energies

Review

Recent Advances in Wastewater Electrocoagulation Technologies: Beyond Chemical Coagulation

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Abstract: This review provides a comprehensive analysis of the recent research trends and application cases of chemical coagulation (CC) and electrocoagulation (EC), which play a crucial role in wastewater treatment. In particular, the principles and process performances of the EC technologies are comparably reviewed with traditional CC technologies. EC offers the advantage of reducing the use of chemical agents and minimizing sludge generation compared to CC. Moreover, recent research cases have demonstrated its effectiveness in removing pollutants from wastewater. With increasing water consumption due to industrial development, the application of coagulation processes in wastewater and sludge treatment is expected to expand to minimize environmental impact. This review provides insights into the current status and future development direction of CC and EC technologies and can serve as foundational information for more efficient and environmentally friendly coagulation systems.

Keywords: wastewater treatment; electrocoagulation; chemical coagulation; sustainability

Citation: Jo, S.; Kadam, R.; Jang, H.; Seo, D.; Park, J. Recent Advances in Wastewater Electrocoagulation Technologies: Beyond Chemical Coagulation. *Energies* **2024**, *17*, 5863. https://doi.org/10.3390/en17235863

Academic Editors: Marin Ugrina and Jelena Milojković

Received: 8 October 2024
Revised: 16 November 2024
Accepted: 20 November 2024
Published: 22 November 2024

1. Introduction

In the 21st century, water and energy have emerged as two of the most pressing challenges in the world. The rapid growth of the global population, coupled with industrialization aimed at meeting these demands, has significantly compromised both the quality and availability of water resources. Around 40% of the population is affected by water contamination, and over 20% faces a shortage of freshwater [1]. Additionally, industries, particularly those known for high water consumption such as textiles, consume around 300 L of freshwater for each kilogram of product. This results in the discharge of substantial quantities of heavily pigmented wastewater into the environment [2]. This leads to pollution of both surface- and groundwater due to contaminants and other harmful organic compounds. Many of these compounds can be carcinogenic, mutagenic, and sometimes teratogenic, posing a risk to living organisms [3]. Moreover, industrial wastewater typically contains very fine suspended solids (SS), dissolved solids, and inorganic/organic particles. Due to their small size and surface charge, aggregating these particles into a heavier mass for effective removal becomes a considerable challenge. A range of both traditional and advanced technologies has been employed to eliminate colloidal particles from wastewater. These methods include ion exchange, membrane filtration, precipitation, flotation, solvent extraction, adsorption, and coagulation, as well as biological and electrolytic approaches [4,5].

Coagulation is one of the most widely used methods in water and wastewater treatment processes, involving various chemicals [6,7]. This approach aligns with the growing trend toward wastewater-to-energy technology, which emphasizes the direct recovery of organic matter from wastewater. To minimize energy input and maximize energy production, these technologies aim to transform waste into resources, such as treated water for reuse and recoverable materials from residuals. This technique comprises three distinct stages: (1) the rapid mixing of the dispersed coagulant into water or wastewater through vigorous agitation, (2) the gentle stirring of the mixtures to encourage the formation of larger flocs by aggregating tiny particles, and (3) subsequent settling of these flocs to the bottom [8]. Coagulation is primarily induced by inorganic metal salts, including aluminum (Al) and iron (Fe). The most frequently used Al-based coagulants are aluminum sulfate, aluminum chloride, and sodium aluminate. For Fe-based coagulants, the common types include ferric sulfate, ferrous sulfate, ferric chloride, and ferric chloride sulfate [9]. However, the use of inorganic coagulants has decreased due to environmental concerns. The presence of chemical compounds can result in toxic residues in sludge, which may pose health risks after extended exposure. Additionally, chemical processes often require significant chemical inputs, which not only elevate the overall cost but also complicate downstream operations. As a result, both synthetic polymeric and natural flocculants have gained high attention in water and wastewater treatment processes. This is attributed to their inherent stability against pH fluctuations, high effectiveness at low dosages, and ease of use [10]. Recently, synthetic polymers like polyaluminum chloride (PAC), polyferric sulfate (PFS), and polyacrylamide (PAM) have become the most commonly utilized coagulants in wastewater treatment because they can produce large shear-stable flocs [11]. Similarly, natural coagulants present a viable alternative to reduce environmental pollution and health risks linked to chemical coagulants. Numerous studies have highlighted the use of natural coagulants derived from various plant species, including Moringa oleifera, Jatropha curcas, banana peels, and bagasse [12]. Both polymeric and natural coagulants demonstrate effective treatment capabilities, positioning them as promising replacements for traditional chemical coagulants. Despite these benefits, the acceptance of synthetic and natural coagulants in water and wastewater treatment facilities has been limited. This is largely due to a lack of industrial confidence in their use, driven by concerns regarding their effectiveness and consistency when utilized on a large scale [13].

In recent years, electrochemical technologies have gained considerable interest for their capacity to utilize various parameters to enhance performance efficiency. One notable method, electrocoagulation (EC) has become increasingly popular as an effective and economical solution for treating wastewater, all while reducing sludge generation. It provides versatility, user-friendliness, and the capacity to manage a range of contaminants [14]. One of the key advantages of EC is its ease of control over the dosing of necessary chemicals. Unlike traditional methods that require the addition of stabilizing agents like chlorides and sulfates, EC utilizes fixed chemical electrodes such as Al and Fe, which simplifies the process and minimizes the need for additional chemical inputs. This reduction in chemical concentration not only lowers the generation of inorganic sludge but also mitigates the risk of producing potentially toxic byproducts. Furthermore, the electrochemical reactions involved in EC allow for the use of various materials, including waste. This approach enhances the stability of coagulants and counteracts the slow corrosion often seen with synthesized coagulants [15]. The application of voltage during the EC process can effectively oxidize soluble organic matter, reducing the energy requirements for subsequent biological treatments. Additionally, the inevitable byproduct, hydrogen ions can be converted to hydrogen gas, which aids in maintaining pH levels and contributes to energy production [16]. Due to these advantages, EC has been extensively used in the treatment of various industrial wastewater, including those from the textile, pharmaceutical, municipal, dairy, petroleum, and paper industries as well as in drinking water treatment [17]. Ongoing advancements in EC research have consistently highlighted the importance of EC and its potential benefits in wastewater treatment.

Therefore, this review paper seeks to engage in a critical analysis of the coagulation processes involved in water and wastewater treatment, with a particular emphasis on chemical coagulation (CC) and EC. Notably, there is a lack of published literature that specifically addresses these two methods in tandem. CC has been a cornerstone of wastewater treatment for a while, evolving through various process modifications and the introduction of innovative natural coagulants. Meanwhile, EC has emerged as a noteworthy alternative to conventional CC techniques. This review aims to deliver a thorough overview of the EC process, including its reaction mechanisms, challenges, and potential avenues for future research. This review will provide a deeper understanding of both CC and EC processes, highlighting their limitations and suggesting possible solutions.

2. Chemical Coagulation

2.1. Fundamentals of Chemical Coagulation Process

Coagulation is a three-phase process designed to eliminate stable particles by creating larger aggregates. As illustrated in Figure 1, the key stages of coagulation involve destabilizing colloidal particles through the addition of coagulants, facilitating the aggregation of these particles into larger flocs, and, finally, allowing these flocs to settle at the bottom. In aqueous environments, the majority of solids or suspended particles are usually relatively small and often have a negative charge. To enhance the sedimentation process, particles need to aggregate into larger flocs. However, this aggregation is hindered by electrostatic repulsive forces that keep negatively charged particles from coming together. As a result, settling takes longer. This issue can be addressed by using a coagulant to destabilize the particles [18]. Destabilization can occur through one or more of the following mechanisms following the addition of a coagulant:

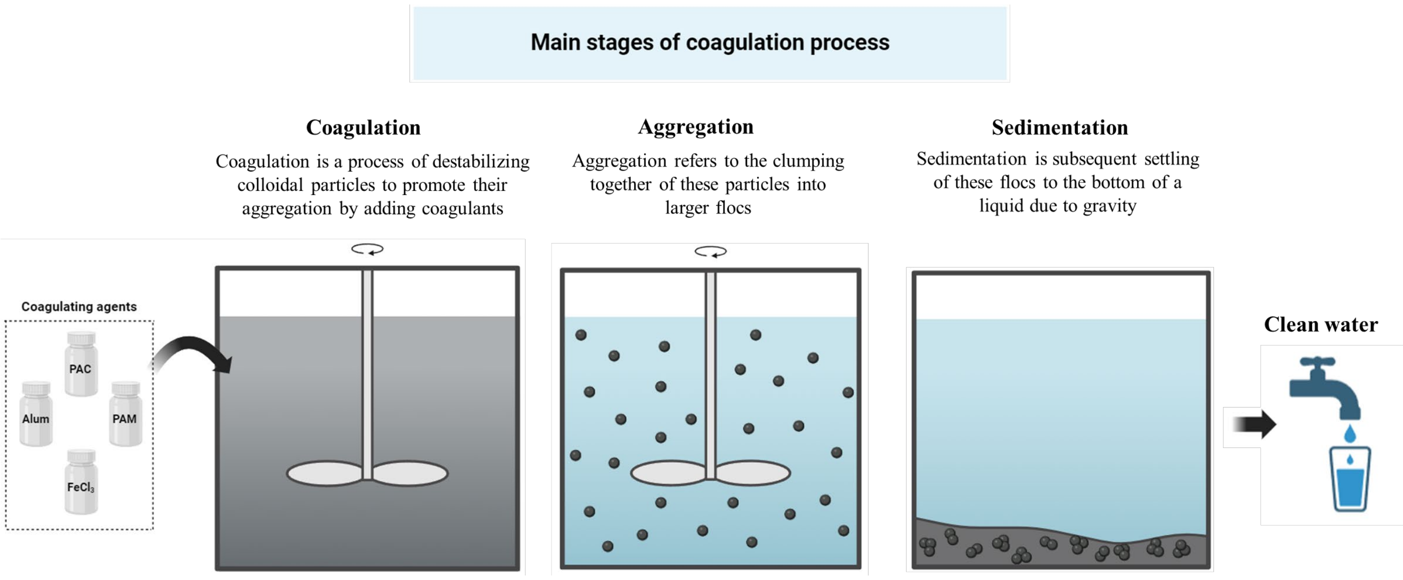

Figure 1. Graphical illustration depicting the main stages of chemical coagulation process.

