



Research Signpost  
37/661 (2), Fort P.O.  
Trivandrum-695 023  
Kerala, India

Evaluation of Electrochemical Reactors as a New Way to Environmental Protection, 2014: 1-16  
ISBN: 978-81-308-0549-8 Editors: Juan M. Peralta-Hernández, Manuel A. Rodrigo-Rodrigo and  
Carlos A. Martínez-Huitle

# 1. Fundamentals of electrocoagulation

Nilson Marriaga-Cabrales and Fiderman Machuca-Martínez

*GAOX Group, Chemical Engineering School, Universidad del Valle  
Calle 13 No 100-00, PBX +57 2 3212100 A.A. 25360 Cali, Colombia*

**Abstract.** Electrocoagulation is an alternative technology for waste water treatment in which are consumed only metallic plates (sacrifice anodes) and direct electrical current. This chapter presents the theoretical fundamentals that govern the electrocoagulation and likewise the conventional chemical coagulation. Also, the chemical and electrochemical reactions that take part in these processes and a discussion of the advantages and disadvantages and the most important parameters of operation are included; finally, some designs of reactors that have been proposed are shown.

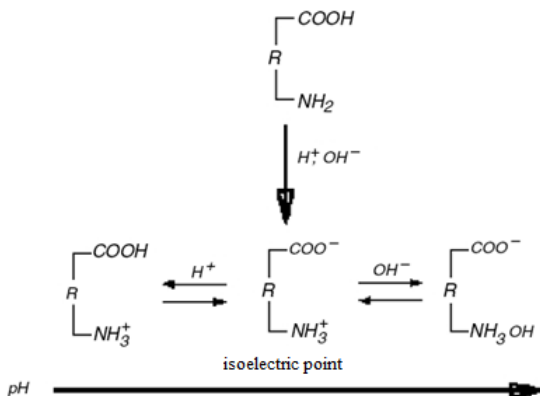
## 1. Electrocoagulation

Electrocoagulation is an alternative waste water treatment that combines electrochemical processes with conventional chemical coagulation. Many studies have been carried out to evaluate the performance of this technique in a lot of waste water [1]. In the electrocoagulation direct electrical current is used to add metal ions into waste water which are subsequently hydrolyzed to generate coagulating species. The entire process is conducted in an electrolytic reactor (batch or continuous) in which a clarified liquid and a sludge are obtained as principal products.

Correspondence/Reprint request: Prof. Nilson Marriaga-Cabrales, Ph.D., Chemical Engineering School Universidad del Valle, Cali, Valle del Cauca, Colombia. E-mail: [nilson.marriaga@correounivalle.edu.co](mailto:nilson.marriaga@correounivalle.edu.co)

### 1.1. Chemical coagulation

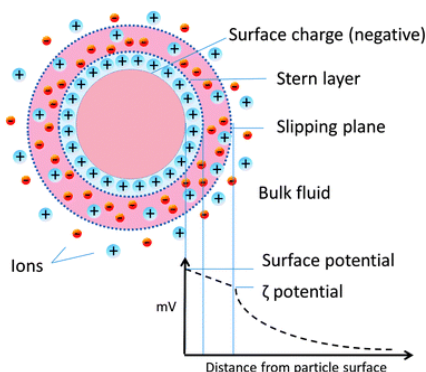
Colloids are small particles with sizes between  $10^{-6}$  and  $10^{-3}$  mm that are present in a lot of varieties of waste waters and industrial effluents and they increase turbidity and color. Generally, the colloids have a surface charge acquired by dissociation of their functional groups or by the preferential adsorption of ions from solution. Due to the dissociation of the functional groups, the colloids can acquire positive or negative surface charge when the pH of the suspension is modified (Figure 1).



**Figure 1.** Primary charge of an organic colloid as a pH function (Adapted from [2]).

**1.1.1. The double layer.** This model is used to visualize the ion atmosphere on the vicinity of the charged colloid and to explain how the electrical repulsive forces operate. Thus, the attraction of a negative colloid makes that some positive ions generate an adjacent layer around the surface of the colloid (Stern layer), all the charges presented in this layer can move together with the colloid. Additional positive ions are attracted by the negative colloid but these are now rejected by the Stern layer, equally other negative ions are attracted by the positive layer; Figure 2 shows the change in the charge density around the colloid and the distribution of positive and negative ions around of it.

