

Heavy Metal Removal from Ore Processing Plant Wastewater by Electrocoagulation Process

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Abstract: Discharging wastewater originating from industries to the receiving environment without any purification causes environmental pollution and endangers biotic life. When the literature is examined it seems that there are studies on acid mine drainage but purification of ore processing wastewater by electrocoagulation (EC) is not seen much. In this study the heavy metal removal from wastewater of ore processing facility (magnetite crushing, screening and washing facility) by using electrocoagulation process was investigated. At the EC process Ferrum-Ferrum electrode was used in parallel. The removed heavy metal parameters have been identified as: Ni^{2+} , Zn^{2+} ve Cr (VI) . In this research study as a result: At removal of Nickel it has been obtained %98,14 efficiency by $21,3\text{mA/cm}^2$ current density, 20 minute contact time and 8,5 pH value, at removal of Zinc, it has been obtained %97,80 efficiency by 16mA/cm^2 current density, 40 minute contact time and 8,5 pH value, at removal of Chrome^{+6} , it has been obtained %98,20 efficiency by 16mA/cm^2 current density, 20 minute contact time and 7 pH value.

Keywords: Electrocoagulation, Magnetite, Wastewater, Removal, Heavy Metal

Introduction

As a result of the rapid population growth in the world and in our country, the needs have also increased. The supply required to meet the demands indirectly caused the increase of industrial facilities and the development of production (Bayar, 2014). With industrialization, environmental pollution has occurred and living life has been threatened. Discharge of solid, liquid and gas wastes before and after industrial plants to receiving environments without treatment has left impaired impacts on the environment that are difficult to repair. These environmental pollution has exceeded nature's absorption capacity and adversely affected living life. In order to minimize these negative effects, it is of great importance to determine the wastes causing pollution and to carry out studies on how to eliminate them (Kasap, 2017; Yılmaz, 2009).

Underdeveloped and developing countries can only treat 5% of waste water. Since the remaining industrial and domestic wastewater is supplied to the environment uncontrolled, underground and aboveground supplies are polluted day by day. As a result of this pollution, the effects of global climate change are being felt intensely. These kinds of effects cause floods, drought and irregularities in annual precipitation rate. These kinds of effects cause floods, drought and irregularities in annual rainfall rate. Water quality is affected by environmental conditions. One of the most important problems of today is the decrease in drinking water resources (Bayar, 2014; Şık, 2015). According to the UNESCO report, it is stated that one billion eight hundred thousand people will experience water shortage in 2025. It is stated that 40% of the population in approximately 80 countries will

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be insufficient to meet their water needs due to the population density and the uneven distribution of water resources in the last decade. By 2025, the amount of water per capita is expected to decrease by half (Öztürk & Çelik, 2008). The need for clean water is an important issue, especially in third world countries. Developed countries like America think that wastewater treatment is a "critical need" due to urbanization, ever-increasing population and climate changes, and they are doing intensive studies on this subject (Güney, 2013). The need for economical, fast and highly transformable, feasible wastewater treatment systems has become a necessity in terms of being integrated into the rapidly developing world in order to ensure a healthy environment in our country's accession and harmonization process to the European Union (Bayar, 2014). With the increase of regulations on wastewater treatment, great efforts are being made to develop new technologies and procedures for water treatment alongside traditional treatment methods (Çebi, 2018). Among the industries that cause environmental pollution, one of the industries with great strategic importance is the mining industry. Due to the different geological structures and tectonic structures in our country, there are a wide variety of mineral ores. Mining, which is one of the important sectors for the economy, includes all activities that provide basic raw materials in sectors such as industry and energy for national development. Mines are among our natural resources and it is inevitable to be used for demands. As a result of these mining activities, wastewater containing high amounts of metal occurs. The fact that these waters reach lakes and rivers without treatment poses a threat to water resources (Yücesoy, 2011). In addition, geological wastes containing heavy metals can cause great damage to the environment and the health of the living creatures around them when they mix into the soil or water resources uncontrolled (İşler, 2019).

The reasons for entering the mining sector in research such as electrocoagulation: 1. Reusing the water it needs during production to deal with the danger of drought as well as environmental pollution. 2. Dewatering the final product. 3. To recover fine ores and by-products released as a result of ore preparation and enrichment processes (Atay, 2019). Electrocoagulation, used as a wastewater treatment technology, is a long-standing method used to remove a variety of pollutants. In the early days, electrocoagulation (EC) was not developed in terms of electrode reliability (especially passivation of electrodes over time) and lack of a systematic approach for reactor design and operation. Thanks to the latest technical developments and the increasing need for small-scale water treatment plants, EC has been brought to the agenda again (Holt et al, 2005). EC is a simple and effective method for wastewater treatment. This method; It is a low cost and environmentally friendly treatment method that can be used in industrial wastewater containing heavy metals, wastewater containing suspended solids, wastewater containing oil, etc. (Karagözoğlu & Malkoç, 2017; Gülyaşar, 2019).

