

INVESTIGATING THE ROLE OF MEMBRANE FILTRATION TECHNOLOGIES IN THE TREATMENT OF NICKEL PLATING WASTEWATER.

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Abstract

The electroplating process used in the manufacturing of chrome, nickel, and copper results in the generation of a significant quantity of wastewater. The primary sources of wastewater are wash water from the plating process, wash water from the plant, and cooling and wash water from the equipment. These wastewaters include a wide variety of metal components, which results in the concentrations being quite distinct from one another. Because metal ions are capable of inflicting significant damage not only on people but also on animals, plants, and the environment as a whole, it is essential to treat effluent from electroplating in order to eliminate these substances. Electroplating wastewater also contains a huge number of complexes, all of which are notoriously difficult to eliminate through the use of standard precipitation methods. According to the findings of this research, the iron reduction co-precipitation method is an effective way to get rid of hexavalent chromium, break down nickel and copper complexes, and lower the amount of chemical oxygen demand (COD). Because the concentration of chromium, nickel, and copper ions remained consistent at 0.1 ppm on average, and the concentration of COD remained steady between 20 and 30 ppm, quick processing by one-time treatment was possible to fulfil the emission limits of India.

Keywords: *Filtration, technologies, treatment, nickel, wastewater*

Introduction

If we want to maintain a clean and healthy environment, we need to confront the growing problem of water pollution and how to best regulate it. This is a problem that affects people all over the world. In order to maintain a healthy life, all living organisms face the challenge of finding clean and pure water on a worldwide scale. At the moment, over 11% of people throughout the world do not have access to clean water for drinking. There may be a scarcity of water for as many as 4 billion people by the year 2050, as reported by the World Health Organization (WHO). Water makes up 70% of the surface of the world; however, 97% of this water is extremely salty, and the remaining 3% is locked up in the earth's crust, glaciers, and ice caps. We only have access to a fraction of one percent of the water in the globe. Because of the enormous increase in population in the domestic, industrial, and agricultural sectors, which consume 8, 22 and 72% of fresh water respectively,

and this has resulted in the generation of a large amount of wastewater that contains a large number of contaminants, there has been an increase in the amount of pollution in the world's water supplies. Dye and hazardous metal pollutants are two key types of contaminants that may be found in aquatic environments. Once these contaminants are present in water, the water is no longer clean and suitable for human consumption, and it is very difficult to remediate contaminated water. The poisoning of hazardous metals has developed into a significant and severe concern that not only threatens the health of people but also the health of the environment. In recent years, the toxicity of heavy metals and their influence on the environment have attracted much noteworthy and widespread attention. This focus has grown steadily over time. Heavy metals that are hazardous to humans are regarded to be toxic components because they have the potential to disrupt the natural environment even at low concentrations and have a propensity to penetrate the food chain. Toxic metal ions are the source of water pollution, and they are created by processes such as electroplating, mining, pigments, alloys, industries related to aerospace, rubber, plastics, and batteries. In addition, nickel is one of the hazardous heavy metal ions that cannot be broken down by biological processes and is found in aquatic environments. Nickel Ni(II) is the 24th most plentiful element and is silver-white in colour, hard, and ductile in nature. Its atomic number is 28, and its atomic mass is 58.71. The most frequent oxidation state for nickel is +2, however the metal may exist in oxidation levels ranging from -1 to +4. Several industrial and commercial applications make use of nickel alloys and nickel compounds in their respective formulations. Ni(II) compounds, when present at low concentrations, have the potential to be employed as enzyme activators and to contribute to metabolic processes. Compounds containing nickel that are used in excessive amounts have a tendency to harm the environment. Some nickel compounds, such as carbonyl, have a naturally carcinogenic effect and are readily absorbed via the skin. The maximum concentration of nickel metal ions that can be found in water that is suitable for human consumption is 0.02 mg/L. If this concentration is exceeded, it can lead to a number of diseases, including diarrhoea, anaemia, hepatitis, kidney damage, gastrointestinal distress, skin dermatitis, and dysfunction in the central nervous system.

