



The Combined Implementation of Electrocoagulation and Adsorption Processes for the Treatment of Wastewaters

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Abstract: Effluent treatment and reuse are essential in order to address the global problem of water scarcity. Additionally, improving the quality of treated wastewater is necessary to reduce its adverse effects on natural water resources and, consequently, on human health. Electrocoagulation and adsorption have been successfully applied separately to treat different wastewaters. Each method has unique benefits, drawbacks, and parameters that affect the effectiveness of treatment. A review of both processes, including their theoretical principles, the effect of operating conditions, and practical applications, is presented to provide an overview of their capabilities. The combination of electrocoagulation and adsorption in a combined process can be used to amplify the advantages of each process while mitigating their limitations. In the present work, the combined process is analyzed in terms of its principles, applications, and integration in a circular economy model.

Keywords: electrocoagulation; adsorption; low-cost adsorbents; wastewater treatment; circular economy

1. Introduction

The mitigation of the effects of water scarcity worldwide is becoming one of the main challenges of the 21st century. The United Nations Water World Development Report estimated in 2019 that the lack of access to clean and safe drinking water sources is responsible for the deaths of around 780,000 people yearly. Additionally, the lack of water due to draughts affects 55 million people and has an economic impact of USD 5.4 billion [1]. Despite this, water consumption by industries has been globally increasing, representing about 22% of all the water provided. It is estimated that by 2050 the water consumed by the manufacturing industries could increase by 400% [2].

In the current context of an increasing concern with water scarcity worldwide, the sustainable use of water resources should be one of the main priorities of the different industries, mainly the high water consumers. Moreover, the effluents from human activities are often loaded with toxic compounds such as heavy metals, antibiotics, and other organics that can negatively impact human health [3]. The presence of heavy metals in drinking water leads to their accumulation in the human body, resulting in nervous system dysfunction, red cell damage, hypertension, and anemia [4]. Antibiotics can cause bacterial resistance, which poses a considerable risk to human health [5]. Organic dyes can cause genetic mutations in human cells and damage the immune and reproductive systems [6]. This problem is more alarming in developing countries, where it is estimated that 70% of the industrial effluents are dumped untreated [7]. The importance of this issue was recognized by the United Nations, which in its Sustainable Development Goals (SDG) to be achieved by 2030, defined under goal number six ("Clean Water and sanitation") the target of improving water quality, wastewater treatment, and safe reuse (Target 6.3) [8].



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Water scarcity and poor water quality are pressing issues that require decentralized wastewater treatment systems to be widely used in big and small industries. These water treatment systems, which may be used as a tertiary treatment of effluents, must be compact, easy to operate, and have low operating and investment costs. Utilizing an integration methodology, combining multiple process units into a single unit to produce smaller, cleaner, less expensive, and more energy-efficient processes is one way to accomplish this goal. Additionally, the costs associated with the process can be reduced by employing low-cost materials.

Wastewaters are conventionally treated using biological [9,10] and physico-chemical processes [11,12]. The use of biological processes can be limited by their strictly regulated conditions, large space requirements, high retention time, significant footprint, and the possible generation of undesired by-products [13]. Moreover, the presence of non-biodegradable or slow degradable compounds in the wastewater can significantly reduce the biological processes' performance [14]. Chemical processes require the addition of chemicals to target specific pollutants, leading not only to an increase in global treatment costs but also to an increase in the concentration of dissolved compounds in the wastewater that may require additional downstream treatment steps. Among the limitations associated with implementing conventional methods, the high investment and operation costs can be a significant impediment to their implementation, mainly in small industries or poor countries.

The electrocoagulation (EC) process is a possible alternative to conventional wastewater treatment methods. Characteristics of the process, such as its flexibility, easy operation, no need for additional chemicals, and its ability to deal with different contaminants, have been increasing the interest in its implementation [15]. The EC process found application in the treatment of different contaminated waters, and several studies have shown the potential of this technology [16–18]. Additionally, there is the possibility of operating the EC process using sustainable energy sources, such as solar cells, windmills, and fuel cells [19]. Although the EC treatment can be applied without adding any chemical agent, some published works reported that the application of EC in waters containing chloride can result in the generation of toxic chlorine compounds, which can be viewed as a secondary source of pollution [20]. The use of adsorbents such as activated carbon has been reported as a possible solution for reducing the toxicity resulting from the electrochemical treatment [21].

Adsorption (AD) is another attractive way of treating wastewaters due to the potential of using low-cost and environmentally friendly adsorbents. Due to their high surface area and well-developed pore structure, activated carbons are the most used adsorbents in wastewater treatment systems. The high price of activated carbon limits its application. Therefore, research has been driven to the search for alternative low lost-cost adsorbents, natural materials that, in some cases, are wastes from industrial or agricultural activities.

Despite the enormous potential of both EC and AD processes for the treatment of wastewaters, the operation of each process presents some potential limitations. The main drawback of the EC process can be its energy consumption, mainly when dealing with highly concentrated effluents due to the high current necessary to generate enough co-agulant for the treatment. The use of the AD process also may present some limitations, namely the saturation of the adsorbent and the competitive effect of some compounds. Combining both processes can be a solution to overcome their limitations while benefiting from their potential.

This review discusses the fundamentals of both EC and AD processes, such as their mechanisms, key operating parameters, and applications in wastewater treatment. Moreover, this review intends to provide a critical analysis of the advantages and limitations of both processes and how their combination in a hybrid process could enhance their capabilities while mitigating their limitations.

2. Overview of Electrocoagulation Process

In its basic form, the EC process is constituted by an electrolytic cell and a pair of metal electrodes connected to a DC power source (Figure 1). The anodes are the sacrificial electrodes consumed during the operation and can be made either from the same or different material as the cathode [22]. The metal ions generated from the electro-dissolution of the anode form different complexed metal hydroxide ion species that can act as coagulants and remove pollutants from the water. Additionally, the hydrogen and oxygen bubbles generated in the anode and cathode, respectively, promote lifting the coagulated particles by electro-flotation [23]. The process's efficiency depends on operational parameters such as the applied current intensity, solution pH and conductivity, inter-electrode distance, electrode material, and configuration.



Figure 1. Schematic representation of the batch electrocoagulation process.

The EC process can be summarized in three successive steps: (i) production of coagulants from the electro-dissolution of the sacrificial anode, (ii) destabilization of the particulate suspension and formation of flocs, and (iii) aggregation of the destabilized particulates and their sedimentation and flotation [24].

The main reaction of the EC is the electro-dissolution of the sacrificial anode:

$$M_{(s)} \rightarrow M^{n+}_{(aq)} + ne^- \tag{1}$$

Simultaneously, at the cathode occurs a hydrolysis reaction where hydrogen bubbles are produced:

$$2H_2O_{(l)} + 2e^- \to H_{2(g)} + 2OH_{(aq)}^-$$
(2)

At the anode occurs the oxygen evolution:

$$2H_2O_{(l)} \to O_2_{(g)} + 4H_{(aq)}^+ + 4e^-$$
(3)

The metal ions (M^{n+}) released to the solution undergo hydrolyzation reactions to produce different metal hydroxide species that can act as coagulants:

$$M_{(aa)}^{n+} + mH_2O \rightleftharpoons \mathcal{M}(OH)_m^{n-m} + mH_{(aa)}^+ \tag{4}$$

where *M* is the electrode material, *n* is the number of electros involved in the reaction, and *m* is the stoichiometric coefficient.

2.1. Chemical Coagulation vs. Electrocoagulation

The pollutants present in wastewaters are often colloidal particles. Due to their stability, these particles are hard to remove from water through physical processes such as sedimentation or flotation [25]. The stability of the colloidal particles in the wastewater results from the balance between attractive van der Waals forces and repulsive forces on the particles' surface, keeping the particles in suspension and preventing their aggregation [26]. The introduction of a chemical agent able to reduce the repulsive forces leads to the prevalence of the attractive forces causing the aggregation of the colloidal particles and consequent formation of large agglomerates that can settle down for easier separation from water.

