Operating Conditions to Avoid the Passivation of Iron Electrodes in Electrocoagulation

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Abstract
The use of electrocoagulation for water treatment has drawn attention in the last few years due to several advantages it holds over traditional coagulation. However, gaps in the current understanding of the complex physicochemical processes performed during its operation have made the systematization of the design and the operation of this kind of systems quite difficult. This study intends to gather some knowledge about the factors that influence the coagulant formation when iron electrodes are used. Also, the electrochemical efficiency is verified at semi-pilot scale when the operation is performed out of the material passivation zone.
This study shows that it is possible to determine the limits of the passivation zone with galvanometric tests at microelectrolysis scale for different conductivities, pH and anions in solution. These results make it possible to design a full-scale reactor with electrochemical efficiencies close to 100%.

Keywords
Electrocoagulation, passivation, electrochemical reactor, iron electrodes, water treatment.

Introduction

The processes normally used for the physical-chemical water treatment, used for purifying drinking water or treating wastewater, include reverse osmosis, ionic exchange, softening, electrodialysis, adsorption in granular activated carbon, and chemical clarification (coagulation-sedimentation-filtration) (AWWA, 1999). From these treatments, the ones most used for technical and economic reasons in Mexico are chemical clarification and softening, even though electrodialysis, ionic exchange and above all reverse osmosis have gained popularity because of a recent reduction in investment and operation costs. The main problem with coagulation and softening is the high rate of sludge formation, as a by-product of the treatment; disposing of this sludge is a problem that has still not been satisfactorily solved.

In the early 80's, the development of water-purification techniques based on electrochemistry turned into an attractive method for the treatment of industrial wastewater. These technologies are

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electrocoagulation (EC) and electroflotation (EF), and they posses the potential to eliminate the disadvantages of conventional clarification. This kind of treatments can be effectively used to remove contaminants from aqueous solutions through electrolysis (Phutdhawong et al., 2000). Some of the applications of EC lie in the clarification of wastewater, the purification of drinking water (Chen et al., 2002), the removal of chromate, cyanide and arsenic from industrial effluents (Balasubramanian and Madhavan, 2001), the removal of fluoride from drinking water (Mameri , 2001), the removal of soluble organic matter (Tsai et al., 1996), the removal of emulsified oils (Hosny , 1996; Biswas and Lazarescu, 1991), the recuperation of phenolic (Phutdhawong et al., 2000) and tannic compounds (Chowwanapoonpohn et al., 2003), among others.

The main advantages of EC over chemical coagulation include the following: 1) EC requires relatively simple equipments, is easy to use and has flexible operation (Chen et al., 2002); 2) During treatment, the liquid is not enriched with anions and the salt content is not increased (Phutdhawong et al., 2000); 3) A sludge production up to 50% lower is achieved and there is a lower concentration of solids dissolved in the treated water, which makes it possible for it to be reused (Ögütveren and Koparal, 1997; Tsouris et al., 2001); 4) EC has the advantage of removing smaller colloidal particles since the applied electric field increases their movement and facilitates their coagulation (Yousuf et al., 2001); 5) The EC process avoids the use of chemical agents, which eliminates the problem of neutralization (Yousuf et al., 2001); 6) Electrolytic processes are electrically controlled without mechanical devices, so less maintenance is required; 7) The components of the system can be manufactured locally.

In the case of electrocoagulation, in contrast with chemical clarification, the coagulant is generated in situ by the electrolytic oxidation of the anode. In this process, ionic species are removed from the water through reaction with: a) ions of opposite charge, and b) the generated metallic hydroxide flocs. This process combines the effects producing gases like H_2 and O_2 through electrolysis and producing polyvalent cations through the oxidation of sacrificial anodes like Fe and Al. Metallic ions can react with the OH^- produced at the cathode during the formation of H_2, forming insoluble hydroxides that adsorb contaminants and contribute to coagulation.