(a) Double-layer compression: It is a mechanism that involves countercharged ions penetrating the double layer around colloids. These counter ions modify the double layer, making it thinner and less voluminous. Continuous double-layer compression by electrolytes diminishes electrostatic repulsion and enhances the van der Waals force, promoting the aggregation of destabilized colloids. The continuously increased aggregation rate makes the tiny flocs formed at the double-layer compression step larger and denser [12,19]. However, the stability of the flocs is influenced by the ionic charge of the coagulant used. Monovalent ions, which carry a weak charge, tend to create large but loosely bound flocs that take longer to settle. In the presence of weakly charged ions, the double layer remains significantly charged, resulting in a strong repulsive force that hinders the likelihood of agglomeration [20].

(b) Sweep flocculation: It is a process that eliminates colloids by trapping them within a net-like framework. This framework is formed by the precipitation of amorphous metal hydroxides during hydrolysis. Theoretically, a higher fractal dimension leads to stronger flocs that are more resistant to breakage. However, flocs formed through sweep flocculation tend to be larger and have a faster formation rate, making them more susceptible to breakage [12,19,21]. The presence of repulsive forces between flocs contributes to this phenomenon. Sweep flocculation primarily entraps colloids within a net-like structure but does not neutralize the repulsive forces among them, leading to the formation of weak flocs [22].

(c) Charge neutralization: It takes place when oppositely charged coagulants adhere to the surfaces of colloids through adsorption. Charge neutralization happens on the colloid surfaces in a patch-wise fashion, referred to as the electrostatic patch mechanism. Different cations attached to the colloid surface create regions with both positive and negative charges. The mixed charge distribution diminishes repulsive forces and enhances the van der Waals interaction between particles. Flocs generated through the charge neutralization mechanism are stronger than those formed by sweep flocculation, yet weaker than those created by interparticle bridging [12,23,24]. Flocs formed through charge neutralization are indeed strong, but their strength is limited because they depend on physical bonds, which are weaker than chemical bonds [22].

(d) Interparticle bridging: It involves polymer chains that are long and highly reactive, extending into wastewater. One end of the polymer chain binds to colloids, while the free ends connect to other colloidal particles. The resultant structure is known as colloid–polymer–colloid, where polymer acts as a bridge. Multiple colloid–polymer–colloids can intertwine, resulting in easily settleable flocs. Theoretically, a low fractal dimension typically leads to weak flocs that are susceptible to breakage. However, these flocs can be quite robust and resistant to fragmentation into smaller clusters. This is due to the presence of various polymers that act as strong bridges formed by numerous chemical bonds among flocs [12,22,25]. A recent study indicated that employing a natural coagulant with an interparticle bridging mechanism can increase floc growth by at least three times compared to using a chemical coagulant. This enhancement is attributed to the capacity of polymeric chains to extend and bind to multiple colloids effectively [26]. Overall, coagulation relies on these mechanisms to destabilize particles and facilitate aggregation, leading to larger flocs that settle more easily. Each mechanism contributes uniquely to the formation of flocs with varying strengths and resistance to breakage.

2.2. Importance in Wastewater Treatment Plants

Wastewater treatment (WWTP) is a critical element of modern urban infrastructure, playing an important role in public health and environmental protection. The most widely used sewage treatment process is the activated sludge, accounting for over 90% of all sewage treatment processes worldwide [27]. This method is based on primary treatment through gravity sedimentation of raw sewage and secondary treatment through the microorganism's metabolism with primarily treated sewage. The widespread use of the activated sludge process is due to its process stability, ease of maintenance, and effective performance in removing various pollutants [28].

However, the activated sludge has several major drawbacks. First, a significant amount of energy is consumed in the aeration process for aerobic microorganism activity during biological treatment. It has been shown that approximately 50–75% of the total energy consumption in WWTP is used in the aeration process [29]. Second, large amounts of activated sludge are generated during the organic matter treatment process, which incurs additional costs and environmental burdens for treatment and disposal [30].

Recently, the field of wastewater treatment has been facing new challenges. Effluent regulation standards are becoming more stringent, and there is an increasing demand for carbon neutrality in wastewater treatment facilities. In these changing environmental conditions, it has become necessary to explore new wastewater treatment methods that can complement or replace the existing activated sludge method [31,32].

In this context, the application of the Chemical Enhanced Primary Treatment (CEPT) process is gaining attention. CEPT recognizes wastewater not as mere waste but as an energy source, aiming to recover it effectively and reduce the load on biological treatment processes. The CEPT process significantly improves the removal efficiency of organic matter and SS in the primary sedimentation stage by using chemical coagulants. The application of CEPT to existing activated sludge processes can be implemented without separate civil engineering work, and its main advantages are as follows [33,34]:

1. Improved Energy Efficiency: By removing more organic matter in the primary treatment stage through CEPT, the load on subsequent biological treatment stages is reduced. This has the positive effect of reducing the energy consumption required for aeration in the bio-processes linked with the CEPT. Compared to the conventional activated sludge process, previous studies reported that the application of CEPT could reduce energy consumption for aeration by up to 50% [35,36]. Moreover, when comparing the entire treatment process, it has been reported that energy savings of up to 71% can be achieved [37].
2. Energy Source Recovery: The primary sludge generated through CEPT has a higher organic content than the primary sludge formed by conventional gravity sedimentation. As a result, CEPT sludge can be used as a more effective raw material for energy recovery processes, such as anaerobic digestion, and it has been reported that methane yield can be increased by 30–40% [38]. Additionally, when CEPT is applied, the amount of low-biodegradability-activated sludge formed in the subsequent biological treatment process decreases, which can reduce sludge treatment costs. This ultimately has the advantage of increasing the value of sewage sludge as an energy source.
3. Greenhouse Gas Reduction: The application of the CEPT process significantly reduces greenhouse gas emissions from wastewater treatment plants. According to recent studies, when CEPT is applied, greenhouse gas emissions from wastewater treatment plants can be reduced by up to 70% compared to the conventional activated sludge method [37]. This is attributed to two factors: reduced aeration due to efficient organic matter removal from the influent, and increased biogas production through anaerobic digestion of recovered sludge.

However, there are still several challenges remaining for the widespread application of the CEPT process. Due to the continuous increase in wastewater generation caused by population growth and industrial development, large quantities of chemicals are required, which can lead to increased operational costs and environmental impacts. Excessive use of chemicals can adversely affect subsequent biological treatment processes, requiring a cautious approach. Additionally, further research is needed on the impact of changes in the physicochemical characteristics of recovered sludge on subsequent treatment processes.

Therefore, it is essential to optimize factors such as the type and amount of coagulant, and operating conditions for the successful application of CEPT (pH, mixing intensity, retention time, etc.). Furthermore, along with optimal conditions, it is necessary to quantitatively verify the impact on subsequent processes.

In summary, while CEPT offers promising advantages in terms of energy efficiency, resource recovery, and greenhouse gas reduction, its effective application requires careful optimization of coagulant type, dosage, and operating conditions. A quantitative assessment of CEPT's impact on subsequent treatment stages is essential to maximize its benefits and minimize potential drawbacks. The following section will explore these aspects in greater detail.

2.3. Types of Chemical Coagulants

WWTPs primarily utilize inorganic coagulants, which can be broadly classified into Al-based and Fe-based coagulants. When these inorganic coagulants are introduced into water or wastewater, they undergo three main reaction stages: dissociation, hydrolysis, and polymerization [39].

1. Dissociation: This initial stage involves the breakdown of the metal salts into their constituent ions. For example, when Al or Fe salts are added to the water, they dissociate into ions such as Al^{3+}, SO_4^{2-}, Fe^{3+}, and Cl^-.
2. Hydrolysis: In this stage, the dissociated ions react with water, leading to the formation of hydroxyl complexes like $Al(OH)_3$ and $Fe(OH)_3$. These hydroxides play a crucial role in the coagulation process by helping to aggregate suspended particles.
3. Polymerization: The final stage involves the reaction of hydrolyzed Al and Fe ions to form larger, more complex structures known as polymeric aluminum and polymeric ferric species. These polymers possess a higher charge density, which effectively bridges and agglomerates suspended particles, thereby enhancing the coagulation process.

