ISSN 2959-6157

The Review of Treatment of Copper Ion in Wastewater and Comparison Between Four Treatment

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Abstract:

This paper presents a comprehensive review of various methods used to remove copper ions from wastewater, highlighting their efficiency and feasibility. The main focus is on adsorption, ion flotation, membrane-based techniques, and electrochemical cells, with a particular emphasis on innovative approaches like the use of graphene oxide electrodes. The comparison and analysis section assesses each method's removal efficiency, operational challenges, and costs, providing a critical perspective on their practical application in industrial settings.

Keywords: Copper ion removal, Wastewater treatment, Adsorption, Electrochemical cell, Membrane filtration

1. Introduction

Heavy metal in wastewater is a serious problem and needs global attention. Recently, the concentration of heavy metal ions in natural water kept rising due to the growth of industry and human activities. For example, chrome plating process, electrochemical processes using cyanide baths, washing processes, electrochemical processing of printed circuit boards, manufacturing of PCBs, and alkaline etching processes.[1] Handling water containing heavy metals with care is essential to prevent harm to the environment and the long-term health of humans and other living beings. Failure to manage it properly could have serious consequences. In 1993, the World Health Organization recommended the maximum concentration of copper ions in drinking water should not be greater than 2 ppm.[2] Intake of too much copper regularly may cause liver damage, abdominal pain, cramps, nausea, diarrhea, and vomiting.[3]

Research in 1992 suggests the concentrations of dissolved copper generally increase in the downriver direction, especially near urban centers. The concentration of copper ions in the St. Louis area reached 2 ppm, and the concentration of copper ions doubled compared to the Minneapolis area. The Research pointed out that copper dissolved in the Mississippi River comes mainly from industrial and municipal wastewater.[4] This means downriver cities using water from the Mississippi River as the drinking water source will need extra treatment to remove copper ions in the water.

Therefore, the paper presents a review that comprehensively and critically discusses the available technologies to expel copper ions from wastewater. The methods discussed in this review are Adsorption, Membrane, Electrochemical Cell, and Graphene Oxide Electrode. Moreover, compare the removal efficiency of each method, and choose the most efficient method as a potential treatment plan for wastewater containing high-concentration copper ions produced by industries nearby the Mississippi River.

2. Method

2.1 *Adsorption*

Ion flotation is a separation technology for recovering and removing metal ions from dilute aqueous solutions. During this procedure, target ions (non-surface active ions) are attached to oppositely charged ions from the surfactant. Gases are introduced at the bottom of the floatation machine, bringing the complexes to the upper part. Finally, a condensed hydrophobic product with concentrated target ions is generated in the upper section of a flotation machine and then recycled.

The removal efficiency of copper II ions depends on the surfactant and collecting treatments. For example (table 1),

in a study, Cu II recovery improved when surfactant-stabilized emulsified oil was used during agglomeration. After flotation for 10 min, Cu recovery increased from ~57% (without emulsifier) to ~81% (with sodium dodecyl sulfate) and ~85% (with potassium amyl xanthate).[5] In another study, researchers found that Cu(II) removal could be enhanced by increasing the oxidation degree of the nano collector (graphene oxide).[6] Overall, as concluded from various studies, the floatation method is highly efficient, and all the researches show a removal efficiency above 80%.

