a significant impact on copper removal efficiency in investigations of

synthetic water samples. After three hours of reaction with the proper salt concentration (0.04 M— 1.5 M), over 90% copper reduction was accomplished. When the salt concentration was less than 0.1 M, the extracted copper clung to the cathode and could be retrieved directly from the water. When the salt concentration was greater than 0.1 M, the copper fell into the water when the electrodes were removed from the water, but the copper can be totally removed by using a bag filter. The copper electrowinning reaction can be described as a first order reaction. A study of the relationship between voltage and copper reduction was also carried out by Tang's study. According to the findings, there is a considerable positive link between voltage and maximum copper reduction. Furthermore, the higher the applied voltage, the higher the chlorine concentrations observed. The longer the electrowinning time, the lower the value of the current efficiency obtained. After three hours of reaction, it was just 14.3%. More research is needed to increase present efficiency.

When actual water samples were studied, 85% copper reduction was obtained after three hours of response when the original copper concentration was 221 mg/L. The copper removal efficiency was reduced to 50% - 70% when the starting copper concentration was less than 100 mg/L. The low copper removal effectiveness of the actual samples is most likely due to high salt content and low copper concentration. More sampling and testing on actual samples is required. On synthetic water samples, continuous reactor and internal circulation reactor studies were also carried out. Copper concentrations for five flow rates over the course of five hours' electrowinning process are presented in Figure 4 and the result of maximum copper reduction with different flow rates for five hours' electrowinning process are presented in Figure 5 (Tang, 2018). The greatest copper reduction was obtained after five hours of reaction when the flow rate was set to 20 mL/min.

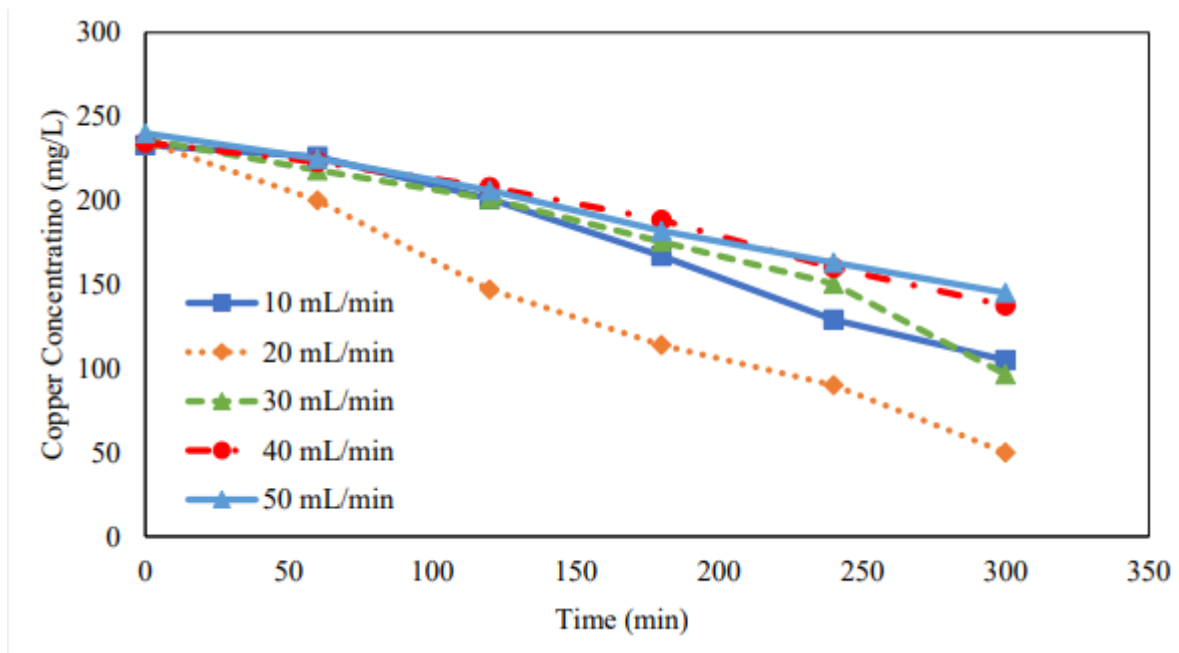


Figure 4. The concentration of copper varies according to reaction time of electrowinning process with different flow rate (Applied voltage: 2.5 V, Salt concentration: 1 M) (Tang, 2018)

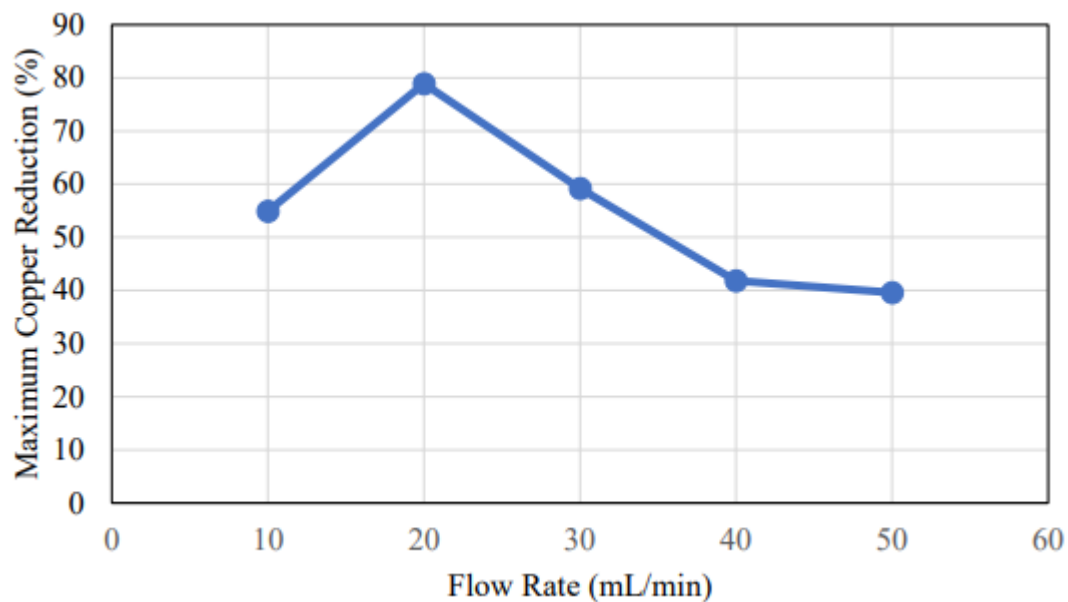


Figure 5. Maximum copper reduction of copper after applying electrowinning with different flow rates (Tang, 2018)