Inorganic coagulants offer several advantages over other types of coagulants. They demonstrate high efficiency in removing various pollutants, including heavy metals, turbidity, Chemical Oxygen Demand (COD), and Biological Oxygen Demand (BOD). Indeed, these metal-based coagulants can achieve impressive removal efficiencies of up to 99.3% for phosphate, 99.5% for SS, and 95.6% for COD [40]. Moreover, these coagulants are commercially available and possess the ability to effectively inactivate bacteria.

Al-based coagulants include $Al_2(SO_4)_3$, PAC, and composite PAC. $Al_2(SO_4)_3$ is the most widely used coagulant, preferred for its cost-effectiveness and efficiency. While it is readily available and inexpensive, it is only effective within a limited pH range (5.5–7.0). PAC is effective over a broader pH range (4.0–8.0) than alum and performs well at low temperatures. It also offers advantages such as rapid reaction and large floc formation but may be insufficient for removing high molecular weight particles and hydrophobic particles [9,41,42].

Fe-based coagulants include $Fe_2(SO_4)_3$, $FeCl_3$, and $FeSO_4$. These are effective over an even wider pH range (4–11) compared to Al-based coagulants and exhibit excellent performance in phosphorus removal. However, they may cause color issues in treated water due to residual iron. $Fe_2(SO_4)_3$ and $FeCl_3$ show high coagulation efficiency but can be corrosive. $FeSO_4$ is relatively inexpensive and effective in phosphorus removal but may require an additional oxidation step [40,42].

As outlined above, each coagulant has unique characteristics along with advantages/disadvantages depending on its type, necessitating appropriate selection based on the application scenario. The main advantages and disadvantages of each coagulant type are summarized in Table 1.

Table 1. Overview of common metal coagulants: merits and demerits as reported in previous studies.

Coagulant	Merits	Demerits	Reference
Aluminum sulfate	Easily accessible, low cost, and low sludge volume index.	Effective in limited pH range, and residual Al ions in the sludge.	[43]
PAC	Fast reaction and bigger flocs.	Insufficient in removing higher molar mass particles and hydrophobic particles.	[44]
Sodium aluminate	Small dosage and efficient in highly contaminated wastewater.	Costly and limited application due to inefficiency in treating low-polluted wastewater.	[45]
Ferrous sulfate	Easily available and less costly.	Alkalinity addition is needed and corrosive.	[46]
Ferric sulfate	Less sensitivity to overdosage.	Alkalinity addition is needed and leaves visible rust-colored strains.	[47]
Ferric chloride	Effective in a broad pH range, easily available, and less costly.	Corrosive and hazardous.	[48]

While these inorganic coagulants with diverse characteristics demonstrate high efficiency, their performance is significantly influenced by various factors. Since optimal operation conditions depend on the coagulant type and dose, coagulation efficiency can be greatly reduced if these conditions are not accurately controlled. Therefore, it is crucial to understand the characteristics of each coagulant and the interactions of various variables that need to be considered in the optimization process to derive optimal operating conditions. This approach can maximize the effectiveness of inorganic coagulants in the wastewater treatment process and enhance treatment efficiency.

2.4. Key Factors Influencing Chemical Coagulation

The efficiency and effectiveness of CC processes in wastewater treatment are significantly influenced by various factors. Understanding and appropriately controlling these factors are essential for achieving optimal wastewater treatment results. The main influencing factors include pH, coagulant dosage, mixing intensity and time, temperature, and wastewater characteristics.

pH is one of the most critical factors in the coagulation process, directly affecting coagulant hydrolysis, charge characteristics, and the surface charge of pollutants. Each coagulant has the recommended optimal pH range, outside of which coagulation efficiency can significantly decrease. For instance, Al-based coagulants are generally most effective in the pH range of 6.5–8.0, while Fe-based coagulants perform optimally in the pH range of 4.5–6.0, where charge neutralization and adsorption bridging mechanisms operate simultaneously [6]. Recent research by Zhou et al. (2023) used molecular dynamics simulations to analyze the impact of pH on coagulation mechanisms, revealing how pH changes alter the structure and charge distribution of coagulant molecules, directly influencing their interaction with pollutants [49].

Coagulant dosage directly impacts both treatment efficiency and economic viability. Li et al. (2022) elucidated the non-linear relationship between coagulant dosage and removal efficiency, demonstrating that increasing dosage beyond a certain threshold does not significantly improve removal efficiency and may lead to problems associated with overdosing [50]. Kurniawan et al. (2020) found that underdosing results in the formation of unstable small flocs, leading to poor sedimentation efficiency and reduced treatment effectiveness [51]. Conversely, recent studies have detailed the problems arising from coagulant overdosing, including increased sludge production, elevated residual metal concentrations, pH changes, and increased electrical conductivity of treated water [52].

Mixing intensity and duration also significantly influences coagulation efficiency. The process typically involves two stages: rapid mixing and slow mixing. Suzuki et al. (2023) reported that the optimal rapid mixing intensity and duration could be varied by the type of coagulant and pollutant characteristics. For instance, polymer coagulants require longer rapid mixing times (60–90 s) compared to metal salt coagulants (30–60 s) [53]. Liu et al. (2024) emphasized the importance of the slow mixing stage, showing that appropriate slow mixing conditions (30 rpm, 20 min) optimize floc growth and structure, enhancing final sedimentation efficiency [54]. Sun et al. (2019) analyzed the impact of mixing intensity on floc morphology and strength, reporting that excessive mixing intensity can lead to floc breakage and reduced treatment efficiency, while insufficient mixing results in inadequate coagulation [55]. However, contrasting these findings, Abbas et al. (2021) used design expert software to analyze optimal conditions for $FeCl_3$ coagulant and found that while pH and dosage significantly affected COD, turbidity, and total suspended solids (TSS) removal, mixing time had no significant impact, and mixing speed only slightly influenced COD removal [56].

Temperature is another crucial factor affecting the coagulation process. Generally, increased temperature enhances molecular motion and chemical reaction rates, potentially improving coagulation efficiency [39]. However, Zhang et al. (2023) observed that coagulation efficiency decreased when temperatures exceeded 30 °C. This phenomenon is attributed to accelerated hydrolysis reactions at high temperatures, resulting in looser floc formation and consequently reduced pollutant removal rates. Conversely, at low temperatures, hydrolysis of coagulant and aggregation of destabilized colloid particles could be inefficient due to weakened Brownian motion. Therefore, maintaining an appropriate temperature range is crucial for achieving optimal coagulation efficiency [57].

Wastewater characteristics, including SS concentration, particle size distribution, and organic matter content, significantly influence the coagulation process. The alkalinity of wastewater affects pH buffering capacity, playing a crucial role in coagulation efficiency. Various ions in wastewater (e.g., Ca^{2+}, Mg^{2+}, SO_4^{2-}) can affect the coagulation efficiency by directly reacting with coagulants or indirectly interfering with floc formation [58]. Previous studies have investigated the effect of molecular weight distribution of organic matter in wastewater on coagulation efficiency. Results showed that higher molecular weight organic matter tends to improve coagulation efficiency, as it more readily combines with coagulants to form larger flocs [59,60].

Recent research has employed various statistical techniques and artificial intelligence-based methodologies to optimize the coagulation process. In particular, response surface methodology (RSM), artificial neural network (ANN), and genetic algorithm (GA) are widely used.

RSM remains an important optimization tool. Abbas et al. (2021) used design expert software to analyze optimal conditions for $FeCl_3$ coagulant. They employed Central Composite Design to design experiments and developed a second-order polynomial model to determine the effects and optimal conditions of independent variables such as pH, dosage, mixing time, and mixing speed [56].

Furthermore, hybrid models combining ANN and GA are being increasingly used for coagulation process optimization. Ejimofor et al. (2021) used an ANN-GA model to optimize the removal of colloidal particles from paint wastewater using clay [61]. Kusuma et al. (2021) employed ANN-GA to optimize turbid water treatment using Ipomoea batatas leaf extract as a green coagulant. These studies demonstrate that ANN-GA hybrid models can provide more accurate predictions and optimal solutions for various coagulants and wastewater types compared to RSM or other optimization techniques [62]. These models can predict optimal operating conditions by considering various process parameters such as pH, coagulant dosage, mixing time, and temperature. They have high potential for application in real-time control systems as they can predict optimal coagulant dosage and operating conditions based on various water quality parameters [39].

While these optimization techniques can significantly enhance the efficiency of the coagulation process, they still have some limitations. Firstly, these models have primarily been validated at laboratory or pilot scales, and further research is needed regarding their applicability in large-scale wastewater treatment plants. Secondly, these optimization techniques mainly focus on pollutant removal efficiency, potentially overlooking other important factors in terms of overall water treatment system efficiency and sustainability.

Therefore, future research should focus on overcoming these limitations and developing more comprehensive and sustainable coagulation process optimization methods. Additionally, the development of adaptive coagulation systems that can rapidly respond to changing wastewater characteristics by combining real-time monitoring and control technologies is necessary. Alongside this, continuous research into new technologies and methods that can reduce or replace the use of CC should be pursued.

