Revista Mexicana de Ingeniería Química

Electrodialysis applied to the removal of iron ions in an aqueous solution

Electrodiálisis aplicada a la remoción de iones de hierro en una solución acuosa

M. Arreola-Castro[1], J.C. Rojas-Montes[1,2**], V.J. Martínez-Gómez[1,2], D. Calla-Choque[3],
M. J. Rodríguez-Rosales[1], R. Pérez-Garibay[4], R. Valencia-Vázquez[1,2]

[1]*Maestría en Sistemas Ambientales, División de Estudios de Posgrado e Investigación, TecNM/IT de Durango, Felipe Pescador 1830 Ote. Col. Nueva Vizcaya, Durango, Dgo. México. C.P. 34080. Mexico.*
[2]*CONACyT-TecNM/IT de Durango, Felipe Pescador 1830 Ote. Col. Nueva Vizcaya, Durango, Dgo. México. C.P. 34080. Mexico.*
[3]*Faculty of Engineering, National Autonomous University of Mexico (UNAM), 04510 Mexico City, Mexico.*
[4]*Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional, Unidad Saltillo. Av. Industria metalúrgica 1062, Parque Industrial Saltillo-Ramos Arizpe, Ramos Arizpe, Coahuila, México. C.P. 25900. Mexico.*

Abstract

Iron is one of the main elements present in surface and ground waters due to mineral leaching or mining industry activities. To avoid the formation of acid mine drainage (AMD), it is necessary to treat the water with the presence of iron to reduce the environmental impact and obtain water that can be reused. In this work, electrodialysis is proposed for removing iron from a solution. To do this, it is necessary to know the appropriate conditions of current density, pH, and concentration to carry out the removal of iron in an analogous solution in concentration to those found in mineral processing. The electrodialysis tests were performed in a two-compartment cell. From the data obtained in the chemical analysis, the removal percentages, the amounts of mass removed, and the removal rates were calculated to determine the best operating parameters. Discussion is also made from the thermodynamics that determines the speciation of iron in the anolyte. The maximum percentage of iron removal reached was 97.15%, with the next parameters: current density of 390 A/m^2, initial iron concentration (C_{Fe}) of 40 mg/L, initial pH value (pH$_i$) of 4, agitation speed (v) of 500 r.p.m. and temperature (T) of 25°C.

Keywords: iron, electrodialysis, removal, current density, diffusion.

Resumen

El hierro es uno de los elementos presentes en agua superficial y subterránea debido a la lixiviación de minerales o por actividades de minera. Para evitar la formación de drenaje ácido de mina (DAM) se requiere dar tratamiento al agua con presencia de hierro para disminuir riesgos ambientales, de salud y para el reusó de esta. Este trabajo plantea la electrodiálisis como un proceso de remoción de hierro, para esto es necesario conocer las mejores condiciones de densidad de corriente, pH y concentración para remover el contenido en una solución análoga en concentración de este metal a las encontradas en el procesamiento de minerales. Las pruebas de electrodiálisis se realizaron en una celda con dos compartimentos. A partir del análisis químico se calcularon porcentajes, masa y velocidades de remoción, para determinar los mejores parámetros. También se hace una discusión desde una perspectiva de la termodinámica, que involucra la especiación del hierro en el anolito. El porcentaje máximo de remoción de hierro fue de 97.15%, con una densidad de corriente de 390 A/m^2, concentración inicial de hierro (C_{Fe}) de 40 mg/L, valor de pH inicial (pH$_i$) de 4, velocidad de agitación (v) de 500 r.p.m y temperatura (T) de 25°C.

Palabras clave: hierro, electrodiálisis, remoción, densidad de corriente, difusión.

1   Introduction

The presence of iron in surface and groundwater waters is quite common mainly due to the leaching of the minerals or by mining industry activities. While it is true that this metal does not represent a health risk, like heavy metals, it can cause aesthetic and organoleptic problems (Ben-Sik-Ali *et al.*, 2013). On the other hand, the presence of this element can promote the generation of acid mine drainage (AMD), which can cause serious environmental impacts, particularly on soil, water resources and aquatic species (Galhardi and Bonotto, 2016). The degree of contamination and environmental repercussions will depend on the content of other elements present in the contaminated water, since an acidic effluent is a potential leaching agent, different ions of other metals can be found. So, waters containing lead could cause gastrointestinal damage, chromium would cause fatigue, irritability, and copper problems of anemia, and intestinal irritation, to mention some examples. In addition, acidity by itself presents toxicity to aquatic organisms, corrodes infrastructure, color, taste and produces water unfit for human consumption (Singh *et al.*, 2011).

The formation of acid mine drainage (AMD) is a natural phenomenon, originated by chemical reactions that occur by the interactions between air, water, microorganism (*Thiobacillus ferrooxidans, Acidithiobacillus ferrooxidans, Leptospirillum ferrooxidans y Acidithiobacillus thiooxidans*) and other rocks that contain sulfide minerals (especially, pyrite -PbS-) that produce acidity in water (Akcil and Koldas, 2006; Cervantes-Macedo, 2014). In addition to the natural phenomenon, the mining activity can also contribute to the formation of AMD by the operations of the mineral extraction process (Simate and Ndlovu, 2014).

Chaparro (2015) indicates that the process of AMD formation begins when sulfide minerals such as pyrite are exposed to the effects of oxygen and water. The pyrite oxidation process can be observed in Equation 1, where oxygen acts as the main oxidizing agent and sulfides are oxidized to sulfates ions.

$$FeS_{2(s)} + \frac{7}{2}O_2 + H_2O \leftrightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (1)$$
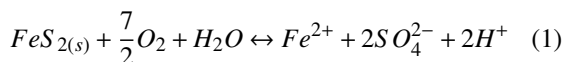
At this stage, the pH remains at values above 4.5. Later, in the presence of atmospheric oxygen, iron ferrous is oxidized to ferric according to Equation 2:

$$Fe^{2+} + \frac{1}{4}O_2 + H^+ \leftrightarrow Fe^{+3} + \frac{1}{2}H_2O \quad (2)$$
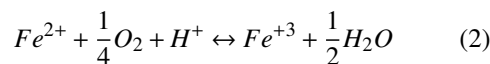
The Fe^{2+} can undergo two processes depending on the pH of the water, if the pH is above 4.5 the process that occurs is described in Equation 3 where the ferrous iron is oxidized and hydrolyzed to form hydroxides that form the red precipitate seen in most mines that generate acid mine drainage.