Sources of Nickel (II) in Environment

Many diverse sectors, including electroforming, electroplating, alloys, aerospace industries, rubber, plastics, batteries, and mining, are responsible for exposing nickel compounds. In addition, they have applications in the fields of medicine and the production of jewellery and cast coins. There are many different kinds of causes of nickel pollution in the environment, such as the manufacture and processing of nickel compounds and their derivatives, the disposal of nickel waste, and the recycling of nickel waste products. Here are some examples. It is also possible to get Ni(II) compounds in the soil, where they can be found in both soluble and insoluble forms. Ni(II) is also found in the natural world, and the species that it takes on are determined in part by the contamination's origin. The many human and industrial sources of waste are disposed of in the form of silicates, oxides, sulphides, and certain soluble forms. The disposal of Ni(II) in air pollution was also contributed by the burning of coal and oil. The sediments and the leaching of the rocks both revealed a considerable concentration of nickel in the water. This nickel was found in both dissolved and undissolved suspended forms. The divalent form of nickel, known as Ni(II), can be found in high concentrations in aquatic environments. The properties of nickel compounds are affected by pH as well as inorganic and organic binding sites.

Nickel Toxicity

The harmful effects of nickel on health are variable depending on the route of exposure, which might be cutaneous, oral, or inhaled. There are two different kinds of exposure, which are referred to as acute exposure

and chronic exposure respectively. Nickel's most harmful effect on human beings is an allergic reaction that is extremely sensitive to nickel's presence. Nickel is not only a known allergy but also a factor in the development of a number of disorders, including dermatitis of the skin, anaemia, hepatitis, kidney damage, gastrointestinal discomfort, and digestive upset. Moreover, it has the potential to cause hypersensitivity, immunomodulation, as well as immunotoxicity in human beings. According to the findings of the International Agency for Research on Cancer (IARC) and the Department of Health and Human Services (DHHS) of the United States, all nickel compounds, including sulphates, chlorides, carbonates, and nitrates, have the potential to cause cancer and are toxic in their natural state. The fact that nickel is taken up so readily demonstrates that it is naturally teratogenic, poisonous, and carcinogenic. The impact of a meal containing nickel metal on the tissues of chickens and pigsmk was investigated by Anke and colleagues. They found that the content of nickel reduced in many tissues of hens and pigs when the concentration of other metals, such as manganese, magnesium, and zinc, increased. It is possible that the growth of chickens might be negatively affected if the zinc content was lowered. Researchers from a variety of fields came to the conclusion that nickel triggers an allergic reaction in the human body. Nickel can be found in the environments of almost 10–20 percent of the world's population. Nickel's interaction with skin may potentially result in the development of dermatitis. It is vital to realise the actual and effective treatment procedure for the remediation of more nickel from our aquatic environment because of the harmful effects that nickel has on human health. There were a few distinct review papers that were published for the treatment of heavy metals using a variety of approaches. Yet, none of them has provided a comprehensive explanation of a single metal ion in particular. As a result, the goal of this work is to conduct an in-depth analysis of various different removal methods for the elimination of nickel ions from aqueous environments. So, by reading this review paper, the younger researchers may acquire entire facts on the path in which they need to begin their study and continue to develop it in the future.

method

The effluent from an electroplating park in Ningbo was utilised in this experiment. The wastewater included chromium, nickel, and copper at the particular amounts that are outlined in table 1. In order to successfully remove the heavy metals from the water, demonstration tests were carried out.

Table 1. concentrations of heavy metal ions in the wastewater coming from an electroplating park in Ningbo.