In the chemical coagulation (CC) process, the pollutants' removal is performed by adding coagulant agents able to neutralize the net surface charge and promoting the aggregation, floc formation, and sedimentation of the pollutants [27]. The CC is traditionally carried out using aluminum and iron coagulants such as aluminum sulfate ($Al_2(SO_4)_3$ ·18 H_2O), aluminum chloride ($AlCl_3$), sodium aluminate ($NaAlO_2$), ferric sulfate ($FeSO_4 \cdot 7H_2O$), ferrous sulfate ($Fe_2(SO_4)_3 \cdot 9H_2O$), and ferric chloride ($FeCl_3 \cdot 6H_2O$) [28]. The hydrolyzation of these compounds results in the formation of insoluble precipitates able to destabilize the suspended particles. Despite being a widely used process for removing turbidity from wastewater [25], the increased dissolved components caused by the added chemicals can complicate the downstream treatments of wastewater [29].

In contrast, in the EC process, the coagulant metal ions are generated in situ by the electro-dissolution of a sacrificial anode [30]. The EC process does not require the addition of external chemicals. Like in the CC process, the coagulants produced by EC can neutralize the repulsive forces promoting the aggregation of the particles for easier separation.

Compared with CC, the sludge produced during the EC process contains less bound water, is acid resistant, and presents more stable and large flocs that can be separated easily by filtration or decantation [30]. Additionally, EC produces about half the sludge of CC, which is an essential advantage due to the potential negative impact of those residuals on the environment. Sludge resulting from wastewater treatment is often characterized by high BOD and COD [31]. Therefore, those residuals may require an additional post-treatment process.

Another critical aspect of a wastewater treatment process is its associated costs. Published works showed that the CC process could present a 2 to 3.5 higher cost for treating the same wastewater than the EC process [32–34].

2.2. Electrocoagulation Process Set-Up

Batch EC is one of the most used set-ups to study EC at a lab scale. In this configuration, plate electrodes are submerged in the wastewater, and the solution is stirred to be homogenized (Figure 1). Despite helping study the different operating parameters of the process, this configuration may not be suitable for large-scale wastewater treatment processes. Continuous EC processes can be a better choice for treating large volumes of water. Graça et al. [35] proposed a continuous EC setup for the defluoridation of water (Figure 2). This continuous EC unit is constituted by a plexiglass structure, consisting of a first compartment containing the electrodes and directly connected to the unit inlet. A second compartment, which receives the water from the first compartment, is connected to a third compartment by a small gap at the bottom of the reactor. This separation prevents the floating solids from the second compartment from passing directly to the reactor outlet. The results showed that in addition to the capacity to treat larger amounts of water, this process also showed the ability to mitigate electrode passivation.



Figure 2. Schematic representation of the continuous electrocoagulation process: (**a**) side view; (**b**) top view (1—inlet, 2—electrodes, 3—outlet) [35] (Reproduced with permission from Graça, N.S., *Industrial and Engineering Chemistry Research*; published by American Chemical Society, 2019.).

Different variations on both batch and continuous EC set-up have been used. An alternative to the typical batch EC set-up involves cylindrical concentric electrodes [36,37]. Another variation uses the anode with a cylindrical shape while the cathode consists of a rotating impeller [38]. Several configurations have been used for the continuous process, including a filter press-cell [39,40] and reactors with rotating screw-type electrodes [41,42].

2.3. Factors Affecting Electrocoagulation

2.3.1. Current Intensity

The intensity of the electrical current applied during the EC is a key factor in the process since it controls the electro-dissolution rate of the sacrificial anode. Faraday's law gives the relationship between the applied current intensity and the rate of the anode dissolution [43]:

1

$$\tau_{Al} = \frac{l}{FzV} \varepsilon_c \tag{5}$$

where *I* is the applied current intensity (A), *z* is the valence number of the metal, *F* is Faraday's constant (94,485 C·mol⁻¹), *V* is the solution volume (m³), and ε_c is the current efficiency.

According to Equation (1), for a specific current intensity, the maximum theoretical electro-dissolution rate corresponds to a current efficiency of 100%. However, experimental results show that the amount of dissolved metal can be higher than the one predicted by Faraday's law with 100% current efficiency [44]. In this case, the process is referred to as having a "super-faradic efficiency". The main explanation for this phenomenon is the chemical dissolution of the cathode caused by the increase in the pH near the surface of the cathode due to the formation of $OH^$ associated with the hydrogen evolution [45]. Additionally, supporting electrolytes such as sodium chloride, often used to increase the solution conductivity, can cause the electrodes' corrosion, leading to values of metal dissolution above the value predicted by Faraday's equation [46].

In addition to the electro-dissolution rate, the current intensity also controls the formation rate and sizes of the bubbles. A high applied current increases the number of bubbles while reducing their size, contributing to faster pollutants removal by floatation [47].

The current intensity can be seen as the main parameter controlling the coagulant dosage during the EC process. The range of applied current intensity will depend on

the characteristics of the wastewater, such as the conductivity and concentration of the pollutants. The low conductivity of the wastewater corresponds to a high electrical resistance between the electrodes. Consequently, high voltages are required to obtain a specific current intensity. The presence of high concentrations of pollutants in the wastewater may require higher dosages of coagulant that can be obtained using a high current/voltage or a higher operation time. However, those operational parameters have a direct impact on the EC process energy consumption and consequently on its operating costs. For constant current intensity, the energy consumption can be determined by using the following expression:

$$EC = I \int_0^t U \, dt \tag{6}$$

where *U* is the value of the voltage applied to the electrodes during the *EC* operation, *I* is applied current intensity, and *t* is the time necessary to treat the volume of the water considered.

2.3.2. Initial pH

The pH is essential in the EC process operation since it affects the conductivity, zeta potential, electrode dissolution, and concentration of metal hydroxide species [43,48]. Since the pH usually changes during the EC, its relationship with the process performance is hard to assess. Therefore, the initial pH is often used to determine the pH effect on the EC process [49].

The optimum initial pH of the EC process depends on the treated wastewater type. Some published works showed that an initial acid pH provides good results for treating laundry wastewater [50], palm oil mill effluent [51], oily wastewater [52], and dairy processing wastewater [53]. In contrast, tannery wastewater [54], municipal wastewater [55], and textile wastewater [56] showed better results at an alkaline pH. The electrode type also plays a vital role in determining the optimal initial pH. Demirbas and Kobya [57] showed that for the treatment of metalworking fluid wastewater by EC, the best results for aluminum electrodes were obtained at pH 6.5, whereas for iron electrodes a pH of 7.5 led to the best results. Therefore, the best pH to carry out the EC process is highly dependent on the wastewater and its interaction with the electrodes.

The pH value Influences the formation of the metal hydroxide species. For aluminum electrodes, the theoretical equilibrium concentration of the different aluminum hydroxide mononuclear species is a function of the solution pH [58]:

$$\log\left[Al^{3+}\right] = \log K_s - 3\log K_w + 3pH \tag{7}$$

$$\log\left[Al(OH)_{n}^{3-n}\right] = \log K_{n} + \log K_{s} - 3\log K_{w} + (n-3)pH$$
(8)

where K_n are the thermodynamic equilibrium constants.

Figure 3 shows the aluminum solubility diagram determined using Equations (7) and (8). It can be noticed that the concentration of the different aluminum species is strongly dependent on the pH.



Figure 3. Aluminum solubility equilibrium diagram [43] (Reprinted from *Chemical Engineering Science, vol. 197*, Graça, Nuno S.; Ribeiro, Ana M.; Rodrigues, Alírio E., Modeling the electrocoagulation process for the treatment of contaminated water, Pages 379–385, Copyright (2019), with permission from Elsevier.).

