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Algae and cyanotoxins removal by coagulation/flocculation: A review

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ABSTRACT

A continuing worldwide problem for drinking water treatment industry is the presence of algae in source water. Algae in drinking water supply can cause significant disturbances including taste and odour, production of disinfection by-product, obstruction to coagulation, clogging of filter, and assimilable organic carbon for growth of biofilm. Algae removal by conventional treatment is more difficult than inorganic particle, due to their low specific density, motility, morphological characteristics and negative surface charge. This review examines the character of freshwater algal populations and their algogenic organic matter from a coagulation/flocculation (C/F) perspective and reviews C/F for their removal. It was suggested that the coagulation mechanism was ''one of mutual attraction and charge neutralisation (CN) of the algae and the incipient hydroxide flocculi'' and as such the hydroxide precipitant should be positively charged. It was observed that on adjusting the zeta potential of an algal suspension with a specific operational range, removal was significantly improved. However, it has been demonstrated that the impact of some algal characteristics means removal by CN mechanism is unfeasible. Removal by CN can be obtained if the algal cell is spherical, free from protruding appendages or polymeric substances and microscopic in size. Deviation from this optimum conformation is common among algae cells and hence the optimum removal conditions cannot always be predicted by charge measurement data. In many instances, even increasing the coagulant dose to enable removal by sweep flocculation mechanism does not improve removal. However, successful clarification relied heavily on the optimisation of preceding C/F and coagulant demand was important in this respect.

Keywords: Algae; Cyanotoxins; Natural organic matter; Coagulation; Flocculation; Water treatment

1. Introduction

Many water sources in the world contain natural organic matter (NOM), which should be eliminated from water prior to its delivery to consumers. Otherwise, there is a potential health hazard caused by disinfection by-products (DBPs), the fouling of membranes and ion-exchange resins, the deterioration of water quality in distribution systems due to bacterial growth, or the oxidation of dissolved iron and manganese to insoluble forms — not to mention the aesthetics of the water delivered, i.e. the colour [1,2].

Algae are photosynthetic, aquatic plants that utilise inorganic nutrients such as nitrogen and phosphorus [3,4]. Cyanobacteria, approximately 2000 species of cyanobacteria identified, are typically referred to as blue-green algae because they perform photosynthesis and are similar in size and colour, even though they are bacteria [5–10]. Algae are ubiquitous in surface water but do not pose a problem to water treatment processes provided