	Raw water concentration	pH	COD _{Cr}	Cr ⁶⁺
Nickel	200.93 ppm	9.8	890 ppm	
Chromium	257.76 ppm	2.9	254 ppm	111.6 ppm
Copper	152.46 ppm	1.2	537 ppm	

Chromium reduction, precipitation and co precipitation

In the first experiment, the effects of direct precipitation separation were measured. In the second experiment, reduced agent reduction-precipitation separation was investigated. In the third experiment, reduced agent reductiontrivalent iron co-separation was evaluated. And in the fourth experiment, iron reduction-coprecipitation separation was investigated. ICP Emission Spectroscopy was used to determine the amount of chromium present. In a nutshell, a standard curve was constructed with the help of five distinct sets of standard solutions, and then the total chromium content in the test solution was calculated and determined. The

concentration of hexavalent chromium in the raw liquid was determined with the assistance of a HZ-7000 electromeasurement equipment, and the sample was evaluated using CV cyclic voltammetry at a pH value of 1. The scanning speed was 20 mV/s, the sample period was 0.5 seconds, and the reference electrode was constructed of Ag/AgCl. The positive and negative electrodes both consisted of graphite. Altogether, measurements were taken from ten different groups, with the first set potential being -1.5 V and the second set potential being +1.5 V. A CV cycle diagram of the raw water and the reacted solution was generated once the measurement was complete.

Nickel reduction, precipitation and coprecipitation

Experiments one through three, in order, explored the separation of iron by sedimentation, the separation of ferric iron via coprecipitation, and the separation of iron via reduction and coprecipitation, respectively. We used the ICPS-7000 standard to determine the amount of nickel present in each sample.

Copper reduction, precipitation and coprecipitation

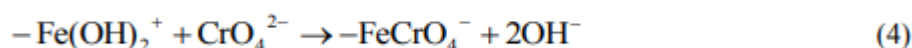
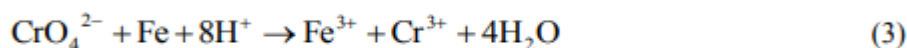
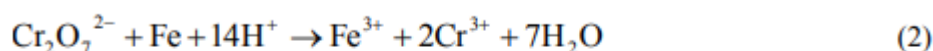
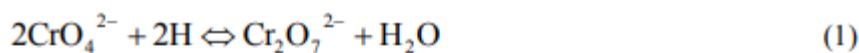
Experiments one through three explored the separation of iron by sedimentation, the separation of ferric iron via coprecipitation, and the separation of iron via reduction and coprecipitation respectively. Using an ICPS-7000, the amount of copper that was found in the samples was calculated.

Results and discussion

After the iron reduction-coprecipitation reaction, the concentrations of heavy metals in liquids were analysed, and changes in the valence of elements were detected by an inductively coupled plasma (ICP) and an electrochemical measurement system to determine the residual concentrations of chromium, nickel, and copper, as well as the reduction ratio of Cr (VI). The efficacy of the removal of heavy metal components over a given time period was indicated by analysing the difference in the concentrations of heavy metal components in the liquid before and after the reaction was carried out. The iron reduction-co-settlement was found to be feasible after being subjected to testing and analysis by both the experimental group and the control group.

Chromium reaction principle and results analysis

The experiment was carried out at room temperature, which is equal to 25 degrees Celsius, and the reaction principle was broken down into two distinct phases: reduction and co-sink. It is hypothesised that the following reaction formulae will take place throughout the experiment:



The insoluble electrolyte chromium hydroxide precipitates as an ion under conditions of perfect reduction (equation 6). These conditions are described in the previous sentence. The equilibrium point for the rate of precipitate dissolution was attained when the rate of decomposition of precipitation was equal to the rate at which precipitation was being formed. The theoretical elution quantity of trivalent chromium in solution might be estimated as follows, in accordance with the K_{sp} of chromium hydroxide at normal temperature:

$$K_{sp} = [Cr^{3+}] [OH^{-}]^3 = 6.3 \times 10^{-31}$$

When the pH of the solution is 12, the dissolution concentration of Cr^{3+} is as follows:

$$[Cr^{3+}] [10^{-2}]^3 = 6.3 \times 10^{-31}, [Cr^{3+}] = 6.3 \times 10^{-25} \text{ (mol/L)}$$

$$Cr^{3+} = 51.996 \times 6.3 \times 10^{-25} = 0.328 \times 10^{-19} \text{ (mg/L)}$$

