

Power Plant Algal Treatment with Focus on the Sonication of *Enteromorpha Prolifera* Macro Algae

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Abstract

While others considering algae as the “light of hoop” to the energy crisis, and as a carbon neutral technology to combat global warming, uncontrolled growth and its eutrophication can be considered a challenging pollution issue. Nevertheless, in the last a few decades algae pollution has become a global issue. The occurrence of algal bloom in water source has posed a serious water safety and unaccounted control and maintenance at substantial added cost. Overgrowing algae have brought negative impacts on power plant and less frequently led to shutdown of the desalination or power plant. The eutrophication which is rarely is eliminated; it could be controlled by mechanical filtration and chemical biocidal methods. This adds another economic burden by the supply of chemical and their neutralizing agent to cope with tight EPA limits. In this work a review of the treatment of algae is carried out which involves chemical, mechanical, electromechanical and as well as the aid of scavengers directly or indirectly and their combination. As plausible results on the sonication treatment have been emerging, recent work of the author was presented as well to show the effectiveness of the sonication technology in the treatment of the *Enteromorpha Prolifera* Macro Algae.

Keywords: *Enteromorpha prolifera*, Algal Treatment, Sonication of Algae, Eutrophication

1. Introduction

Water is essential for life in the form of drinking in so much to power plant for cooling. Because of the limitation of fresh water and the abundance of sea water the latter is been used and treated for drinking via desalination and for cooling via biocide, demineralization, buffering or whatever required treatment process. However, emerging contaminants are biggest threat to optimum functioning of the power and desalination plants. Harmful algal blooms (HAB), frequently referred to as ‘red tides’ due to their vibrant colors, are of a great concern for desalination plants due to the high yield of biomass of microalgae present in ocean waters.

Moreover, during their growth period, variety of substances are produced by some of these algae. These compounds range from noxious substances to potent neurotoxins that constitute significant public health risks if they are not effectively and completely removed prior to human consumption. Macroalgal blooms in power plant is another significant operational issues that result in (a) an increasing in chemical consumption, (b) increasing in membrane fouling rates, and in extreme cases, (c) a plant to be taken off-line.

To cope with these issue the plant operator needs to develop a full proof mitigation plan starting from control management of algal population while adopting different strategies at initial

level. Early algal bloom detection by power plant engineer is essential for better mitigation of algal bloom so that operational adjustments can be made to ensure that production capacity uncompromised. Beside it is also equally important to know the type of algal species and related toxic substances if any, the surrounding growth promoting factors (nutritional, climatological, hydrological), and the different treatment option, and present state of knowledge to avoid catastrophic plant shutdown.

In recent years, pollution has become a global issue and overgrowing algae have brought negative impacts on power and desalination plant. The occurrence of algal bloom in sea water source has posed two sided threats (i) a serious water safety and maintenance problem to water supply systems and (ii) their bloom poses threat to water quality by releasing the toxins., including (a) *Pseudo-nitzschia australis*, a producer of domoic acid; (b) *Pseudo-nitzschia australis*; (c) *Alexandrium catenella*, a producer of saxitoxin; (d) *Dinophysis* sp., a producer of okadaic acid; (e) *Heterosigma akashiwo*, a producer of brevetoxins; (f) *Chattonella marina*, a producer of brevetoxins; (g) *Cochlodinium* sp.; (h) *Lingulodinium polyedrum*, a producer of yessotoxin all due to an algal bloom. Algal bloom are rarely eliminated by common mechanical filtration and chemical/biocide methods. To efficiently remove algae from water, methodologies like physical, chemical, mechanical and biological treatments are either individually or combined has to be adopted.

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Literature review is still missing for the treatment of algae based on the current and new emerging treatment technologies covering chemical and electro-mechanical (sonic wave) and biological scavenging methods. This work fill this literature gap by reviewing the recent strategies with the goal to provide some recommendations on less harmful treatment such as the use of sonication.

Problem of *Enteromorpha prolifera* bloom: Algal blooms from *Enteromorpha prolifera* has become nuisance not only at some sea shore of Abu Dhabi and regional power plants, but globally as it has great threat to the many coastal regions. In china the *Enteromorpha prolifera* has become an annual occurrence in the region over the past six summers. In 2012 it swathed 28,900 km² (11,158 mi²), twice as much as the previous biggest bloom in 2008. (Fig. 1).



Figs. 1: Tourists bathat a beach covered by a thick layer of green algae *Enteromorpha prolifera* in Qingdao, China in 2012. Photograph: China (FotoPress/Getty Images)

Pumping of surface algal scums from inshore areas has been proven as un-effective old practice to temporarily protect recreational users of freshwater lakes from exposure to toxic cyanobacteria. Filtration also has been used less effectively in purification of drinking water supplies. For the last 2 years, vast accumulations of the unattached filamentous green alga "*Enteromorpha prolifera*" have occurred during summer along the coastal region of the Yellow Sea, China. Therefore, an alternative effective method to mitigate such algal blooms is becoming necessity.

Eutrophication of algae in the power plant in the GCC region has been reported more often. It typically start at the outfall and crawl upstream near the discharge water channel, resulting in unpleasant smell, possible interruption in the discharge pumps, create a suitable culture for herbivore and zooplankton, as well as increasing the risk of initiation red-tides bloom at the sea discharge [1]. This is additional to the increase in the economic burden and associated environmental risk of the current and common chemical treatment. Recent published work draw the relationship between red tides and green tides of *Enteromorpha prolifera*. It concluded that the decomposition or completing life span, green algae released ammonium and phosphate into seawater. These regenerated nutrients becoming a potential nutrients source of any opportunistic microalgae including the *Enteromorpha* and may lead to red tides [1].

Although it is strange in appearance, the *Enteromorpha prolifera* algae is reportedly nontoxic to humans or animals, bu it leaves behind it the toxic gas hydrogen sulfide. The green "carpet" create on the surface can dramatically change the ecology of the environment beneath it, blocks sunlight from entering the ocean, consuming the dissolved underwater oxygen, and leading to complete suffocating of marine life.

