

Review

Technical Considerations for Designing an Electrocoagulation Reactor for Wastewater Treatment: A Brief Review

Ismael Salvador Solano Huerta ¹, Gabriela Roa Morales ^{1,*}, Patricia Balderas Hernández ^{1,*},
Carlos Eduardo Barrera Díaz ¹, Thelma Beatriz Pavón Silva ², Pedro Ávila Pérez ¹ and Israel Rodríguez Torres ³

- ¹ Centro Conjunto de Investigación en Química Sustentable (CCIQS) UAEM-UNAM, Carretera Toluca-Atlacomulco, Km 14.5, Toluca 50200, Estado de México, Mexico; ismaelsolano045@gmail.com (I.S.S.H.); cebaread@uaemex.mx (C.E.B.D.); pavilap@uaemex.mx (P.Á.P.)
- ² Facultad de Química, Universidad Autónoma del Estado de México, Paseo Colón, Colonia Universidad, Toluca 50120, Estado de México, Mexico; tbpavons@uaemex.mx
- ³ Instituto de Metalurgia, Universidad Autónoma de San Luis Potosí, Av., Sierra Leona 550, Lomas 2^a Sección, San Luis Potosi 78210, San Luis Potosi, Mexico; learsi@uaslp.mx
- * Correspondence: groam@uaemex.mx (G.R.M.); pbalderash@uaemex.mx (P.B.H.); Tel.: +52-(722)-2766610 (ext. 7716 or 7724) (G.R.M. & P.B.H.)

Abstract: Within the field of wastewater treatment, various treatment systems stand out, including those that use chemical reagents to promote a precipitation reaction. Among these chemical methods are electrochemical processes such as electrocoagulation systems, which have gained prominence due to their ease of operation and the cost-benefit associated with the accessibility of the coagulant material. This article aims to guide the implementation of the electrocoagulation process in various water remediation systems as an improvement option for any treatment train. Electrocoagulation is analyzed from the perspective of Electrochemical Engineering. Various essential aspects of electrocoagulation are addressed, including its definition, the types of reactions occurring within the reactor, hydrodynamics, the variables that need to be controlled and their influence on the process's hydrodynamics, the factors to consider in the design of an electrocoagulation reactor, and some results obtained with this technique in the treatment of various wastewater and/or substrates. All of this is presented from a practical and easy-to-apply approach, providing a reference point for those interested in implementing this technology.

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1. Introduction

Due to increasing industrialization and population growth, water use as an essential resource and the waste generated by anthropogenic activities have grown exponentially. These effects have created an imbalance that has increased the flow of wastewater to be treated and decreased the availability of drinking water, in addition to repercussions on the environment and biodiversity caused by the pollution of these waters [1–4]. As a result, wastewater treatment and reduction of wastewater toxicity have been developed, and treatment plants have been designed and built [5,6]. Nevertheless, when raw wastewater characteristics are not considered and highly contaminated water is fed to a treatment train designed to treat slightly polluted wastewater, the environmental problem reappears due to not using an adequate treatment [7].

Most treatment plants are designed based on fixed-film biological treatment or suspended growth systems [8]. They are the most widely used worldwide technologies due to their easy access, and they are classified as conventional treatment systems [9]. These systems are designed to treat wastewater with low organic loads, whose values in concentration are 300–400 mg L⁻¹ BOD₅, and 800–1000 mg L⁻¹ COD [8], showing efficiencies of 88%. However, when highly polluted wastewater is treated, the efficiency percentage falls to 42% because toxic agents destroy microorganisms that mainly reduce BOD₅ and COD [10]. This decrease in efficiency affects both the social and the environmental sectors and the treatment plant itself. The discharge limits established in the current regulations on the matter could be constantly exceeded and generate economic sanctions or contract recessions since the current needs require quality control in the effluent that provides the security of maintaining a decent and habitable environment in balance [11,12].

For this reason, treatment alternatives have been developed to increase the biodegradability of contaminants in wastewater, such as adsorption, photocatalysis, ultrasound, electrochemical processes, among others [13]. Electrochemical treatments being one of the processes that has attracted attention for its easy application.

2. Electrochemical Engineering

Electrochemical Engineering is a technological discipline whose purpose is to design and operate equipment and processes where chemical and electrical energies intervene, characterized by using the electron as a reagent to initiate sequences or oxidation-reduction reactions [14]. Electrochemistry, from an environmental point of view, can be applied for several purposes. But, the remediation of soils, gaseous, and liquid effluents highlight [15], particularly for treating liquid effluents, the electrocoagulation, and electrooxidation techniques stand out [16].

The performance and efficiency of electrochemical processes in reactors depend mainly on the phenomena occurring inside, such as cell hydraulics and mass transport. Since their quantification is difficult, these phenomena can be represented through mathematics models, so it is necessary to simplify the problems of fluid dynamics and mass transport in the reactor and obtain quantitative data that represent the complexity of the transport of electrochemical species in wastewater [1].

Therefore, we know that the phenomena present in an electrochemical reactor will depend on the reaction rate or electrochemical kinetics, the fluid dynamics of the flow, mass transport, the current and potential distribution, and thermodynamics [16,17].

3. Electrocoagulation (EC)

The coagulation-flocculation technique is characterized by the consumption of polymers (reagents based on aluminum and iron) and pH-stabilizing reagents, which increases the operational cost of the process [18,19]. Likewise, the floc formation techniques were implemented to improve the low efficiency of settlers or clarifiers, where colloidal particles and remaining solids in suspension, due to their small density and tiny size, are not easy to remove by gravity [20]. Electrocoagulation is an electrochemical technique proposed as an economic response to conventional coagulation-flocculation methods.

Electrocoagulation has been a desirable treatment technique due to its simplicity of operation, low energy consumption, and the generation of high-quality effluents [21]. Good efficiencies have been reported to treat various municipal, and industrial wastewaters [22] EC can remove many pollutants such as heavy metals, suspended solids, refractory organic material, dyes, fats, and oils [23]. A benefic characteristic of this technique is the possible oxidation of chloride ions (secondary reaction) [15], resulting in a strong-oxidizing agent that helps disinfect wastewater eliminant pathogens [24].

The electrocoagulation process has managed to carve out a place among other treatment systems due to the accessibility of the materials used to make the electrodes (mainly aluminium and iron) [25], which translates into savings in logistics and energy. A clear example is the reduction of environmental impact due to the lack of dependence on coagulant polymers (which end up in waste sludge and can be difficult to dispose of), or the energy savings compared to a biological system, which requires prolonged aeration and therefore leads to high energy costs [26]. Another advantage is that the electrodes can increase their durability if the current is reduced to find an ideal dosing point, which would also result in energy savings. Recent studies have explored the possibility of using the sludge resulting from electrocoagulation as pigments, giving added value to a waste product [27].