Coagulation is first performed by the reduction of the net surface charge (compression of the diffuse double layer) to the point where colloidal particles previously stabilized by electrostatic repulsion can approach one another enough for the Van der Waals forces to permit agglomeration (AWWARF, 1991). One of the proposed mechanisms for the formation of metallic hydroxides (Yousuf et al., 2001) when using iron anodes is the following:
Anode:

$$Fe = Fe^{2+} + 2e^-$$

$$Fe^{2+} + 2OH^- = Fe(OH)_2$$

Cathode:

$$2H_2O + 2e^- = H_2 + 2OH^-$$
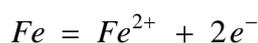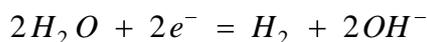
This ion generation is followed by the electrophoretic concentration of particles around the electrode, which neutralize their charge by coagulating. The freed adsorbents form long chains of polyhydroxides different from those formed by iron when it is added in chemical salts, since they have a different hydrated structure. This situation makes it possible to more easily remove, retain and dehydrate waste sludge.

The formed sludge removes the contaminants present in water through complexation or electrostatic attraction. In the proximity of the electrodes, the increase in the concentration of positively charged hydroxide polymers attracts anions such as bicarbonates and sulphates, which promote the precipitation of calcium and magnesium; this causes the partial softening of the water. The use of iron electrodes is preferred over that of aluminium electrodes, due to problems with the disposal of sludge containing the latter and to the passivation that it originates in the electrodes.

In its simplest form, an electrocoagulation reactor is an electrolytic cell constituted by an anode and a cathode. When the electrodes are connected to an external power source, the material of the anode will be electrochemically oxidized and the cathode will be subject to reduction. One way of increasing the efficiency of this technique is to use an alternating current that delays the normal mechanisms of

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electrode attack. This technology has also been applied through the use of electrodes in series; the water to be treated flows through them or through fluidized bed units. These units are equipped with non-consumable metals, between which a bed of aluminium particles is kept in turbulent flow using compressed air (Xiong et al., 2001).

All these studies have been directed towards the determination of the power required to produce a controlled amount of coagulant and the proper operation characteristics, including transport properties, residence time, voltage, Z potential, pH, chemical constituents of water, and characteristics of the electrodes optimizing the process. The electrocoagulation mechanisms have not yet been fully understood, however, and there are few considerations of the factors that allow for an effective and generic design; in addition, the problem of passivation of the electrodes has not yet been solved.

The objective of the present work is the study of the behaviour of the variables that intervene in the formation of coagulant in an electrochemical cell, through tests in microelectrolysis, with the objective of later applying the discovered criteria to the design of a reactor at semi-pilot scale.

Materials and Methods of the Study

The study mainly concerns the analysis of the parameters of interest in the formation of the coagulant; that is to say: the maximum current density that can be used before the electrodes passivize or important parasite reactions occur, the pH interval in which the electrochemical reactions of interest are not affected, the influence of electrical conductivity and the type of support electrolyte. Due to the wide range of conductivities that can be encountered in the different kind of waters that can be treated, it was necessary to characterize the anodic behaviour of the study material in a wide interval of conductivities. In the present study, the system response was analyzed between 1,000 and 100,000 μS/cm, in order to cover both municipal and industrial wastewater. With respect to pH, the studied interval (between 5 and 9) was adopted from the theoretical chemical coagulation zone that relates the different iron species that form as a function of pH and the dominant form of coagulation (Arboleda , 2000).

Initially, the phenomena of electrode passivation were studied; i.e., voltage was increased and the maximum current density at which an increase in electric resistance is not observed was measured.

In order to achieve this objective, the electrochemical techniques of voltammetry as well as chronoamperometry, were used. They were performed with magnetic stirring using distilled water, nitrogen atmosphere and salt as an electrolytic support medium. The electrochemical cell was a conventional three-electrode cell for microelectrolysis experimentation.
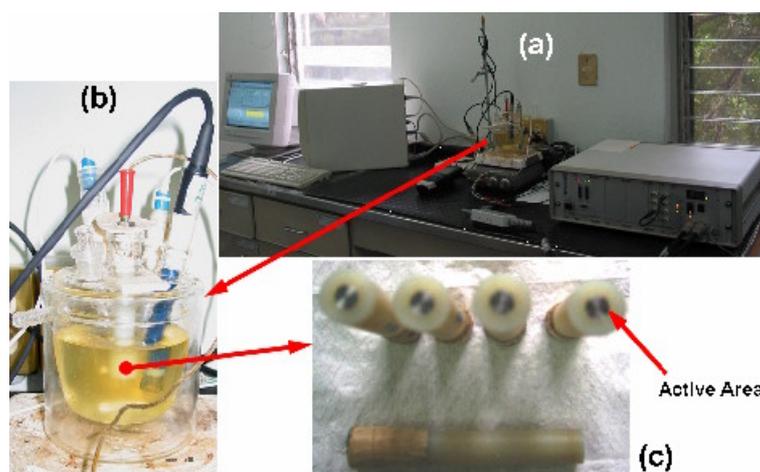
Figure 1. (a) Experimental montage, (b) conventional three-electrode cell, and (c) work electrode

