Hungarian University of Agriculture and Life Sciences

Szent István Campus

MSc in Environmental Engineering

Coagulation and Sedimentation of Algae in Wastewater

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1 - Introduction and Objectives

Currently, 1.1 billion people globally require improved access to water supplies, and 2.4 billion are at risk of contracting waterborne illnesses including typhoid fever, cholera, diarrhea, etc. because of inadequate sanitation facilities.

By 2025, 2/3 of the world's population will be living in water-stressed conditions, and more than 1.8 billion people will experience complete water scarcity. The serious condition calls for the growth of cost-effective treatment methods, efficient management of water resources, and source water protections.

Algal blooms typically occur when there are high nutrient concentrations, especially when there are warm, sunny, and calm hydraulic conditions. Harmful algal blooms (HABs) are the proliferation of microscopic algae that significantly increase health risks to the environment by producing toxins (i.e., Microcystis (MCs)) or bioactive compounds that accumulate in shellfish or fish, or by accumulating Microcystis aeruginosa biomass that negatively impacts the co-existing organisms and alters food chains. The onset of an algal bloom leads to the death of livestock and aquatic species as well as a catastrophic decline in water quality (Department *et al.,* 2020).

The increasing occurrence of harmful algae blooms globally poses significant challenges to water management. In water treatment utilities, coagulation is the first treatment process of the multi-barrier strategy designed to address algae-laden source water. Since the coagulation efficiency directly impacts all downstream treatment processes, it is critical to optimize coagulation conditions to remove algal cells to the extent possible without causing cell damage. Moreover, the importance of coagulation extends to source water management. Coagulation-based processes have demonstrated great potential as in-lake measures to mitigate eutrophication and control algal blooms.

Coagulation and sedimentation are commonly used processes in wastewater treatment to remove suspended algae and other particles from the water. The process involves the addition of chemicals, such as alum or ferric chloride, which form flocs that trap algae and other impurities.

Algae are particularly difficult to remove from water, as they are often small and have a negative charge on their surface. Calcium chloride can effectively neutralize the negative charges of algae cells, causing them to clump together and settle out of the water.

Overall, calcium chloride can be an effective and cost-efficient coagulant for algae coagulation in water treatment systems. However, as with any chemical treatment, proper dosing and monitoring are essential to ensure optimal performance and minimize potential health or environmental risks.

In this research, we studied the effect of $CaCl_2$ as a coagulant to enhance the coagulation process to remove algae from wastewater where we use three cylinders to make the experiments and the concentrations that we used is 0 for the control sample and 400 mg/L and 800 mg/L.

In this research, we investigate the effectiveness of using $CaCl_2$ as a coagulant aid in accelerating the process of sedimentation and coagulation of algae in wastewater.

2 - Literature review

2.1-Algae

There exists an extensive variety of eukaryotic microorganisms capable of carrying out photosynthesis known as algae. These algae species can be found in diverse ecological environments such as freshwater, seawater, snow, soil, and hot springs, among others. Their total number of species exceeds 50,000 (Raven et al., 2014).

Microorganisms that are capable of carrying out photosynthesis have the unique ability to rapidly multiply and proliferate in vast numbers. In order to sustain this growth, these organisms require a source of inorganic materials such as carbon dioxide, as well as light energy and an abundance of vital nutrients like nitrogen and phosphorus. This intricate web of environmental factors and biological needs creates a delicate balance that is essential for the continued growth and survival of these vital microorganisms (Raven et al., 2014).

Figure: 1 Algae

Algae can be broadly categorized into filamentous (often break off from the lake bottom to form masses that resemble rafts on the water's surface), macroalgae (algae that can be seen without the use of a microscope), and planktonic forms (free-floating microscopic plants that are identified under the microscope and usually measured in micrometers). These algae are typically a sign of higher nutrient concentration in a certain water body when they are present in the water. Lakes are categorized as oligotrophic, mesotrophic, eutrophic, and hypereutrophic based on the amount of nutrients present. Algal blooms are brought on by an excess of nutrients and can clog screens, affect the taste and odor of drinking water, make a body of water look unattractive, and hurt the local economy by reducing the recreational use of the water. Some of the toxic algal blooms release poisons that can seriously endanger both people and animals.

Algae have been used for a very long time, and phycologists are always trying to understand their economic significance and all the good and bad things about them. Primary producers, a source of nutrition for both humans and animals, a provider of antibiotics and medications, a purifier of wastewater, source of biofuel, a fertilizer, and a pollution controller by fixing CO2 are just a few of the advantageous roles that algae play. Biofuels such as biodiesel, biohydrogen, and methane can be produced from microalgae biomass (Demirbas, 2010). Additionally examined as potential commercial uses for microalgae were dietary supplements, fatty acids, stable isotopic biochemistry, phycobiliproteins, and carotenoids. (Milledge, 2011). Microalgae are still not economically viable for commercial use despite substantial research. There is extensive documentation on the commercial development of microalgal biotechnology (Olaizola, 2003). Typically, the cost to harvest microalgae is between 20 and 30 percent of the cost to produce microalgal biomass (Molina Grima et al., 2003). Algal harvesting additionally requires significant energy input. 90% of the entire cost of producing algal biomass from open ponds is thought to be incurred by harvesting and dewatering equipment (Amer et al., 2011).

2.2 - The role of algae in wastewater treatment:

Wastewater, which is generated from various human activities, typically contains nitrogen (N) and phosphorus (P), two important nutrients that play a significant role in the growth and development of aquatic plant and animal life. However, if these nutrients are not effectively removed before discharging into the environment, they can lead to a harmful buildup that can be detrimental to the delicate ecosystem. This unwanted buildup can occur in lakes, streams, rivers, and other water sources, resulting in a process known as eutrophication, whereby water bodies become densely populated with algae and other plant life.

Excess nutrients in water can lead to the rapid and extensive growth of algae blooms, which can persistently shade and consume oxygen from the water, leading to environmental degradation and toxicity that can adversely impact the health of local fish and other aquatic species. To prevent this scenario from occurring, strict limits are often placed on the discharge of nitrogen and phosphorus, to ensure that the delicate balance of the ecosystem is maintained and that the health of the environment is preserved for years to come. Consequently, removing nitrogen and phosphorus from wastewater is crucial for environmental protection and the sustainability of our planet's aquatic resources.

Wastewater treatment processes have traditionally been viewed as a means to dispose of the unwanted nutrients of nitrogen (N) and phosphorus (P) that are present in wastewater. However, more recent technological advancements have made it possible to turn these nutrients into valuable resources through the use of algae. This innovative approach involves growing algae in the wastewater and using its natural capabilities to consume the nutrients present in the water while producing valuable biomass that can be harvested and sold.

This method of wastewater treatment with algae not only facilitates the recovery of N and P but also provides a cost-effective and environmentally friendly solution. Rather than wasting resources through conventional disposal methods, algae-based wastewater treatment represents a significant step forward in the shift towards a more sustainable and circular economy. By harnessing the power of these natural organisms, wastewater treatment can become a critical source of raw materials, leading to reduced waste, lower costs, and greater environmental protection for future generations to come (Kube et al., 2018).

Algae have an important role in the purification of wastewater (sewage water), where the algae carry out the process of photosynthesis, which results in the release of oxygen, which is used by the bacteria present in the same place and works to break down complex organic materials and convert them into simple nutritional forms Algae benefits from it, grows and multiplies, and this leads to speeding up the purification process and ridding the water of its excessive loads.

2.3 - Microalgal harvesting methods

2.3.1 - Coagulation and flocculation

Microalgae cells are distributed, have a density close to the growing medium, and have a negative surface charge. Slow natural sedimentation is the product of this steady system. Pre-flocculation or coagulation is an effective harvesting technique for these microalgae (Chen et al., 2011). Utilized are substances known as flocculants, which balance the negative charge and enable microalgae to aggregate. It has been suggested that flocculation is a better method for collecting microalgae since it can be applied on a large scale and with a variety of microalgae species (Molina Grima et al., 2003). Electrostatic patch (or patching), bridging, or sweep flocculation are all methods of inducing flocculation (Vandamme et al., 2013).
(Chen et al., 2011) says that the main process involved in the flocculation of microalgae is surface charge neutralization. The ideal chemical coagulant would be cheap, nontoxic, effective at low dosages, renewable, sustainable, and allow reuse of the culture media. It would also prevent biomass contamination (Molina Grima et al., 2003). In the past, numerous researchers have harvested microalgae by using a wide variety of salts as coagulants. Despite being cost-effective, the flocculation chemicals can be dangerous and pollute the algal biomass (Lee et al., 2009). Inorganic, organic, or polyelectrolyte flocculants can be used as flocculants depending on their chemical composition (Chen et al., 2011).

Microalgal cells are flocculated using inorganic chemical flocculants such as multivalent cations of aluminum sulfate, ferric chloride, and ferric sulfate that, at an ideal pH, produce polyhydroxy complexes that neutralize and reduce the negative surface charges on microalgal cells (Chen et al., 2011). The electronegativity and solubility of these multivalent salts determine how effective they are. Faster coagulation is caused by more electronegative ions. Similar to how less soluble salts work better (Barros et al., 2015). Metal coagulants can easily cause flocculation, but they are not environmentally friendly, and the increased dissolved solids, contaminated biomass, altered growth medium, and coloration prevent their use in the harvesting of algae for biofuel or animal feedstock. Ferric salts are less effective than aluminum salts (Shelef et al., 1984). It is possible for organic flocculants or polyelectrolytes to be cationic, anionic, or non-ionic (such as polyacrylamide or polyethyleneimine). The physical connection between cells that cationic polymers create allows them to flocculate, but electro-repulsion prevents anionic or non-ionic polymers from producing flocs in microalgae. The features of the polyelectrolyte, such as charge and functional groups on the surface of microalgae, growth media pH, and density of the algal culture, all affect how well it may cause flocculation (Chen et al., 2011). Cationic polyelectrolytes, according to the article, produced up to 35 times more concentrated biomass than metal salts. In contrast to anionic polyelectrolytes, which do not flocculate, cationic polyelectrolytes with high charge density are more effective flocculants for harvesting microalgae, and the effective dose decreases with an increase in coagulant molecular weight (Uduman et al., 2010).

Chemicals or microorganisms can flocculate; however, the excess flocculant requirement frequently renders this process too expensive for large-scale operations. Its downstream usage for food or feed is constrained by additional drawbacks such as high sensitivity to pH, contamination of harvested biomass, and recycling of flocculants, which likely render it uneconomical for commercial use (Pushparaj et al., 1993). When the biomass concentration is high and the stirring speed is slow, this approach is more effective. The effectiveness of flocculation can also be influenced by the ionic strength, pH, molecular weight, and charge density of the flocculant (Molina Grima et al., 2003). Similar to this, the number of nutrients like phosphorus and nitrogen, alkalinity, ammonia, dissolved organic matter, algal type, and temperature of the algal culture can similarly affect the ideal coagulant dose (Show et al., 2015). Polymer dosing has a substantial impact on flocculation efficiency; however, it is challenging to1 achieve optimal polymer dosing due to the fluctuation of numerous factors throughout the algal development cycle. Weak bridging and lose flocs are caused by low dosage, whereas electrostatic hindrance is caused by heavy dosing, which reduces bridging potential (Gerardo et al., 2015). Harvesting microalgal biomass during the stationary growth phase may be facilitated by low zeta potential, low metabolic activity, and significant intercellular connections (Danquah, Ang, et al., 2009). For more efficient harvesting, flocculation is typically employed in conjunction with other harvesting methods.