An electrocoagulation reactor is versatile since the design includes two-unit stages in a single process: coagulation and flocculation. Its principal function is to act as a dosing reactor; since the addition of the coagulant agent can be controlled by the current density supplied. The oxidation product generated, called flocs, are settled at the bottom when they are large enough. As a result, the flocs less dense are raised to the surface (thanks to the formation of H_2 like reduction product of the water) of the treated effluent and removed mechanically by dragging, thus removing impurities from wastewater [25].

A general arrangement of an electrochemical reactor, in this case an electrocoagulation reactor, is an electrolytic cell, as shown in Figure 1. The cell is composed of a power source that supplies the electric current to a tank (body of the reactor) where the anode is known as a sacrificial electrode (M) due your oxidation (Equation (1)) dosing the cations (M^{n+}) and a inert cathode where the water is generally reduced [26].

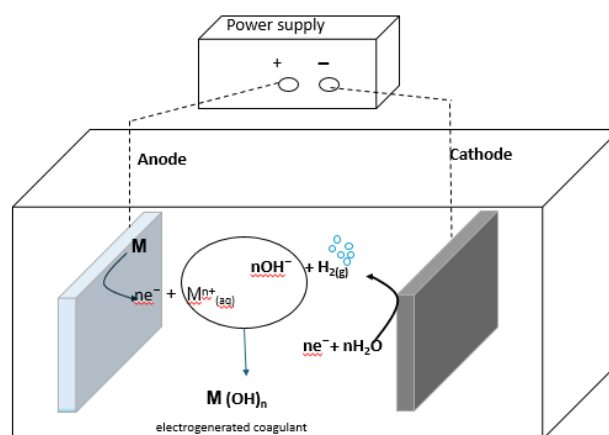
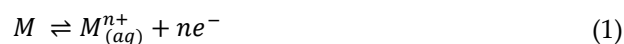


Figure 1. Electrolytic cell, electrocoagulation process and general consequent reactions, in the anode, M, are electrogenerated the cations " M^{n+} " forming the coagulant $M(OH)_n$.

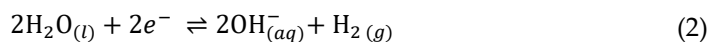
Any process that involves oxidation-reduction reactions when using a metallic material as an electrode, and an energy source, reaction can be theoretically generalized according to the reactions (1)–(3) [22,28]

The cations released in the anode (Equation (1)) react with the hydroxyl ions produced for reduction of the water (Equation (2)) forming the coagulant (Equation (3)), destabilizing the charges of the colloidal compounds and suspended organic matter (coagulation). The formed products are polynuclear hydroxide and hydroxide complexes with adsorbent characteristics (flocculation) [19].

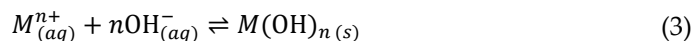
Anode:



Cathode:



General reaction in solution:



When the flocs are small and light, they are brought to the surface of the water by the H_2 formed in the cathode. Subsequently, the flocs increase in quantity and form larger aggregates gaining enough weight to precipitate, this effect is more effective with the increase in pH associated with the hydroxide ions that are formed in the cathode [29].

It is important to mention that electrocoagulation has reported that the sacrificial electrode material that can be used in water treatment are iron, aluminum [30,31], copper [31,32], zinc [31] and magnesium [33].

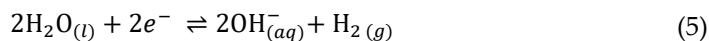
For the reader's practical purposes and in a way that can be explained in detail, the reactions presented below correspond to an electrocoagulation system with copper electrodes [31,32,34].

The electrical current supplied oxidizes the anode, producing metal cations, in this case, cupric ions (Equation (4)). The water electrolyzes at the cathode producing hydroxyl ions and tiny hydrogen bubbles (Equation (2)). Cupric ions react with hydronium ions to form hexahydrated copper compounds (Equation (6)); at this point, there is a decrease in the pH of the substrate. The copper hexahydrate in contact with the hydroxide ions produced by the cathode form copper hydroxides; at this point, the pH of the substrate increases (Equations (7) and (8)).

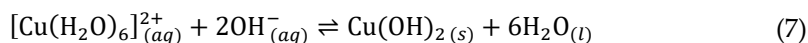
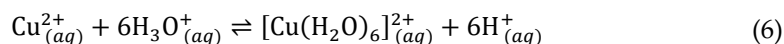
Anode:



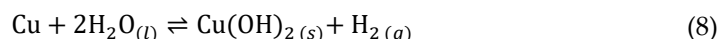
Cathode:



Reactions in solution:



General reaction:

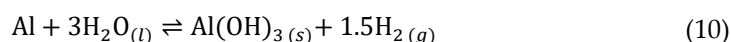


Other hand also shows most common reactions in electrocoagulation systems that utilize different electrodes: aluminum (Reactions (9) and (10)), iron (Reactions (11) and (12)), magnesium (Reactions (13) and (14)) and zinc respectively (Reactions (15) and (16)) [30–35]:

Anode reaction with Aluminum:



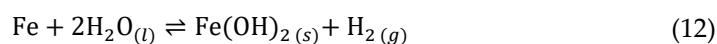
General reaction with Aluminum:



Anode reaction with Iron:



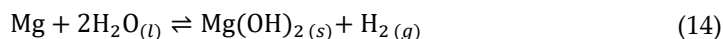
General reaction with Iron:



Anode reaction with Magnesium:



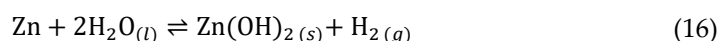
General reaction with Magnesium:



Anode reaction with Zinc:



General Reaction with Zinc:



Cathodic reactions are always reduction processes, leading to water hydrolysis at this electrode. Therefore, in every electrocoagulation system, regardless of the cathode material, the reduction of water will occur, (see reaction Equation (5)).

4. Design Criteria for an Electrocoagulation Reactor

The main design criteria of any electrochemical cell must respond to the demands of the of origin of the wastewater to be treated, having operational simplicity at low cost, reliability of maintenance and operation related to the space and time required, and the versatility to adapt to any situation [22,26]. The advantage of an electrochemical system concerning energy supply is that it can be supplied by green systems based on wind or solar energy [31,32,36]. Furthermore, the by-products produced, such as hydrogen gas generated in the water electrolysis and the sludge generated in the process, can be recovered [37]. Depending on its characteristics, the residual sludge can be recirculated and used as polymers since its composition allows coagulation by charge neutralization, or as an adsorbent material for other contaminants [38].

