

# Electrochemically and Ultrasonically-Enhanced Coagulation for Algae Removal

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## Abstract

At the global level, the augmenting presence of harmful algae blooms constitutes important dares to water treatment plants (WTPs). In WTPs, coagulation remains the primary process of the applied procedure to treat algae-contaminated water. Such a chemical process influences the following techniques; thus, regulating coagulation parameters to eliminate algae at the maximum degree without provoking cell deterioration is more than crucial. This work aims to review coagulation-founded methods for algae elimination. First, investigations concentrating on algae elimination using the chemical process are discussed. The introduction presents the widespread algae encountered in the water treatment field. Then, habitually utilized experimental techniques and emerging methods in coagulation investigations are summarized with typical findings. Next, the newest expansions in improved algae elimination, launched by electrochemically and ultrasonically-enhanced coagulation, are discussed. Workable thoughts for applying coagulation to eliminate algae in WTPs are also debated. The paper finishes by defining restrictions and dares related to the present literature and suggesting trends for subsequent studies. The charge neutralization mechanism efficiently removes solubilized microcystins (MCs), and enhanced coagulation configuration is also found to be more efficient for their removal. However, considerations should be taken to avert that the acid introduction has no unwanted effect in killing algae treatment to avoid the solubilized MCs level elevation. If such techniques are well-optimized and controlled, both algae and solubilized MCs could be efficaciously removed by ultrasound-enhanced coagulation and electrocoagulation/electrooxidation.

#### **Keywords**

Harmful Algal Blooms (HABs), Electrocoagulation (EC), Electrooxidation (EO), Ultrasound (US), Machine Learning (ML), Reactive Oxygen Species (ROSs)

#### **1. Introduction**

A flourishing population of phytoplankton microorganisms in aquatic ecosystems, like eukaryotic algae and cyanobacteria, is more than an essential constituent [1] [2] [3]. Nonetheless, harmful algal blooms (HABs) could exist below some ecological circumstances conducting to immoderate aggregation of algal biomass, exhaustion of dissolved oxygen, and inherent formation of toxins [4] [5] [6]. In water treatment and human safeguard, some algal types that form toxins remain of noteworthy worry [7] [8]. Such poisonous substances could provoke unfavorable human health influences [9] [10]. Several HAB-producing species generate disagreeable taste and odor (T&O) substances [11]. Even if cyanobacteria repeatedly remain the most difficult harmful algal category, numerous other eukaryotic algae also worsen water quality by forming toxins [12]. Table 1 presents the frequent algae of interest and their likely influences on water quality. Even if HABs could exist naturally, the effects of human activities (e.g., expanded nutrient charge and hydrologic change) have been related to the augmenting recurrence of HAB cases [13] [14]. The severe effects of HABs on water safety have been confirmed broadly in many instances, during which potable water supply had to be suspended because of poisonous HABs [15] [16]. Since climate alteration is foreseen to modify the recurrence, distribution, and gravity of HABs, vigorous management procedures must be elaborated to dominate the harmful impacts of HABs in natural waters and furnish enough supplies of protected potable water [1].

Water treatment plants (WTPs) use a multi-barrier procedure to deal with algae-infected source water [1] [19] [20]. In traditional potable water treatment techniques, coagulation remains largely the opening treatment unit [8] [21] [22]. However, its performance immediately influences all downstream treatment stages [23] [24] [25]. Destroyed algal cells could liberate toxins, T&O compounds, and additional cellular metabolites that generate disinfection by-products (DBPs) [15] [26] [27]. Thus, the main objective of coagulation, besides the following solid-liquid separation methods (*i.e.*, clarification and filtration), remains to increase the elimination of algae without touching the cell integrity [7] [10] [28]. The significance of coagulation in treating algae issues overpasses treatment plants [2] [3] [5].

Regarding water management, the basic procedure to stop and dominate eutrophication and algae-linked troubles is to decrease the nutrient charges into waterbodies [6] [11] [19]. Comparatively, defining point-source nutrients related

Classification	Common genera of interest	Biological characteristics	Importance
Cyanobacteria (blue-green algae)	Anabaena, Aphanizomenon, Cylindrospermopsis, Lyngbya, Microcystis, Oscillatoria, Phormidium, Planktothrix	<ul> <li>Cell walls are composed of peptidoglycan and a layer of lipopolysaccharide (Gram-negative)</li> <li>Pigments include chlorophylls, phycobilins, and carotenoids</li> <li>Contain specialized structures: aerotopes, heterocytes, and akinetes</li> <li>Various morphologies: unicellular, colonial, filamentous</li> </ul>	<ul> <li>Produce cyanotoxins (cyclic peptides, alkaloids, and endotoxins)</li> <li>Produce T&amp;O compounds</li> <li>Clog water intake and filter</li> <li>Increase in organic matter</li> </ul>
Chlorophyta (green algae)	Chara, Cladophora, Hydrodictyon, Pithophora, Scenedesmus	<ul> <li>Have flagella in at least one life stage</li> <li>Various morphologies: unicellular, colonial, filamentous</li> </ul>	• Some genera produce T&O compounds
Bacillariophyta (diatoms)	Aulacoseira, Cyclotella, Melosira, Nitzschia, Pseudonitzschia, Synedra, Tabellaria	<ul><li>Cell walls are made of silica</li><li>Two forms: centric and pennate</li><li>Many have spines or stellate</li></ul>	<ul> <li>Only one marine genus</li> <li>(<i>Pseudonitzschia</i>) produces a toxin</li> <li>(domoic acid)</li> <li>Some genera produce T&amp;O</li> <li>compounds</li> </ul>
Dinophyceae (dinoflagellates)	Ceratium, Peridinium	<ul><li>Unicellular with two dissimilar flagella</li><li>Many have lorica made of cellulose</li></ul>	<ul> <li>Many marine genera produce toxins</li> <li>Only one freshwater toxin-producing species (<i>Peridiniopsis polonicum</i>)</li> <li>Some genera produce T&amp;O compounds</li> </ul>
Chrysophyceae (golden algae)	Chrysosphaerella, Dinobryon, Uroglen	<ul> <li>Unicellular with one or two dissimilar flagella</li> <li>Unique siliceous cyst</li> <li>Some have lorica</li> </ul>	• Some genera produce T&O compounds
Euglenophyceae (euglenoids)	Euglena, Phacus	<ul> <li>Generally, spindle-shaped</li> <li>No cell walls, but enveloped by a proteinaceous pellicle</li> </ul>	• A few species (e.g., <i>Euglena sanguinea</i> ) produce a toxin (euglenophycin)
Haptophyta	Prymnesium	Usually with two flagella and a unique haptonema	• <i>Prymnesium parvum</i> produces a toxin (prymnesin)
Phaeophyceae Xanthophyceae Rhodophyta		• Commonly known as brown, yellow-green, and red algae, respectively.	• Rarely in large quantities, not a concern

Table 1. Frequent algae of interest to water treatment [1] [17] [18].

to urban and industrial wastes stays simple and satisfies regulatory discharge limits using advanced processes for improved nutrient elimination [12] [14] [29]. Nonetheless, attempts at point-source nutrient lowering are frequently useless because of the primarily unregulated nutrient inputs from nonpoint sources (e.g., agricultural drainage, soil erosion, urban runoff, and household septic systems) [30]. Actions to decrease nonpoint-source nutrients (e.g., applying best management practices in agriculture) could be expensive, and it could take several years to depict marks of amelioration [1]. This can follow from the internal cycling of nutrients aggregated in the sediment because of constant external charge. Therefore, there is an augmenting agreement that geoengineering actions are indispensable to deal with the internal legacy phosphorus (P) charge inside a water body [1] [13]. Processes founded on coagulation and precipitation have set significant capacity in decreasing eutrophication and dominating algal blooms [31] [32] [33]. This method uses coagulants with ballast materials to sink agglomerated algal flocs into the sediment [1]. P-sorbent materials could be used in integration to eliminate P in the water column and diminish its liberation from the deposit. These in-lake actions will be more and more significant to water management because they can engender a direct amelioration in water quality and consequently reduce the time gap until the long-term preventive precautions (like external nutrient decrease) enter into impact [34].