The results of the calculations show that the concentration of trivalent chromium in the dissolution is extremely low, and that the majority of the chromium ions that were left over were of the hexavalent kind. Figures 1 and 2 illustrate the findings of a cyclic voltammetry (CV) test conducted on the untreated raw water and treated liquids, respectively. The concentration of Cr^{6+} in the solution may be determined in the fourth quadrant of the redox coordinate axis by measuring the vertical distance that separates the highest point of the cycle curve from the X-axis. Following then, starting from the greatest point in the fourth quadrant, the curve descends steadily until it reaches the third quadrant. The transformation from Cr^{6+} to Cr^{3+} is a linguistic representation of this alteration. The vertical lengths from the highest point of the fourth quadrant to the X axis before and after the response are represented by vertical lines with a length ratio of 206: 0.48 in the two figures that are located above this one. The length ratio provided a visual representation of the changes in valence that occurred in the hexavalent chromium found in the liquid both before and after the reaction.

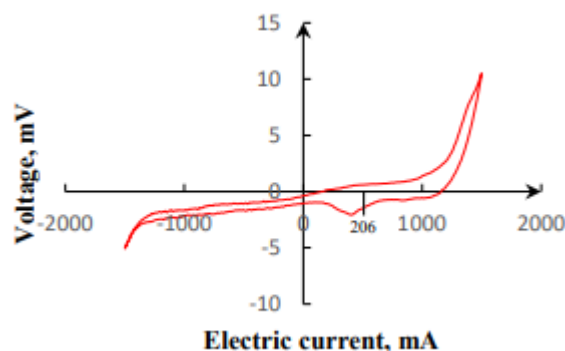


Figure 1. Chromium content before treatment.

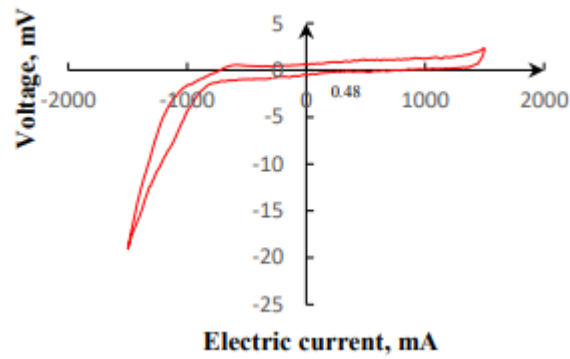


Figure 2. Chromium content after treatment.

Table 2. Measured chromium concentrations in treated water.

	Cr	Cr ⁶⁺	COD _{Cr}
Experiment One	134 ppm	82 ppm	176 ppm
Experiment Two	2.01 ppm	0.24 ppm	153 ppm
Experiment Three	1.02 ppm	0.08 ppm	89 ppm
Experiment Four	0.092 ppm	0.06 ppm	35 ppm

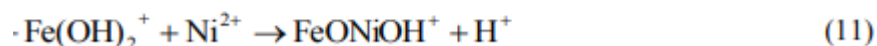
In the iron reduction-coprecipitation technique, the treatment efficiency of Cr and the reduction efficiency of Cr 6+ could be estimated if the findings of table 2 were taken into account. Since the hexavalent chromium ions must first be decreased before the precipitation process can begin, the technique of direct precipitation cannot be utilised in the treatment of chromium wastewater. Not only did the iron reduction approach (equations (2) and (3)) demonstrate reduction rates of 99.95% for hexavalent chromium, but it also had a positive effect. The effects of co-precipitation with ferric iron and chromium were better than those of the separate precipitation when the same reducing conditions were used for chrome wastewater. After the process, the iron and chromium ions that were formed attained the effect of co-precipitation when subjected to particular circumstances.