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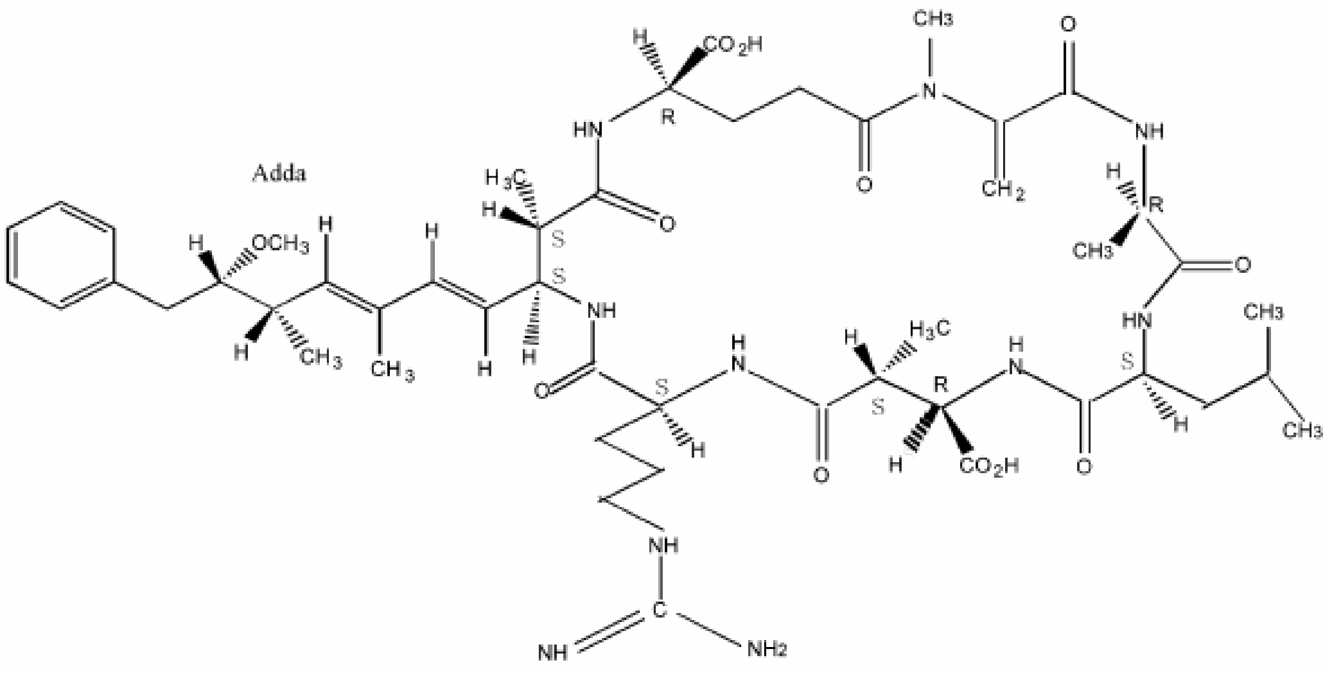
populations are relatively low. However, seasonal algal blooms can dramatically increase populations on relatively rapid timescales and as a result water treatment process efficiency can be impaired. On one occasion this has led to the presence of algae in treated water or even to the closure of a particular site. For example, in the Anglian Region of the UK, a cyanobacteria bloom of 400,000 cells mL^{-1} of Microcystis could not be treated, resulting in the treatment plant being out of service for an 8-week period [3,11]. Furthermore, algal cells and associated algogenic material are trihalomethane (THM) precursors which have resulted in the restriction of chlorine usage [12–15]. Similarly, the potential for toxin release by cyanobacteria, in particular from Microcystis, has resulted in the World Health Organisation setting a guideline value of 1 $\mu g\ L^{-1}$ for the associated toxin, microcystin-LR (MCLR) [16–19]. The structure of MCLR is shown in Fig. 1; this compound is a cyclic heptapeptide containing 3-amino-9-methoxy-2,6,8-trimethyl-10-phenyldeca-4,6-dienoic acid (ADDA), with leucine (L) and arginine (R) in the variable positions [20]. Finally, the presence of offensive taste and odour compounds including 2-methylisoborneol (2-MIB) and geosmin in the resultant drinking water supply has also been attributed to high algal populations [3].

Algae are traditionally characterised according to differences in pigmentation and cell complexity arising as a result of evolution [3]. Cyanobacteria existed prior to all algal phylum and are prokaryotic cells [21]. Algae evolved as a result of primary endosymbiosis, whereby a prokaryotic cell engulfed a bacterium on two occasions to produce eukaryotic green and red algal phyla, differentiated by the quantity of chlorophyll a in the cell pigmentation. Current opinion is that secondary endosymbiosis, whereby eukaryotic cells engulfed other eukaryotic cells, produced phyla including diatoms, chrysophytes, cryptomonads, brown algae and dinoflagellates [22]. Within a particular phylum, the species can vary significantly in terms of their morphology and other important functionalities including the composition and quantity of excreted extracellular organic matter (EOM). This suggests that a water treatment process may well be able to successfully remove a number of species from particular phyla, while struggle with others [3].

Consequently, it is required that algae are removed from drinking water, preferably during the initial stages, i.e. coagulation/flocculation (C/F), to ensure minimal impact on subsequent processes [23–25]. This paper seeks to review algae and cyanotoxins in surface waters, and their removal in water treatment, and understand how C/F may be more efficient in algae removal.

2. Algae and cyanotoxins in surface waters

In the context of drinking water treatment, NOM refers to the complex matrix of organic compounds present in natural waters. The NOM in source waters has important influences on many aspects of water treatment, including the performance of unit operations (e.g. oxidation, coagulation, filtration), and the potential for forming harmful DBPs. In addition, NOM remaining after



Adda : 3-amino-methoxy-10phenyl-2,6,8-trimethyl-deca-4,6-dienoic acid

Fig. 1. The structure of microcystin-LR [20].