2.3.3. Inter-Electrode Distance

The inter-electrode distance determines the electrostatic field between the anode and the cathode. The intensity of the electrostatic field is inversely proportional to the distance between the electrodes. Decreasing too much distance between the electrodes generates a strong electrostatic attraction that can lead to degradation by the collision of the metal hydroxides responsible for forming the flocs. However, a weak electrostatic field caused by a large inter-electrode distance causes a slow movement of the released ions between the anode and the cathode, hindering the formation of metal hydroxide flocs [59]. Therefore, it is necessary to determine the optimal inter-electrode distance that corresponds to a maximum pollutant removal efficiency. The inter-electrode distance generally used in the EC processes is between 0.5 and 3.0 cm [60].

2.3.4. Electrode Arrangement

In addition to the basic two-electrodes set-up presented in Figure 1, the EC process can be operated with several electrodes. The operation with multiple electrodes opens the possibility of connecting the electrodes in different arrangements. The connections between the electrodes and the power source can be established in three ways [61].

Two possible electrode arrangements are monopolar, meaning that each electrode is charged with one polarity. One of those arrangements is called series monopolar (SM) (Figure 4a), where the internal electrodes are connected to each other but are not connected to the outer electrodes, which are connected to the power source. The other arrangement is called parallel monopolar (PM) (Figure 4c). In this case, all the electrodes are connected in pairs to the power source. In the PM arrangement, the electrical current is divided between all the electrodes proportionally to their resistance, requiring a lower potential difference when compared with serial arrangements, where the electrical current flows through all the electrodes.



Figure 4. Electrodes configuration: (a) series monopolar (SM); (b) series bipolar (SB); (c) parallel (P).

Alternatively, the EC process can be performed using a series bipolar configuration (SB) (Figure 4b), where the inner electrodes are not connected to each other or the outer electrodes, which are the only ones connected to the power source. In this configuration, the inner electrodes have different polarities in each face.

Comparative studies of the different configurations suggest that the P configuration generally presents lower operational costs, whereas the SB configuration presents, in some cases, higher pollutant removal and requires lower maintenance [61,62]. However, these studies are not conclusive since the EC optimal performance depends on the various operating parameters, the water matrix, and the pollutant type [63].

2.3.5. Electrode Material

The most common electrode material used in the EC process is aluminum (Al) Under the electrical current, the electro-dissolution of the sacrificial anode leads to the release of aluminum cations $(Al)^{3+}$ The main anodic and cathodic reactions using aluminum electrodes are shown in Equations (9)–(11). During the EC process, the dissolved cations present in the electrolytic solution can undergo different hydrolysis reactions producing several aluminum hydroxide monomeric species such as $Al(OH)^{2+}$, $Al(OH)^+_2$, $Al(OH)^+_3$, $Al_7(OH)^+_{17}$, and $Al_8(OH)^{4+}_{20}$ [64], the concentration of each aluminum hydroxide species depends upon the solution pH [43]. The formation of aluminum flocs during the EC process can be attributed mainly to the formation of $Al(OH)_3$ [65,66].

Anode:
$$Al_{(s)} \rightarrow Al_{(aq)}^{3+} + 3e^-$$
 (9)

Cathode:
$$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aa)}$$
 (10)

$$Overall: 2Al_{(s)} + 6H_2O_{(l)} + O_{2(g)} \rightarrow 4Al(OH)_{3(s)} + 4H_{2(g)}$$
(11)

Another widely used electrode material is iron (*Fe*). Like the aluminum electrodes, the coagulants are generated in situ by the electro-dissolution of the sacrificial anode. Two mechanisms were proposed for the dissolution of the iron electrode depending on the solution pH [67]. Mechanism 1 occurs at high pH, where the in-

volvement of oxygen can lead to further Fe^{2+} oxidation into Fe^{3+} . In mechanism 2, at lower pH, there is no further oxidation. The main anodic and cathodic reactions using iron electrodes are shown in Equations (12)–(17). The $Fe(OH)_2$ and $Fe(OH)_3$ form a gelatinous suspension, which can remove the pollutant particles by either complexation or particle destabilization [68].

In mechanism 1,

Anode:
$$Fe_{(s)} \rightarrow Fe_{(aa)}^{2+} + 2e^{-}$$
 (12)

 $Cathode: \qquad 2H_{(aq)}^+ + 2e^- \rightarrow H_{2(g)} \tag{13}$

$$Overall: 4Fe_{(aq)}^{2+} + 10H_2O_{(l)} + O_{2(g)} \rightarrow 4Fe(OH)_{3(s)} + 8H_{(aq)}^+$$
(14)

In mechanism 2,

Anode:
$$Fe_{(s)} \to Fe_{(aq)}^{2+} + 2e^{-}$$
 (15)

Cathode:
$$2H_2O_{(l)} + 2e^- \to H_{2(g)} + 2OH_{(aq)}^-$$
 (16)

$$Overall: \qquad Fe_{(aa)}^{2+} + 2OH_{(aa)}^{-} \rightarrow Fe(OH)_{2(s)}$$
(17)

Copper has been used as alternative electrode material in the EC process. A comparative study performed between Al and Cu electrodes showed that copper electrodes perform better than Al electrodes in the treatment of printing wastewater [69]. The copper cations (Cu^{2+}) are released into the electrolytic solution by electro-dissolution of the sacrificial anode while hydrogen is produced in the cathode surface. The main cathodic and anodic reactions are described in Equations (18)–(20). The hydrolysis of the copper cations results in the formation of monomeric and polymeric species such as $Cu(OH)^{2+}$, $Cu(OH)^{+}_2$, $Cu(OH)^{-}_4$, $Cu_2(OH)^{4+}_2$, $Cu(H_2O)^{+}_2$, $Cu(H_2O)^{+}_2$, and $Cu(H_2O)_5OH^{2+}$ [70]. The negatively charged colloidal particles can be adsorbed into the amorphous ions hydroxides, causing their neutralization and consequent precipitation due to their higher mass [71].

Anode:
$$Cu_{(s)} \rightarrow Cu_{(aq)}^{2+} + 2e^-$$
 (18)

Cathode:
$$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aa)}$$
 (19)

$$Overall: 2Cu_{(s)} + 4H^+_{(aq)} \rightarrow 2Cu^{2+}_{(aq)} + 2H_{2(g)}$$
(20)

Additionality, other materials such as zinc and magnesium have been considered alternatives to aluminum and iron as sacrificial anodes [72]. The mechanisms of electro-dissolution and precipitation are as described for aluminum, iron, and copper electrodes. The reactions for the electro-dissolution of the sacrificial anodes and the formation of the respective metal hydroxides $Zn(OH)_2$ and $Mg(OH)_2$ are described in Equations (21)–(24).

$$Zn_{(s)} \to Zn_{(aq)}^{2+} + 2e^{-}$$
 (21)

$$Mg_{(s)} \to Mg_{(aa)}^{2+} + 2e^{-}$$
 (22)

$$Zn_{(aq)}^{2+} + 2H_2O_{(l)} \rightarrow Zn(OH)_{2(s)} + 2H_{(aq)}^+$$
(23)

$$Mg_{(aq)}^{2+} + 2H_2O_{(l)} \to Mg(OH)_{2(s)} + 2H_{(aq)}^+$$
(24)

Due to their low cost and high efficiency, iron and aluminum have been extensively used as electrode materials. However, depending on the wastewater, the process configuration, or the process application, other materials might perform better. Prajapati et al. [71] showed that copper electrodes performed better in treating rice-grain-based biodigester effluent when compared with aluminum and iron electrodes. Using solar-photovoltaic electrocoagulation, Hussin et al. [73] showed the superior performance of perforated zinc electrodes in removing lead from water.

2.3.6. Other Factors

The temperature is an operating parameter that usually is not considered in EC studies. In most cases, the processes are carried out at room temperature. Nevertheless, some published works report a positive effect of the temperature increase on the process performance in terms of pollutants removal and operation costs [74,75]. However, increasing the solubility of the metal hydroxides and shrinkage of the coagulant pores at high temperatures may have a detrimental effect on the EC process [76,77].