The design of an electrochemical cell can be classified according to different criteria, such as flow direction, circulation mode, type of connection, and the cell's purpose [15].

Flow direction according to the reactor configuration: According to the available space, the type can be selected between one or the other; for large flows, a horizontal model is usually used, see Figure 2A, while for experimental tests or small flows, vertical flow is used, see Figure 2B [39].

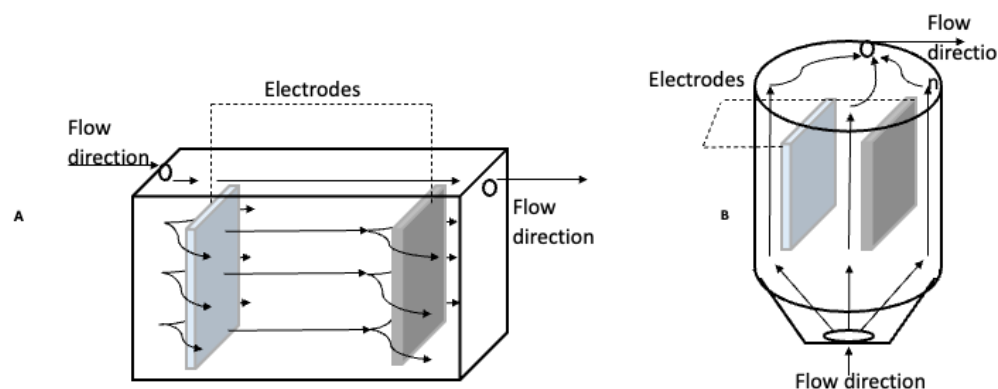


Figure 2. (A) Horizontal configuration EC reactor. (B) Vertical configuration EC reactor.

Flow circulation according to the configuration of the electrodes: the arrangement and position of the electrodes can contribute to the hydrodynamics of the reactor; the arrangement must distribute the flow evenly without dead or stagnation zones. The most common configurations are shown below (Figure 3) [15].

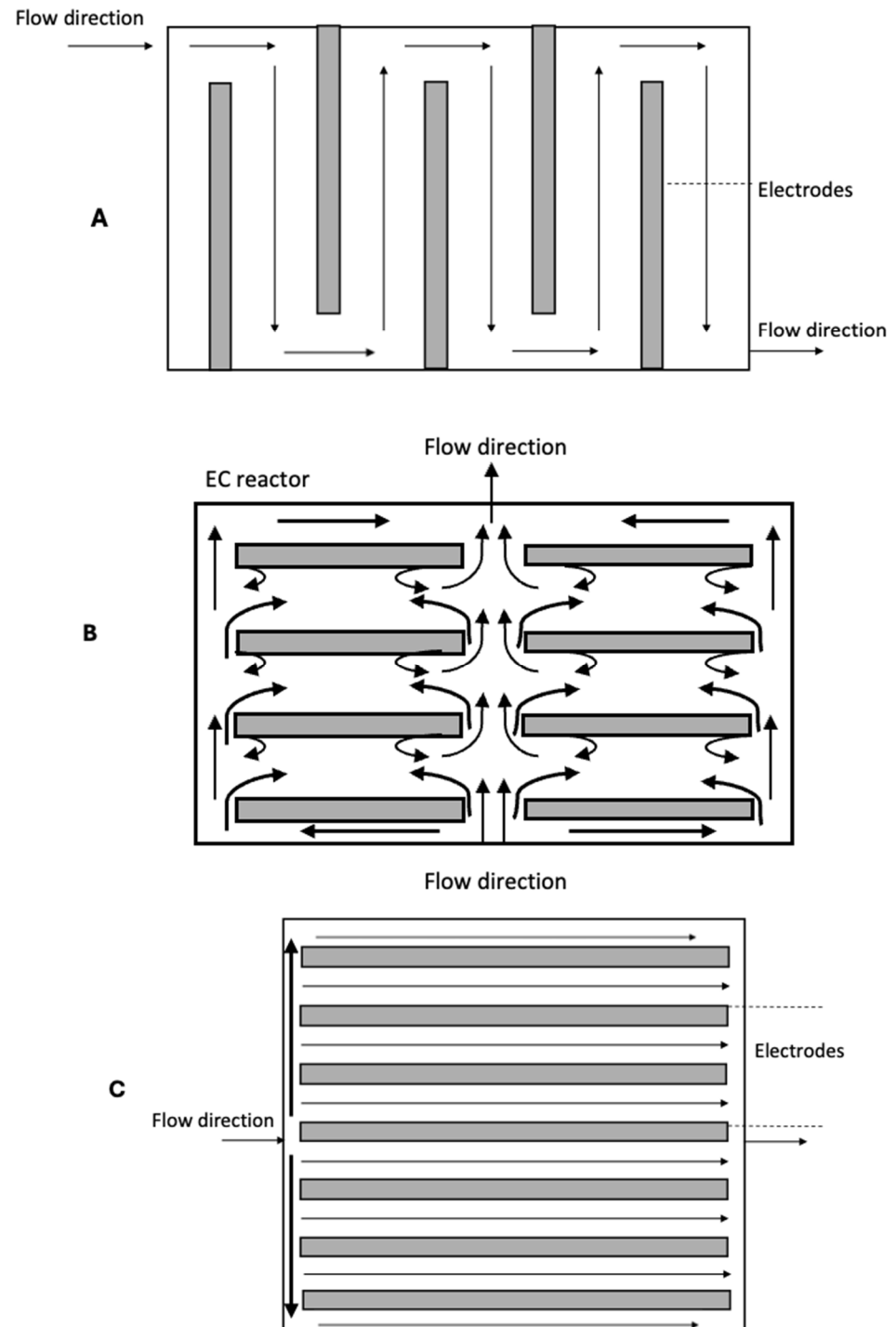


Figure 3. (A) EC reactor with single channel configuration, the flow is transported in only one direction, the walls of the channel are the electrodes, top view. (B) EC reactor with series electrode configuration, the flow is transported between the electrodes, in continuous flow it creates vortices that helps its homogenization, top view. (C) EC reactor with parallel electrode configuration, the flow is transported between the electrodes in a single direction, top view.

Electrical connection type: the appropriate connection type will depend on the desired final quality and the cost of the treatment; for example, Demirci et al. (2015) and Khaled et al. (2019) [39,40] they mention a monopolar connection (Figure 4A) offers a better efficiency/cost ratio; however, if a better quality is preferred in the effluent, a bipolar connection (Figure 4B) will be necessary.