Depending on the use of the microalgae, coagulation and flocculation, filtering, and centrifugation are among the most popular harvesting procedures. Coagulation and flocculation are the greatest options for producing biofuels and improving water quality based on the six key criteria. Similarly, filtration and centrifugation are the ideal methods for harvesting biomass for high-value items like food for humans and animals. For harvesting microalgae for various uses of microalgae and water quality restoration, coagulation and flocculation, filtration, and centrifugation may be utilized alone or in combination.

2.3.2 - Chemical coagulation/flocculation

The key strategy for the economically efficient optimization of microalgal harvesting procedures is chemical coagulation/flocculation. Application of these techniques is necessary primarily due to the substantial amounts of microalgal cultures that must be processed and the requirement for an all-purpose technique that can be used with a wide range of species (Uduman et al., 2010). The suspension is 20–100 times more concentrated after this harvesting process (Vandamme et al., 2013). Before dewatering, it improves the effective particle size, greatly lowering the energy need (Molina Grima et al., 2003). Coagulation/flocculation is usually followed by gravity sedimentation for the low-cost harvesting of microalgae (Smith et al., 2012).

While flocculation is dependent on adding cationic polymers to the broth, coagulation entails adjusting pH or adding electrolytes (Papazi et al., 2010). The coalescence of finely divided particles in suspension onto bigger aggregates, followed by the agglomeration of these into larger flocs, which sink to the bottom of the vessel, leaving a clear supernatant, is one method to characterize chemical coagulation/flocculation. Flocculation can be brought about in a variety of ways, including electrostatic patching (or patching), which happens when a charged polymer binds to an oppositely charged particle, locally reversing that charge, and creating a patch that will connect with oppositely charged patches; (ii) bridging (forming a bridge between two different particles), which happens when polymers or colloids bind to the surfaces of the particles; and (iii) sweep flocculation (Vandamme, et al., 2013). The concentration of coagulant/flocculant species, cellular concentration, and surface qualities like net charge and hydrophobicity, as well as pH and ionic strength of the broth, all have a significant impact on this process (Papazi et al., 2010). Because of the considerable fluctuations in pH, dissolved CO_2, zeta potential, and particle size over the cultivation period, the microalgal growth phase also affects flocculation (Shelef et al., 1984). Therefore, it is advantageous to think about harvesting microalgal biomass during the stationary phase. The zeta potential is lower in this phase, which results in lower metabolic activity and cell mobility in the microalgae, and stronger intercellular connections. The larger particle size, which may be the result of cell agglomeration, also supports this. Additionally, the circumstances of storage prior to harvest are common. Low settling rates are caused by photosynthesis, which increases metabolic rate and unicellular movement in the presence of daylight (Danquah et al., 2009). Chemical coagulation/flocculation should ideally: I do not contaminate the biomass; (ii) produce a high-efficiency biomass settler; (iii) permit the reuse of the culture medium;(iv) take environmental effect into account; and (v) be inexpensive and non-toxic when used on a wide scale (Molina Grima et al., 2003).

The objective of the succeeding operations is to influence the choice of the right coagulant, as it does for all harvesting techniques. The application of ferric salts has been proven to cause the microalgae to turn brown, and yellow in color. Cell viability and the photosynthetic system, however, showed no effects. In this sense, ferric salts cannot be used if pigment extraction is the goal. On the other side, a cheaper and speedier coagulant, like aluminum salt, should be used if the goal is to lower the entire production cost. Cell lysis was detected (10–25%) when utilizing aluminum salts, potentially because of accelerated cell aggregation or cell membrane instability (Papazi, et al., 2010).

Although coagulation/flocculation followed by gravity sedimentation is a low-cost method for harvesting microalgae, the cost of the coagulant accounts for a sizeable amount of the entire procedure (4–7%). As a result, using naturally occurring coagulants and flocculants like phosphates, carbonates, calcium, and magnesium ions, which are typically found in wastewater, brackish water, or seawater, have been investigated (Smith et al., 2012). However, phosphate-based coagulation is only practical for phosphate-rich wastewater because microalgae hoard phosphate when it is given to a free medium in addition to utilizing it for metabolism. However, as magnesium ions can be cheaply acquired from wastewater and have efficiencies comparable to those of Al^{+3} and Fe^{+3} ions, using them as coagulants may be advantageous. Additionally, adding lime to the culture broth can improve the effectiveness of coagulation (Schlesinger et al., 2012).

The necessary coagulant dose is also influenced by the broth's ionic strength. For instance, because the chemical activity of the coagulant is decreased by the presence of marine salts, the flocculation of marine microalgae requires five to ten times greater coagulant dose than that of freshwater ones (Uduman et al., 2010).

2.3.3. - Gravity sedimentation

Despite the crude nature of the procedure, sedimentation is highly energy-efficient and effective for a variety of microalgae (Rawat et al., 2011). Gravity sedimentation should therefore be chosen for microalgal harvesting when the final product has a very low value, such as biofuels (Molina Grima et al., 2003).

The procedure efficiency depends on microalgal density; hence this method's dependability is limited. A relatively slow sedimentation process caused by microalgal settling rates of 0.1 to 2.6 cm per hour limits the use of this technology for routine harvesting because most of the biomass degrades during the settling time (Christenson et al., 2011). In this approach, it is typical to use a coagulation/flocculation phase before gravity sedimentation to speed up microalgal settling (Chen et al., 2011).

Due to microalgal auto-flocculation, lamella-type separators and sedimentation tanks produced the highest results for microalgal harvesting utilizing gravity sedimentation, recovering 1.6% TSS and 3% TSS, respectively (Show et al., 2014). Although using sedimentation tanks is thought to be a straightforward and affordable method, the concentration that may be achieved without prior coagulation or flocculation is quite low. Similar to this, lamella-type separators' ability to concentrate microalgae is low and unstable, necessitating additional thickening. Utility companies that treat water use a multi-barrier approach to deal with algae-contaminated source water. In traditional drinking water treatment techniques, coagulation is typically the initial step in the process. The efficiency of coagulation directly influences all subsequent therapy procedures. Toxins, T&O compounds, and other biological metabolites can be released by damaged algal cells, which may result in the creation of disinfection byproducts (DBP) (Chisti, 2007); To maximize the removal of algal cells while preserving cell integrity, coagulation, and the subsequent solid-liquid separation techniques (such as clarifying and filtration) are used. Coagulation is crucial for dealing with algae issues outside of treatment facilities. Reducing the nutrient loads entering waterbodies is the main technique from the perspective of water management to prevent and control eutrophication and algae-related issues. Regulatory discharge restrictions can be reached by using cutting-edge technology for increased nutrient removal. Point-source nutrients connected to urban and industrial wastes are generally simple to identify. However, because of the highly unregulated nutrient inputs from nonpoint sources, point-source nutrient reduction measures are frequently ineffective (agricultural drainage, soil erosion, urban runoff, household septic systems, etc.) (Gonçalves, et al., 2013). It may take years or even decades for nonpoint-source nutrient reduction measures, including using best management practices in agriculture, to demonstrate improvement. This could be brought on by the internal cycling of nutrients that have built up in the sediment as a result of constant external loading. As a result, there is a growing understanding that actions to address internal legacy phosphorus (P) loading within a water body must be taken through geo-engineering. Engineering methods based on precipitation and coagulation have shown tremendous promise for reducing eutrophication and managing algal blooms (Gonçalves, et al., 2013). In this method, aggregated algal flocs are sunk into the sediment using coagulants and ballast materials. Combinations of P- sorbent materials can be utilized to remove P from the water column and lessen sediment discharge. Such lake treatments are crucial to water management because they may directly improve the water's quality while bridging the time until longer-term preventive actions (such as external nutrient reduction) take effect (Marcilla et al., 2013).

Although coagulation is one of the most well-known methods for treating water, it still significantly relies on an empirical method called the jar test. The coagulation process is made more challenging by several interrelated variables, such as those from water matrices and operational circumstances. The various biological characteristics of algae add to the system's complexity(Atabani et al., 2012).

When dealing with complicated water matrices, the conventional colloidal models and flocculation theories can fall short in describing the interaction mechanisms in the coagulation process and are thus of limited help in forecasting the results (Becker, 2013). Despite the expansion of this field's study, the experimental setups used in these investigations are frequently very different. Additionally, many studies lack a thorough explanation of the experimental circumstances, which makes it challenging to compare and transfer knowledge between other coagulation systems. Traditional coagulants have been in use for many years and, when applied under ideal circumstances, produce good results. To achieve the regulatory objectives, coagulants, however, frequently need to be administered at a greater dosage for water that is algae-rich. This procedure produces a lot of sludge, which must be thoroughly treated before disposal, increasing the overall operating costs (Papazi, et al., 2010). Additionally, there has been an ongoing discussion on the environmental effects and long-term safety of these conventional coagulants (e.g., the potential adverse effects of aluminum and synthetic polymer coagulants). Therefore, a variety of novel coagulants based on materials of natural origin have been developed in response to the need for new types of coagulants that are safe, effective, and economical. Combining coagulation processes with novel approaches like electrochemical processes and sonication is another recent advancement in algae removal (Danquah, Gladman, et al., 2009). These hybrid treatment methods could use renewable energy and require less chemicals during the coagulation process.

2.3.4 - Microbiological composition of sewage

The composition of sewage is largely comprised of microorganisms, including bacteria, viruses, and protozoa, making it an ideal environment for their growth and proliferation. While a majority of these microorganisms are harmless and often utilized in biological sewage treatment, there are also numerous pathogenic microorganisms present, many of which are excreted in high concentrations by symptomatic individuals and carriers of various diseases. Sewage hosts a multitude of dangerous bacteria including those responsible for causing cholera, typhoid fever, and tuberculosis. Additionally, harmful viruses, such as those that cause infectious hepatitis, as well as protozoa that cause dysentery and parasitic worms in their egg form can also be found in sewage. Overall, the complex microbiological composition of sewage underscores the importance of proper wastewater management to safeguard both public and environmental health (Abdel-Raouf et al., 2012).

2.4. - Conventional sewage treatment technology

2.4.1. - Preliminary treatment of sewage

Large solids carried by sewers that could restrict plant flow or harm equipment are removed during the initial treatment of sewage. These substances are made up of floating debris like rags, wood, feces, and larger grit particles. By running the sewage through bars spaced 20–60 mm apart and periodically raking the material that has been retained from the bars, large floating objects can be eliminated (Tebbutt, 1997). By lowering the flow velocity to a level where grit and silt will settle but the organic matter will remain in suspension, typically in the range of 0.2 to 0.4 m/s, grit can be eliminated (Gray, 2004).