The macro algal growth of ulva (60% in mineral content) showed to cause bottom channel sedimentation and wall calcination, and initiation of surface corrosion adding to reduction in cooling efficiency. Algal growth also promotes Bio-film formation due to the excretion of exopolysaccharides. This also cause a larger ecological and environmental problems by creating a suitable culture for the anaerobic bacteria that in turn provide a nutrition ground for other types of algae and breed for insect and other zooplankton species [1]. Eutrophication at near sea power plant break out the intrinsic equilibrium of the aquatic ecosystem into sea shore and causing damage of the water ecosystem leading to gradual degeneration of its functions. As a result, water quality deteriorates and sunlight necessary for photosynthesis of underwater plants is hindered causing water super-saturation and deprivation of dissolved oxygen stressing the aquatic animals and resulted in great death to them.

Eutrophic systems tend to accumulate large amount of organic carbon, then a shift into organic matter biochemical composition [2]. Thick layer of "green scum can also formed on water surface by thick layer algae of cyanophyta and green algae, and causing the release of toxins and organic matters infusion and decomposition into harmful gases that can poison the fish and seashell. Fortunately no toxins has been reported from *Enteromorpha prolifera*, however, one cannot rule out the mentioned toxins as result of algal death, depleting the dissolved oxygen and suffocating underwater marine. Leading to other Cyanobacteria toxins (cyanotoxins) including cytotoxins and biotoxins which are responsible for acute lethal, acute chronic and sub-chronic poisonings of wild/domestic animals and humans. The biotoxins include the neurotoxins; anatoxin-a, anatoxin-a(s) and saxitoxins plus the hepatotoxins; microcystins, nodularins and cylindrospermopsins [3]. Increased nitrite concentration in the eutrophic water lead to product of nitrite nitrification process which thought to be strong carcinogen. Considering the gulf region and nearly 96% desalination water dependency of UAE, it is worth mentioning that Algal blooms is the night mere of the desalination plant operator and raising problem in maintaining the efficiency and performance of the desalination units. Shutdown in Oman and UAE was reported due to an invaded red-tide species that lasted few weeks that caused a major economic burden.

2. *E. prolifera* Collection and Characterization

On the basis of morphological characters and measurements taken from the local power plant and local sea shore (see fig 1), algae is described as *Enteromorpha prolifera* f. *capillaris* (Kützing) V.J.Chapman a strain of Chlorohyta that belong to Kingdom: Plantae, Phylum kingdom of Chlorophyta – green algae and classify as Ulvophyceae of Order Ulvales [4].

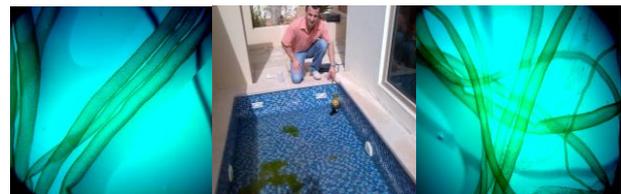


Fig. 1. Microscopic view of healthy algae at 1st and 20th day after basine cultivation

Enteromorpha habitat however is distributed throughout the world, in a wide variety of environments. *Enteromorpha* can tolerate salinities varying from freshwater to seawater, and *Enteromorpha* has also been reported to be able to survive in salt springs and salt mines. *Enteromorpha* can also grow on a wide variety of substrates, on sand, mud, or rock, and concrete or can also grow without any substrate. Sometime algae detached from the muddy substrate, rise to the surface, and then continue to grow (Xiaowen, 2009, [5]) covering the surface of the water with a green layer of algae due to its tremendous potential to divide vegetatively.

Prolifera is characterized by the regular longitudinal rows of relatively small cells which are usually angular, square or short rectangular. It appear as single cylindrical filament, sometimes partially flat or branching, small size, large surface area so the absorption of nutrients is fast. Algae basal cells produce the holdfast. Appears as green, filamentous, branched, monosiphonous, and benthic macroalga and has hollow thalli with longitudinal rows of quadrangular to polygonal cells. Each cell has single nucleus, contains starch grains, single large pyrenoid large parietal chloroplasts, and vacuoles that reach up to 40% of cell volume. Vegetative propagation is by fracture or fragmentation of each filament, portion or cell while has tremendous potential to germinate into new daughter algae at appropriate conditions (Fig. 2).

There are reports that somatic cells of the algae serves as a potential propagule bank of *E. prolifera* due to its tremendous growth potential. It has Extreme tolerance of the cells against low temperature of 0°C even after several months at high saline medium and at no light (Xiaowen Z et al 2010, [6]). *Enteromorpha* also known to be tolerant against high doses of metal toxicity (Andrade, 2004, [7]).

Blooms of algal biomass will not only block oxygen for fish and other aerobic/breathing organism which causes death, but also hinder the photosynthesis and fixation by masking the sun. Consequently, some algal biomass release toxins, and accumulate in fish and shellfish which consumed by water birds or humans leading to poisoning. Algal biomass following death will start to decay and decompose which consumes a large amount of oxygen in the water. Luckily *Enteromorpha prolifera* is not toxic to people, but it can adsorb a huge quantity of oxygen, choking marine life and as it rots it releases unpleasant smell.

The optical micro graphs view showed that the fronds are tubular, though often more or less flattened and moderately-branched. The arrangement of the cells, in longitudinal and transverse rows in the central part of the frond is the characteristic of this species. They have cylindrical chloroplasts seeming to fill the cell and the usually single and central paranoids.