The experimental montage (Figure 1) includes a 250 mL double-jacket cell manufactured from glass and with openings for a platinum auxiliary electrode (Radiometer Analytical E31MOO1 M241 Pt), a calomel reference electrode with a ceramic joint for protection (Radiometer Analytical REF 401), and a cylindrical work electrode made from 1045 steel embedded in PVC, with an exposed circular shaped work area of 0.3318 cm^2 and the following chemical composition:

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Table 1. Chemical composition

Component	% (Weight)
C	0.42 – 0.5
Fe	98.51 – 98.98
Mn	0.60 – 0.90

A pH meter (HACH SensION 2), a conductivity meter (HACH SensION 5) and a HACH DR/2010 equipment to determine iron concentration were used as auxiliary equipment. The tests were performed an Autolab PGSTAT 30 potentiostat, connected to a computer with the corresponding software (GPES, General Purpose Electrochemical Software) that allowed the acquisition and analysis of the results. The potentiostat allows a maximum current of 1 ampere and a maximum potential of 10 volt. The studied variables in this stage were: the material of the electrode, pH and conductivity of the solution, and the influence of electrolytes that can normally be found in the water to be treated. Each test was repeated at least three times to insure that the behaviour was repetitive.

Once the previous vas completed, a piston flow electrocoagulation unit was built (Figure 2) to treat a maximum of 0.1 L/s, with electrodes measuring 5 cm x 10 cm x 0.5 cm connected in parallel, separated 0.5 cm from one another, and made from commercial-grade iron. The current was fixed through the use of a power source that allows a maximum of 10 ampere and 20 volt.
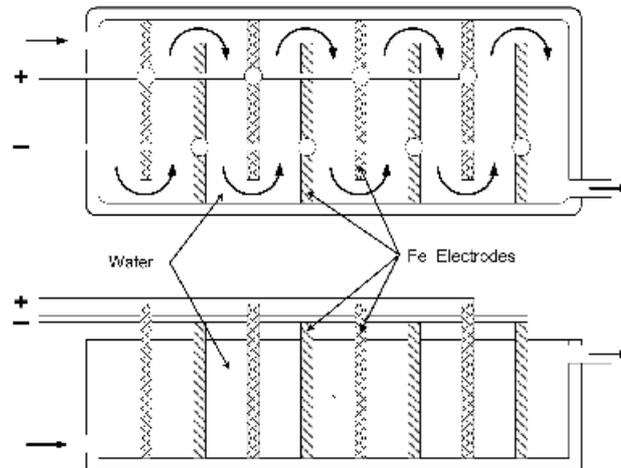
Figure 2. Schematic representation of the piston flow electrocoagulation unit

The electric current established in the cell by means of a power source is an indicator of the reaction rate and is defined as the charge increment (dq) flowing through a plane per unit of time (t).

$$I = \frac{dq}{dt} = \frac{coulomb}{s}$$

A useful measure of the amount of charge flowing through the system is Faraday's constant (F), defined as the charge transported by one mol of electrons and equal to 96,485 coulomb/mol. According to Faraday's Law, q = n F m, and thus:

$$I = \frac{dq}{dt} = n F \frac{dm}{dt}$$

$$\int_0^t I \, dt = n F \int_0^m dm$$

$$I \, t = n F m$$

And since:

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$$t = \frac{V}{Q}$$

it follows that:

$$\frac{m}{V} = \frac{I}{Q\,n\,F}$$

i.e., the production of moles (m) per reactor volume unit (V) is a function of the applied current (I), of the test flow (Q) and the number of electrons involved in the reaction (n).

$$\frac{m}{V} = \frac{I}{Q\,n\,F}$$

yield, calibration tests were performed at different conductivities, flow rates, electrode numbers, and applied current levels. The used solution was made of water from the laboratory supply, conditioned with salts to fix conductivity. Once the flow, study current, pH, and conductivity of the water at the reactor exit were established, a sample was taken to determine the amount of iron produced.

