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# The Potential for Using Bubble Modification Chemicals in Dissolved Air Flotation for Algae Removal

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**Abstract:** This paper investigates the potential for using surface modified bubbles in the treatment of algae using dissolved air flotation (DAF) instead of upstream coagulation and flocculation. Bubble modification is attempted by adding either metal coagulant, surfactant or polymers direct to the saturator. In this way, the chemical characteristics most suitable for removing small algae cells using this technique are examined. Optimum removal using metal coagulant, aluminium sulphate, was 60%; however, both a decrease in the magnitude of the zeta potential and microfloc generation occurred concurrently, thus accounting for the improved removal. In contrast, there was no change in system zeta potential and no microfloc generation when using cationic surfactant cetyltrimethyl-ammonium bromide (CTAB), for which 63% removal was achieved. An average of 95% removal was achieved using the cationic polymer, PolyDADMAC, with no change to system zeta potential. The results therefore confirm that there is a potential for adapting the conventional DAF process to operate without upstream coagulation and flocculation. A chemical with both a hydrophobic component in addition to a high molecular weight, hydrophilic, highly charge component is advised for the process.

**Keywords:** Bubble, coagulant, dissolved air flotation, polymer, surfactant

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## INTRODUCTION

Dissolved air flotation (DAF) is frequently used to treat algae laden water as it takes advantage of both their natural tendency to float and the very low density flocs that form on coagulation (1). The DAF process floats particles using microscopic bubbles that are produced by saturating recycled water with air at high pressure and subsequently releasing it at atmospheric pressure. The generated bubbles attach to influent particles, raising them to the surface. Efficient flotation relies on effective collision and attachment of bubbles and particles, achieved by coagulating influent particles to increase their size and decrease their negative charge respectively (1,2). The latter minimises repulsive effects between the particles and the strongly negatively charged bubbles. However, coagulation of algae is frequently reported to fail due to variable morphology (3), metabolically excreted organic matter (4), and their ability to react to changes in their immediate environment (5,6), leading to poor flotation. A flotation process that did not rely on coagulation would therefore be advantageous.

It is proposed that surface modification of the bubble, as opposed to the particle, could remove the requirement for upstream coagulation or greatly improve overall removal. This can be achieved by adding chemicals to the saturator of DAF process, which then coats the bubbles as they form, generating functionalised surfaces. This concept of particle collector modification has been investigated for depth filtration where media has been functionalised with cationic collectors such as metal hydroxides (7). However, contamination of such collectors can occur in water with high influent loadings, reducing the lifetime of such media (8). This issue is averted in modification of bubble surfaces as they are continually replenished. There is also potential to utilise surface modified bubbles in addition to upstream coagulation in order to further improve the particle removal obtained conventionally or reduce dose requirements. The specific surface function of the bubble depends on the chemical coating. For example, anionic surfactants have been demonstrated to make bubbles surface more negative (9,10) while the use of cationic surfactants have been shown to produce positively charged bubbles (9–12). Similarly, the application of di- and trivalent metal coagulants have been shown to alter bubble charge, attributed to adsorption of the positively charged aluminium and magnesium hydroxide precipitates with hydroxylated dissolved species making a more minor contribution. For example, bubble charge reversal occurred at pH 10 using $10^{-3}$ M $MgCl_2$ (13) and $10^{-2}$ M $MgCl_2$ (14) while aluminium was observed to reverse charge at pH 7 for concentrations of $5 \times 10^{-6}$ M (15), $10^{-5}$ M (14) and $10^{-4}$ M (16). The use of poly(diallyldimethylammonium chloride) (polyDADMAC) type polymer, Catfloc, has also been shown to create positively charged bubbles (17). Algae are negatively charged (18), thus in order to ensure good bubble-cell attachment, generating bubbles with positively charged functional sites is appropriate. However, charge may not be key to guaranteeing bubble-cell attachment. For example, polymer bridging between bubble and cell may also be important.

Surfactants and polymers have been utilised in the saturator with the intention of lowering the air/water surface tension (19). However, to date, only one published study has utilised such chemicals to produce a positively charged bubble that has subsequently been used to improve removal.

Malley (17) revealed that, when using positively charged bubbles created by dosing Catfloc to the saturator, comparable removal to that obtained by conventional coagulation-DAF was obtained when treating low color, low turbidity water. Overall, while it is acknowledged that surface modified bubbles can be produced, little research has been conducted in applying these bubbles in DAF for cell removal. Consequently, there is no understanding of which would be the most appropriate chemical to use.

