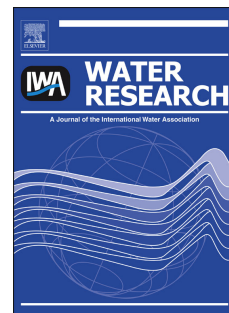


Accepted Manuscript

Title: The impact of differing cell and algogenic organic matter (AOM) characteristics on the coagulation and flotation of algae

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PII: S0043-1354(10)00256-3

DOI: [10.1016/j.watres.2010.04.016](https://doi.org/10.1016/j.watres.2010.04.016)

Reference: WR 7968

To appear in: *Water Research*

Received Date: 13 January 2010

Revised Date: 16 April 2010

Accepted Date: 16 April 2010

Please cite this article as: Henderson, R.K., Parsons, S.A., Jefferson, B. The impact of differing cell and algogenic organic matter (AOM) characteristics on the coagulation and flotation of algae, *Water Research* (2010), doi: 10.1016/j.watres.2010.04.016

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1 The impact of differing cell and algogenic organic matter (AOM)

2 characteristics on the coagulation and flotation of algae

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12

13 **Abstract:**

14 The aim of this study was to compare the coagulation and flotation of different algae

15 species with varying morphology and algogenic organic matter (AOM) composition

16 in order to link physical and chemical algae characteristics to treatment. *Microcystis*

17 *aeruginosa* (cyanobacteria), *Chlorella vulgaris* (green algae), *Asterionella formosa*

18 and *Melosira* sp. (diatoms) were treated by coagulation with aluminium sulphate and

19 flotation. The AOM was extracted and treated separately. Analyses included cell

20 counts, dissolved organic carbon, aluminium residual and zeta potential. Removal

21 efficiencies in the range 94-99 % were obtained for each species. Cells, AOM and

22 aluminium were concurrently removed at a coagulant dose that was related on a log-

23 log basis to both cell surface area and total charge density, although the relationship

24 was much stronger for the latter. This was attributed to a significant proportion of the

25 coagulant demand being generated by the AOM. The implications of such findings

are that relatively simple charge measurements can be used to understand and control coagulation and flotation of algae.

Introduction

Algae are ubiquitous in rivers and reservoirs that supply drinking water treatment works. On a seasonal basis, algae population densities can soar, challenging the removal efficiency of treatment processes. A commonly employed treatment chain for algae removal is coagulation-flocculation-dissolved air flotation (DAF). During DAF treatment, negatively charged, microscopic bubbles collide and attach to influent particles, floating them to the surface where they are removed. Successful flotation is reliant upon influent particles having both a minimum particle diameter of approximately 10-30 μm (Edzwald, 1995), and a surface charge that approaches neutral (Han et al., 2001), equating to a zeta potential of approximately -10 mV to +5 mV (Henderson et al., 2008d), to ensure effective particle-bubble collision and attachment efficiencies respectively. Algae are negatively charged and many common species are less than 10 μm in diameter therefore coagulation and flocculation processes are included to adjust the size and charge of the algae cells accordingly. If coagulation is unsuccessful, poor flotation can occur which results in high coagulant and cell residuals causing downstream filter blockage or breach (Henderson et al., 2008a, Henderson et al., 2008b). Residual algal matter can form disinfection by-products (DBP) such as trihalomethanes (THM) (Chen et al., 2008, Nguyen et al., 2005) or be responsible for offensive taste and odour compounds or toxic metabolites (Haider et al., 2003, Rosen et al., 1992).

Coagulation of algae cells can be difficult as a result of their widely variable physical and chemical characteristics (Henderson et al., 2008b), including complex cell morphologies, such as spinal appendages preventing close contact of cells (Bernhardt and Clasen, 1991); cell motility, enabling liberation from flocs (Pieterse and Cloot, 1997); variable surface charge (Henderson et al., 2008d); or algogenic organic matter (AOM) sterically interfering to prevent agglomeration, increasing the negative charge at the cell surface and complexing with metal coagulants thus raising residual coagulant concentration (Bernhardt et al., 1985, Pivokonsky et al., 2006, Takaara et al., 2004). These characteristics generally act to increase coagulant demand and it has been suggested that consequently coagulant cannot be added on a stoichiometric basis (Bernhardt et al., 1985), as is usual for inert, inorganic particles (Stumm and O'Melia, 1968). Earlier studies suggested that only microscopic, spherical cells can be coagulated according to charge neutralisation mechanisms (Bernhardt and Clasen, 1994, Tilton et al., 1972) thus allowing optimum coagulant dosage to be estimated stoichiometrically. However, these conclusions resulted from studies investigating coagulation followed by direct filtration and may not apply for flotation processes. While numerous studies on the flotation of algae have been conducted (Edzwald, 1993, Kempeneers et al., 2001, Teixeira and Rosa, 2006), no studies have investigated the link between coagulation-flotation and algal characteristics. Specifically, the impact of variable morphology and AOM composition on coagulation and removal by flotation requires investigation and this will be the focus of the current paper.

The authors recently undertook a study examining the AOM characteristics of four algae species –*Chlorella vulgaris* (micro, spherical, green algae), *Microcystis aeruginosa* (micro, spherical cyanobacteria), *Asterionella formosa* (large, elongated,

colonial diatom), and *Melosira* sp. (large, filamentous diatom) (Henderson et al., 2008c) (Table 1). The major differences in AOM characteristics were associated with charge density, hydrophobicity, protein content and molecular weight (MW). AOM from *C. vulgaris* had a charge density of 3.2 meq g⁻¹ and a hydrophobicity of 11 % whereas that of *M. aeruginosa* had a charge density of 0.1 meq g⁻¹ and a hydrophobicity of 30 %. Much less protein was present in AOM extracted from the diatoms - *A. formosa* and *Melosira* sp., compared with *C. vulgaris* and *M. aeruginosa*. Additionally, *C. vulgaris* and *M. aeruginosa* had larger MW AOM in comparison to *A. formosa* and *Melosira* sp., where 45 % of *M. aeruginosa* AOM was greater than 500 kDa in comparison to less than 10 % of *C. vulgaris* AOM (Henderson et al., 2008c). It is anticipated that the differences may impact considerably on coagulant dose for optimum removal. Hence, the major objective of this study was to treat the aforementioned algal cultures using coagulation-flocculation-DAF and link the coagulation conditions required for treating each species by flotation to algal physical and chemical character.