Table 1 Comparison of Ion flotation method

Collector	Experimental conditions	Removal efficiency	Reference
sodium dodecyl sulfate (SDS)[16]	[SDS]total = 5.85 mmol /L, [EtOH] = 0.5% (v/v), total = 5 h, flotation stages = 3	85%	Xanthopoulos et al., 2021
Potassium amyl xanthate (KAX)[6]	KAX (200 g KAX/t sample), for 5 min at 1000 rpm, stirred for 3 min at an impeller speed of 1000 rpm, Flow rate of 1 L/min	~83%	Hornn et al., 2021
SDS[17]	pH 8, contact time of 60 min, surfactant dosage of 0.2 g, Pressure = 137.89 kPa.	98.6%	Pooja et al., 2021.
Dry baker's yeast and cetylpyridinium bromide (CPB)[18]	pH 4.5, biosorbent 0.5% w/v, 10 min, CPB 0.01 M, molar ratio CPB/Cu(II) 1 : 2	97.09%	Stoica et al., 2015.
Silica nanoparticle (SNP) development[19]	pH 6.0, Cu(II) 15 mg/L, SNP 90 mg/L, CTAB 35 mg/L, Fotation column height 750 mm	94.5±4.7%	Hu et al., 2017
Anti and syn 2-hydroxy-3,5- di-tert-butyl-benzaldoxime[20]	pH 8.5 to 9.5, Cu(II) 200 mg/L, molar ratio of surfactant/metal 1 : 2	100%	Stoica et al., 2012
Sodium diethyldithiocarbamate (DEDTK)[21]	pH 3, Cu(II) 50 mg L^{-1}, air flow rate 1.8 L min-1 , foaming agent 39.6 g m^{-3}	96.4%	Strel'tsov et al., 2010
Xanthates [22]	pH 2.5 to 5.5, 10% excess of xanthate, air flow rate 100 cm^3 min^{-1}	100%	Lazaridis., 2004
Potassium O-ethyl dithiocarbonate (KEtD)[22]	pH 4.5, KEtD 1.10 equivalents of Cu(II), flotation time 5 min	100%	Lazaridis., 2004
DEDTK[21]	foaming agent 39.6 g/m^3, pH 3.0	96.4%	Strel'tsov et al., 2010

Adsorption is another method for the removal of heavy metal ions like copper II ions. It is a surface process (see figure), and this involves the interaction of a fluid with a solid surface to form chemical or physical bonds. The adsorption efficiency may depend on pH, temperature, pressure, and the nature of the gas. For example (table 2), increasing of pH causes the removal efficiency to increase according to an investigation of Fe3O4 nanoparticles due to more negative surface as explained by the researchers. Also, the effectiveness of this process depends on the number of pores present (Saleh, 2018; Saleh and Ali, 2018). The adsorption isotherms are used to study the interaction between pollutants and adsorbents. These isotherms explain how adsorbates distribute, retain, or move from liquid or gas to adsorbent under consistent temperature and pH. The Langmuir maximum adsorption capacity (qmax) is a commonly used isotherm to characterize the metal sorption capacity of diverse materials, a widely accepted parameter in research (Shaheen et al., 2012). (Shaheen, S.M., Derbalah, A.S., Moghanm, F.S., 2012. Removal of heavy metals from aqueous solution by zeolite in competitive sorption system. Int. J. Environ. Sci. Dev. 3 (4), 362–367.)

Table 2 Comparison of adsorption method

Adsorbents	Adsorption capacity (mg/g)	Maximum removal efficiency	Reference

Wheat straw[7]	7.05	99.8%	(Wu et al. 2009)
Eggshell waste[8]	142.86	93.17%	(Zheng et al. 2007)
TiO2 nanotubes/ CNT[9]	83–124	/	(Sadegh et al. 2017)
SiO2[10]	6.35	/	(Manyangadze et al. 2020)
Fe_3O_4 nanoparticles[11]	369.0–523.6	98%	Xin et al. 2012
As-produced Carbon nanotubes (CNTs)[7]	8.25	/	Wu (2007)
NaOCl-modified CNTs[7]	47.39	/	Wu (2007)
activated carbons (AC)[13]	19.50	/	Rao et al. (2009)
Sawdust[14]	37.17	/	Ahmad et al. (2009)
Zeolite[15]	8.13	/	Sljivic et al. (2009)

2.2 *Membrane*

Membrane filtration methods in copper removal are considered to be relatively highly effective, easy to install, low in operational cost, and space-saving. Membranes are used to separate pollutants from passing while letting cleaned water flow through them. The development of technology leads to an increase in the use of membranes to extract heavy metal ions from water. The primary membrane techniques in metal ion removal are ultrafiltration, nanofiltration, reverse osmosis, and electrodialysis.