Fig. 2. Collected Algal, Daughter Algal filaments, Microscopic view by Motoc 1000

For the collected algal the overall percentage of elemental carbon, hydrogen, nitrogen, oxygen and sulfur are measured using “Flash 2000 (CHNO-S)” instrument. Each part is comprised of series of measurements that starts from the calibration of the instrument to the final result. The actual heating value also is measured using the Parr600 bomb calorimeter. The elemental analysis a long with the calorific value provides the overall percentage of carbon, hydrogen, nitrogen, oxygen and sulfur present in the sample and the amount of chemical energy that can be converted into thermal energy if the feedstock subjected to oxidation. These values are listed in table 1 along. Surprisingly the calorific value of the *Prolifera* is very low to even sustain biomass combustion. Proximate analysis of the moisture content, volatile, fixed carbon and inorganics are also measured by the Simultaneous Thermo gravimetric Analysis using the TGA as depicted in . figure 3 that shows the large content of inorganic metal of *Prolifera*. The iCAP 6000 Spectrometer Series is used to measure the inorganic elemental components of the *Prolifera*. It is an inductively coupled argon plasma optical emission spectrometers (ICP-OES) which use an Echelle optical design and a Charge Injection Device (CID) solid-state detector to provide elemental analysis. Most samples are liquids that are pumped through a nebuliser to produce a fine spray. The large droplets are removed by a spray chamber and the small droplets then pass through to the plasma. The solvent is evaporated. The residual sample decomposed to atoms and ions that become excited and emit characteristic light which is measured, giving a measurement of the concentration of each element type in the original sample. Using the measurement of inorganic elements, the overall materials present in the algae and their composition are listed in table 2.

Table 1: Summary of FLASH elemental Analysis

N (%)	C (%)	H (%)	S (%)	O (%)	Ash (%)	Calorific Value (MJ/kg)
0.53±0.01	19.70±0.01	3.18±0.01	2.49±0.01	22.23±0.01	51.87±0.05	7.1±0.1

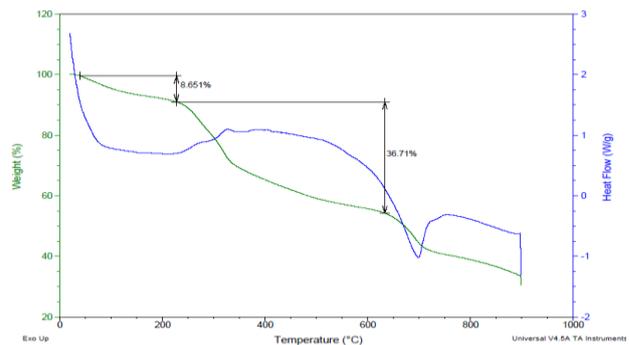


Fig. 3. STA results of *E. Prolifera*

Table 2: Summary of ICP metal elemental analysis

P (ppm)	K (ppm)	Al (ppm)	Ba (ppm)	Zn (ppm)	Ca (ppm)	Na (ppm)	Mg (ppm)	Mn (ppm)
39,800	33,000	4.941	0.0013	700	18,000	39,300	22,000	80

2. Possible Treatment Approach

Literature to study the response of various common treatment methods available for controlling the algae include the followings:

1. *Physical/mechanical* process such as filtration and barriers,
2. *Biological process* such as slow sand filters or activated sludge,
3. *Chemical process* such as coagulation, flocculation and chlorination,
4. *Electro-chemical* even though is adopted to relatively small effected areas
5. Electromagnetic/Electromechanical including radiation, i.e. ultraviolet light and Electromechanical or sonication [1–4].

2.1 Physical and mechanical methods: Their deployment is cumbersome, expansive, requires intensive labor, and continuous follow-up. Algal are not eliminated and the bloom is typically recurring. Pumping of surface algal scums from inshore areas has proven to be an effective mechanism but does not last due to choking of pumps. It removes the algae temporarily [12]. Mechanical control involves the uses of filters, pumps, and barriers (e.g. curtains, floating booms) to remove or exclude HAB cells.

2.2. Biological methods: These are typically slow adding the impracticality to adopt and accommodate industrial constrains. Biological control organisms include species that scavenge on, infect or decompose intruding algal [13]. Biological control method of algal bloom could include enhancement of existing predators involves the use of other organism or pathogen (i.e. virus, bacteria, parasite, zooplankton, and shellfish) that can kill, lysis, or remove or reduce the HAB cells. The method used depends on the scale of red-tide or algal bloom of the species. Among these are copepods, and ciliates, that graze and scavenge on algae and dianoflagellates and some viruses, parasites and bacteria that hold promise as control agent because they are abundant in marine system. There exist some diatoms that exhaust nutrients vary fast in the surface layer, which will reduce the growth of the algae, i.e. *Chattonella*. In the past filter feeding fish have been examined and found to consume some large algae. Lu and coworker used *Oreochromis* (tilapia) to control algal blooms [14]. Recently, the isolation of novel control species through the genetic engineering has been suggested as another promising technique [15].

2.3 Chemical treatments: Chemical control methods currently are the most common. It involves the use of chemical or mineral compounds to kill, inhibit, or remove HAB cells or algal bloom. However, buffering large water volume and bubbling the treatment residuals not only adds economic burden but also risk exceeding EPA thresholds. Numerous approaches have been suggested under chemical treatment and description of these chemical and other emerging methods are detailed below:

1. One of the chemical strategies involves the treatment of blooms with flocculants clay, which scavenge on suspended particles, including algal cell from the sea water and carry them to bottom as sediments. Flocculation refers to a process by which a “flock” that removes fine particulates by binding with them and causing them to clump together [16]. Clay flocculation can be considered successful in managing the marine environment from algae.