Insert Table 1

Materials and Methods

Algae Cultivation. The following freshwater algae cultures were obtained from the Culture Collection of Algae and Protozoa (CCAP), (Oban, Scotland): *Chlorella vulgaris* (211/11B – Delft, Holland); *Microcystis aeruginosa* (1450/3 – Esthwaite Water, Cumbria, England); *Asterionella formosa* (1005/9 – Esthwaite Water, Cumbria, England), while *Melosira* sp. (JA386 – Redesmere, Cheshire, England) was obtained from Sciento, Manchester, UK. Growth conditions have previously been

described (Henderson et al., 2008c). Algae were harvested for experiments in the early stationary phase.

AOM Extraction. AOM was extracted from all bulk algae suspensions with the exception of *Melosira* sp. by centrifuging at 10,000 G for 15 minutes and subsequently filtering the supernatant through a 0.7 µm filter (Whatman GF/F glass microfibre). AOM therefore comprises both extracellular organic matter (EOM), any intracellular organic matter (IOM) that may have been present, and also loosely bound organic matter, which may be dislodged via centrifugation (Henderson et al., 2008c)

Algae Cell Characterisation. The algae systems were assessed using the following methods:

- a) Cell concentration – a light microscope was used to manually count cells with a haemocytometer and Sedgewick Rafter cells as appropriate. Samples were left to settle onto the grids for 15 minutes. At least 100 cells were counted in triplicate.
- b) Cell surface area – images of cells were obtained microscopically and sized using a scale generated using a graticule. The dimensions were used to produce surface areas using basic geometric shapes as follows: *C. vulgaris* and *M. aeruginosa* were sized using a spherical surface area = $4\pi r^2$; *A. formosa* and *Melosira* sp. were sized using a cylindrical surface area = $2\pi r^2 + 2\pi rh$. In each case the dimensions of 100 cells were measured.
- c) Charge density – The back titration method utilised was adapted from an established method (Kam and Gregory, 2001). The specific procedure was that utilised for determining AOM charge density was previously reported (Henderson et al., 2008c). Three different volumes of algae were analysed.

d) Zeta potential – A Malvern Zetasizer 2000HSA (Malvern, UK) was utilised to determine the zeta potential of the system.

Coagulation and Dissolved Air Flotation. Stock algae suspensions were diluted prior to treatment to a concentration more often observed in supply reservoirs using deionised water to which 0.5 mM NaHCO₃ and 1.8 mM NaCl had been added. See Table 2 for initial algal concentrations. Bench scale coagulation and flotation was undertaken using an EC Engineering Dissolved Air Flotation Batch Tester, Model DBT6 (Alberta, Canada). Aluminium sulphate coagulant was added to 1 litre of algae suspension at the beginning of a 2 minute rapid mix (200 rpm), during which pH was adjusted to either pH 5 or 7 using 0.1 M NaOH or 0.1 M HCl as required. Coagulation and flotation experiments were undertaken at pH 7 for all algae species and additionally at pH 5 for *M. aeruginosa* and *C. vulgaris*. It has previously been observed that algae may not start agglomerating until more than 7 minutes of slow mixing has passed (Henderson et al., 2006), attributed to a lag time in charge neutralisation (Clasen et al., 2000). For this reason flocculation time was 15 minutes of slow mixing (30 rpm) rather than 5 minutes which is usually more normal for flotation processes. After flocculation, the paddles were gently removed and air saturated deionised water with 0.5 mM NaHCO₃ and 1.8 mM NaCl was supplied at a pressure of 450 kPa and recycle ratio of 12 %. The algae-bubble agglomerates were allowed to float for 10 minutes.

Samples of the clarified water were obtained from sampling ports located 5 cm from the vessel base for analyses by cell count and zeta potential as previously described and DOC using a Shimadzu TOC-5000A analyser. All analyses were performed in triplicate.

The same coagulation-DAF experiment was also undertaken for AOM extracted from *C. vulgaris*, *M. aeruginosa* and *A. formosa* at pH 7. Samples were adjusted to approximately 5 mg L⁻¹ by dilution using deionised water with 0.5 mM NaHCO₃ and 1.8 mM NaCl. At the early stationary phase, cell concentrations for *C. vulgaris*, *M. aeruginosa* and *A. formosa* were 1.2 x 10⁷ cells mL⁻¹, 1.5 x 10⁷ cells mL⁻¹ and 2.9 x 10⁵ cells mL⁻¹ respectively., thus requiring the extraction of approximately 140 mL, 350 mL and 900 mL respectively of algae per jar test to provide sufficient AOM. Subsequent analyses included residual aluminium by atomic absorption spectroscopy using a Perkin Elmer AAnalyst 800 (Perkin Elmer, Beaconsfield, UK), DOC and zeta potential.

Results and Discussion

Algae System Characterisation

M. aeruginosa and *C. vulgaris* cells are microscopic spherical cells and therefore had far greater initial cell concentrations and smaller individual cell surface areas when compared with the much larger diatoms of *A. formosa* and *Melosira* sp. (Table 2). Charge equivalents, presented on a per cell basis, were in the range 0-1.88 peq cell⁻¹ where *M. aeruginosa* had the smallest charge density and *Melosira* sp. the largest. The charge density of each species increased with increasing pH. This is attributable to dissociation of carboxylic acid groups, similar to that observed for natural organic matter (NOM) (Kam and Gregory, 2001). AOM concentration for the cell concentrations examined in this study were in the range 0.6-1.5 mg L⁻¹ as C. By comparison of the charge density of AOM alone (Table 1) and the whole system of

cells and AOM, an estimate of the contribution of charge by AOM was calculated. AOM was found to contribute 84%, 5% and 30% of the charge of the system for *C. vulgaris*, *M. aeruginosa* and *A. formosa* respectively while for *Melosira* sp. the AOM had negligible charge density (Table 2).