This dynamic equilibrium resulting in the formation of a counter-ions diffuse layer having a high concentration near the Stern layer and then gradually decreases with distance until a balance is achieved with the concentration of the counterion within the suspension. The thickness of this double layer depends on the type and concentration of the ions present in the solution.



**Figure 2.** Double layer configuration

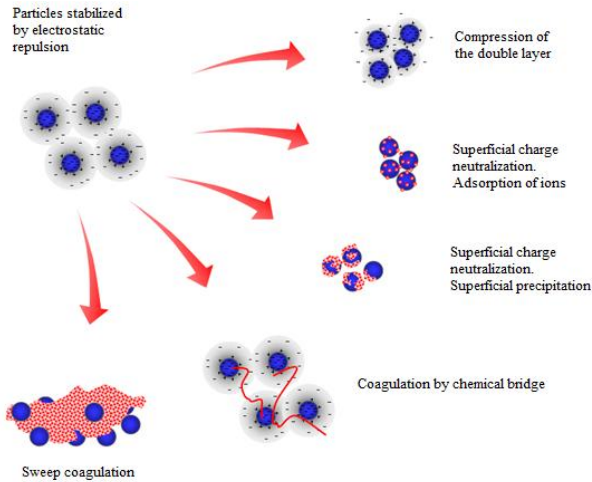
**1.1.2. Zeta potential.** The colloid and their ionic atmosphere produces a electric net potential between the colloid surface and the ion cloud. The potential is greater at the surface of the colloid and gradually falls with distance, then it approaches zero towards the end of the diffused layer. There is a slipping plane, close to the Stern layer, in which the ions layer moves together with the colloid and the other ions do not.

This potential is known as the zeta potential and is an indirect measure of the surface potential of the colloid. The higher the magnitude of the zeta potential will be greater the force of repulsion among the colloids and the suspension will be more stable [3].

**1.1.3. Coagulation.** Usually can be achieved by neutralizing the net charge of the colloidal particles by the increased concentration of counterions in the diffuse layer, mechanism of charge neutralization, thereby decreasing the repulsive forces. By decreasing the zeta potential values close to  $\pm 10$  mV, the double layer is compressed and the coagulation of the colloids is possible because they begin to dominate the attractive forces.

When the counterions have less valency higher concentration of them will be required to neutralize the charge of the colloid. Thus, a divalent ion is 30 to 60 times more effective in neutralizing charges that other monovalent and a trivalent ion is 700 to 1000 times more effective than the monovalent (rule of Schultze-Hardy and DVLO theory) [2].

To carry out coagulation by neutralization usually hydrolysable species are used such as  $\text{Al}^{3+}$  y  $\text{Fe}^{3+}$  that at acid pH generates ions-complexes soluble, e.g.  $[\text{M}(\text{H}_2\text{O})_6]^{3+}$ ,  $[\text{M}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$ ,  $[\text{M}(\text{H}_2\text{O})_4(\text{OH})_2]^+$  and even polynuclear-ions complexes are generated [4,5]. These complex ions may also be deposited on the surface of the colloids contributing with the charge neutralization (superficial precipitation).

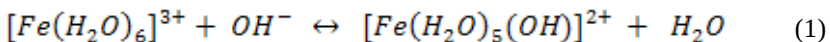


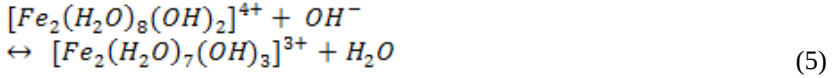
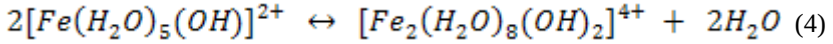
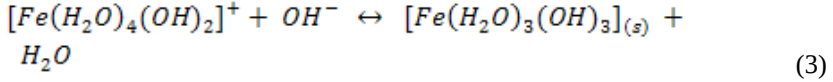
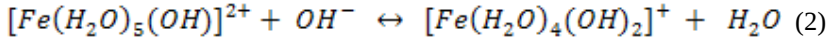
**Figure 3.** Colloids coagulation mechanisms (Adapted from: [7])

It is also possible to use polymers with high charge density that can adhere electrostatically to oppositely charged colloids achieving their agglomeration, coagulation by chemical bridge. Another alternative is to generate species insoluble amorphous (non-crystalline) with high superficial area, thus, are obtained voluminous flocs that catch and precipitate the colloids, mechanism of sweep coagulation (Figure 3).