This study investigates the potential for treating algal laden water by flotation using surface modified bubbles without pre-coagulation. A preliminary chemical screening trial is reported where bubble modification is attempted by dosing positively charged surfactant, metal coagulant and polymers into the saturator – a process that will be referred to as posiDAF from hereforth. Specifically, this research aims to assess a) the maximum removal efficiency achievable for *Microcystis aeruginosa* (a species of cyanobacteria commonly referred to as a blue-green algae) without conventional coagulation and flocculation; and b) the most appropriate chemical character for use in the production of surface modified bubble for algae treatment. The current study focuses on the interaction between algae, algal organic matter and the bubble modification chemicals. As such the work excludes the influence of residual natural organic matter to provide clarity in resolves the respective influences of each component. Further, given that previous studies outlines above have demonstrated that the chemicals used in the current work all generate positively charged bubbles no further work on direct measurement of bubble charge will be reported. Instead, the work focuses on understanding the influence of chemical choice on the efficacy of the process, an area which has received considerably less attention.

## MATERIALS AND METHODS

### Cultivation of Microcystis Aeruginosa

Cultures of *M. aeruginosa* (1450/3 – freshwater, Esthwaite Water, Cumbria, England) were obtained from the Culture Collection for Algae and Protozoa (CCAP) (Oban, Scotland). Cells were cultivated in sterilised Jaworski Media using conical flasks that were shaken at 75 rpm (Patterson Scientific Bibby Stuart SO1 shaker, Luton, UK) and incubated at 20°C under 24 hour radiation using Sun-glo 30 W aquatic lighting. Algae were harvested at the onset of the stationary phase when they had reached maximum cell concentration of $2 \times 10^7$ cells $mL^{-1}$. *M. aeruginosa* cells had an average diameter of 5.5 µm respectively as measured microscopically for 100 cells.

## PosiDAF Chemicals

The chemicals trialled in this research are outlined in Table 1 and include the metal coagulant, aluminium sulphate, the surfactant cetyltrimethylammonium bromide (CTAB), and polymers poly(ethyleneimine) (PEI), chitosan, poloyamines-Magnafloc LT31 and Agefloc A50, and polyDADMAC. Note that the charge of these chemicals is stable for all pH ranges with the exception of chitosan, PEI and CTAB. The surfactant would only become less positively charged for very high pH (10 or 11). With the exception of aluminium sulphate, the charge density of each chemical was analysed using a back titration method (20). Initially, the charge density of cationic surfactant, CTAB, was calculated from the chemical formula and subsequently used to standardise the charge of anionic poly(vinylsulphonic acid) sodium salt (PVSA). A 1 meq $g^{-1}$ solution of PVSA was then used to measure the charge density of the remaining chemicals by back titration. Each solution was buffered to pH 7 or pH 5 as appropriate using 1 mM $NaH_2PO_4/Na_2HPO_4$ or $CH_3COOH/NaCH_3COO$ respectively) and the indicator ortho-Toluidene blue was added. Decrease in the $UV_{635}$ absorbance (Jenway 6505 UV/Vis) signified neutralisation, coinciding with a colour change from blue to pink-purple. Three different volumes of cationic chemical were analysed in this way.

## PosiDAF Experiments

A bench scale flotation jar tester was used for all PosiDAF experiments (EC Engineering Dissolved Air Flotation Batch Tester, Model DBT6, Alberta, Canada). One liter samples were prepared by diluting the concentrated algae solution to $7.5 \times 10^5 \pm 2.3 \times 10^4$ cells $mL^{-1}$ using DI water buffered and ionised with 0.5 mM $NaHC0_3$ and 1.8 mM NaCl and adjusted to pH 7 using HCl. The same buffered DI water was added to the saturator along with aliquots of stock chemical, shaken vigorously, and adjusted to pH 7. The solution was then saturated with air at a