treatment may support bacterial growth in distribution systems [26]. The nature, distribution, and reactivity of organic matter (OM) in source waters are determined by a variety of biogeochemical phenomena occurring in the natural water system and its watershed, namely the nature and strength of interactions among organic source materials, biological cycles, soil chemistry, and hydrology [27]. For many surface water systems, algal productivity is an important source of NOM and DBP precursors [28–31]. Extracellular products, compared to whole cells and cell fragments, often represent the more significant contribution to the concentration of total organic carbon [32]. The degree of influence that algae have on NOM depends on the type of aquatic environment [33]. In freshwater systems, the influence of algae on NOM generally becomes more significant as production of organics in a water body dominates the contribution by runoff from the watershed [34,35]. In general, the NOM in large or highly productive lakes and reservoirs is influenced greatly by algae, while the NOM in small or low productivity lakes and reservoirs originates more from terrestrial sources [26].

Since the NOM matrix of surface waters changes seasonally, it is reasonable to propose that the nature of dissolved organics in natural water may be related to seasonal shifts in algal speciation and dominance [36]. While the total concentration of dissolved organic carbon (DOC) may, in some cases, be relatively constant over the seasons, the character or quality of the organic matrix is likely to vary. The most prevalent historical model of aquatic NOM is similar to the model of NOM in soils; that is, organics are thought to be primarily lignin-based and highly aromatic. A newer model suggests that aquatic NOM can be significantly different from NOM in soils depending on influences to the NOM sources [36]. In this model, NOM is primarily aliphatic [26]. Furthermore, natural organic substances, when measured as DOC, have levels in the range of 0.1–115 g C m^{-3}, with 5.75 g C m^{-3} being reported as a global average for streams [2]. DOC fraction consists of amino acids, fatty acids, phenols, sterols, sugars, hydrocarbons, urea, porphyrins, or polymers [37]. The polymers include polypeptides, lipids, polysaccharides, and humic substances. The make-up of organic substances for the average river water is 20% fulvic acids, 10% humic acids, 30% hydrophilic acids, 10% carbohydrates, 6% carboxylic acids, and 4% amino acids [2,38–45].

On the other hand, the blue-green algae or cyanobacteria represent a diverse group of organisms that produce potent natural toxins [46–49]. There have been case reports of severe morbidity and mortality in domestic animals through drinking water contaminated by these toxins. Microcystins, in particular, have been associated with acute liver damage and possibly liver cancer in laboratory animals [50]. Although, there has been little epidemiologic research on toxin effects in humans, a study by Yu [51] found an association between primary liver cancer and surface water. Surface water drinking supplies are particularly vulnerable to the growth of these organisms; current US [47] drinking water treatment practices do not monitor or actively treat for blue-green algal toxins including the microcystins. After a monitoring survey in Florida found organisms and microcystins (among other cyanobacterial toxins) in surface water sources used for drinking water supply, a pilot ecological study was performed using a Geographic Information System (GIS) to evaluate the risk of primary hepatocellular carcinoma (HCC) and proximity to a surface water treatment plant at cancer diagnosis [52,53]. The study linked all HCC cancers diagnosed in Florida from 1981 to 1998 with environmental databases. A significantly increased risk for HCC with residence within the service area of a surface water treatment plant was found compared to persons living in areas contiguous to the surface water treatment plants. However, this increased risk was not seen in comparison to persons living in randomly selected ground water treatment service areas or compared to the Florida cumulative incidence rate for the study period, using various comparison and GIS methodologies. Furthermore, these findings must be interpreted in light of significant issues of latency, high population mobility, and the lack of individual exposure information. Nevertheless, the issue of acute and chronic human health effects associated with the consumption of surface waters possibly contaminated by blue-green algal toxins merits further investigation [47].

3. Algal removal in water treatment

Coagulation has historically been employed in water treatment practice to decrease levels of turbidity and NOM [38]. However, selection of specific coagulation processes has been traditionally based on raw water turbidity and is not usually optimised for the removal of NOM [39]. In actual practice, operational decisions for coagulation processes are usually empirically based on past performance, rather than on accurate models that account for a water's organic quality. Therefore, there is a need to better understand coagulation performance in relation to the organic character of water supplies. Such an understanding would be particularly valuable in efforts to reduce DBP formation and improve overall treatment efficiency [26].