Stirring speed is another parameter that may impact the performance of the process. The stirring speeds for wastewater treatment are usually within 80–300 rpm [51,78,79]. Results of the study of this parameter show that an increased stirring speed enhances the mobility of the metal hydroxides flocs inside the EC reactor, increasing the pollutant removal efficiency. However, a too high stirring speed can reduce the EC performance due to the breaking down of the flocs [25].

Since the EC process is based on electrical current, the conductivity of the water is an essential parameter of the process. Wastewater with low conductivity requires a high voltage to obtain a specific current intensity, increasing the EC process energy consumption (see Section 2.3.1). Conductivity is related to another process parameter, which is the supporting electrolyte. The addition of a supporting electrolyte is necessary when the wastewater presents a low conductivity. The most typical electrolyte used in EC is sodium chloride (NaCl); however, other electrolytes such as potassium chloride (KCl) and sodium nitrate (NaNO₃) are also used [79].

Most studies involving EC are performed using direct current (DC). However, using DC leads to the passivation of the electrodes due to forming an oxidation layer on the cathode, reducing the flow of the electrical current and lowering the pollutant removal efficiency. The use of alternating current (AC) has been suggested to avoid the problem of electrode passivation [80]. The passivation of the electrodes during the EC process is caused by the accumulation of an inhibiting layer on the electrode's surface. The formation of this passivating layer contributes to an increase in the system's overall resistance, which impacts the current and potential applications during the EC process. The electrode passivation is undesirable for the EC operation since it reduces its energetic efficiency.

2.4. Application of the EC Process on Wastewater Treatment

Treatment processes based on EC have been used to treat several kinds of wastewaters, such as industrial wastewater [81], municipal wastewater [82], textile wastewater [83], and laundry wastewater [84]. This versatility of EC is related to its capacity to remove several types of pollutants such as total organic carbon (TOC) [22], chemical oxygen demand (COD) [85], heavy metals [86], suspended solids (SS) [87], oil emulsions [52], turbidity [88], and color [89]. Table 1 presents a summary of the treatment of different types of wastewaters using the EC process.

In the context of industrial wastewaters, the EC process has been widely used in the treatment of effluents containing persistent organic pollutants (POPs) such as perfluorooctanoic acid [90], perfluoroalkyl substances [91], and trichloroethylene [92]. In addition to being a huge water consumer, the textile industry also produces effluents containing hazardous compounds such as dyes. The EC process found application in removing several dyes, such as Reactive Blue 198, Reactive Yellow 145, Reactive Blue 19, Congo Red, and Acid Blue 25 [93–95].

Another important application of the EC process is in treating urban wastewaters, which has been used to remove pollutants such as turbidity, color, phosphorus compounds, COD, and BOD [96–98]. Additionally, the EC process showed the ability to remove active pharmaceutical compounds found in municipal and hospital wastewaters [99].

Wastewater	Initial Concentration of Pollutants	Electrodes	Removal Efficiency	Reference
Industrial wastewater	873 mg/L (COD)	Fe	91.7%	[100]
Municipal wastewater	143 mg/L (TSS) 68 mg/L (particulate BOD)	Fe	95.4% (TSS) 99% (particulate BOD)	[101]
Textile wastewater	1400 mg/L (Ácid Red 336)	Al	99% (turbidity) 95% (color)	[102]
Textile wastewater	278 ADMI (color) 339 mg/L (COD) 610 mg/L (silica)	Fe	88.1% (color) 70.5% (COD) 100% (silica)	[103]
Cold meat industry Wastewater	3482 mg/L (COD)	Al	92.9%	[104]
Palm oil mill effluent	25,500 mg/L (COD) 15,600 mg/L (BOD) 12,300 mg/L (TSS)	steel wool	95% (COD) 94% (BOD) 96% (TSS)	[105]
Carpet cleaning wastewater	20.4 mg/L (methylene blue substances) 674 mg/L (COD) 122 NTU (turbidity)	Al	85.5% (methylene blue substances) 84.4% (COD) 90.5% (turbidity)	[106]
Hospital wastewater	32.5 mg/L (ciprofloxacin)	Al	90.4%	[107]
Simulated phenolic wastewater	327 mg/L (total phenolic content) 1118 mg/L (COD)	Zn/SS	84.2% (total phenolic content) 40.3% (COD)	[108]
Olive mill effluent	57,800 mg/L (COD) 2420 mg/L (polyphenol)	Al	76% (COD) 91% (polyphenol) 95% (dark color)	[109]
Landfill leachate	11,000 mg/L (COD)	Fe	65.9%	[110]
Wastewater from an industrial park	2300 mg/L (COD) 7450 mg/L (color (Pt-Co)) 550 NTU (turbidity) 1080 mg/L (TOC)	Си	89% (COD) 97% (color) 91% (turbidity) 48% (TOC)	[111]
Pulp and paper industry bleaching effluent	255 CU (color) 620 mg/L (COD) 210 mg/L (BOD)	Al	94% (color) 90% (COD) 87% (BOD)	[112]
Cork boiling wastewater	1594 mg/L (COD) 880 mg/L (TOC) 38.6 mg/L (TN) 271 mg/L (TSS)	Al/SS	93.5% (COD) 82.5% (TOC) 88.9% (TN) 99% (TSS)	[113]
Tannery wastewater	14,001 mg/L (COD) 6000 mg/L (TDS)	carbon-steel	23% (COD) 76% (TDS)	[114]

Table 1. Electrocoagulation is used to treat different wastewaters (COD—chemical oxygen demand; BOD—biochemical oxygen demand; TDS—total dissolved solids; TSS—total suspended solids; TOC—total organic carbon; TN—total nitrogen).

3. Overview of the Adsorption Process

Adsorption is the process of transferring molecules (adsorbates) from a gas or a liquid into a solid surface (adsorbent) and holding them through physical or chemical intermolecular interactions [115]. In the case of the interaction forces between the adsorbent surface and the adsorbed molecules being physical, the process is denominated physisorption. This process is reversible due to the weak nature of the attraction van der Waals forces

between the adsorbent and the adsorbate. It occurs at low temperatures and is exothermic, with the heat of adsorption comparable to the latent heat of condensation [116]. In contrast, when the adsorbed molecules are held to the solid surface through chemical bonding, the process is called chemisorption. In this case, the molecules adsorbed to the solid surface are hardly removed due to the strong nature of the forces involved. This process is usually irreversible. It occurs at high temperatures with a high heat of adsorption [116].

The AD process's efficiency depends on the adsorbent material used, which should present a high affinity towards the target pollutants to treat the wastewater effectively. Different materials can be used as adsorbents: activated carbons, zeolites, clay materials, industrial by-products, agricultural waste, biomass, and polymeric materials [115,117,118]. The efficiency of the process is also dependent on other factors, including surface area, pore structure, adsorbent surface chemistry, the nature of the adsorbate, the presence of competing adsorbates, temperature, and pH [116].

The AD mechanism can be explained by the intra-particle model, which describes the AD process occurring in four steps [119]:

- 1- Bulk diffusion: transport of the adsorbate molecules in the solution phase.
- 2- <u>Film diffusion</u>: transport of the adsorbate molecules from the bulk solution to the adsorbent surface through a hydrodynamic boundary layer (film).
- 3- Intra-particle diffusion: transport of the adsorbate molecules from the adsorbent external surface through the adsorbent pores.
- 4- Adsorption: uptake of the adsorbates on the adsorbent.

The reverse mechanism can be used to describe the desorption process.

A dynamic equilibrium is established when, at a constant temperature, the adsorption and desorption rates are equivalent. In these conditions, adsorption isotherms relate the amount of adsorbate in the solid phase (q_e) and its equilibrium concentration in the liquid phase (C_e). Among several options, the most used isotherm models are Langmuir, Freundlich, Temkin, Dubinin–Radushkevich, Sips, and Redlich–Peterson [4,120]. Table 2 presents a summary of the isotherm models.

