

Current density and residence time in the electrocoagulation process and its influence on Fe²⁺ reduction

[Densidad de corriente y tiempo de residencia en el proceso de electrocoagulación y su influencia en la reducción de Fe²⁺]

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Received: 29 December 2020; Accepted: 14 January 2021; Published: 22 January 2021

Resumen

El presente trabajo de investigación tuvo como variables de estudio la densidad de corriente de 20, 40 y 80 mA/cm² y tiempos de residencia de 10, 20, 40 y 60 minutos, dentro de estos parámetros de evaluación se tomaron valores de pH, conductividad y porcentaje de remoción de Fe²⁺ antes y después del proceso de electrocoagulación de muestras de drenaje ácido de mina (DAM) artesanal, la cantidad de muestra DAM por ensayo fue 350 mL por ensayo, de los resultados obtenidos se pudo observar que por la densidad de corriente de 80 mA/cm² y tiempo de 40 minutos se obtuvo el mayor porcentaje de remoción (76.20%), así mismo se obtuvo un porcentaje mínimo de remoción de 17.97% a 20 mA/cm²; los porcentajes de remoción se atribuye al efecto de la densidad de corriente del proceso de electrocoagulación, la cual permite incrementar los valores iniciales de pH del efluente que a su vez permite la formación de precipitados y coprecipitados en este caso de Fe²⁺.

Palabras clave: Electrocoagulación, Drenaje ácido, Densidad de corriente.

Abstract

The present research work had as study variables the current density of 20, 40 and 80 mA/cm² and residence times of 10, 20, 40 and 60 minutes, within these evaluation parameters values were taken of pH, conductivity and Fe²⁺ removal percentage before and after the electrocoagulation process of artisanal acid mine drainage samples (AMD), the amount of AMD sample per test was 350 mL per test, from the results obtained it could be observed that For the current density of 80 mA/cm² and a time of 40 minutes, the highest percentage of removal was obtained (76.20%), likewise a minimum percentage of removal of 17.97% was obtained at 20 mA/cm²; The removal percentages are attributed to the effect of the current density of the electrocoagulation process, which allows increasing the initial pH values of the effluent, which in turn allows the formation of precipitates and co-precipitates, in this case of Fe²⁺.

Keywords: Electrocoagulation, Acid Drainage, Current Density.

1. Introduction

Since its inception, humanity has had the need to use metals and has always sought methods to extract them; In this way, since those remote times, mining has existed and with it the effects of the process, whether in the air, soil or bodies of water, which are being attended to with increasing intensity; A very particular case is that of the generation of acidic waters from mining and extractive activities; This phenomenon occurs due to the release of mineral sulfur agents to the water and in combination with the air (oxidation) they alter the initial conditions of the water, such as pH, to values lower than 7, in a similar way this acidification process occurs due to the high dissolution of sulfates in bodies of water, this runs the risk of significantly altering and / or modifying river habitats. Sulfides are rare minerals in the earth's crust, however, in certain geological situations the abundance of these minerals increases, becoming the majority, thus in these cases the high content of Au, Ag, Fe, Cu, sulfides Zn and Pb have caused their exploitation and use by man throughout history; Pyrite (FeS_2) is the most common sulfide in nature, found in hydrothermal formations, igneous rocks and sedimentary deposits, sulfides are stable and very insoluble under the reducing conditions that exist in the subsoil, but the exposure of these minerals to conditions atmospheric destabilizes its structure through oxidation reactions; the oxidizing agent for this process to take place can be oxygen (O_2) or ferric iron (Fe^{3+}); on the other hand, depending on the absence or presence of microorganisms that catalyze the weathering reactions, we speak of abiotic or biotic oxidation, respectively. Acid Mine Drainage (AMD) consists of the appearance of waters with a pH typically between 2 and 4 and high concentrations of metals as a consequence of underground exposure to metallic sulphides during mining. AMD is one of the most serious types of water pollution, due to its nature, extent and difficulty of resolution, as well as the economic costs of its traditional remediation; The rivers affected by this type of pollution are characterized by their acidity, as well as by the high content of sulfates and heavy metals in their waters and by the metallic content of their sediments. The damage produced can cause the loss of water resources by making the water useless for human, agricultural or industrial consumption. (Arango, 2005); (Chen et al., 2002) and (Yilmaz, 2005).