**Table 1.** Description of chemicals utilised in the chemical trial

| Chemicals | Supplier | Structure | Molecular weight (Da) or intrinsic viscosity (cp) | Preparation of stock solution | Charge density of stock (meq $g^{-1}$) |
|---|---|---|---|---|---|
| *Metal coagulant* | | | | | |
| 1. Aluminium sulphate | Fisher Scientific (UK) | $Al_2(SO_4)_3 \cdot 14H_2O$ | 594 | 10 mg $mL^{-1}$as Al prepared using DI water | Not measured |
| *Surfactant* | | | | | |
| 2. Cetyltrimethyl-ammonium bromide (CTAB) | Sigma (UK) | $CH_3(CH_2)_{15}N(CH_3)_3Br$ | 364.5 | 1 mM prepared using Dl water | 2.8 |
| *Polymers* | | | | | |
| 3. PoIy(ethyleneimine) (PEI) | Fisher Scientific (UK) | $(-CH_2CH_2NH-)_n$ | 50,000–60,000 | 1 mg $mL^{-1}$ prepared using DI water | 12.1 |
| 4. Chitosan (deacetylating grade) | Fisher Scientific (UK) | $(C_6H_{11}NO_4)_n$ | 100,000–300,000 | 1 mg $mL^{-1}$ prepared using I mM acetic acid | 4 at pH 5/2.9 at pH 7 |
| 5. Magnafloc LT31 (Polyamine) | CIBA (UK) | Not disclosed (N.D.) | N.D., 350–650 cp | 1 mg $mL^{-1}$ prepared using DI water | 7.2 |
| 6. Agefloc A50 (Polyamine) | CIBA (UK) | Not disclosed (N.D.) | N.D., 600–900 cp | 1 mg $mL^{-1}$ prepared using DI water | 7.2 |
| 7. PolyDADMAC | Sigma Chemicals (UK) | $((CH_2)_2C_4H_6(CH_3)_2N^+)_n$ | 100,000–200,000 | 1 mg $mL^{-1}$ prepared using DI water | 6.2 |

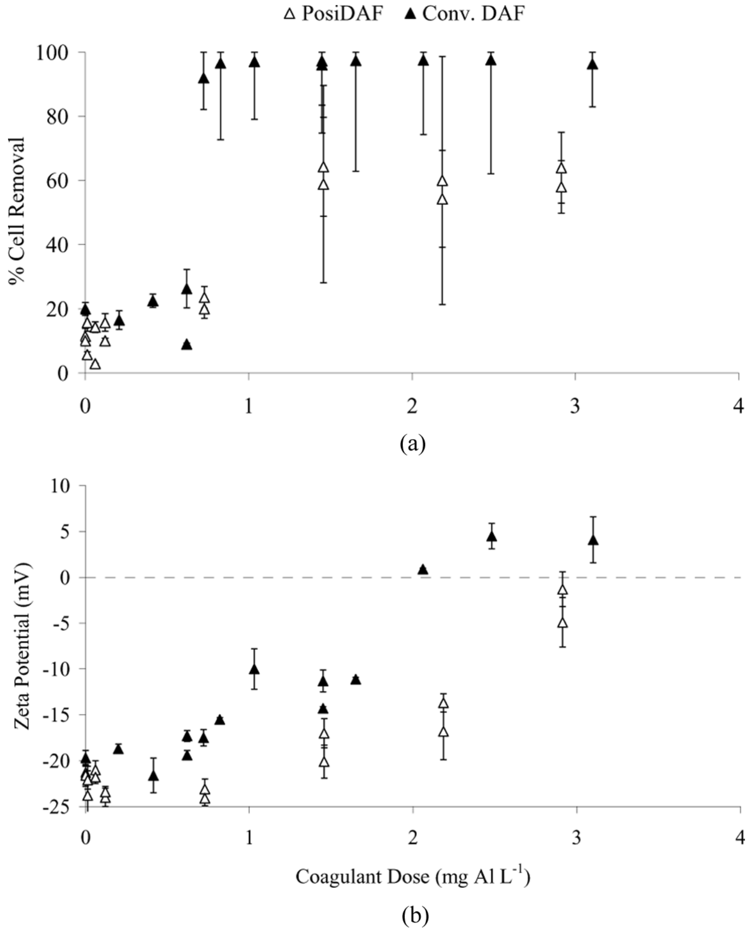
pressure of 450 kPa, shaken for 30 seconds (until gauge pressure stabilisation) and then added to the algae solution using an equivalent recycle ratio of 20%. A recycle ratio of 20% was selected in order to ensure that a sufficient number of bubbles were available to float the suspension despite the high particle number and small size of the algae, which would normally have been decreased and increased respectively as a result of coagulation and flocculation, Hence, poor removal can be attributed to inefficient bubble modification rather than insufficient availability of bubbles for flotation. The algae were allowed to float for 10 minutes. When using chitosan, experiments were undertaken additionally at pH 5.