EC process is a method of wastewater treatment with an electrolysis system using a metal electrode and a double-sided (anode and cathode) mechanism. It is based on the principle of forming coagulants by electrically dissolving the electrode material used during the process (Yılmaz & Karagözoğlu, 2019). In this study, the raw wastewater generated in the ore preparation phase (crushing and screening plant) of the Chrome-Magnesite plant operating in the Konya region was taken. It was transported according to standard methods and stored in the laboratory. Heavy metal removal efficiency has been investigated in the EC process. The pH value of the wastewater is 8.5 and its electrical conductivity is 35 μ S/cm. Electrocoagulation application was carried out by rotating iron-iron (Fe-Fe) electrodes to treat the ore washing wastewater of the Chrome-Magnesite crushing and screening plant.

In the electrocoagulation (EC) process, the heavy metal removal efficiency of the raw wastewater was investigated by optimizing the solution environment pH, current density and reaction contact time. The characterization of ore washing wastewater taken from the Chrome-Magnesite crushing and screening plant is given in Table 1.

Table 1. Crushing and screening plant ore washing wastewater characterization

Parameters	Measurement Value
pH	8, 5
Conductivity	395 μ S/cm
COD	103 mg/L
Chromium (IV)	10 mg/L
Zinc	5,74 mg/L

In the study, the removal efficiencies of Nickel, Zinc, Chromium (VI) with different electrodes, different pH values, different currents and different durations were examined.

Material and Method

The studies were carried out in a glass plexiglass (mica) reactor at room temperature and Fe-Fe electrode pairs were used. Rectangular electrodes with side lengths of approximately $6 \times 12 \text{ cm}^2$ were used in the reactor, and the average weight of the electrodes used was measured around 100 grams. During the EC process, 2 plexiglass reactors were used simultaneously and the wastewater volume used was approximately 500 mL and the mixing speed was 100 rpm. While pH adjustment was made in the reactor, solutions of HCl and NaOH (0.1 N-1 N) were used, while the required doses of NaCl were used for conductivity adjustment. The EC reactor assembly used is shown in Figure 1.



Figure 1. Visual presentation of EC process in the laboratory

DC power supply with 0-30 V / 0-5 A current density was used in the reactor, and the effects of pH, reaction time, current density and electrode types on removal efficiency were investigated. Coagulant precipitation process: At the end of the reaction, the treated waste water was taken into 500 mL measure and it was waited for sludge to settle for 1 hour. Precipitated sludge amounts were recorded by reading, and pollutant removal efficiencies were calculated in the samples taken from the supernatant after treatment.

Results and Discussion

Within the scope of the study, firstly, pH optimization, Current optimization and Time Optimization were carried out by using Fe-Fe electrodes and Nickel, Chromium (VI) and Zinc removal efficiencies at different pH, current density and contact times were examined.

pH Optimization and Pollution Removal Using Fe-Fe Electrode

At this stage of the study, Nickel, Chromium (VI) and Zinc removal efficiencies at pH 3, 5, 7 and 8.5 (original pH) were investigated by using Fe-Fe electrodes for 20 minutes of contact time, current density of 10.67 mA/cm^2 . The graphic below was created as a result of this experiment.

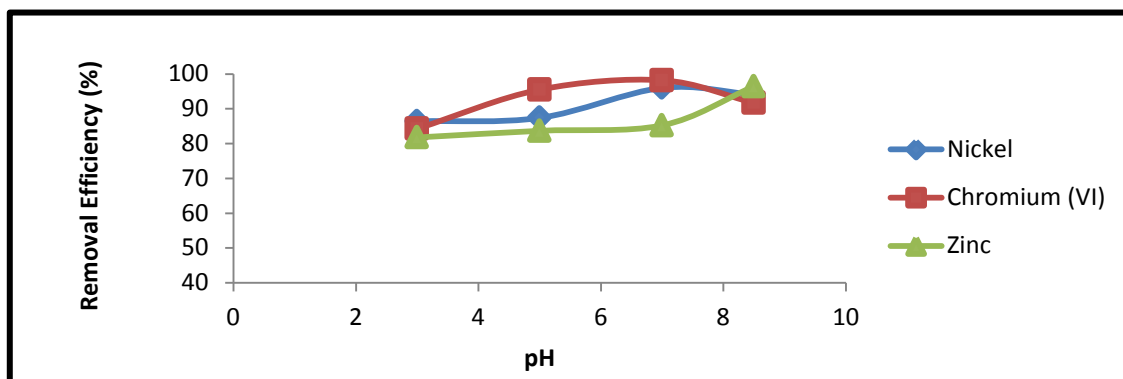


Figure 2. Nickel, Chromium (VI) and Zinc Removal Efficiency (pH Optimization)