2. Chemical algae removal methods may still considered as cost-effective and practically deployable, because the existing workflow would not be significantly changed and there would be no increase in the amount of large-scale equipment and structures. Chemical agents that commonly used are including: i) chlorine, ii) chlorine dioxide, and iii) ozone that could kill, inhibit, or remove algae cells. Nevertheless, chemicals are probably non-specific and thus may kill co-existing algae and other organisms. Numerous studies have showed that pre-treatment with pre-oxidants such as chlorine, chlorine dioxide, ozone, or permanganate can enhance algae removal by chemical coagulation processes [17-26]. Chemical coagulation is an essential step in conventional water treatment processes for algae removal [20,21]. The chemical pre-oxidants are powerful oxidants and can improve algae coagulation by: i) inactivating algal cells, ii) destabilization of algal cells, or iii) liberating extracellular organic matter (EOM). Chlorine acts to kill the algae by first penetrating through the cell wall then destroying enzymes within the cytoplasm. The major disadvantages of chlorine are formation of the environmental pollutants, including Tetra halo methanes (THMs) and haloacetic acids (HAAs), which are harmful by-products.
3. Preoxidation with potassium permanganate would promote the aggregation of algae cells. In addition to adsorption of its reducing product MnO₂ into algae floc, it increases their specific gravity. Permanganate may also induce the release of EOM, which probably enhances the incorporation of MnO₂ into algae floc [18]. Chlorine coupled with permanganate, therefore, has been proved to be in synergistic action in inactivating algae cell and enhance the algae removal in reservoir water. This combined use in pre-treatment also has the advantage of controlling the formation of THMs and safely for drinking water [19]. To efficiently remove algae from drinking water, a strengthening process or combined process of coagulant and chlorine, and with the dosage of potassium permanganate (≈0.3 mg/l) is investigated on three selected water supply and purification plants during the algae outbreak period [20]. The results show that the algae density increases with the increase of water temperature. When the algae density in raw water is less than 106 cells/l, more than 98% of algae can be removed with a coagulant dosage of 13 mg/l. When the algae density is increased to more than 107 cells/l, i.e. during algae outbreak period, more than 96% of algae can be removed using the coagulant and chlorine at approximately 20 mg/l and 4.0 mg/l dosages, respectively. [21] studied the removal of *M. aeruginosa* cells by alum flocculation using a jar test apparatus. They indicated that all cells were removed without sign of membrane damage. Thus the chemical treatment and mechanical action did not damage the cultured *M. aeruginosa* cells and, more importantly, did not result in additional release of cell metabolites above background concentrations. For pilot plant experiments, which consisted of coagulation/flocculation and sedimentation and finally filtration, most of the cells were removed intact and no additional microcystin/toxins was found in the finished water..

2.4 Electro-chemical treatment: Alternative method to the coagulation/sedimentation process, electrocoagulation combined with electroflotation (ECF) technology has attracted

considerable attentions in water and wastewater treatment. Usually, the following processes take place in the ECF system: (a) metal ions release at sacrificial anode through electrolytic oxidation, which are considered as efficient coagulants; at the same time, the oxygen and hydrogen microbubbles are generated at the anode and cathode, respectively; (b) the coagulants react with pollutants and larger flocks are formed; (c) the flocculated particles are removed through sedimentation or lifted to the surface by the microbubbles aeration that adhered to them [22,23]. Besides, the anodic oxidation, cathodic reduction and electrophoretic migration of the ions may also promote the pollutants removal [13]. Compared with conventional coagulation, the coagulants produced in situ in the ECF could offer many advantages, i.e. (i) no anions such as sulphates and chlorides would be introduced in the ECF system, which are always coupled with traditional coagulants [24]; (ii) the coagulants produced by electrolytic oxidation are of high efficiency, and less dosage would be required as compared with conventional coagulants [25]; (iii) pH buffering is unnecessary since ECF performs well in a large pH range [26]; (iv) alkalinity is not consumed during ECF process as the OH⁻ ions are generated at cathode. Moreover, in ECF process, the microbubbles produced at the anode and cathode could also contribute to the separation of pollutants through flotation [27].

Generally, cyanobacteria (often called blue-green algae) have a lower density than that of water due to their gas vacuoles for adjusting the content of water [28]. Thus, it is difficult to remove the cyanobacteria through sedimentation. On the other hand, the ECF process with the combination of coagulation and flotation might be an effective method for the algae removal. Poelman et al. [29] found that excellent separation of cyanobacteria (>90%) can be achieved by electrolytic flocculation, with relatively low energy consumption (0.3kWh/m³). Alfafara et al. [30] demonstrated that the electroflotation alone also exhibited a maximum algae removal of 40–50%. While complete removal of algae was obtained by Ghernaout et al. [31] when treating Keddara raw water by the electrocoagulation using aluminum electrodes. The algae removal by electro-coagulation–flotation (ECF) technology was investigated by Gao and coworkers [32]. The results indicated that aluminum was an excellent electrode material for algae removal compared with iron. The optimal parameters determined were: current density (1mA/cm²), pH (4–7), water temperature (18–36°C), algae density (0.55E9–1.55E9) cells/l. Under the optimal conditions, 100% of algae removal was achieved with the energy consumption as low as 0.4kWh/m³. The ECF performed well in acid and neutral conditions. At low initial pH of 4–7, the cell density of algae was effectively removed in the ECF, mainly through the charge neutralization mechanism; while the algae removal worsened when the pH increased (7–10), and the main mechanism shifted to sweeping flocculation and enmeshment. Furthermore, initial cell density and water temperature could also influence the algae removal. Gao et al. [33] also investigated the effectiveness and mechanisms of algae removal by ECF process using aluminum electrodes. It was also investigated in the presence of Cl⁻ ions. The results showed that the addition of Cl⁻ ions (1.0, 3.0, 5.0 and 8.0mM) promoted the algae removal in terms of both the cell density and chlorophyll reduction, which could be attributed to the following two reasons. Firstly, active chlorine could be generated in the ECF when Cl⁻ ions were present. The electrochemically generated active chlorine was demonstrated to be effective for the inactivation of algae cells with the aid of the electric field in the ECF. Secondly, the Cl⁻ ions in the algae solution could enhance the release of Al³⁺ from the aluminum electrodes in the ECF. ECF technology was reported as the

most effective way for algae removal, from both the technical and economical points of view. Nevertheless the main drawback is that the pH of water increases after ECF, since OH⁻ directly produced at cathode and increase of current density increase energy consumption [32]. The addition of chloride ion (brine solution) on ECF can cause corrosion and alleviated formation of oxide film by Cl⁻ ions were observed on the anode surface [33]. Table 1 summarize the chemical biocidal treatment and their reported effective dosage.