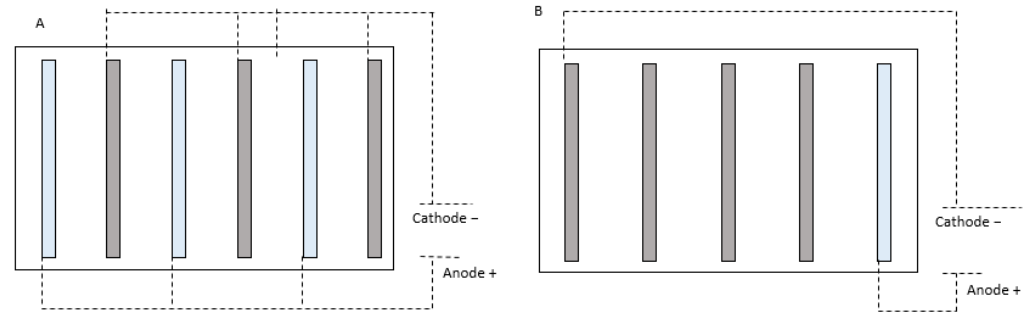


Figure 4. (A) EC reactor with monopolar electrical configuration, (B) reactor with bipolar electrical configuration.

Various authors have considered various configurations to develop their experiments. In the experimental part, the most common is to use an electrolytic cell with two electrodes, but in practical testing, the most commonly used configurations tend to be a monopolar configuration, a horizontal hydraulic flow, and a parallel electrode configuration.

Both continuous and batch systems are used, such as the case of Asaithambi (2023) [41], which used a batch system and used a continuous flow reactor, a series electrode arrangement, and a monopolar connection; or the case of Bhuvanendran et. al., 2024 [42], which used a continuous system, a horizontal flow, a parallel electrode arrangement, and a monopolar connection. These are some examples of practical systems that were used on a pilot scale.

In electrocoagulation reactor design, a minimum volumetric space must be considered to achieve better reaction efficiency and eliminate the by-products formed zones [43,44]. An electrocoagulation reactor is composed of three parts (Figure 5). At the top, the flotation zones the upper region of the reactor where the less dense flocs form the supernatant and foams, which can be easily eliminated from the system. The intermediate zone or reaction zone, where the electrodes are located, and the phenomenon of destabilization of the particles occur. And the lower area or sedimentation zone where the densest sludge formed in the reaction zone is deposited can be removed by controlled purges or pumping systems.

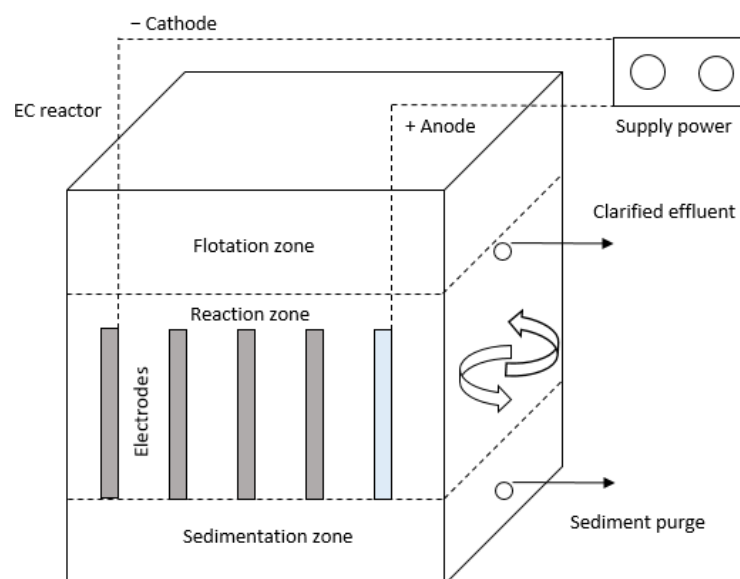


Figure 5. EC reactor zones.

5. Control Variables and Design Parameters of an Electrocoagulation Reactor

An engineer or specialist who wishes to use electrocoagulation to purify any wastewater must know the variables on which the process depends, how this influences and controls the process (Table 1), and the design parameters that are considered during the implementation (Table 2), either in laboratory tests, in pilot tests or real scale. A process variable is the numerical representation without a fixed value subject to the substrate hydrodynamics and its frequent changes. The design parameter will be a qualitative or quantitative value, set by the characteristics of the system of treatment and whose value will be the reference for the design and implementation of the reactor [45]. The variables considered as design parameters will be marked with an asterisk (*) for practical purposes. Each variable has a purpose that is fundamental to the operation of an electrocoagulation system, as shown in Tables 1 and 2, among all of them, the main variables that truly determine the functionality of the process are electrical conductivity, pH and current. Depending on the pH in the reactor, different coagulant species will form, and depending on the current, the dosage of coagulant ions used to destabilize the sludge charges will vary and electrical conductivity ensures electrochemical cell functionality [46,47].

Table 1. Control variables and effect of the electrocoagulation process.

Variable Process	Units	Variable Analysis	Reference
pH	pH	<ul style="list-style-type: none"> The effect of pH is directly related to the reaction rate inside the reactor; therefore, it influences the capacity to form flocs in the substrate. The ideal working pH for wastewater treatment is a neutral value between 6 to 8. The quantity of the chemical species of interest Will be a function of the pH; therefore, its control is recommended. 	[46,48]
Electrical conductivity	$\mu\text{S}/\text{cm}$	<ul style="list-style-type: none"> It is the capacity of the treated substrate to allow the electric current to pass through it; a high electrical conductivity means high concentrations of total dissolved solids Low electrical conductivity promotes increased ohmic resistance. 	[19,49]
Current density	A/m^2	<ul style="list-style-type: none"> It is the way to measure the current supplied by electrode area; with higher current density, the efficiency would be better; however, increased electrode wear is observed. The applied density range will always vary; this will depend on the concentration of the contaminant and the type of substrate to be treated. 	[50–52]
Limiting current density	A/m^2	<ul style="list-style-type: none"> It is the maximum point of current supplied to the treated substrate; the ion concentration released by the anode reaches its maximum point where ion precipitation and passivation of the electrode occur. The limiting density will be a function of the electrical conductivity of the treated substrate. It determines the limit of the useful current density in the reactor, preventing current losses under the form of heat. 	[52]
Electric current	A	<ul style="list-style-type: none"> In an electrochemical cell, the coagulant dosage will be proportionally related to the intensity of the current supplied; it will determine the number of ions released in the treated substrate. Very high values can lead to undesirable side reactions. 	[20,47,53]
Resistivity	Ω	<ul style="list-style-type: none"> A higher resistance increases the treated substrate's temperature, decreasing the process's efficiency. The increase in resistance is related to the passivation of the electrode, a long distance between electrodes, a low conductivity in the treated substrate, or a generation of excess hydrogen gas between the electrodes. 	[20,47,53,54]