Coagulation remains one of the most proven water treatment methods; however, applying coagulation stays utterly dependent on an experimental procedure, the jar test [1] [21] [35]. Several depending parameters, including those from water matrices and running circumstances, make the coagulation phenomenon more complex [22] [23] [24]. The various biological properties of algae complicate the situation [19] [36]. The conventional colloidal models and flocculation principles occasionally need to be revised to define the relationship pathways in the coagulation method. They remain as well of restricted employment in anticipating the results when treating complex water matrices [25] [37] [38]. Even with the expanding investigation campaign in this domain, empirical circumstances are frequently similar in such investigations [6] [14]. In addition, numerous publications are short of an explained illustration of practical cases, rendering the juxtaposition among various coagulation setups hard [39] [40] [41]. Nevertheless, traditional coagulants have been primarily utilized for several decades and provided acceptable efficiencies under below-optimized circumstances [42] [43] [44]. Nonetheless, coagulants frequently require algae-laden water injections at a bigger dosage to satisfy the regulatory targets [6] [7] [10]. Such a procedure produces a considerable quantity of sludge that needs substantial treatment before disposal and adds to the global working costs [45]. Also, there has been an unceasing discussion about the long-term security and ecological effects of such usual coagulants (like the inherent negative impacts of aluminum [29] [46] [47] and synthetic polymer coagulants) [48] [49].

Consequently, the demand for novel kinds of coagulants, which are secure, performant, and cost-effective, has pushed the expansion of new coagulants founded on materials of natural origin [1] [50] [51]. Another fresh progress in algae elimination is integrating coagulation methods with emerging processes like electrochemical techniques [6] [52] [53] and sonication [54]. Such combined treatment technologies can be powered via renewable energy and decrease the chemical need in the coagulation method. However, even if encouraging outcomes have been noticed in lab-scale experiments performed below well-controlled parameters, such strategies must be reliable for field deployment [1].

Recently published review papers present significant comprehensions on the

observation and elimination of cyanobacteria and cyanotoxins [4] [15] [55]; however, the field of such publications, which include several treatment technologies, does not furnish a complete survey of coagulation-founded techniques [1]. Also, surveys focusing on the global implementation of the coagulation method [56] [57] do not treat the specific dares of algae-infected water. Researchers [58] discuss the effects of algal features on the solid-liquid separation of algae and illustrate the significance of regulating coagulation in the following clarification stage. Ghernaout et al. [2] presented some ameliorations in this domain and shortly displayed the contribution of coagulation in algae and cyanotoxins elimination. The field has progressed highly over the last twelve years by suggesting novel methodologies, improving diverse coagulant materials, and combining new technologies with coagulation. Therefore, even with writing this work, there is a need for a review paper furnishing a thorough survey of the latest advance in algae elimination and domination via coagulation-founded methods. Thus, this work aims to include the usage of coagulation for algae elimination in water treatment and its implementation to deal with eutrophic water bodies. Coagulation/flocculation-founded methods are among the most common processes for harvesting algal biomass [59].

Nonetheless, it must be mentioned that coagulation's principal aim is to recover high-purity algal biomass efficiently. Besides, algae-related troubles in water treatment, like toxins and T&O substances, are no longer a worry because algal species are frequently preselected and cultivated in a controlled medium. Consequently, this work will not examine investigations concerning coagulation in algal biomass harvesting. However, a more detailed overview of this subject may be found in such references [1] [59].

Ren *et al.* [1] recently discussed the savoir-faire in utilizing coagulation-founded methods to deal with algae-impacted water. They defined the interfacial phenomena in the coagulation process regarding colloidal chemistry and algal properties. They also outlined the empirical procedures frequently utilized in coagulation investigations to estimate floc characteristics, distinguish and observe algal cells, and describe coagulant materials. Also, they debated the advance in the expansion of coagulant materials. In this work, we display the emerging coagulation methods founded on the electrochemical phenomenon and sonication for enhanced algae removal. Further, we focus on the troubles related to coagulation-founded techniques for algae removal in water treatment and in-lake algae control. Lastly, we display the restrictions of existing coagulation investigations and suggest opportunities for future study.

## 2. New Coagulation Method for Algae Elimination

## 2.1. Electrochemical Process

## 2.1.1. Electrooxidation

In an electrochemical cell, the oxidation of a matter may be initiated by either direct electron transfer to the anode (anodic oxidation) or a chemical reaction with species electrogenerated at the anode surface (mediated oxidation) [60] [61]

[62]. The oxidation route is mainly controlled by the features of the electrode and solution chemistry [63] [64] [65]. Following the strength of interaction with hydroxyl radicals produced in the electrooxidation (EO) of water, anode materials could be classified into active and non-active anodes (Table 2) [66] [67] [68]. The active anodes boost strong chemisorption of 'OH and could advance higher oxidation states on the surface [1]. An excellent instance is the mixed metal oxide electrodes prepared by coating the titanium substrate with a film of mixed oxides (like RuO<sub>2</sub>, IrO<sub>2</sub>, and Ta<sub>2</sub>O<sub>5</sub>) [69]. Such materials are valuable anodes for the oxygen evolution reaction (OER) thanks to their low overpotential for OER vet show low oxidizing power, conducting to partial oxidation of substances. Further, at the non-active anodes, the interaction with physisorbed 'OH is weak, leading to poor OER efficiency; even so, a strong oxidizing power promotes total oxidation [60] [70]. On the other hand, boron-doped diamond (BDD) electrodes produce a considerable quantity of loosely adsorbed 'OH that is so efficacious at oxidizing refractory pollutants and demobilizing algal cells [71] [72].

The current density (current per unit area of the electrode, mostly expressed as mA/cm<sup>2</sup>) is a critical parameter determining the EO reaction rate [1]. At low current intensities, the electrochemical method is under current control; thus, an augmentation in the present leads to a more considerable elimination of algal cells [6]. Nonetheless, as the current keeps augmenting, the elimination efficiency attains a plateau because the reaction becomes kinetically restricted by algae's mass transfer to the anode surface. An additional elevation in current raises the competing OER, decreasing the current efficiency [73] [79]. Most EO tests on algae were performed in lab-scale tank reactors mixed by continuous stirring [74] [85]. Specially engineered flow reactors have presented noticeable amelioration over tank reactors in treating wastewater samples [87]. To favor the mass transport of algae in the EO method, a commercial filter-press flow cell reactor (Electro MP-Cell) was employed, and the hydrodynamics of the reactor was assessed and modeled as a continuous stirred-tank reactor [82]. Even if the device was not optimized, it revealed the large capacity of flow reactors in eliminating algal cells [1].