2.5 Electromechanical via Sonication: Using chlorine, ozone, chlorine dioxide and in combination with potassium permanganate as preoxidant lead others the removal of algae by coagulation [34,35,36]. However, because some preoxidants are found to stimulate the release of Microcystin from algae cells [37] or formation of disinfection by-products (DBPs) [38], Ultrasound-enhanced coagulation was emerged. Using this method, *Microcystis aeruginosa* (common species of toxic algae) removal is studied by Zhang and Zhang [39]. These results reported that sonication significantly enhances the reduction of algae cells, solution UV254, and chlorophyll-a without increasing the concentration of aqueous microcystins.

The main mechanism involved the destruction of gas vacuoles during ultrasonic irradiation inside algae cells that acted as ‘nuclei’ for acoustic cavitation. The efficiency of cyanobacteria coagulation depends strongly on the coagulant dose and sonication conditions. When the coagulant dose was 0.5 mg/l, 5 second of ultrasonic irradiation increased algae removal efficiency from 35% to 67%. As further sonication lead to slight enhancement to the coagulation efficiency due to better mixing, and the optimal sonication time was 5 second. The most effective sonication intensity was 47.2 W/cm², and the highest removal ratio of *M. aeruginosa* was 93.5% by the sonication–coagulation method. Experiments with reservoir water showed that this method could be successfully applied to natural water containing multiple species of algae. Algae removal by ultrasonic irradiation–coagulation is carried also be by Liang et al. [40] who stated that the sonication time has more prominent effect than sonication intensity on the removal of algal.

Numerous studies have indicated that ultrasonic irradiation inhibit eutrophication followings two mechanisms: i) by direct penetration and breaking down gas vesicles in algae cells, ii) inhibits the process of photosynthesis and therefore hinders the algal growth. Moreover, ultrasound application is considered as pollution-free or as “green chemical technique” and may have a promising future for the control of algae growth [39–48].

A few studies have directly examined the effect of ultrasonic irradiation on enhancing coagulation for algae removal. In water treatment it is difficult to remove algae cells due to special characteristics such as negative surface potential and that their metabolites are prone to adsorb colloidal particulates [40]. Ultrasonic irradiation can alter the characteristics by breaking down their gas vesicles, thus achieving better algae removal efficiencies by enhanced coagulation. Although optimal ultrasound parameters are determined, the technique is still not fully tested for large-scale and practical application. The drawback of ultrasound is that it is thought that cannot work adequately on massive water bodies due to its limited irradiation range. New emerging sonicator manufacturers however claimed that they break this barrier and their range can reach as far as several hundred meters long. Table 2 summarizes the reported literature on electrochemical treatment of algal.

“Ultrasound” basically emits a sound beyond the frequency that can normally be heard in air by the human ear. In air, human ear can hear sounds between 20 Hz and 20,500 Hz. Sound travels at 4710 feet/sec or roughly 0.9 miles/sec in fresh water, over 4 times faster than in air. That’s over 3,200 miles per hour. Some algae, fungi and bacteria have gas vesicles and are affected (ruptured) by ultrasound waves and consequently causing death to them.

When plants absorb ultrasonic waves, the associate energy is converted into heat, leading to a “thermal” effect. Therefore, the consequence of ultrasound on plant cells and tissues is not only mechanical but thermal as well [49]. It is reported that due to both actions mechanical vibration and thermal heating the cell wall, vesicles and nucleus membrane are ruptured and cell is succumbed according to Ahn et al .[50] and Taylor D. [51]. Advantages of ultrasound treatments are numerous amongst these are:

- inhibit eutrophication by breaking down gas vesicles in algae cells.
- impairs the process of photosynthesis and therefore controls algae growth.
- a pollution-free and “green technique” use
- less laborious and easy to implement

2.6 Reported literature on Ultrasound treatment:

Documented biological effects of sonication on plant cells includes chromosomal anomalies, disruption or collapse of gas vesicles and subsequent loss of buoyancy, damage to or destruction of cellular organelles, cell death, changes in cellular osmotic potential, inhibition of photosynthesis and cell division, destruction of cell membranes, and formation of free radicals [49, 50,52, 53,54,55,56]. These effects have been reported after short exposures to ultrasonic waves, from several seconds, as in the work of Lee et al. [54], to two minutes in the work of Zhang et al. [52], Hao et al. [53], Ahn et al [56] and Soar [50]. They reported that algal cell densities and chlorophyll-a concentrations of *Microcystis aeruginosa* were significantly decreased after 3 days of ultrasonication when 20 kHz applied twice daily for 2-minute exposures.

Ultrasound also has been used to reduce algal biofilms in some water treatment facilities. The application of ultrasonic irradiation to control cyanobacterial blooms in eutrophic systems including *M. aeruginosa* and *Spirulina platensis* has been documented by many researchers. Laboratory and greenhouse studies by Wu and Wu, 2007, [49], demonstrated that ultrasonic waves of 20 kHz, aimed directly at water chestnut (*Trapa natans*) stems and petioles, caused severe damage and plant death. These findings indicate that ultrasound may hold promise as a new control technique for this invasive weed species. Earlier work of Soar [56], shows that he submersed aquatic macrophyte, Eurasian watermilfoil (*Myriophyllum spicatum*) is also susceptible to ultrasound.

Working Mechanism: The ultra sonic waves typically target the i.) *Gas Vesicles* ii) *Contractile vacuole* and *plasmalemma*, as well as iii) the biofilm and weakening the cell wall [40].

- **Gas Vesicles:** Each algal cell has thousands of gas vesicles. It represents a stiff but hollow cylindrical structures with conical ends made of proteins. As blue-green algae create carbohydrate mass or better termed ballast during sunlight hours, they gain enough weight to be heavier than water and sink. This allows them to find necessary nutrients near the bottom or at lower depths. As the carbohydrate ballast is consumed, they slowly

rise to the surface and sonic waves can damage these vesicles as explained by Hutchinson,2010, [57].