Analysis of the Passivation of Electrodes in Microelectrolysis
The influence of conductivity and pH on passivation
This study was performed by rising the electric current at a rate of 0.0000666 A/s, at four different conductivities (1,000, 5,000, 10,000 and 100,000 μS/cm) set with NaCl and three pH values (5, 7 and 9) fixed with NaOH or HCl depending on the desired pH.

The results show (Figure 3) that for conductivities in the order of 1,000 μS/cm, the response of the potential to the increase in current is linear up to the maximum voltage allowed by the equipment and shows maximum current densities of 0.05 A/cm^2. At 5,000 μS/cm, there was no evident passivation of the material up to current densities of 0.1 A/cm^2. For larger conductivities, the passivation of the electrode is evident for current densities greater than 0.3 A/cm^2. The system response in the non-passivation zone was not affected by pH, since the curves produced at the three pH levels of the study overlap for the 4 studied cases.
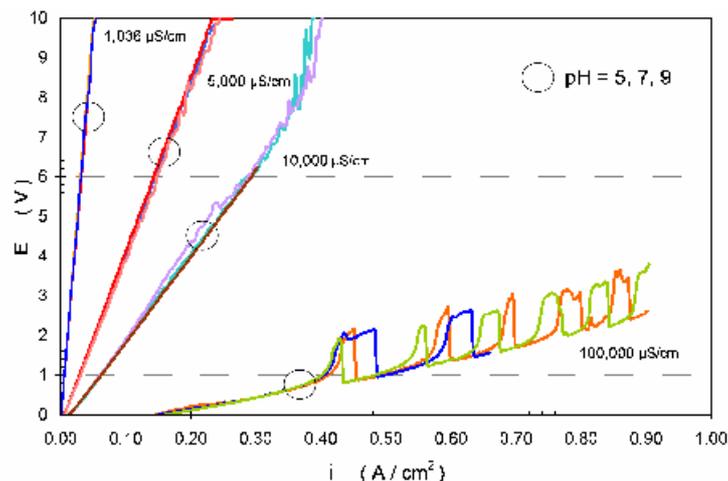
Figure 3. The effect of conductivity and pH on the passivation of iron

The influences of conductivity and pH on the production of Fe in the non-passivation zone.
The total iron production in the non-passivation zone was verified through chronopotentiometry (Figure 4); conductivity was fixed with NaCl, pH was fixed at 5, 7, and 9 with NaOH or HCl, and current density was fixed at 0.040 A/cm^2 for 65 seconds to obtain a theoretical Fe^{2+} concentration of 0.999 ppm according to Faraday's Law. Theoretical iron is calculated assuming that all of the applied

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current is used to transform Fe^0 into Fe^{2+}. The current density for this test was chosen based on the highest that can be applied to low conductivities, given the maximum voltage allowed by the equipment (10 V).
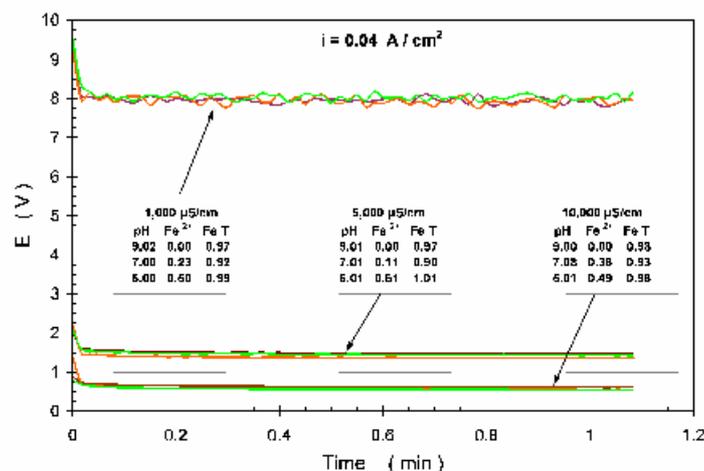
Figure 4. The effect of conductivity and pH on iron production at constant current density