1) Ultrafiltration

Ultrafiltration is a membrane technique that works at low transmembrane pressures. Since the sizes of the pores are 2-100 nanometers, much larger than dissolved heavy metal ions in hydrated forms or as low-weight complexes[23], heavy metal ions are likely to be able to pass the membrane. Thus, it is necessary to enlarge the ions or change the structure of the membrane to enhance efficiency.

Micellar-enhanced ultrafiltration (MEUF) is a method that adds surfactant over the critical micelle concentration (CMC)[24]. The surfactant aggregates into micelles that react with heavy metal ions to form metal-surfactant particles that can be blocked by the membrane. Polymer-enhanced ultrafiltration (PEUF) is a method that uses water-soluble polymers to complex heavy metal ions to form larger particles[25]. Polymers are usually chemicals containing functional groups like sulfonate, phosphonic, or amine, which allows them to provide electrons into metal ions' empty orbits to form coordinate bonds.

However, MEUF and PEUF methods have several disadvantages: the recycling process of the surfactant and polymers will be needed to reduce the cost, which is still a complicated step in the process. Also, the large amount of metal ions in industrial wastewater requires many surfactant inputs to meet the need for reaction rate and efficiency[23]. Thus, MEUF and PEUF are more suitable to be used for wastewater that contains low-concentration heavy metal ions.

Membrane modification is another method to apply to ultrafiltration membranes. A common modification is layer-by-layer (LbL) electrostatic self-assembly to form polyelectrolyte multilayers (PEMs)[23]. This method can change the shape of ultrafiltration membranes and offer the characteristics needed. PEM modification is considered to be able to form membranes with high flux and good separation characteristics. C.Magnenet's team used ultrafiltration polyethersulfone (PES) membranes to be modified with poly allylamine hydrochloride (PAH) and poly acrylic acid (PAA) layer-by-layer to make copper removal membranes[23].

The membrane efficiency is defined as the percentage ratio of copper ions concentration in the permeate and the concentration in the flow-in water. Using MEUF modification with cellulose membrane and sodium dodecyl benzene sulfate (SDBS) as the surfactant, the removal efficiency can reach over 90% under the pH of 3-5. Using the PEUF modification method with PES membrane and poly acrylic acid-co-maleic acid as complexing agents, the removal efficiency has a maximum value of 99.84%[24].

2) Reverse osmosis

Reverse osmosis is a separation process that uses a semi-permeable membrane to block heavy metal ions and allow smaller particles to pass. The pore size of the

membrane is 0.5-1.5 nanometers, much smaller than ultrafiltration membranes[26]. Reverse osmosis has a wide range of applications in industry and environmental water purification processes. RO membrane's permeate flux is proportional to operating pressure, feed temperature and inversely proportional to feed concentration. The copper ion removal efficiency using hydroxyl (OH) functionalized graphene RO membrane reaches 100%, while boron (B-) functionalized graphene RO membrane has an efficiency of 98%[24]. Thus, RO membranes are considered one of the most effective processes for heavy metal ion removal.

3) Nanofiltration

Nanofiltration can be considered a relatively new advancement among various membrane separation methods[25]. Its separation sizes are located in the upper limit in reverse osmosis and the lower limit in ultrafiltration, encompassing MWCO values ranging from 100 to 1000 Daltons[24]. The critical difference between reverse osmosis and nanofiltration is that the latter blocks the way of only divalent salts and allows monovalent salts to pass, while reverse osmosis retains both types. Nanofiltration membranes consist of polymer composites of thin-film of chemical groups with negative charges. Using polyethersulfone NF membranes, the removal efficiency reaches 92% with a pH of 5 under the pressure of 4 bars[24].