Insert Table 2

Algae-Coagulant Interactions

A log linear relationship between the ratio of the coagulant dose (as aluminium) to cell charge equivalence (coagulant:charge ratio) and the zeta potential was observed for all four algae systems coagulated at pH 7 (Figure 1). This relationship is relevant as it quantifies the effectiveness of coagulant in neutralising the charge of the algal system. Figure 1A depicts the relationship when coagulation the entire algal system, including cells and associated AOM, while Figure 1B shows the relationship when coagulating only AOM extracted by centrifuging and filtration. The gradients of the log-linear relationships in Figure 1A were 22.8, 13.6, 9.5 and 11.0 mV meq mg⁻¹ for *C. vulgaris*, *M. aeruginosa*, *A. formosa* and *Melosira* sp respectively, indicating that the coagulant was significantly more effective at neutralising the charge of *C. vulgaris* in comparison to the other three species. The coagulant:charge ratios required to achieve neutralisation were 183, 456, 1290 and 2781 mg meq⁻¹ for *Melosira* sp., *C. vulgaris*, *A. formosa* and *M. aeruginosa* respectively. These ratios are comparable with the literature as one study determined that the spherical cyanobacteria, *Synechocystis minuscular*, required a coagulant (Al):charge ratio of 1400 mg meq⁻¹ at pH 6 for complete neutralisation (Bernhardt and Clasen, 1994).

The resulting gradients for Figure 1B were 16.3, 20 and 11.5 mV meq mg⁻¹ for *C. vulgaris*, *M. aeruginosa* and *A. formosa* respectively and thus, while the gradient obtained for *A. formosa* was very similar to that observed for the entire system, those of *C. vulgaris* and *M. aeruginosa* were less than and greater than those obtained for the entire system, respectively. The coagulant:charge ratio required to achieve neutralisation for *C. vulgaris* was 263 mg meq⁻¹, as opposed to the much larger values of 2426 and 6017 mg meq⁻¹ for *A. formosa* and *M. aeruginosa* respectively. The coagulant:charge ratio was therefore 1.7 times less than that required for neutralisation of the entire *C. vulgaris* system while that of *A. formosa* and *M. aeruginosa* was 1.9 and 2.2 times greater.

Insert Figure 1

In general, differences observed in zeta potential vs coagulant dose curves are explained in terms of varying pH, charge density or complexation of coagulant. However, each experiment was conducted at the same pH and the coagulant dose was normalised against the charge density of the algae or AOM. Hence, the different doses required to achieve a neutral zeta potential and gradient reflect a difference in coagulant interaction mechanism with the cells and AOM, particularly with respect to complexation. It is known that at pH 7 the concentrations of dissolved cationic hydrolysis products are relatively low and the system is dominated by the negatively charged aluminate ion (Al(OH)₄⁻) and by amorphous Al(OH)₃ precipitate (Duan and Gregory, 2003). This precipitate has an isoelectric point at pH 8 as a result of surface ≡Al–OH⁺ groups and is thus positively charged at pH 7. Hence, surface complexation is likely to occur between these cationic sites and dissociated –COOH groups which

are generally attributed to charge in an algae system (Bernhardt et al., 1985). Adsorption of negatively charged AOM and cells to amorphous precipitates may also occur such that a net decrease in negative charge results (Duan and Gregory, 2003). A low gradient such as that exhibited by *A. formosa* indicates that this neutralisation mechanism is relatively inefficient in comparison to larger gradients, such as that exhibited by *C. vulgaris*.

Explanation for the differences in efficiency of neutralisation lies in the system character and particularly that of the AOM as it will be closely associated with the cells. For example, the *M. aeruginosa* system required approximately six times the coagulant:charge ratio of *C. vulgaris* for complete neutralisation. This increased to 22 times in the case of the AOM. The AOM of *M. aeruginosa* has a very low charge but a significant protein concentration of 0.64 mg protein mg⁻¹ DOC (Table 1) and, while that of *C. vulgaris* is also significant at 0.40 mg protein mg⁻¹ DOC, previous studies have demonstrated that only the cyanobacteria protein and not green algae proteins have the appropriate characteristics for protein-coagulant complexation (Pivokonsky et al., 2006; Takaara et al., 2004; Takaara et al., 2007). The fact that the gradient of the AOM curve for *M. aeruginosa* was relatively steep but that charge neutralisation was not instigated until a much larger coagulant:charge ratio had been achieved suggests that initially aluminium coagulant was consumed by protein complexation such that it was unavailable for charge neutralisation. In the case of *A. formosa*, the relatively high coagulant:charge ratio that was required for neutralization relates to both an increased point of onset of neutralization as well as a relatively low gradient. To date, no studies have addressed the protein-coagulant complexation reactions from AOM other than that extracted from *C. vulgaris* and *M. aeruginosa*. This represents an area for future research, which would clarify the following proposed hypothesis.

The fact that the onset point of neutralization lies between the other two systems infers a moderate influence of protein-coagulant complexation. However, comparison of the protein:DOC ratio for the AOM from *A. formosa* reveals the lowest level of the three at 0.2, suggesting that the protein complexing power of AOM from *A. formosa* may be similar to that of *M. aeruginosa* and the difference may be just related to total mass of available protein. In terms of the lower gradient, the size of the carbohydrates appears important. In the case of *A. formosa* the carbohydrates were predominately less than 1 kDa in size (81% of total) compared to 30% and 38% for the AOM from *C. vulgaris* and *M. aeruginosa* respectively. These types of carbohydrates are known to exhibit a low affinity for coagulant such that very large doses are required (Bernhardt et al., 1985). The mechanism in this case is either a reduced complexation process or direct adsorption onto precipitate. In either case, a shallower gradient can be expected as each unit of coagulant has less impact.