Among the alternatives to control acidic water we have the so-called primary (preventive) methods; secondary methods (containment) and tertiary methods (remediation), the latter are intended to collect and treat these. Remediation treatments generally achieve their objectives due to the use of chemical agents, which should be used in a controlled way according to their need, which does not happen, since we almost always use chemical compounds in excess in order to achieve the expected modifications. In this way, substances are added that the bodies of water did not have, however there are treatments that follow the principles of chemical neutralization but with the advantage of the controlled use of reactants and products, such processes are called electrochemicals, which generate in situ the agents necessary for the control processes, in this case of acidic waters, but that can be used in theory in all bodies of water to be treated, with the difference of the control of electrolyte conductivity, initial pH, anodes and cell cathodes, electrical parameters of the process, volume of water body, among others; Among these methods we have the so-called electrocoagulation, which in our case was used in search of reducing the cation content and increasing the initial pH of the water samples. Among other forms of control of this type of water we have the use of so-called wetlands, which although designs can be made, their application depends on the facilities for their installation (Nina, 2008).

(Park et al., 2015) reported that dissolved Fe, Al, Cu and Zn / Ni can be recovered from AMD through selective precipitation; In the cation exchange experiments (CEM) and the anodic exchange plate (AEM) they demonstrated high loss of Fe (around 40-50%) caused by precipitation at the cathode; for the reduction of Fe a salt bridge (SB) was used; the cathode reaches a high concentration of hydroxide generated by the cathodic reaction that can be used as a neutralizing agent, this neutralizing agent produced by electrochemical reactions can be used to selectively recover dissolved metals; Based on the results, it is possible to oxidize Fe (II) to Fe (III), while producing neutralizing agents for the selective recovery of dissolved metals; (Ghosh et al., 2008) evaluated the elimination of Fe (II) by electrocoagulation, using aluminum

electrodes; varied the initial concentrations of the iron cation and determined that the elimination of this cation occurs in two stages, the oxidation of the cation +2 to +3 and the subsequent formation of complex hydroxides of this cation and aluminum, the current densities used vary from 0.01 mA/m², to 0.04 mA/m²; measurements showed that Fe (II) elimination increases with current density; the highest iron removal was around 99.2% with a time of 35 minutes.

The basic principle of electrocoagulation is the electrolysis process; During electrocoagulation, the most important chemical reactions involve the dissolution of metal cations at the anode and the formation of hydroxyl ions and hydrogen gas at the cathode, the current passes through a metal electrode, oxidizing the metal to its cation, simultaneously, the water is reduced to hydrogen gas and the hydroxyl ion (OH⁻), in this way electrocoagulation introduces metal cations in situ, using sacrificial anodes (typically iron or aluminum) that need to be periodically replaced; cations destabilize colloidal particles by neutralizing charges, in addition to producing complex species of monomeric and polymeric hydroxide as coagulants; These coagulants form amorphous metal hydroxide precipitates; its high adsorption properties confer a strong affinity for dispersed particles and dissolved contaminants; thus, the pollutants can be separated from the aqueous phase by coagulation, the hydrogen bubbles in the cathode promote turbulence in the system and bind with the pollutants, reducing their relative specific weight, consequently, they improve the separation process by flotation (Mollah, et al., 2001).

2. Materials and Methods

The sample consisted of 20 liters of acid mine drainage solution from the sierra zone of the La Libertad region. Table 1 provides information on the effluent used. Table 2 indicates the variable and its level used in the present investigation. Table 3 provides information on the electrocoagulation cell construction.