Anode type	Composition	Oxidation potential (V)*	Overpotential of OER (V)*	Studies on algae inactivation
	RuO <sub>2</sub> /Ti	1.4 - 1.7	0.18	[73] [74] [75] [76] [77]
	IrO2-Ta2O5/Ti	1.5 - 1.8	0.25	[78]
Active	Pt	1.7 - 1.9	0.30	[78]
	Graphite	1.7	-	[74] [79]
	BDD	2.2 - 2.6	1.3	[72] [78] [80]-[85]
Non-active	Magnéli oxides (Ti <sub>4</sub> O <sub>7</sub> -Ti <sub>5</sub> O <sub>9</sub> -Ti <sub>9</sub> O <sub>17</sub> )	2.2 - 2.7	1.3	[86]

Table 2. Experiments on algae demobilization categorized by anode materials utilized in electrooxidation (EO)
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\*Potential values (vs. normal hydrogen electrode) are obtained from references [1] [69] [86].

In electrochemical engineering, the occurrence of electrolytes remains necessary for the electrochemical method to progress [1] [88]. In lab-scale trials, NaCl or Na<sub>2</sub>SO<sub>4</sub> is frequently injected into the algae suspension as the supporting electrolyte to reach the desired conductivity [89]. If chloride (Cl<sup>-</sup>) exists, EO forms chlorine (Cl<sub>2</sub>) [90] [91], hypochlorous acid (HClO) [92], and/or hypochlorite (ClO<sup>-</sup>), following the aqueous pH (Figure 1(a)) [52] [69] [70]. Such active chlorine species can accelerate the oxidation rate through numerous reaction pathways in addition to the coexisting direct oxidation at the anode surface and reactive oxygen species (ROSs)-mediated oxidation [1] [64]. Researchers [80] examined the EO demobilization of Microcystis aeruginosa employing a sandwich-type device with a solid polymer electrolyte. They illustrated that the synergistic influence of *in-situ* produced ozone  $(O_3)$  [93] and  $Cl_2$  species boosted the demobilization of cells and decomposition of microcystins (MCs) when 30 mg/L Cl<sup>-</sup> was introduced. Scientists [83] likewise demonstrated that the main route of M. aeruginosa demobilization was provoked by the electrogenerated active chlorine, and the level of oxidants was highly dependent on the Cl- (100 - 1000 mg/L). Practically, the BG-11 medium, primarily utilized for cultivating freshwater algae, carries approximately 18 mg/L Cl<sup>-</sup> [1] [94].



**Figure 1.** Schematic reaction pathways in (a) electrooxidation (EO) and electro-Fenton (E-F) reactions and (b) electrocoagulation (EC) and electroflotation (EF) processes [1].

In addition to the active chlorine, different chlorine oxoacids and oxyanions (e.g., chlorine dioxide ( $ClO_2$ ), chlorite ( $ClO_2^-$ ), chlorate ( $ClO_3^-$ ), and perchlorate  $(ClO_{4}^{-})$  could be generated via either direct oxidation of chloride or reaction with hydroxyl radicals formed by the oxidation of water [70]. Among these, chlorine dioxide and chlorite frequently exist considerably lower than active chlorine. Further, chlorate and perchlorate have insufficient oxidizing capabilities than hypochlorite, so the generation of such species competes for chloride and is expected to diminish the oxidation performance [69]. Also, since chlorite, chlorate, and perchlorate could cause toxicity and harmful health impacts, their maximum levels are regulated or considered for regulation [95] [96] [97]. One more dare related to the occurrence of chlorides in EO, particularly at more significant levels, is the possible generation of toxic organochlorinated DBPs like trihalomethanes and haloacetic acids [87]. The typical chloride concentration in freshwater ranges from 1 to 250 mg/L [87]. For example, increased chloride levels have been detected in U.S. rivers during the last years, particularly in urban areas, influenced by anthropogenic sources like road salt and wastewater [98]. As a result, it is not a suitable procedure to use EO for algae demobilization in chloride-rich source water or add extra chlorides as a supporting electrolyte [1].

The actual efficacy in generating active chlorine is likewise influenced by the characteristics of the anode [1]. Mixed metal oxide electrodes (especially those founded on RuO<sub>2</sub> and IrO<sub>2</sub>) are seen to be the most performant in the occurrence of chloride. The RuO<sub>2</sub>-founded anode was proven to boost hypochlorite generation [69]. Investigators [77] tested algae demobilization utilizing a  $RuO_2$ -Ti anode in simulated surface waters with low Cl levels (0 - 18 mg/L). They demonstrated that active chlorine and hydrogen peroxide  $(H_2O_2)$  were the main species inhibiting M. aeruginosa cells. While the level of chorine augmented with the elevation in Cl<sup>-</sup> level, the level of H<sub>2</sub>O<sub>2</sub> diminished. The occurrence of Cl<sup>-</sup> ameliorated the oxidation performance because of the considerable efficacy of RuO<sub>2</sub>-founded anode in forming active chlorine. In the absence of chloride, the generation of hydroxyl radicals and related ROSs from the EO of water dominates. As discussed previously, such a mechanism promotes non-active anodes like BDD. When source water carries additional salts (like sulfates, phosphates, and carbonates), BDD anodes could form persulfate, perphosphate, and percarbonate, and a greater oxidation efficacy can be obtained [87] [99]. As an illustration, researchers [78] juxtaposed the demobilization efficacy of M. aeruginosa below three electrode materials (BDD, IrO2-Ta2O5/Ti, and Pt) with various electrolytes (Na<sub>2</sub>SO<sub>4</sub>, NaNO<sub>3</sub>, and Na<sub>2</sub>HPO<sub>4</sub>). BDD anode achieved a much greater demobilization efficacy (about 99%) than the other two (10% -20%) below the identical working circumstances. The most excellent effectiveness was reached with 30 mM Na<sub>2</sub>SO<sub>4</sub> as the electrolyte. The *in-situ* electrochemical formation of persulfate was proved, and 'OH and reactive sulfate species like  $SO_4^{-}$  both participated in the increased oxidation of algal cells.

EO mainly implies the phenomena on the anode [100] [101] [102]. To completely take advantage of the electrochemical setup, cathodic phenomena (like the *in-situ* formation of  $H_2O_2$ ) may be combined with EO [1] [103]. When iron ions are introduced into the electrolyte [104] [105] [106], a hybrid setup consisting of EO and the electro-Fenton (E-F) [107] technique can considerably boost the oxidation efficacy (**Figure 1(a)**). Long *et al.* [84] examined an electrochemical device with a BDD anode, and a carbon felt cathode for demobilizing *M. aeruginosa.* When 0.2 mM Fe<sup>2+</sup> was introduced, the elimination rate was augmented 15 times. The significant amelioration was attributed to the synergistic impact among radicals generated by the BDD anode and the E-F technique. The Fe<sup>2+</sup> was regenerated on the anode surface [108] [109] [110]; thus, the Fe<sup>2+</sup>/Fe<sup>3+</sup> cycle persisted in the device to transform electrogenerated H<sub>2</sub>O<sub>2</sub> to 'OH. The EO/E-F apparatus was efficient in a large pH interval, and the elimination rate was hardly influenced by the pH interval of 3 to 9 [1].