According to Dominguez and Zhou, the effect of brine concentration was studied at 2 M NaCl to simulate the actual brine concentration from the discharge and 1 M brine for potential pre-dilution of the discharge on site. After 30 hours in 2 M brine, copper had been removed by 50%, and after 72 hours, it had been 99% removed, with a concentration of 1 ppm. After 19 hours and 92% after 72 hours, the system at 1 M brine had eliminated more than 50% of Cu (II) ions. At 1 M NaCl, floc development was gradually observed over time. At 2 M NaCl, on the other hand, flocs formed practically instantly. The pump was switched off after 72 hours to allow any precipitates to settle. After the precipitate settled out, the Cu (II) concentration in each brine solution was 24.5 ppm and 1.3 ppm at 1 M NaCl and 2 M NaCl, respectively. The system removed more than 50% of copper after running 19 hours and 92% after running 72 hours.

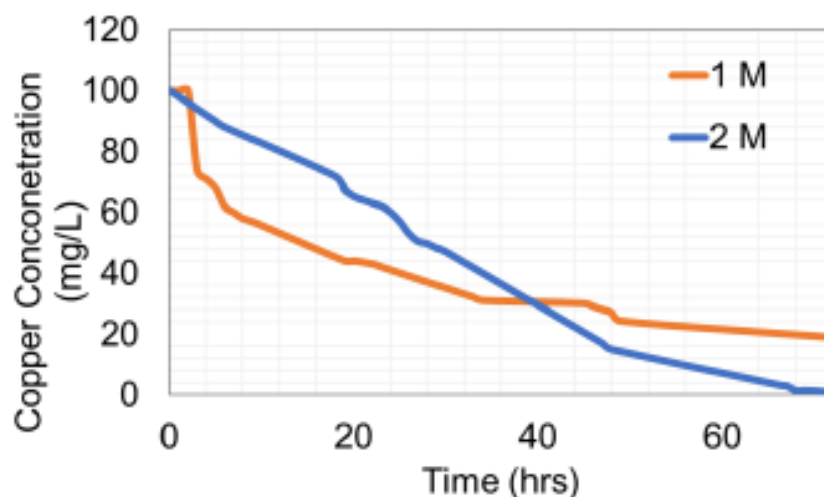


Figure 6. Effect of Synthetic Brine Solution on Cu (Dominguez and Zhou, 2019)

The salient part is that the graph presented shows a linear trend at 2 M copper concentration measurement. According to Tang's research, the copper concentration could be expressed by equation below, where k is the rate constant of copper reduction. The kinetic of copper reduction occurs as a first order reaction (equation 1).

$$[\text{Cu}^{2+}]_t = [\text{Cu}^{2+}]^0 * e^{-kt}$$

When salt concentrations increase, the rate of constant of copper induction decrease (Figure 7). In other words, it could be expressed that half-life of first order reaction increases, as increasing salt concentration (equation 2).

$$t_{(1/2)} = \frac{0.693}{k}$$

For this reason, copper concentration gradually decreased in 2 M, compared to 1 M solution.

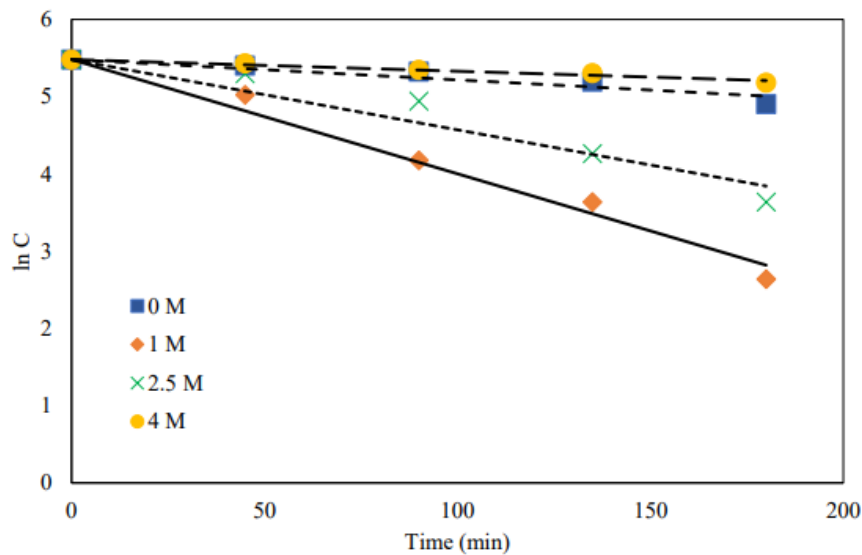


Figure 7. A semi log plot of the course of copper electrowinning with four different salt concentration (0, 1, 2.5, 4M) (Tang, 2018)

As seen in table 2, the current efficiency rapidly increased in first hour, because the copper concentration is rapidly decreased during this period, the increase of current efficiency leveled off after 60 minutes (Tang, 2018).