$$Fe^{3+} + 3H_2O \leftrightarrow Fe(OH)_{3(s)} + 3H^+ \quad (3)$$
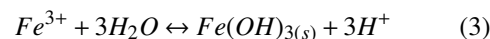
If the pH of the water is at values of $\leq$ 4.5, the process that will most likely happen is the oxidation of ferrous to ferric iron and the latter will act as the main oxidizing agent of the pyrite replacing the atmospheric oxygen and generating more acidity as shown in Equation 4, it is worth mentioning that this cycle repeats itself so that each time the acidity of the effluent is increased.

$$14Fe^{3+} + FeS_{2(s)} + 8H_2O \leftrightarrow 2SO_4^{2-} + 15Fe^{2+} + 16H^+ \quad (4)$$
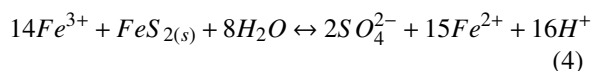
Although mining activities can contribute to the formation of this type of drainage, it is also true that this industry has adequate places for the disposal of the effluents that are generated, however, the natural process that takes place through the biogeochemical cycle of water, transports and deposits them in ponds, streams, rivers, lakes and nearby aquifers, causing severe degradation of water quality. Once these effluents are produced, they can last for hundreds, or perhaps thousands of years, so full extraction of the sulfides or acid mine drains are recommended as they are generated (Shim *et al.*, 2015).

In order to prevent the formation of these AMD, it is necessary to treat the water to eliminate the iron it contains even before the formation of this type of effluent, whether it is effluent from the mining industry or water basins that stimulate water acidification, because once they are generated they are difficult to control and treatment can be very costly (Aguiar *et al.*, 2016; Grande *et al.*, 2010). However, the most common methods are focused on sanitation once they have been generated, for example, the chemical method of adding lime (CaO); this process has the disadvantage that it requires the addition of considerable volumes of this compound so this option is sometimes unviable for the control of acid generation (Watten *et al.*, 2005). Other alternatives to control these drains are the methods of bacterial

inhibition (temperature control and dissolved oxygen limitation) or the use of other alkalizing agents (lime, limestone, caustic soda, sodium carbonate and ammonia), however, all these processes are only attenuating the problem, so it is advisable to attack the problem even before it originates (Johnson and Hallberg, 2005).

The methods for removing metals, including iron, are not new and are very varied, being able to use processes such as ion exchange, adsorption, oxidation, membrane processes, electrochemical processes, coagulation-flocculation (Abdulhadi *et al.*, 2020; Aragaw, 2020; Dyer *et al.*, 2012; Laverde-Cerda *et al.*, 2019; Torbaghan and Khalili Torghabeh, 2019). Of these processes, the electrochemical and membrane methods attract attention (Torres-Santillan *et al.*, 2019), since they have the advantage of not requiring the addition of alkalizing reagents, mentioned above, during the process that can lead to another type of pollution (mainly generation of sludges containing heavy metals), both processes converge in a process known as electrodialysis, this it has the particularity of separating the ions that are present in an aqueous solution (Baker, 2012).

Electrodialysis is an electro membrane separation process which is based on the selectivity of the ion exchange membranes. These membranes contain functional groups with fixed electrical charges in a polymeric matrix, so that they allow the permeation of the oppositely charged ions in a solution, under the influence of a continuous electrical field (Koter and Warszawski, 2000). Electrodialysis is applied to extract ionic chemical species from aqueous solutions. In general, the feed is a solution containing ions which, when treated by electrodialysis, generates two solutions as products: a diluted one and a concentrated one (Martí-Calatayud, 2014).

The main application that has been given to this technique is the salts removal from seawater and brackish water, so they are commonly classified as desalination processes (Kabay *et al.*, 2008; Strathmann, 2010). However, they have also given good results for the removal of other inorganic components, for example for the removal of anions such as arsenic (Ortega *et al.*, 2017), nitrates and chlorides (El Midaoui *et al.*, 2002), fluorides (Amor *et al.*, 2001; Banasiak *et al.*, 2007) and sulfates (Serrano-Meza *et al.*, 2020). It has also been used for the removal of metal cations such as zinc (Kariduraganavar *et al.*, 2012), copper (Caprarescu *et al.*, 2011; Cifuentes *et al.*, 2009) and lead (Abou-Shady *et al.*, 2012; Mohammadi *et al.*, 2004).

In the specific case of iron, few investigations have been focused on its removal, in a work carried out by Ben-Sik-Ali *et al.* (2013) focused on iron removal from brackish water by evaluating the variables of applied cell voltage, flow rate, initial pH, initial concentration and ionic strength of the solution, reaching percentages close to 100% when working with small iron concentrations (2 mg/L), 8 V, feed flow of 15 L/h, pH of 3 and ionic strength of 0.04 M.

This work focused on adapting the electrodialysis process to achieve the iron removal cations in typical concentrations found in mineral processing to prevent the formation of acid mine drains and obtain water with low iron content, which can be reused in some processes or disposed without affecting the environment. The tests were carried out in an electrodialysis cell at a laboratory scale from a synthetic solution. For the development of the electrodialysis process, variables such as current density, initial iron concentration and pH were studied to know the importance of its intervention and repercussion in the process.

2 Experimental

2.1 Experimental development

Figure 1 shows the electrodialysis cell used for the development of the tests (polymethylmethacrylate cell). It has an approximate capacity of 425 cm^3 and is partitioned by means of a cation exchange membrane (CMI-7000, Membranes International lnc.; polymer structure of gel polystyrene-divinylbenzene, functional group sulphonic acid, electrical resistance <30 Ω/cm^2 in 0.5 M NaCl, permselectivity 94%). The power supply was made with a direct current power source (Tektronix, PWS4305). A 1 cm thick lead plate was used as the anode, while a 1 mm thick stainless-steel plate was used as the cathode, both with an effective surface area of 84 cm^2. Before and after each test the electrodes were polished with different grades of silicon carbide sandpaper (80, 120 and 220) and then washed in a 0.5 M hydrochloric acid solution to remove any possible residue formed during the previous experiments.