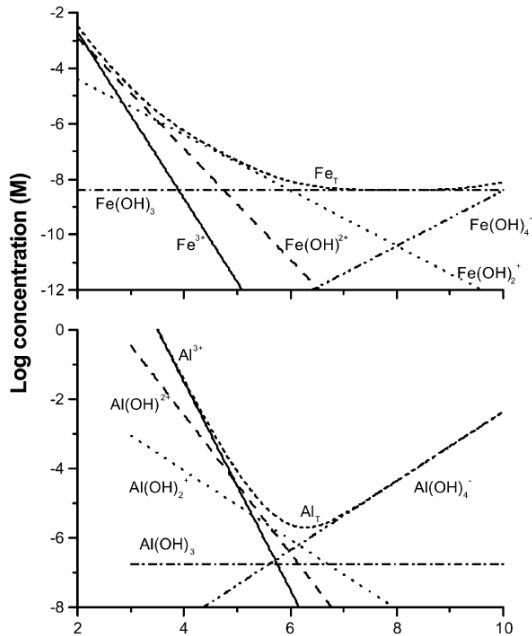
**1.1.4. Metallic complexes.** At pH close to 3.0 the cations of iron and aluminum produces hexa-aquo-coordinated complexes dissolved in water,  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ . For iron ions the polarization of the coordinated water molecules is strongly dependant on the charge of the cation (oxidation state  $2^+$  or  $3^+$ ). Thus, the ferric complexes are more acid than the ferrous complexes, therefore, the hydroxylation i.e substitution of water molecules by hydroxyl anions, in these complexes ocure at a different pH range. At room temperature the hydroxylation of  $\text{Fe}^{2+}$  in water begin at pH about 7.0 whereas for  $\text{Fe}^{3+}$  begin at pH 4-5 [6].

The hydroxylated complexes are not stable as monomeric species in solution therefore are condensed by nucleophilic substitution caused by the hydroxyl ligands. For hexa-aquo complexes,  $[\text{Fe}(\text{H}_2\text{O})_h(\text{OH})_{6-h}]^{(2-h)+}$ , the condensation proceeds by elimination of a water molecule and formation of hydroxo bridges (olation mechanism).





As the pH is increased, these hydroxylated species are transformed in species polynuclear-amorphous insoluble with zero valence that precipitate causing sweep coagulation (Figure 4), even it is possible to precipitate colloids with zeta potential greater than  $\pm 10$  mV [8]. Usually, these insoluble products are abbreviated and are written as  $Fe(OH)_{3(s)}$ . A similar mechanism is found when exist  $Fe^{2+}$  or  $Al^{3+}$  dissolved into the water [4].



**Figure 4.** Concentrations of monomeric hydrolysis products of  $Fe^{3+}$  and  $Al^{3+}$  in equilibrium with the amorphous hydroxides, at zero ionic strength and 25 °C (Adapted from: [4])

Generally this latter mechanism performs best to remove colloidal and dissolved organic matter that when particles are destabilized by neutralization charge. The details involved in the process can become highly complexes incorporating electrostatic phenomena, adsorption/desorption, stearic forces and even hydrodynamic effects [9,10]

On the other hand, it has been found that the kinetics of oxidation of ferrous species, by dissolved oxygen, accelerates significantly only in alkaline medium [11] and  $\text{Fe}(\text{OH})_{3(s)}$  is obtained [12] which have been proved to be an useful adsorbent in the wastewater treatment [13]. If the oxidation of ferrous hydroxide is partially achieved double-layered hydroxides are obtained called green rust, oxyhydroxides-ferrous-ferric [14] characterized by its high capacity anion exchange[15,16].

## 1.2. Basic concepts

In the conventional chemical coagulation are added water-soluble inorganic salts containing hydrolysable metal cations, usually are used aluminum sulfate or ferric chloride. In the electrocoagulation technique these cations are generated *in situ* through the electrolytic dissolution of sacrificial anodes, usually iron or aluminum plates are used (Figure 5).