Table 1. Initial characterization of the artificial chrome plating effluent used in the research

Property	Initial value
Temperature (°C)	23.5
Fe (+2) (ppm)	637.33

Table 2. Levels of the study variables

Independent variables of study	Levels of study
Factor (A): Current density (mA/cm ²)	20,40, 80
Factor (B): Rffluent residence time (minutes)	10, 20, 40 y 60
Dependent variable of study	
Fe reduction porcentaje (+2)	

Table 3. Electrocoagulation cell installation conditions

Sample: Solution AMD	Number of electrodes: 02 per cell
Volume of test container: 500 mL	Electrode spacing: 5 cm
Applied voltage: Defined by the required current density	Cathodes: AISI 304
Treatment time: Variable	Anodes: Aluminum 1xxx
Operation type: Batch	Electrode size: Defined by cell type and size

Experimental sequence

2.1.- Preparation of the working electrodes:

As working electrodes, AISI 304 steel and 1000 series aluminum plates were adapted, they will be cleaned superficially, until they do not have any contaminants such as oils, grease or dust, as well as the lids of each of the plastic containers used as cells, they were drilled with the help of a metal or hot plate, in order to mount all the accessories of the equipment necessary to carry out the electrocoagulation process. The total number of electrode plates will be twice the number of tests to be carried out (two steel plates per electrocoagulation test).

2.2.- Design and construction of the electrocoagulation cell:

The electrocoagulation cell was designed by computer, in order to obtain the maximum benefit from the agitation of the cell (circular cells will be tested for this); Once the type of cell was defined, it was built, which will be plastic or similar material, each cell will have a volume of 350 mL (having to build one for each test). Table 3, shows some of the characteristics of the cell to be used for the present investigation.

2.3.- Preliminary tests of electrolytic cell.

At this stage of development, pilot tests were carried out in order to rule out failures in the electrolytic cell system, thus avoiding delays and other inconveniences. If a fault is detected, such as lack of electrical continuity between the components, broken cables, among others, they are corrected.

2.4.- Electrocoagulation:

Once the previous step described was achieved, we proceeded to the round of electrocoagulation tests, at the study levels indicated above, this round 33 of tests was carried out randomly, trial by trial, each one of them was coded and packed in order to achieve in the right way. Each electrocoagulation test was performed for each proposed level, with solution volumes of 350 mL each, leading to their respective analysis of 100 mL of each; The basic installation of the developed process is presented in Figure 1.

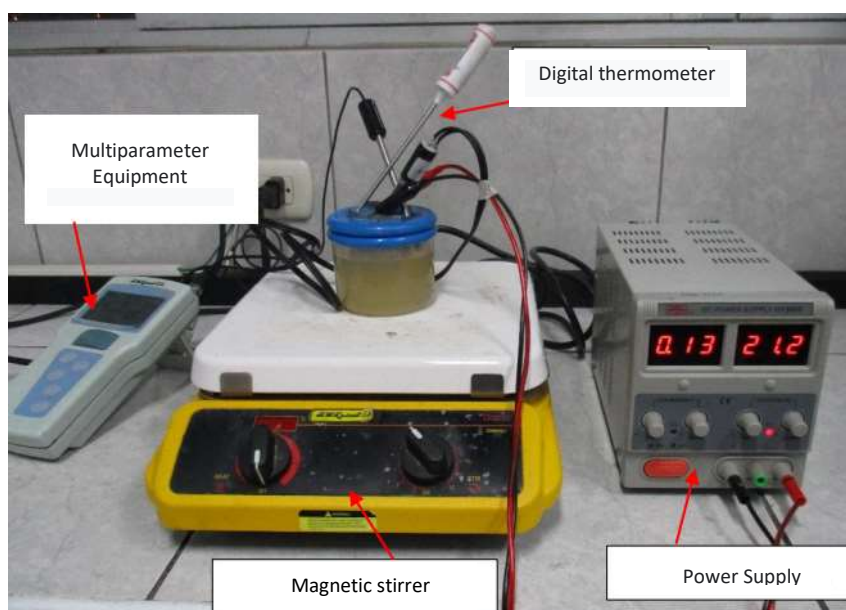


Figure 1. Electrocoagulation process of one of the AMD samples.