In the cathodic compartment (catholyte) a 0.2 M conductive solution of sodium chloride (NaCl) was used, while in the anodic compartment (anolyte) the solutions (feed water) had a 0.01 M concentration of ammonium sulfate -$(NH_4)_2SO_4$-, to provide
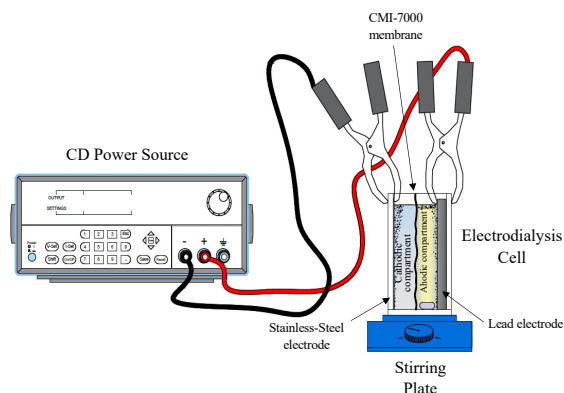
Fig. 1. Experimental scheme used in electrodialysis tests.

conductivity, and different concentrations of iron (Fe), the test were performed in triplicate. All the solutions were made from deionized water and the analytical grade reagents: heptahydrated iron sulfate, ammonium sulfate and sodium chloride. The pH value was adjusted at the beginning of the tests with a solution of 1 M of sulfuric acid (H_2SO_4) or 1 M of sodium hydroxide (NaOH), according to the required value and measured with a Hanna brand pH-meter (HI98103). The stirring speed (*v*) for the tests was 500 r.p.m. carried out with a stirring grid (IKA, Topolino). The experiments were carried for 60 minutes out in batch mode at an initial temperature (T) of the electrolytes of 25° C. To study the effect of current density (D, A/m ^{2}), four levels were analyzed (45, 90, 200 and 390 A/m^2), to determine the effect of the initial iron concentration (C_{Fe}), concentrations of 15, 25 and 40 mg/L of iron were analyzed, and finally, to determine the effect of the initial pH value of the feeding solution (pH_i), values of 2, 4 and 6 were evaluated. All materials used were reagent grade brand Sigma-Aldrich.

Sampling was done at specific time intervals, taking a sample from the cell, and then determining its concentration with an atomic absorption spectrophotometer (Varian SpectrAA 220 FS). During the development of the tests, cell voltage and temperature were monitored. In addition, thermodynamic simulation was performed using HSC Chemistry 6.1R software to determine the predominance areas of the different species, as well as the speciation of the electrolytes. Finally, from the data obtained in the chemical analysis, calculations were made to determine the percentage of removal

achieved for each time interval, and for each of the tests.

2.2 Data analysis

Equations 5, 6 and 7 were used to determine the percentage of iron removal (%R), mass of iron removed (M_t) and removal rate (V_t) in each interval, respectively.

$$\%R = 100 - \frac{C_f(100)}{C_i} \tag{5}$$

$$M_t = C_{t-\Delta t} - C_t \tag{6}$$

$$V_t = \frac{M_t}{t} \tag{7}$$

Where C_f, C_i y C_t are the final, initial and interval t iron concentrations -mg/L-. Δt is the time interval between the concentration to be known and a previous known concentration and t is a determined time both expressed in minutes.

3 Results and discussion

3.1 Evaluation of current density in iron removal

The first variable studied was the current density with different initial concentrations of iron. The results achieved in each of the electrodialysis tests for the different concentrations studied are shown in Figure 2. For all the concentrations analyzed there is a defined behavior, as the current density increases (from 45 to 390 A/m^2) there is an increase in the percentages of iron removal in the anolyte from 63 to 94%, 68 to 90% and 75 to 97% for the initial concentrations of 10, 25 and 40 mg/L, respectively (Figure 2a-c). Reaching slightly higher removal percentages with the highest concentration as shown in Figure 2d. It is important to note that during the first 10 minutes of the tests, the slopes are steeper, which is a clear indication of a higher removal rate during this time. This indicates that the removal process would be dominated by the diffusion of the ions and that once their presence is scarce, the transfer speed tends to decrease. The removal values are above those reported by Ben-Sik-Ali *et al.* (2013) in their work, where they report removal percentages of around 60% under similar conditions.
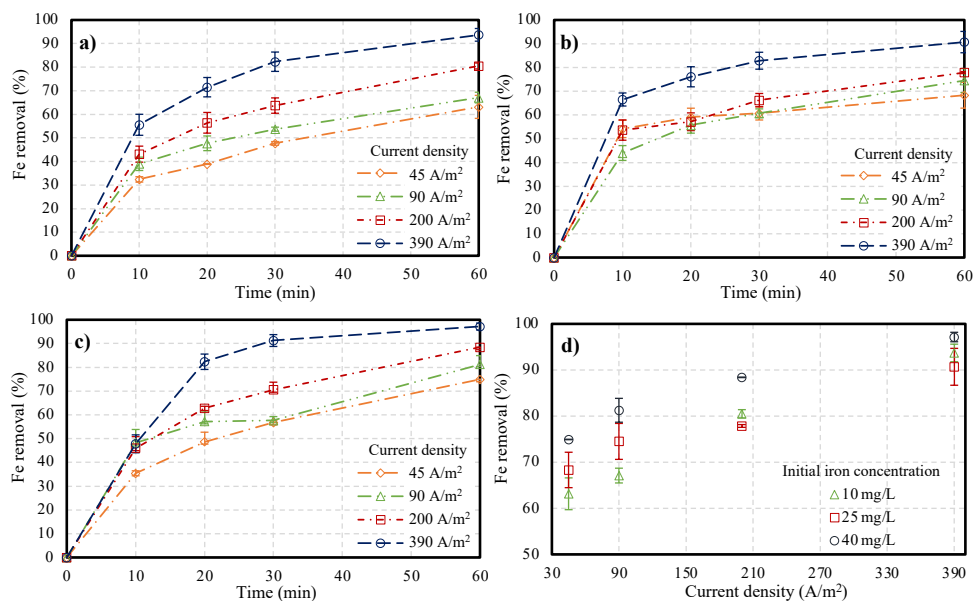
Fig. 2. Effect of current density on the percentage of iron removal for a) C_{Fe}=10 mg/L, b) C_{Fe}=25 mg/L and c) C_{Fe}=40 mg/L. d) Iron removal percentage as a function of current density and initial iron concentration. pH_i= 4, v = 500 r.p.m., t=60 minutes and T = 25°C.

The results obtained were the expected ones, because a higher current density results in a higher cell voltage and consequently a higher driving force of the ions. This behavior has been previously reported by Ben-Sik-Ali *et al.* (2013) because they observed that the ion transport between the compartments of the cell was proportional to the applied current. This is demonstrated by analyzing the cell voltages obtained during the tests. Figure 3 shows the monitoring of this parameter during the experiments for the different initial concentrations of iron. The conduct of this variable is completely associated with the iron removals achieved, since the highest iron removals correspond to the highest cell voltages recorded which in turn belong to the highest current density, this shows that the driving force to perform the diffusion of ions is higher as the cell voltage increases. On the other hand, the behavior observed in the removal during the first 10 minutes is also present in the cell voltages, since the highest voltages are recorded, and the decrease is pronounced during this time interval.