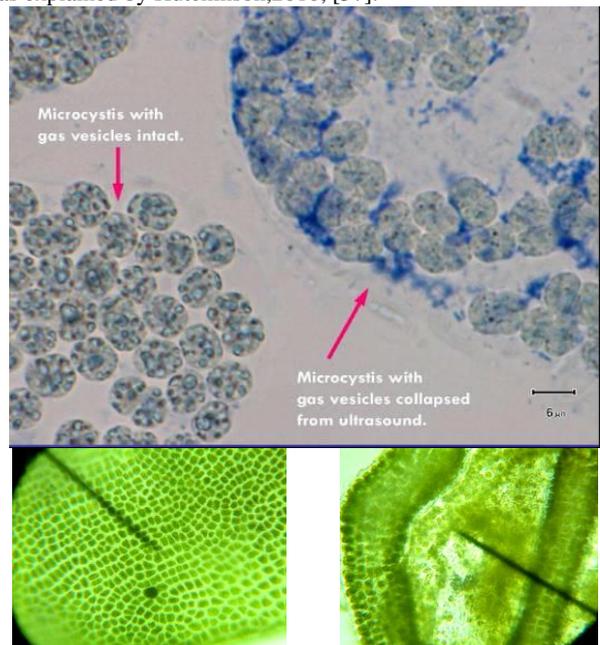


Fig. 5. Blue-green algae with ultrasonically damaged gas vesicles – photo (below other’s work on *prolifera*) Before/After

- **Contractile vacuoles and plasmalemma:** Contractile vacuoles are osmoregulatory organelles on the algae outer sheath surface and allow the inflow of water and nutrients into and out of the cell through specialized membrane transporters called aquaporins. They are connected to the plasmalemma or inner cell wall that lies beneath the outer sheath. The ultrasound causes the plasmalemma to detach from the outer wall and the contractile vacuole. When this occurs, the internal cell begins to shrink as it can no longer control its internal pressure, receive nutrients, expel waste, or protect itself from external bacterial attack. The mode of action appears to be by disruption of the connections between the plasmalemma and the algal cell walls causing loss of membrane integrity, probable leakage of cytoplasm and a collapse of the cell into a dense brown mass.

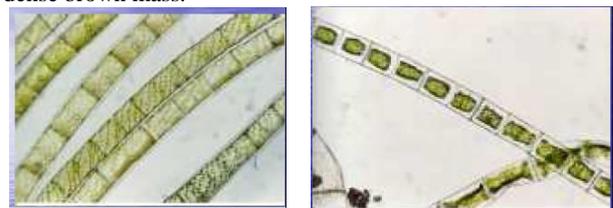


Fig. 6. Algae (Spirogyra, left), from the source without sonication and after 7 days exposure to ultrasound.

Figure 2 shows how the plasmalemma is coming away from the cell wall. It shows that the cells have shrunk. There is increased granulation of the cytoplasm, indicating loss of chloroplast structure and loss of connectivity with other cells and the external environment.

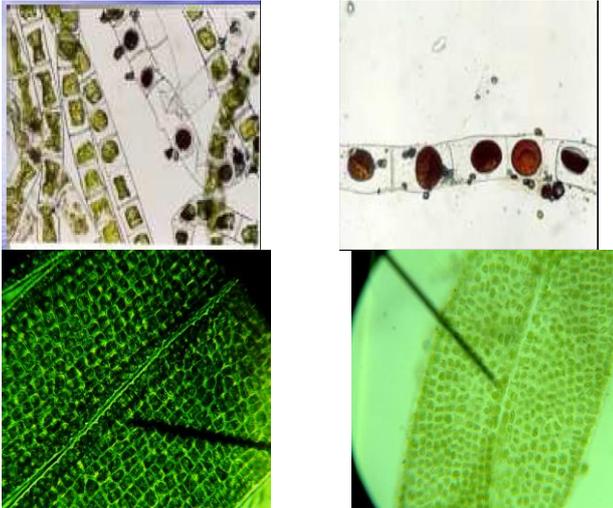


Fig 7: After 14 days exposure as more evidence of cell shrinkage, (right) some forming denser circular brown agglomerations in the center of the cell (below other's work on *prolifera* before and after exposure).

There is some evidence of cytoplasm leakage from the cells, indicating further damage to the cell wall [57]. Figure 7 shows the treatment after two weeks and three weeks exposure, as well as before and after and shows complete breakdown of cell structure.

- **Ultrasound waveform** the laboratory sonic bath are typically carried out at intensified conditions and characterized with continuous frequency signature ($\approx 40\text{kHz}$) and high amplitude (up to 500Watt). The signal of some industrial sonicators however for algal removal are depicted in figure 8. They vary from pulsating signal of 1 to 2 seconds duration and low amplitude of 0.5-1Vpp (5-25Watt) to modulated amplitude and longer burst signals that last several seconds. In general the effective frequency needs to be above the audible frequency range of humans of 20,000 Hz [49,56]. Complete destruction of algal species can take up to 4 to 5 weeks with the relatively low power continuous (24-hour) application as stated in the work of Xiaoge et al. [58] and Kotopoulis et al. [59]. The shape of the waveform still needs further study to better correlated to the species in question as one waveform may control specific stains while has no effect on another. Sound waves are generated by a submersed transducer and more effectively placed near the water surface where algal present. The emitters are typically submerged in the polluted water and an influenced field similar to the sonic cone is created with longer effectiveness range to the blue green microalgal, followed with roaming green-algal and shortest to biofilm.