2.5. Limitation of Chemical Coagulant

Chemical coagulants, particularly inorganic metal salts, are widely used in wastewater treatment. However, their use presents several significant limitations that manifest in environmental, operational, and health aspects. The use of chemical coagulants significantly affects the pH and alkalinity of water. Al- and Fe-based coagulants, in particular, release hydrogen ions, lowering pH and reducing alkalinity. This can impact other stages of the treatment process and may necessitate additional chemical use for pH adjustment.

Since the CC process generates substantial amounts of sludge containing hazardous and toxic substances, process costs would be raised for efficient treatment and disposal. The use of inorganic salt coagulants can increase sludge volume by 37–97%, negatively affecting subsequent processes such as anaerobic sludge digestion [40,63]. For instance, Al can reduce the specific methanogenic activity of methanogenic and acetogenic bacteria by 50–72% [64].

Excessive use of coagulants can leave residual metals in treated water, potentially harming aquatic life. These metals can disrupt physiological processes, leading to impaired growth, reproduction, and survival rates in fish and other aquatic animals. They may also bioaccumulate in the tissues of organisms, affecting the entire food chain [42]. Al-based coagulants, in particular, may leave Al salts in residuals, and long-term exposure to water containing these residuals has been associated with an increased risk of Alzheimer's disease [41], but whether the link is causal is still open to debate. However, previously published epidemiological studies of Al and Alzheimer's disease have shown statistically significant positive relations [65]. In response to these concerns, the US Environmental Protection Agency (EPA) has established a secondary standard of 0.05 to 0.2 mg/L for Al in drinking water [66]. Fe-based coagulants, while effective over a wider pH range and excellent for phosphorus removal, can leave residual Fe causing color issues in treated water, necessitating additional treatment [67]. This residual Fe can impart a yellowish or reddish tint to the water, which may affect consumer perception and acceptance. Although it does not pose health risks, the EPA has set a threshold of 0.3 mg/L for Fe in domestic water use, including drinking water, due to concerns about aesthetic quality [68].

Coagulated sludge can cause problems in both subsequent aerobic biological treatment and sludge treatment. The aggregated and dense structure of coagulated sludge can limit the access of bacteria and enzymes to organic matter within flocs, while residual coagulant concentrations can alter microbial activity in activated sludge processes, acting as inhibitors and affecting the settleability of activated sludge [34,69].

Al-based coagulants, in particular, can have severe impacts on aquatic environments depending on pH levels. Al has the lowest solubility between pH 5.7 and 6.2 but tends to exist in solution outside this range. Studies have shown that the combination of pH below 5.5 and dissolved Al concentrations above 0.5 mg/L can pose a serious threat to aquatic ecosystems [69].

In the case of Fe-based coagulants, while they primarily precipitate as $Fe(OH)_3$, resulting in relatively low concentrations of dissolved Fe^{3+}, the residual Fe^{3+} can damage important biomolecules such as DNA, proteins, and lipids through the following reactions:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH\bullet + OH^- \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO\bullet + H^+ \quad (2)$$

Fe^{3+} ions do not directly form oxygen-free radicals but play a crucial role in promoting and amplifying their formation. This underscores the importance of managing Fe^{3+} concentrations in water treatment systems, as excessive Fe^{3+} can negatively impact microbial activity and overall treatment efficiency [70].

Chemical coagulants are highly corrosive and can shorten the lifespan of treatment facilities, leading to increased long-term maintenance costs. Additionally, the effectiveness of chemical coagulants is sensitive to changes in water quality, requiring continuous adjustment of dosage in response to changing wastewater characteristics, which increases operational complexity [71].

Lastly, the environmental impacts of producing and transporting chemical coagulants should also be considered. This can increase the overall environmental footprint of the wastewater treatment process [26].

In conclusion, while chemical coagulants are effective in wastewater treatment, their use presents several significant limitations. Considering the environmental impacts, operational issues, and potential risks to health and ecosystems. The use of these coagulants should be approached with caution, and where possible, more sustainable alternatives should be explored.

3. Electrocoagulation

EC is a method for treating wastewater that utilizes electrical currents to eliminate contaminants. This process neutralizes negatively charged particles by forming hydroxide complexes in the water. These complexes aid in aggregating SS, which strengthens the floc that eventually settles under the force of gravity. Additionally, it generates coagulants on-site through the electrical dissolution of specific metal electrodes such as Al, Fe, copper (Cu), or stainless steel (STS). At the anode, metal ions are released, while hydrogen gas is generated at the cathode [72]. The core principle of EC is based on "electrolysis," which involves using electricity to decompose compounds. This concept was introduced by Michael Faraday in 1820. The process occurs in an electrolyte solution, facilitating the transfer of ions between the electrodes. In the EC cell, positive ions move toward the cathode, where they undergo reduction, while negative ions migrate toward the anode and experience oxidation [73,74]. EC has a rich history as a water treatment technology. It was first proposed in London in 1889 and implemented in sewage treatment facilities for a decade [75]. In 1909, J.T. Harries received a patent in the United States for electrolysis technology that employed Al and Fe electrodes for wastewater treatment [76]. At that time, EC was not commonly used for water treatment, primarily due to the high costs associated with power and investment. However, it began to gain recognition for its effectiveness in removing both organic and inorganic pollutants from groundwater and surface water, especially when compared to traditional CC methods. It was not until 1984 that EC was implemented to treat significant volumes of drinking water in the United States [77]. Following extensive research in the late 20th century, the adoption of EC has grown due to advancements in technology that reduce electrical power consumption while enhancing effluent throughput rates. Today, the EC is recognized as a cost-effective solution for treating surface and wastewater. It boasts numerous benefits, such as environmental stability and versatility. EC is also energy-efficient and safe, offering selectivity and ease of automation, all of which enhance its overall cost-effectiveness.

3.1. Fundamentals of Electrocoagulation

The EC unit comprises an electrolytic cell containing a cathode and an anode, which are connected to an external power source and submerged in an electrolytic solution. In this setup, the anode acts as the coagulant, releasing metal cations when DC is applied to the cell. When the cell is connected to an external power supply, the anode material undergoes electrochemical corrosion due to oxidation. Consumable metal plates are commonly utilized as sacrificial electrodes to continuously generate ions in the water. These ions neutralize the charges of various particles, triggering the coagulation process. The released ions eliminate unwanted contaminants through either chemical reactions and precipitation or by facilitating the aggregation of colloidal particles, which can then be removed by flotation. As water containing colloidal particles, oils, or other impurities passes through the applied electric field, processes such as ionization, electrolysis, hydrolysis, and free-radical generation may occur. The occurrence and efficiency of these processes depend on specific factors, including the type of electrode material, current density, pH levels, and the presence of contaminants. These reactions can modify the physical and chemical characteristics of both water and contaminants. Consequently, this reactive and energized state allows for the release and destruction or reduction in solubility of contaminants in the water [73,78]. The mechanism of EC is quite intricate, involving multiple processes that work together to eliminate pollutants from water. The literature presents a diverse range of perspectives regarding the primary mechanism and reactor configurations involved. However, as per the literature, the EC process typically includes the following mechanisms. Figure 2 represents the EC process, illustrating the key reactions, including the generation of metallic cations, formation of metal hydroxides, oxidation of pollutants, and aggregation and removal of contaminants through sweep flotation.

(1) Sacrification of anode material: When the anode material is exposed to electrical current, it undergoes sacrification, leading to the generation of metallic cations.
(2) Hydrolysis at the cathode: Hydrolysis occurs at the cathode, generating hydroxyl ions (OH^-).
(3) Formation of metal hydroxides: The metallic cations interact with hydroxyl ions to form metal hydroxides, which have strong adsorption capabilities to bind pollutants.
(4) Oxidation of pollutants: Pollutants are oxidized to form fewer toxic species.
(5) Reaction with metal oxides: Metal oxides react with pollutants, facilitating the formation of neutralized matter.
(6) Aggregation and coagulation: The neutralized matter aggregates and adsorbs onto the metal hydroxides, followed by sweep coagulation and removal from the water.
(7) Sweep flotation: Some of the neutralized matter interacts with gasses generated in the system, leading to the entrapment of gas within the flocculated structures, which follows the process of sweep flotation [79]. Overall, the EC process generally includes chemical reactions that take place when an electric current flows through electrodes. The primary electrode reactions are as follows [14].