2.4.2 - Primary treatment of sewage

Following the removal of the coarse debris, sewage is directed to sedimentation tanks with the intention of gravity-removing the settleable solids, which can make up to 70% of the total settleable solids. A properly constructed sedimentation tank may eliminate 40% of the BOD as settleable solids. With varying clearance rates reported for diverse organisms, pathogen elimination during the first therapy is highly variable (Horan, 1989).

2.4.3 - Secondary treatment of sewage

The secondary treatment method seeks to lower the BOD by removing organic materials.
For the aerobic oxidation of BOD, a wide range of biological unit actions are accessible. Based on their microbial populations, all processes can be divided into fixed film or scattered growth processes. Organic chemicals are absorbed into the biofilm and aerobically destroyed in fixed film reactors that have biofilms connected to a fixed surface. Microorganisms freely interact with wastewater in suspended (like activated sludge) growth reactors and are maintained in suspension by mechanical agitation or mixing with air diffusers (Horan, 1989).

Several researchers have noted that while biological oxidation systems can eliminate over 90% of dangerous bacteria from sewage, there are many ways to eliminate viruses. Adsorption is regarded to be the main method of virus elimination. 90% of the solid flocs and sewage are removed in suspended growth reactors through intimate mixing, whereas film reactors' lesser surface areas for biological adsorption sites result in a range of decreases.

2.4.4 - Tertiary treatment of sewage

The final stage of treatment tries to eliminate all organic ions. It can be carried out chemically or biologically. When compared to chemical treatments, which are typically too expensive to be used in most places and which may cause secondary pollution, the biological tertiary treatment technique seems to perform better. Additionally, the price of a wastewater system rises significantly with each new treatment step (Abdel-Raouf, et al., 2012).

It is projected that a full tertiary procedure that removes ammonium, nitrate, and phosphate will cost nearly four times as much as primary treatment. In order to remove heavy metals, organic compounds (refractory and toxicants), and soluble minerals, quaternary treatment will be between eight and sixteen times more expensive than primary treatment, respectively(Abdel-Raouf, et al., 2012).

Modern treatments typically rely on highly sophisticated technological processes such as chemical precipitation, ozonation, reverse osmosis, or carbon adsorption. These methods include those intended to eliminate specific nutrients, such as phosphorus or nitrogen, which under some circumstances can promote eutrophication. The removal of tiny particles can permit discharges below the goal criteria, especially in small-scale applications, for general improvements in effluent quality. These systems comprise sand or gravel filters for filtering, lagoon storage, and land application. (Gray, 2004).

Total nitrogen and phosphorus concentrations in some industrial and agricultural wastewater are up to three orders of magnitude higher than those in naturally occurring water basins. In order to remove the easily settled materials (primary treatment) and oxidize the organic material present in wastewater, the standard primary and secondary treatment methods have been used in an increasing number of locations (secondary treatment). The result is an effluent that is discharged into natural water bodies that are transparent and appears to be clean. However, due to the release of refractory organics and heavy metals, this secondary effluent is highly concentrated in inorganic nitrogen and phosphorus and causes eutrophication as well as further long-term issues(Abdel-Raouf, et al., 2012).

According to (Abdel-Raouf, et al., 2012), the organic matter was being destroyed by chemoorganotrophic microorganisms, and the natural purification processes revealed that both aerobic and anaerobic mechanisms were in use. Additionally, they stated that current biological wastewater treatment techniques still rely on the same kinds of self-purification that occur naturally. The distinction is that they are housed in facilities intended to expedite the treatment process.

2.4.5 - Disinfection of wastewater

Disinfection is the process of treating effluent to eliminate all pathogens. Sterilization is a different word that is occasionally used to describe the eradication of microorganisms. The elimination of all microbes is sterilization. While sterilization is not a goal of wastewater treatment, disinfection signifies the elimination of all disease-causing germs. However, using disinfection techniques on wastewater will cause a significant decrease in all microorganisms, bringing bacterial counts down to a safe level. In general, any technique that eliminates microorganisms can be used to disinfect an area. Microorganisms can be eliminated using a variety of physical or chemical techniques in some situations. Physical techniques could involve boiling, burning, or exposure to X-rays or UV rays, among other things. Theoretically, chemical techniques might involve the use of powerful acids, alcohols, or a range of oxidizing substances or surface-active agents (such as special detergents). However, the treatment of wastewater for the eradication of pathogens necessitates the employment of constant, cost-effective, and practical techniques that can be applied to vast volumes of wastewater that have undergone varying degrees of treatment. In the past, chlorine was mostly used for disinfection in wastewater treatment methods. Because chlorine is a superior disinfectant agent and, until recently, was accessible at a fair price, it has become widely used. However, chlorination is no longer the disinfectant of choice for wastewater treatment due to the rising expense of chlorine, the fact that it is poisonous to fish and another biota even at low concentrations, as well as the risk that potentially dangerous chlorinated hydrocarbons may occur. As a result, it is quite likely that ozone (ozonation) or ultraviolet radiation will be used more frequently in the future to disinfect wastewater. In addition to being powerful disinfectants, ozone, and UV light also leave no hazardous aftereffects. Ozone will also increase the amount of dissolved oxygen in water. However, ozone must be produced, and it has only lately started to economically outperform chlorination. Recent research has examined the cost and efficacy of using ultraviolet light in big wastewater treatment facilities. While the research is still ongoing, UV light presently seems to be a disinfectant that is both effective and cost-competitive with chlorination. Both chlorine and ozone are used as chemical disinfectants, and their respective roles in disinfection will be discussed. However, because chlorine is still widely employed as a disinfectant, our main focus will be on the theory and application of chlorination(Abdel-Raouf, et al., 2012).

Hybrid methods have been developed to treat polluted water.

The operating cost of the wastewater treatment plant is highly expensive (Abdel-Raouf, et al., 2012).

Disadvantages of conventional treatment processes:

1-The efficiency is not stable depending on the nutrient to be removed.

2- High cost to operate.

3- The chemical processes often cause secondary pollution.

4- Loss of valuable potential nutrients (N, P) (de la Noüe, et al., 1992).

2.4.6 - Microalgae Treatment Method:

Due to their capacity for absorbing nutrients and converting them to biomass, microalgae are regarded as one of the more advantageous wastewater agents (Chinnasamy et al., 2010).

Nitrogen, phosphorus, and other nutrients in the wastewater are effectively absorbed by microalgae during the wastewater treatment process to support their growth. Microalgae release oxygen freely through their photosynthetic processes, and microorganisms in the wastewater use this oxygen. By assimilation of HCO3 from CO2 through respiration, microalgae also fix CO2.

In the last 50 years, the importance of microalgae has been emphasized in wastewater treatment as a biological treatment system due to its ability to accumulate nutrients, heavy metals, pesticides, and organic and inorganic materials in their body cells, thus eliminating these materials from the aquatic environment (Kalesh et al., 2005) (Jothinayagi et al., 2009).

It can absorb many radioactive metals in its cells as well, and reduce both chemical and biochemical oxygen demand.

Where wastewater contains organic and inorganic substances and microbes,

Organic compounds in wastewater contain at least one carbon atom that can be chemically and biologically oxidized to produce carbon dioxide.

BOD exploits the ability of microorganisms to oxidize organic material to carbon dioxide and water by an oxidizing agent (molecular oxygen).

Therefore, biochemical oxygen demand is a measure of the respiratory demand of bacteria metabolizing the organic matter present in wastewater.

Excess BOD can deplete the dissolved oxygen of receiving water leading to fish kills and anaerobiosis, thus its removal is a primary aim of wastewater treatment.

It has been proven that several water algae are able to take up various heavy metals selectively from aqueous media and accumulate these metals in their cells.

This method has also been used due to its low cost compared to conventional treatment systems.

Many scientists have confirmed that using algae is an economical way to remove heavy metals from wastewater and obtain high-quality reusable water (Filip et al., 1979)

(Kiran, et al., 2007) (Pandi, et al., 2009).

The harvested algae can be used for agricultural purposes in terms of the availability of nitrogen and phosphorus, or it can be fermented for energy (Palmer, 1969).

The most pollution-tolerant genera include eight green algae, five blue-greens, six flagellates, and six diatoms.

Wastewater treatment system by alga cultures has proved high efficiency in removing N and P in a short period of time (Lavoie et al., 1985).

In previous studies, the ability of Chlorella vulgaris the removal of nutrients has been studied. They found that the results indicated a nutrient removal efficiency of 86% inorganic N and 70% inorganic P (Lau, et al., 1996).

In other studies, they found the elimination of nitrogen (50.2%) and phosphorus (85.7%) in industrial wastewater treatment and the elimination of phosphorus (97.8%) in domestic wastewater treated by algae (Lau, et al., 1996).

Based on many studies, coagulation, and flocculation are effective methods for removing algae from wastewater.

Coagulation is a chemical process in which a chemical compound, a “coagulant”, is added to the water, in order to destabilize the suspended particles and promote the creation of flocs.

A ‘Stable colloidal particle’ is a colloidal particle that remains as a separate entity in the water, i.e., in a dispersed state.

The reason colloidal particles tend to remain in the dispersed state is that their surface is electrically charged, usually with a negative charge.

Coagulation treatment is usually carried out before sedimentation and filtration. During the process, a coagulant is added to water, and its positive charge neutralizes the negative charge of suspended contaminants.

Neutralization causes suspended particles to bind together (hence the term). In clumps known as “flocs”, these particles sink to the bottom of the treatment tank. They can then be more easily filtered out of water.

Several factors can influence the effectiveness of coagulation and sedimentation processes in removing algae from wastewater. These factors include the concentration and type of algae present, the type and dosage of coagulant employed, and the hydraulic retention time of the sedimentation basin. Despite the use of these processes, some wastewater may still contain residual algae, necessitating additional treatment methods to ensure efficient removal.