Maximum nickel removal efficiency was obtained as 96.02% at pH 7. Removal efficiency was measured as 86.4% at pH 3, 87.3% at pH 5 and 94.08% at pH 8.5 (original pH). Maximum chromium (VI) removal efficiency was obtained as 98.20% at pH 7. Removal efficiency was measured as 84.30% at pH 3, 95.50% at pH 5, and 91.70% at pH 8.5 (original pH). Maximum zinc removal efficiency was 96.46% at pH 8.5 (original pH). Removal efficiency was measured as 81.77% at pH 3, 83.68% at pH 5 and 85.24% at pH 7. Considering the heavy metal removal efficiencies after pH optimization, it has been determined that the optimum pH is 8.5 (original pH).

Current Density Optimization And Pollution Removal Using Fe-Fe Electrodes

At this stage of the study, using Fe-Fe electrodes for 20 minutes contact time, pH 8.5 (original pH), current density 10.67 mA/cm², 16 mA/cm², 21.3 mA/cm², 26.67 mA/cm², 32 mA/cm², 37.33 mA/cm², 42 mA/cm² Nickel, Chromium (VI) and Zinc removal were investigated. The graphic below was created as a result of this experiment.

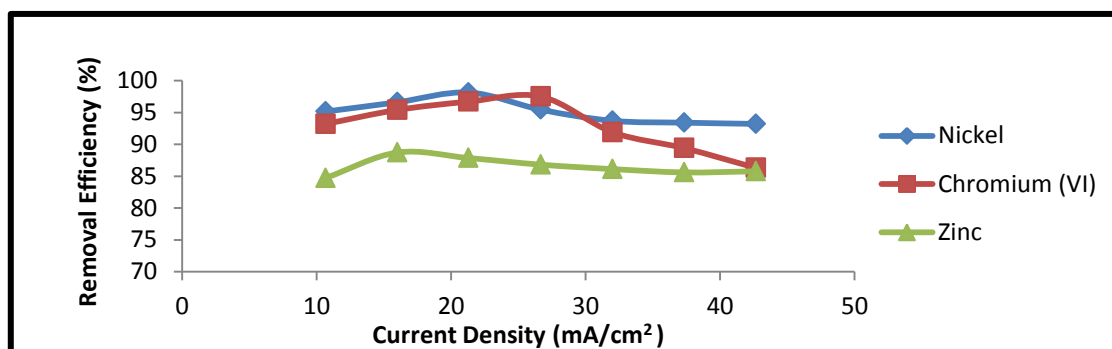


Figure 3. Nickel, Chromium (VI) and Zinc removal efficiency (current density optimization)

Maximum nickel removal efficiency was obtained as 98.14% and current density at 21.3 mA/cm². The current density is 95.15% at 10.67 mA/cm², 93.69% at 32 mA/cm², and the removal efficiency 93.20% at 42.67 mA/cm². Maximum chromium (VI) removal efficiency was obtained as 97.50% and current density at 26.67 mA/cm². The current density is 93.20% at 10.67 mA/cm², 91.90% at 32 mA/cm², and the removal efficiency 86.30% at 42.67 mA/cm². Maximum zinc removal efficiency efficiency was obtained as 88.72% and current density at 16 mA/cm². The current density is 87.85% at 21.3 mA/cm², 86.11% at 32 mA/cm², and the removal efficiency 85.76% at 42.67 mA/cm². After the current density optimization, considering the heavy metal removal efficiencies, it was determined that the optimum current density is 16 mA/cm².

Time Optimization and Pollution Removal Using Fe-Fe Electrodes

At this stage of the study, nickel, chromium (VI) and zinc removal efficiencies were investigated at the original pH value of 8.5, constant current density of 16 mA/cm² and contact time between 0-40 minutes using Fe-Fe electrodes. The graphic below was created as a result of this experiment.