A large plurality of experimentation on EO demobilization of algae has been performed in lab-scale setups [1] [69] [87]. As a stand-alone process, EO is not a functional technique for algae elimination, at least in terms of water treatment, due to likely side contamination troubles like the generation of DBPs throughout the method. One of the main barriers to scaling up the EO technique for functional exercise is linked to the decay of anode activity. During persistent running, a polymer film of oxidation by-products may aggregate on the electrode surface, leading to the passivation of the anode. BDD is less susceptible to electrode fouling thanks to its inert surface, even if it is still vulnerable to corrosion from anodic oxidation [60]. The first surface can be oxidized through duration, becoming more hydrophilic [111]. The alteration in surface chemistry may affect the electron transfer with redox couples on the electrode that, in turn, can influence the EO performance. EO could be better appropriate as a pre-oxidation stage to be integrated with electrocoagulation (EC) (debated in Section 2.1.2), chemical coagulation, or membrane filtration [112] [113] [114]. The following study can be dedicated to developing such a combined treatment technique and examining the contribution of EO to it.

#### 2.1.2. Electrocoagulation (EC)

In the classic disposition of an electrocoagulation (EC) device (**Figure 1(b)**), the dissolution of sacrificial anodes (usually in iron or aluminum) liberates metal ions that form flocs in coagulation [115] [116] [117]. **Table 3** summarizes the main routes encountered in EC using Fe and Al electrodes [118] [119] [120].

For instance, in the case of an Al anode, following the aqueous pH, the electrogenerated  $Al^{3+}$  ions could be converted into different monomeric and polymeric Al species [1]. Among them,  $Al(OH)_3$  is the predominant species (*Reaction* (13) and *Reaction* (14), **Table 3**) that results in the production of precipitates [123] [124] [125]. Theoretically, the amount of metal ions liberated from the anodic oxidation is stoichiometrically linked with the number of electrons passing across the electrode [126] [127] [128]. Supposing the EC technique is run under constant current, the quantity of coagulant *m* may be quantified by Faraday's laws of electrolysis (Equation (16)):

Fe Mechanisms	Medium	Reaction		
	. 1	$2\mathrm{Fe}_{(\mathrm{s})} - 4\mathrm{e}^{-} \rightarrow 2\mathrm{Fe}_{(\mathrm{aq})}^{^{2+}}$	$(E^{\circ} = +0.447 \text{ V})$	(1)
	Anode	$2H_2O_{(1)} - 4e^- \rightarrow O_{2(g)} + 4H_{(aq)}^+$	$(E^{\circ} = -1.229 \text{ V})$	(2)
<i>Mechanism # 1</i> (pH 2)Solution		$2Fe_{(aq)}^{2+} + 4OH_{(aq)}^{-} \rightarrow 2Fe(OH)_{2(s)}$		(3)
	Cathode	$8H^{\scriptscriptstyle +}_{\rm (aq)}+8e^{\scriptscriptstyle -}\to 4H^{\phantom -}_{\rm 2(g)}$	$(E^{\circ} = 0.000 \text{ V})$	(4)
	Total	$2Fe_{(s)} + 6H_2O_{(1)} \rightarrow O_{2(g)} + 4H_{2(g)} + 2$	$\operatorname{Fe}(\operatorname{OH})_{2(s)}$	(5)
		$2Fe_{(s)} - 4e^- \rightarrow 2Fe_{(aq)}^{^{2+}}$	$(E^{\circ} = +0.447 \text{ V})$	(1)
	Anode	$\operatorname{Fe}_{(\operatorname{aq})}^{2+} - e^{-} \rightarrow \operatorname{Fe}_{(\operatorname{aq})}^{3+}$	$(E^{\circ} = -0.771 \text{ V})$	(6)
		$\operatorname{Fe}_{(s)} - 3e^{-} \rightarrow \operatorname{Fe}_{(aq)}^{3+}$	$(E^{\circ} = +0.037 \text{ V})$	(7)
Mechanism # 2		$2Fe_{(aq)}^{2+} + 4OH_{(aq)}^{-} \rightarrow 2Fe(OH)_{2(s)}$		(3)
(pH 7)	Solution	$2Fe^{^{3+}}_{(aq)} + 6OH^{^-}_{(aq)} \rightarrow 2Fe\left(OH\right)_{^{3(s)}}$		(8)
	Cathode	$8H_2O_{(1)} + 8e^- \rightarrow 4H_{2(g)} + 8OH_{(aq)}^-$	$(E^{\circ} = -0.828 \text{ V})$	(9)
	Total	$3Fe_{(s)} + 8H_2O_{(l)} \rightarrow Fe(OH)_{2(s)} + 2Fe_{(s)}$	$e(OH)_{3(s)} + 4H_{2(g)}$	(10)
	Anode	$\operatorname{Fe}_{(s)} - 3e^{-} \rightarrow \operatorname{Fe}_{(aq)}^{3+}$	$(E^{\circ} = +0.037 \text{ V})$	(7)
Mechanism # 3	Solution	$2Fe_{(aq)}^{3+} + 6OH_{(aq)}^{-} \rightarrow 2Fe(OH)_{3(s)}$		(8)
(pH 12)	Cathode	$8H_2O_{(1)} + 8e^- \rightarrow 4H_{2(g)} + 8OH_{(aq)}^-$	$(E^{\circ} = -0.828 \text{ V})$	(9)
	Total	$2\mathrm{Fe}_{(\mathrm{s})} + 6\mathrm{H}_{2}\mathrm{O}_{(\mathrm{l})} \rightarrow 2\mathrm{Fe}(\mathrm{OH})_{3(\mathrm{s})} + 3\mathrm{H}_{2}\mathrm{O}_{(\mathrm{l})}$	$H_{2(g)}$	(11)
<b>Al Mechanism</b> (pH 7)	Anode	$\mathrm{Al}_{(\mathrm{s})} - 3\mathrm{e}^{-} \rightarrow \mathrm{Al}_{(\mathrm{aq})}^{3+}$	$(E^{\circ} = +1.660 \text{ V})$	(12)
		$2H_2O_{(l)} - 4e^- \rightarrow O_{2(g)} + 4H^+_{(aq)}$	$(E^{\circ} = -1.229 \text{ V})$	(2)
	Solution	$\mathrm{Al}_{(\mathrm{aq})}^{^{3+}} + \mathrm{3OH}_{(\mathrm{aq})}^{^{-}} \rightarrow \mathrm{Al}\big(\mathrm{OH}\big)_{\!\!3(s)}$		(13)
		$\mathrm{Al}\big(\mathrm{OH}\big)_{4(\mathrm{aq})}^{-} \to \mathrm{OH}_{(\mathrm{aq})}^{-} + \mathrm{Al}\big(\mathrm{OH}\big)_{3(\mathrm{s})}$		(14)
	Cathode	$8H_2O_{(1)} + 8e^- \rightarrow 4H_{2(g)} + 8OH_{(aq)}^-$	$(E^{\circ} = -0.828 \text{ V})$	(9)
	Total	$Al_{(s)} + 5H_2O \rightarrow O_{2(g)} + (7/2)H_{2(g)} +$	$Al(OH)_{3(s)}$	(15)