Table 2. Summary of the isotherm models.

Model	Equation	Description
Langmuir [121]	$q_e = \frac{Q_{max}k_L C_e}{1+k_L C_e}$	Assumes monolayer adsorption and a homogenous surface energy distribution. (Q_{max} is the maximum adsorption capacity (mg g ⁻¹), k_L is the Langmuir constant (L mg ⁻¹))
Freundlich [122]	$q_e = k_F C_e^{1/n}$	Assumes a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface. (k_F is the Freundlich constant (mg g ⁻¹) (L mg ⁻¹) ⁻ⁿ , <i>n</i> is the intensity of adsorption constant)
Sips [123]	$q_e = \frac{K_S C_e^{n_S}}{1 + a_S C_e^{n_S}}$	This model results from the combination of both the Langmuir and Freundlich models. It has the ability to take into account the heterogeneity of the adsorbent surface while overcoming the limitations associated with the increased adsorbate concentrations of the Freundlich model. (K_S is the Sips model constant (L mg ⁻¹), a_S is the Sips constant (L mg ⁻¹), n_S is the Sips
Redlich-Peterson [124]	$q_e = \frac{K_{RP}C_e}{1 + a_{RP}C_e^{\beta}}$	It is a hybrid model of the Langmuir and Freundlich isotherms. It can be used to describe adsorption on both homogeneous and heterogeneous surfaces. (K_{RP} is the Redlich–Peterson constant (L mg ⁻¹), a_{RP} is the Redlich–Peterson constant (L mg ⁻¹), and β is the Redlich–Peterson exponent)

Model	Equation	Description
Temkin [125]	$q_e = B_T ln(A_T C_e)$	Assumes uniform binding energy distribution and a linear decrease in the heat of adsorption with the surface coverage. (A_T is the Temkin isotherm equilibrium binding constant (L mg ⁻¹), and B_T is the Temkin
		isotherm constant)
Dubinin– Radushkevich [126]	$q_e = Q_s exp(-k_{DR}\varepsilon^2)$	Assumes a Gaussian distribution of energy onto a heterogeneous surface. (Q_s is the theoretical isotherm saturation capacity (mg g ⁻¹), k_{DR} is the Dubinin–Radushkevich isotherm constant (mol ² J ⁻²), and ε is the Polanyi potential)

The rate at which the adsorption occurs can be limited by mass transfer resistances depending on the temperature and the adsorbent and adsorbate characteristics. The two primary resistances occurring during the adsorption process are the resistance to external diffusion, which is related to the mass transference between the bulk solution and the external surface of the adsorbent, and the intraparticle resistance, which is related to the mass transfer through the adsorbent internal porous structure [127]. Several kinetic models have been proposed to describe the adsorption rate, including pseudo-first-order (Equation (25)), pseudo-second-order (Equation (26)), Avrami fractional-order (Equation (27)), and intraparticle diffusion (Equation (28)) models [128,129]. Determining the process's rate constant is fundamental to understanding the dynamics of a specific adsorption problem [130].

$$q_t = q_e \left(1 - e^{-k_1 t} \right) \tag{25}$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$$
(26)

$$q_t = q_e \left[1 - e^{-(k_3)^n} \right]$$
 (27)

$$q_t = k_4 t^{1/2} + C (28)$$

where q_t (mg g⁻¹) is the amount adsorbed at any time t (min), k_1 (min⁻¹) is the rate constant of the pseudo-first-order model, k_2 (g mg⁻¹ min⁻¹) is the rate constant of the pseudo-second-order model, k_3 (min⁻¹) is the Avrami kinetic constant, k_4 (mg g⁻¹ min^{-1/2}) is the intra-particle rate constant, n is the fractional adsorption order, and C (mg g⁻¹) is the thickness of the boundary layer.

3.1. Adsorption Process Set-Up

The AD process is often carried out in batch mode to study the removal of several pollutants [131–133]. However, this operation mode may present some limitations from a scaling-up perspective. Therefore, a continuous or semi-continuous operation mode appears to be a more feasible option for developing large-scale AD systems. Fixed-bed columns (Figure 5) are one of the most used dynamic AD systems presenting several advantages, including the capacity to treat large volumes of solution with high removal efficiency, simple set-up, and easy scaling up from laboratory scale [134]. The performance of the fixed-bed AD mode has been studied in the treatment of several contaminated wastewaters, including paper-making wastewater [135], tannery wastewater [136], and textile wastewater [137]. Despite the fixed-bed mode being considered more efficient in most cases, Dichiara et al. [138] proposed a methodology to choose either batch or fixed-bed processes when the goal is to remove pollutants above a specified threshold while minimizing the amount of adsorbent needed. It was shown that above a critical effluent concentration, the batch process could be more efficient than the fixed-bed process.

The fixed-bed AD process is usually carried out in two steps. In the saturation or loading step, the column is fed with a pollutant solution until the adsorbent reaches saturation. This step is followed by a desorption or regeneration step, where the column is fed with the solvent until the adsorbent is regenerated. However, this operative scheme presents two major drawbacks: one is the need for high temperatures or a chemical regenerant to get an operative bed, which increases the process costs and causes an additional waste disposal problem, and the second is the lack of efficiency since the adsorbent is only partially used during the fixed-bed operation.

A possible alternative to the conventional fixed-bed process is using a cyclic process such as parametric pumping, where the evolution of the process occurs in successive flow direction changes coupled with the variation of a thermodynamic variable such as temperature (Figure 6). The column is never completely saturated or regenerated, allowing a continuous cyclic operation. This process is based on the fact that the adsorption equilibrium of the solute changes with a thermodynamic variable (temperature, pressure, and pH) [139]. The study of this process at the lab scale showed its ability to remove several compounds from water, such as phenol [140], toluene [141], urea [142], and oxalic acid [143]. Otero et al. [144] studied the purification of wastewater containing 500 mg L⁻¹ of either phenol or 4-nitrophenol using a thermal pilot scale parametric pumping unit. After ten cycles, it was possible to reduce the concentration of phenol to C/C_F = 0.0003 and the concentration of 4-nitrophenol to C/C_F = 0.0013.



Figure 5. Schematic representation of the fixed-bed adsorption process.



Hot half cycle

Cold half cycle

Figure 6. Schematic representation of the parametric pumping process.

3.2. Factors Affecting Adsorption

3.2.1. Adsorbent Material

The adsorbents can be prepared from organic materials with high carbon content, such as algae, rice husks, bark, fruit waste, peat moss, agricultural waste, and organic industrial products [145]. The inorganic adsorbents are produced from ores, metal oxides, soil, clays, zeolites, and metal hydroxides [145,146].

Activated carbons are one of the most used adsorbent materials applied in the treatment of wastewaters. Characteristics such as well-developed surface area, high microporosity, and good removal efficiency justify its popularity [147]. However, its difficult regeneration, which may require high temperatures or chemical regenerants, is a significant drawback [148]. Therefore, the activated carbon is usually replaced and disposed of [149]. Polymeric resins are a possible alternative to activated carbons, which can be produced with various physical properties such as functionality, surface area, and porosity. The possibility of customizing some physical properties of the polymeric resins for the selective removal of specific compounds is a significant advantage of this kind of adsorbent [150]. However, the high cost of this kind of material can be a significant impediment to its widespread application in wastewater treatment processes.

3.2.2. Adsorbent Dosage

The dosage of adsorbent material determines the amount of available binding sites and the adsorbent surface area, directly affecting the adsorbate uptake and equilibrium time [151,152]. However, it has been reported that the adsorption capacity may decrease beyond an optimal amount of adsorbent. This decrease in capacity can be attributed to the change from a low amount of adsorbate to an increasing amount of adsorbent, leading to the existence of unsaturated biding sites [153]. Another explanation is the reduced available adsorbent surface area due to aggregation or an overlapping of the binding sites [154].