Another parameter that is important to know is the speed of removal as a function of current density, since from this it is possible to determine what type of process dominates the electrodialysis system. Figures 4a-c show that the amount of iron transferred from one compartment to another reached its maximum during the first 10 minutes of the process. This had already

been inferred in the removal graphs from the slopes observed in those graphs. Recalling the percentage removal graphs, important differences (changes of 29, 22 and 22% for the lowest and highest current density with the initial concentrations of 10, 25 and 40 mg/L, respectively) were obtained according to the different current densities; however, analyzing the results obtained in the removal rates, these differences are no longer important because the ratio of change in removal rate (0.42, 0.31 and 0.26 for the initial concentrations of 10, 25 and 40 mg/L) is much smaller than the change in current density ratio (8.6).

Examining the tests in more detail, for a concentration of 10 and 25 mg/L (Figure 4a and b) increasing the current density results in an increase in the obtaining values in the first 10 minutes of 0.32-0.56 and 1.1-1.66 mg/min when the current density is increased from 45 to 390 A/m^2. However, when working with a concentration greater than 40 mg/L the results varied (Figure 4c), since from a current density of 90 A/m^2 the removal rate is very similar (approximately 1.9 mg/min). It should be noted that the change in the rate is not large when compared to that obtained at 25 mg/L (only 0.30 mg/min), on the other hand, it also highlights that the decrease in rate obtained at 20 minutes is not as drastic as the one found at lower concentrations. This is a clear indication that the process is dominated by the
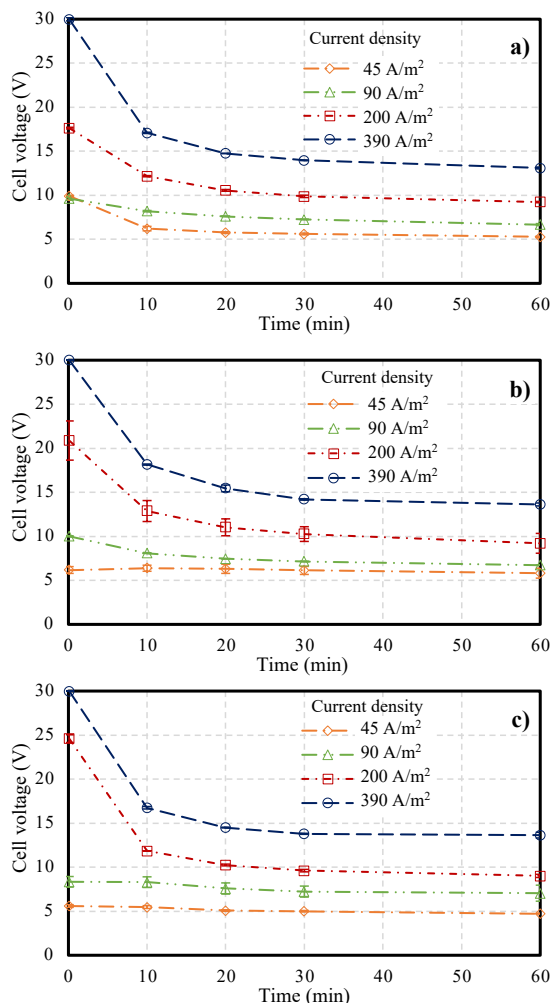
concentrations end up in very similar percentages,

Fig. 3. Cell voltage for iron removal electrodialysis for a) C_{Fe}=10 mg/L, b) C_{Fe}=25 mg/L y c) C_{Fe}=40 mg/L. pH_i=4, v=500 r.p.m. and T=25°C.
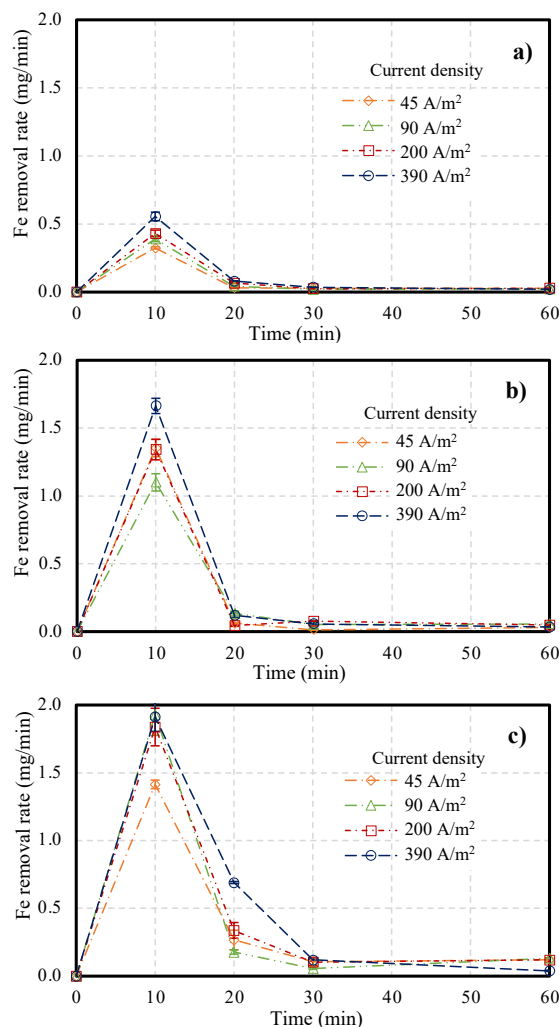

Fig. 4. Effect of current density on the iron removal rate for a) C_{Fe}=10 mg/L, b) C_{Fe}=25 mg/L y c) C_{Fe}=40 mg/L. pH_i=4, v=500 r.p.m., T=25°C.

diffusion of iron ions from one compartment to another, so that the removal rates are mostly due to a poor availability of iron ions in the anolyte than to the change in current density.

3.2 Evaluation of initial iron concentration in iron removal

As previously mentioned, as the initial iron concentration increases, higher removals occur. These differences can be seen in Figure 5, however, this does not occur in all current densities used in this work, this statement is only fulfilled when working at low current densities (45 and 90 A/m²). As a higher density is used (200 and 390 A/m²) the iron removals of the lower

while for the higher concentration it still maintains the tendency to be the highest removal. These differences are due to a greater disposition of iron ions as the initial iron concentration increases.