Anode:

$$M_{(s)} \rightarrow M^{n+}_{(aq)} + ne^- \quad (3)$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad (4)$$

Cathode:

$$2H_2O + 2e^- \rightarrow 2OH^-_{(aq)} + H_2\,(g) \quad (5)$$

$$M^{n+} + nOH^- \leftrightarrow M\,(OH)_n \quad (6)$$

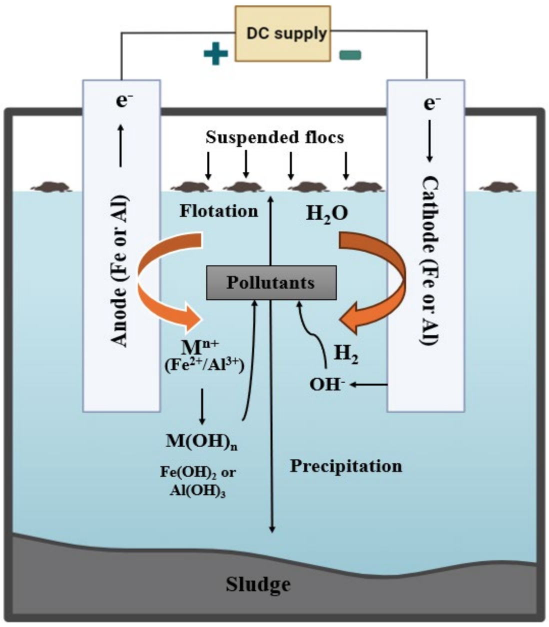

Figure 2. Schematic representation of reactions occurring in the electrocoagulation process.

3.2. Application of Electrocoagulation in Wastewater Treatment and Limitations

EC equipment is engineered for ease of use, affordability, and versatility in treating various types of effluents. This section provides a broad overview of how EC is utilized in the treatment of different types of wastewater. To date, extensive research has been conducted on its effectiveness in treating wastewater from diverse sources, including municipal facilities, textile industries, oil-related operations, urban environments, industrial sectors, and palm oil effluents. The successful removal of pollutants from these diverse wastewater sources highlights its reliability as an alternative technology for wastewater treatment [80]. For biologically resistant wastewater, such as hospital effluent, traditional biological treatments may not be effective. In these cases, EC has emerged as a promising solution, which can remove up to 88.75% of the antibacterial drug Ciprofloxacin [81]. Additionally, EC has proven effective in treating wastewater containing pollutants, such as TiO_2 nanoparticles, commonly used in pharmaceutical and culinary industries. A recent study reported that EC can remove 95% of these nanoparticles [77]. Microplastics, tiny plastic particles resulting from consumer products and industrial waste, are another significant emerging pollutant. Researchers have investigated the use of EC to treat wastewater containing microplastics, finding removal rates of 93.2% for polyethylene, 91.7% for polymethyl methacrylate, 98.2% for cellulose acetate, and 98.4% for polypropylene [82]. Table 2 summarizes the applications of EC in treating various organic and inorganic pollutants across different sectors. Recent studies indicate that EC is a highly effective method for treating diverse wastewaters, including those with elevated COD, demonstrating significant removal efficiencies while generating minimal solid waste. Consequently, implementing EC treatment systems offers numerous advantages, such as faster organic matter separation, stronger pH buffering capability, reduced secondary pollution, and easier automation [83]. Furthermore, it can operate effectively across a broad spectrum of conditions, including high salinity and varying pH levels, throughout electrochemically supported potential redox reactions. It is clear that EC technology is rapidly advancing and holds significant potential to supplant traditional wastewater treatment approaches.

Table 2. Application of electrocoagulation for treating various industry effluents.

Type of Wastewater	Pollutants	Electrode Configuration (Anode–Cathode)	Operational Conditions	Removal Efficiency	Reference
Tannery wastewater	COD, BOD, TDS, and Cr	Fe-Al	Continuous (flow rate = 6 lpm; current density = 20 mA/cm^2)	46% Cr, 42% COD, 42% TDS, and 35% BOD	[84]
Textile wastewater	COD and TOC	Al-Al	pH = 5.6; current density = −52.5 mA/m^2; time = 33.9 min	68% COD and 69% TOC	[85]
Refinery wastewater	Selenium	Fe-Fe	pH = 5 to 8; current density = 15.3 mA/cm^2; voltage = 3.20 V and time = 360 min	90% selenium	[86]
Oily wastewater	COD and Turbidity	Al-STS	pH = 7; electrode spacing = 1 cm; temperature = 20–22 °C	90% COD and Turbidity = 99%	[87]
Palm oil mill effluent	COD	Al-Al	pH = 4.5; current density = 56 mA/cm^2; time = 65 min	75.4% COD	[88]
Food industry wastewater	COD and TSS	Fe-Fe	pH = 10; current density = 86.4 mA/cm^2; time = 20 min	100% TSS and 98.94% COD	[89]
Pharmaceutical wastewater	Color and COD	Al-STS	pH = 4.5–10.5; current density = 3.47–12.15 mA/cm^2; voltage = 1–15 V; time = 30–150 min	58.35% COD and 97.83% color	[90]
Municipal wastewater	TSS and BOD	STS-STS	pH = 7.0; current = 0.80 A; time = 5 min	95.4% TSS and 99% BOD	[91]

Although EC has proven effective for treating wastewater pollutants at the laboratory scale, scaling this technology for industrial applications presents challenges. One significant challenge is the high capital investment required, primarily due to the cost associated with construction and electrode materials. Commonly used electrode materials include Fe, Al, and STS. These electrodes are sacrificial and hence necessitate regular replacement. Moreover, electrode passivation can diminish overall process efficiency and increase electricity consumption. Therefore, further investigation is needed into aspects such as the proton–electron transfer mechanism, consistent performance improvements, and the development of more cost-effective anode and cathode materials [92]. The other critical challenges in scaling up EC technology are reactor operation mode and configuration. The batch and continuous operation modes are the most representative in various laboratory-scale studies. Since real wastewater continuously flows into the system, continuous mode should be introduced for successful practical application. The design of reactor configurations mainly depends on electrode arrangement. Various reactor configurations can be classified into monopolar or dipolar setups, either in series or parallel connections [93]. Among them, the most available reactor configuration for practical application is a monopolar parallel connection due to its high performance, easy electrode maintainability, and low energy consumption [77]. A future study has to be directed to demonstrate how to select and integrate appropriate reactor configuration and operation mode. Optimum standardization of comprehensive reactor designs will help the EC accelerate achieving successful practical applications and unravel reaction complexities in real wastewater [94]. Long-term operational stability is also a significant concern in EC treatment systems. Performance failures have been observed in pilot-scale studies due to various factors, including electrode degradation, floc clogging, insufficient biofilm development, and reduced activity. Addressing these issues is essential for the successful large-scale implementation of EC technology. Although both small- and large-scale EC technologies can achieve simultaneous hydrogen production, the rates are generally lower compared to laboratory studies, highlighting the need for further optimization. High electricity consumption is another major challenge that directly impacts operating costs. The success of EC technology will rely heavily on minimizing both operational and management expenses [77]. Finally, the characteristics of flocs, including their strength, size, weight, and compaction, significantly influence the EC process. Denser flocs may settle over time, while floc size tends to increase with current intensity and duration due to enhanced coagulation. However, prolonged exposure can lead to floc breakage due to shear forces [95]. In summary, while EC offers promising results for various wastewater types, further advancements in reactor design, operational stability, energy efficiency, and floc management are needed to support its widespread industrial application. Additionally, integrating the EC process with other treatment methods is advisable to address these limitations and improve the overall efficiency of the treatment system.

3.3. Synergistic Approaches: Integration of Electrocoagulation with Conventional Techniques

Over the years, extensive research has focused on addressing the challenges associated with EC and enhancing its performance for large-scale applications. One effective strategy has been integrating the EC with traditional methods such as CC, adsorption, and biological treatments. Numerous studies have explored the feasibility of this integration, aiming to achieve faster reaction rates, higher removal efficiency, and reduced operational costs. Figure 3 provides a graphical illustration of the integration of EC with traditional methods.

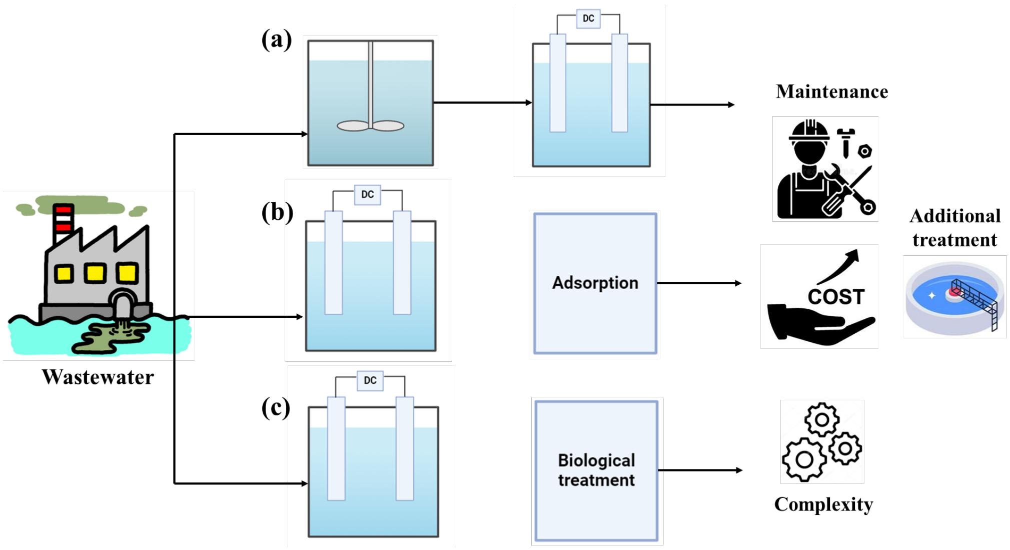

Figure 3. Integration of electrocoagulation with (**a**) chemical coagulation, (**b**) adsorption, and (**c**) biological pretreatment.