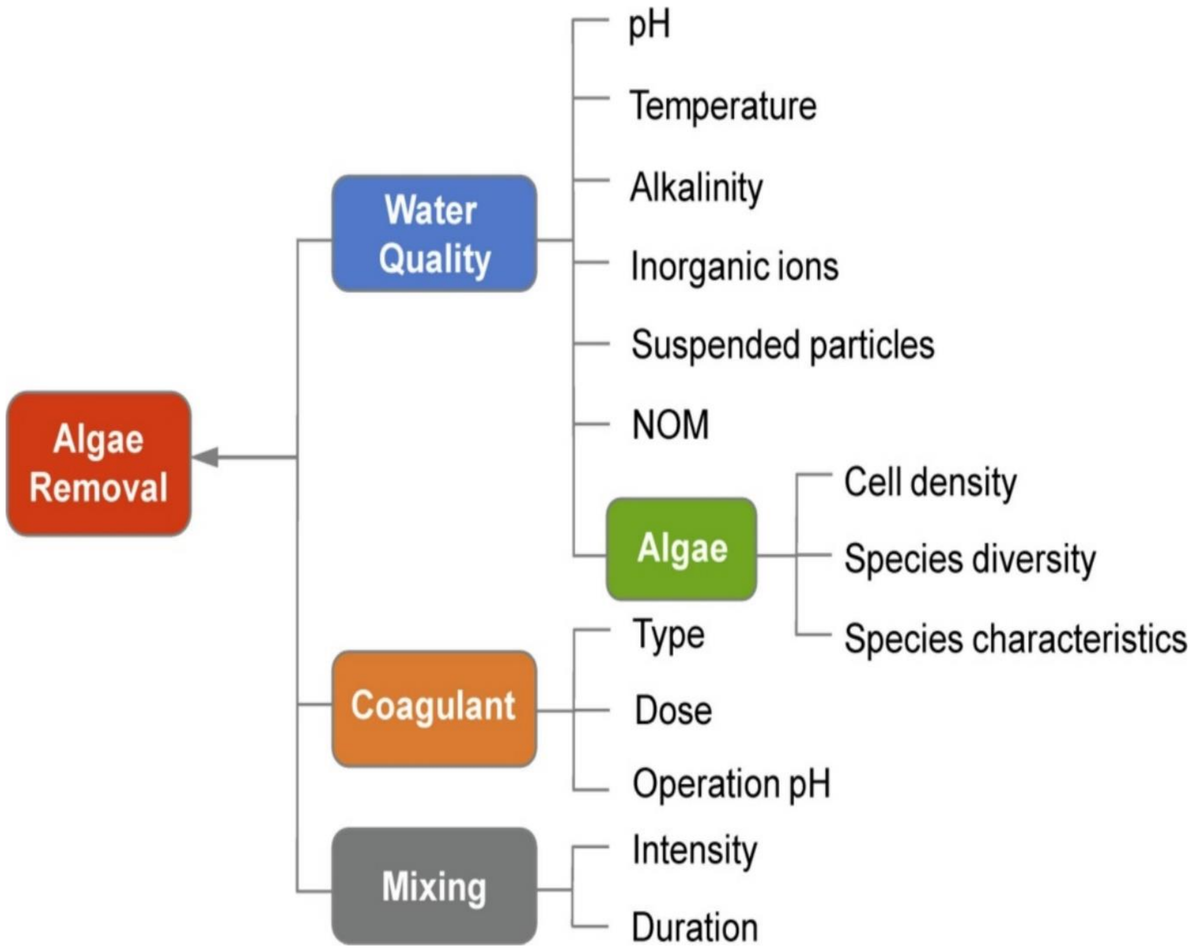

Figure 2: The primary influencing factors that determine the performance of coagulation in algae removal

Coagulation is a process in which a chemical (such as alum or ferric chloride) is added to the water to destabilize and clump together the suspended particles, including algae. Flocculation is then used to further aggregate these clumps, making them easier to remove from the water. Both these processes are commonly used in wastewater treatment plants to remove algae and other impurities from the water. Some of the articles mentioned the use of electro-coagulation as another method for removing algae from wastewater.

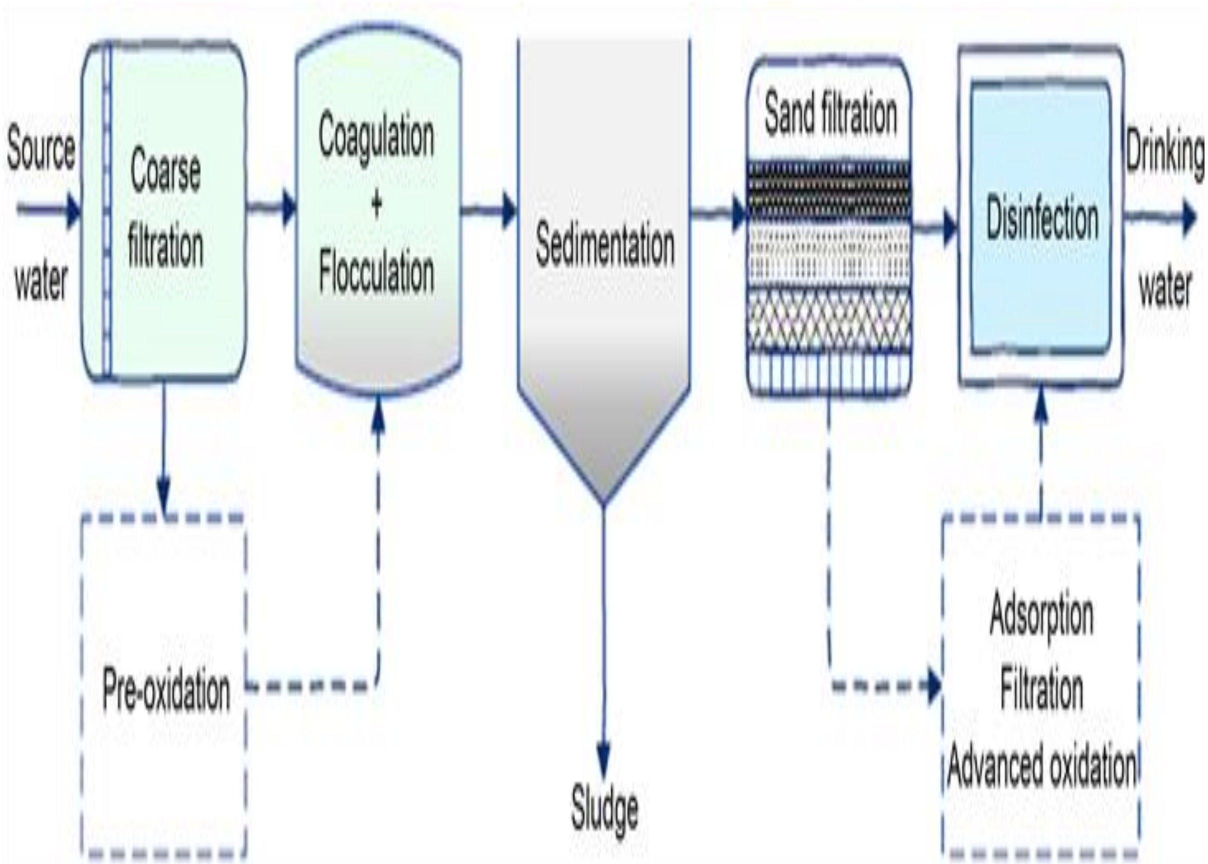

Figure3: Overview of water treatment processes

2.5. - Theory of Coagulation

Coagulants are substances that are commonly used to induce the destabilization of negatively charged colloids and dissolved matter in aqueous solutions. According to classical theory, there are four mechanisms of coagulation, which include double-layer compression, charge neutralization, adsorption and inter-particle bridging, and enmeshment in a precipitate. These mechanisms are employed to facilitate the aggregation and removal of colloidal particles from the solution, which is especially important in water treatment processes. Figure (4) (Department et al., 2020).

When colloidal particles carry a negative charge, they tend to attractions with a positive charge, forming a dense layer called the Stern layer around the particle. Additionally, a diffuse layer is formed due to the equilibrium between excess positive ions that are attracted to the negative core of the colloids and repulsion forces from the Stern layer. Together, these layers are referred to as the double layer in the interfacial region of colloid particles. When a positively charged, coagulant is introduced to the colloidal system, the double layer is compressed due to the electrostatic attraction between the ions and colloids. While double-layer compression is not a significant factor in water treatment for colloid destabilization, it plays a crucial role in natural aquatic systems, such as the formation of deltas in estuaries.

Colloidal destabilization can occur through two methods: charge neutralization and inter-particle bridging. Charge neutralization involves the electrostatic interaction between the coagulant and counter-ions, resulting in the neutralization of charges. Inter-particle bridging, on the other hand, involves the use of polyelectrolytes with highly active surfaces and linear or branched structures as coagulation aids, which promote the aggregation of micro-flocs during the flocculation process. The polyelectrolyte adsorbs colloidal particles and extends its linear or branched chains to attach other particles, forming inter-particle bridges. At higher coagulation dosages, hydroxide precipitates are generated. These insoluble, amorphous precipitates entrap or enmesh colloids, a process known as sweep coagulation or enmeshment. (Department et al., 2020).

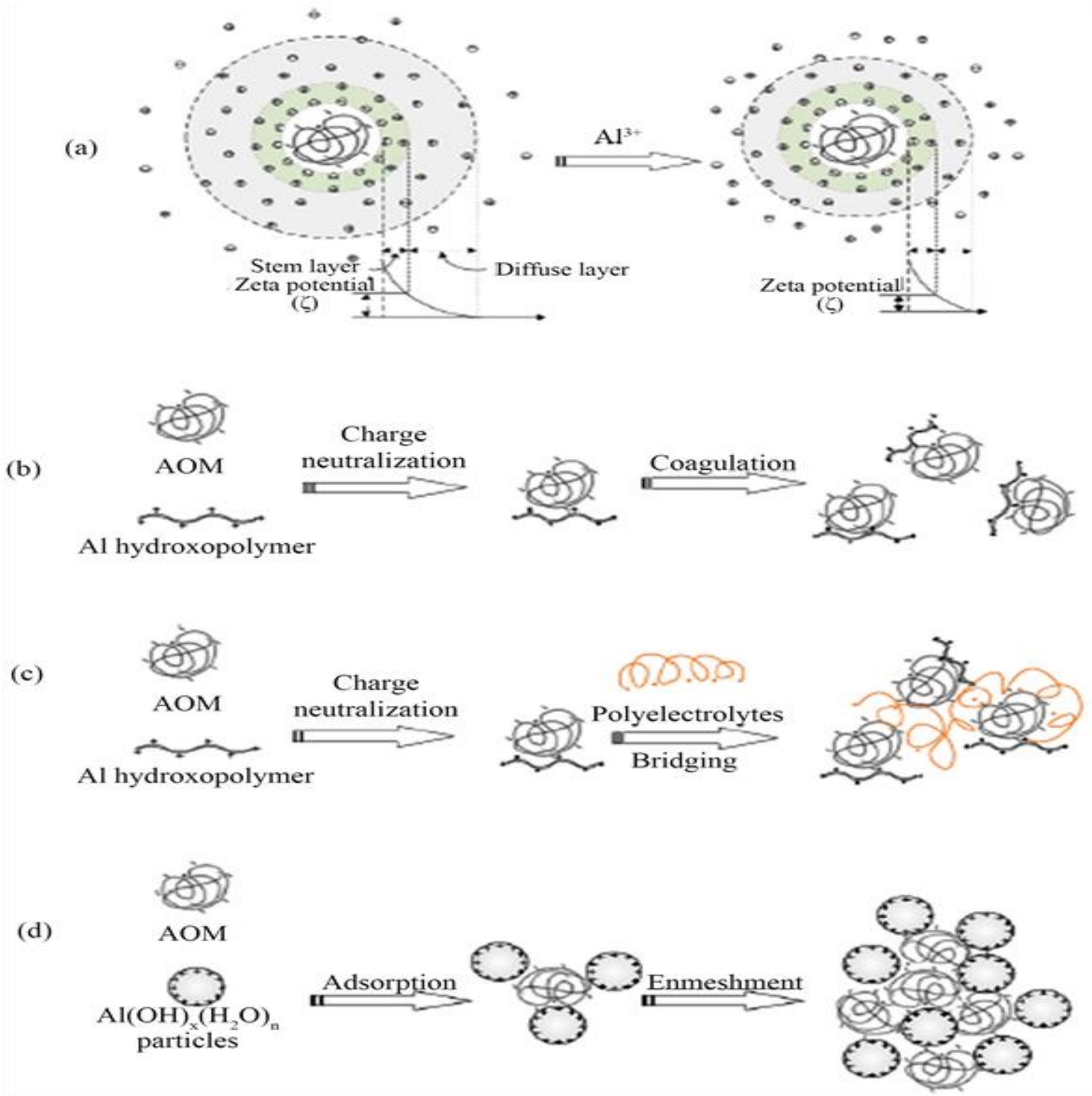

Figure 4: Pathways of coagulation process: (a) Double layer compression; (b) Charge neutralization; (c) Inter-particle bridging; (d) Sweep coagulation

In the field of water treatment, coagulants play a crucial role in removing impurities and suspended particles from the water. To ensure optimal performance, coagulants are evaluated based on two key criteria. The first criterion involves determining the appropriate coagulant and chlorine dosage for achieving the desired level of water quality. The second criterion involves ensuring that the water meets the required standards for safe consumption.