Removal Efficiencies of Cells, AOM and Aluminium

Cell Removal

There were four coagulation regions for *C. vulgaris* at pH 5 (Figure 2): Zone 1 – a region of no removal at low doses; Zone 2 - an initial zone of removal at low dose that coincided with a reduction in the magnitude of the zeta potential (ZP) to +3.8 mV; Zone 3 - a restabilisation zone where ZP values were highly positive at +15 mV; and Zone 4 – a secondary removal zone at high coagulant doses. Coagulant doses were normalised to surface area which has previously been demonstrated to be a useful preliminary indicator of coagulant dose (Henderson et al., 2008b). The coagulant doses giving the maximum removal efficiency for Zone 2 and Zone 4 removal were

0.0195 g m⁻² (289 mg meq⁻¹) and 0.742 g m⁻² (11,027 mg meq⁻¹) respectively achieving 97.7 % and 96.8 % removal respectively. This sequence of removal zones is commonly observed for both organic and inorganic systems at pH 5, where Zone 2 removal is attributed to charge neutralisation mechanisms while Zone 4 is attributed to sweep flocculation mechanisms (Duan and Gregory, 2003). In contrast, no restabilisation zone was observed for *M. aeruginosa* at pH 5, even upon reaching highly positive ZP values of +18.9 mV (Figure 2). Furthermore, in contrast to *C. vulgaris*, a far lower dose of 0.0087 g m⁻² was required to obtain good removal corresponding to a ZP of -4.2 mV. It is proposed that the absence of a restabilisation zone is attributable to large MW proteins and carbohydrates acting as polymer aids and overcoming repulsive electrostatic forces. This is supported by previous work that showed that at pH 5 such polymers are only partially deprotonated (Bernhardt et al., 1985). In contrast, it is suggested that AOM did not prevent restabilisation of *C. vulgaris* systems at pH 5 as the AOM was smaller with ~5 % larger than 500 kDa compared to ~45 % for *M. aeruginosa* (Henderson et al., 2008c) and therefore would not be as efficient a polymer aid.

Insert Figure 2

At pH 7, no restabilisation zone was observed for any of the algae systems. Optimum coagulant doses were 0.7 to 1.36 mg L⁻¹ as Al, which when normalised for cell count were in the order 1.1 < 4.3 < 31.4 < 290 pg cell⁻¹ for *M. aeruginosa*, *C. vulgaris*, *A. formosa* and *Melosira* sp. (Table 3). The value obtained for *M. aeruginosa* is comparable with that obtained for the similar organism, *Synechocystis minuscula*, which had a coagulant demand at pH 6 of 1 pg Al cell⁻¹ (Bernhardt and Clasen, 1994). Doses per charge and surface area were also calculated as 383, 927, 508 and 154 mg Al meq⁻¹ and 0.078, 0.012, 0.085 and 0.053 pg µm⁻² for *C. vulgaris*,

M. aeruginosa, *A. formosa* and *Melosira* sp. respectively. Corresponding zeta potentials at optimum removal were -14.5 ± 1.6 , -10 ± 2.2 , -13.5 ± 0.4 and 1.4 ± 0.3 mV for the same species. Optimum removal was similar for all species at between 94.8 and 99.7 % cells removed.

Insert Table 3

The dose required for *C. vulgaris* at pH 7 in terms of surface area was four times higher than at pH 5 (Figure 2). This observation is a reflection of firstly the decrease in charge density of the system, which was three times lower at pH 5. Secondly, dissolved cationic hydrolysis species as opposed to amorphous hydroxide precipitates dominate and these are more effective neutralisers. Interestingly, the corresponding coagulant:charge ratio decreased by only 1.3 times, as it only reflected the difference in alum speciation having already been normalised for charge density. In contrast, the optimum coagulant demand of *M. aeruginosa* at pH 5 was $0.0087 \text{ pg } \mu\text{m}^{-2}$, only 1.4 times less than that required at pH 7. This is primarily a result of the change in alum speciation as the charge density of these algae was much lower than that of *C. vulgaris* and therefore less significant.

AOM Removal

The coagulant dose required to achieve maximum removal of AOM was $0.8 < 1.2 < 1.5 \text{ mg Al mg}^{-1} \text{ DOC}$ for *C. vulgaris*, *M. aeruginosa* and *A. formosa* respectively (Figure 3) at zeta potential values of 3.8 ± 0.8 , 1.0 ± 0.3 and -7.9 ± 0.7 mV for the same species. Additionally, AOM was relatively treatable with removal efficiencies of 71 %, 55 % and 46 % for *C. vulgaris*, *M. aeruginosa* and *A. formosa* respectively. In general these removal efficiencies are greater than those observed in a previous

study where AOM was coagulated using ferric chloride and removed by sedimentation to yield removal efficiencies of 18 %, 25 and 50 % at pH 5 for the species *M. aeruginosa*, *Scenedesmus quadricauda*, *Dictyosphaerium pulchellum* respectively (Widrig et al., 1996). The doses required to achieve maximum removal efficiency are consistent with literature values for NOM which has a coagulant demand of approximately 1 mg Al mg⁻¹ at neutral pH (Duan and Gregory, 2003). *M. aeruginosa* required a larger dose than *C. vulgaris*, despite having a lower charge density of 0.1 meq g⁻¹ compared with 3.2 meq g⁻¹ (Table 1), attributed to protein-coagulant complexation increasing coagulant demand. The high coagulant demand of *A. formosa* can be explained by the low MW AOM causing inefficient flocculation, where cross linking of the small MW AOM-aluminium compounds is required to build flocs. The high removal efficiency of *C. vulgaris* AOM is a result of the material being both highly charged and of relatively large MW such that flocculation is efficient.