Voltage	V	<ul style="list-style-type: none"> The voltage is directly proportional to the applied current and inversely proportional to the resistivity of the treated substrate. The measured voltage will be a function of the voltage generated by the electrochemical cell. In the electrochemical cell, the voltage must be measured to calculate the energy consumption of the cell. 	[20,47,53,54]
Zeta potential	mV	<ul style="list-style-type: none"> To produce stable flocs, it seeks to reduce the repulsive forces between the colloids and suspended material. The addition of a coagulant can suppresses the double layer of colloidal particles, promoting the aggregation of the contaminant of interest. 	[42]
Hydraulic retention time ¹	min	<ul style="list-style-type: none"> It is the treatment time of the substrate, the time it takes for the oxide-reduction reaction to promote coagulation-flocculation, and the elimination of the by-products formed. 	[55,56]
Flow ¹	L/min	<ul style="list-style-type: none"> It is the flow to be treated; it must be according to the hydraulic retention times of the reactor. 	[56,57]
Temperature	°C	<ul style="list-style-type: none"> An increase in temperature in the electrocoagulation process indicates increased ohmic resistance in the reactor. High temperatures modify the physical characteristics of the treated substrate, diminish its viscosity, and alter the kinetic characteristics regarding the formation of the floc. The temperature has a potentiating or inhibiting impact depending on the nature of the pollutant. The range of variation requires an understanding of the electrocoagulation mechanism and the contaminant to be treated. 	[58–60]
Stirring speed	rpm (Batch)	<ul style="list-style-type: none"> The stirring speed increases the collision between the ions anodically generated and the contaminating compounds. Therefore, maintaining adequate stirring will prevent the break-up of the flocs formed and increase the contaminant's removal efficiency. 	[60,61]
Initial concentration of the contaminant ¹	mg/L	<ul style="list-style-type: none"> Characterizing the substrate to be treated is the initial and fundamental step of the all-design. This characterization will adapt the process to ensure quality is met according to the established criteria. If the initial concentration of the contaminant is high, it is helpful to recycle a part of the treated effluent to dilute the untreated substrate; this can solve the problem and improve it. Electrochemical systems, especially electrocoagulation, have reported good efficiencies at high COD levels. 	[5,62]
Electrode contact area ¹	cm ²	<ul style="list-style-type: none"> As it increases, there is better use of the voltage and current supplied. The resistance of the cell decreases with increasing contact area between the electrode and the treated substrate. There is a close correlation between contact area and cell performance. 	[63]

¹ Control Variables considered as design parameters too.

Table 2. The design parameters that are considered during the process implementation.

Design Criteria	Units	Variable Analysis	Reference
Kind of cell	---	<ul style="list-style-type: none"> It will depend on the flow to be treated and whether the process will be continuous or batch. It will depend on the space available for its implementation; they can be handled with horizontal or vertical flow. The cell type should not affect the versatility of operational use and preventive or corrective maintenance; simple systems are recommended to reduce costs. 	[15,39]
Operation mode	----	<ul style="list-style-type: none"> Batch system: the volume of the treated substrate is constant; the substrate is treated in cycles; it lacks a feed and an 	[8,27]

		<p>outlet. This mode of operation is used for experimental laboratory treatments.</p> <ul style="list-style-type: none"> • Continuous system: it has a feed flow and an outlet for the treated substrate. This mode of operation is used in pilot and industrial treatment systems. 	
Electrode distance	cm	<ul style="list-style-type: none"> • The spacing can reduce or increase the ohmic resistance of the cell; at a shorter distance, ohmic resistance will decrease. • A shorter distance helps to minimize energy consumption. • Optimal spacing promotes electrostatic attraction between the formed flocs and the displacement of coagulating ions. 	[50,54]
Electrode arrangement	---	<ul style="list-style-type: none"> • The arrangement of electrodes influences hydrodynamics; it can create stagnant or turbulent zones affecting positively or negatively electrolysis. • The arrangement of the electrodes can be monopolar or bipolar; the appropriate type of connection will depend on the cost/efficiency ratio required. • The monopolar connection is used to obtain a linear electrical distribution. • The bipolar connection takes advantage of the electric field generated by the current supplied between the anode and the cathode. 	[64,65]
Electrode material	----	<ul style="list-style-type: none"> • Depending on the characteristics of the material, different benefits may be obtained, e.g., making sure that the material does not form by-products that could affect the quality of the substrate treated. • Always consider its abundance, production, cost, and maintenance. • The materials used are metals capable of generating destabilizing cations, such as Al, Fe, Ag, Ba, Ca, Cd, Cr, Cs, Fe, Mg, Si, Sr, Zn, and Cu. 	[66,67]
Electrode shape	---	<ul style="list-style-type: none"> • The electrode shape should not affect the performance of the process; it can be circular, cylindrical, trapezoidal, or rectangular. • Some studies have reported higher treatment efficiencies using perforated electrodes than conventional plates. 	[59,68]
Cell material	---	<ul style="list-style-type: none"> • It should not interfere with the electrolysis produced by the electrodes. • The cost of the material and its installation must be feasible. 	[69]
Cell size	cm ³	<ul style="list-style-type: none"> • The cell volume will be a function of the flow to be handled and the dimensioning of the different reactor zones: flotation, zone reaction, and sedimentation. • It must be verified that the volume considered allows the correct operation of each zone, ensuring the process quality. 	[44,70]
Kind of current supplied: Direct current (dc) Alternating current (AC)	V	<ul style="list-style-type: none"> • The DC is generally used in experimental tests; this often results in operational challenges since the electron flow in one direction promotes electrode passivation. The AC is 	[71,72]

typically used to ensure the electrodes' equal wear and avoid passivation.

- The change in the electrode polarity leads to the evolution of the interfacial reactions in the system, improving the process performance.
- The ionic dosage of the coagulant does not vary from one type of current to another.

Hydrodynamics of the electrocoagulation cell: The performance and efficiency of the electrochemical processes in reactors depend significantly on the phenomena within it, such as cell hydraulics and mass transport [39]. It is common to observe mass transport by convection in an electrocoagulation reactor, where the driving force of the flow tends to be external. Several studies have been conducted to show the impact of the hydrodynamic behavior in the design of electrocoagulation reactors [73], the H₂-H₂O flow and hydraulic pressure inside [74,75], and the flow pattern in the cell [76].