Among the equipment used we have: Multiparametric pH / ORP / EC / DO / Pressure / Temperature Meter (Hanna Instruments); pH / mV (0.00 to 14.00 pH / \pm 600.0 mV); EC (0 to 9999 μ S/cm; 0.000 to 200.0 mS/cm); Glass ceramic heating magnetic stirrer; variable speed of rotation; Variable regulation laboratory power supply, (0 - 30) V, (0 - 5) A; Model HY3005D, RSR Electronics, Inc.

3. Results

Reduction percentage of divalent iron:

Table 4 and Figure 2 show the average values of the Fe²⁺ removal percentage from the acid mine drainage, with respect to time and current density used in the electrocoagulation process.

Table 4. Average values of the Fe²⁺ removal percentage, present in acid mine water.

Time (minutes)	Current density (mA/cm ²)		
	20	40	80
10	17.97 %	25.28 %	26.84 %
20	35.79 %	40.78 %	44.98 %
40	42.81 %	59.10 %	76.20 %
60	40.78 %	50.22 %	70.35 %

From the aforementioned figure, the increase in the percentage of removal of the Fe²⁺ cation is evidenced, with respect to the increase in the current density in the evaluated times of the electrocoagulation process, as can be seen in Table 4, the maximum removal percentage was 76.20% for a time of 40 minutes and 80 mA/cm²; This trend can also be seen in Figure 2, for the 40-minute times the maximum removal potential is reached according to the variables evaluated, from this time there is a pronounced drop in the slope of the graph; This phenomenon is associated with the inverse process of initiation, that is, the difference in the concentration of cations, since at the beginning it is high but during the electrocoagulation process it decreases due to the formation of stable and unstable compounds based on divalent iron, in addition to the formation of products on the surface of the metals used for the electrocoagulation process, the products that are generated by electrocoagulation are simple or complex hydroxides, this being the main cause of the removal of the cationic content of the electrolyte; the statement made is supported by the decrease in the cation content and the conductivity data of the electrolyte used shown in table 5 and figure 3, in the case of conductivity, this decreases this would be due to the elimination or reduction of the ions of Fe²⁺, that is to say, the decrease in cations in solution, since having less presence of these decreases the conductivity, because as the electrocoagulation process is carried out, the formation of the typical products of this occurs, finally the changes were measured of pH of the acid solutions evaluated, these data are shown in table 6 and in Figure 4, of the latter it was observed that this increase in this with the passage of time and the current density used, the increase in pH is It should be due to the generation of OH⁻ groups, in the process of decomposition of water.