Table 2. Estimated Current Efficiency (V = 2.5 V) (Tang, 2018)

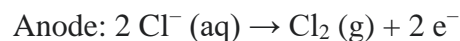
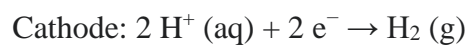
Reaction time (min)	Copper Concentration (mg/L)	Current (A)	Current Efficiency (%)
0	237	0.14	0
30	141	0.11	23.4
60	51	0.11	22.7
90	15	0.11	18.1
120	2.9	0.11	14.3

Based on past work, preparing testing at a wastewater treatment plant necessitates larger-scale studies than previously. Also, only 1 M solution was applied for this research because it was decided to achieve 50% copper removal effectively. Before conducting experiments with wastewater treatment plant samples, copper removal at the large tank would be performed to ensure that testing may be conducted in a high volume of synthetic waste brine solution. After the research with a large tank, actual waste brine would be used for the removal of copper in electrowinning.

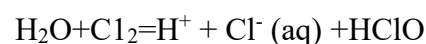
2.2.3. Unresolved Studies

Before maximizing to utilize electrowinning for copper removal, challenges that need to be addressed have emerged. One of the priority challenges is aqueous chlorine. A high value-added oxidation reagent produced conventionally by a chlor-alkali electrolysis

process, which can lead to considerable CO₂ emissions. (Pang and Miseki, 2022). According to PSU studies, during the copper electrowinning process, chlorine was discovered at the highest concentration of 89 mg/L. Chlorine can be manufactured by the electrolysis of a sodium chloride solution called as brine, which is known as the Chloralkali process (Du, 2018). There are three industrial ways for extracting chlorine from chloride solutions that all follow the equation below.



The chlorine mixed with water will produce hypochlorous acid (HOCl). The following equation presents the hydrolysis reaction (USEPA 1999; White 1992).



Total chlorine residual is the total amount of free and combined chlorine existing in water. Breakpoint chlorination could be defined as periodic switching from chloramines to free chlorine has been used by utilities to control distribution system nitrification (Hua and Baggett, 2012). After the breakpoint, the average total chlorine gradually increased. The majority of wastewater applications necessitate the measurement of total chlorine. The chlorine concentration in reused wastewater can be as high as several ppm. In discharged

wastewater, the allowed concentration is low, typically less than 0.05 ppm (Emerson, 2013).

Dechlorination procedures are acceptable in accordance with the chlorine levels. Chlorine concentration should be measured from actual waste brine as well as copper removal.

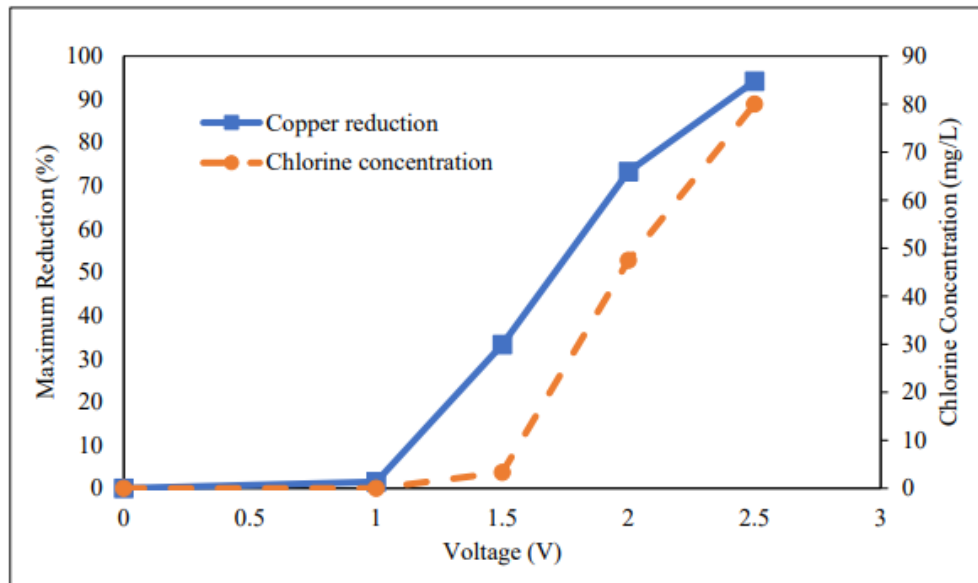


Figure 8. Effects of Brine Concentration on Copper Removal and Chlorine Production. The concentration of sodium chloride was controlled at 1 M (Tang, 2018)

Chapter 3

Materials and Methods

3.1. PSU Copper source and samples

Particularly, the copper associated with the heat exchanger corrosion is discharged into the sewer system through the waste brine from University Park. The samples were taken from the steam plant in University Park. A total of 114 liters of actual wastewater from University Park plant were transported to the Laboratory in Penn State Harrisburg, preferably the same day, and storage there to run the experiment next day. To avoid any oxidation of the waste brine it is critical to run the experiment as soon as possible.

3.2. Electrowinning Devices

An electrowinning lab scale equipment is the Goldbug System, provided from Precious Metals Processing Consultants, Inc. A power supply rectifier, pump, plug cables, canister carrying the cylindrical cathode and anode cell, and hose barb are all part of the apparatus. The unit, which employs a very high surface area cathode, is small enough to fit into the smallest drag-out tanks while being powerful enough to recover enormous tanks of concentrated cyanide strip solutions. Dimensions of collection canister is equal as 16 inches long. Additionally, It has five and half inches of outside diameter, and 10ft² of total cathode surface area. Optimum output voltage of goldbug ranges from 2.5 to 4 voltage, according to PMPC manual. After five minutes of mixing, check to see if the solution is still actively stripping by submerging a gold-plated item with a known thickness of gold plating and ensuring that the gold is not being attacked. When all stripping action has been determined, submerge the Goldbug system in the solution and turn it on immediately.