One of the primary challenges in water treatment is the presence of turbidity caused by dissolved substances and negatively charged particles, such as algae. Coagulation is the process of destabilizing these suspended particles by adding positively charged coagulants, such as H+ and Al3+. This destabilization process promotes the formation of larger particles, or flocs, which are easier to remove through sedimentation and filtration.

To optimize the coagulation process, it is important to carefully select the appropriate coagulant and adjust the dosage to match the specific characteristics of the water being treated. Factors such as pH, temperature, and the composition of the water can all impact the effectiveness of the coagulant.

In addition to selecting the appropriate coagulant, it is important to ensure that the water meets the necessary quality standards for safe consumption. Turbidity is one of the key parameters that is monitored to assess water quality. By carefully controlling the coagulation process, it is possible to achieve the desired level of turbidity reduction and ensure that the water is safe for consumption.

2.6. - Common Coagulants for Water Treatment

Ferric sulfate, aluminum sulfate, or ferric chloride, classed as aluminum or iron salts, are common coagulants for water treatment.

A coagulant is a type of chemical that is utilized to eliminate suspended solids from drinking water by neutralizing them. This is achieved with the aid of positively charged molecules that provide effective neutralization of water. In order to meet specific water quality criteria, it is necessary to remove suspended and dissolved impurities from water and wastewater.

These impurities may include silt, organic matter, mineral substances, industrial pollutants, and microorganisms such as bacteria, algae, and viruses. The coagulation-flocculation process aims to transform the small, suspended particles into larger flocs so that they can be removed by filtration or settle out of the water.

In order to address the issue of algae-contaminated source water, water treatment utilities utilize a multi-barrier strategy. The first step in conventional drinking water treatment processes is typically coagulation. It is important to note that the efficiency of coagulation directly affects all downstream treatment steps. When algal cells are damaged during the treatment process, they can release toxins, taste, and odor (T&O) compounds, and other cellular metabolites that have the potential to lead to the formation of disinfection byproducts (DBPs). Therefore, the primary goal of coagulation, along with subsequent solid-liquid separation processes such as clarification and filtration, is to maximize the removal of algal cells without damaging the integrity of the cells.

The importance of coagulation in addressing algae problems extends beyond just treatment facilities. From a water management standpoint, the fundamental strategy to prevent and control eutrophication and algae-related problems is to reduce nutrient loads into water bodies. While point-source nutrients associated with municipal and industrial wastes are relatively easy to identify and regulatory discharge limits can be met by employing advanced techniques for enhanced nutrient removal, efforts in point-source nutrient reduction are often ineffective due to largely unregulated nutrient inputs from nonpoint sources. These nonpoint sources include agricultural drainage, soil erosion, urban runoff, household septic systems, and other sources.

Therefore, it is critical to implement effective measures to reduce nutrient loads from both point and nonpoint sources to address algae-related problems in water bodies. Coagulation plays a vital role in this process by removing algal cells from the source water and preventing the formation of DBPs. By employing a multi-barrier approach and implementing effective nutrient reduction measures, water treatment utilities can ensure the provision of safe and high-quality drinking water to consumers (Department et al., 2020).

3 - Methods of the studies

Used algae: Corella vulgaris sp. From agrochemistry laboratory.

Salts used as coagulants during the experiment: $CaCl_2$.

In the experiment conducted, distilled water was mixed with the selected ion to form a solution, which was then added to three glass cylinders. Afterward, an algae sample was poured into each cylinder, and the experiments were set at three different cation concentrations, namely 0, 400, and 800 mg/l.

To monitor the sedimentation efficiency of the suspension, photographs were taken of the three columns, which were back-illuminated, at various intervals. Specifically, one photograph was taken every five minutes during a 35-minute settling period. The camera used in the experiment was a Fujifilm FinePix S8600 camera, set to manual mode and configured to take photographs at a resolution of 4608 x 2592 pixels (16:9, L, fine quality), with a shutter speed of 60, and an aperture of F2.9.

The rationale behind this experiment is that the color change observed in the glass cylinders is an indicator of sedimentation efficiency. This concept is similar to the concept of turbidity measurement. As noted by Grayson et al., the coagulation capacity, which affects the stability of aggregates, can be inferred from the grain size, which, in turn, determines the sedimentation rate. This rate can be calculated using Stokes' law, where larger grains settle faster, and thus, the soil suspension clears sooner.

Therefore, the more efficient the coagulation, the faster the settling rate, which, in turn, leads to a lighter glass cylinder. However, achieving perfect efficiency is very challenging since colloidal particles do not settle out due to Brownian motion, except when they form larger aggregates.

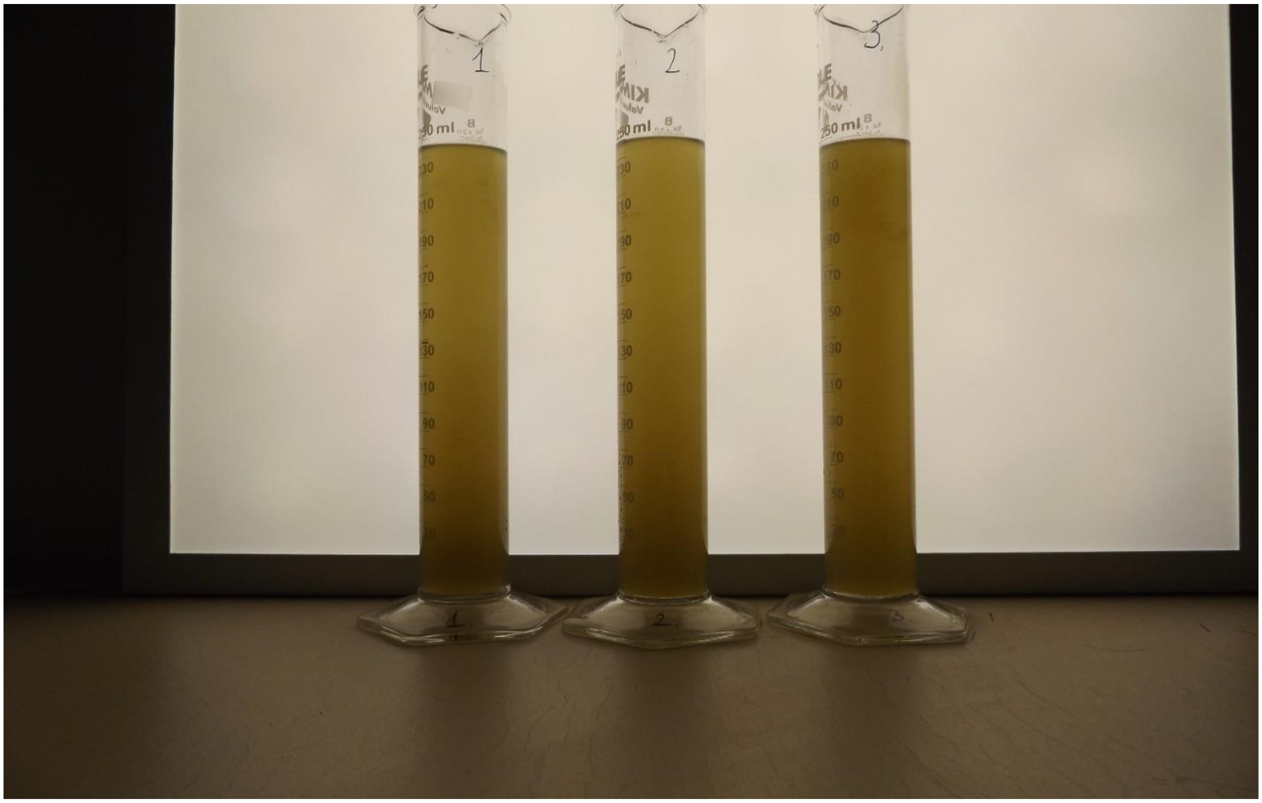

Figure 5: shows the first step of the experiment in 0 minute where $CaCl_2$ added