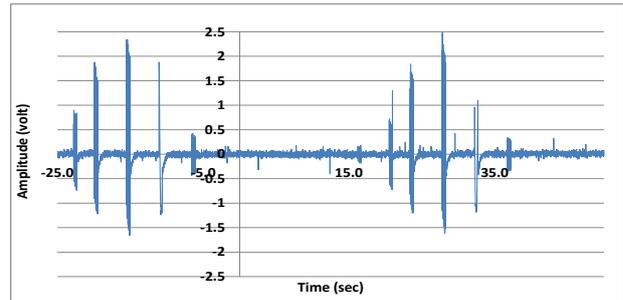


Fig. 8. Common industrial sonicator signals with short and high amplitude and different pulsating signals

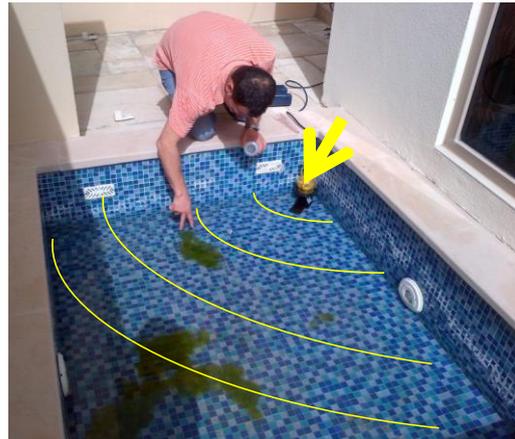
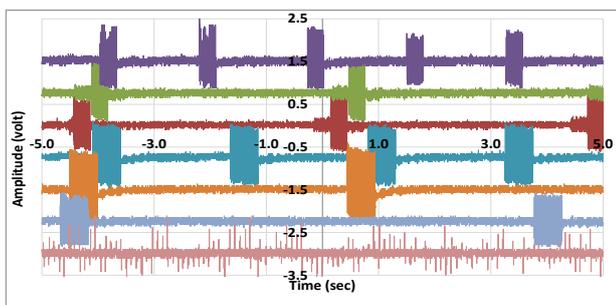


Fig. 9: Application of sonication to *prolifera* in benchscale open basin

It reaches as far as 650m in calm water to disinfect blue micro algae, and up to 250m for the green micro algae and near 120m to the biofilm. Application of sonication to the algal resulted in oozing, pigment reduction, pertenance, and significant reduction on chlorophyll-a. Some of these results produced in our lab are depicted in figure 9.



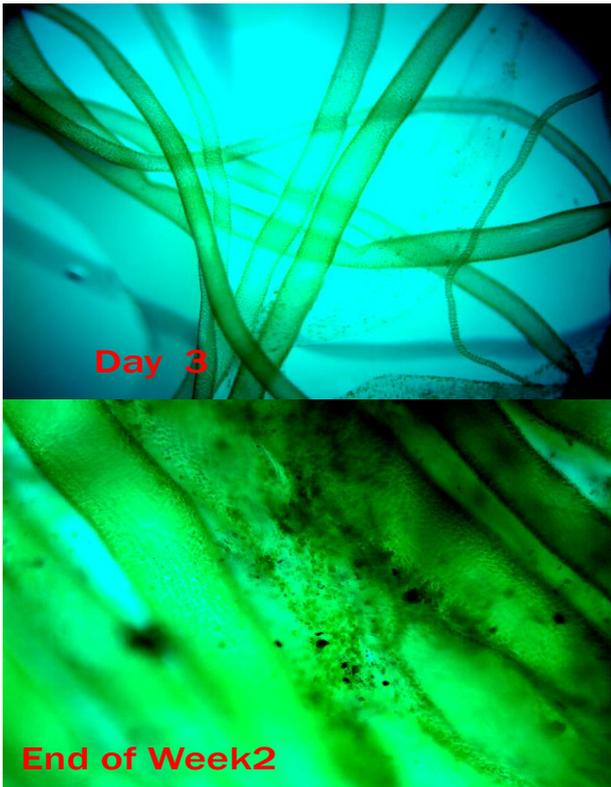


Fig. 10: Microscopic view of nearly healthy algae at 3rd and after sonicated on the 15th day taken from open basin experiment of fig. 9.

3. Conclusion

In this work a review on the *Enteromorpha prolifera* Macro algae eutrophication is presented. This algal strains appears to invade the water basin in the Gulf region and some part of the gulf shore. Initially the physical appearance, proximate and elemental compositions as well as the heating value of the such algal is determined and presented to confirms it strain as the macro “*Ulva Enteromorpha prolifera*”. Secondly a literature review is presented on the current and new emerging treatment technologies covering physical, chemical and electro-mechanical (sonic wave) methods.

Commonly used chemical treatment agents include chlorine, chlorine dioxide, and ozone which could kill, inhibit, or remove algae cells. This has been thought is the best cost-effective technology. Chlorination can cause a leaky cell membrane, but no change in cell morphology or to the surface charge of algae and flocks. Chlorine dosage however affected the level and nature of released intracellular organics [60]. The major disadvantages of chlorine are formation of THMs and haloacetic acids (HAAs), which are harmful by-products. Some preoxidants are found to stimulate the release of Microcystin from algae cells into the water. In addition, certain preoxidants may expedite the formation of disinfection by-products (DBPs). Chemical treatment depends on anionic potential and some of oxidant like preoxidants releases toxins. They can increase the THM and HAA of water.

Amongst the promising mitigation/treatment methods (between physical, biological, electro-chemical, electro mechanical) is the use of the sonication method. It is a pollution-free or a “green electrochemical” technique. This work reviewed some favorable work of this method additional to the author’s work. Currently, the author is investigating the practicality of large

scale application of sonic waves, and its combined presence with lower chemical dosage to enhance the treatment of *prolifera*. Reported results on this method show the effectiveness of the low amplitude and long duration. However, signal form also needs to be correlated to the species in question as one waveform may control specific stains while has a lesser or no effect on another.

As the acoustic pressures may surpass the NURC by over 35 dB, caution should be taken when using these techniques where aquatic or semi-aquatic animals are present within the surrounding habitat.