Figure 9. Copper Electrowinning System (PMPC, 2017)

3.3. Operating Conditions

The electrowinning procedure for copper removal was tested at each copper concentration and at room temperature. The initial concentration is 100 mg/L of copper and the volume of tank is 32.5 L for 80 hours. After the research at 32.5 L tank, a follow-up research had been conducted copper removal at a 1000 L tank for as many hours as an experiment at small size tank. When measuring the initial concentration of actual waste brine from University Park, about 35mg/L is the initial copper concentration. The power supply was set to 2~3 volts for operating several run, because previous PSU studies by other researchers adopt 2.5 and 2.8 voltage in electrowinning, each.

3.4. Synthetic Waste Brine Solution

About 60 mg/L Cu stock solution was prepared using copper (II) sulfate pentahydrate (CAS 7758-99-8). Making 1 M NaCl, Morton table salt without iodide and salt (CAS 7647-14-5) was used. The solutions were made for a 80-hour course of a synthetic copper brine solution of 1000 L. In order to imitate the real brine concentration from the discharge, the effect of brine concentration was examined at 1 M brine for probable pre-dilution of the discharge on site. Also, hourly copper removal for 50 hours was measured instead of current efficiency because the parameter of amperage display was not working.

3.5. Copper Removal from Actual Wastewater

The tank were filled with samples taken the day before from University Park, and then the cathode was introduced into the solution. About 114 liters of waste brine were used in total. The pump was connected to the system to recirculate the waste brine in the tank, reaching the same concentration of the waste brine. Specified voltages were selected from 2 volts to 3 volts for each experiment. The initial concentration of each lab was set to about 35mg/L. Because researches at the laboratory had to be done fast because of avoiding any oxidation, each lab study run 6 hours to identifying copper removal efficiency considering voltage performance. Additionally, in order to measure considering a magnitude of the voltage in many experiments, about 38 liters were used in each lab study.

3.6. Chlorine Analysis

After every hour operation from actual waste brine, the chlorine concentration of

sample water was tested by USEPA Method 8021. Because from 0.00 to 2.00 mg/L is the chlorine concentration detection range, the samples have to be diluted prior to analysis. First, A blank sample cell containing 10 mL of material was prepared, cleaned, and then fitted into the cell holder, and pressed zero. Second, DPD-Free Chlorine Powder Swirl the pillow into 10 mL of sample water. Clean the prepared sample cell, then put it into the cell holder and press READ

Chapter 4

Results and Discussion

4.1. Copper Removal from Synthetic Waste Brine Solution

Before running the system at a large tank, it had to be examined whether the system removed more than 50% of copper after running 19 hours and 92% after running 72 hours. The initial concentration is 100 mg/L of copper and the volume of tank is 32.5 L. The decreased effect of copper concentration is presented in figure 10. This finding is backing past studies from former researchers. The remarkable point is that more than half of the copper had been removed after only a few hours of operation, whereas achieving 90% removal took a little longer than expected considering a steeper decline at a start phase. There was a significant decrease in the early stage at former experiments though, the initial reduction rate was exceedingly high in this study.

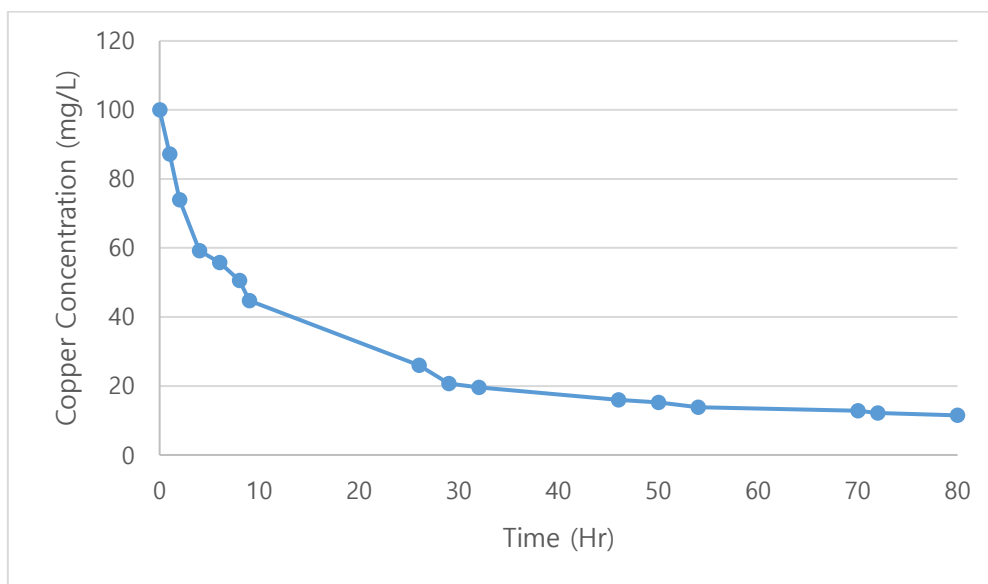


Figure 10. Copper Concentration at a 32.5 L tank

Power consumption estimation should be considered for operating electrowinning system. From 30 hours to 80 hours after running the electrowinning system, there was about only 9 mg/L of copper removal from synthetic waste brine solution. Just in terms of allocation of time resources and cost-effective, 90% copper removal for 80 hours is not very efficient rather than 80% removal of copper for 30 hours. If long-term operating electrowinning system is not considered enhancing removal efficiency, adjusting experiment time may be needed in the light of amount of copper removal in a part of the future research. Hourly removal of copper could be expressed by equation below. Estimated copper reduction of each phase are presented in Table 1.

$$\text{Hourly Removal (mg/hr)} = \frac{\text{Initial Concentration} - \text{Final concentration (mg/L)}}{\text{Times (hr)}} * \text{Volume of Tank (L)}$$

Table 3. Hourly Copper Removal at a 32.5 L tank for 50 hours

Phase (hr)	Initial Concentration (mg/L)	Final Concentration (mg/L)	Hourly Removal (mg/hr)
~10	100	43.6	183.3
10~20	43.6	32.57	35.85
20~30	32.57	20.33	39.78
30~40	20.33	17.51	9.17
40~50	17.51	15.2	7.51

The goal was to verify substantial removal of copper from wastewater in this lab. The effect of brine concentration was studied at 1M NaCl and 58kg of NaCl was needed. Then, about 483 g (= 483,000 mg) of copper sulfate pentahydrate was put at a 1000 L tank

for making 100 mg/L Cu stock solution. But because of avoiding overuse copper sulfate pentahydrate, it was compromised to apply about 60 mg/L copper stock solution. In this lab, research had been conducted copper removal at a 1000 L tank for 80 hours and identified whether the data is similar with an experiment at small size tank. At 1 M brine, copper had a 90% removal after 80 hours. Sample from University Park can be used for copper removal because 90% of copper are removed after a certain amount of time at a 1000 L tank, as well as a 32.5 L tank.