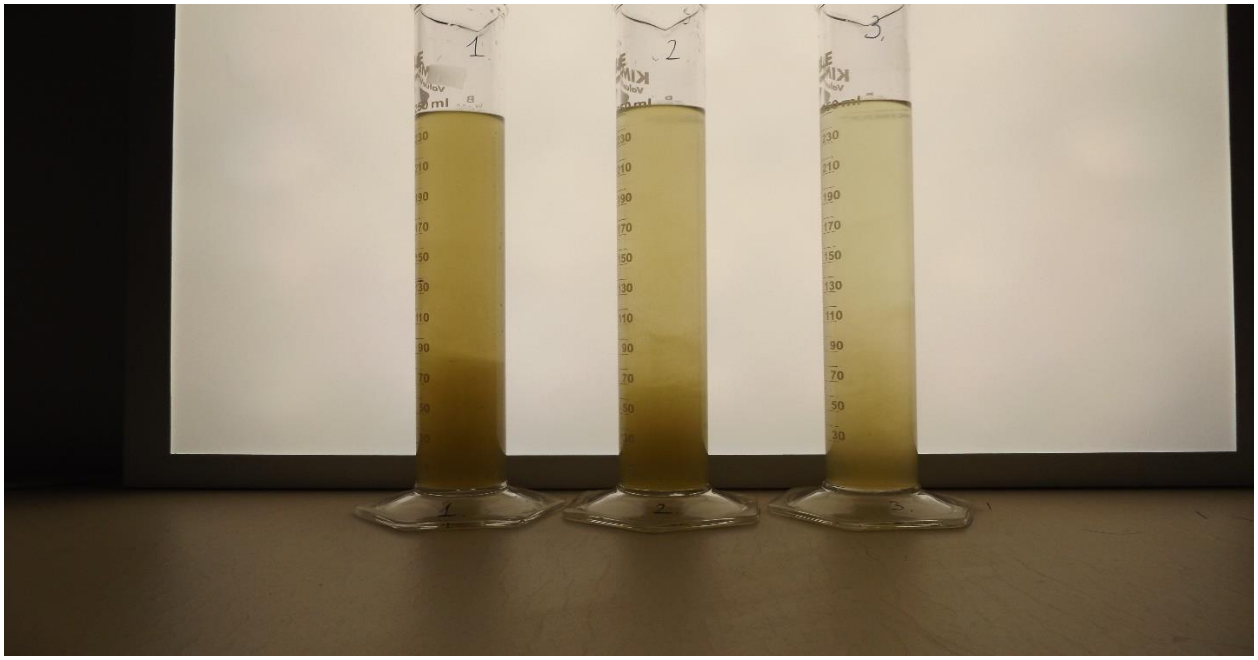

Figure 6: During the experiment

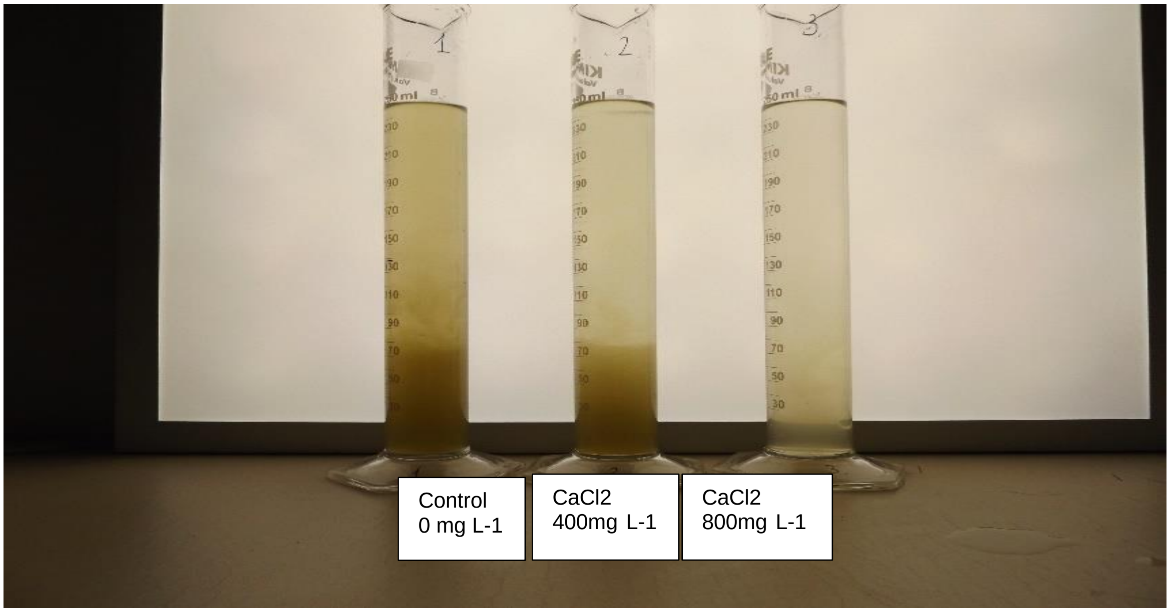

Figure 7: shows differences in turbidity after 35 minutes

Sedimentation efficiency and experimental design. The percentages in the columns indicate the settling efficiency, where 0% is the removal efficiency value of the initial suspension.

The analysis of the photographs was performed automatically using a program written for this purpose. The program performs the analysis on the vertical central third of the glass column (35 pixels wide), where it averages the RGB colour depth value row by row. Averaging these values column by column (400 rows of values, excluding the notches in the glass cylinder) gives a typical colour depth. For each column, for each photo, there will be one such averaged data (0-35 minutes per five minutes, so 8 photos, 8 data/column).

Comparison:

If a comparison is made between the images that were taken of the three cylinders during the experiment that was conducted (Figures 5,6,7), we notice that in figure (5) the percentage of turbidity is very high, and that is very normal due to the zero-time image taken.

While in Figure (6) we notice less turbidity, therefore, greater sedimentation, especially in the third cylinder which contains 800 mg/L of Calcium Chloride, and thus the presence of this salt help in accelerate the coagulation process compared to the control sample.

The last picture (figure 7) proves the hypothesis and shows the same results, where we see a large sedimentation rate. In the following chart, we show the ratio of removal efficiency.

3.1. - Functional evaluation, columnar sedimentation

1. Row by row, we aggregate and average the middle third of the columns (30-38 pixels wide), from the meniscus to the bottom of the column (sedimentation ground). The resulting data represents the RGB colour depth.

2. These data (typically 385-410 rows) are averaged to give the average column brightness. For each column, each photograph, there will be one such averaged data (0-35 minutes per five minutes, so 8 photographs, 8 data per column).

3. The same is done for the background between columns.

4. Based on the data measured on the water-filled columns, 95.6% of the total luminosity passes through the glass column, so this is used to correct the background values to obtain the pure 100% condition.

5. We correct the background value associated with the column (due to the minimum but different brightness of the photographer). That is the (modified) background minus the measured value. We call this the AA value.

6. This gives 8 values, already corrected for background and opacity (AA values)

7. The starting point for each column is taken to be the position of that column at time 0. This (already corrected) value is subtracted from all time values so that starting from the zero point we obtain the rate of decrease or change from the starting point. (BB values)

8. These values, if divided by the 0th time instant value of the column (in negative), give the relative throughput at that time. 0% represents the initial, agitated state, while 100% represents the ion-exchanged water state. These points are plotted as a function (of time).

4 - Results

During the procedure, photographs of the settled algae were taken every five minutes, and the data points, cleaned by the background correction described above, were plotted and compared. Such a series of functions is shown in Figure (8), where different concentrations of $CaCl_2$ solution are plotted as a function of translucency (or settling efficiency, y-axis) and time (x-axis). It can be observed that the sedimentation (brightening) follows a definite exponential function for all t concentrations.

The sedimentation efficiency of the control solution (with no added chemical) after 35 minutes was approximately 30%. However, when the minimum chemical addition (400 mg/l) was added to the suspension, the settling efficiency increased to 55%, while higher concentrations of the chemical resulted in a settling efficiency of almost 80%.

While these findings provide some useful information about the sedimentation efficiency of the suspension, it is essential to note that this alone is not sufficient. The endpoint of the settling efficiency measurement does not reveal information about the dynamics of the process, which is crucial in understanding the coagulation behavior of the suspension.

It is important to note that coagulation involves the formation of larger aggregates from smaller particles. Therefore, the dynamics of the coagulation process, such as the rate of aggregate formation and the size of the formed aggregates, are crucial in understanding the sedimentation behavior of the suspension.

Moreover, it is worth mentioning that the concentration of the chemical added to the suspension also affects the dynamics of the coagulation process. Specifically, higher chemical concentrations tend to promote faster aggregate formation, leading to a more rapid settling of the suspension. However, excessively high chemical concentrations may result in undesirable effects, such as the formation of large, unstable aggregates that may eventually break apart and result in reduced settling efficiency.

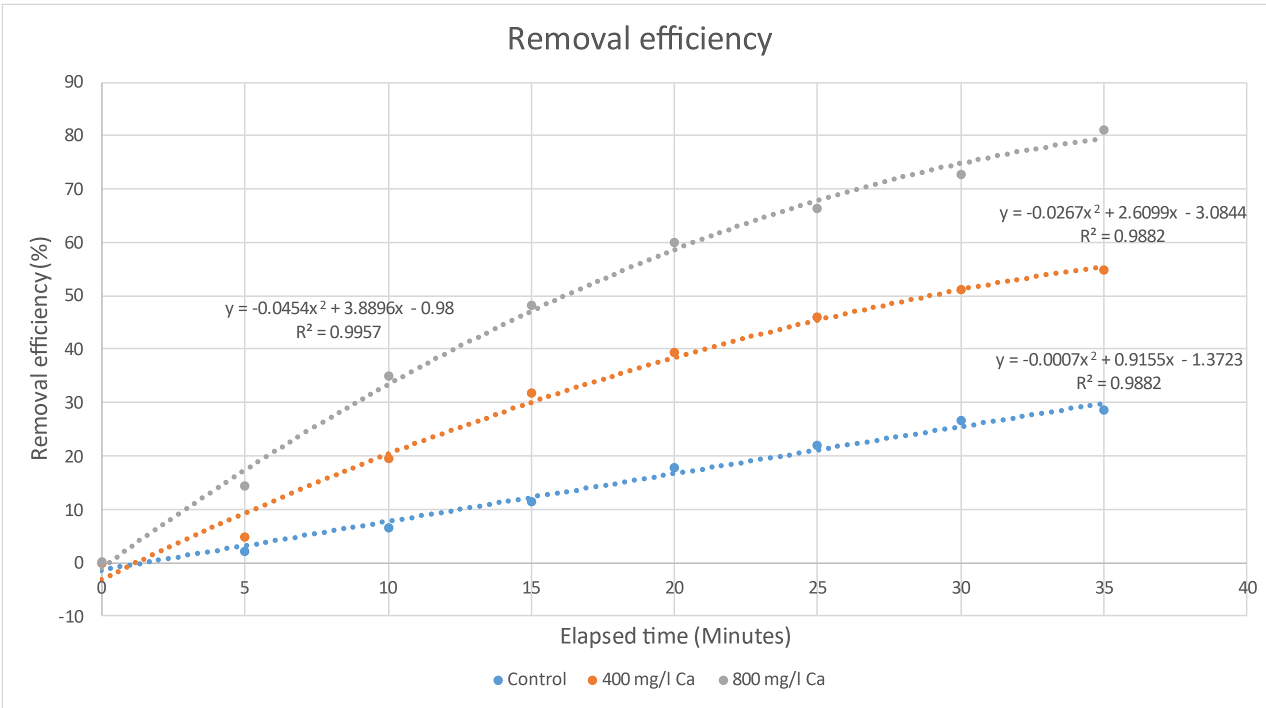

Figure 8: shows the removal efficiency through the time

The high value of R2 shows the satisfactory agreement of the experimental data with the quadratic model.

In all cases of this study, the values of R2 were found to be higher than 0.9 for all responses, thus, it can be said that the quadratic model has a good fitness for the data.

	Control	400 mg/l Ca	800 mg/l Ca
0	0.00386	0.00494	0.01601
5	2.11312	4.68946	14.26717
10	6.48464	19.44112	34.91116
15	11.41236	31.66385	48.33417
20	17.88291	39.40486	60.00613
25	21.86425	46.05413	66.33929
30	26.56178	51.07153	72.7889
35	28.58131	54.82487	81.07608

Figure 9: shows the results of removal efficiency through the time

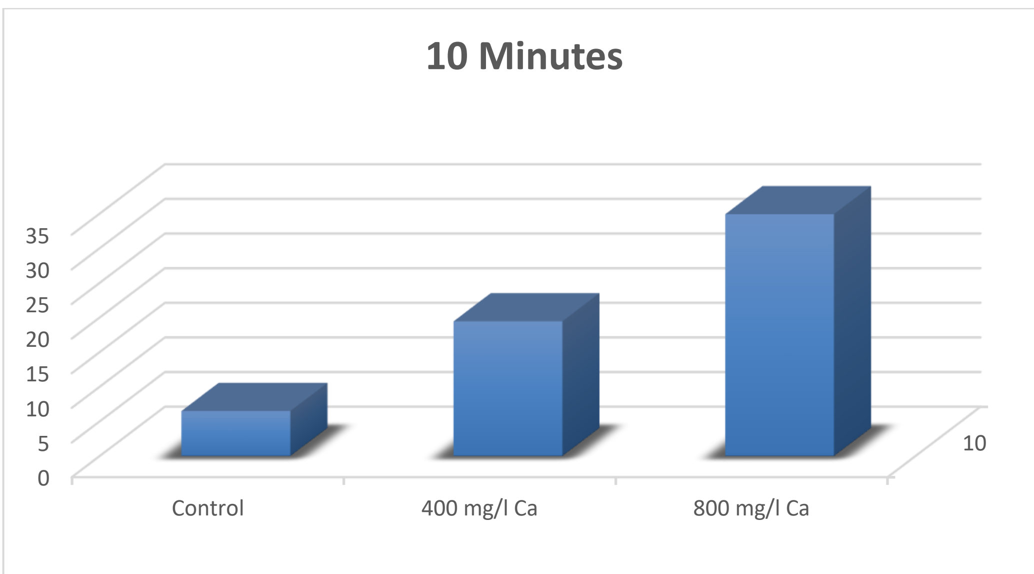

Figure 10: comparison of control, 400, 800 mg/l samples at 10 minutes

As shown in Figure 10, our results indicate that the removal efficiency of the control sample after 10 minutes was approximately 6.4, while the 400 mg/L sample showed a significantly higher removal efficiency of 19.4, almost three times higher than the control sample. Furthermore, the 800 mg/L sample exhibited a removal efficiency of 34.9 after ten minutes, which is more than five times higher than the control sample. These findings suggest that increasing the concentration of calcium in the solution accelerates the removal process, resulting in better outcomes in a shorter period of time.