3.3.1. Electrocoagulation and Chemical Coagulation-Based Process

CC remains a prevalent method for treating wastewater from various industries but often leaves behind dissolved and SS, which need further treatment. The combination of CC with EC could enhance process efficiency and lower overall costs. Numerous studies have explored the use of CC with appropriate coagulants prior to EC. This combination aims to enhance pollutant removal while also minimizing both the cost and duration of the EC treatment phase. For example, a hybrid CC-EC method was employed to treat wastewater from the slaughterhouse industry. The method utilized PACl as a chemical coagulant up to 100 mg/L in the first stage (CC), followed by the application of Al electrodes at 40 V in the EC stage. The findings indicated that this hybrid approach effectively treated slaughterhouse wastewater, achieving over 99% removal of COD and BOD [96]. In another study, a combined EC-CC process was used to treat brewery wastewater. Operating the EC-CC system at 5 W for 20 min with Al electrodes and dissolved aluminum sulfate yielded consistent removal rates of 26% for COD, 74% for reactive phosphorus, 76% for TP, and 85% for TSS. Despite significant energy consumption, the EC-CC treatment proved economically viable when considering potential savings from reduced discharge fees. Notably, at the lower power setting of 5 W, recovery costs were 23% higher than at a 10 W supply, indicating effective processing at reduced power input [97]. A recent study investigated a combined approach of CC and EC at the pilot scale to eliminate fluoride from tungsten-melting wastewater. The pilot tests effectively reduced fluoride concentrations, with operational costs ranging from USD 0.99 to 1.51/m^3 of wastewater. The cost analysis revealed that the three most significant expenses in the CC process were liquid caustic soda, aluminum sulfate, and solid waste management. In contrast, the primary costs associated with the EC advanced treatment included the Al electrodes fee, electricity charges, and solid waste disposal [98]. These studies indicate that the combined application of CC and EC greatly improves pollutant removal from various types of wastewater. However, it is crucial to highlight that in the combined CC-EC process, CC is implemented first to manage the pollutant entering the subsequent EC stage. While the high effectiveness of the combined CC-EC method has been extensively examined in lab-scale studies, it has been less frequently evaluated at the pilot scale. This is primarily due to the significant drawback of elevated operational costs associated with CC, electrode replacement, and electricity usage.

3.3.2. Electrocoagulation and Adsorption-Based Process

Adsorption is a promising alternative technique for achieving substantial reductions in pollutants from various industrial effluents. However, the operating cost tends to be high due to the need for adsorbent regeneration and disposal. Incorporating EC prior to the adsorption process can enhance pollutant removal efficiency and lower overall operating costs. An investigation was carried out using EC as the sole treatment method, allowing for simultaneous EC and adsorption with Al electrodes. The study utilized a central composite design to optimize pH, current density, and reaction time to assess their effects on the removal of COD, total organic carbon (TOC), and TSS from landfill leachate. Under optimal conditions of pH 7.35, a current density of 15.29 mA/cm^2, and a reaction time of 57 min, the removal efficiencies were 83.56% for COD, 73.12% for TSS, and 85.58% for TOC [99]. Similarly, another study explored the effectiveness of combining EC with adsorption using natural zeolite for treating industrial wastewater. The study utilized response surface methodology to optimize various operational parameters, including pH, current density, reaction time, and zeolite dosage. Optimal conditions of pH 7, a current density of 38 mA/m^2, an electrolysis duration of 20 min, and a zeolite dosage of 0.183 g/mol resulted in 92% COD removal and 97% turbidity reduction [100]. Additionally, a study assessed a solar photovoltaic power EC-assisted adsorption system for treating pharmaceutical wastewater. A COD removal rate of 95.5% was achieved at optimum conditions of 20 min reaction time, 6.656 mA/cm^2 current density, and a temperature of 45 °C with an operating cost of USD 0.273/m^3 of wastewater [101]. It is crucial to note that all these studies employed EC as a preliminary treatment before adsorption, ultimately enhancing overall process efficacy. However, the integration of EC and adsorption presents significant challenges, including the need for electrode replacement, adsorbent regeneration, and process optimization. As a result, this combined approach is infrequently examined in pilot-scale studies.

3.3.3. Electrocoagulation and Bioprocess-Based Treatment

EC combined with biological treatments has emerged as an effective technology for addressing heavily contaminated industrial effluents. While biological treatments have demonstrated significant potential in removing organic pollutants from wastewater, they often struggle with non-biodegradable and toxic substances. In this context, EC presents a promising solution that can be integrated with biological processes to improve contaminant removal. A study was conducted to assess the effectiveness of integrating EC with biological fungal treatment to treat tannery wastewater. RSM was employed to examine how different conditions influenced treatment efficiency. The findings revealed that using Al-Fe electrodes under optimal conditions resulted in removal efficiencies of 96% for COD and 97% for Cr^{6+} [102]. In another study, EC combined with biological treatment effectively addressed wastewater from the oil industry. The process of EC followed by aerobic biofiltration significantly increased the biodegradability of total petroleum hydrocarbons, achieving reductions of 95% in COD and 98% in total petroleum hydrocarbons [103]. A more recent study explored a modified biological integrated EC method for treating municipal wastewater, aiming to reuse the treated water for irrigation. This combined approach achieved notable removal efficiencies: 78.8% for turbidity, 56.8% for hardness, 28.4% for conductivity, 37.4% for total dissolved solids (TDS), 98.3% for TSS, 27.6% for chloride, 26.7% for NH_3-N, 78% for BOD, 81% for COD, and an impressive 99.9% for total coliforms. The process consumed 9.9 Wh/L of energy, with an operational cost of USD 0.76/m^3 of municipal wastewater [104]. However, this approach faces challenges, including the complexity of the integrated system, the need for additional equipment, higher maintenance costs, and the optimization of operational parameters, which limits its broader application.

3.4. Next-Generation Approaches: Electrocoagulation Integration with Emerging Technologies

The integration of EC with traditional approaches such as biological treatment, CC, and adsorption often falls short of effectively removing contaminants like dyes, salts, and surfactants. Furthermore, these conventional methods are complex and require significant investment. Considering these challenges, researchers have focused their efforts on developing innovative hybrid technologies that can integrate with EC. This advancement aims to simplify processes, lower operational costs, and enhance the removal of contaminants from wastewater.

3.4.1. Electrocoagulation-Membrane-Based Treatment

Membrane separation processes offer great simplicity and energy efficiency compared to other separation techniques, making them ideal for eliminating contaminants. Several membrane-based methods, including ultrafiltration (UF), reverse osmosis (RO), forward osmosis (FO), membrane distillation (MD), nanofiltration (NF), electrodialysis (ED), and membrane bioreactors (MBR) have demonstrated superior effectiveness in removing pollutants from different industrial wastewater. However, these technologies face significant challenges, mainly fouling, which can lead to increased operational costs despite their ability to eliminate nearly all contaminants. To mitigate this issue, pretreatment methods are often employed before the membrane processes to improve efficiency and reduce costs. In this context, integrating the EC as a pretreatment step before membrane technology presents a versatile and promising solution for water treatment characterized by reduced space requirements, minimal chemical usage, and enhanced efficiency. For example, a hybrid EC-membrane technology for industrial wastewater treatment is illustrated in Figure 4. Numerous studies have investigated integrating various membrane technologies with EC to improve the removal of contaminants from industrial effluents. One study, for instance, combined EC with UF and RO to remove pollutants from hospital wastewater. UF uses a membrane with pore sizes of 1 to 100 nanometers to retain larger molecules, while RO employs a membrane with pore sizes of approximately 0.0001 microns to remove dissolved salts and small contaminants. The EC-UF configuration resulted in TSS, TDS, BOD, and COD removal efficiency of 95.12%, 97.53%, 95.18%, and 97.88%, respectively, with an operating cost of USD 3.92/m^3 of wastewater. In contrast, the EC-RO configuration demonstrated even higher efficiencies with TSS, TDS, BOD, and COD removal rates of 97.64%, 99.85%, 97.88%, and 98.38%, respectively, at an operating cost of USD 4.02/m^3 of wastewater. When the treatment scale was increased to 50 m^3/day, the operating costs dropped to USD 0.89/m^3 for EC-UF configuration and USD 0.93/m^3 for EC-RO configuration [105]. In another study, EC was integrated with UF membrane to treat palm oil mill effluent, revealing that using a bipolar electrode significantly enhanced coagulation efficiency. The removal efficiencies for TDS, TSS, COD, and BOD were 59.1%, 99.9%, 96.8%, and 96%, respectively, with an estimated operating cost of USD 2.71/m^3 and an energy requirement of 6.20 kWh/m^3 [106]. FO is recognized as an innovative membrane technology for freshwater production, operating on the principle of natural osmotic pressure gradients. A lab-scale hybrid EC-FO setup was tested for treating produced water, achieving a maximum flux of 1.2 LPM under optimal conditions with a current density of 10 mA/cm^2 and a residence time of 10 min for the EC process. This configuration effectively removed 99% of TSS, 98% of turbidity, and 16% of conductivity [107]. MD, another separation technique, involves vapor molecules passing through a porous hydrophobic membrane. Utilizing EC as a pretreatment for MD offers several advantages, particularly in preventing membrane wetting, which occurs when water permeates through the membrane pores. A study on a hybrid EC-MD process for treating produced water from hydraulic fracturing found that EC effectively reduces TOC, which is crucial for minimizing membrane fouling during the MD process [108]. ED is an electrically powered membrane process that drives ions through a membrane using an electric current. It boasts high selectivity, excellent recovery rates, and the ability to remove most contaminants from raw water. However, additional treatment steps are often necessary for effective wastewater treatment. One study demonstrated the success of a hybrid EC-ED process in treating tannery wastewater, achieving a COD removal efficiency of 92% when Al electrodes were used while eliminating NH_3-N, chromium (Cr), and color. When Fe electrodes were employed, the COD removal efficiency was 87%, with complete removal of NH_3-N, Cr, and color [109]. Additionally, a submerged membrane reactor was integrated with EC for greywater treatment. With a voltage gradient of 1.26 V/cm, the removal efficiencies for turbidity, color, COD, NH_3-N, and total phosphorous (TP) were found to be 100%, 99.7%, 92%, 94.1%, and 96.5%, respectively [110]. While utilizing EC as a pretreatment method marks a significant advancement in water treatment technology, membrane fouling remains a critical challenge for long-term operation. Researchers have extensively studied the various types of fouling, their causes, and potential mitigation strategies. By examining particle size distribution, differing influx ratios, and the condition of fouled membranes, it has been found that approximately 75–85% of the initial flux can be recovered when filtering EC-treated wastewater [111]. Furthermore, pore-blocking models have been developed to analyze the nature of fouling on membranes exposed to various effluents. Hermia's models are notably recognized for their effectiveness in evaluating types of fouling in membrane filtration processes [112]. Ultimately, a fully optimized and controlled EC process can significantly enhance membrane filtration performance by minimizing fouling, presenting substantial potential for efficiently treating industrial effluents while reducing energy consumption and costs.