However, it is difficult to quantify and correlate these transport phenomena with performance and efficiency because it is necessary to represent the transport phenomena involved through mathematical models. To describe the mass transport and reactor hydraulics, avoiding a complex mathematical model, the problem should be simplified to obtain qualitative parameters that describe the transport of electrochemical species and analytically solve the transport phenomena. One way to facilitate this analysis is by looking for experimental data correlating with the involved variables [14,15].

Production of electroactive species: The coagulant species formed in the sacrificial electrode will be proportional to the amount of electrical energy supplied. Therefore, it can be deduced that the number of electroactive species will determine and affect the number of by-products formed and thus the formation rate of the floc, as well as the mass transport [15,67]. Therefore, a variant of Faraday's law (Equation (17)) can be used to calculate the number of electroactive species supplied

$$m = \frac{I * t}{nF} \quad (17)$$

where m will be the number of released ions by the electrode during the anodic reaction; I is the intensity current supplied to the reactor (A); t is the treatment time (s); F is Faraday's constant (96,500 C/mol), and n is a stoichiometric relationship where the number of the exchanged electron will be equal to each released mol from the electrode

The Hydraulic of the cell: The hydrodynamic conditions, and how these influence mass transport, can be correlated through dimensionless numbers. The number value of the Reynolds number (Re) describes the flow regime into the reactor, either laminar, transition, or turbulent flow. For a Re number lower than 2000, the flow will be laminar. For a Re number higher than 4000, the flow will be turbulent, and a Re number from 2000 up to 4000 corresponds to a transition flow [77]. If the velocity of the substrate increases from Re_1 to Re_2 , a rise in mass transport will be observed, increasing the surface concentration of floc in the electrode, which produces an augmentation of reaction rate [15]. The Re number can be calculated by:

$$Re = \frac{lc * u * p}{\mu} \quad (18)$$

where lc is the hydraulic diameter of the reactor (m); u is the linear velocity of the treated substrate (m/s); p is the density of the treated substrate (kg/m³), μ is the dynamic viscosity of the treated substrate (kg/m s).

Reaction rates: The study of reaction rates is extensive since it will depend on the system used [78]. For designing an electrocoagulation reactor, it is feasible to use batch-

type processes in the experimental stage to determine the operating conditions and the factors that may affect the process [57]. For the researcher, it is essential to know the reaction rate because, in an electrocoagulation system, the essence of the process will be the rate of floc formation.

To determine the reaction rate ($-r$), the linear behavior of the treatment must be analyzed and based on this determine which rate law will describe the process. The reaction rate analysis is fundamental since the final design conditions, such as treatment time and reactor dimensions, can be determined [79,80].

The reaction rate is given by:

$$-\frac{dC}{dt} = r - kC^\alpha \quad (19)$$

where r is the reaction rate based on mass (consumption rate of reagents or generation rate of products in any physical or chemical process) (mg/L s); C is the pollutant concentration in the effluent (mg/L), k is the reaction kinetic constant (s^{-1}), and α is the reaction order.

The kinetics behavior in any batch system will be linear according to the following rate laws.

Zero-order reaction:

$$-r = k_0 \rightarrow C = -k_0t + C_0 \quad (20)$$

where the units for the constant k_0 are (mg/L min) and C_0 is the concentration influent

First-order reaction:

$$-r = k_1 \rightarrow \ln C = -k_1t + \ln C_0 \quad (21)$$

where the units for the constant k_1 are (min^{-1})

Second-order reaction:

$$-r = k_2 \rightarrow \frac{1}{C} = -k_2t + \frac{1}{C_0} \quad (22)$$

where the units for the constant k_2 are (L/mg·min)

Sometimes the process tends to have adsorption mechanisms due to the characteristics of the floc formed. As a result, other kinetic models to describe the experimental data are considered; for example, in heavy metal removal processes, the behavior does not follow the previous rate laws but rather rate laws of pseudo-order kinetics [26,60].

Pseudo-first order reaction:

$$-r = k_{s1}(C - C_0) \rightarrow \ln(C - C_0) = -k_{s1}t + \ln C \quad (23)$$

where the units for the constant k_{s1} are (min^{-1})

Pseudo-second order reaction:

$$-r = k_{s2}(C - C_0)^2 \rightarrow \frac{1}{(C - C_0)} = -k_{s2}t + \frac{1}{C} \quad (24)$$

where the units for the constant k_{s2} are (g/mg·s). For this kind of rate law, C_0 is the equilibrium concentration in the pseudo-first-order equation [79]. C_0 and C in the pseudo-second-order equation are the adsorption capacities of the adsorbent at the equilibrium and for the time t , respectively.

The approach to analyzing the experimental kinetic data involves developing a linear form for each possible pseudo-order model; that is, an equation of type $y = mx + b$, whose slope will be the speed constant k . Once the reaction rate is obtained in a batch system, the reactor volume for continuous systems can be calculated [26].

The models to obtain reaction rates depend on the chemical species to be eliminated and the sacrificial anode, since it has been reported that with Mg anodes to eliminate Pb^{2+} it is adjusted to second order, Fe anode to eliminate Cu^{2+} , Ni^{2+} and Zn^{2+} was adjusted to Pseudo first order, Al anode to eliminate as was adjusted to first order, Fe anode to eliminate as was adjusted to Pseudo Second Order [60]

pH effect: The mass transfer and floc formation will depend on the pH solution in the treated substrate. Many pollutants present in wastewater are in colloidal form, colloids with a generally negative charge which, when supplying a positive charge such as the cations released by some metal, these colloids are adsorbed in the flocs formed will be neutralized in the hydroxo-metal complexes [81,82]. But on what parameter will the abundance of these neutralizing species depend? The answer is the pH. One way to understand the mechanics of the process is with the species distribution diagrams. A species diagram allows obtaining the existence and abundance of different chemical species produced during the treatment and how they behave according to the pH of the solution [23].

To better understand pH effect in the formation the of coagulant electrogenerated to eliminate the present pollutants species in wastewater were elaborated the species distribution diagrams with Hydra-Medusa™ software (1997) (Royal Institute of Technology, Stockholm, Sweden), when are using copper electrodes in the electrolysis cell. The Figures 6 and 7 were obtained considering two concentrations of Cu^{2+} electrogenerated and the concentrations of ions that may be present in the wastewater such as Cl^- , NO_3^- , PO_4^{3-} , SO_4^{2-} , which is information that must be fed to the software.