For a continuous fixed-bed AD process, the amount of adsorbent is directly proportional to the bed height. Therefore, the increase in the bed height corresponds to an increase in adsorbent amount, surface area, and saturation time. Baral et al. [155] showed that for Cr(VI) removal, the increase in the bed height corresponded to an increase in the throughput volume due to higher contact time. Likewise, Nazari et al. [156] reported that the column height increased treated effluent volume and saturation time. However, they concluded that removing cephalexin at a low bed height was beneficial because not all the adsorbent surface was accessible to cephalexin molecules in a high bed column, decreasing the adsorbent efficiency.

3.2.3. Concentration of Pollutants

The effect of the pollutant's concentration depends on its proportion relative to the available binding sites on the adsorbent surface. At low concentrations, only a small fraction of the adsorption sites on the adsorbent surface will be occupied. A further increase in the pollutants' concentrations increases the occupied fraction until no available sites exist. At this point, the adsorbent reaches saturation [157]. Therefore, for a fixed amount of adsorbent, the percentage of the pollutant removed by AD decreases with increased concentration. However, Dogan et al. [158] reported that the adsorption capacity of hazelnut shells increased with the initial concentration of the dye methylene blue. Likewise, Garg et al. [159] observed that increasing the concentration of methylene blue from 50 mg/L to 250 mg/L led to an increase in rosewood sawdust adsorption capacity from 12.49 mg/g to 51.4 mg/g. These results can be explained by the higher driving force to mass transfer when a fresh adsorbent is in contact with a higher concentration of pollutant [160]. In addition to the target pollutant, the presence of co-existing substances in the water can also affect the performance of the adsorption process. Therefore, for a specific water treatment problem, the impact of co-existing substances on the adsorption should be investigated [161].

The concentration of pollutants in the column's inlet for continuous fixed-bed AD significantly impacts the process's dynamic behavior. Due to an increased driving force to mass transfer and consequent increase in the adsorption rate, a high inlet concentration results in a faster saturation of the adsorbent bed and an early breakthrough of the pollutants [162]. Conversely, a low inlet concentration results in a later breakthrough due to a slower saturation of the binding sites on the adsorbent surface [163].

3.2.4. Temperature

The effect of the temperature on the AD process will depend on the nature of the process from a thermodynamic perspective. The thermodynamic parameters Gibbs energy change (ΔG), enthalpy change (ΔH), and entropy change (ΔS) can be calculated using the following equations:

$$\ln K = \frac{-\Delta G}{RT} \tag{29}$$

$$\Delta G = \Delta H - T \Delta S \tag{30}$$

The AD process is favorable and spontaneous when, at a specific temperature, the ΔG is negative. Negative values of ΔH indicate that the process has an exothermic nature. In this case, the adsorption capacity decreases with the temperature increase. An exothermic AD process can involve either physisorption or chemisorption, or both. However, a positive value of ΔH (endothermic process) suggests the occurrence of only chemisorption [164]. The level of organization of the solutes at the liquid/solid interface is determined by ΔS . A positive value ($\Delta S > 0$) corresponds to an increase in randomness and is associated with a dissociative mechanism. However, the low randomness associated with a negative value ($\Delta S < 0$) corresponds to an associative mechanism [164,165].

Determining the thermodynamic parameters based on experimental adsorption data is fundamental for understanding the relationship between the temperature and the process performance and its further optimization [166].

3.2.5. Solution pH

A critical parameter for evaluating pH's effect on AD is the point of zero charge (pH_{pzc}). This parameter is defined as the pH at which the sum of positive surface charges balances the sum of negative surface charges and is indicative of the surface properties of the adsorbent [167]. The pH_{pzc} is determined by comparing the initial pH with the equilibrium pH of electrolyte solutions containing the adsorbent. At the pH_{pzc}, the solution pH does not change from the beginning until the adsorption equilibrium is reached [168]. Below the point zero charge value (pH < pH_{pzc}), the surface is positively charged, whereas above this value, it is negatively charged. Therefore, it is usually easier to adsorb a cation below pH_{pzc} and an anion above this value. However, other interactions may be stronger than purely electrostatic forces, making the effect of surface charge less important. Dash et al. [168] studied the adsorption of toxic reactive dyes on modified coal fly ash and observed that cationic dye favorably adsorbed for pH > pH_{pzc}. In contrast, anionic dye adsorption occurs when pH < pH_{pzc}.

The pH used to treat different wastewaters depends on the properties of the target pollutants and the adsorbent used. Chowdhury et al. [169] studied the adsorption of Basic Green 4 dye on Ananas comosus leaf powder at a pH range from 2 to 10 and observed that the maximum adsorption was obtained at pH 10. In contrast, Dawood and Sen [170] showed that the Congo red dye adsorption on pine cones was higher at pH 3.5.

3.3. Applications of Low-Cost Adsorbents

Many low-cost adsorbents have been studied as alternatives to conventional adsorbents to remove different types of pollutants from wastewater. The apparent advantage of this kind of material is the reduction in the costs associated with the wastewater treatment process. Additionally, using by-products from different activities such as agriculture and industry minimizes their disposal problems [171]. Table 3 summarizes different low-cost materials and their respective adsorption capacity for target pollutants.

Material	Adsorbate	Adsorption Capacity	Reference
Pineapple leaf powder	Methylene blue	$9.28 \times 10^{-4} \text{ mol/g}$	[172]
Grapefruit peel	U(VI)	140.79 mg/g	[173]
	Methyl orange	17.2 mg/g	
	Methylene blue	15.9 mg/g	
Banana pool	Rhodamine B	13.2 mg/g	[174]
Danana peer	Congo red	11.2 mg/g	[1/4]
	Methyl violet	7.9 mg/g	
	Amido black 10B	7.9 mg/g	
	Pb(II)	$4.47 imes10^{-5} ext{ mol/g}$	
Oliva stona wasta	Ni(II)	$3.63 imes10^{-5} ext{ mol/g}$	[175]
Onve stone waste	Cu(II)	$3.19 imes10^{-5} ext{ mol/g}$	[175]
	Cd(II)	$6.88 imes10^{-5} ext{ mol/g}$	
Maize cob	2,4-Dichlorophenol	17.94 mg/g	[176]
Sugarcane bagasse	Hg(I)	35.71 mg/g	[177]
Peanut husk	Neutral red	37.5 mg/g	[178]
Potato peel charcoal	Cu(II)	0.3877 mg/g	[179]

Table 3. Adsorption capacities of different low-cost materials for the removal of various pollutants from water.

Material	Adsorbate	Adsorption Capacity	Reference	
	Cu(II)	59.77 mg/g		
	Cd(II)	125.63 mg/g		
Orange peel	Pb(II)	141.84 mg/g	[180]	
	Zn(II)	45.29 mg/g		
	Ni(II)	49.14 mg/g		
Red mud	Phosphate	0.23–0.58 mg/g	[181]	
Rice straw	Cd(II)	13.9 mg/g	[182]	
Ground wheat stems	Cd(II)	0.1032 mmol/g	[183]	
Iron-containing fly ash	As(VI)	19.46 mg/g	[184]	
Steel-making slag	Cu(II)	6.2–17.4 mg/g	[185]	
	Crystal violet	184.68–270.88 mg/g		
Sewage sludge	Indigo carmine	30.82–60.04 mg/g	[186]	
	Phenol	5.56–42.04 mg/g		
	Cd(II)	90.7 mg/g		
Ulva seaweed	Zn(II)	74.6 mg/g	[187]	
	Cu(II)	57.3 mg/g		
Palm seed coat	o-Cresol	19.58 mg/g	[188]	
Pinewood	Basic Blue 9	556 mg/g	[189]	
Lathar industry wasta	Cr(VI)	133 mg/g	[100]	
Learner moustry waste	As(V)	26 mg/g		
Rice husk	Safranine	838 mg/g	[191]	

Table 3. Cont.