4) Electrodialysis

Electrodialysis is a method that uses electric fields as forces to move ions. Cations and anions in the concentrated solution migrate towards the diluted solution, driven by the disparity in salt concentration. They traverse the CEMs (Cation Exchange Membranes) and AEMs (Anion Exchange Membranes)[25]. The dissimilarity in salinity on both sides of the membrane assists in facilitating the transportation of ions via the IEMs (Ion Exchange Membranes). This process can be harnessed to generate electricity by utilizing electrodes, namely an anode and a cathode. Normally, a large-scale ED system contains multiple CEMs and AEMs in the middle of cathodes and anodes. After an operating time of 120 minutes, copper ion removal efficiency is kept at 95%[27]. Nevertheless, the ED method shows a high cost of membranes and the requirement of electric potential[25].

The form of experiment data of several types of membrane is listed[24,25] (Table 3):

Table 3 Comparison of membrane

Membrane Type	Membrane material	Other ingredients	Initial Concentration	pH	Removal Efficiency
Ultrafiltration (MEUF)	Cellulose	Sodium dodecyl benzene sulfate (SDBS) or sodium dodecyl sulfate (SDS) as surfactant	1.6–8 mM (mg/L)	3.0-5.0	>90%
Ultrafiltration (PEUF)	Polyethersulfone(PES)	poly(acrylic acid-co-maleic acid)-PMA as complexing agent	100 and 400 (mg/L)	Maximum at 5	99.84%
Reverse Osmosis	Graphene	/	0.5 – 3.0 M (mg/L)	-	100.0%(for OH- graphene), >98.0% (for B-and 95.0%(for NH-graphene)
Reverse Osmosis	Spiral bound	/	50-200 ppm	2-10	96.1% at 50 ppm, 94.2 at 200 ppm
Nanofiltration	Polyethersulfone (PES)	Magnetic graphene-based composite (MMGO) to hybrid MMGO and PES polymer	200.0 (mg/L)	5.0	92.0%
Nanofiltration	polyethersulfone (PES)	Fe_3O_4@SiO_2–CS bionanocomposite to modify	100.0 (mg/L)	5.0	98.61%

2.3 *Electrochemical Cell*

Electrochemical processes have gained lots of interest and attention in recent years since it is a cost-efficient method and is widely used in treating industrial wastewater (figure 1). It actually has several advantages over other methods, for example, it doesn't need to react in a specific temperature or pressure, and it can adjust to the change in the flow rate. The electrochemical process involves the application of electricity to allow a current to flow through a metal-bearing solution in an aqueous medium. This solution comprises a cathode plate and an insoluble anode. During this treatment, heavy metals are precipitated as hydroxides in a weakly acidic or neutralized electrolyte. The selection of the electrode material is crucial as it not only determines specific application possibilities but also plays a vital role in enhancing the method's efficiency in dealing with different types of contaminated compounds.

During the process, copper sulfate and nickel sulfate serve as the electrolyte. Following the passage of the current, the following reactions occur:

At the cathode, the element with a higher reduction potential tends to gain an electron and undergo reduction through the oxidation process. Due to copper having a more positive standard reduction potential value, it is treated and removed from the solution before nickel. As the treatment progresses, hydrogen and oxygen are generated at the cathode and anode, respectively, within a few minutes.