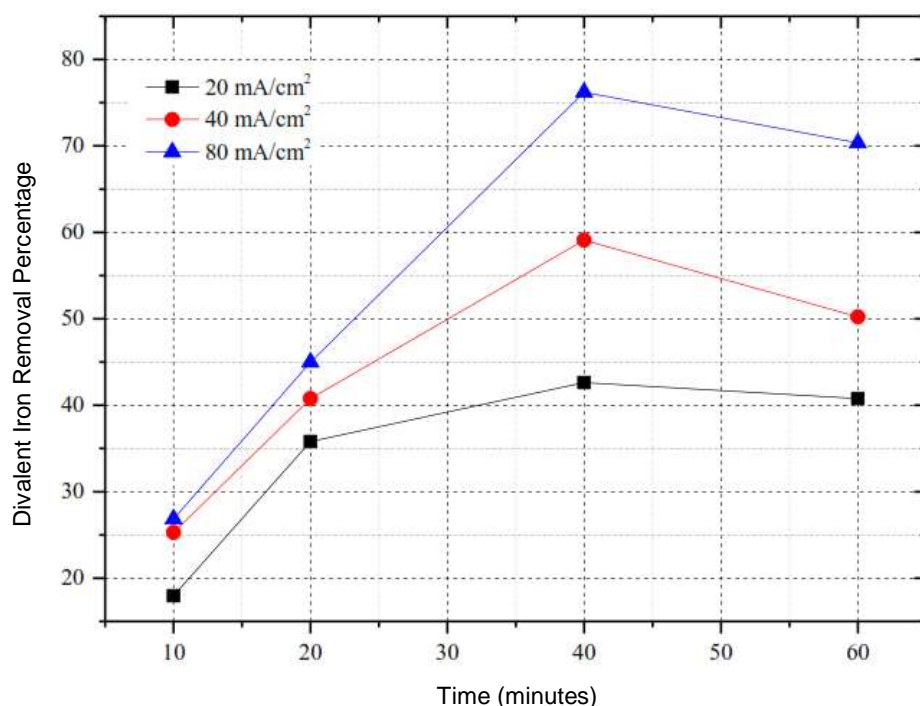


Figure 2. Fe²⁺ removal percentage from acid mine drainage.

Table 5. Average values of electrical conductivity of the solutions used

Time (minutes)	Conductivity (uS/cm)		
	20	40	80
10	28.35	26.38	24.6
20	22.90	15.14	9.40
40	21.12	8.74	6.60
60	14.90	6.14	5.60

Table 6. Average pH values of the different AMD samples

Time (minutes)	Conductivity (uS/cm)		
	20	40	80
10	2.56	3.05	3.51
20	2.90	3.79	4.75
40	3.73	5.31	6.20
60	4.38	6.26	6.73