It is worth mentioning that analyzing the results as a function of the removal percentage provides biased information on the conditions that may prefer iron removal, because the initial masses are not similar and therefore it is imprecise to compare them as a function of the initial concentration. The results are discussed below from the perspective of mass removed, since it provides information on the capacity of the system in terms of iron transfer and the limitation associated with the availability of iron in the anolyte.
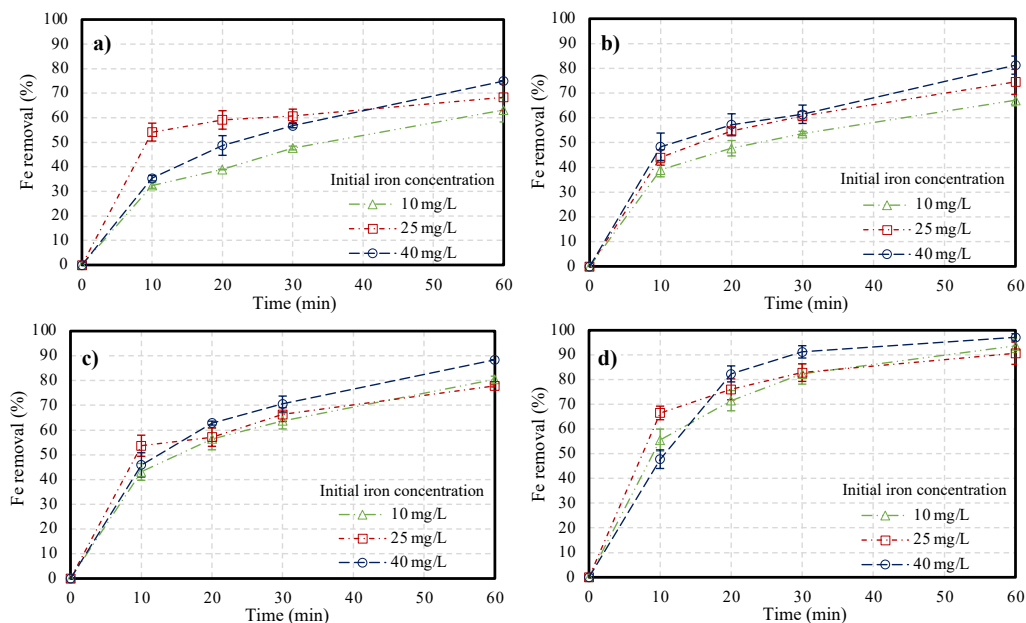
Fig. 5. Effect of the initial concentration on the percentage of iron removal for a) D=45 A/m^2, b) D=90 A/m^2, c) D=200 A/m ^{2} and d) D=390 A/m^2. pH$_i$=4, v=500 r.p.m. and T=25°C.
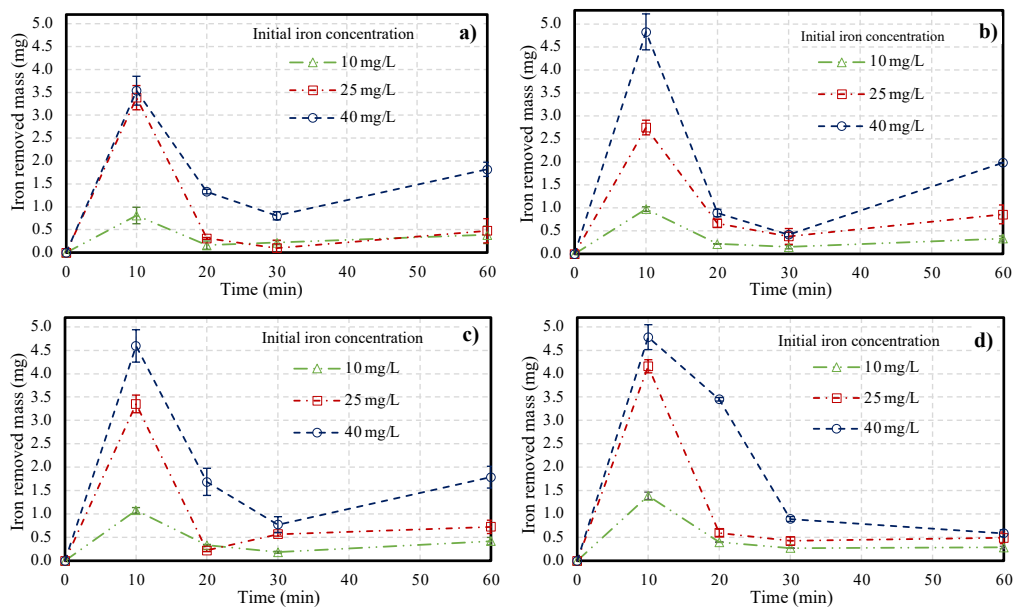

Fig. 6. Iron removed mass for different initial concentrations for a) D=45 A/m^2, b) D=90 A/m^2, c) D=200 A/m^2 and d) D=390 A/m^2. pH$_i$=4, t=60 minutes, v=500 r.p.m. and T=25°C.

Figure 6 shows the results of removed mass, the results are revealing, because they demonstrate that the factor that can define the efficiency of the process is the initial concentration, because despite having a large amount of energy, if there is no availability of ions the process will not be efficient. This is more evident in the first 10 minutes of the tests; this justifies the monitoring of the kinetics of the process because

it is decisive for a process in batch regime since taking the final results of the tests does not show a complete picture of what happens in the whole test.

Analyzing Figures 6a-d it is observed that there is a limit of mass diffusion from one compartment to another, this is determined by Faraday's laws and is demonstrated in the results obtained in these tests. For example, for an initial concentration of 10 mg/L a considerable increase in current density from 45 to 390 A/m² only resulted in a change of 0.58 mg (0.81 to 1.39 mg) of removed mass during that period, that is, an increase of energy in the magnitude of eight only increases by 1.71 times the removed mass. A similar case occurs if the results obtained for 25 and 40 mg/L are analyzed, since the difference in removed mass is 0.78 mg (from 3.38 to 4.16 mg) and 1.25 mg (from 3.53 to 4.78 mg), respectively, with the same change in current density. On the other hand, observing the case of the initial concentration of 40 mg/L from a density of 90 A/m² the removals remain practically constant (≈ 4.7 mg), this shows that under these conditions the process is dominated by ion diffusion independently of the current applied in the system.