Insert Figure 3

Aluminium Residual

Residual aluminium data revealed that high Al residuals of up to 65 % could be anticipated for aluminium doses of less than 0.5 mg Al mg⁻¹ DOC at pH 7 (Figure 4). The lowest aluminium residuals of 0.4 %, equating to a residual of 10-35 µg l⁻¹, were achieved for doses of greater than 0.8 mg Al mg⁻¹ C (Figure 4), which is concurrent with optimum AOM removal (Figure 3). This high initial residual and subsequent lowering of aluminium at higher aluminium:DOC ratios has previously been observed for humic acid systems, where a dose of 0.54 mg Al:mg C was required to ensure low aluminium residuals (Jekel and Heinzmann, 1989). Similarly, a study examining the coagulation of AOM originating from *Chlorella* with iron determined that residual

iron was always found in the filtrate for doses of $<0.2 \text{ mg Fe mg C}^{-1}$ but never at doses of $1 \text{ mg Fe mg C}^{-1}$ (Bernhardt et al., 1985). This trend has been attributed to the coordination of AOM to metal-hydroxide polymers at low concentrations thus preventing the cross linking and clustering of Al-hydroxide polymers which consequently only becomes possible at higher doses (Bernhardt et al., 1985, Jekel and Heinzmann, 1989), when simultaneous removal of both AOM (Figure 3) and aluminium (Figure 4) occurs. The fact that residual aluminium in the *M. aeruginosa* systems was similar to those of *C. vulgaris* and *A. formosa* indicates that protein-Al complexates did not remain dissolved in solution and were bound into flocs by the aforementioned mechanisms.

While the treatability of cells, AOM and aluminium has been demonstrated, their concurrent removal must also be considered. If cells were removed preferentially, then high residual AOM and consequently high aluminium levels could result. At the dosages required to achieve maximum removal of , the ratios of coagulant:DOC were calculated to be 0.93, 1.4 and $1.7 \text{ mg as Al mg}^{-1} \text{ DOC}$ at pH 7 for *C. vulgaris*, *M. aeruginosa* and *A. formosa* respectively, such that each was greater than the 0.8 mg mg^{-1} required for low residuals of both aluminium and AOM. Hence, for the optimum coagulant doses, it is anticipated that removal of all three components would result.

Insert Figure 4

Relationships Between AOM Character and Removal

The study demonstrated that, with appropriate application of coagulant, good removal could be anticipated for all of three system components – cells, AOM and aluminium,

irrespective of algae species. The key difference between the systems was in the coagulant dose required to achieve maximum removal. Analysis of the data presented in this study, compared with that of another study (Bernhardt and Clasen, 1994) reveals a log-log relationship between optimum dose and both cell surface area and charge density (Figure 5). The relationship between coagulant dose and charge density appears stronger than that of surface area, attributable to the fact that the dissolved organic component is also taken into account in the former. This is most important as the charge demand generated by some species is predominantly associated with the AOM component. For instance, in the case of *C. vulgaris*, 84 % of the charge is associated with the AOM. Other studies have reported a relationship between the concentration of algae and coagulant dose and have attributed this to increases in surface area and thus charge density (Stumm and O'Melia, 1968, Tilton et al., 1972); however, these early studies were concerned with only one type of microscopic, spherical algae. Extending the analysis across multiple species then reveals the importance of understanding the impact of charge density in determining the optimum dose (Figure 5). Detailed analysis of how the coagulant interacts with AOM to reduce the charge reveals a number of different actions which describe the zeta profiles away from the optimum point. The work presented here suggests the two important characteristics of the associated AOM are the complexing strength of the protein components and the size of the carbohydrates as they appear to influence the onset point of neutralization and the rate of neutralization respectively. Together these describe the how the zeta potential of the system changes with coagulant addition and provides a route to determining the sensitivity of the system to changes in dose. Further work is required to confirm such suggestions by detailed analysis of the protein complexation relationships as previously reported for *C. vulgaris* and *M.*

aeruginosa (Takaara et al., 2004). However, if confirmed, these two components provide potential diagnostic signals with which to track and predict changing coagulation requirements for algal systems.

The findings outlined here indicate a similar relationship to that observed for NOM, where coagulant dose was closely related to the charged component of the water (Sharp et al., 2006). The implications of such findings are that relatively simple charge measurement via zeta potential can be used to understand and control coagulation and flotation of algae, irrespective of morphological differences. Zeta potential is now being used in understanding practical issues related to the coagulation of NOM rich waters within a region of the UK and has resulted in lower residuals, more stable systems and lower coagulant demands in certain sites (Sharp et al., 2007). Surface area also provided a relationship with coagulant demand which could be utilised to understand changes in dose requirements as different species predominate in feed reservoirs. In contrast, monitoring cell counts without reference to species, will not give an indication of coagulant demand as, on a per cell basis, the coagulant demand required for optimum removal varied between species by orders of magnitude. Similarly, monitoring algae with respect to taxonomic grouping will not give any indication as to the coagulant demand.

Insert Figure 5

Conclusions

Specific conclusions are as follows:

1. Addition of coagulant to algae systems caused a neutralisation of the negative charge of both cells and AOM even at pH 7, although the efficiency of neutralisations varied with differing system characteristics.

2. Good cell removal efficiencies in the range 94-99 % were obtained for all algae treated provided sufficient coagulant was added.
3. High MW, protein-rich AOM appears to act as a polymer aid in *M. aeruginosa* systems, resulting in the absence of a restabilisation zone at pH 5.
4. AOM removal efficiency was in the range 46-71 %.
5. Residual aluminium was always low provided sufficient coagulant had been added to ensure the maximum removal efficiency of AOM had been achieved.
6. A strong correlation between charge density and coagulant dose was observed for all algae species at pH 7. The indications are that charge measurements would provide a robust control for algae irrespective of physical and chemical characteristics.