The use of agricultural by-products is one of the most economically attractive ways to produce low-cost adsorbents able to remove many types of pollutants such as phenol [192], COD [193], heavy metals [194], dyes [195], and gases [196]. Several agricultural wastes have been showing potential to be used as low-cost adsorbents, including hazelnut shell [197], corncob [198], grapefruit peel [199], olive stone [200], sugarcane bagasse [201], potato peel [202], rice straw [203], orange peel [204], and wheat stem [205]. These materials can be used in their natural form after being washed, ground, and sieved to the desired particle size. Additionally, pre-treatments can enhance the functional group potential and increase the number of active sites [206]. Moreover, biochars made from biomass pyrolysis are becoming increasingly important as a carbonaceous material used in pollution reduction [207].

Another important source of low-cost materials is industrial waste. These waste materials, if not reused, are sent for disposal in landfills. Therefore, in addition to the advantage of their reduced cost, the use of industrial wastes also contributes to minimizing their disposal problem. The main industrial by-products used as adsorbents include fly ash [208], steel industry wastes [209], red mud [210], fertilizer industry wastes [211], leather industry wastes [212], and paper industry wastes [213].

Sludges produced in several wastewater treatments can be reused as adsorbents to remove pollutants from aqueous solutions [214–216]. Otero et al. [186] studied the potential of sewage-sludge-based adsorbents to remove organic pollutants. Li et al. [217] showed the effectiveness of wine processing waste sludge for removing Cr(III) from an aqueous solution. Neilsen and Bandosz [218] produced adsorbents from sewage sludge, fish waste, and mixtures of both. Those adsorbents were effective in the removal of pharmaceuticals from water.

Due to its abundance, chitin is an economically attractive material to be used as an adsorbent. It is estimated that annually more than 1362×10^6 tons of chitin can be obtained from fisheries of crustaceans [145]. Chitosan, which can be chemically prepared from chitin, has been used as an adsorbent to remove several pollutants [219–221]. Other sea materials, such as seaweed, have also been used as low-cost adsorbents [187,222,223].

Clays, soils, and ore minerals are other sources of materials used for producing low-cost adsorbents. Clays are a particularly interesting material due to their large surface area, raging up to $800 \text{ m}^2/\text{g}$ [145]. Soils have been used as adsorbents to remove

pesticides [224] and phenolic compounds [225]. Ore minerals were applied to remove organic pollutants [226].

4. Combined Electrocoagulation and Adsorption Processes

The EC and AD processes have shown great potential for treating several wastewaters. Both processes have merits and difficulties when applied individually to remove target pollutants. Therefore, any process resulting from the combination of the two technologies should be able to take advantage of their potential while mitigating their weak points. Table 4 presents some potential limitations of both processes.

Table 4. Summary of the limitations of the EC and AD processes.

EC Limitations	AD Limitations	
 Need for periodic replacement of the sacrificial anodes Passivation of the cathodes Formation of chlorinated organic compounds in waters containing chloride Sludge disposal High energy consumption 	 Adsorbents cost Adsorbent regeneration may require extreme conditions or chemicals Loss of adsorption capacity in each regeneration cycle Pore blocking due to suspended solids 	

The combination of the EC and AD processes can be used to amplify the advantages that each process presents in treating wastewaters. As a first step, the EC process reduces the pollutant loading and the suspended solids concentration, which can benefit the AD process by delaying the adsorbent saturation and preventing clogging. Additionally, each adsorption/regeneration cycle could result in the adsorbent losing some of its capacity; as a result, delaying adsorbent saturation helps to increase its useful life [227]. Alternatively, the application of the AD process as a post-treatment step results in a reduction in energy consumption by decreasing the removal requirements of the EC part of the integrated process and consequently reducing the voltage/current necessary to carry out the process. This combined process characteristic can be especially important when the effluent contains different pollutants. Moreover, removing the different pollutants can have different efficiency in each process. Therefore, combining both processes will result in a good overall removal performance.

Furthermore, the integration of both processes also presents advantages associated with process intensification principles; namely, using a compact unit reduces its space requirements and improves its mobility, increasing its versatility. The integration also results in the reduction of energy consumption and, consequently, operating costs. Additionally, the possibility of using low-cost materials in the combined process reduces the investment costs associated with its implementation. These advantages are crucial for implementing this process in small industries.

4.1. Applications of Combined Electrocoagulation and Adsorption Processes

Wastewater treatment processes combining EC with AD have been used to remove target pollutants. Table 5 summarizes processes combining EC and AD to treat different wastewaters.

Wastewater	Adsorbent	Electrodes	Removal Efficiency	Reference
Industrial wastewater	Ectodermis of Opuntia	Al	84% (COD) 78% (BOD) 97% (color) 98% (turbidity) 99% (fecal coliforms)	[228]
Aqueous solution	Granular activated carbon	Zn	99.88% (Pb(II))	[19]
Textile wastewater	Crude Tunisian clay	Fe	96.87% (color) 89.77% (COD) 84.46% (TSS)	[229]
Beverage industry wastewater	Activated carbon	Al	98.66% (COD) 92.15% (TSS) 90.12% (color)	[230]
Semiconductor wastewater	Activated carbon	Al	67.25% (fluoride)	[231]
Produced water	Coconut shell activated carbon	Al/Fe	98.39% (COD) 93.54% (TDS) 75.16% (ammonia) 97.56% (oil content) 92.5% (phenol)	[232]
Nitrate- contaminated ground water	Zeolite	Al	96% (nitrates)	[233]
Automobile wastewater	Activated carbon	Al	71.58% (COD) 77.91% (surfactant)	[234]
Tanning wastewater	Eggshell	Al	99% (Cr(VI))	[235]
Anaerobic wastewater	Granular activated carbon	Al	100% (COD) 100% (BOD) 96.5% (turbidity) 97.5%	[236]
Paper mill	Granular	Al / Fe	(prosprorus) 98.97% (COD)	[237]
effluent Model solution	activated carbon Red onion skin	Al	97% (Cr(VI))	[238]
Cellulose and paper industry wastewater	Granular activated carbon	Al	93% (humic acid)	[239]
Dye solution	Banana peel	Al	99% (methylene blue)	[240]
Mine waters	Rice straw activated carbon	Al	95.2% (sulphate)	[241]
Dairy wastewater	Granular activated carbon	Al	99.39% (turbidity) 87.12 (COD)	[242]

Table 5. Combined electrocoagulation and adsorption on the treatment of different wastewaters (COD—chemical oxygen demand; BOD—biochemical oxygen demand; TDS—total dissolved solids; TSS—total suspended solids).

Several combinations of electrodes and adsorbents have been used in the combined EC and AD processes to treat different wastewaters. This characteristic of the process increases its versatility in dealing with specific pollutant removal problems.

Wang et al. [243] applied EC combined with peanut shell adsorption to remove malachite green from an aqueous solution. They found that with an adsorbent dosage of 5 g/L, the removal efficiency increased significantly, requiring lower current density and shorter operating time than the EC process alone. At optimal conditions, the removal efficiency of 98% was obtained in 5 min, corresponding to an increase of 23% relative to the removal obtained by the EC process in 60 min. Moreover, it was concluded that the combined process reduces 94% of the unit energy and electrode material demand compared to the EC process alone.

Yang et al. [244] studied the removal of several micropollutants from real municipal wastewater using graphene adsorption and simultaneous electrocoagulation/electrofiltration. They concluded that the main mechanisms involved in the combined process were carbon adsorption, size exclusion, electrostatic repulsion, EC, and electrofiltration. The removal efficiencies obtained with the combined process were the following: di-n-butyl phthalate 89%, di-(2-ethylhexyl) phthalate 85%, acetaminophen 99%, caffeine 94%, cefalexin 100%, and sulfamethoxazole 98%.