According to the pH and anion total concentration, these anions in contact with copper ions will form hydroxo-metal polynuclear complexes and $M(OH)_n(s)$ species. The ions concentrations of the Figure 6 were obtained of industrial wastewater. Figure 6 shows that insoluble species formation of $Cu_3(PO_4)_2(s)$ and $Cu_3SO_4(OH)_4(s)$ to pH= 5 with 10% and 80% receptivity in abundance, in pHs of 6 to 8.5 the predominant species is $Cu_4SO_4(OH)_6(s)$ and $Cu(OH)_2(s)$ from pH= 9. All species are important for the processes of EC.

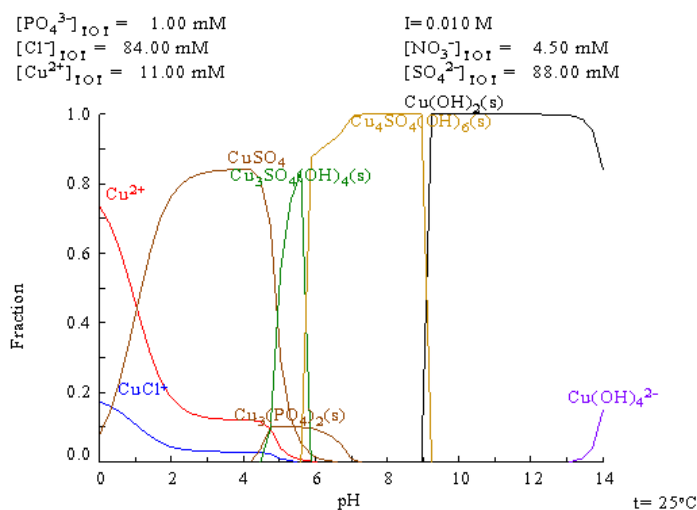


Figure 6. Species distribution diagrams to 11 mM Cu^{2+} and ions presents in the industrial wastewater $[Cl^-] = 84$ mM, $[NO_3^-] = 4.5$ mM, $[PO_4^{3-}] = 1$ mM, $[SO_4^{2-}] = 88$ mM, (Hydra-Medusa™ software, Royal Institute of Technology, Stockholm, Sweden (1997)).

The ions concentrations of the Figure 7 were obtained of municipal wastewater. Figure 7 shows the formation of $Cu_3(PO_4)_2(s)$, $Cu_4SO_4(OH)_6(s)$ and $Cu_4SO_4(OH)_6(s)$, between pH 5 to 7 with 5%, 25% and 60% receptivity in abundance and from pH 8 to 11 the predominant species is $Cu(OH)_2$.

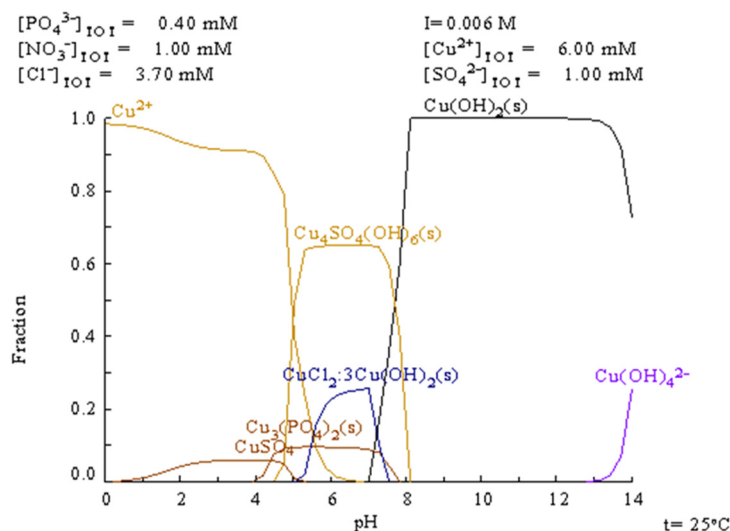


Figure 7. Species distribution diagrams to 6 mM Cu^{2+} and ions presents in the industrial wastewater $[\text{Cl}^-] = 3.7 \text{ mM}$, $[\text{NO}_3^-] = 1 \text{ mM}$, $[\text{PO}_4^{3-}] = 0.4 \text{ mM}$, $[\text{SO}_4^{2-}] = 1 \text{ mM}$, (Hydra-Medusa™ software (1997), Royal Institute of Technology, Stockholm, Sweden).

If we remember, the compound of interest for electrocoagulation is the insoluble form of metal hydroxide $\text{M}(\text{OH})_{n(s)}$, which with the help of the diagrams, we can determine at what pH the compound is formed and thus determine an operational condition. In this way, the formation of polynuclear hydroxo complexes will be avoided soluble. The insoluble hydroxo complexes would help the process too much, the production of the compound of interest would be promoted to make the process more efficient. In this case, the optimal treatment pH for industrial and municipal wastewater would be between 6–11 and 5–11, respectively.

The importance of the mentioned considerations is that an imbalance between the criteria, such as the reaction rate, the formation of the electroactive species, the supplied current, the pH, and the influence of the flow in the cell, could promote undesirable reactions, for consequent efficiency losses, and other possible operating problems. Thus, a well understanding of these principles will allow the correct operation of an electrocoagulation reactor.

6. Operative Cost

Process efficiency and operational economic cost: A numerical value that specifies the efficiency achieved is obtained using relationships between terms of interest [24]. Efficiency can be calculated using the following equation:

$$R = 1 - \left(\frac{c_f}{c_0} \right) \times 100 \quad (25)$$

where R is the removal percentage of the process; c_f is the final concentration of the pollutant (mg/L), and c_0 is the initial concentration of pollutant (mg/L).

The calculation of the super-faradaic efficiency (FE) is used to determine if the concentration of the formed coagulant ion is according to the actual expenditure of the sacrificial electrode. Values greater than 100% could indicate the presence of ions in the treated substrate, which despite not coming from the sacrificial electrode, can be beneficial for the process as it entails less energy expenditure and treatment time. On the other hand, if the value is less than 100%, it may indicate a loss of the current supplied in the form of heat [43].

$$\text{FE} = (\text{experimental mass} - \text{consumed of electrode}) / (\text{theoretical mass} - \text{Consumed of electrode}) \times 100 \quad (26)$$

The economic operating cost is a fundamental parameter in any process. The cost analysis plays an essential role in selecting a treatment technique; the technique must be economically attractive while obtaining an effluent with the required environmental standards [6]. The operational costs of electrocoagulation can be classified in three terms [21,83].