Similarly, Figure 11 shows that after 20 minutes, the removal efficiency in the control sample was 17.8, while it was 39.4 in the 400 mg/L sample and 60 in the 800 mg/L sample. This indicates that the removal efficiency in the 400 mg/L sample was twice as high as that of the control sample, whereas the removal efficiency in the 800 mg/L sample was only three times higher than that of the control sample. These findings highlight the importance of finding an optimal concentration of calcium to maximize removal efficiency while avoiding any negative effects of excessive calcium concentrations.

After 30 minutes, the removal efficiency of the control sample was 26.5, whereas the 400 mg/L sample exhibited a removal efficiency of 51, and the 800 mg/L sample showed a remarkably higher removal efficiency of 72.7, as illustrated in Figure 12. This confirms our earlier observations that the concentration of calcium in the solution plays a crucial role in enhancing the removal efficiency of the tested samples.

Therefore, based on our findings, we conclude that the concentration of calcium in the solution significantly influences the removal efficiency of the samples. Increasing calcium concentration accelerates the removal process and leads to better outcomes in a shorter time. However, it is essential to determine the optimal concentration of calcium to avoid any adverse effects and ensure the best possible removal efficiency.

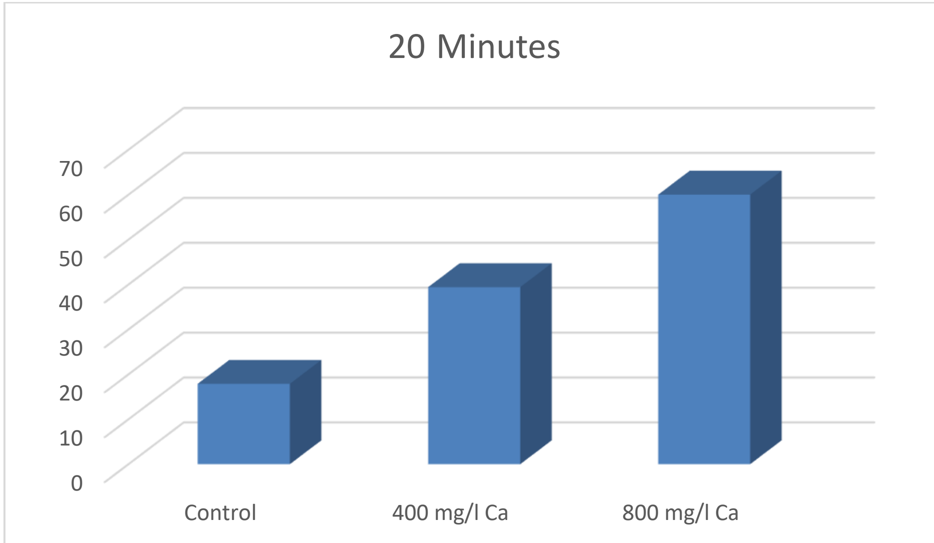

Figure 11: comparison of control, 400, 800 mg/l samples at 20 minutes

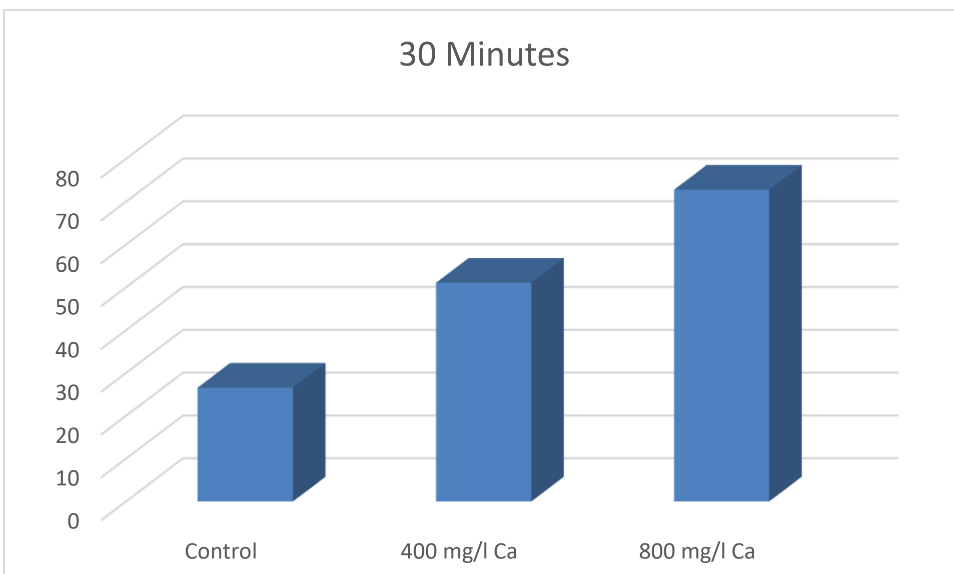

Figure 12: Comparison of control, 400, 800 mg/l samples at 30 minutes

5 - Conclusion and recommendations

This work studied the role of Calcium Chloride as an uncommon coagulant for the treatment of wastewater and to enhance microalgae removal by coagulation.

The findings of this work may provide some new solutions for developing wastewater treatment technology and algae removal where we use $CaCl_2$ as a coagulant to enhance the efficiency of coagulation and sedimentation of algae in wastewater as the results show.

It is important to note that the use of calcium chloride for water treatment and algae removal should always be carefully considered, and its effects on water quality and treatment efficiency should be appropriately evaluated before use.

We know that $CaCl_2$ is more readily available than metal salts and does not have the same environmental impact. Studying $CaCl_2$ also suggests a potential economic impact for the industry if calcium can replace primary coagulants in drinking water production. The following economic benefit would result from the reduced requirement of $Al_2(SO4)_3$: (a) $CaCl_2$ costs less than this primary coagulant, (b) the amount of sludge is reduced, (c) the amount of chemicals used for pH adjustment is potentially decreased.

The effectiveness of calcium chloride as a coagulant for algae coagulation depends on several factors, including the concentration of calcium chloride, the pH of the water, and the type of algae present. In general, higher concentrations of calcium chloride and lower pH values can improve coagulation efficiency. It may also be necessary to add additional coagulants or flocculants to optimize the process.

Here are some recommendations to consider when using calcium chloride:

1-Determine the appropriate dosage: The dosage of calcium chloride required for coagulation varies depending on the type and quantity of algae present in the water. It is essential to carry out jar tests to determine the appropriate dosage.

2-Monitor the pH of the water: The pH of the water can affect the effectiveness of coagulation. The optimum pH range for the use of calcium chloride as a coagulant is between 6.5 and 7.5.

3-Allow time for coagulation: It is essential to allow sufficient time for coagulation to occur. The duration of coagulation depends on the type and quantity of algae present in the water. Typically, it takes between 30 minutes to an hour.

4-Use a settling tank: Once coagulation occurs, the water needs to be settled to allow the algae to settle to the bottom. A settling tank should be used for this purpose, and the water should be left undisturbed for several hours.

5-Monitor effectiveness: The effectiveness of coagulation can be monitored by measuring turbidity levels. If the turbidity levels remain high after coagulation, it may be necessary to increase the dosage of calcium chloride or use another type of coagulant.

6. Summary

The pollutants can enter water bodies at various points and non-point sources, and wastewater discharge remains a major pathway. The increasing occurrence of harmful algae blooms globally poses significant challenges to water management. In water treatment utilities, coagulation is the first treatment process of the multi-barrier strategy designed to address algae-laden source water. Since the coagulation efficiency directly impacts all downstream treatment processes, it is critical to optimize coagulation conditions to remove algal cells to the extent possible without causing cell damage. This work was motivated by the assumption that the induced coagulation of particles may accelerate sedimentation in such wetlands and by that help reduce the amount of material that is lost from the vicinity of the diffuse source. Our specific aim was to laboratory-test the effectiveness of calcium cation coagulants in accelerating the process of sedimentation. We tested the effect of Ca^{+2} in 400, 800 mg/L doses added to cylinders filled with algae samples with distilled water compared with the control cylinder which does not have any cation inside and photographs were taken every 5 minutes for 35 minutes, it yielded rapid stabilization of algae. This proves the effectiveness of Ca^{+2} to increase the efficiency of coagulation and therefore sedimentation this cation is environmentally friendly, and it is not harmful to humans and animals.