$$\eta_{Cr^{6+}} = \frac{\text{stock}C_{Cr^{6+}} - C_{Cr^{6+}} \text{ filtrate}}{\text{stock}C_{Cr^{6+}}} \times 100\% = 99.95\% \quad (7)$$

$$\eta_{Cr} = \frac{\text{stock}C_{Cr} - C_{Cr} \text{ filtrate}}{\text{stock}C_{Cr}} \times 100\% = 99.96\% \quad (8)$$

Nickel reaction principle and results

The experiment was carried out at normal room temperature, and the reaction principle was broken down into two distinct phases: reduction, and co-sinking. The following are hypothesised to be the reaction formulas [7] observed in the experiment:



According to the potential of the standard electrodes of Fe and Ni, which are $E^0 \text{Fe} = -0.409\text{V}$ and $E^0 \text{Ni} = -0.233\text{V}$, the oxidation of nickel ions is larger than that of iron ions, which is why iron is able to reduce nickel ions (equation (9)). Nevertheless, as reaction time grew, the decreased nickel attached to the surface of the iron, which caused the reaction rate to drop. As a result, it was hypothesised that there was an ideal moment in time for the reaction to take place. When the solution's pH rose, nickel ions began to precipitate out of solution as hydroxides. So, based on the K_{sp} of nickel hydroxide, one might use equation to determine the theoretical elution concentration of nickel ion in solution (10).

$$K_{sp} = [\text{Ni}^{2+}] [\text{OH}^-]^2 = 5.48 \times 10^{-16}$$

When the pH of the solution is 12, the following equation describes the concentration of Ni^{2+} in the dissolved state:

$$[\text{Ni}^{2+}] [10^{-2}]^2 = 5.48 \times 10^{-16}, [\text{Ni}^{2+}] = 5.48 \times 10^{-12} \text{ (mol/L)}$$

$$\text{Ni}^{2+} = 58.69 \times 5.48 \times 10^{-12} = 0.322 \times 10^{-6} \text{ (mg/L)}$$

According to the findings of the calculations, the concentration of nickel ions in the solution might be lowered by less than 0.1 ppm if direct precipitation was used to remove nickel from wastewater that contained nickel that was present with free ions.

Table 3. Measured nickel concentrations in treated water.

	Ni	COD _{Cr}
Experiment One	11.63 ppm	194 ppm
Experiment Two	2.367 ppm	86 ppm
Experiment Three	0.081 ppm	25 ppm

Throughout the process of iron reduction and co-settlement (equation 11), the amount of time that had passed had a substantial impact on the variations in nickel content. This is seen in figure 3. At 30–40 minutes into the experiment, the response rate reached its maximum. When forty minutes had passed since the beginning of the reaction, the concentration of nickel in the filtrate had dropped to less than 0.1 parts per million (ppm), and it had already started to climb. Hence, the best amount of time for the reaction was forty minutes. Using the data found in table 3, we were able to determine the treatment effectiveness of the iron reduction-co-settlement technique, which is denoted by the symbol Ni. In most cases, a significant quantity of complexing agent was included in the nickel plating process. This contributed to the production of complexed nickel molecules, which made it challenging to precipitate the nickel. Despite the fact that the nickel wastewater was precipitated as a result of an increase in pH directly.