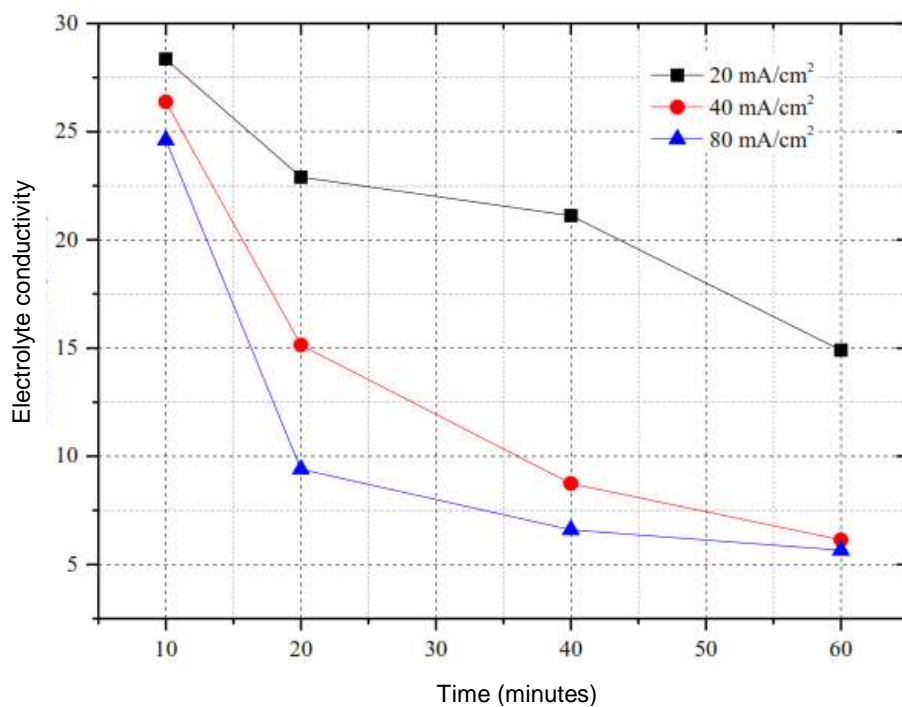


Figure 3. Average values of electrical conductivity of the solutions used

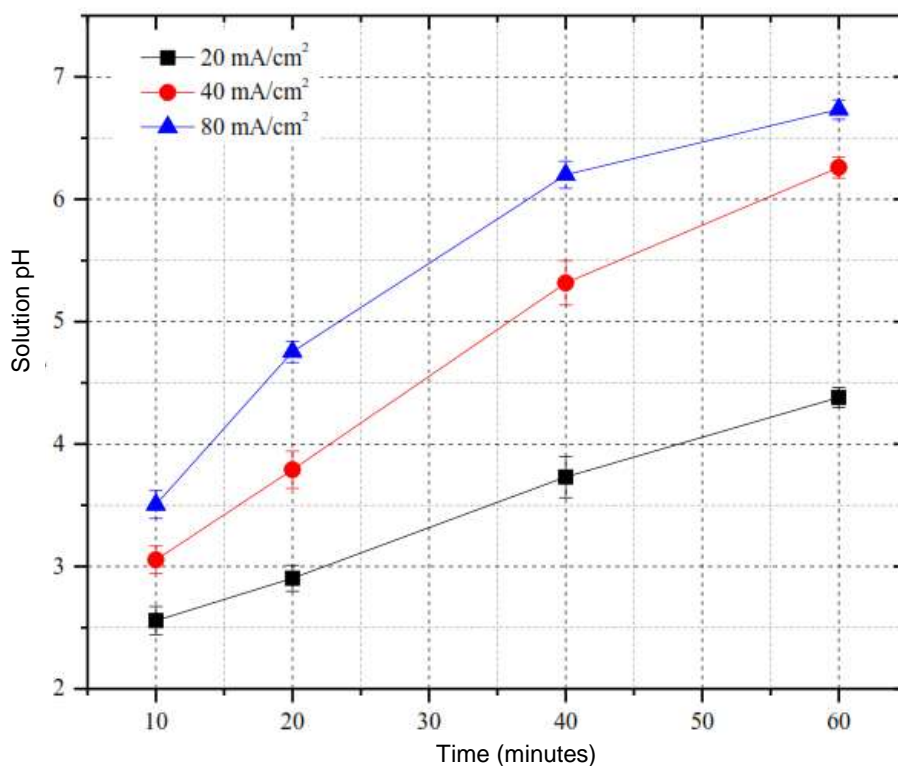


Figure 4. Average pH values of the different AMD samples.

Regarding the current density (Zhu et al., 2011) expresses that it is one of the most important operating parameters of the electrocoagulation process, thus in their case they achieved the elimination of antimony with current densities between (55.5-166, 7) A/m² reached a plateau when the current density was 167 A/m², this reaffirms the trend of results obtained in the present investigation, that is, the direct relationship between the current density and the removal percentage Fe⁺² ions, until reaching a threshold value of current density as a function of time in which the removal percentage does not increase significantly due to the decrease in the initial ionic concentration, since compounds are generated at starting from the metal cations present in solution. Likewise (Lu et al., 2015), in their work they state that the OH⁻ ion formed in the cathode increases the pH of the evaluated solution and therefore induces the precipitation of metal ions as corresponding hydroxides and co-precipitation with iron hydroxides, this would explain the trend of the pH increase in all tests from an initial pH of 2.56 to a pH of 6.73; In the same research, the residence time is evaluated, reaching the conclusion that a longer residence time causes a longer contact time between heavy metal ions and flocs, which could also increase the removal efficiency, which is why in our case Fe²⁺ ions precipitated in greater quantity as a function of the increase in treatment time. For (Nariyan et al., 2017) the removal of metals from mine water with electrocoagulation is promising since it would generate sludge in the pH range of 6 -7 and metal oxides that will not be discharged into receiving water courses; in this case the pH of the solution will be adjusted to neutral during the reaction time, which is one of the benefits of this method. The pH near the cathode is alkaline as hydrogen is released and near the anode is acidic as H⁺ is produced.

4. Conclusions

- The increase in the current density and the treatment time of the electrocoagulation process increased the percentage of reduction of Fe²⁺; thus the highest percentage of was 76.20%, obtained with a current density of 80mA/cm² and 40 minutes.
- The increase in the current density and the treatment time of the electrocoagulation process, decreased the electrical conductivity of the treated effluent and increased their pH values

Acknowledgments

Special thanks to the Composite Materials Laboratory of the School of Materials Engineering for its support in the development of this research.

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