Table 3. Electrocoagulatio	n (EC) mechanisms	s using Fe (pH 2, 7, an	nd 12) and Al (pH 7)	electrodes [61] [10	9] [121] [122].
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$$m = \frac{I \times t \times M_M}{n \times F} \tag{16}$$

where: *I* is the applied current, *t* is the electrolysis time; *F* is the Faraday's constant (96,485 C/mol); *m*,  $M_{M_0}$  and *n* are the mass, molar mass, and valence of the anode materials, respectively [129] [130] [131]. The actual amount of dissolved metal ions has mainly been observed to be bigger than the theoretical value, and this could be affected in part by the chemical dissolution of the anode as expressed in *Reaction* (1) and *Reaction* (7) for Fe and *Reaction* (12) for Al [132] [133] [134]. The chemical dissolution is promoted at acidic pH, which can be induced by OER at the anode [1]. Also, the pitting corrosion of the anode in the occurrence of electrolyte anions can participate in the augmentation of dissolved metal ions (this is why EC is defined as accelerated corrosion) [135].

The anodic dissolution of the Fe anode mostly liberates ferrous ions (Fe<sup>2+</sup>)

(see *Mechanism* #1 (pH 2), **Table 3**), accompanied by a negligible quantity of ferric ions (Fe<sup>3+</sup>) (see *Mechanism* #2 (pH 7), **Table 3**). The coexistence of Fe<sup>2+</sup> and Fe<sup>3+</sup> (*Mechanism* #2 (pH 7), **Table 3**) leads to a more complex system than what is presented with the Al anode (Al *Mechanism*, **Table 3**). In a neutral media (*Mechanism* #2 (pH 7), **Table 3**), soluble Fe<sup>2+</sup> ions could be oxidized into Fe<sup>3+</sup>, followed by the subsequent formation of Fe(OH)<sub>3(s)</sub> [1]. At higher pH (*Mechanism* #3 (pH 12), **Table 3**), Fe<sup>3+</sup> is transformed to Fe(OH)<sub>3(s)</sub>. Even if Fe(II) species could lead to floc generation, Fe(III) species, especially Fe(OH)<sub>3(s)</sub>, are the favored species for performant coagulation. The occurrence of Fe(II) species is commonly related to the lower current efficiency of the Fe anode in EC devices. Several investigations established that below the identical circumstance, Fe anode could attain only 70% - 80% of the performance of Al anode in dealing with *M. aeruginosa* cells [136] [137].

The flocs produced in EC can precipitate like in the traditional coagulation-decantation technique [138]. Electrolysis of water can take place as minor reactions forming oxygen gas (Reaction (2)) at the anode and hydrogen gas (Reaction (4), Reaction (9)) at the cathode. In addition, the microbubbles may attach to the flocs and carry them to the surface [6] [139]. Integrating such two methods is known as electrocoagulation-flotation (ECF). The combined setup may be run either in one electrochemical cell or independently in two units [1]. As an illustration, researchers [140] assessed the elimination of *Chlorella vulga*ris employing an ECF apparatus with Al electrodes for the EC module and IrO<sub>2</sub>-Ti electrodes in a separate electroflotation (EF) chamber. The gas/solid ratio in ECF was lower than that in traditional dissolved air flotation, showing that the smaller bubbles electrogenerated in ECF were more performant in interacting with algal cells. When non-sacrificial electrodes are utilized, the device is run mainly by EF, as no metal ion-induced flocs are produced. As a result, the elimination performance of algal cells is lower than those with sacrificial anodes [141]. Non-sacrificial electrodes also need higher current densities; thus, this may only apply to sensitive metal contamination, such as algae harvesting for food products.

Ren *et al.* [1] listed new investigations on eliminating algal cells by EC/EF techniques. In addition to the kind of anode, the reduction efficacy is related to more parameters, comprising the current density, inter-electrode distance, and the occurrence of electrolyte salts [6]. Identical to the EO method, the elimination of algal cells in EC is increased with the elevation in current density to some level where an additional augmentation boosts the secondary reactions, which can provoke serious harm to algal cells and excessive remaining metal ions [137]. A shorter gap between the anode and cathode reduces the internal resistance of the electrochemical cell, decreasing the energy compulsion [142]. Moreover, a short inter-electrode gap is helpful for the mass transfer between algal cells and electrogenerated species. EC elimination performance is considerably improved with chlorides [143]. As mentioned above concerning the EO method, algal cells can be destabilized because of the oxidation impact of active

chlorine species formed at the anode. In addition, the activity of an Al electrode decays over time because of the generation of a passive oxide film [1]. The pitting corrosion provoked by active chlorine may efficiently eliminate the oxide film and form porous structures on the anode surface [143]. Consequently, more metal species can be dissolved for coagulation when chloride exists.

Juxtaposed to chemical coagulation, EC needs less coagulant, forming less sludge [8] [144]. This could be related to numerous distinctive benefits of the EC system: 1) metal ions are *in-situ* formed and consumed, so averting the overdoing of coagulant; 2) algal cells may be destabilized as a consequence of their interactions with electrogenerated active species; 3) charged algal cells could migrate to the oppositely charged electrode; and 4) the electric field itself could likewise harm cells via inducing transient pores in the membrane [67] [131] [145]. Besides, the alkalinity consumption associated with the generation of flocs is buffered by the  $OH^-$  formation at the cathode; thus, alkalinity adjustment could not be indispensable in EC devices [1].

For ideal water sources that need no amendment of electrolytes [88], electrochemical techniques comprising EO and EC may be run without injecting coagulants or oxidants, so avoiding the necessity for storage and handling of chemical products [1]. Further, electrochemical devices are compact in size and simple to adapt to automation juxtaposed to traditional techniques [69] [139]. Also, renewable energy from sources like solar photovoltaics [146] [147] [148], wind, and biomass [5] [19] could be employed to power the electrochemical methods [29] [149]. For example, a hybrid device using the power produced from a microbial fuel cell with nitrifying and denitrifying biocathodes and a sacrificial Fe anode was proved for the EC elimination of *M. aeruginosa* cells [150] [151]. Such distinctive properties can align well with the interests of decentralized treatment needs or small-scale facilities in rural areas [152] [153] [154]. In general, eliminating algae via electrochemical methods stays at the early step of technology expansion [6] [11]. Even if the idea and individual parameters of the technique have been validated in lab studies, some of the simulated conditions could not satisfy the demand of real-world utilizations. More research remains to be performed on actual circumstances in algae-laden water sources. Thus, knowledge could be efficiently transferred to pilot and full-scale operations [1].