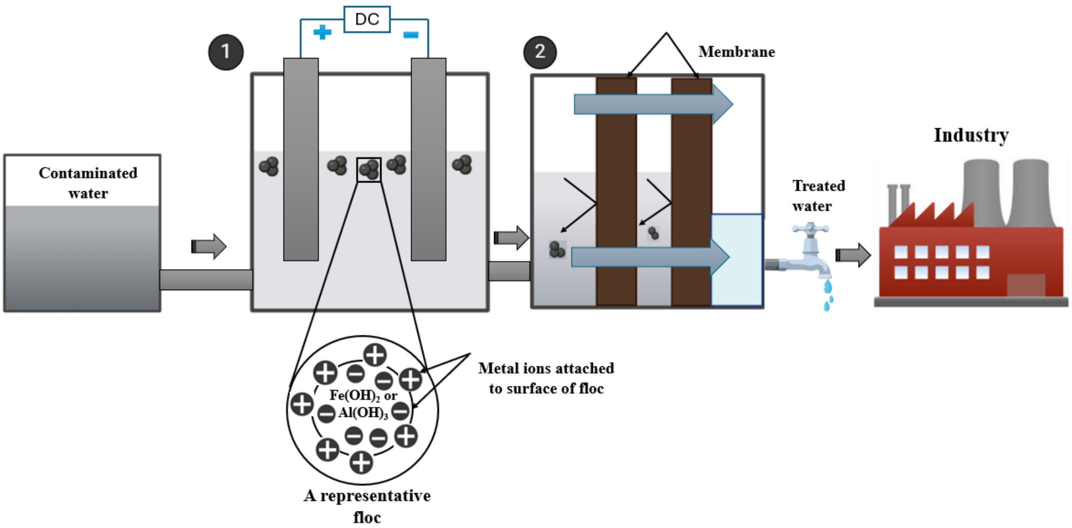

Figure 4. Schematic depiction of hybrid electrocoagulation-membrane technology for treating industrial effluents.

3.4.2. Electrocoagulation–Electrochemical Processes

Hybrid EC-membrane-based processes have shown great potential for wastewater treatment. Several electrochemical-based processes such as electrooxidation, ozonation, Fenton, and their integration with EC have also shown promise. However, there is a growing need to explore and adapt these technologies to improve treatment efficiency and effectively address the full spectrum of contaminants found in wastewater. EC has already proven effective in removing numerous pollutants and microbial pathogens. When combined with advanced electrochemical methods, it not only improves treatment efficiency but also supports environmental sustainability. This combination is user-friendly and characterized by low energy consumption and ease of operation [113]. Advanced oxidation processes, in particular, are highly effective as they generate a variety of reactive species capable of breaking down organic pollutants. Different methods for generating radicals include electroreduction, electro-Fenton, photo-Fenton, and ozonation [114]. Overall, integrating EC with various electrochemical processes offers a holistic approach to wastewater treatment, leveraging the strengths of both technologies.

Among the various electrochemical treatment systems, the combination of EC and electrooxidation (EO) is frequently utilized for wastewater treatment. EO is a sophisticated oxidation method that relies on electrolytic reactions occurring at the surface of the electrodes. In this process, pollutants present in the wastewater are drawn to the electrode surface, where they undergo oxidation after adsorption. Using EC as a preliminary treatment, colloidal and suspended particles can be rapidly coagulated, enabling the EO system to eliminate any remaining pollutants. A combined EC and EO process has been employed to treat industrial wastewater. Using the EC system alone, the removal efficiencies for COD, BOD, total coliforms, color, and turbidity were recorded at 85.6%, 46.4%, 99%, 52%, and 83.8%, respectively, at a current density of 80 mA/cm^2. In contrast, the hybrid EC-EO system rapidly coagulated and eliminated colloidal particles, while the EO component effectively addressed the remaining particles, achieving over 99% removal of all contaminants [115]. In another investigation, the combined EC-EO method was utilized for water treatment. Although EO effectively removed certain trace organic compounds, its performance was limited by the presence of dissolved organic carbon. However, when paired with EC, the removal of these trace contaminants improved, and the interference from dissolved organic carbon was mitigated. This synergistic approach resulted in higher pollutant removal rates than when each method was applied individually [116]. Additionally, research on the EC-EO integration for treating industrial container wash wastewater, characterized by high levels of COD and phosphorus, demonstrated significant removal rates of 97% for phosphorus and 95% for COD, successfully meeting discharge regulations [117]. These findings highlight the potential of the combined EC-EO process to enhance wastewater treatment by effectively addressing a variety of pollutants. Nonetheless, it is essential to note that this hybrid system may not be universally effective for all types of wastewater, particularly those containing surfactants and cleaning agents. Therefore, further research is essential to optimize operational parameters, assess the applicability of these processes across different wastewater types, and evaluate the scalability and cost-effectiveness of this combined approach.

Ozonation is a highly effective technology that utilizes ozone as a powerful oxidant to break down various pollutants, including dyes. This process generates hydroxyl radicals, solid and non-selective oxidants, allowing for the indirect oxidation of a wide range of contaminants. Although ozonation has been extensively researched on a pilot scale due to its high efficiency, it has limitations when dealing with high-molecular-weight pollutants. To address this, a synergistic method that combines EC with ozonation has emerged as a promising solution. One study evaluated the effectiveness of the EC-ozonation process in treating greywater. Under optimal conditions—using Fe electrodes, a neutral pH, an ozone concentration of 47.4 mg/L, and a current density of 15 mA/cm^2—significant reductions were achieved: 85% for COD and 70% for TOC [118]. Another investigation proposed a combined ozone-assisted EC approach for degrading color and COD in distillery spent wash. This continuous process attained impressive removal rates of 97.3% for COD and 98.7% for color [119]. Additionally, a study introduced a method that integrates sedimentation, EC, and ozonation for wastewater treatment, achieving remarkable removal efficiencies of 90.9% for COD, 100% for color, 73.7% for total solids (TS), and 99.7% for SS [120]. These findings collectively illustrate the potential of the combined EC-ozonation approach for enhancing wastewater treatment by leveraging the strengths of both methods. Nonetheless, further research is essential to optimize the process and assess its applicability to various wastewaters, aiming for the cost-effective scalability of this combined treatment strategy.

Electro-Fenton (EF) is an advanced oxidation technique designed to eliminate persistent organic pollutants by generating hydroxyl radicals through specific mechanisms. This process is categorized into homogeneous and heterogeneous EF based on the mechanism of pollutant degradation. In homogeneous EF, the catalyst dissolves, leading to the generation of hydroxyl radicals, which subsequently oxidize organic compounds. Conversely, heterogeneous EF occurs when Fe^{2+} is replaced with Fe^{3+} or other transition metal ions. While EF processes are highly effective for treating various pollutants, they require pH adjustments, which can increase operational costs. To address these limitations, combining EC with EF has been proposed to enhance efficacy. One study introduced a dual anode system that integrates EC and EF processes to treat leachate concentrate, achieving a removal rate of 57% for organic materials and 60% for NH_3 under specific conditions. The radicals produced by this dual-electrode system effectively oxidized both organic substances and other persistent pollutants [121]. Another research effort implemented a combined EC and EF approach to treat tannery wastewater, resulting in a COD removal rate of 88.1 ± 4.8% and complete elimination of Cr. This combined method demonstrated a lower global environmental impact compared to using each process individually [122]. Additionally, a recent study explored a novel integration of heterogeneous EF and EC for the efficient removal of Cu-ciprofloxacin complexes. Under optimal conditions, removal efficiencies of 99.6% for Cu, 96.4% for ciprofloxacin, and 83.6% for TOC were achieved. The primary mechanism involved the degradation of Cu-ciprofloxacin complexes into smaller molecules, releasing Cu^{2+} ions [123]. These findings collectively highlight the potential of combined EC-EF processes for effectively removing contaminants from wastewater. However, further research is necessary to optimize the parameters, evaluate scalability, and assess the cost-effectiveness of this integrated approach.