Further work is required to assess the application of such a model to real systems as opposed to those artificially created using laboratory monocultures. It is anticipated that the principles of the charge dependent process described in this paper should be applicable in such a situation.

Acknowledgements

The authors would like to thank the EPSRC, Anglian Water, Northumbrian Water, Thames Water, and Yorkshire Water for their financial support.

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Figure and Table Headings

Figure 1. Coagulant dose:charge equivalent ratio vs. zeta potential at pH 7 for **A.** the entire system (cells and AOM) and **B.** the extracted AOM.

Figure 2. Dose response curves depicting coagulant demand in terms of surface area at pH 5 and 7 for **A.** zeta potential, and for normalised removal based on cell count for **B.** *C. vulgaris* and **C.** *M. aeruginosa*.

Figure 3. Normalised AOM removal achieved by coagulation and flotation at pH 7 using aluminium sulphate.

Figure 4. Normalised residual aluminium upon coagulation and flotation of AOM at pH 7 using aluminium sulphate, where **A.** shows all results, and **B.** shows results where residual aluminium is less than 2 %.

Figure 5. The relationship between coagulant demand for maximum removal and both charge density and surface area of the algae systems with literature data (Bernhardt and Clasen 1994, Henderson et al. 2008b).

Table 1. Key AOM characteristics for *C. vulgaris*, *M. aeruginosa*, *A. formosa* and *Melosira* sp. at pH 7 (adapted from Henderson et al. (2008c))

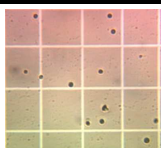

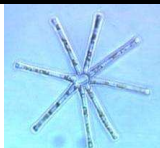

Table 2. Key cell characterisation data for *C. vulgaris*, *M. aeruginosa*, *A. formosa* and *Melosira* sp.

Table 3. Summary data for coagulation conditions required for maximum removal at pH 7.

Table 1.

	<i>Chlorella vulgaris</i>	<i>Microcystis aeruginosa</i>	<i>Asterionella formosa</i>	<i>Melosira</i> sp.
AOM (ng cell ⁻¹)	0.0029	0.00095	0.019	0.65
Charge Density (meq g ⁻¹)	3.2	0.1	1.0	Neg.
Hydrophobicity (%)	11	30	20	32
Carbohydrate:DOC (mg as glucose mg ⁻¹ as C)	1.1	0.7	1.0	0.8
Trans-/hydrophilic carbohydrates (%)	95	77	90	83
Protein:DOC (mg as Bovine Serum Albumin mg ⁻¹ as C)	0.40	0.64	0.19	0.16
Protein:carbohydrate (mg mg ⁻¹)	0.4	0.6	0.2	0.2
AOM >30 kDa (%)	62	55	9	30
AOM <1 kDa (%)	30	38	81	53

Table 2.

	<i>Chlorella</i>		<i>Microcystis</i>		<i>Asterionella</i>	<i>Melosira</i>
	<i>vulgaris</i>		<i>aeruginosa</i>		<i>formosa</i>	<i>sp.</i>
	pH 5	pH 7	pH 5	pH 7	pH 7	pH 7
Cell images						
Initial Cell concentration (cells ml ⁻¹)	$5.0 \times 10^5 \pm 5 \times 10^4$		$6.0 \times 10^5 \pm 1.5 \times 10^4$		$5.0 \times 10^4 \pm 1.2 \times 10^4$	$1.9 \times 10^3 \pm 550$
Surface area (μm ² cell ⁻¹)	55 ± 30		95 ± 34		370 ± 95	5500 ± 845
AOM concentration (mg L ⁻¹ as C)	1.5 ± 0.15		0.6 ± 0.01		1.0 ± 0.2	1.2 ± 0.4
Charge						
Equivalents per cell (including associated AOM)	0.004	0.011	negligible	0.002	0.062	1.88
(peq cell ⁻¹)						
% Charge Contributed by	-	84	-	5	30	negligible

AOM

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Table 3

	<i>Chlorella</i> <i>vulgaris</i>	<i>Microcystis</i> <i>aeruginosa</i>	<i>Asterionella</i> <i>formosa</i>	<i>Melosira</i> sp.
Optimum Coagulant Dose (in terms of cell number, surface area and charge density)				
pg cell ⁻¹	4.3	1.1	31.4	290
g m ⁻²	0.078	0.012	0.085	0.053
mg meq ⁻¹	383	927	508	154
Optimum Zeta Potential (mV)	-14.5 ± 1.6	-10 ± 2.2	-13.5 ± 0.4	1.4 ± 0.3
Optimum Cell Removal (%)	94.8	97.3	98.8	99.7