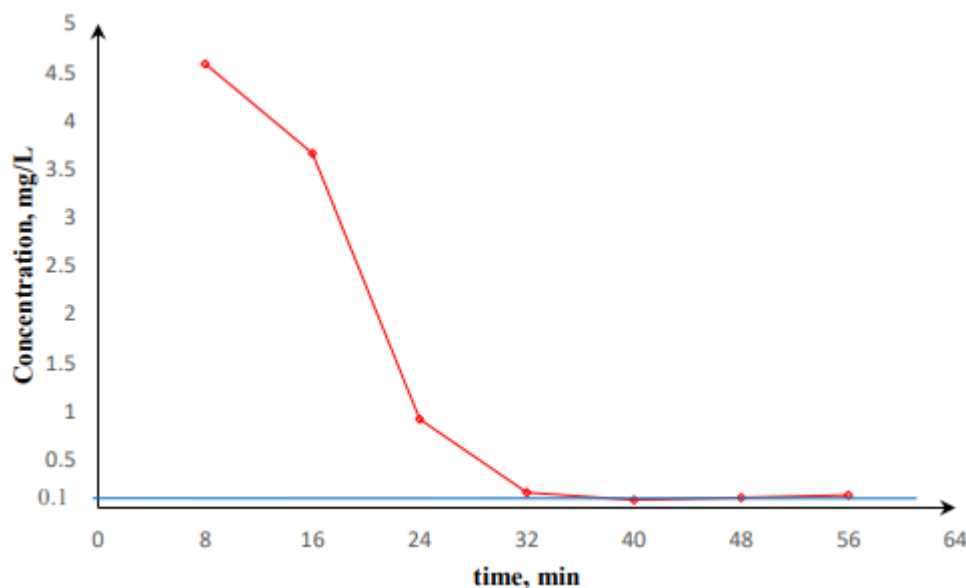


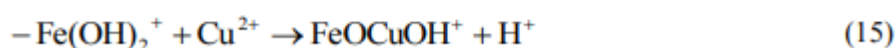
Figure 3. Variations in the concentration of nickel in the filtrate as a function of reaction time.

technique, the concentration of nickel in the filtrate was still quite high, and the resulting molecule was thought to be a complexed form of nickel. Nevertheless, the removal rate of heavy metal nickel reached 99.95% in the experimental group that used iron reduction and co-sinking. This indicates that the iron reduction and co-sinking approach had some influence on the disintegration of the complex.

$$\eta_{\text{Ni}} = \frac{\text{stock}C_{\text{Ni}} - C_{\text{Ni}} \text{ filtrate}}{\text{stock}C_{\text{Ni}}} \times 100\% = 99.95\% \quad (12)$$

Copper reaction principle and result analysis

Throughout the course of the experiment, there was a noticeable crimson coating on the surface, and scientists determined that it was reduced copper. The experiment was carried out at room temperature, and the reaction principle was broken down into two distinct components: reduction and co-sink. The following are hypothesised to be the reaction formulas observed in the experiment:



According to the reaction formula, the primary cause for the decrease in the amount of copper was the reduction of copper ions, which was followed by their co-precipitation in the precipitate. The amount of copper metal that was reduced by iron wrapped around the surface of the iron (equation (13)), which stopped any further reaction from occurring, rose as the reaction time grew. As a direct consequence of this, the optimum level of reduction efficiency was accomplished in the minimum amount of time. Copper and iron ions precipitated as hydroxides when the pH of the reaction was gradually raised, and the theoretical concentration of copper ion in solution could be determined using the K_{sp} of copper hydroxide according to the equation (14) given above.

$$K_{sp} = [\text{Cu}^{2+}] [\text{OH}^-]^2 = 4.8 \times 10^{-20}$$

When the pH of the solution is 12, the dissolution concentration of Cu^{2+} is:

$$[\text{Cu}^{2+}] [10^{-2}]^2 = 4.8 \times 10^{-20}, [\text{Cu}^{2+}] = 4.8 \times 10^{-16} \text{ (mol/L)}$$

$$\text{Cu}^{2+} = 63.54 \times 4.8 \times 10^{-16} = 0.305 \times 10^{-10} \text{ (mg/L)}$$

According to these calculations, the amount of copper ions that dissolve in solution is completely insignificant. As can be seen in figure 4, the reaction of iron reduction and co-precipitation (equation (15)) stabilised after approximately twenty minutes. This occurred as the reduced copper metal wrapped the surface of the iron carrier, which decreased the effective reaction area and consequently slowed the reaction rate gradually. After that, the effectiveness of the iron reduction-coprecipitation method's Cu treatment and Cu^{2+} reduction was determined using the data presented in table 4. After doing the math based on the concentration of the raw water, it was determined that the reduction process was extremely important since it was responsible for around 88.06 percent of the overall processing efficiency. The elimination rate of the heavy metal copper reached 99.94% in the experimental group that utilised the iron reduction-coprecipitation approach, demonstrating that the treatment was effective.