For comparison, conventional coagulation and flotation was undertaken whereby the chemical was added to 1 L of algae sample (prepared as described previously) at the beginning of a 2 minute rapid mix (200 rpm) during which pH was adjusted. The suspension was then mixed at 30 rpm for 15 minutes after which the paddles were gently removed and pressurized (450 kPa), air saturated, buffered, deionized water was supplied at an equivalent recycle ratio of 12%. Algae flocs were floated for 10 minutes. Residual samples were analyzed as follows: cell counting using a haemocytometer and light microscope (100 cells were counted per analyses); zeta potential (ZP) using a Malvern Zetasizer 2000HSA (Malvern, UK); and DOC using a Shimadzu TOC-5000A analyser. All analyses were performed in triplicate and with respect to DOC errors were less than 2%. ZP analyses was undertaken at least 7 minutes after chemical addition to ensure that no further change in ZP would occur (6) and were found to be stable. At no time was the bubble charge measured. Chemical addition was reported in terms of the effective concentration added to the 1 litre cell suspension for both PosiDAF and conventional DAF experiments, allowing direct comparison of the dosages required.

## RESULTS

### Coagulant

The maximum removal obtained when using aluminium sulphate in the saturator, with a 20% recycle ratio, was 60% which occurred over the dose range of 1.46 to 2.9 mg $L^{-1}$ over which the removal was at a plateau (Fig. 1). This plateau coincided with a decrease in ZP from $-18.5$ to $-1.3$ mV, significantly less than the initial ZP of $-22.6 \pm 1.2$ mV. Microflocs were observed when analysing residual cells microscopically and by the naked eye after the algae system was exposed to the turbulent flotation conditions. The DOC of the system remained constant at $0.68 \pm 0.1$ mg $L^{-1}$. In comparison, when the coagulant was added



(a)

(b)

***Figure 1.*** Comparison of (a). % cell removal and (b). zeta potential, of PosiDAF and conventional coagulation and flotation using aluminium sulphate at pH 7.

traditionally to the jar and flotation conducted with a recycle ratio of 12%, removal of 98% was consistently observed once the dose exceeded $0.72\,\mathrm{mg\,L^{-1}}$ corresponding to ZP values between $-10 \pm 2.6\,\mathrm{mV}$ to $4.1 \pm 2.4\,\mathrm{mV}$ (Fig. 1). This demonstrates that upon coagulating conventionally there was more interaction of the coagulant with the algae cells in comparison to when using PosiDAF, suggesting that a proportion of the coagulant remained associated with the bubble. However, both the slight decrease in ZP and microfloc generation indicates that a significant proportion of the coagulant was associated with the cells in the bulk aqueous phase. Optimum dose ranges for PosiDAF convert to $5 \times 10^{-5}$

to $10^{-3}$ M and are therefore within the concentration that has been determined to generate positive bubbles (14,16).

## Surfactant

The optimum removal obtained when adding the cationic surfactant, cetyltrimethylammonium bromide (CTAB) to the saturator was 63% (Fig. 2) which occurred over the dose range of 0.0022 – 0.0040 mM (meq $l^{-1}$). Removal then decreased, beginning to stabilize at 42%. The ZP remained constant at $-19.3 \pm 1.3$ mV and microflocs were not observed at any time. The DOC remained consistent at $0.72 \pm 0.29\,\mathrm{mg\,L^{-1}}$. In comparison to when the surfactant was utilised as a conventional coagulant it was observed that aggregation of the algae cells did not occur until a dose of 0.14 mM had been added and optimum removal of 97% required addition of 0.39 mM, approximately 100 times more chemical than that required for PosiDAF, indicating that a different removal mechanism was predominant. Optimum removal by conventional methods coincided with charge reversal of the ZP to $6.2 \pm 0.0$ mV. Hence, the surfactant did not interact with the algae until relatively large doses had been added. This suggests that bubble modification occurred and was responsible for the improved removal observed at low surfactant doses. The CTAB dose required for optimum removal by PosiDAF is comparable with that required to create a positively charged bubble as measured by Kubota and