Mass-consumed of the electrode (sacrificial anode): This theoretical value obtained from a variant of the Faraday equation helps determine the mass of the electrode consumed per volume of the substrate treated. This equation and its analysis allow determining the useful life of the sacrificial anode.

$$m_{SA} = \frac{I * t * M}{nFV}. \quad (27)$$

where m_{SA} is the mass-consumed of the sacrificial anode by volume of treated water (kg/m^3); I is the intensity current supplied to the reactor (A); M is the molar mass (g/mol); n is the number of electrons by mol of electrode; F is Faraday's constant ($96,500 \text{ C}/\text{mol}$), and t is the treatment time (s) and V is the volume of treated substrate (m^3).

Energy consumption: this relationship helps to determine to know the energy consumed by the volume of the treated substrate.

$$EC = \frac{P * I * t}{V} \quad (28)$$

where EC is the energy consumption by volume of treated substrate (kWh/m^3), P is the cell voltage measured, I is the constant current supplied (A), V is the volume of treated substrate (m^3), and t is the treatment time (h).

Chemical consumption: Although this parameter is not a mathematical relationship, the design should incorporate the economic cost of both cell materials and used chemical reagents by volume of treated substrate (a stabilization of pH is sometimes required). In general, electrocoagulation for wastewater treatment does not involve chemical reagents since the number of inorganic salts dissolved in the effluent is high. Where ChC is chemical consumption (kg/m^3)

$$\text{ChC} = \text{Mass of used chemical reagents}/\text{volume of treated substrate} \quad (29)$$

Total operational cost: this parameter involves the complete addition of the expenses in the process.

$$OC = aEC + bm_{SA} + cChC \quad (30)$$

where OC is the total operational cost ($\text{\$/USD}/\text{m}^3$ treated substrate), a is the cost of energy ($\text{\$/USD}/\text{kWh}$), b is the cost per kilogram of mass of aluminum consumed from the sacrificial anode ($\text{\$/USD}/\text{kg}$ aluminum consumed), c is the cost per kilogram of cell materials or chemical reagents used ($\text{\$/USD}/\text{kg}$ materials or chemical reagents consumed), EC is the energy consumption (kWh/m^3 treated solution), m_{SA} is the mass-consumed of the sacrificial anode by volume of treated water (kg/m^3), and ChC is the number of cell materials or chemical reagents used per volume of treated solution (kg/m^3). A study of Cd removal by EC with Al electrodes demonstrated that the cost of operation is $\text{\$}0.039 \text{ USD m}^{-3}$ to remove 100% of Cd in 5 min using 1.6 kW h m^{-3} [43].

7. Summary of Electrocoagulation Results from the Last Ten Years

Table 3 summarizes studies carried out on electrocoagulation to treat various types of wastewaters over the last ten years. The purpose of the table is to follow up on the innovations in electrocoagulation and to demonstrate the versatility of electrocoagulation for treating any wastewater and its ease of being coupled to other treatment methods. It should be pointed out that electrocoagulation is one more stage of any treatment, and as such, it must be applied; the engineer or specialist who needs to implement this technology on an industrial scale must take into account the design criteria of a treatment train to increase the efficiency of the treatment of the effluent considered.

Table 3. Control variables of the electrocoagulation process.

Author	Process' Output	Treated Substrate	Electrode Material (Sacrificial Anode and Cathode), and/or Counter Electrode	pH	Treatment Time (min)	Current Density Applied (mA/cm ²)	Efficiency Percentage (%)
[84]	Continuous	Sb contained in mine wastewater	Fe-Fe	8	3.5	0.06–2.12	75 for Sb
[85]	Batch	Hardness in mining waters containing phosphates	Al-Al	7	30	22.2	83.8 for hardness (CaCO ₃)
[86]	Batch	Indigo carmine in synthetic water	Mg pure-304 Stainless Steel AZ31 Magnesium alloy-304 Stainless Steel	7.83	150	2–5	99 for color 84 for TOC
[87]	Batch	Vinasse (wastewater from ethanol production using sugarcane)	Al-Fe/cultivation of <i>D. subspicatus</i>	6.4	240 (Time only for electrocoagulation process)	20	66 for TOC 75 for nitrogen removal 98 for turbidity
[88]	Semi-continuous	Wastewater from the tanning industry	Processes including four steps: Sedimentation/porous filter/electrocoagulation/biomass filter	7	15 (Time only for electrocoagulation process)	20 A (current density nonreported)	83.33 for COD 66.43 for BDO5 84 for chromium
[89]	Batch	Wastewater from the dairy industry	Al-Al	Non-reported	60	12 V (current density non-reported)	93.33 for BDO5 82.42 for COD 76.81 for SS
[90]	Continuous	Oil synthetic solution	Al-Fe	Non reported	60	10	85 for CDO
[91]	Batch	Wastewater from pig slaughterhouse	Al-Fe	2.43	100	25	97 for COD
[92]	Continuous	Cyanobacteria	Al-Al/anionic flocculants	7–8	2.2	37	34.8 for bacterial inactivation
[93]	Batch	Wastewater from the printing ink industry	Al-Al	Non reported	30	156	51 for COD
[94]	Batch	Dairy Wastewater	Fe-Fe	9	60	30 V (current density non-reported)	98 for COD
[95]	Continuous	Synthetic wastewater with microplastics	Ni-Ni	8	50	5 A (current density non-reported)	81 for microplastic

8. Conclusions

It is expected that the information collected can be used to promote the review of basic design knowledge, and the specifications and considerations that the engineer or specialist needs and must address to implement this technology in a treatment train were pointed out. In addition, the hydrodynamics of electrocoagulation was addressed towards the critical points. Some design considerations will depend on the treated substrate's various factors and technical issues; not all wastewaters will behave similarly. So, it is recommended that before establishing design considerations, physicochemical characterization

of the substrate should be made, and from characterization to choose the process conditions and the pertinent design for its treatment.

This topic can be divided into several specific sections; therefore, interdisciplinarity is recommended to implement this type of project.

The reader must be made clear that several factors still intervene in the mass transport and the hydrodynamics of the reactor, so the information analyzed in this paper is only a guide to entering the design and understanding what goes on inside an electrocoagulation reactor

As seen from the text, this technique has been very well studied and is supported by several authors who have obtained excellent efficiencies using only this technology. However, the use of this technology must be considered in a continuous treatment system for the treatment of large volumes of effluents; it should be clarified that the expected efficiency will depend on this technology and the appropriate arrangement of a treatment train. The versatility of electrocoagulation stands out to adapt to any process, treat almost any kind of wastewater, generally with low operating costs and a compact design that facilitates its implementation.

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