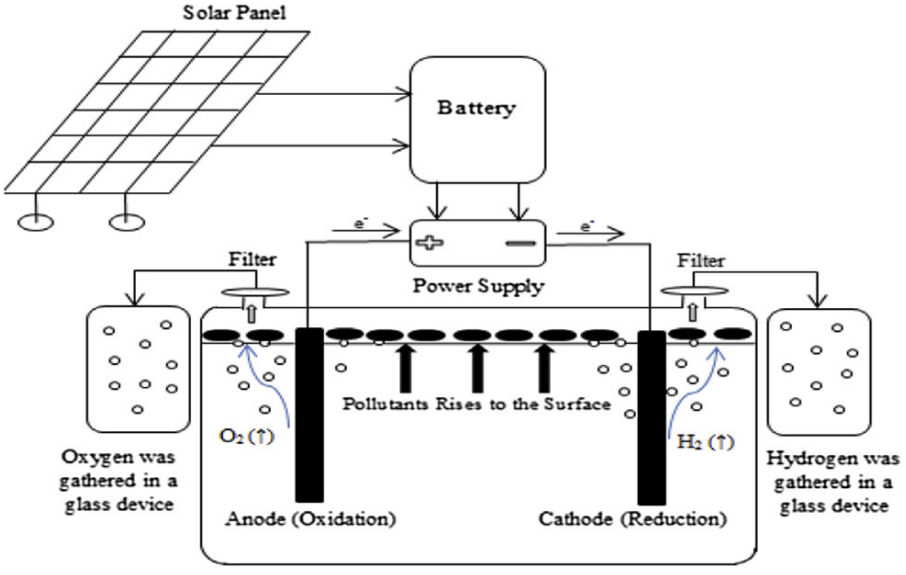

Figure 1: Electrochemical processes

In this study, a platinum-coated titanium panel anode has proven to be an excellent electrode. It not only provides significant electrical conductivity but also demonstrates superior durability. This ensures that the treatment can be extended without fear of damaging the electrode and decreasing electrochemical performance. Unlike conventional electrochemical processes, platinum does not participate in the reduction reaction (due to requiring a very large current for reduction), making the reaction at the anode a simple water electrolysis process.

Consequently, the sole focus should be on maintaining and enhancing the quality of the cathode. Previous studies by Naohide[28], Kobya[29], and Kashefialasl[30] have revealed that the current density not only determines the coagulant dosage and bubble generation rate but also influences solution mixing and mass transfer at the electrodes. Consequently, the charge loading value becomes the primary factor affecting the overall process efficiency, and this parameter itself is influenced by both cathodic and anodic reactions, which rely on the electrode's performance. Therefore, any improvement aimed at prolonging the cathodic reduction can be considered a valuable alternative factor.

The removal efficiency of copper ions mainly depends on the electrode material and the arrangement of the electrode. Compared to other works such as Nanseu-Nikki[31], Kabdash[32], and Safaei[33] (table 4), the electrochemical method demonstrates remarkable efficiency in removing metals, often yielding 95 to 99% removal rates for heavy metals. However, the main challenge lies in its cost-effectiveness, as the high initial investment and expensive electricity supply hinder its widespread adoption. To address this issue, integrating a solar energy source and utilizing economical materials like conductive carbon fiber cloth could prove highly beneficial for enhancing the practicality and broader implementation of electrochemical methods.

Table 4 Comparison of removal efficiency form different processes after 20 h treatment

The removal efficiency of the process after 20 h treatment				
	total collected metals (g)	overall removal efficiency of metals (%)	removal efficiency of coppers (%)	removal efficiency of nickels (%)
result of heavy metals removal process at far range after 20 hours	3.676	71	95	42
result of heavy metals removal process at medium range after 20 hours	3.765	96.5	98	55
result of heavy metals removal process at close range after 20 hours	3.762	97	98	45

2.4 *Using Graphene Oxide Electrode*

Recently, a new method to treat heavy metals in wastewater using graphene oxide electrodes was developed. The treatment method is based on the electrochemical deposition-based mechanism.[34] The graphene oxide electrodes provide positions for ions to form an electrical double layer by electric-field migration. This processing ultimately leads to heavy metal ion solid forms on the electrode.

The research team synthesized a new electrode called the 3D graphene oxide electrode (CF-GO). This was achieved by consolidating graphene oxide onto conductive carbon felt (CF) substrates through electrophoretic deposition. The microstructure of the 3D graphene oxide electrode (CF-GO) was obtained by scanning electron microscope (SEM). The SEM image shows the graphene oxide coating formed flower-like 3D structures surrounding each carbon felt fiber. Additionally, the image showed that the 3D CF-GO electrode had a surface area that was three times larger than that of the bare CF. High-density surface area can provide more binding sites for heavy metal ions to bind with surface functional groups.

The research designed a treatment system that can function in direct current (DC) and alternating current (AC) and deal with high and low concentrations of heavy metal wastewater. The wastewater treatment system is performed within a flow device, which contains one piece of 1 cm^2 CF-GO as the cathode, one piece of 1 cm^2 bare CF as the anode, and two pieces of Kimwipes, preventing contact between two electrodes.