3.3 Evaluation of initial pH value in iron removal

Finally, the influence that the initial pH value has on the iron removal in the electrodialysis process was evaluated. For the concentration of 10 mg/L only current densities of 45 and 200 A/m² were evaluated, the results are shown in Figure 7a and b. In both cases the removals achieved at a pH_i value of 4 and 6 are very similar (close of 64%), however, this percentage decreases considerably when working at a pH_i value of 2 with an approximate removal of 44%. Taking as a reference the Eh-pH diagram (Pourbaix diagram) in Figure 7c and according to the conditions of the solution and the iron concentration (10 mg/L), the predominant species in the system for all the pH values studied would be ferrous iron (Fe^{2+}). According to these results, the pH variable should not have any interference on the electrodialysis process. However, this type of diagram only gives a general visualization, so we proceeded to make a speciation diagram, this is shown in Figure 7d.

Considering this graph, the presence of the ferric iron species (Fe^{3+}) is identified, the concentration of this species increases as the pH value becomes more acidic. This agrees with the results observed in the iron removal, which indicates that the working valences of the species influence the diffusion of these, it is

then concluded that ions with higher valence require a greater amount of energy to perform the diffusion from one compartment to another. Due to this, the more acidic pH values show less removal than in the electrodialysis cell. It is worth mentioning that the pH values are referred only to initial values, since the water oxidation reaction ($2H_2O \rightarrow O_2 + 4H^+ + 4e^-$; $E° = -1.23$ V$_{SHE}$) and its consequent generation of hydrogen ions can modify the pH value in the anodic compartment, such reaction will be affected to a lesser or greater extent by the current densities used during the tests. In this case there are no considerable changes since we worked with relatively low current densities.

To determine whether the pH behavior described above is maintained with the other concentrations, tests were performed with a concentration of 25 mg/L and different pH_i values. Figure 7a shows that the removal percentages achieved for a pH_i value of 2, 4 and 6 were 76, 74 and 79%, respectively. As it can be seen in Figure 8a, at the beginning of the test there is a greater migration of cations towards the cathode compartment when the pH tends to be neutral, however, from the 30th minute this trend changes to the point where the final removals are very similar to each other. This behavior is different from that observed at a concentration of 10 mg/L. These small changes are associated with the water oxidation reaction that results in the generation of H⁺ ions by acidifying the anolyte. This leads to changes in the pH values reached at the end of the tests from the initial values, as shown in Figure 8b. It is worth noting what was found in the tests performed with pH_i value of 4 and 6, since they end in a pH like the test performed at a value of 2 (slightly below 2), which favors the speciation of iron to be similar so that final removals achieved are very alike.

Finally, the tests were performed with a concentration of 40 mg/L using the different pH_i values, the results are shown in Figure 9a and b. The removals for these tests are in the range of 64-75% and 69-88% for the densities of 45 and 200 A/m², respectively. However, what is relevant in these experiments is the behavior associated with the pH_i values for both densities, since in both series of tests the removals observed with a value of 6 are below the other two levels studied. These results are not consistent with those observed so far with lower concentrations of iron, since the pH_i values less acidic were those that reached the best removals of iron. It should be noted that this behavior is only observed when there is a very high concentration of iron, so it is important to rely on thermodynamics to explain what

happens in this series of tests, because it is clear that under these conditions the more acidic values promote a greater diffusion in the process.

This change is associated with a different speciation of iron than that observed for lower concentrations, which can be corroborated in the species distribution diagram in Figure 9c. The concentration of ferrous iron (Fe^{2+}) shows a decrease from a pH of approximately 4.7, this decreases the presence of the species that require less energy to be transferred, resulting in a lower ferrous:ferric ratio ($Fe^{2+}:Fe^{3+}$). This does not occur with more acidic

pH_i values, as these promote a higher concentration of ferrous iron species (Fe^{2+}) according to the speciation diagram in Figure 7d (10 mg/L). This diagram shows that speciation takes place in a different way, since the decrease in ferrous iron does not occur so considerably until a pH_i value of approximately 6 is reached and it occurs more gradually than at a higher concentration. This confirms that speciation will determine the final iron removal, and this factor is linked to the ratio $Fe^{2+}:Fe^{3+}$ that is presented in the anodic compartment, so a higher ratio will allow the diffusion process to be carried out more efficiently.

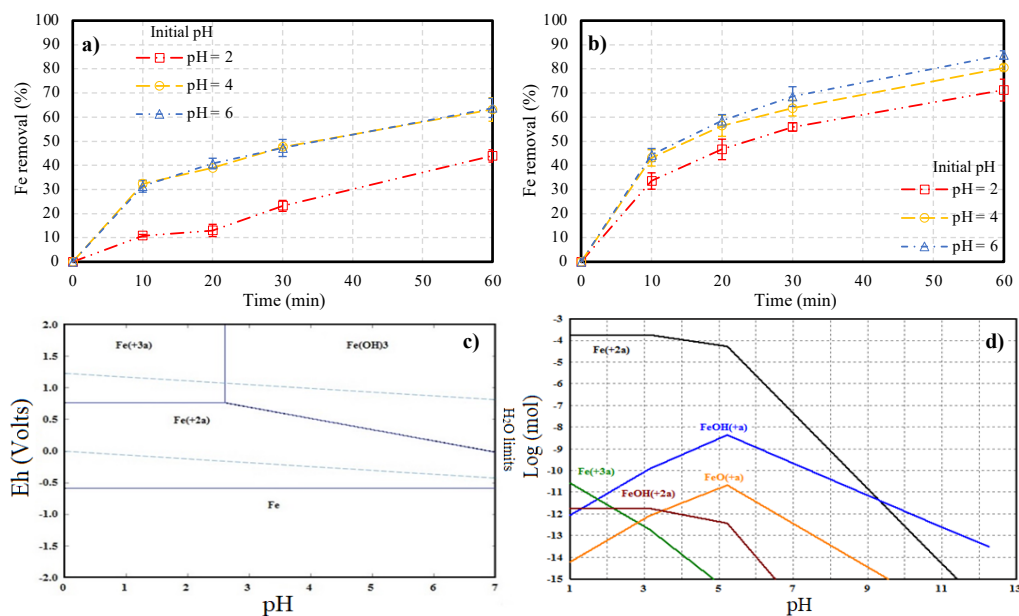Fig. 7. Effect of the pH_i value on the percentage of iron removal a) D=45 A/m^2 and b) D=200 A/m^2. C$_{Fe}$=10 mg/L, v=500 r.p.m. and T=25°C. c) Pourbaix diagram of the Fe-S-H$_2$O system, Fe=1.79x10^{-4} M, S=1.79x10^{-4} M and d) Distribution diagram of iron species for C$_{Fe}$=10 mg/L.