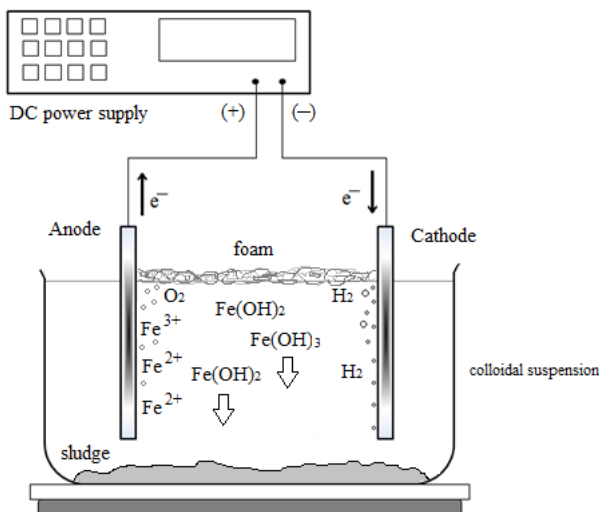


Figure 5. Electrocoagulation cell scheme.

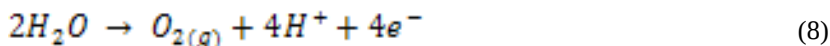
**1.2.1. Electrochemical and chemical reactions.** The reactions that take place during the electrocoagulation have not been fully identified because they depend on the waste water characteristics, some general reactions have been proposed equating to the reactions that take place during chemical corrosion.

The electrocoagulation can be considered as a process of accelerated corrosion caused by imposing a potential more noble than the reversible potential of the anode. Thus, it has been proposed that the reactions are tightly bounded by the pH of the suspension. When iron or aluminum anodes are used in water and the pH is below 4.0, actually the exact magnitude of pH is uncertain for electrolytes other than pure water, are presented the next reactions:

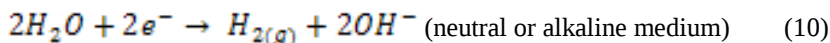
Anode:



If the oxygen evolution potential is reached then:



Cathode:



The global reaction rate depends on the mechanism of electrodisolution of the metal, the pH, the temperature and agitation regime. For pH less than 4.0 the ferrous oxide (FeO) is soluble, there are not protective film on the metal surface, and thus the metallic dissolution process is faster.

Likewise, the ferrous or aluminum cations electrogenerated can react with anions such as oxalates, carbonates, phosphates, etc., or with molecular oxygen produced on the anode to form insoluble products on electrode surface causing passivation and diminishing the rate of dissolution.

Also, the rate of oxidation of  $Fe^{2+}$  to  $Fe^{3+}$  in water is only significant to alkaline pH as long as the sample maintains saturated with  $O_2$ . Morgan y Lahav (2007) found that when the pH was maintained at 9 the oxidation of  $Fe^{2+}$  was produced almost immediately but at pH 6 only 40% of  $Fe^{2+}$  was

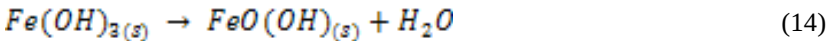
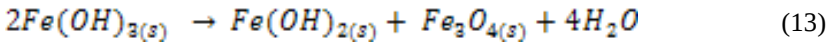
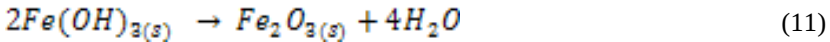
oxidized after 250 minutes [11]. However, the oxidation of  $\text{Fe}^{2+}$  can also be instantaneously achieved through the creation of oxidizing species produced for oxidation of chloride ions on the anode [17].

When the electrocoagulation cell is operated at low current densities the molecular oxygen is not produced and is obtained mostly  $\text{Fe}^{2+}$ ; in some cases, it is possible that the chemical dissolution of the metal produces more metallic cations, that those produced through electrolytic process, and the theoretical concentrations established by Faraday's law are exceeded [18].

For pH between 4 and 7 approximately the electrogenerated metallic cations undertake chemical reactions of hydrolysis. Then, aluminum hydroxides flocs are precipitated with a white color, these complexes reach their lower solubility with a pH between 6.0 and 6.5. For the iron, ferrous hydroxides flocs are precipitated with a dark greenish color, these ferrous hydroxides reach their lower solubility with a pH between 11.0 and 11.5.