In summary, integrating EC with emerging technologies such as membrane processes and advanced electrochemical techniques presents a promising approach for addressing highly contaminated wastewater. This combination reduces the formation of passive films on electrode surfaces, boosts radical generation, and improves the degradation of pollutants. As outlined in Table 3, comprehensive research highlights the effectiveness of EC combined with membrane and electrochemical technologies in eliminating a range of contaminants, including phenols, dyes, oils, heavy metals, COD, BOD, and TDS, achieving high removal rates. These integrated processes demonstrate enhanced treatment efficiency compared to traditional methods, making them well suited for managing residual effluent and promoting sustainable practices in water and wastewater treatment. However, it is crucial to address the long-term sustainability and cost-effectiveness of these integrated systems, particularly concerning electrode replacement and power consumption. Therefore, long-term pilot-scale studies should be conducted to better understand the economic viability and operational implications of these advanced technologies in real-world applications.

Table 3. Summary of electrocoagulation integrated with membrane and electrochemical-based processes.

New Integration Technology	Hybrid Process	Wastewater	Operating Conditions	Results	Reference
Membrane-based integration	EC-UF and EC-RO	Hospital wastewater	Electrode configuration: 2A-2C-2B) and (4A-2C-2B); current density: 88.5 A/m^2.	EC-UF: 95.12% TSS, 97.53% TDS; 95.18% BOD and 97.88% COD removal. EC-RO: 97.64% TSS, 99.85% TDS; 97.88% BOD, and 98.38% COD removal.	[105]
	EC-UF	Palm oil mill effluent	Electrode configuration: 2A-2C-2B.	59.1% TDS, 99.9% TSS, 96.8% COD, and 96% BOD removal.	[106]
	EC-FO	Produced water	EC: 10 mA/cm^2, 10 min residence time. FO: 1.2 LPM FS-DS flowrate in PRO mode.	99% TSS, 98% turbidity, 16% conductivity.	[107]
	EC-MD	Hydraulic-fracturing-produced water	Al/Fe electrodes	Effective TOC removal, insoluble species were effectively coagulated rather than dissolved.	[108]

	EC-ED	Tannery wastewater	Al: 0.371 mS/cm at 45 min. Fe: 1.5 mS/cm at 75 min.	92% COD and 100% NH_3-N, Cr, color for Al electrodes. 87% COD and 100% NH_3-N, Cr, color for Fe electrodes.	[109]
	EC-Submerged MBR	Gray water	EC: AL electrodes at voltage gradient of 1.26 V/cm.	100% turbidity, 99.7% color, 92% COD, 94.1% NH_3-N and 96.5% TP.	[110]
Electrochemical integration	EC-EO	Industrial wastewater	EC: current density of 80 mA/cm^2. EO: boron-doped diamond anode and Fe cathode.	EC: 85.6% COD, 46.4% BOD, 99% total coliforms, 52% color, 83.8% turbidity. Hybrid EC-EO: 99% contaminant removal.	[115]
	EC-EO	Drinking water	EO: boron-doped diamond electrodes, current density of 14.8 mA/cm^2. EC: Fe electrodes, current density of 1.85–11.1 mA/cm^2.	EO is affected by the presence of dissolved organic carbon. EC removed 74 ± 7% dissolved organic carbon from water. Hybrid EC-EO effectively removed all contaminants.	[116]
	EC-EO	Industrial container wash water	EC followed by EO with boron-doped electrodes and current density of 0.12 A/cm^2.	The EC-EO hybrid process removed 97% phosphorus and 95% COD. EC-EO reduced treatment cost around 3.3 times more than individual.	[117]
	EC-ozonation	Gray water	60 min electrolysis time, pH 7.0, 47.4 mg/L ozone, 15 mA/cm^2 current density.	85% COD, 70% COD were removed. EC with Fe electrodes exhibited high catalytic activity.	[118]
	EC-ozonation	Distillery spent wash	Al electrodes	Combined ozone-assisted EC approach achieved 97.3% COD and 98.7% color removal.	[119]
	EC-ozonation	Fiberboard industry wastewater	EC: Al anode and Fe cathode with current density of 214.3 A/m^2. Ozonation: flow of 2.5 g/h at initial pH of 7.4.	Hybrid process achieved 90.9% COD, 100% color, 73.7 TS, and 99.7% SS.	[120]
	EC-EF	Leachate concentrate	Dual anode system, electrical charge of 7 Ah/L, potential of 7 V, pH 7.	57% organics, 60% NH_3 were removed. Most of the fulvic and humic substances were removed.	[121]
	EC-EF	Tannery wastewater	EC: mild steel electrodes. EF: air diffusion cathode and boron-doped diamond anode.	The hybrid 2h EF-5 h EC process achieved 88.1 ± 4.8 COD and total elimination of Cr. The electrical energy consumption was reduced to 1.7 times.	[122]
	EC-EF	Heavy metal wastewater	N-Co/Fe-PC cathode and graphite anode. Current: 2–150 mA, pH: 3–7.	99.69% Cu, 96.40% Ciprofloxacin, and 83.62% TOC removed.	[123]

4. Conclusions and Future Perspective

Coagulation is a method used to eliminate contaminants from wastewater effectively. Both synthetic and natural coagulants have been recognized as effective materials in this process. Natural coagulants have been utilized for decades, even before the advent of chemical coagulants. However, the latter have gained significant popularity recently despite their drawbacks, such as high costs and the production of toxic byproducts. This has prompted a shift towards natural coagulants, which are more cost-effective and environmentally friendly. Nonetheless, concerns regarding their effectiveness on a larger scale often limit their use.

EC has emerged as a highly efficient and eco-friendly technology for contaminant removal in water and wastewater treatment. Like other treatment methods, EC faces challenges, including electrode passivation and substantial energy consumption, mainly due to the lower conductivity of specific wastewater. Additionally, EC is less effective at removing stable, persistent organic compounds to levels that meet discharge regulations. Our findings suggest that integrating EC with established treatment methods, such as CC, adsorption, and biological treatment, presents a promising avenue for enhancing wastewater treatment efficiency. However, this integrated approach faces several challenges related to operational economics, including high operational costs, the need for adsorbent regeneration, process optimization, and increased maintenance expenses. Furthermore, these methods have yet to be studied at the pilot scale. In this context, emerging technologies like membrane processes and advanced electrochemical techniques, particularly when integrated with EC, offer significant potential. Utilizing EC as a pretreatment method before these advanced techniques provides several advantages, including increased permeate water volume, improved water quality, reduced membrane fouling, and lower operational costs for hybrid systems. However, for the commercialization of hybrid EC processes, several challenges must be addressed. These include minimizing the consumption of sacrificial electrodes, which necessitates further research into cost-effective alternatives. Additionally, more pilot-scale studies are needed to evaluate the effectiveness of hybrid EC processes on various industrial wastewater. Long-term assessments should also be conducted to determine the efficacy of different hybrid EC systems. Addressing these research gaps and challenges will significantly enhance the field of hybrid EC processes, providing sustainable and cost-effective solutions for water and wastewater treatment.

Author Contributions: S.J., writing—original draft preparation, writing—review, and editing; R.K., writing—original draft preparation and writing—review and editing; H.J. and D.S., writing—review and editing; J.P., conceptualization, writing—review and editing, supervision, and funding acquisition. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Chosun University 2023 [grant number K208702003] and “Regional Innovation Strategy (RIS)” through the National Research Foundation of Korea (NRF), funded by the Ministry of Education (MOE) [2021RIS-002].

Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript.

CC: chemical coagulation; EC: electrocoagulation; SS: suspended solids; Al: aluminum; Fe: iron; PAC: polyaluminum chloride; WWTP: wastewater treatment plant; CEPT: chemical enhanced primary treatment; COD: chemical oxygen demand; BOD: biological oxygen demand; TSS: total suspended solids; RSM: response surface methodology; ANN: artificial neural network; GA: genetic algorithm; Cu: copper; STS: stainless steel; TOC: total organic carbon; TDS: total dissolved solids; UF: ultrafiltration; RO: reverse osmosis; FO: forward osmosis; MD: membrane distillation; NF: nanofiltration; ED: electrodialysis; MBR: membrane bioreactor; TP: total phosphorous; EO: electrooxidation; TS: total solids; Cr: chromium; EF: electro-Fenton; EPA: US Environmental Protection Agency

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