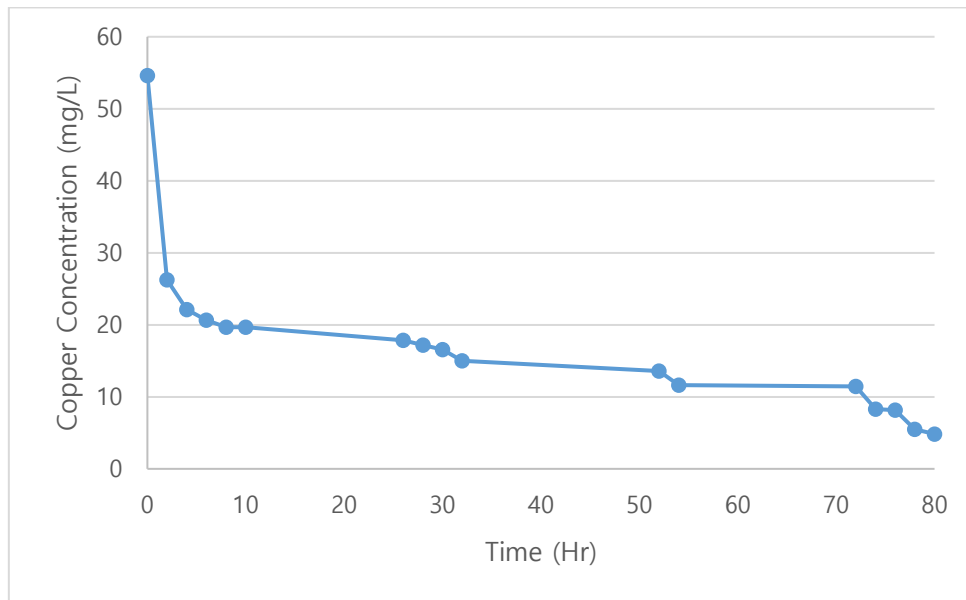


Figure 11. Copper Concentration at a 1000 L tank

Additionally, copper is removed 622 mg per hour from copper stock solution in a large tank. One of the salient parts are that a drastic decline at a start phase like former studies. Although hourly removal increase in some phases at a 1000 L tank, the longer time of electrowinning, on the whole, the lower value of the hourly copper removal was get (Table 2). Compared to previous PSU study, the copper electrowinning reaction can be also described as a first order

reaction. It could be related to current efficiency directly. Further studies need to be conducted to improve current efficiency. What has to be remembered is that the findings of 1000 L tank study should take variables, especially given the large volume of tank. If other variables played no small part in copper removal in a 1000 L tank, the alternatives of reducing variables should be devised in order to raise precision.

Table 4. Hourly Copper Removal at a 1000 L tank for 50 hours

Phase (hr)	Initial Concentration (mg/L)	Final Concentration (mg/L)	Hourly Removal (mg/hr)
~10	54.6	19.65	3495
10~20	19.65	18.53	112
20~30	18.53	16.55	198
30~40	16.55	14.44	211
40~50	14.44	13.74	70

4.2. Copper Removal from Actual Waste Brine

Copper removal was conducted with samples collected from Pennsylvania State University Wastewater Treatment Plant after tests in small tanks and a large tank. Experimental studies are divided into three sections at 2, 2.5 and 3 voltage performance in order to verify result value more elaborate and apply typical voltage for maximizing reduction. Each part had been conducted for about 6 hours, because researches at the laboratory had to be done fast because of avoiding any oxidation, each lab study run 6 hours to identifying copper removal efficiency considering voltage performance. Figure 12 showed a dramatic effect at 3 voltage by about 74% reduction from 33.5 to 8.65 mg/L for only 6 hours, whereas only 30% reduction was recorded at 2 V and 2.5 V. It concludes between 2.5

V and 3 V would be more suitable than other voltages for copper removal in PSU Wastewater Treatment Plant. To meet land application rules, the excess copper concentration had to be decreased by 50% in less than 30 hours for both runs. However, because Goldbug system could be applied from 2.5 to 4 voltages, more various voltages should be studied to identify ideal voltage ranges for copper removal. Also, follow-up copper removal studies would be needed to do long-term electrowinning from actual waste brine. Along the way, several factors have to be considered, such as current efficiency, finding how to achieve 50% copper removal effectively. If current efficiency patterns are similar as previous studies, straightforward ways of retaining current efficiency in long-term operation are needed to be devised. The preferred options, in order of priority, are needed to do several experiments to test benefited verification, then apply the optimum alternative plan to the University Park plant. Above all, several findings back up that using electrowinning system is applicable to carry out copper removal from actual waste brine from University Park plant.