Figure 1

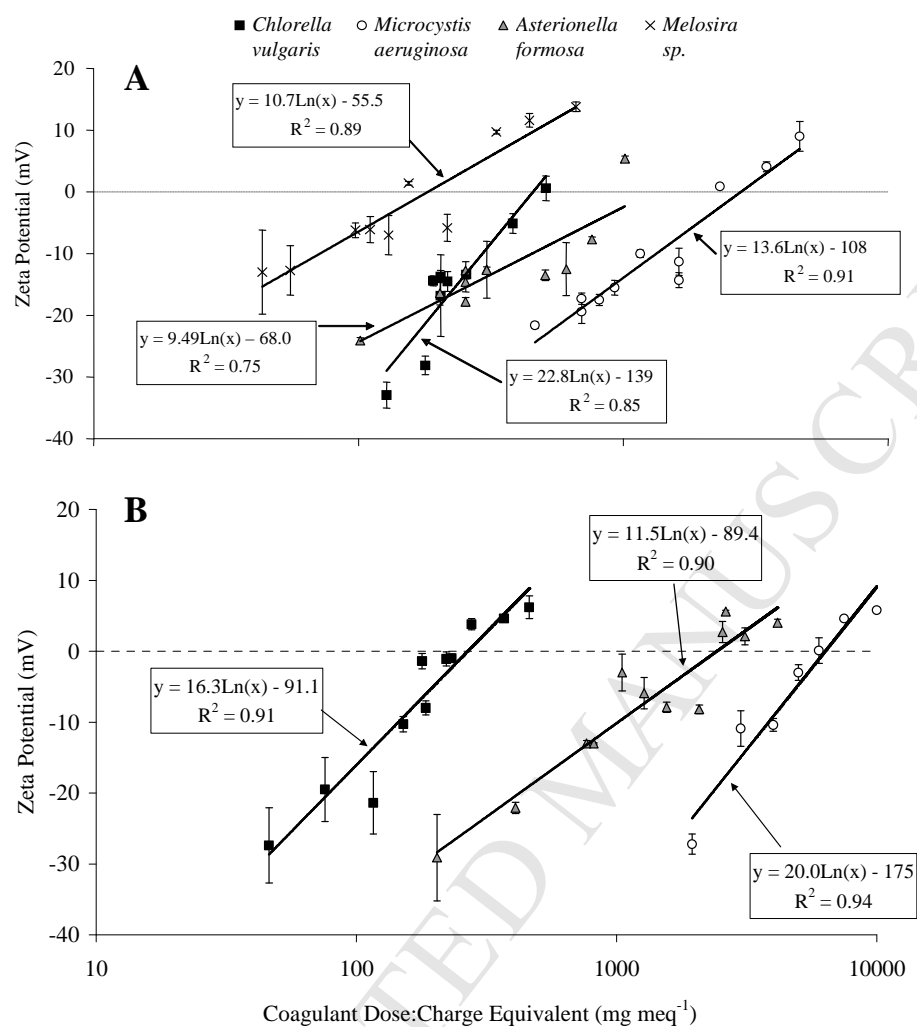


Figure 2

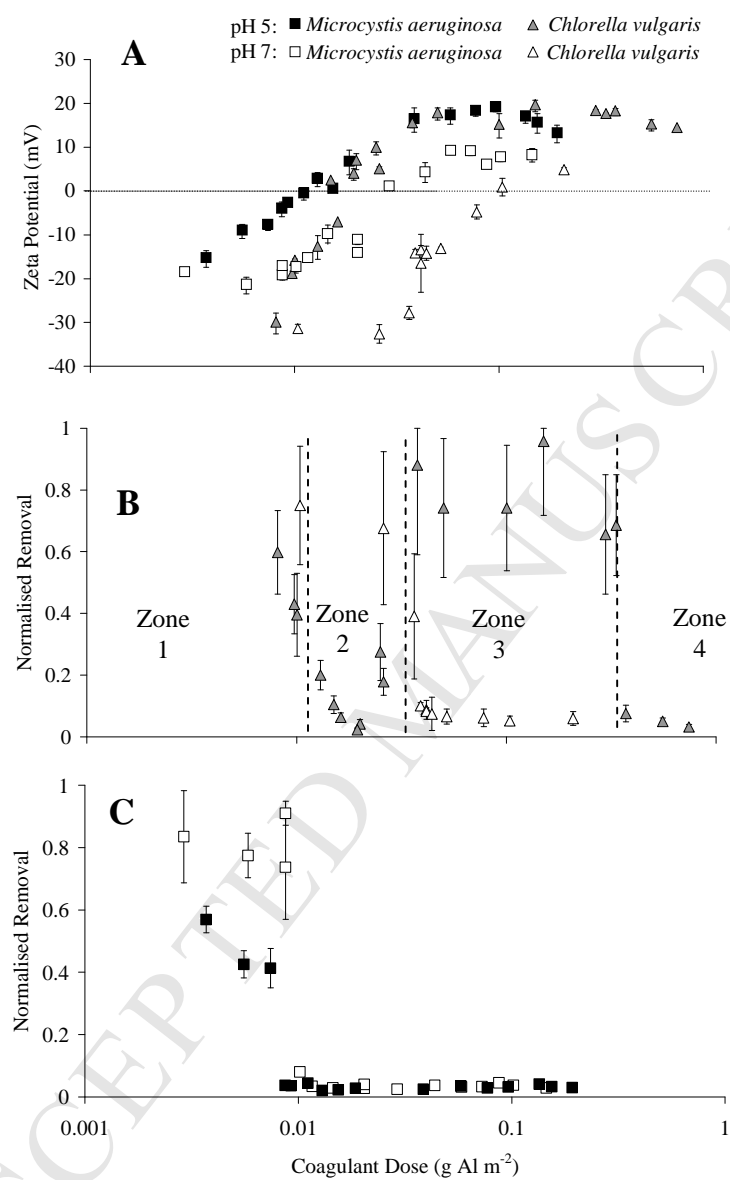


Figure 3

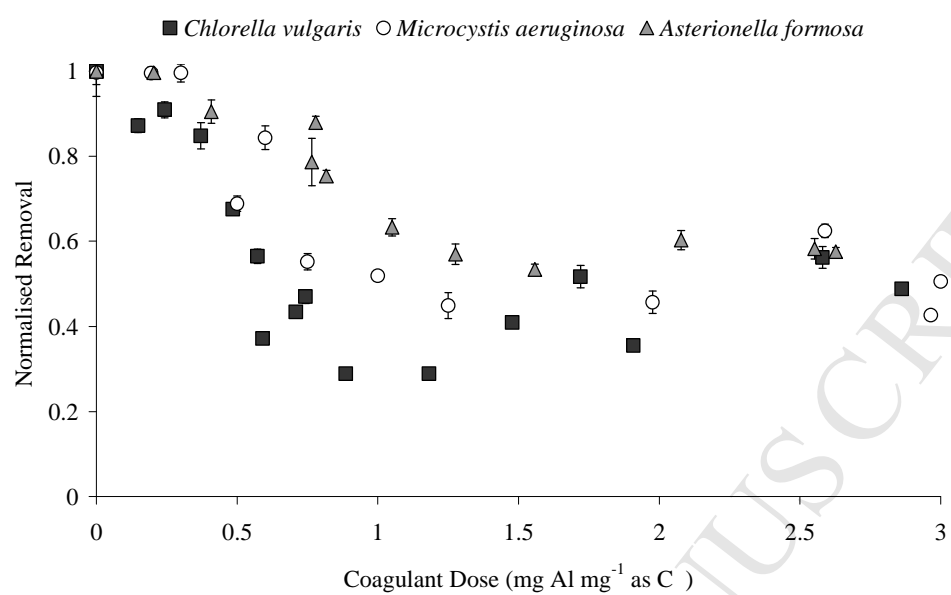


Figure 4

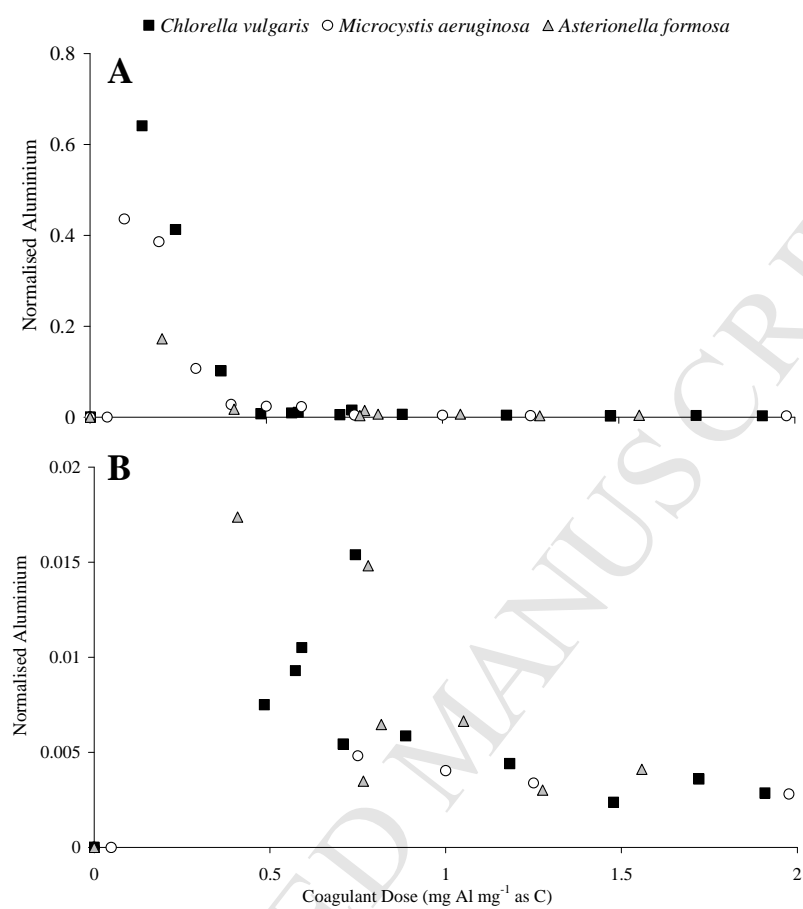
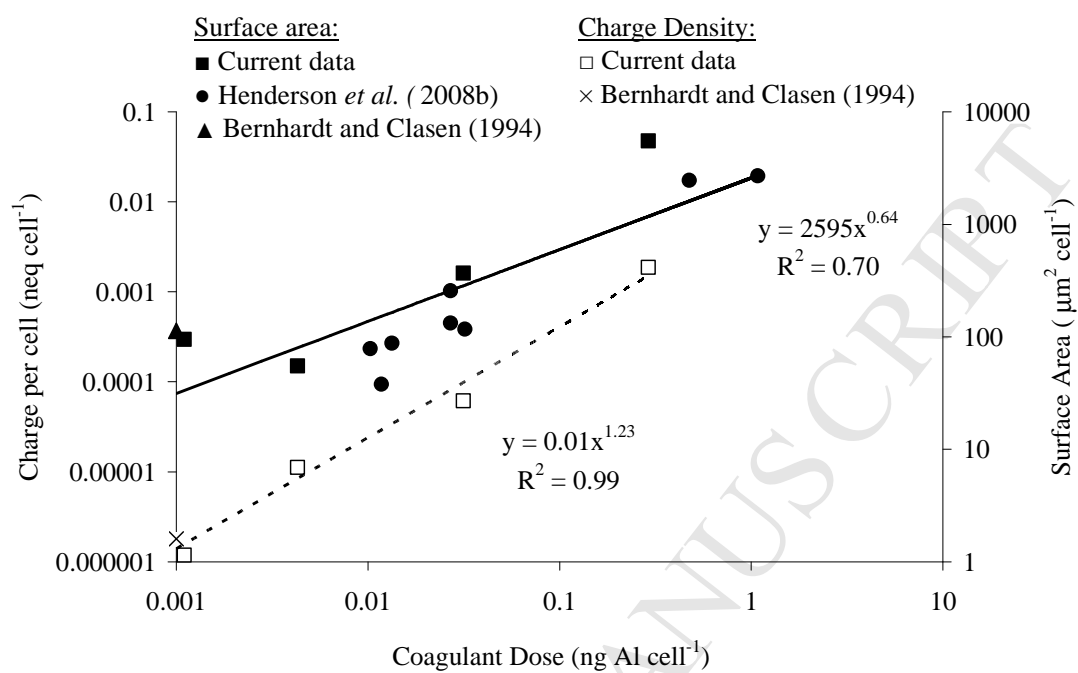


Figure 5



The impact of differing cell and algogenic organic matter (AOM) characteristics on the coagulation and flotation of algae

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2010-06

Rita K. Henderson, Simon A. Parsons and Bruce Jefferson, Water Research, Volume 44, Issue 12, June 2010, Pages 3617-3624

<http://dx.doi.org/10.1016/j.watres.2010.04.016>

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