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8 - References

1. Abdel-Raouf, N., Al-Homaidan, A.A. and Ibraheem, I.B.M. (2012) ‘Microalgae and wastewater treatment’, *Saudi Journal of Biological Sciences*, 19(3), pp. 257–275. Available at: https://doi.org/10.1016/j.sjbs.2012.04.005.
2. Amer, L., Adhikari, B. and Pellegrino, J. (2011) ‘Technoeconomic analysis of five microalgae-to-biofuels processes of varying complexity’, *Bioresource Technology*, 102(20), pp. 9350–9359. Available at: https://doi.org/10.1016/j.biortech.2011.08.010.
3. Atabani, A.E. *et al.* (2012) ‘A comprehensive review on biodiesel as an alternative energy resource and its characteristics’, *Renewable and Sustainable Energy Reviews*, 16(4), pp. 2070–2093. Available at: https://doi.org/10.1016/j.rser.2012.01.003.
4. Barros, A.I. *et al.* (2015) ‘Harvesting techniques applied to microalgae: A review’, *Renewable and Sustainable Energy Reviews*, 41, pp. 1489–1500. Available at: https://doi.org/10.1016/j.rser.2014.09.037.
5. Becker, E.W. (2013) ‘Microalgae for Human and Animal Nutrition’, in *Handbook of Microalgal Culture*. John Wiley & Sons, Ltd, pp. 461–503. Available at: https://doi.org/10.1002/9781118567166.ch25.
6. Chen, C.-Y. *et al.* (2011) ‘Cultivation, photobioreactor design and harvesting of microalgae for biodiesel production: A critical review’, *Bioresource Technology*, 102(1), pp. 71–81. Available at: https://doi.org/10.1016/j.biortech.2010.06.159.
7. Chinnasamy, S. *et al.* (2010) ‘Microalgae cultivation in a wastewater dominated by carpet mill effluents for biofuel applications’, *Bioresource Technology*, 101(9), pp. 3097–3105. Available at: https://doi.org/10.1016/j.biortech.2009.12.026.
8. Chisti, Y. (2007) ‘Biodiesel from microalgae’, *Biotechnology Advances*, 25(3), pp. 294–306. Available at: https://doi.org/10.1016/j.biotechadv.2007.02.001.
9. Christenson, L. and Sims, R. (2011) ‘Production and harvesting of microalgae for wastewater treatment, biofuels, and bioproducts’, *Biotechnology Advances*, 29(6), pp. 686–702. Available at: https://doi.org/10.1016/j.biotechadv.2011.05.015.
10. Danquah, M.K., Ang, L., *et al.* (2009) ‘Dewatering of microalgal culture for biodiesel production: exploring polymer flocculation and tangential flow filtration’, *Journal of Chemical Technology & Biotechnology*, 84(7), pp. 1078–1083. Available at: https://doi.org/10.1002/jctb.2137.
11. Danquah, M.K., Gladman, B., *et al.* (2009) ‘Microalgal growth characteristics and subsequent influence on dewatering efficiency’, *Chemical Engineering Journal*, 151(1), pp. 73–78. Available at: https://doi.org/10.1016/j.cej.2009.01.047.
12. Demirbas, A. (2010) ‘Use of algae as biofuel sources’, *Energy Conversion and Management*, 51(12), pp. 2738–2749. Available at: https://doi.org/10.1016/j.enconman.2010.06.010.
13. Department, D.G.E. *et al.* (2020) ‘Coagulation Process for Removing Algae and Algal Organic Matter—An Overview’, *Open Access Library Journal*, 07(04), p. 1. Available at: https://doi.org/10.4236/oalib.1106272.
14. Filip, D.S. *et al.* (1979) ‘Residual heavy metal removal by an algae-intermittent sand filtration system’, *Water Research*, 13(3), pp. 305–313. Available at: https://doi.org/10.1016/0043-1354(79)90211-2.
15. Gerardo, M.L. *et al.* (2015) ‘Harvesting of microalgae within a biorefinery approach: A review of the developments and case studies from pilot-plants’, *Algal Research*, 11, pp. 248–262. Available at: https://doi.org/10.1016/j.algal.2015.06.019.
16. Gonçalves, A.L., Pires, J.C. and Simões, M. (2013) ‘Lipid production of Chlorella vulgaris and Pseudokirchneriella subcapitata’, *International Journal of Energy and Environmental Engineering*, 4(1), p. 14. Available at: https://doi.org/10.1186/2251-6832-4-14.
17. Gonçalves, A.L., Pires, J.C.M. and Simões, M. (2013) ‘Green fuel production: processes applied to microalgae’, *Environmental Chemistry Letters*, 11(4), pp. 315–324. Available at: https://doi.org/10.1007/s10311-013-0425-3.
18. Gray, N.F. (2004) *Biology Of Wastewater Treatment (2nd Edition)*. World Scientific.
19. Horan, N.J. (1989) ‘Biological wastewater treatment systems: theory and operation.’, *Biological wastewater treatment systems: theory and operation.* [Preprint]. Available at: https://www.cabdirect.org/cabdirect/abstract/19911364078 (Accessed: 29 April 2023).
20. Jothinayagi, N. and Anbazhagan, C. (2009) ‘Heavy Metal Monitoring of Rameswaram Coast by Some Sargassum species’.
21. Kalesh, N.S. and Nair, S.M. (2005) ‘The accumulation levels of heavy metals (Ni, Cr, Sr, & Ag) in marine algae from southwest coast of India’, *Toxicological & Environmental Chemistry*, 87(2), pp. 135–146. Available at: https://doi.org/10.1080/02772240400029744.

22. Kiran, B., Kaushik, A. and Kaushik, C.P. (2007) ‘Biosorption of Cr(VI) by native isolate of Lyngbya putealis (HH-15) in the presence of salts’, *Journal of Hazardous Materials*, 141(3), pp. 662–667. Available at: https://doi.org/10.1016/j.jhazmat.2006.07.026.
23. Kube, M. *et al.* (2018) ‘The impact of wastewater characteristics, algal species selection and immobilisation on simultaneous nitrogen and phosphorus removal’, *Algal Research*, 31, pp. 478–488. Available at: https://doi.org/10.1016/j.algal.2018.01.009.
24. Lau, P.S., Tam, N.F.Y. and Wong, Y.S. (1996) ‘Wastewater Nutrients Removal by Chlorella Vulgaris: Optimization Through Acclimation’, *Environmental Technology*, 17(2), pp. 183–189. Available at: https://doi.org/10.1080/09593331708616375.
25. Lavoie, A. and de la Noüe, J. (1985) ‘Hyperconcentrated cultures of Scenedesmus obliquus: A new approach for wastewater biological tertiary treatment?’, *Water Research*, 19(11), pp. 1437–1442. Available at: https://doi.org/10.1016/0043-1354(85)90311-2.
26. Lee, A.K., Lewis, D.M. and Ashman, P.J. (2009) ‘Microbial flocculation, a potentially low-cost harvesting technique for marine microalgae for the production of biodiesel’, *Journal of Applied Phycology*, 21(5), pp. 559–567. Available at: https://doi.org/10.1007/s10811-008-9391-8.
27. Marcilla, A. *et al.* (2013) ‘A review of thermochemical conversion of microalgae’, *Renewable and Sustainable Energy Reviews*, 27, pp. 11–19. Available at: https://doi.org/10.1016/j.rser.2013.06.032.
28. Milledge, J.J. (2011) ‘Commercial application of microalgae other than as biofuels: a brief review’, *Reviews in Environmental Science and Bio/Technology*, 10(1), pp. 31–41. Available at: https://doi.org/10.1007/s11157-010-9214-7.
29. Molina Grima, E. *et al.* (2003) ‘Recovery of microalgal biomass and metabolites: process options and economics’, *Biotechnology Advances*, 20(7), pp. 491–515. Available at: https://doi.org/10.1016/S0734-9750(02)00050-2.
30. de la Noüe, J., Laliberté, G. and Proulx, D. (1992) ‘Algae and waste water’, *Journal of Applied Phycology*, 4(3), pp. 247–254. Available at: https://doi.org/10.1007/BF02161210.
31. Olaizola, M. (2003) ‘Commercial development of microalgal biotechnology: from the test tube to the marketplace’, *Biomolecular Engineering*, 20(4), pp. 459–466. Available at: https://doi.org/10.1016/S1389-0344(03)00076-5.
32. Palmer, C.M. (1969) ‘A Composite Rating of Algae Tolerating Organic Pollution2’, *Journal of Phycology*, 5(1), pp. 78–82. Available at: https://doi.org/10.1111/j.1529-8817.1969.tb02581.x.
33. Pandi, M., Shashirekha, V. and Swamy, M. (2009) ‘Bioabsorption of chromium from retan chrome liquor by cyanobacteria’, *Microbiological Research*, 164(4), pp. 420–428. Available at: https://doi.org/10.1016/j.micres.2007.02.009.
34. Papazi, A., Makridis, P. and Divanach, P. (2010) ‘Harvesting Chlorella minutissima using cell coagulants’. Available at: https://doi.org/10.1007/s10811-009-9465-2 (Accessed: 29 April 2023).
35. Pushparaj, B. *et al.* (1993) ‘Microbial biomass recovery using a synthetic cationic polymer’, *Bioresource Technology*, 43(1), pp. 59–62. Available at: https://doi.org/10.1016/0960-8524(93)90083-N.
36. Raven, J.A. and Giordano, M. (2014) ‘Algae’, *Current Biology*, 24(13), pp. R590–R595. Available at: https://doi.org/10.1016/j.cub.2014.05.039.
37. Rawat, I. *et al.* (2011) ‘Dual role of microalgae: Phycoremediation of domestic wastewater and biomass production for sustainable biofuels production’, *Applied Energy*, 88(10), pp. 3411–3424. Available at: https://doi.org/10.1016/j.apenergy.2010.11.025.
38. Schlesinger, A. *et al.* (2012) ‘Inexpensive non-toxic flocculation of microalgae contradicts theories; overcoming a major hurdle to bulk algal production’, *Biotechnology Advances*, 30(5), pp. 1023–1030. Available at: https://doi.org/10.1016/j.biotechadv.2012.01.011.
39. Shelef, G., Sukenik, A. and Green, M. (1984) *Microalgae harvesting and processing: a literature review*. SERI/STR-231-2396. Technion Research and Development Foundation Ltd., Haifa (Israel). Available at: https://doi.org/10.2172/6204677.
40. Show, K.-Y. and Lee, D.-J. (2014) ‘Chapter 5 - Algal Biomass Harvesting’, in A. Pandey et al. (eds) *Biofuels from Algae*. Amsterdam: Elsevier, pp. 85–110. Available at: https://doi.org/10.1016/B978-0-444-59558-4.00005-X.
41. Show, K.-Y., Lee, D.-J. and Mujumdar, A.S. (2015) ‘Advances and Challenges on Algae Harvesting and Drying’, *Drying Technology*, 33(4), pp. 386–394. Available at: https://doi.org/10.1080/07373937.2014.948554.
42. Smith, B.T. and Davis, R.H. (2012) ‘Sedimentation of algae flocculated using naturally-available, magnesium-based flocculants’, *Algal Research*, 1(1), pp. 32–39. Available at:

https://doi.org/10.1016/j.algal.2011.12.002.
43. Tebbutt, T.H.Y. (1997) *Principles of Water Quality Control*. Elsevier.
44. Uduman, N. *et al.* (2010) ‘Dewatering of microalgal cultures: A major bottleneck to algae-based fuels’, *Journal of Renewable and Sustainable Energy*, 2(1), p. 012701. Available at: https://doi.org/10.1063/1.3294480.
45. Vandamme, D., Foubert, I. and Muylaert, K. (2013) ‘Flocculation as a low-cost method for harvesting microalgae for bulk biomass production’, *Trends in Biotechnology*, 31(4), pp. 233–239. Available at: https://doi.org/10.1016/j.tibtech.2012.12.005.

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Signed below, Hala Haitham Hammadi, student of the Szent István Campus of the Hungarian University of Agriculture and Life Science, at the MSc Course of Environmental Science declare that the present Thesis is my own work and I have used the cited and quoted literature in accordance with the relevant legal and ethical rules. I understand that the one-page-summary of my thesis will be uploaded on the website of the Campus/Institute/Course and my Thesis will be available at the Host Department/Institute and in the repository of the University in accordance with the relevant legal and ethical rules.

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As primary supervisor of the author of this thesis, I hereby declare that review of the thesis was done thoroughly; student was informed and guided on the method of citing literature sources in the dissertation, attention was drawn on the importance of using literature data in accordance with the relevant legal and ethical rules.

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