In addition to conventional coagulation, several newer processes for improving the removal of NOM before final disinfection are currently being investigated. These efforts are being driven by the anticipated introduction of the US EPA's Disinfection/Disinfection By-Products Rule. Treatment processes being studied include coagulation enhancement by pH adjustment, adsorption to granular activated carbon, and membrane filtration processes [40,41]. Another process with potential to enhance removal of DOC is preozonation, or pretreatment with ozone prior to coagulation. Several researchers have investigated the interactions by which preozonation alters the stability of particles, organic compounds, and algae [42–44]. However, the reported performance of preozonation for organics removal is variable and appears to be site specific. Preozonation selectively modifies fractions of the NOM matrix, but overall removal is difficult to predict [45]. A plausible reason for the variable benefits of ozonation may be related to the varying composition of the NOM matrix in aquatic systems [26].

Ives conducted some of the original research into the significance of surface charge with respect to algal coagulation [54]. It was suggested that the coagulation mechanism was "one of mutual attraction and charge neutralisation (CN) of the algae and the incipient hydroxide flocculi" and as such the hydroxide precipitant should be positively charged [3]. In a more recent study, the flocculation mechanism of *Synechocystis minuscula* (diameter of 6 μm) using alum coagulant was investigated [3]. It was determined that at pH 5 charge reversal was achieved with 7 mg L–1 as Al and cells started to form distinctive aggregates [3]. It was suggested that aggregation occurred as a result of the cationic aluminium hydroxo complexes interacting with the algal surface, in accordance with the principle of adsorption coagulation with CN [55,56]. Certain coagulation experiments have taken surface charge into account by measuring the zeta potential (ZP) when examining conditions for optimal removal [3]. On comparing two studies [57,58], it was observed that on adjusting the ZP of an algal suspension with a specific operational range, removal was significantly improved. The range was noted to alter depending on the clarification procedure. To illustrate, for both sedimentation examples the bands are fairly narrow, with optimum removal occurring at between –5 to 0 mV and –8 to 0 mV for Seine and Nile river water, respectively [58]. Use of flotation as opposed to sedimentation widened the ZP range for optimum removal; such that successful removal was obtained at more negative ZP ranges of –15 to 0 mV [59]. Additionally, the residual turbidities were much lower for dissolved air flotation (DAF) processes than for sedimentation [3]. This occurred irrespective of phyla, where green algae were represented by *Chlorella vulgaris* and *Pediastrum*, diatoms by *Cyclotella* and *Melosira* and cyanobacteria by *Synechocystis miniscula*. Furthermore, the varying morphology did not appear to impact on the requirement to operate within a specific ZP range whilst *Chlorella* and *Synechocystis* are micro-algae with spherical cells, *Cyclotella*, *Melosira* and *Pediastrum* are barrel shaped with spines, filamentous and disc shaped, respectively [3].

The relationship between algae cell destabilisation by reduction of the magnitude of the ZP and coagulant dose has been shown to be time dependent, particularly for relatively low Al doses [3,60]. For example, on dosing 1 mg L^{-1} of Al to 1 × 10^6 cells mL^{-1} of the spherical cyanobacteria cells, *Synechocystis*, the ZP took over 6 min to decrease to the final value. The time lag was reduced to 2 min when the dose was increased to 10 mg L^{-1}. This phenomenon was attributed to algae actively influencing the surface charge by ion transfer across the cell membrane to restore the negative charge, as has been discussed in previous studies [61,62]. It was supposed that higher Al dosages disrupted the cell repair mechanism, leading to more immediate destabilisation. This observation held for four additional species of algae—the spherical green algae *Chlorella* and other cyanobacteria species including spherical Microcystis and filamentous *Pseudanabaena* and *Planktothrix*. It was further concluded that algae may therefore need more time to flocculate than other particles. This was demonstrated when comparing kaolin, NOM and the spherical green algae *Chlorella* vulgaris, where steady state floc size was achieved after 4, 5 and 25 min, respectively [63]. Furthermore, no observable growth was observed for the *C. vulgaris* until after 7 min [3].