#### 2.2. Ultrasound (US)-Enhanced Coagulation

By applying ultrasound (US, with a frequency higher than 20 kHz) into an algae-laden suspension, cavity bubbles are formed via nucleation from preexisting bubbles or surface crevice sites [1]. Bubbles then contract and expand along with the acoustic wave and induce cavitation effects in two distinct modes: stable cavitation (where bubbles oscillate over many cycles); and transient cavitation (where bubbles proliferate in a few cycles and collapse in a burst) [155] [156]. In the former case, a streaming flow driven by bubble oscillation forms a shear force, provoking mechanical destruction to cells. Transient cavitation is interesting in sonochemistry-related methods. The violent collapse of cavitation bubbles produces micro-jetting close to the surface. More importantly, the energy liberated from the rapid collapse is highly localized to a hotspot that could attain around 5000 K and 1000 bar [155] [157]. Extreme temperature and pressure break bonds, forming free radicals that initiate chemical reactions. Following the solution chemistry, a series of ROSs (like 'OH,  $'O_2^-$ ) and H<sub>2</sub>O<sub>2</sub> may be produced and harm different components of cells via oxidation [157] [158] [159].

The sonochemistry activity could be adjusted by changing the device parameters that then control the impact of US on algae [1]. The frequency of the US is linked with the amount and size of cavitation bubbles. At lower frequencies, mechanical impacts resulting from the collapse of bubbles dominate. At higher frequencies, the augmented nucleation and short time of growth lead to smaller bubbles, and a shorter bubble lifetime permits more radicals to liberate and migrate to the interface. The chemical influences begin to be dominant [155] [157] [158]. The impact of frequency on algae elimination and demobilization has been established in numerous investigations [79] [160] [161] [162]. As an illustration, Wu et al. [160] depicted that sonication at 20 kHz induced harm to M. aeruginosa primarily via direct rupture of cells; however, at 580 kHz, more radicals were generated, conducting to the demobilization of cells with less mechanical deterioration. The frequency impact is particularly significant in the experiments on cyanobacteria with gas vacuoles. The size of the gas vacuole is mostly below one µm, and the resonance size of a bubble is inversely related to the frequency of US [1]. Sonication at 1700 kHz was observed to be more performant in pushing gas vacuoles to collapse and cell inhibition as the frequency is closer to the resonance frequency of gas vacuoles [157] [162] [163]. Nonetheless, it must be remembered that as the cavitation threshold is elevated at higher frequencies, higher power intensities are requested to cause cavitation [79] [157] [158].

As a rule, a higher power density is directly linked with the elevation in cavitation bubbles and sonochemical activity [156] [164]. US intensity is determined by measuring the acoustic power entering the system via calorimetry and expressed as power supplied per unit volume, W/mL [1]. US dosage (J/mL) considers the duration of exposure and is obtained by multiplying density (W/mL) by time (s). While a higher intensity can boost the ultrasonic impact on algae, the intensity must be augmented with care since the necessary liberation of algal organic matter (AOM) resulting from cell harm and death was observed at higher US intensities [79] [163] [165]. US has as well been assessed for eliminating algal toxins and T&O compounds. Effective decompositions of MCs, 2-methylisoborneol, and geosmin via sonication were detected in some reports [166] [167]. Since the decomposition was solely attained at relatively higher US intensities, enhancing coagulation with concomitant elimination of toxins could not be a practical procedure. More AOM, comprising toxins and T&O compounds, can be liberated at such intensities as established in lab-scale tests [79] [165].

Ren *et al.* [1] listed fresh investigations concerning eliminating algae with US-enhanced coagulation. Using sonication below the suitable dosage can change the cell surface structure and destabilize the cells by decreasing the zeta potential. Thus, a similar or even better coagulation reduction could be attained at a low coagulant injection [79]. Different system components touch the best favorable circumstances; however, various investigations could still detect some general tendencies. It has been depicted that mid-range frequencies of about 500 kHz are more performant at demobilizing algal cells, and high US density and dosage could elevate the possibility of severe cell deterioration [157] [160]. Considering functional parameters involving reduction rate (turbidity, total organic carbon, or cell count), US dosage and coagulant dosage furnish a more thorough indicator to estimate the performance of US-enhanced coagulation [1].

The key sonication parameters (frequency, density, and dosage) dominate the pivotal working conditions [1]. Also, the sonication performance may be affected by additional factors in the sonication system. For example, higher dissolved gas concentrations participate in the augmentation of nucleation bubbles and lower the cavitation threshold. Dissolved gas can also directly influence the reaction mechanisms at the interface of collapsing bubbles; for instance, oxygen concentration can dictate the type and proportion of ROSs formed in the sonochemical process [155] [156]. Likewise, the occurrence of solid particles could intervene with neighboring bubbles and furnish nucleation sites for cavitation via crevices and defects on the surface of the particles. As an illustration, Wang et al. [168] utilized TiO<sub>2</sub>/biochar as a catalyst in the sonication pretreatment to boost ROSs generation. They depicted that the catalyst increased the oxidation impact on the cell membranes of *M. aeruginosa* and augmented the following coagulation elimination of cells [168]. A subsequent investigation may be performed to suggest new materials to promote the US-enhanced coagulation technique. Practically, a hybrid material with a core-shell structure can be carefully conceived so that the granules can boost the demobilization of algal cells as a sonocatalyst in the sonication pretreatment. In addition, the coating shell may be perforated and eroded by the mechanical shear force and micro jetting of sonication, so liberating the core component as a coagulant to eliminate cells in the following coagulation method [1].

Using the US as a stand-alone technique to dominate algal blooms in natural waterbodies has failed, particularly with lower US employment intensities [169] [170]. Eliminating algal cells only lasted briefly before the population recovered to its original level [158]. Higher powers proved efficacious in inactivating algae; however, different aquatic organisms (like Daphnia magna, a phytoplankton grazer) were also demobilized at these intensities [169]. Also, the related energy consumption and high operating cost may be a worry for the implementation in large open water areas. The following research may focus on the possibility of US-enhanced coagulation to reduce algal blooms. Integrating low-intensity US for cell demobilization and low coagulant injection for cell elimination can be a cost-saving strategy to treat algal blooms in natural waterbodies [1].

## 3. Applied Features of Algae Elimination in Water Treatment Technologies

WTPs embrace a multi-barrier procedure to treat water damaged by algae-related troubles (see **Figure 2**). The train of solid-liquid separation processes (*i.e.*, coagulation, flocculation, sedimentation or flotation, filtration [171] [172]) remains so efficient in eliminating algal cells when run below-optimized circumstances [173] [174] [175].

Nonetheless, such methods can potentially eliminate low-molecular-weight dissolved organic substances like cyanotoxins and different cellular metabolites, which could result in DBPs generation [176] [177]. Consequently, the global objective of solid-liquid separation treatment is to maximize the elimination of algal cells while preserving cell integrity [1] [178] [179].