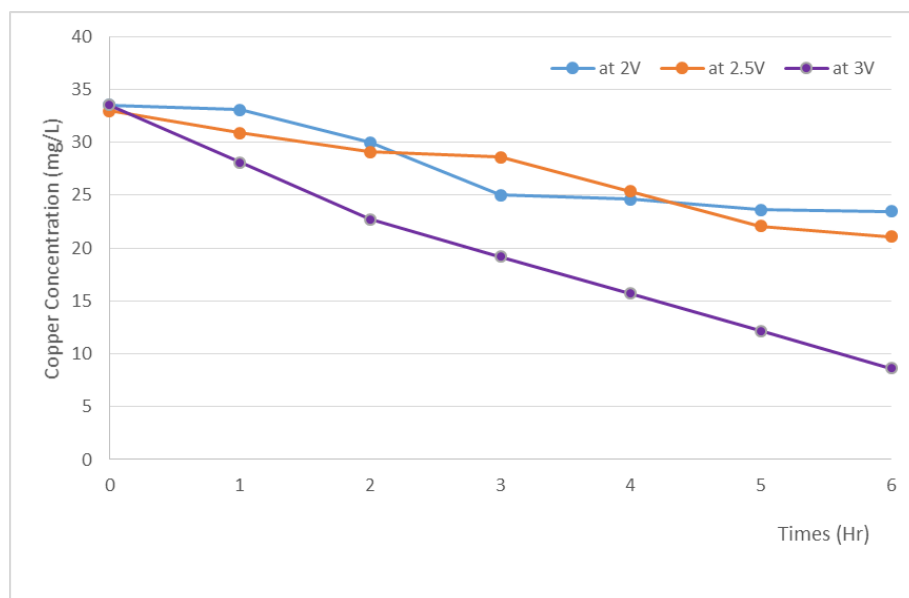


Figure 12. Effect of actual waste brine on copper concentration as a function of time at specified voltage performances

As mentioned in literature review, electrowinning system also produces chlorine through hydrolysis reaction of water and gaseous chlorine which is made from cathodic-anodic coupling reaction. Considerable amount of chlorine was detected during the copper electrowinning process, with the highest concentration at about 170 mg/L of total chlorine (Figure 13). Free chlorine forms the bulk of total chlorine, and combined chlorine increased after 6-hour. If copper removal from actual waste brine had taken longer, total chlorine would be increased after the breakpoint. Adequate ventilation system needs to be considered to ensure that there is sufficient air exchange because wastewater treatment plant workers should avoid inhalation issues. To provide against long-term experiments at wastewater treatment plant, ventilation system would be designed considering spatial constraints. It should also be noted that chlorine can react violently with many combustible materials. In compliance with the chlorine levels, dechlorination processes are allowed, but not at this stage considering apply a dechlorination. More in-depth studies are required because maximizing efficiency of removing copper is crucial as well as ramping up the amount of reduction.

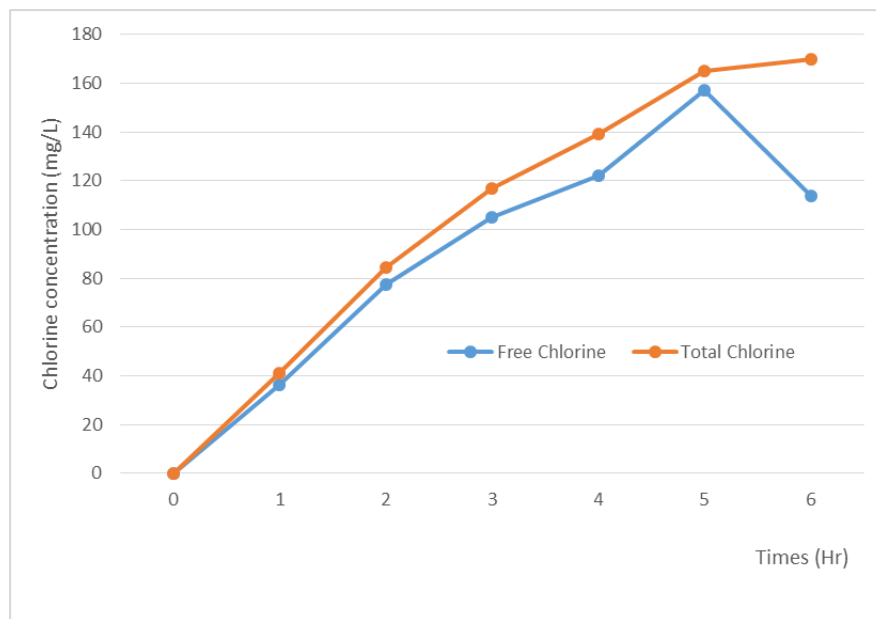


Figure 13. Effect of actual waste brine on Free and Total Chlorine concentration as a function of time

To organize copper removal studies using synthetic waste brine solution and actual wastewater, several findings could testify that copper removal using electrowinning system is workable to carry out a full-scale study on the spot at University Park. But because of liquid chlorine, to guarantee enough air exchange, a proper ventilation system must be considered for safety's sake.

Chapter 5

Conclusions

Copper removal efficiency through electrowinning was demonstrated from direct experimental verification with two studies. In a pilot study, the findings from Dominguez and Zhou are proven that the system removed more than 50% of copper after running 19 hours and 92% after running 72 hours. At 1 M brine, copper had a 90% removal after 80 hours at a 1000 L large tank and identified that the results are comparable to findings at a small size tank. University Park wastewater could be treated for copper removal because 90% of copper is removed after 80 hours in both a large and small tank. Copper removal from waste brine at Penn State University's Steam Plant was also investigated. A substantial reduction was shown at 3 voltage in only 6 hours rather than at 2 and 2.5 V. Considerable amount of chlorine was detected during the copper electrowinning process, with the highest concentration at about 170 mg/L of total chlorine. A proper ventilation or dechlorination processes may be needed. Overall, it was identified that copper removal from actual waste brine in University Park could be investigated, but more various voltages should be investigated to find proper voltage for long-term copper removal. Also, current efficiency would be needed to conduct in copper removal, in order to achieve 50% copper removal effectively, as well as about chlorine level issue.