If the  $\text{Fe}^{2+}$  is oxidized, the ferric hydroxides begin to precipitate yellowing flocs; this are insoluble as well in a wide window of pH and they are more insolubles than those ferrous hydroxides. The solubility constant for ferric hydroxides in water is  $2 \times 10^{-39}$  while for the ferrous hydroxide is  $1 \times 10^{-14}$  [19].

If pH is increased then the sweep coagulation is enhanced due to the polymerization of iron oxyhydroxides ( $\text{FeO}(\text{OH})$ ) that catch more colloids; pH to reach the minimum solubility of  $\text{Fe}(\text{OH})_3$  in water is in the range of 7.0 to 8.0. In addition, there may be the formation of green rust:



It is also possible to form iron oxides such as magnetite ( $\text{Fe}_3\text{O}_4$ ) and maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) that are characterized because of the showing magnetic susceptibility. However, the details involved in the process can become highly complex including electrostatic phenomena (charge neutralization, compression of the double layer), adsorption, desorption, steric forces and hydrodynamic effects [4].

The electrocoagulation involves the following consecutive steps:

- i) *Anodic dissolution*: generation of metal cations product of dissolution of sacrificial anodes due to the passage of direct electric current.

- ii) *Generation of coagulants*: The metallic cations react with hydroxyl ions ( $\text{OH}^-$ ) generating hydroxylated species, ions-complexes positively charged. Several kind of ions-complexes can be formed depending on the pH of the suspension, so that these ions-complexes can present several possibilities of molecular weights. When pH is acid the metal cations and ions-complexes may destabilize the colloidal particles by neutralizing the superficial charges (charge neutralization). At higher pH the ions-complexes are completely hydrolyzed to generate insoluble amorphous species (oxides, hydroxides and oxyhydroxides) that cause sweep coagulation.
- iii) *Flotation*: Due to cathodic reaction small bubbles of hydrogen are produced and in some cases, oxygen bubbles are produced by water electrolysis at the anode. It is possible that these bubbles are adhered to the coagulated particles due to superficial phenomena and, through natural buoyancy, rise to the surface along with the foam which can be easily removed afterwards.
- iv) Additionally, some other physicochemical reactions could happen: cathodic reduction of compounds such as nitrates and nitrites, reduction of metal cations, electrodeposition of cations, and generation of metal oxides and hydroxides on the electrode surfaces (*passivation*).

On the other hand, the electrocoagulation presents a serie of advantages and disadvantages [20, 21].

### 1.2.2. Advantages for electrocoagulation

- i) Produces effluent with less total dissolved solids (TDS) content as compared with chemical treatments. If this water is reused, the low TDS level contributes to a lower water recovery cost.
- ii) The electrolytic processes in the electrocoagulation cell are controlled electrically with no moving parts, thus requiring less maintenance.
- iii) More effective and faster organic matter separation than in coagulation.
- iv) pH control is not necessary, except for extreme values.
- v) The amount of chemicals required is small: metal cations are introduced without corresponding sulphate or chlorine ions; there is no need for an alkalinity supply to have a reaction. By eliminating competing anions using a highly pure iron or aluminium source, lower metal residuals are obtained.
- vi) The amount of sludge produced is smaller (50–70 %) when compared with coagulation: the sludge formed in the EC method with Fe contains higher content of dry and hydrophobic solids than that produced in coagulation by the action of  $\text{FeCl}_3$  followed by the addition of NaOH or lime.

- vii) The operating costs are much lower than in most conventional technologies.
- viii) The electrocoagulation technique can be conveniently used in rural areas where electricity is not available, since a solar panel attached to the unit may be sufficient to carry out the process.