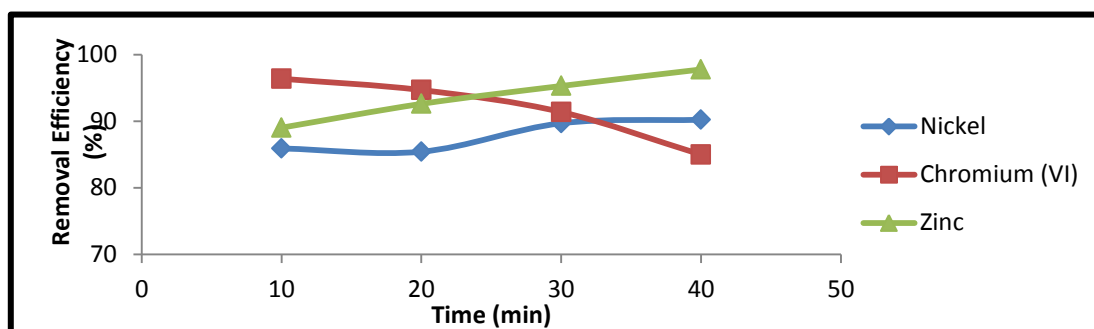


Figure 4. Nickel, Chromium (VI) and Zinc removal efficiency (operation contact time optimization)

The maximum nickel removal efficiency was 90.23% and contact time was obtained in 40 minutes. If the contact time was 85.92% in 10 minutes, the contact time was 85.44% in 20 minutes and the contact time was 30 minutes, removal efficiency was measured as 89.71%. Maximum chromium (VI) removal efficiency was 96.40% and contact time was obtained in 10 minutes. If the contact time was 94.70% in 20 minutes, the contact time was 91.40% in 30 minutes and the contact time was 40 minutes, removal efficiency was measured as 85%. The maximum zinc removal efficiency was 97.80% and the contact time was obtained in 40 minutes. If the contact time was 89.05% in 10 minutes, the contact time was 92.62% in 20 minutes and the contact time was 30 minutes, removal efficiency was measured as 95.31%. As the time increased, an increase in removal efficiency was observed. Considering the heavy metal removal efficiencies after contact time optimization, it was determined that the optimum contact time was 20 minutes.

Conclusions

pH optimization: It was determined that the optimum pH (original pH) in pH optimization is 8.5. At this pH value, nickel removal efficiency 94.08%, chromium (VI) removal efficiency 91.70%, zinc removal efficiency 96.46% was measured. $\text{Fe}(\text{OH})_3$ formation has the highest removal efficiency in the pH range of 8,0–8,5. Because the solubility of $\text{Fe}(\text{OH})_3$ formed in this pH range is very low and flocs occur in the environment (Çebi, 2018). In the study where chromium (VI) removal was performed using iron electrodes, it was stated that besides chromium (VI) reduction of iron electrodes, an additional reduction reaction occurred on the cathode electrode surface to the EC process. It was stated that as a result of this reaction, $\text{Cr}(\text{OH})_3$ was formed and precipitation was observed (Aygün, 2015). Maximum nickel (96.2%), Maximum chromium (VI) (98.20%) was obtained at pH 7 as removal efficiency. Maximum zinc (96.46%) was obtained at pH 8.5 as removal efficiency. Nevertheless, optimum pH (original) 8.5 was preferred to adjust the pH, as it would give an additional pollution to the water with the use of chemicals and due to the high removal efficiency. In a study, similar results were obtained in Chromium (III) measurements, and a decrease in removal efficiency was observed after pH: 7 (Gülyaşar, 2019). In another study, when the pH value is 5-9, it was observed that the zinc removal efficiency increased as the time increased (over 90%) (Türk, 2016).

Current density optimization: In the current density optimization, it was determined that the optimum current density is 16 mA/cm^2 . At this current density, nickel removal efficiency 96.60%, chromium (VI) removal efficiency 95.40%, zinc removal efficiency 88.72% were measured. Maximum nickel (98.14%) removal efficiency at 21.3 mA/cm^2 , Maximum chromium (VI) (97.50%) removal efficiency at 26.67 mA/cm^2 and maximum zinc (88.72%) removal efficiency at 16 mA/cm^2 it was obtained. Despite this, 16 reasons for choosing the optimum current density: 1. Adequate amount of expense has been provided 2. The more basic the wastewater environment, the higher the potential difference (voltage) value. In this case, it also increases the amount of electrical energy consumption, depending on the Faraday Law (Türk, 2016). With this, energy consumption will also be reduced.

Time optimization: It has been determined that the optimum contact time in time optimization is 20 minutes. During this contact period, Nickel removal efficiency was measured as 85.44%, chromium (VI) removal efficiency 94.70%, zinc removal efficiency 92.62%. Maximum nickel (90.23%) removal efficiency contact time was achieved in 40 minutes, Maximum chromium (VI) (96.40%) removal efficiency contact time was 10 minutes, Maximum zinc (97.80%) removal efficiency contact time was obtained in 40 minutes.

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