It has been demonstrated that the impact of some algal characteristics means removal by CN mechanism is unfeasible. Removal by CN can be obtained if the algal cell is spherical, free from protruding appendages or polymeric substances and microscopic in size [61]. Deviation from this optimum conformation is common among algae cells and hence the optimum removal conditions cannot always be predicted by charge measurement data [3]. In many instances, even increasing the coagulant dose to enable removal by sweep flocculation (SF) mechanism does not improve removal. For example, the diatoms *Asterionella formosa* and *Fragillaria crotonensis* are so large that filter clogging occurs rapidly and increasing coagulant addition only decreases run times [3]. Pieterse and Cloot [61] noted that large algal cells such as the aforementioned can no longer be treated as colloidal entities, and therefore discussion of system "destabilisation" may not be appropriate. They identified the likelihood of the presence of an additional short range force of mutual attraction (universal gravitation) favouring the coagulation process [3,61].

EOM acting as a polymer aid can also decrease the amount of coagulant required, for example, the green algae *Dictyosphaerium pulchellum* had an EOM composition that enhanced flocculation, when present in small concentrations (0.1–2.0 mg L^{-1} as C). However, at increased EOM concentrations (> 1–2 mg L^{-1} as C) flocculation was inhibited for a dose of 3 mg L^{-1} as Fe, and only when 10 mg L^{-1} as Fe had been added was coagulation satisfactory [3]. This was attributed to either steric hindrance or to metal complexation. Another study determined that the coagulant demand did not wholly correlate with cell surface area as 0.25 mg L^{-1} as Al was required for destabilisation of *Pseudanabaena* compared to 1 mg L^{-1} for a similar surface area of *Synechocystis* — both of which are cyanobacteria, the former filamentous and the latter spherical [3,60].

4. Enhanced coagulation

4.1. Why algogenic organic matter extracted from algae is difficult to remove?

When the algae populations increase, treatment processes can be adversely affected [64–74]. For example, coagulant demand is increased and floc formation is poor or membrane fouling is increased [75,76]. This is a result of not only increased cell concentration but also associated algogenic organic matter (AOM) which can form a substantial component of the algae system [77]. AOM arises extracellularly via metabolic excretion, forming EOM or intracellularly due to autolysis of cells, forming intracellular organic matter, and is known to comprise proteins, neutral and charged polysaccharides, nucleic acids, lipids and small molecules, of which polysaccharides can comprise up to 80–90% of the total release [78,79]. The intracellular organic matter proportion increases with increasing age of the algae system. AOM provides a significant contribution to the heterogeneous mixture of compounds that forms dissolved organic matter (DOM) in algal systems. Understanding the character of DOM, and therefore AOM, is essential in order to determine the level of process interference and treatability that may be anticipated [74].

The first major investigation into AOM character from a treatment perspective was undertaken by Bernhardt and team [80,81]. It was demonstrated that molecular weight (MW) and the concentration of DOC, carbohydrates and uronic acid was highly variable, depending on both species and culture age. MW is particularly important as high-MW AOM can act as a flocculant aid while low-MW AOM can increase the negative charge at the surface of particles [80,82]. A later study showed that alginate, which is frequently used as a model for AOM and comprises two uronic acids, has a similar capacity for Al ions as fulvic acid [83]. More recent investigations have demonstrated that proteins can interfere with coagulation [84], while both proteins and polysaccharides have been shown to foul membranes [74,76].

In related fields involving treatment of organic systems, including that of NOM and wastewater biomass, additional parameters have been shown to be useful for linking OM character to treatment. For example, NOM is frequently characterised in terms of specific UV absorbance (SUVA), hydrophobicity, charge density and ZP [85,86]. Furthermore, the character of soluble microbial products and extracellular polymetric substances in biomass, in terms of protein:carbohydrate ratios, charge density, hydrophobicity and MW distribution, has been linked to flocculation and membrane fouling potential [87]. Additionally, information on OM character has been gained from fluorescence excitation–emission matrices which can provide information specifically on protein and humic/fulvic-like substances in DOM and sewage effluent [76,88–92].

On the other hand, water purification treatment is greatly affected by the existence of algae when the water supply source is eutrophic [93,94]. They include coagulation interference, abnormal smell/taste, filter clogging, toxic substances, residue of soluble metals, and generation of THM [95]. Algae are often pretreated with chlorine for the reason that coagulation treatment is not easy, but its treatment is limited by generation of THM [96]. There are several reports that chlorine treatment improves the sedimentation of algae, but this reported method is not regarded well in terms of the improvement of coagulation. On the other hand, there is no report about how the algae treated with chlorine will change. According to comparative experiments of Al-based coagulant and Fe-based coagulant about the generation of algae floc, it is reported that Al-based coagulant is better than Fe-based coagulant [90].