Where
Fe^{2+} = Ferrous ion (Fe^{2+})
Fe^T = Total iron (includes Fe^{2+} and Fe^{3+})
pH = Initial pH of the water

These experiments confirm the results obtained in the previous section, showing that there is no passivation in the electrodes when they are submitted to a constant current if the current density is under 0.3 A/cm^2. It is also observed that pH has no effect on the potential response of the electrode; however, pH does considerably affect the predominant iron species in the solution (at a higher pH, the proportion of Fe^{2+} becomes proportionally smaller). At a pH of 7, also, there is a lower iron production than there is at a pH of 5 and 9. This indicates that a neutral pH reduces the electrochemical efficiency of the reaction at the three studied conductivities. It is interesting to notice as well that the theoretical Fe^{2+} calculation matches the measured total iron (Fe^T) values; this indicates that all of the applied current is used to produce Fe^{2+}, some of which transforms into Fe^{3+} in the solution depending on the pH.

The effect of different anions on passivation

The effect on the current density of using NaCl, NaSO4, and NaNO3 as support electrolytes was analyzed through linear sweep voltammetry at a rate of 0.01025 V/s and a conductivity of 5000 μS/cm. This was done in order to analyze the effects that different anions in the solution may have on the passivation of the electrodes.

At a pH of 5, the effect of each of the anions was analyzed separately; the pH was fixed through HCl, H_2SO_4 or HNO_3, depending on the anion used to fix the conductivity. At pH levels of 5 and 10, the three ions were combined as follows: a) 100 ppm of NaCl + 100 ppm of $NaSO_4$ + enough $NaNO_3$ to reach a conductivity of 5,000 μS/cm (A = B = 100 ppm in Figure (5); b) 1000 ppm NaCl + 1000 ppm $NaSO_4$ + enough $NaNO_3$ to reach a conductivity of 5,000 μS/cm (A = B = 1,000 ppm in Figure 5).

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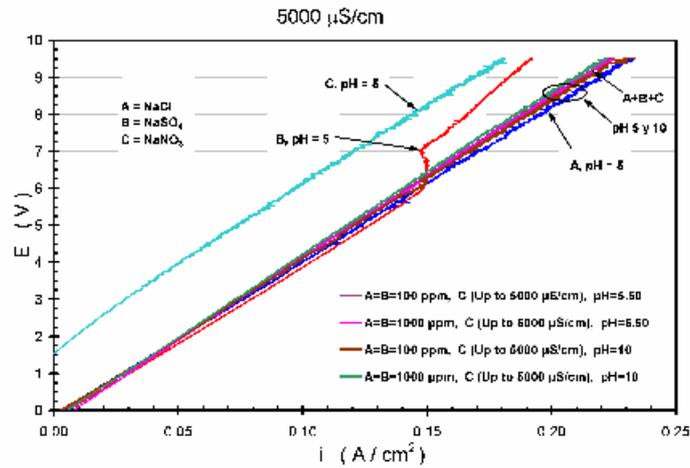
Figure 5. Effect of different ions and pH on iron passivation at constant conductivity

The results show that there is a higher energy consumption in the presence of nitrate from the beginning of the sweep, and in the presence of sulphate starting at approximately 0.15 A/cm². It was also observed that mixing all three anions yields the same system response as chloride alone at any of the extreme pH levels of this study. This protective effect of chloride towards electrode passivation during electrocoagulation had been previously observed (Guohua, 2004) for carbonates and sulphates.

Equivalent responses by varying current and voltage

The responses obtained when performing potential and current sweeps were practically identical (Figure 6), as long as the sweep rates corresponded to the slopes observed in the system. In the case of this study, these rates were calculated and the results were compared against those of both kinds of tests.