References

- Ab Hamid, N.H., Bin Mohd Tahir, M.I.H. (2022). The Current of State-of-Art of Copper Removal from Wastewater: A Review, *Water*, 14(19), p3086-3100
- Agarwal, M. (2015). Heavy Metal Sources Impacts & Removal Technologies, *International Journal of Engineering Research and Technology*, 3(3), ETWQQM – 2014
- Agouborde, L., Navia, R. (2009). Heavy Metals Retention Capacity of a Nonconventional Sorbents Developed from a Mixture Industrial and Agricultural Waste, *Journal of Hazardous Materials*, 167(1-3), p536-544
- Apiratikul, R. and Pavasant, P. (2008) Batch and Column Studies of Biosorption of Heavy Metals by *Caulerpa lentillifera*. *Bioresource Technology*, 99, 2766-2777
- Belkacem, M. (2008). Treatment characteristics of textile wastewater and removal of heavy metals using the electroflotation technique, *Desalination*, 228(1-3), p245-254
- Bhardwaj, A. A., Vos J. G. (2021). Ultrathin Silicon Oxide Overlayers Enable Selective Oxygen Evolution from Acidic and Unbuffered pH-Neutral Seawater, *ACS Catalysis*, 11(3), p1316-1330

Buteau S., Valcke M. (2010). Probabilistic Human Health Risk Assessment for Quarterly Exposure to High Chloroform Concentrations in Drinking-Water Distribution Network of the Province of Quebec, Canada, *Journal of Toxicology and Environmental Health*, 73(23), p1626-1644

Cesiulis, H., Tsyntaru, N. (2023). Eco-Friendly Electrowinning for Metals Recovery from Waste Electrical and Electronic Equipment (WEEE), *Coatings*, 13(3), p574-584

Chamber, A. J. (2014). An Evaluation of Anode Corrosion and Gas Emissions during Gold Electrowinning, *the University of Utah*

Chang, J. (2009). The electrochemical phenomena and kinetics of EDTA–copper wastewater reclamation by electrodeposition and ultrasound, *Separation and Purification Technology*, 68, p216-p221

Chang, Y. K., Chang, J. E. (2002). Integrated copper-containing wastewater treatment using xanthate process, *Journal of Hazardous Materials*, 94(1), p89-99

Cifuentes, L. (2009). The use of electrodialysis for metal separation and water recovery from CuSO₄–H₂SO₄–Fe solutions, *Separation and Purification Technology*, 68(1), p105-108

Dominguez, T., Zhou, G. (2019). Electrowinning for Copper Removal from Waste Brine Solution, *22nd Annual Environmental Chemistry & Microbiology Student Symposium*, Penn State Harrisburg, University Park, PA

Du, F. (2018). Sodium hydroxide production from seawater desalination brine: process design and energy efficiency, *Environmental Science & Technology*, 52(10), p5949–5958

El Samrani, A.G., Lartiges, B.S. (2008). Chemical Coagulation of Combined Sewer Overflow: Heavy Metal Removal and Treatment Optimization, *Water Research*, 42, p951-960

Emerson Process Management (2013). *Measurement of Total Chlorine in Municipal Wastewater Effluent* (LIQ_ADS_4950-10). Retrieved from <https://www.emerson.com/documents/automation/application-data-sheet-measurement-of-total-chlorine-in-municipal-wastewater-effluent-rosemount-en-68474.pdf>

Estay, H., Barros, L. (2021). Metal Sulfide Precipitation: Recent Breakthroughs and Future Outlooks, *Minerals*, 11(12), p1385-1411

Evans, R. B. (2004). Chlorine: State of the Art, *Lung*, 183(3), p151–167

Fu, F. and Wang, Q. (2011). Removal of Heavy Metal Ions from Wastewaters: A Review. *Journal of Environmental Management*, 92, p407-418.

Gode, F., Pehlivan, E. (2006). Removal of chromium (III) from aqueous solutions using Lewatit S 100: the effect of pH, time, metal concentration and temperature, *J Hazard Mater*, 136(2), p330-337

González-Munoz, M. J., Rodriguez, M. A. (2006). Recovery of heavy metals from metal industry waste waters by chemical precipitation and nanofiltration, *Desalination*, 200(1-3), p742-744

Gorgievski, M. (2009). Copper electrowinning from acid mine drainage: a case study from the closed mine "Cerovo", *J Hazard Water*, 170(2-3), p716-721

Gower, W. (2020). Factors that affect anode life in electrowinning, *emew Blog*, <https://blog.emew.com/factors-affect-anode-life-electrowinning>

Gul, A., Hruza, J. (2021). Fouling and Chemical Cleaning of Microfiltration Membranes: A Mini-Review, *Polymers (Basel)*, 13(6), p846-870

Guo, Y., Li, C. (2023). The Performance of Ultrafiltration Process to Further Refine Lactic Acid from the Pre-Microfiltered Broth of Kitchen Waste Fermentation, *Membranes*, 13(3), p330-344

Hannula, P., Khalid, M. K. (2019). Energy efficient copper electrowinning and direct deposition on carbon nanotube film from industrial wastewaters, *Journal of Cleaner Production*, 207(10), p1033-1039

Harharah, R. H., Abdalla, G. M. (2022). A Study of Copper (II) Ions Removal by Reverse Osmosis under Various Operating Conditions, *Separations*, 9(6), p155-167

Heredia, J.B., Martin, J.S. (2009). Removing heavy metals from polluted surface water with a tannin-based flocculant agent, *Journal of Hazardous Materials*, 165(1-3), p1215-1218

Hua, G., Baggett, C. (2012). Effectiveness of Periodic Breakpoint Chlorination on Distribution system Nitrification Control for Pinellas County Utilities, *Florida water Resources Journal*, p56-64

Jack, F. (2014). Electrocoagulation for the removal of copper from distillery waste streams, *Journal of The Institute of Brewing*, 120(1), p60-64

Jiang L., Tu.Y. (2018). Application of reverse osmosis in purifying drinking water, *ICEMEE* 2018, 01037