Moreover, the types of algae and the concentration in wastewater depend on residence time, climate and weather, amount of pollutants entering the pond, and dimensions of the pond [97]. Normally, small unicellular types of algae develop first, e.g., *Chlorella*. Because of their physical dimensions they are difficult to remove by the processes listed in Table 1. Longer residence times lead to the development of larger algae and other plankton, which is more readily removed. The algae concentration affects the choice of removal process and the rate of treatment. Because of their light density, the dried weight of suspended solids is not an efficient measure of concentration. Algae are normally measured in volumetric or areal standard units [97]. In surface water supplies, concentrations may be as high as 30,000 cells per mL, this can be much higher in nutrient-rich waste treatment effluents. A combination of processes may be the best treatment, e.g., copper sulphate addition and microstraining (Table 1), as used on surface water supplies in London, England [97,98].

However, a wide range of technologies are available for treatment of drinking water sources contaminated with cyanobacterial toxins [99–101]. Studies undertaken in operating commercial plants have shown progressive reductions in microcystin concentrations along the treatment sequence. Raw water containing low toxin concentrations has been successfully treated in plants using powdered activated carbon (PAC) [99]. Conventional coagulation/clarification treatment is only partially effective and becomes less so if prechlorination is used, as this redistributes cyanobacterial toxins into the free water solution [102]. When high concentrations of cyanobacterial colonies enter the plant, the particulate load on the flocculation and clarification system will block filters, causing whole cells and free toxin to pass through the system. The chlorine demand of the "finished" water rises under these circumstances, so that the normal residual concentration of chlorine may decrease to zero, allowing dissolved toxin to enter the distribution system [103].

Table 1
Algae removal processes: merits and flaws [97]

Process	Advantages	Limitations
Copper sulphate	Simple and inexpensive	Creates toxicity: only some algal forms attacked
Chlorine	Simple and inexpensive	High doses needed: not all algae attacked
Coagulation and settling	Positive removal of all types of algae	High chemical doses needed: difficult sludges produced
Sand filters	Positive removal of all types of algae	Rapid filter clogging may occur
Microstraining	Simple and inexpensive	Not all algal forms removed
Air flotation	Positive removal of all types of algae	Not all algal forms removed; sludges may be difficult to handle

Conventional treatment is therefore effective in reducing cyanobacterial toxins when the problem is minor but increasingly ineffective as the problem escalates [99].

The most cost-effective solutions to the removal of microcystins and cylindrospermopsin from drinking water depend very much on the other requirements of the system, in particular the need to remove other harmful organic compounds. The highest level of protection currently operating for removal of unwanted organic chemicals from drinking water, which includes the cyanobacterial toxins, is postclarification ozonation followed by granulated activated carbon filtration. However, if the major problem is intermittent, with seasonal cyanobacterial blooms, other systems with lower operating costs may be applicable. As long as prechlorination is avoided and the coagulation/clarification system can handle the fluctuating organic load, the addition of PAC may be sufficient to remove dissolved toxins and cyanobacterial tastes and odours. DAF technology has proved capable of handling variable cyanobacterial loads, as has (on a smaller scale) upflow sludge blanket clarification [104]. In the future, titanium oxide/UV oxidation and membrane filtration may prove to be cost-effective options [99].

Post-treatment chlorination can provide a last defence against microcystins and cylindrospermopsin in the drinking water supply, but only if a residual chlorine level of at least 0.5 mg L^{-1} is maintained in the finished water for more than 30 min at neutral pH. While this is commonly achieved in normal water treatment, the circumstances of a major cyanobacterial bloom in the raw water may override the chlorination, allowing harmful toxins to reach the consumer [105]. If postchlorination or postozonation are not practiced, there is an increased possibility of cyanobacterial toxins reaching the consumer, which must be recognised in assessing finished water safety [99].

Because a substantial proportion of the population in the developing world does not have access to treated water, consumption of cyanobacterial toxins is more likely among them. Often surface water is the only supply, with seasonal eutrophication [94]. Very low-cost methods of purifying water from pathogens and toxins are needed. Boiling is common practice to reduce enteric disease transmission, but it does not remove microcystins or cylindrospermopsins. It is possible that low-cost slow sand filters can be developed, based on 44-gal drums half filled with sand, for remote and rural families. These would reduce hazards from protozoa, bacteria, and metabolisable organic contaminants as well as to cyanobacterial toxins [99].