### 1.2.3. Disadvantages for electrocoagulation

- i) The use of electricity may be expensive in many places.
- ii) The electrode processes involve considerable overvoltages, which are due to anode passivation and to deposition on the cathode. It is possible to reduce power consumption by using alternating pulses of direct current, varying the period of polarization [22].
- iii) High conductivity of the wastewater suspension is required. The overpotential caused by the suspension resistance can be minimized if the conductivity of the suspension is increased by using a support electrolyte. Chloride ions are beneficial because they can break the passivating layers at the anode through the mechanism of pitting corrosion. Additionally, it is possible to diminish the overvoltage by increasing the area of the electrodes and by decreasing the distance among them.
- iv) High concentrations of iron and aluminium ions in the effluent that have to be removed.
- v) Gelatinous hydroxide may tend to solubilize in some cases.
- vi) The hydroxide suspension does not have an appropriate hydraulic grain size, which makes it difficult to separate; and the deposit thereby formed is difficult to dewater and cannot be recycled.

But the main limitation is that electrocoagulation is only effective to remove insoluble substances (colloids) and certain types of ions. The technique is not effective to remove soluble substances such as ammonium, sugars, organic acids, solvents, phenols, alcohols, and so on [21].

**1.2.4. Current efficiency.** The theoretical amount of metal dissolved depends on the quantity of electricity passed through the electrolytic solution and can be derived from Faraday's law:

$$W = \frac{j \times t \times M}{n \times F} \quad (15)$$

where  $w$  is the mass of electrode material dissolved (grams of the metal per  $\text{cm}^2$ ),  $j$  the current density (Amperes per  $\text{cm}^2$ ),  $t$  the time in seconds;  $M$  the relative

molar mass of the electrode concerned,  $n$  the number of electrons in oxidation reaction,  $F$  the Faraday's constant, 96,485 Coulombs per mole.

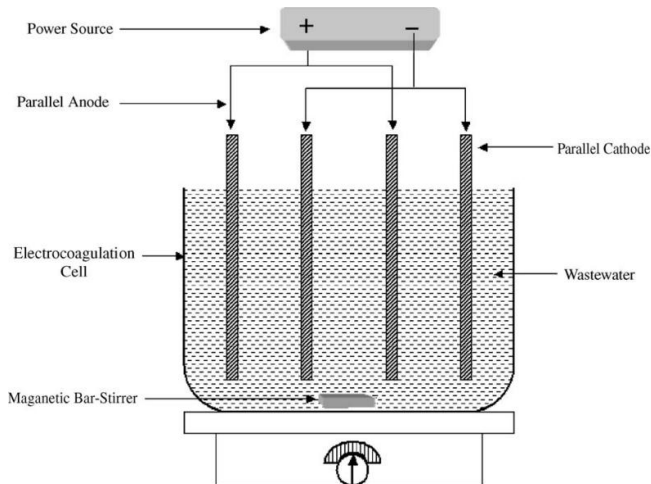
When the amount of metal that actually dissolves, measured by atomic absorption for example, is compared with the theoretical value calculated from Faraday's law, it is possible to calculate a current efficiency. Thus, this parameter allows evaluating the performance of the electrolytic process for different operating conditions.

**1.2.5. Power consumption.** It is important to specify the energy consumed during the treatment, it is usually calculated by the power consumption.

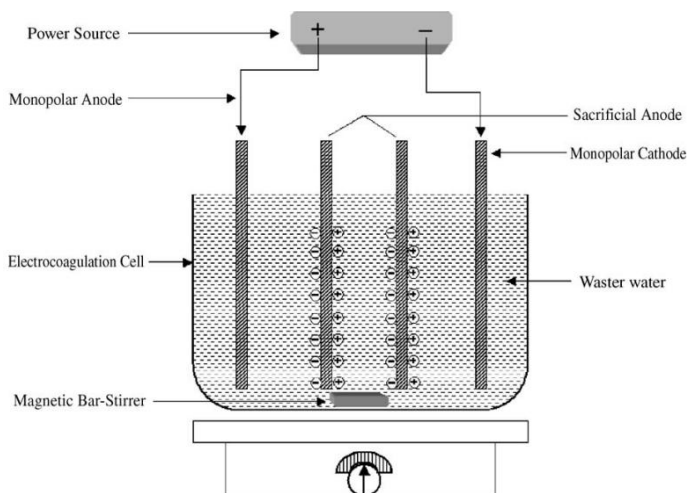
$$W = \frac{v \times i \times t}{1000 \times V} \quad (16)$$

$W$  is the power consumption ( $kWh\ m^{-3}$ ),  $v$  represents the voltage supplied in volts,  $i$  the electric current (Amperes),  $V$  is the volume of sample in  $m^3$  and  $t$  is the residence time in hours.