#### **3.1. Pretreatment**

In some WTPs, pretreating using oxidants increases algae elimination in coagulation [180] [181] [182]. The oxidants tested are chlorine, chlorine dioxide, ozone, permanganate, and ferrate [56] [57]. If employed at a proper dosage, pre-oxidation ameliorates algae removal primarily via four routes: first, pre-oxidation modifies the structure of algal cells, and such impact is very significant for demobilizing the motile species that can get away from agglomerated flocs [183] [184]; second, pre-oxidation decreases the surface charge of algal cells, so augmenting the agglomeration of destabilized cells [56] [185]; third, pre-oxidation detaches the surface-bound extracellular organic matter (EOM) from algal cells [186], and the desorbed EOM may assist cell bridging to produce larger flocs [1] [187]; fourth, in the examples of permanganate and ferrate, *in-situ* produced MnO<sub>2</sub> or Fe(III) precipitate particles could adsorb onto the cell surface, and boost agglomeration and such amorphous species possess a large surface area that can as well adsorb some dissolved organic substances [188] [189]. However, overdosing on oxidants could lead to grave cell lysis and intracellular organic matter (IOM) liberation (involving toxins) regardless of the kind of oxidant implied [56]. IOM is more hydrophilic and includes more organic nitrogen compounds (like amino acids and proteins) [21]. Also, IOM is a more potent precursor than EOM for carbonaceous and nitrogenous DBPs [1] [188]. Since pre-oxidation can constitute a danger of liberated toxins and DBPs precursors to downstream techniques, pre-oxidation must regularly be accompanied by strict control to determine the oxidant demand that attains cell modification without compromising cell integrity. New advances in the pretreatment of algae-laden water proposed that methods founded on advanced oxidation processes could be feasible options for traditional oxidants [190]. Pre-oxidation employing Fe(II)-mediated UV/H<sub>2</sub>O<sub>2</sub> and UV/persulfate depicted encouraging findings in eliminating algal cells and decreasing the liberation of AOM and toxins [191] [192]. More studies are requested to estimate the efficiency of such methods in complex water matrices and evaluate the practicability in actual cases.



**Figure 2.** Flow diagram of a usual traditional water treatment train (the dashed line indicates the optional treatment unit) [1].

Researchers proposed that powdered activated carbon (PAC) comes after pre-oxidation to diminish the hazard of liberated toxins [1] [193]. As a rule, PAC is injected before coagulation (e.g., raw water intake, rapid mixing) to guarantee an adequate contact time. However, the PAC performance in retaining toxins could be influenced by the dose, carbon type, contact time, and interference from organic matter [194]. Besides, PAC particles can work as ballast compounds in coagulation and benefit flocs' aggregation and settling [57] [195]. Therefore, pre-oxidation and PAC must be considered when utilizing a jar test to find the optimal coagulation circumstance.

#### 3.2. Coagulation-Flocculation

Below appropriate circumstances in the coagulation-flocculation technique, algae interact with coagulants to form flocs that could be retained in the next clarification treatment stage [1] [2] [7]. Even if most investigations have been dedicated to the critical contributions of coagulants and working pH in the coagulation reduction of algae (Figure 3), the impacts of mixing circumstances still need to be considered [10] [14]. Scientists proposed that rapid mixing [24] might not be indispensable when the WTPs are run under sweep flocculation circumstances [174] [196]. However, appropriate mixing circumstances remain significant in that enough energy must be furnished to guarantee the mixing of coagulant and the development of flocs while averting the floc breakup because of overmixing [197]. Because the target of the jar test is to simulate the wanted circumstances in the full-scale operation, the mixing process is envisaged to mirror the actual events to the extent possible. A usual jar tester is equipped with multiple overhead stirrers, and the mixing energy input could be reached from the chart depicting the relationship between velocity gradient (G value,  $s^{-1}$ ) and paddle rotation speed (rpm) [1]. Even though it is primarily employed in laboratories, there are better instruments than the magnetic stirrer for mixing in the coagulation test. The rotating speed of the stirring bar noted in numerous investigations cannot be correlated to the mixing energy. Also, the flow pattern formed by a magnetic stirrer is characterized by a strong vortex with upwelling



**Figure 3.** Major factors dictate coagulation efficacy in algae elimination [1].

at the outer wall and downwelling in the axial core [198]. The introduced dye was observed to accumulate around the vortex axis with magnetic stirring [198], proving that this flow pattern could result in the inefficacious mixing of coagulants near the vortex funnel [1].

When pre-oxidation is not applied, it is usually trusted that coagulation does not provoke algae deterioration [199]. Nonetheless, there has been proof proposing that cell rupture and lysis can happen below low pH or mechanical stress [200] [201] [202]. Ghernaout *et al.* [7] proved that the jar tests of enhanced coagulation (pH 6 and alum dose 15 mg/L) as only one stage of water treatment, without chlorination and filtration, ameliorate the elimination of organic matter and algae at 97% and 99%, respectively. Notable cell deterioration and metabolite liberation were detected with *Anabaena circinalis* and *Cylindrospermopsis* below low pH circumstances (pH < 5), while *M. aeruginosa* depicted higher resistance to acidic events [201]. Scientists [200] observed compromised cell integrity and metabolite liberation with *A. circinalis*, even if the hydraulic cases in the mixing satisfied the adopted guidelines. Such findings reveal the significance of fundamental coagulation parameters, and plants must inspect and regulate operations to avert cell harm resulting from localized acidic environmental or excessive shear stress [1].

Numerous reverse osmosis (RO) desalination plants are in regions susceptible to marine algal blooms [1]. Without suitable pretreatment, the algae and related AOM in RO feed water may lead to irreversible membrane fouling [203], provoking severe negative impacts on the plant's operation. Therefore, coagulation pursued by a clarification method is frequently implemented in desalination plants to ameliorate the feed water quality [204].

Nonetheless, because of seawater's elevated salinity and alkalinity, coagulants could require to be injected at a higher dosage or even become inefficient [1]. Seawater possesses an average salinity of 35% (*i.e.*, ~ 0.7 M in ionic strength), and freshwater typically contains an ionic strength lower than 0.01 M [205].

Such dissimilarity influences metal salt hydrolyzing species' concentrations and distribution profiles in coagulation methods. For example, Al is more dissolvable in seawater as the minimum solubility of Al augments with augmented ionic strength. The minimum solubility of Al salts is also higher in warmer waters, attaining ~ 270  $\mu$ g/L at 35°C [205]. Since several desalination plants are located in warm water areas (like the Mediterranean region and the Gulf countries), the elevated concentration of residual Al can be carried over to RO membranes, provoking precipitative scaling as aluminum hydroxides or aluminum silicates. Further, the solubility of Fe salts is less influenced and stays under 1  $\mu$ g/L below an extensive range of circumstances. Thus, Fe salts are constantly employed in full-scale RO desalination plants to avert scaling trouble [204].