1) Direct current (DC)

Eternal voltage was applied to the water treatment system. Cu, Cd, and Pb were chosen to represent the heavy-metal pollutants, and an initial concentration of 100 ppb was used. Figure 2 shows the results of the water treatment system removing Cu, Cd, Pd, and the mixture of those three heavy metals. The water treatment system shows an increased removal ability as the voltage increases for Cu, Cd, Pd, and the mixture of those three heavy metals. The removal ability showed an increasing trend as Cd < Cu < Pb. As the flow rate increases from 5 mL/min to 10 mL/min, the removal ability slightly decreases.

At 20 V, the remaining Cu, Cd, and Pb concentrations were 1.3, 2.3, and 0.74 ppb. The remaining concentration for those three heavy metals is all below the United States safe drinking level. The research also tested the water treatment system with two bare CFs. It shows some ability to remove heavy metals. However, it is much worse than CF-GO. This means more surface area provided by CF-GO helps more heavy metals to bind and form solids. Figure 2d shows the results of the system treating wastewater containing multiple heavy metals. At 20V, starting with 100ppb for each heavy metal, the removal efficiency for Cu, Cd, and Pb is 97.8%, 97.6%, and 98.6%, which is all below the United States safe drinking level.

In 1500 mL large quantity testing, the graphene oxide electrode wastewater treatment shows better removal efficiency than the adsorption method. After 1500mL heavy metal mixture containing 100ppb of each heavy metal flowed through the graphene oxide electrode wastewater, the Cu, Cd, and Pb concentration was lower than 5 ppb. Compared to the adsorption method, 77.5, 99.2, and 54.8 ppb, the graphene oxide electrode wastewater treatment exhibits a stronger removal efficiency.

The wastewater treatment system also tested its ability to remove high-concentration heavy metal wastewater (figure 2). The graphene oxide electrode wastewater treatment can treat high concentrations of up to 10,000 ppb. The removal efficiency for Cu, Cd, and Pb is 97.7%, 97.3%, and 98.5% for 1000 ppb under 20V. The removal efficiency for Cu, Cd, and Pb is 96.5%, 94.8%, and 98.5% for 10000 ppb under 20V.