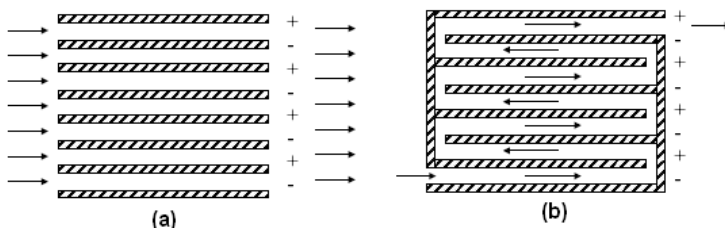
**1.2.6. Electrocoagulation reactor designs.** There are two possible arrangements, monopolar and dipolar (Figure 6 and Figure 7) in series and parallel connections. From these basic configurations have been proposed designs with vertical, horizontal and perforated plates, designs with cylindrical electrodes or rotating disc and also filter press type reactors.



**Figure 6.** Monopolar electrodes in parallel connections (Adapted from [23]).



**Figure 7.** Bipolar electrodes in parallel connections (Adapted from: [23]).

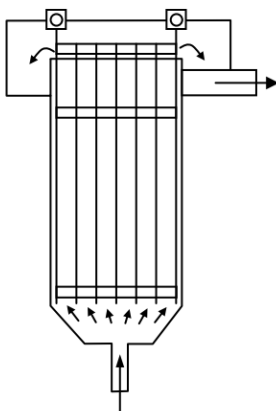


**Figure 8.** Electrodes setup in relation with the flow direction (Adapted from: [24]).

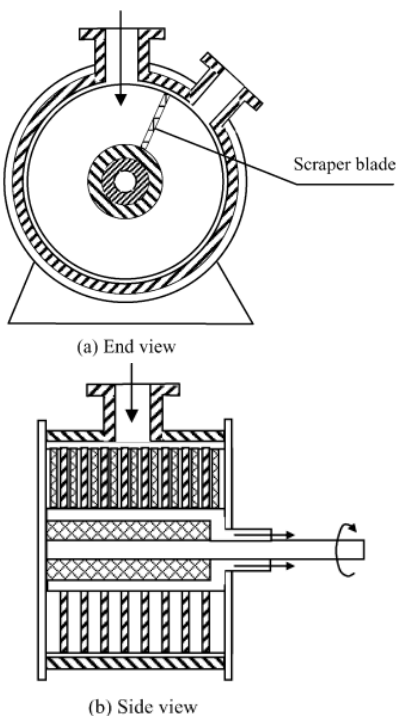
The water that flows within the reactor can be conducted in two different ways, through multiple channels (a) or through a single channel (b) as is shown in Figure 8. Multiple channels are simple in the flow arrangement but the flowrate in each channel is also small. When the electrode surface passivation cannot be minimized otherwise, increasing the flowrate by using a single channel flow is recommended.

There is also a reactor type filter press, which is similar to the industrial filters, wherein the anode, the cathode and a membrane (if necessary) are in the same module, thus cleaning and maintenance is very simple.

The tall vertical-plate reactor uses electrodes made of flat steel plates whose vertical dimension significantly exceeds the horizontal dimension (Figure 9). The plates are typically arranged in a nonconductive case that may



**Figure 9.** Tall vertical-plate reactor (Adapted from: [24]).



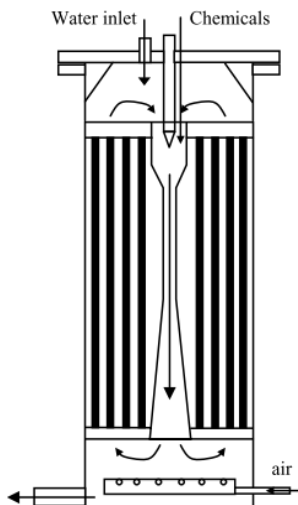
**Figure 10.** Electrocoagulation unit with cylindrical electrodes (Adapted from: [24]).

be open or closed at the top. The open case allows electrical contact above the solution level, while a closed case requires submerged contacts. Submerged contacts typically erode at a rate faster than the plates unless they are coated with an insulating material. This problem complicates the assembly.