#### 3.3. Clarification

When sedimentation is employed, the coagulation-flocculation is mostly run below the sweep flocculation pathway to produce large and compact flocs of algae that can defeat the fluid drag and buoyancy [1] [2] [174]. As a substitute clarification method, dissolved air flotation (DAF) has been adopted as distinctly convenient for dealing with algae-laden water thanks to the fact that the density of algal cells is usually low and numerous species with gas vacuoles possess sufficient buoyancy [206]. Robust, even if smaller flocs keeping a particle size distribution of 10 - 30 µm are supposed to provide the best elimination effectiveness in DAF [207]. In DAF, large flocs are not requested, and the shear stress and turbulence when injecting air bubbles could break the large flocs. DAF is very performant in capturing small flocs, so it is a robust method relatively insensitive to the coagulant selection and operation regime [208]. The substantial efficacy of DAF in eliminating algal cells has been proved in many cases [208] [209]. In addition, a DAF device could cancel the necessity for a traditional coagulation-flocculation treatment stage. Without coagulation-flocculation, microbubbles can be functionalized with cationic surfactants or polymers to reach stronger cohesion between bubbles and algae. Cell eliminations above 90% were attained [210].

#### 3.4. Filtration

In the traditional treatment train, filtration is the last primary stage to eliminate algae from water physically [1]. In the filter, granular media are employed, and their characteristics could influence the filtration effectiveness. Filtration can efficiently retain algae trapped in flocs.

Free cells may escape from the filter media following the filter makeup and algae properties. Researchers [211] explored the impact of algal biodiversity on the elimination efficacy utilizing a lab-scale treatment setup comprising coagulation, sedimentation, and sand filtration. The raw water samples collected from three eutrophic lakes had cell densities of  $3.93 - 13.1 \times 10^5$  cells/mL, and 25 - 55 algal species were observed. Their findings proposed that species with a needle, filament, or plate-like morphologies or protruding structures like thorns or fla-

gella harmed the global elimination efficacy. Also, higher removal efficacies were detected in raw water with more extraordinary algal biodiversity. Species with an elongated shape or larger size could interact with tiny algae through bridging or sweeping routes. The residual algae in the filtration effluent mainly consisted of smaller cells with a spherical shape, like those from the genera of *Gloeocapsa* and *Chlorella*. Identically, other scientists [212] followed the effect of cell morphonology on the filtration reduction rate with a pilot-scale in-line filtration setup (coagulation followed by filtration). The cell numbers of spherical *M. aeruginosa* were invariably higher than those of *Aphanizomenon flos-aquae* (filamentous) in filtered water. In contrast, a constant breakthrough of *Aphanizomenon* in filtered water was noted by researchers [213] in a traditional potable WTP that was observed during a bloom season.

## 4. Conclusions

Using coagulation for eliminating algae remains complicated as such a process is affected by several factors. The critical elements implicated in the coagulation method may be grouped into three classes: water quality parameters comprising those linked with algae features, coagulant parameters, and mixing circumstances. Several of such factors interact with each other via either direct or indirect relationships; thus, the variation of one parameter could touch the efficacy of the overall technology [1]. The summary and analysis of present investigations on coagulation techniques for algae elimination lead to the subsequent conclusions and recommendations for future study:

1) Most coagulation investigations concentrate on only one or two factors' impacts while maintaining the remaining fixed conditions. One of the frequent procedures is to examine the implications of coagulation circumstances (i.e., coagulant, dosage, and operation pH) on reducing some algae species utilizing the same water parameters. The other is to contrast the elimination efficiencies of various algae below the same coagulation conditions. Until now, decisive predictions could not be made concerning how a certain algal species would respond to the modification in coagulation circumstances. Several findings published in the literature are case-specific, making it hard to directly juxtapose the different investigations' conclusions. It is crucial to describe complete data regarding trial circumstances, like the parameters of raw or synthetic water samples, the properties and density of algal cells, the composition and features of coagulants, and the parameters of treated water. The hydraulic circumstances for mixing in the jar test must also meet the guidelines in full-scale operation. For new coagulation technologies, which imply the electrochemical process or the application of sonication, a full detailing of the reactor configuration must be comprised in the literature in addition to the usually reported water parameters and coagulation circumstances. It is also critical to study real-world conditions when performing tests if such techniques are expected to be utilized in practical applications.

2) To maximize algae elimination, the traditional water treatment train regu-

lates the entire solid-liquid separation technology (comprising coagulation, clarification, and filtration as multiple barriers). Even if most algae elimination is realized through clarification, filtration also captures the residual algae [214]. Utilizing settled water quality in a jar test as the exclusive efficacy indicator could lead to an augmented coagulant introduction being determined as optimal without any critical benefit to the finished water quality. It could be helpful to combine a filter column into the jar tester to simulate the solid-liquid separation process in the traditional water treatment plant. The optimal running circumstance to retain algae is assessed, considering the optimized effectiveness of the global system instead of a single unit [1].

3) Pre-oxidation must be avoided because of the possible lysis of algae cells; further, algal growth may be controlled with more frequent cleaning of the basins, especially in summer periods, and coverage of open sedimentation basins would be avoided to benefit from solar radiation disinfection and oxygen diffusion from the air. Chlorine can be maintained as a final disinfectant if organic precursors are sufficiently removed. It remains to be seen that the conventional water treatment (clarification + filtration + chlorination) will continue to be a viable solution for drinking water from source waters containing organic matter as their quality deteriorates and water quality standards become more difficult to achieve [3].

4) During the previous years, with the fast expansion of machine learning (ML), there has been an increasing interest in employing ML algorithms to deal with complicated troubles in environmental science and engineering [215]. ML is superior to conventional statistical analysis in modeling complex systems (like the coagulation phenomenon) with weak or nonlinear relationships between numerous variables [1]. In some preliminary trials, ML algorithms were trained to predict the treated water quality founded on the coagulant injection or assess the coagulant injection to attain the wanted effluent quality [215]. Also, ML algorithms can be trained with various monitoring data [216] [217] [218] to ameliorate the forecasts for HABs and estimate the threat to water utilities and the general public [219] [220] [221]. Until now, employing ML to explore the coagulation elimination of algae has been rare [222]. The following studies may concentrate on leveraging ML to divulge the interactions between different factors and elucidate the divergent behaviors of algal species in response to the alteration of coagulation circumstances. One more crucial aspect of ML is that a robust algorithm can only be obtained when a broad and diverse range of data sets are utilized in the training process. A large dataset concerning the troubles and solutions related to algal blooms needs cohesive efforts from monitoring systems, water utilities, and research communities. The development of ML algorithms must concentrate on predicting the coagulation circumstances in response to the changing algal features and water parameters, diminishing the need for trial-and-error optimization procedures such as jar tests. In the future, intelligent control systems powered by ML will be combined with the entire water treatment process [1].

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## **Conflicts of Interest**

The authors declare no conflicts of interest regarding the publication of this paper.

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## Abbreviation

AOM	Algal organic matter
BDD	Boron-doped diamond
DAF	Dissolved air flotation
DBPs	Disinfection by-products
E-F	Electro-Fenton
EC	Electrocoagulation
ECF	Electrocoagulation-flotation
EF	Electroflotation
EO	Electrooxidation
EOM	Extracellular organic matter
HABs	Harmful algal blooms
IOM	Intracellular organic matter
MCs	Microcystins
ML	Machine learning
OER	Oxygen evolution reaction
PAC	Powdered activated carbon
RO	Reverse osmosis (RO)
ROSs	Reactive oxygen species
T&O	Taste and odor
US	Ultrasound
WTPs	Water treatment plants