Furthermore, as conventional water treatment, i.e. C/F and sedimentation, is largely practiced in the entire world, enhanced coagulation (EC) may be considered as a promising technology [106–108]. Indeed, reducing pH to 4–6 is proven efficient in the NOM and algae removal [109].

4.2. Why enhanced coagulation?

As NOM is almost always negatively charged overall the pH of natural water it has a strong affinity to cationic additives such as metal coagulants [104]. Consequently, coagulation is regarded as an effective technology when removing DOM. Coagulation with Fe or Al salts is specifically good at removing hydrophobic and high MW OM such as humic and fulvic acids. It is not so good at removing the uncharged and hydrophilic OM such as alkyls and polysaccharides. UV_{254} and SUVA (which is the ratio of UV absorbance at 254 nm in m^{-1} to DOC concentration in mg L^{-1}) both give relative indications of the hydrophobic content in water. They give reasonable predictions of the formation of THMs [110] and are good predictors of the performance of coagulation; whereas SUVA increases so does the removal of DOC (Fig. 2). If water is hydrophobic in nature (SUVA >4) 50% removal of DOC will normally be achieved, but if the water is hydrophilic in nature (SUVA <2.5) much lower removal efficiencies will be achieved. High SUVA waters tend to be from upland or moorland catchments whilst lowland sources and groundwater have SUVA values of less than 2.5 [104].

Moreover, NOM is generally described as a poorly

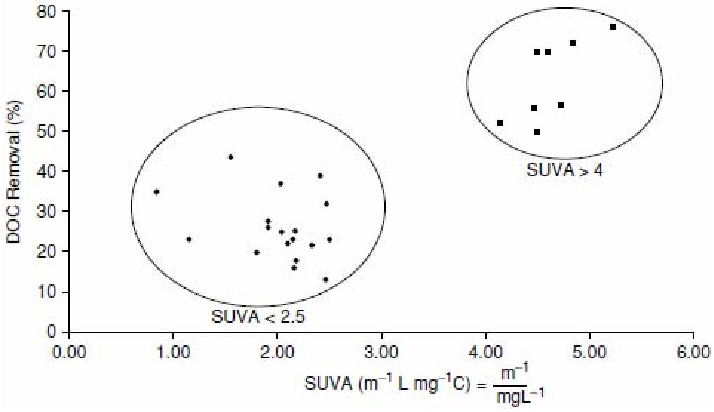


Fig. 2. Relationship between SUVA and DOC removal by coagulation [104].

defined mix of organic substances with variable properties in terms of acidity, MW and molecular structure [111]. Functionally, the OM is predominantly phenolic and carboxylic in nature, but also contains alcohol, purine, amine and ketone groups and is often described as a weak anionic polymer [111]. The mechanisms of coagulation with regard to NOM removal are CN for colloidal material and charge complexation/precipitation for soluble compounds with additional removal occurring due to adsorption on to precipitated flocs and metal hydroxides [112]. Accordingly, optimisation of the coagulation process occurs under acidic conditions between the isoelectric point of the coagulant and the NOM; pH 4.5–5.5 for Fe based system and pH 5–6 for Al based coagulants [111,113].

Given that the coagulation of NOM is predominately charge related for both soluble and colloidal material then the electrical character of the NOM is likely to be a key parameter in describing the process [111]. Characterisation in this regard relates to either surface potential (expressed as ZP or electrophoretic mobility) or the total surface charge (measured as colloidal charge or charge density) [114]. ZP indicates the surface potential of the colloidal system and is commonly related to the stability of the colloidal materials under any given set of water characteristics. However, it does not necessarily provide a proportional indication of the amount of coagulants required for destabilisation. In contrast, the total surface charge of the raw water is proportional to the theoretical coagulant demand providing a CN mechanism prevails. Previous attempts to link the coagulation of NOM to the charge character of the water have found that optimum doses occurred at a range of ZPs between –8 and +8 mV depending on the water source and the pH of coagulation [114]. Hence indicating that complete neutralisation of the charge is not required, only that the barrier generated by electrostatic repulsion is minimised or removed [111].