For water treatment, a cylindrical design can be used as shown in Figure 10. It can be efficiently separate the suspended solids from waste water. In order to prevent any blockings, scraper blades are installed inside the cylinder. The electrodes are so fitted that they are at the open space of the teeth of the comb.

An alternative of cylindrical design is given in Figure 11 where a venturi is placed in the center of the cylinder with water and coagulants flowing inside it to give a good mixing. The electrocoagulation reactor can be operated in continuous as well as in batch mode. For batch operation, the case of small amount of laundry wastewater or for the water supply of construction sites, the automation is an important issue.

The design of these reactors is still a developing field and exhibits high empirical content. However, a more detailed and comprehensive analysis of the designs used was written for Chen (2004) whom studied over 300 publications related to this topic [24].



**Figure 11.** Rod electrodes in a cylinder electrocoagulation unit (Adapted from: [24]).

## Acknowledgements

This work was supported by a grants (No. 1106-521-28599, CI 2758, CI 2744) from Universidad del Valle (Cali, Colombia) and the Colombian Administrative Department for Science Technology and Innovation (Colciencias).

## References

1. Emamjomeh, M., Sivakumar, M. 2009, *Journal of Environmental Management*, 90, 1663.
2. Sincero, A., Sincero, G. 2003. Physical-Chemical treatment of water and wastewater.. s.l.:CRC Press.
3. Savarovsky, L. 2000. Solid-Liquid separation. 4th ed. s.l.:Butterworth-Heinemann.
4. Duan, J., Gregory, J. 2003, *Advances in Colloid and Interface Science*, 100-102, 475.
5. Hogg, R. 2000, *Int. J. Miner. Process.*, 58, 223.
6. Jolivet, J., Tronc, E., Chanéac, C. 2006, *C. R. Geoscience*, 338, 488.
7. Martínez-Navarro, F., 2007. Tratamiento de aguas residuales industriales mediante electrocoagulación y coagulación convencional. s.l.:Tesis (Ph.D) Ingeniería Química. Universidad de Castilla La Mancha.
8. Xiao, F., Zhang, X., Ma, J. 2009, *Separation and Purification Technology*, 68, 273.
9. McMinn, W., Keown, J., Allen, S., Burnett, M. 2004, *Water Research*, Volumen 38, 1873.
10. Rossini, M., Garcia Garrido, J. & Galluzzo, M. 1999, *Wat. Res.*, 33(8), 1817.
11. Morgan, B., Lahav, O. 2007, *Chemosphere*, 68, 2080.
12. Génin, J., Ruby, C., Géhin, A., Refait, P. 2006, *C.R. Geoscience*, 338, 433.
13. Streat, M., Hellgardt, K., Newton, N. 2008, *Process Safety and Environmental Protection*, 86, 1.
14. Génin J-M, Christian Ruby C., Géhin A., Refait P., 2006, *C. R. Geoscience*, 338, 420.
15. Ruby C., Usman M., Naille S., Hanna K., Carteret C., Mullet M., François M., Abdelmoula M., 2010, *Applied Clay Science*, 48, pp. 195.
16. Kok-Hui, G., Teik-Thye, L., Zhili, D. 2008, *Water Research*, 42, 1343.
17. Gendel, Y., Lahav, O. 2010, *Journal of Hazardous Materials*, 183, 596.
18. Sasson, M., Calmano, W. & Adin, A. 2009, *Journal of Hazardous Materials*, 171, 704.
19. Kemmer F. 1988. *The NALCO Water Handbook*. 2nd ed. s.l.:McGraw Hill Company.
20. Ghernaout, D., Naceur, M., Aouab, A. 2011, *Desalination*, 270, 9.
21. Moreno-Casillas H.A., Cocke D.L., Gomes J.A., Morkovsky P., Parga J.R., Peterson E., 2007, *Separation and Purification Technology*, 56, 204.

22. Eyvaz, M., Kirlaroglu, M., Aktas, T., Yuksel, E. 2009, Chemical Engineering Journal, 153, 16.
23. Mollah, M., Morkovsky, P., Gomes, J., Kesmez, M., Parga, J., Cocke, D.L. 2004, Journal of Hazardous Materials, B114, 199.
24. Chen, G. 2004, Separation and Purification Technology, 38, 11.