Table 4. Copper concentrations in water that has been treated were measured.

	Cu	COD _{Cr}
Experiment One	9.8 ppm	249 ppm
Experiment Two	5.15 ppm	64 ppm
Experiment Three (After Reduction)	18.2 ppm	346 ppm
Experiment Three (After Precipitation)	0.0922 ppm	23 ppm

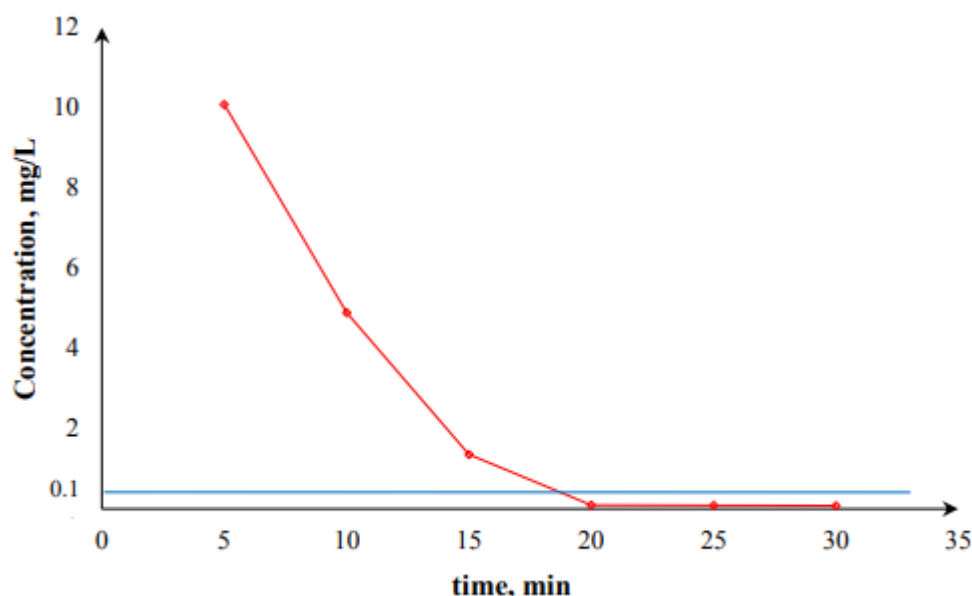


Figure 4. Variations in the amount of copper in the filtrate as a function of reaction time.

$$\eta_{\text{Cu}^{2+}} = \frac{C_{\text{Cu}^{2+}} \text{ before.reduction} - C_{\text{Cu}^{2+}} \text{ after.reduction}}{C_{\text{Cu}^{2+}} \text{ before.reduction}} \times 100\% = 88.06\% \quad (16)$$

$$\eta_{\text{Cu}} = \frac{\text{stock.C}_{\text{Cu}} - C_{\text{Cu}} \text{ filtrate}}{\text{stock.C}_{\text{Cu}}} \times 100\% = 99.94\% \quad (17)$$

Conclusion

According to the findings of this research, the effluent from electroplating may be safely handled using the iron reduction-precipitation principle. The wastewater contains chromium, nickel, and copper. When it came to the treatment of the chromium wastewater, the decrease rate of hexavalent chromium was absolutely necessary. The elimination rate was raised to 99.96% when the iron reduction technique was combined with the coprecipitation method. The reduction rate of hexavalent chromium was reduced at a rate of 99.95% in a short amount of time utilising the iron reduction method. In addition, the best removal rates of 99.95% and 99.94% were achieved for the treatment of nickel and copper wastewater when the reaction time was either 40 minutes or 30 minutes. This was the case for both nickel and copper wastewater. When the effluent from chromium-nickel-copper electroplating was treated using the iron reduction-coprecipitation technique, there was a significant improvement in the quality of the treated water under specific circumstances.

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