On the other hand, microcystins are largely retained within the cyanobacterial producer-cell, although an importance for microcystin export has recently been suggested [115,116]. A sudden increase in the concentration of dissolved microcystin in the water column can occur after the collapse of a bloom and consequent cell lysis [117]. Apart from this occurring as a natural phenomenon, high concentrations of dissolved microcystins have been found after algicide treatment of cyanobacterial blooms [118]. The ambient concentration of dissolved microcystin is a function of several factors such as dilution, photodegradation, adsorption to particles and biodegradation. The relative importance of the processes influencing the dissolved microcystin concentration during and after a cyanobacterial bloom is difficult to estimate. Microbial degradation may be a major pathway for the elimination of microcystins, although a lag phase seems to be required in some cases [118,119]. Even though the concentration of dissolved microcystins in inland waters seldom exceeds 20 μg L^{-1}, concentrations in the range of 900–1800 μg L^{-1} have been reported [117]. The high concentrations were found after algicide treatment of a water bloom [115,120].

Dissolved microcystins are efficiently removed by CN so EC would be more convenient here [109]. However, some precautions must be taken to ensure that the acid adding has not a secondary effect in the form of algicide treatment to avoid the dissolved microcystins concentration increase. Consequently, both algae and dissolved microcystins may be efficiently removed by EC when appropriate rapid mixing and acid/coagulant dosage are guaranteed [109,121].

In conventional C/F, CN in the rapid mixing device and *SF* in the following mixing device would be better designed by focusing on the removal of dissolved microcystins and algae, respectively.

6. Conclusions

The main conclusions drawn from this review are:

1. Seasonal algal blooms can dramatically increase populations on relatively rapid timescales and as a result

water treatment process efficiency can be impaired. Furthermore, algal cells and associated algogenic material are THM precursors which have resulted in the restriction of chlorine usage.

2. It was suggested that the coagulation mechanism was "one of mutual attraction and CN of the algae and the incipient hydroxide flocculi" and as such the hydroxide precipitant should be positively charged. It was observed that on adjusting the ZP of an algal suspension with a specific operational range, removal was significantly improved. However, it has been demonstrated that the impact of some algal characteristics means removal by CN mechanism is unfeasible. Removal by CN can be obtained if the algal cell is spherical, free from protruding appendages or polymeric substances and microscopic in size. Deviation from this optimum conformation is common among algae cells and hence the optimum removal conditions cannot always be predicted by charge measurement data. In many instances, even increasing the coagulant dose to enable removal by *S*F mechanism does not improve removal.

3. Water purification treatment is greatly affected by the existence of algae when the water supply source is eutrophic. They include coagulation interference, abnormal smell/taste, filter clogging, toxic substances, residue of soluble metals, and generation of THM. Algae are often pretreated with chlorine for the reason that coagulation treatment is not easy, but its treatment is limited by generation of THM. Chlorine treatment improves the sedimentation of algae, but this reported method is not regarded well in terms of the improvement of coagulation. On the other hand, there is no report about how the algae treated with chlorine will change. According to comparative experiments of Al-based coagulant and Fe-based coagulant about the generation of algae floc, it is reported that Al-based coagulant is better than Fe-based coagulant.

4. Raw water containing low toxin concentrations has been successfully treated in plants using powdered activated carbon. Conventional coagulation/clarification treatment is only partially effective and becomes less so if prechlorination is used, as this redistributes cyanobacterial toxins into the free water solution. When high concentrations of cyanobacterial colonies enter the plant, the particulate load on the flocculation and clarification system will block filters, causing whole cells and free toxin to pass through the system. The chlorine demand of the "finished" water rises under these circumstances, so that the normal residual concentration of chlorine may decrease to zero, allowing dissolved toxin to enter the distribution system. Conventional treatment is therefore effective in reducing cyanobacterial toxins when the problem is minor but increasingly ineffective as the problem escalates.

5. Since dissolved microcystins are efficiently removed by CN, EC would be more convenient for their removal. However, some precautions must be taken to ensure that the acid adding has not a secondary effect in the form of algicide treatment to avoid the dissolved microcystins concentration increase. Consequently, both algae and dissolved microcystins may be efficiently removed by EC when appropriate rapid mixing and acid/coagulant dosage are guaranteed.

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