Narayanan and Ganesan [245] used batch EC with an Al–Fe electrode pair combined with adsorption using granular activated carbon to remove Cr(VI) from synthetic effluents. They identified that the combined effect of chemical precipitation, coprecipitation, sweep coagulation, and adsorption are the main mechanisms involved in the Cr(VI) removal. The results showed that adding adsorbent to the process provides a higher Cr(VI) removal rate, requiring lower current intensities and operating time than the conventional EC process.

Castañeda-Díaz et al. [246] studied the removal of the cationic dye malachite green and the anionic dye remazol yellow from aqueous solutions using EC followed by an AD process. The AD was performed in a packed column with carbonaceous material from industrial sewage sludge and commercial activated carbons as adsorbents. Batch and continuous set-ups were tested for the EC part of the process. The results showed that the continuous EC–AD process was more efficient than the EC alone.

Rubí-Juárez et al. [247] performed a comparative study of the COD and turbidity removal from car wash wastewater using an EC process followed by AD and simultaneous EC–AD. Removal of 78% for COD and 92% for turbidity was obtained after 60 min using aluminum electrodes. After AD with commercial granular activated carbon (GAC) using a dose of 22.5 g/L, the final removals were 99.97% and 98% for COD and turbidity, respectively. The simultaneous EC–AD process using aluminum electrodes and a GAC dosage of 22.5 g/L provided a final removal of 94% for COD and 98% for turbidity.

Nizeyimana et al. [248] studied the removal of copper and nickel ions from synthetic wastewater through AD with low-cost and sustainable activated green tea residue combined with EC with iron electrodes. The adsorbent was prepared without applying any activating agents. The optimized combined process presented a removal efficiency of almost 100% for both copper and nickel ions. Moreover, they concluded that the combined process is the cheapest due to lower adsorbent dosage and energy consumption than the single AD and EC processes.

Bazrafshan et al. [249] proposed a sequential chemical coagulation process with poly aluminum chloride (PAC), EC with aluminum electrodes, and AD with pistachio nutshell ash. The process was applied to the treatment of actual textile wastewater. The chemical coagulation step with a PAC dosage of 30 mg/L presented removals of 40% for COD, 34% for BOD5, and 44.5% for dye. After the EC step with an applied voltage of 60 V, the removals obtained were 93.1, 88.8, and 98.6% for COD, BOD5, and dye, respectively. The combined process, including the AD step, provided 98, 94.2, and 99.9% removals for COD, BOD5, and dye, respectively. The authors concluded that the combined process presents a superior performance compared with processes alone in textile wastewater treatment.

4.2. The Combined Process from the Perspective of Circular Economy

The circular economy (CE) concept appears as an alternative to the traditional linear economy approach based on the "take-make-use-dispose" model, in which there is a

continuous resource throughput, and the products are usually disposed of as waste at the end of their life cycle. The CE model aims for more sustainable use of raw materials and energy while reducing the volume of waste. In a linear economy model, economic growth is coupled with the negative consequences of resource depletion and environmental degradation. However, in the CE approach, the raw materials and products are kept in the economy for as long as possible, and the wastes are regarded as secondary raw materials that can be recycled and reused [250]. The European Commission recognized the importance of this issue and proposed an action plan to promote the implementation of the CE [251].

Reusing treated wastewater in applications such as agriculture, industrial processes, toilet flushing, and irrigation of parks and recreation grounds can be an essential element of the CE model [250,252]. Moreover, sludges produced from wastewater treatment can be a valuable source of nutrients [253]. From this perspective, wastewater can be regarded as a resource instead of a waste. The water reuse strategy is becoming increasingly important in the present context of water scarcity worldwide. However, when using conventional centralized wastewater treatment plants, the economic aspect can be a significant obstacle to the widespread implementation of water reuse projects [254]. A solution to this limitation can be the development of decentralized wastewater units able to be used far from the centralized wastewater treatment plants usually located near urban centers. To facilitate their application, these treatment units should be efficient, compact, easy to operate, and have low investment and operating costs.

Using waste materials to produce added-value products is also a way to move several manufacturing processes toward a zero-waste circular economy [250]. In this context, the use of wastes as raw materials to produce low-cost adsorbents fits well in the CE model. From the perspective of wastewater treatment, using these kinds of adsorbent materials reduces the costs of the process, facilitating their implementation. This aspect is crucial in developing decentralized wastewater treatment systems outside urban centers.

Despite the potential of EC and AD processes in wastewater treatment, their wastes can represent a significant challenge. Therefore, implementing strategies for valorizing these wastes is fundamental for those processes' sustainability and economic viability. In recent years, there has been an increasing interest in strategies to valorize the EC process wastes [255]. The use of the sludge resulting from EC process operation to produce fertilizers [256], pigments [257], construction materials [258], adsorbents [259], and catalysts [260] are possible ways to valorize this by-product. In addition to these applications, EC sludge has also been considered an alternative energy source. The energy can be obtained from the sludge by combustion, anaerobic digestion, pyrolysis, and gasification [261]. Hydrogen generated at the cathodes by water electrolysis is another potentially valuable by-product of the EC process. The hydrogen recovered during the EC process can be used as an alternative energy source or a reactant for industrial processes [262].

After an adsorption-based wastewater treatment, the saturated adsorbents are traditionally disposed to landfill or regenerated and reused. Hazardous compounds in the adsorbents make their disposal in landfills potentially detrimental to the environment. However, the regeneration of the saturated adsorbents may represent a large part of the treatment process costs. Moreover, the regeneration process can cause secondary pollution due to the addition of regeneration agents and the concentration of contaminants [263]. Alternative strategies for the valorization of spent adsorbents have been proposed, including their application as fertilizers [264] and catalysts [265], and in the production of cementitious materials [266] and energy production [267].

The combination of EC and AD for the treatment of wastewaters has the characteristics to be part of a CE model. First, this combined process has the potential to be used for decentralized wastewater treatment facilitating the implementation of water reuse projects and, consequently, more sustainable use of water resources. Another characteristic of the process is the possibility of using low-cost adsorbents produced from waste. Finally, the wastes produced during the wastewater treatment with the combined process can be valorized into useful materials. In addition to the obvious economic advantage, using this kind of materials also reduces waste from several manufacturing activities. Figure 7 shows a schematic representation of the combined process application with low-cost materials for wastewater treatment, the different routes for valorizing its wastes, and the possible applications of the treated water.



Figure 7. The combined process from the perspective of a circular economy.

5. Conclusions

AD and EC processes were discussed based on the available literature. Several aspects of the processes were addressed, including their theoretical principles, the effect of operating conditions, and practical applications.

Published research has demonstrated the efficiency of the EC process for removing different contaminants from water in a range of concentrations. Additionally, EC is regarded as a cost-effective process that offers a variety of advantages, including portability and simplicity of use, and permits automation and combination with other techniques. Additionally, the EC process's suitability for use as a sustainable water treatment method is increased by the possibility of running it using renewable energy sources, such as solar cells, wind turbines, and fuel cells.

The available research on AD demonstrates its potential for use as a method to extract pollutants and analytes from aqueous solutions. In addition, the accessibility, affordability, and technical viability of low-cost adsorbents for wastewater treatment applications make them very appealing. The ability to use AD as a continuous or semi-continuous process also makes it attractive for industrial applications.

Despite both processes' great potential for treating a variety of wastewaters, using each method separately has some drawbacks. Combining the strengths of both processes to create a hybrid process is one way to get around these constraints while still maximizing their potential. The available literature showed different applications of the combined process in treating various kinds of wastewater. Furthermore, the combined process has several qualities that make it appropriate for use as a decentralized wastewater treatment method and in a zero-waste CE model. Finding a good balance between the effectiveness of the treatment and its operating costs is one of the main challenges when developing this kind of treatment. Therefore, more study should be conducted on this subject to broaden the applicability of those processes.

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