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Table 1: Summary of the literature review on chemical biocidal treatment

Type of algae	Group/Paper	Methodology	Affecting Factors	Results and conclusion/ Comments
Cyanobacterium Microcystis aeruginosa	D. Burch and Renate M.A. Velzeboer [21]	Chemical treatment (alum and flocculation) Aluminum sulphate (alum)	Concentration of alum and application of flocculation	Cells were removed without damage to membrane integrity. Thus the chemical treatment and mechanical action did not damage the cultured M. aeruginosa cells and, more importantly, did not cause additional release of cell metabolites above background concentrations.
Blue green algae (Cyano bacteria)	Qiaohui Shen, Jianwen Zhu, Lihua Cheng, Jinghui Zhang , Zhen Zhang Xinhua Xu[20]	Coagulation with Chlorination (alkaline aluminium chloride) + peroxide treatment (KMnO ₄)	1)Water Temperature 2) Dose of Coagulant	1)Algae density increase with increase of water temperature. 2) 98% of algae can be removed with a coagulant dosage of 13 mg L ⁻¹ . During algae outbreak period, 96% algae can be remove during the coagulant and chlorine of dosages of approximately 20 mg L ⁻¹ and 4.0 mg L ⁻¹ , respectively. Chlorine coupled with permanganate, has been proved to be in synergistic action in inactivating algae cell, pre-treatment helps to remove THM
Cyanobacteria	Shanshan Gao, Jixian Yang, Jiayu Tian, Fang Ma, Gang Tu, Maoan Du [32, 33]	Fe or Al Electrode	1)Nature of electrode 2) Effect of current density (0.5-5mA/cm ²) 3)pH range 4)Effect of temperature	1)Iron electrodes were observed to be less efficient as compared with aluminum electrodes (78.9% vs. 100%) [33,34]. No anions such as sulfates and chlorides would be introduced in ECF systems, coagulant produced by ECF has high efficiency, pH adjustment is unnecessary, alkalinity is not consumed (15-18) Difficult to remove caynobacteria by sedimentation due low density than water (19) No anions such as sulfates and chlorides would be introduced in ECF systems, coagulant produced by

			<p>5)Electrolysis time [32]</p> <p>6) Effect of Chloride concentration -1-8mM(33)</p>	ECF has high efficiency, pH adjustment is unnecessary,
Blue green Algae	Y.M. Chen, J.C. Liu, Yih-Hsu Ju, [34]	Cationic N-Cetyl-N-N-N-trimethylamm onium bromide (CTAB), anionic sodium dodecylsulfate (SDS),and the nonionic Triton X-100 SDS+Chitosa n	<p>1)The electrostatic interactions between collector and algae surface plays a critical role in the removal.</p> <p>2)Effects of pH</p> <p>3)ionic strength</p> <p>4)air flow rate</p> <p>5)alkalinity on flotation efficiency</p>	10% of algae removal was achieved when SDS and Triton X-100 were used, respectively; and 90% algae was removed when CTAB was used. Upon the addition of 10 mg ⁻¹ of chitosan, over 90% algae was removed when SDS was used as the collector.
Microcystis aeuroginosa	Min Ma, Ruiping Liu, Huijuan Liu, Jiuhui Qu, organic [60]	Chlorintaion+ alum coagulation	<p>1)Effects of chlorination - surface charge, cell integrity, and release of intracellular organic matter (IOM)</p> <p>2) influence alum coagulation.</p>	Chlorine inactivation of algae was dominated by the released IOM, rather than by the cell lysis. Released IOM increased the alum dose to electro-neutralize these organics. DOM species with sufficient MW, such as protein, showed positive effects to aid coagulation. However, the formation of protein-coagulant complexes inhibited algae removal and thus increased alum demand.

Table 2: Summary of the literature review on sonic wave treatment

Type of algae	Group and Paper	Methodology	Affecting Factor	Results and conclusion	Inference
<i>Microcystis aeruginosa</i> (permitted level of microcystis-1µg/l)	Guangming Zhang,Panyue Zhang, Maohong Fan[39]	Cogulation with/without sonic waves 1)Coagulant PolyAluminum Chloride-PAC + 2)Sonication Power	1)Coagulation dose 0.5mg/l-3mg/l 2)Sonication time-1-5s 3)Sonication Intensity-0-15.8W/cm ²	1)Coagulant dose-3mg/l PAC -9% removal of algae without sonictaion.Highest cell reduction (algae) was 93.5% with a PAC dose of 3 mg/l and sonication time of 60 s 2)Sonication time 1-5s 3) Increasing the ultrasonic intensity from 23.6 W/cm ² to 47.2 W/cm ² greatly improved the algae removal. But further increase and at high intensity diminishes the performance. Optimum 47.2W/cm ² (50W). 4)30Wand 5S sonication decrease concentration of the UV254(solution UV254 represents both algae cell density and the concentration of organic impurities), removes chlorophyll a. Measurement of the aqueous microcystins showed that the M. aeruginosa solution had a microcystin concentration of 0.21–0.27 mg/l. Coagulation reduced 5.1%–19.2% of microcystins, which were barely influenced by ultrasonic treatment. 5)Optimum coagulation time-5s-helps in cavitation of nuclei then rupture happened	Control of irradiation duration for massive application and practical application in large scale
<i>Spirulina platensis</i>	G. Zhang, P. Zhang, B. Wang, H. Liu[41]	Sonication	Sonication time	1-5s	
Blue green algae	Liang Heng, Nan Jun, He Wen-jie, Li Guibai Desalination [40]	Sonication	1)Sonication intensity -Effect of various ultrasound frequenciesand power supplies 2)Sonication time-irradiation duration (time)	The ultrasonic treatment at 40 kHz and 60W for 15 s can improve algae coagulation removal by 12.4% as compared with direct coagulation The optimal irradiation duration is determined as 15 s. In conclusion, ultrasonic irradiation-coagulation proves effective for algae removal.	Sonication intensity has less role on algae removal.
<i>Anabaena sphaerica</i> (Blue green)	Spiros Kotopoulis, Antje Schommartz, Michiel Postema [59]	Sonication	Sonication frequency	Algal forced to sink. This supports our hypothesis that heterocysts release nitrogen under sonification in the clinical diagnostic range. As supported by previous studies, under identical pulse length and pulse repetition, eradication is most effective close to heterocyst resonance, at a driving frequency of roughly 1 MHz.	The acoustic pressures should be less than 35 dB . Harmful for aquatic or semi-aquatic animals are present.
Cyanobacteria	Xiaoge Wu, Eadaoin M. Joyce, Timothy J. Mason [58]	Sonication	Sonic Intensity (frequency, power)	Hydrodynamic cavitation offers a potential treatment for algae blooms however this requires a number of passes through the reaction zone	Large scale application