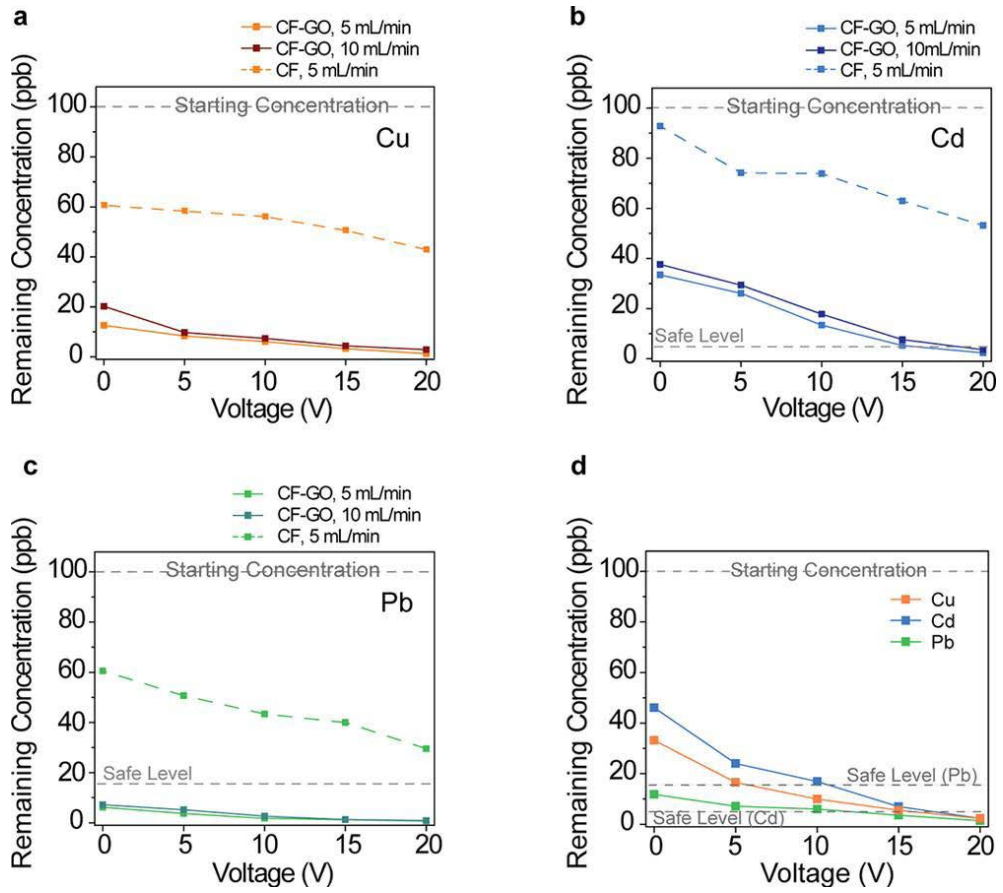

Figure 2: Figure a, b, and c shows the removal ability of Copper, Cadmium, and Palladium ions separately as the voltage increases. Figure d shows the removal ability of the Copper, Cadmium, and Palladium ions mixture as the voltage increases.

2) Alternating current (AC)

The graphene oxide wastewater treatment system can selectively recover metal ions from a pollution mixture by adjusting the AC amplitude, frequency, and offset. As shown in Figure 3, a heavy metal ions mixture solution containing around 1000ppm of Cu, Cd, and Pd. The system begins with -3.5 V and +1 V AC voltage at 50Hz, and the result shows over 99.9% of Pb was removed from the heavy metal wastewater mixture in 8 hours. Then the system was tuned to -4 V and 0 V at 50 Hz, and the Cu concentration rapidly decreased in 2 hours. Lastly, the system was tuned to -5 V and - 2 V at 4 MHz, and more than 99.9% of Cd ions were recovered.

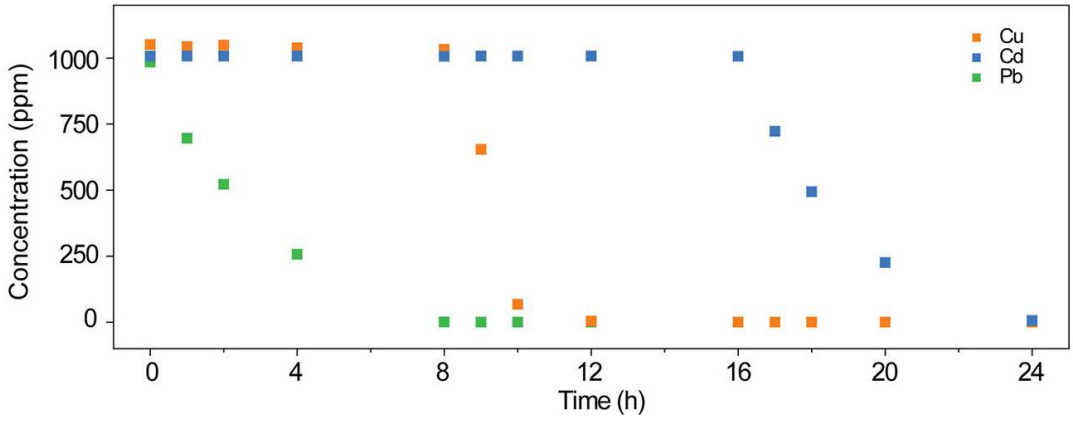

Figure 3: The figure shows the Copper, Cadmium, and Palladium ions were removed separately under different amplitude, frequency, and offset settings.