Kang, S.Y., Lee, J.U. (2004). Competitive adsorption characteristics of Co^{2+} , Ni^{2+} , and Cr^{3+} by IRN-77 cation exchange resin in synthesized wastewater, *Chemosphere*, 56(2), p141-147

Lee, M. Y., & Roth R. (2019). The Impact of Filtration on TTHMs Concentrations, *Penn State Harrisburg*

Lemos, F. A., and Sobral, L. G. S. (2006). Copper electrowinning from gold plant waste streams, *Minerals Engineering*, 19(5), p388-398

Li, Y., Liu, F. (2010). Removal of copper from aqueous solution by carbon nanotube/calcium alginate composites, *Journal of Hazardous Materials*, 177(1-3), p876-880

Liu, L., Chen, X. (2022). Enhancing the Antifouling Ability of a Polyamide Nanofiltration Membrane by Narrowing the Pore Size Distribution via One-Step Multiple Interfacial Polymerization, *ACS Applied Materials & Interfaces*, 14(31), p36132-31642

Liu, Y., Wang, H. (2023). Removal of Copper Ions from Wastewater: A Review, *International Journal of Environmental Research and Public Health*, 20(5), p3885-3907

Loo, S. L., Fane, A. G. (2012). Emergency water supply: A review of potential technologies and selection criteria, *Water Research*, 46(10), p3125-3151

Lu, J., Dreisinger, D.B. (2002). Copper electrowinning from dilute cyanide solution in a membrane cell using graphite felt, *Hydrometallurgy*, 64(1), p1-11

Minnesota Department of Health. (n.d.). Water Treatment Using Carbon Filters: GAC Filter Information. Retrieved from <https://www.health.state.mn.us/communities/environment/hazardous/topics/gac.html>

Moats, M. S., Hiskey, J. B. (2000). Effect of copper, acid, and temperature on the diffusion coefficient of cupric ions in simulated electrorefining electrolytes, *Hydrometallurgy*, 56(3), p255-268

Naik, P.K., Das, S.C. (2000) Aqueous SO₂ Leaching Studies on Nishikhal Manganese Ore through Factorial Experiment. *Hydrometallurgy*, 54, p217-228

Nompumelelo, K. S. M., Edward, N. N. (2023). Fabrication, Modification, and Mechanism of Nanofiltration Membranes for the Removal of Heavy Metal Ions from Wastewater, *Chemistry Select*, 8(33)

Oztekin, E., Altin, S. (2016). Wastewater Treatment by Electrodialysis System and Fouling Problems, *The Online Journal of Science and Technology*, 6(1), p91-99

Panagopoulos, A., Haralambous, K. J. (2019). Desalination brine disposal methods and treatment technologies – A review, *Science of the Total Environment*, 693, 133545

Pang, R., Miseki, Y. (2022). Enhanced HClO production from chloride by dual cocatalyst loaded WO₃ under visible light, *Catalysis Science & Technology*, 12(9), p2935-2942

Pombo, F. R. (2011). Copper removal from diluted cyanide wastewater by electrolysis, *Environmental Progress & Sustainable Energy*, 32(1), p52-59

Precious Metals Processing Consultants (2017). Gold-bug: Operating Instruction. Palisades Park, NJ: PMPC

Qasem, N. A. A., Mohammed R. M. (2021). Removal of heavy metal ions from wastewater: a comprehensive and critical review, *NPJ Clean Water*, 36

Rahimi, M. (2018). A thermally regenerative ammonia battery with carbon-silver electrodes for converting low-grade waste heat to electricity, *Journal of Power Sources*, 373, p95-102

Sadrabadi, S. H., Naderi, H. (2022). Removal of copper ions from dilute sulfuric acid solutions: Effect of solution composition and applied potential, *International Journal of Mining and Geo-Engineering*, 56(3), p239-247

Shahid, P., Kali, F. (2017). Evaluation of Drinking Water Disinfectant Byproducts Compliance Data as an Indirect Measure for Short-Term Exposure in Humans, *International Journal of Environmental Research and Public Health*, 14(5), p548-563

Sillanpää, M., & Shestakova, M. (2017). In *Electrochemical Water Treatment Methods: Fundamentals, methods and full scale applications* (1st ed., pp. 47–130). Butterworth-Heinemann, an imprint of Elsevier.

Smara, A., Delimi, R. (2005). Electroextraction of heavy metals from diluted solutions by a process combining ion-exchange resins and membranes, *Separation and Purification Technology*, 44(3), p271-277

Song, H.J., Yoon, H. (2020). Electrocatalytic Selective Oxygen Evolution of Carbon-Coated $\text{Na}_2\text{Co}_{1-x}\text{Fe}_x\text{P}_2\text{O}_7$ Nanoparticles for Alkaline Seawater Electrolysis. *ACS Catal*, 10, p702–709

Subramanya, M. (2021). Electrowinning of Copper from Industrial Waste Streams, *International Journal of Engineering Research & Technology*, 10(8), p122-131

Tang, L. (2018). Dissolved Copper Removal by Electronwinning Process from Waste Brine Solution, *Penn State University*

Teh, C. Y., Budiman, P. M. (2016). Recent Advancement of Coagulation-Flocculation and Its Application in Wastewater Treatment, *Industrial & Engineering Chemistry Research*, 55(16), p4363-4389

USEPA (1999). Guidance Manual Alternative Disinfectants and Oxidants. United States Environmental Protection Agency, Office of Drinking Water, Cincinnati, Ohio

Ying, X., Fang, Z. (2006). Experimental research on heavy metal wastewater treatment with dipropyl dithiophosphate, *Journal of Hazardous Materials*, 137(3), p1636-1642

Yu Y. (2015). Electrowinning of Zinc for the anode of Rechargeable Hybrid Aqueous Batteries, *the University of Waterloo*

Zuo, K., Garcia-Segura, S. (2023). Electrified water treatment: fundamentals and roles of electrode materials, *Nature Review Materials*, 8, p472-790