Conductivity was fixed at 5,000 μS/cm for each of the studied ions (chloride, sulphate and nitrate) at a pH of 5.
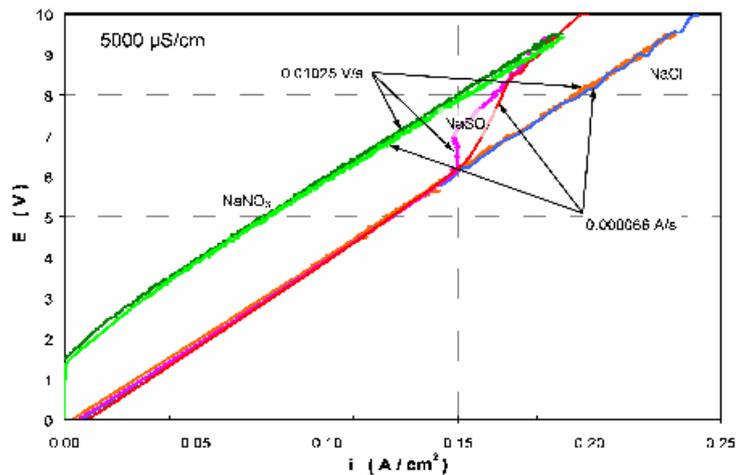
Figure 6. Equivalence in the responses of potential and current sweep

The results show that at equivalent sweep rates the responses are the same; thus, both methods can be used indistinctively for the study of interesting electrocoagulation phenomena. The advantage of controlling the current (or the current density for a given area) is that this is the parameter of interest for establishing the amount of iron ions produced.

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PISTON FLOW ELECTRO-COAGULATION CELL

Once the analysis of the factors that influence the production of the coagulant was concluded, the next stage in the study was to verify the efficiency of the system in the production of coagulant at semi-pilot scale in a piston flux reactor.

In order to calibrate the coagulant production of the system, the following were varied for a flow rate of 0.053 L/s: applied current (2 A, 6 A and 10 A), solution conductivity (2,500, 5,000 and 7,000 μS/cm), and the number of active electrodes in the cell (2, 4, and 6); in addition, coagulant production was also measured at operation flow rates of 0.045 L/s, 0.06 L/s, and 0.10 L/s. Conductivity was fixed using table salt (NaCl); the pH was that of water, which varied between 7.5, for the lowest conductivity, and 6.5 for the highest. The iron concentration at the cell exit was measured using HACH equipment, but some measurements were performed through atomic absorption. The results show an acceptable correlation between the two methods, with a tendency to separate as the concentration of iron ions increases (Figure 7).
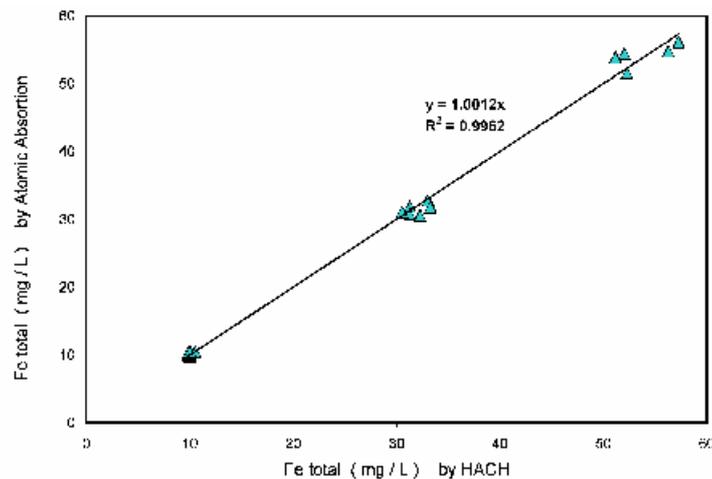
Figure 7. Comparison of total iron measurements in HACH and atomic adsorption equipments