3. Comparison and analysis

3.1 *Efficiency*

The efficiency of copper ions removal methods is the most crucial aspect of determining the availability of the method. We chose one representative removal efficiency data of each method and listed them together in table 5:

Table 5: Comparison of efficiency from different methods

Method	Material/Condition	Removal efficiency
Adsorption	Fe_3O_4	98%
Electrochemical method	Graphene Oxide Electrode 20 V, 5 mL/min	98.7%
Ion floatation	Sodium dodecyl sulfate (SDS) [SDS] total=5.85 mmol/L, [EtOH]=0.5%(v/v), total=5 h, flotation stages=3	85%
Membrane-based	Polyethersulfone (PES) with poly (acrylic acid-co-maleic acid)-PMA as complexing agent	99.84%

This form shows that absorption, electrochemical and membrane-based methods all have an excellent removal efficiency above 98%, while the ion floatation method reaches an efficiency of 85% (ion flotation efficiency can reach a much higher amount under more challenging experiment conditions). All copper ion removal methods have high removal efficiency under certain experiment conditions. Except for these representative examples, the efficiency number of other examples is basically over 80%. This illustrates that all methods are highly effective.

3.2 *Feasibility and cost*

The feasibility of each method determines whether it can be used in actual conditions to solve realistic problems. Feasibility includes the evaluation of operational difficulty, facility requirements, operating time, and other factors. Cost is another crucial aspect to consider in choosing suitable methods.

Electrochemical treatment is suggested because of its metal selectivity. It needs no consumption of chemicals. Pure metals can be attained through this process. On the contrary, the initial solution pH that contains copper ions is required to be controlled. Additionally, electricity is needed to operate, which must be generated with large-scale facilities if used in wastewater treatment. All those factors show that this method has a high capital and running cost[35]. A specific application in electrochemical treatment, graphene oxide electrode, is only tested at room temperature and pH=7 conditions. Thus, it is still not determined whether this method can be used in actual conditions since wastewater is not likely to be in experimental conditions.

Absorption has a low operability difficulty, together with high flexibility and design simplicity. The cost of absorption is relatively low. Moreover, the pH level slightly affects the absorption efficiency. In contrast, excess waste production remains a problem since extra work is required to eliminate those compounds[35].

Ion flotation has high feasibility since it has a low operability difficulty. A bubble addon is exerted into the facility to help with the separation process[35], enhancing operational simplicity. Still, the maintenance and operational cost is high for this method.

Membrane methods are granted for their high separation selectivity. However, the disadvantage in operating is considerable because of membrane fouling. Membrane fouling refers to the accumulation of ions blocked on the membrane that hinders the water flow[23]. Additional work to clean the membrane is required, enhancing the operational difficulty and cost. Also, reverse osmosis methods need high pressure to push the liquid through the membrane. This requirement increases the cost and the facility size.

In conclusion, all methods have their own advantages and disadvantages in feasibility and cost. In order to choose the most suitable one for wastewater treatment, the factories should find out the best one according to their own condition, including budget, size/scale, environment, and so on.

5. Conclusion

In this paper, we discussed mechanisms, copper ion removal efficiency, and other aspects of the membrane-based method, electrochemical method, adsorption, and ion flotation. These methods all have excellent removal efficiency (generally over 90%). We compared those aspects to analyze the advantages and disadvantages of feasibility

and cost. Since the benefits of the methods are different, it is hard to find a perfect method for industrial wastewater treatment. Thus, factories and industries should consider their own situation to determine the way they choose to remove copper ions in wastewater according to the advantages and disadvantages that we have discussed.

Our research has several limitations. Not all copper ion removal methods are covered in this research, such as chemical precipitation or photocatalysis. Also, much data that is discussed in this research is from experimental conditions, so the results of the research are more likely theoretical. Currently, industries near the Mississippi River use chemical precipitation methods to remove copper ions in wastewater because of its simplicity and low cost. All four methods in this research have relatively higher costs, so they are generally not applied to be used in industries. Thus, more research on those methods is needed to optimize the feasibility and reduce the cost to make them available in the future.

Acknowledgement

All the authors contributed equally to this work and should be considered as co-first author.

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