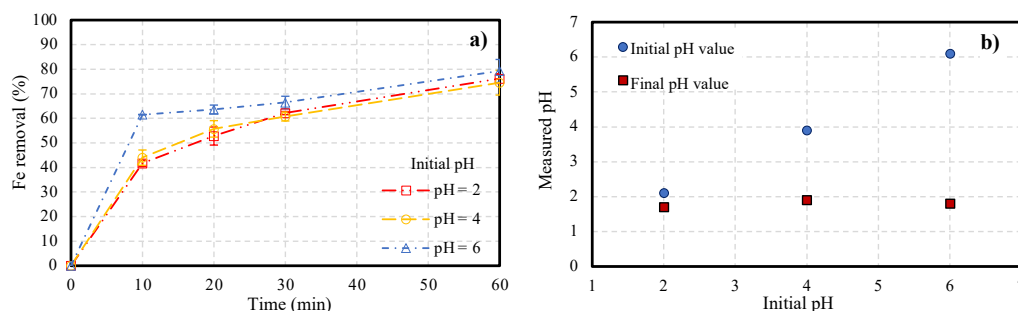Fig. 8. a) Effect of the pH_i value on the percentage of iron removal. b) Variation of the pH before and after the electrodialysis tests. D=90 A/m^2, C$_{Fe}$=25 mg/L, v=500 r.p.m. and T=25°C.
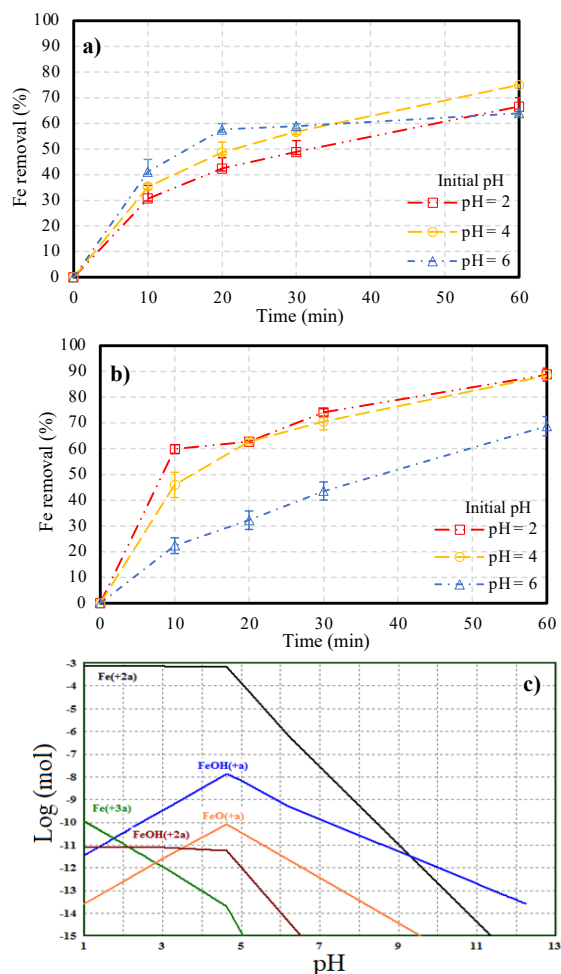
Fig. 9. Effect of the pH_i value on the percentage of iron removal a) D=45 A/m^2 and b) D=200 A/m^2. C$_{Fe}$=40 mg/L, v=500 r.p.m. and T=25°C. c) Distribution diagram of iron species for C$_{Fe}$=40 mg/L.

Conclusions

The use of the CMI-7000 membrane was effective in carrying out the iron removal in a synthetic solution. The highest percentage of removal obtained was 97.15% under the following operating conditions: time of 60 minutes, current density of 390 A/m^2, initial concentration of 40 mg/L, pH_i value of 4, stirring speed of 500 r.p.m. and initial temperature of 25°C. The initial iron concentration variable in the solution is decisive in the amount of mass removed without showing any dependence on current density, reaching removal values of 19.33 mg during the first 10 minutes with an initial concentration of 40 mg/L,

pH_i value of 4 and current density of 90 A/m^2. The effect that the pH_i value has on the iron removal varies mainly according to the initial concentrations of iron. For a lower number of ions in solution (10 mg/L) the increase of the pH_i value to values close to neutrality favors a higher percentage of removal, while, for a higher concentration (40 mg/L) more acidic values favor a higher removal. For an intermediate concentration (25 mg/L), the removal values were similar because the final pH of the tests were very similar due to the oxidation of water and the generation of hydrogen ions (H$^+$). The effect of pH on iron removal by electrodialysis is supported by thermodynamic simulation, where the predominant species are iron ferrous (Fe^{2+}), however, as changes in the pH of the anolyte occur, other species increase (the higher the acidity) or decrease (the higher the alkalinity). This conditions the iron removal, by the number of oxidation of the species that compromise in less or more measure the energy that acts on the ions, so that the removal will depend directly on the ratio of ferrous to ferric ions (Fe^{2+}:Fe^{3+}).

References

Abdulhadi, B., Kot, P., Hashim, K., Shaw, A., Muradov, M. and Al-Khaddar, R. (2020). Continuous-flow electrocoagulation (EC) process for iron removal from water: Experimental, statistical and economic study. *Science of The Total Environment*, 143417.

Abou-Shady, A., Peng, C., Almeria O, J. and Xu, H. (2012). Effect of pH on separation of Pb (II) and NO$_3^-$ from aqueous solutions using electrodialysis. *Desalination*, 285, 46-53.

Aguiar, A.O., Andrade, L.H., Ricci, B.C., Pires, W.L., Miranda, G.A. and Amaral, M.C.S. (2016). Gold acid mine drainage treatment by membrane separation processes: An evaluation of the main operational conditions. *Separation and Purification Technology*, 170, 360-369.

Akcil, A. and Koldas, S. (2006). Acid Mine Drainage (AMD): causes, treatment and case studies. *Journal of Cleaner Production*, 14(12), 1139-1145.

Amor, Z., Bariou, B., Mameri, N., Taky, M., Nicolas, S. and Elmidaoui, A. (2001). Fluoride removal from brackish water by electrodialysis. *Desalination*, 133(3), 215-223.

Aragaw, T.A. (2020). Recovery of iron hydroxides from electro-coagulated sludge for adsorption removals of dye wastewater: Adsorption capacity and adsorbent characteristics. *Surfaces and Interfaces*, 18, 100439.

Baker, R.W. (2012). Membrane Technology and Applications. Editorial Wiley, United Kingdom.