The influence of conductivity on coagulant production

Figure 8 shows that the iron ion production in the cell is very close to the theoretical yield for the operation conditions of the system, without being significantly affected by the difference in conductivities. However, the larger errors were observed at the maximum studied concentration; this suggests that at high iron ion productions the electrochemical efficiency is affected. On the other hand, it is also observed that iron production depends only on the applied current, and that conductivity (during the study interval) does not significantly affect the results.
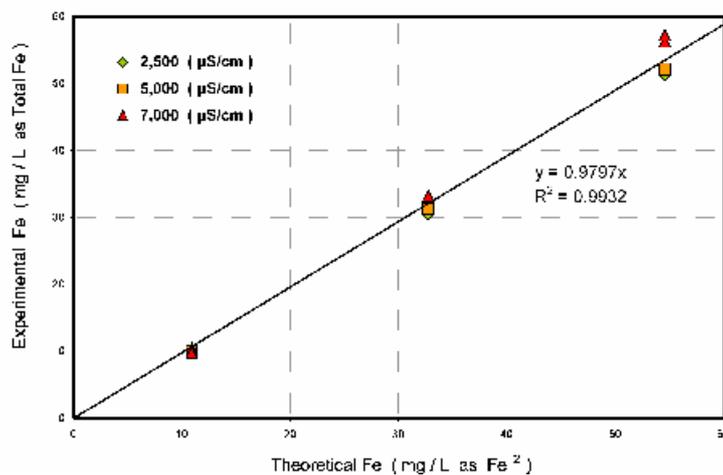
Figure 8. Theoretical versus experimental iron at different conductivities

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The influence of operation flow rate on coagulant production

At the three studied flow rates, the maximum discrepancy between theoretical and measured coagulant yield was lower than 4% and the highest experimental error are observed when the flow is lowest (Figure 9), however, this difference is of no significance, and it requires of a deeper study to be understood.
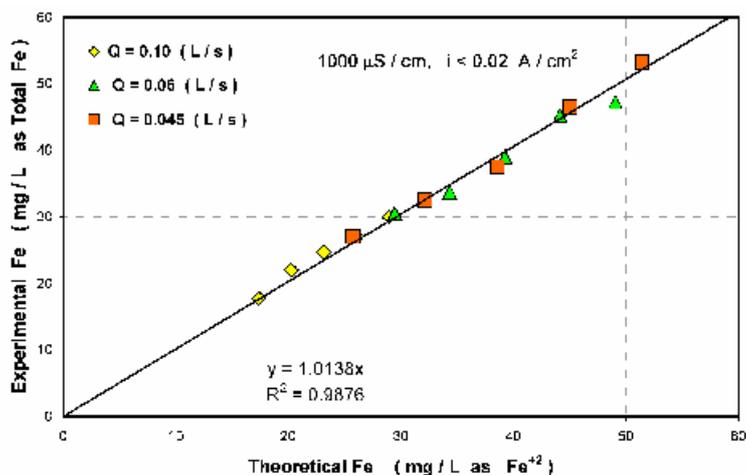
Figure 9. Theoretical versus experimental iron at different flows

Conclusions

It was found in this study that in an electrocoagulation reactor it is convenient to fix current density, based on the conductivity of the water to be treated, and that the electrodes' tendency to passivate is a direct function of the conductivity of the water to be treated. Linear sweep voltammetry is a useful tool for establishing the adequate current density limits in order to avoid the passivation of the material used as a work electrode. In general, it was observed that small current densities ensure a more stable electrochemical behaviour; in addition, this also favours a lower energy consumption and thus a reduction in operation costs.

On the other hand, the studied pH interval does not influence the passivation of the iron electrodes, which facilitates the operation of the system and makes it possible to optimize this variable without affecting coagulant production. One aspect that must be considered during electrocoagulation is that the pH of the water to be treated is an important factor in the efficiency of coagulation; this is so because pH determines the predominant iron ion and thus favours or hinders the formation of floccules that trap the contaminants present in the water.

The presence of chlorides is another one of the factors that make this treatment technology more efficient; first, it increases the conductivity of water and thus reduces energy consumption; it also protects the electrodes from passivation, even in the presence of ions that have the opposite effect.

The high iron production reduces the electrochemical efficiency; this causes the theoretical iron production, according to Faraday's Law, not to be fully reached in practice.

Finally, flow rate seems to be another factor that influences the electrochemical efficiency of the system (a more detailed study is needed), possibly because the flow speed increase in the vicinity of the electrodes reduces the accumulation of deposits and, consequently, passivation of the material.

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Nomenclature

Symbol	Description	Units
dq	charge increment	coulomb
E	Electric tension	volt
F	Faraday's constant	coulomb/mol
I	Electric current	ampere
i	Current density	A / cm^2
m	ions produced	mole
n	number of electrons	-
Q	Flow	L / s
q	electric charge	coulomb
t	Time	second
T	Total	
V	Volume	liter

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