Banasiak, L.J., Kruttschnitt, T.W. and Schäfer, A.I. (2007). Desalination using electrodialysis as a function of voltage and salt concentration. *Desalination*, 205(1), 38-46.

Ben-Sik-Ali, M., Jellouli-Ennigrou, D. and Hamrouni, B. (2013). Iron removal from brackish water by electrodialysis. *Environmental Technology*, 34(17), 2521-2529.

Caprarescu, S., Vaireanu, D.I., Cojocaru, A., Maior, I. and V., P. (2011). A 3-cell electrodialysis system for the removal of copper ions from electroplating wastewater. *Optoelectronics and Advanced Materials*, 5(12), 1346-1351.

Cervantes-Macedo, A.H. (2014). Caracterización del drenaje ácido y de las rocas asociadas a una mina para evaluar su posible aplicación en un sistema de tratamiento pasivo. Tesis de licenciatura en Ingeniería de Minas Y Metalurgista Universidad Autónoma de México, México.

Chaparro, L. (2015). Drenajes ácidos de mina formación y manejo. *Revista ESAICA*, 1, 53-57.

Cifuentes, L., García, I., Arriagada, P. and Casas, J.M. (2009). The use of electrodialysis for metal separation and water recovery from $CuSO_4$-H_2SO_4-Fe solutions. *Separation and Purification Technology*, 68(1), 105-108.

Dyer, L.G., Richmond, W.R. and Fawell, P.D. (2012). Simulation of iron oxide/silica precipitation in the paragoethite process for the removal of iron from acidic zinc leach solutions. *Hydrometallurgy*, 119-120, 47-54.

El Midaoui, A., Elhannouni, F., Taky, M., Chay, L., Menkouchi Sahli, M.A., Echihabi, L. and Hafsi, M. (2002). Optimization of nitrate removal operation from ground water by electrodialysis. *Separation and Purification Technology*, 29(3), 235-244.

Galhardi, J.A. and Bonotto, D.M. (2016). Hydrogeochemical features of surface water and groundwater contaminated with acid mine drainage (AMD) in coal mining areas: a case study in southern Brazil. *Environmental Science and Pollution Research*, 23(18), 18911-18927.

Grande, J.A., de la Torre, M.L., Cerón, J.C., Beltrán, R. and Gómez, T. (2010). Overall hydrochemical characterization of the Iberian Pyrite Belt. Main acid mine drainage-generating sources (Huelva, SW Spain). *Journal of Hydrology*, 390(3), 123-130.

Johnson, D.B. and Hallberg, K.B. (2005). Acid mine drainage remediation options: a review. *Science of The Total Environment*, 338(1), 3-14.

Kabay, N., Arar, Ö., Samatya, S., Yüksel, Ü. and Yüksel, M. (2008). Separation of fluoride from aqueous solution by electrodialysis: Effect of process parameters and other ionic species. *Journal of Hazardous Materials*, 153(1), 107-113.

Kariduraganavar, M.Y., Kittur, A.A. and Kulkarni, S.S. (2012). Ion Exchange Membranes: Preparation, Properties, and Applications. In: Ion Exchange Technology I: Theory and Materials, (I. Dr and M. Luqman, eds.), Pp. 233-276. Editorial Springer Netherlands.

Koter, S. and Warszawski, A. (2000). Electromembrane Processes in Environment Protection. *Polish Journal of Environmental Studies* , 9(1), 45-56.

Laverde-Cerda, E., Altamirano-Briones, A., Zárate-Pozo, P., Sandoval-Pauker, C., Ramos-Guerrero, L., Munoz-Bisesti, F. and Vargas-Jentzsch, P. (2019). Iron removal for kinetics studies on Fenton Treatments: A new approach based on ferrocyanide. *Revista Mexicana de Ingeniería Química*, 19(1), 159-164.

Martí-Calatayud, M.C. (2014). Study of the transport of heavy metal ions through cation-exchange membranes applied to the treatment of industrial effluents. Tesis Doctoral Programa de Posgrado Ingeniería y Producción Industrial, Universitat Politecnica de Valencia, Espana.

Mohammadi, T., Razmi, A. and Sadrzadeh, M. (2004). Effect of operating parameters on Pb^{2+} separation from wastewater using electrodialysis. *Desalination*, 167, 379-385.

Ortega, A., Oliva, I., Contreras, K.E., González, I., Cruz-Díaz, M.R. and Rivero, E.P. (2017). Arsenic removal from water by hybrid electro-regenerated anion exchange resin/electrodialysis process. *Separation and Purification Technology*, 184, 319-326.

Serrano-Meza, A., Garzón-Zúniga, M., Barragán-Huerta, B., Estrada-Arriaga, E., Almaraz-Abarca, N. and García-Olivares, J. (2020). Anaerobic digestion inhibition indicators and control strategies in processes treating industrial wastewater and wastes. *Revista Mexicana de Ingeniería Química*, 19(Sup. 1), 29-44.

Shim, M.J., Choi, B.Y., Lee, G., Hwang, Y.H., Yang, J.-S., O'Loughlin, E.J. and Kwon, M.J. (2015). Water quality changes in acid mine drainage streams in Gangneung, Korea, 10years after treatment with limestone. *Journal of Geochemical Exploration*, 159, 234-242.

Simate, G.S. and Ndlovu, S. (2014). Acid mine drainage: Challenges and opportunities. *Journal of Environmental Chemical Engineering 2(3)*, 1785-1803.

Singh, R., Gautam, N., Mishra, A. and Gupta, R. (2011). Heavy metals and living systems: An overview. *Indian Journal of Pharmacology*, 43(3), 246-253.

Strathmann, H. (2010). Electrodialysis, a mature technology with a multitude of new applications. *Desalination*, 264(3), 268-288.

Torbaghan, M.E. and Khalili Torghabeh, G.H. (2019). Biological removal of iron and sulfate from synthetic wastewater of cotton delinting factory by using halophilic sulfate-reducing bacteria. *Heliyon, 5(12)*, e02948.

Torres-Santillan, E., Vargas-García, J., Ramirez-Meneses, E., Manzo-Robledo, A. and Hernandez-Perez, M. (2019). Induced electrochemical reduction of nitrates species on interface of Pt/MWCNTs prepared by vapor-phase impregnation-decomposition method. *Revista Mexicana de Ingeniería Química*, 18(2), 431-439.

Watten, B.J., Sibrell, P.L. and Schwartz, M.F. (2005). Acid neutralization within limestone sand reactors receiving coal mine drainage. *Environmental Pollution*, 137(2), 295-304.