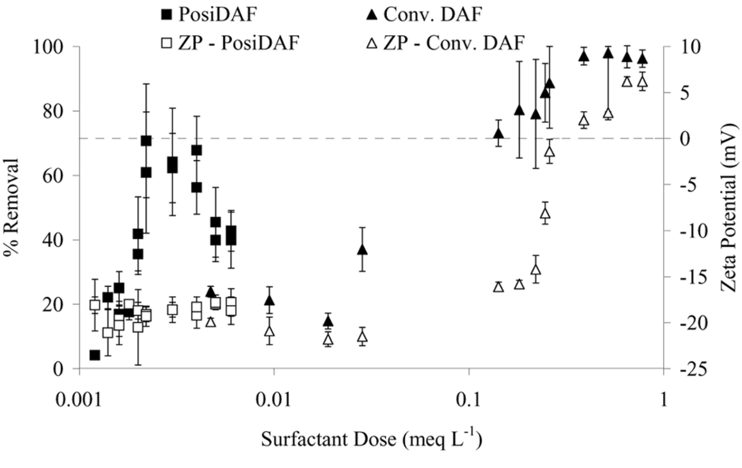


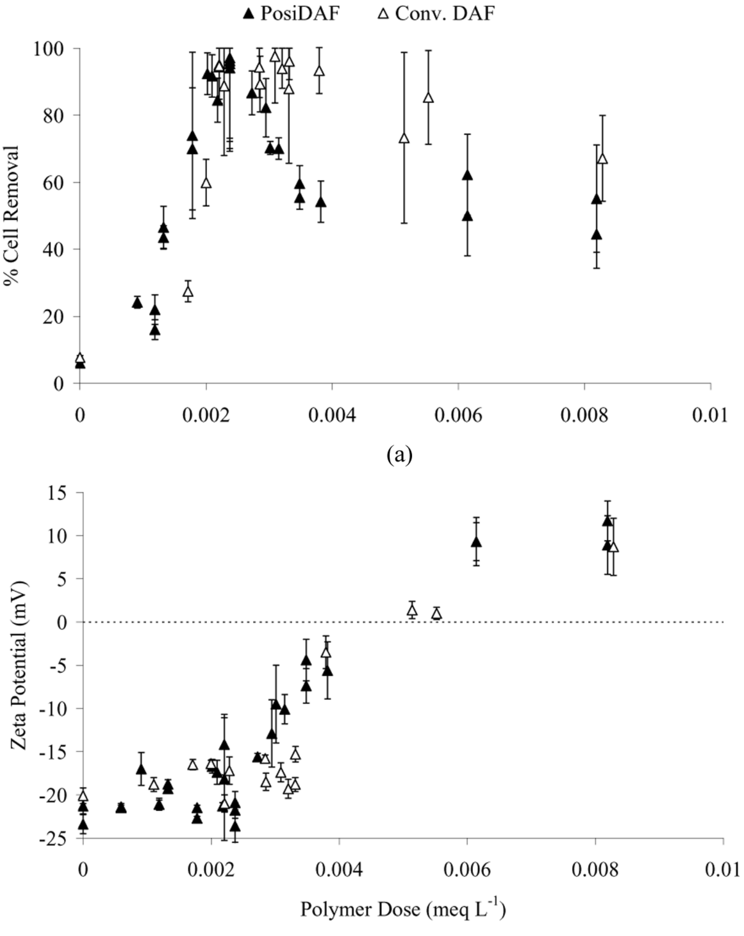
***Figure 2.*** Comparison of PosiDAF and conventional coagulation and flotation using cationic surfactant (CTAB) at pH 7.

Jameson (11) who showed a concentration of greater than 0.001 mM was required for charge reversal.

## Polymers

Optimum removal obtained for PosiDAF using polymers was variable and in the order 68, 76, 78, 87, and 95% for chitosan (pH 7), Magnafloc LT31, PEI, Agefloc A50, and polyDADMAC respectively. With the exception of PEI, all exhibited a peak in removal followed by a subsequent decrease, stabilizing at approximately 45%, as illustrated in the example of polyDADMAC (Fig. 3). The optimum dose range was narrowest in the case of chitosan (pH 7), where optimum removal was obtained at 0.0024 meq $L^{-1}$ (0.83 mg $l^{-1}$), and widest for polyDADMAC at 0.0020–0.0027 meq $L^{-1}$ (0.32–0.44 mg $L^{-1}$) (Fig. 3). The dose range obtained for the latter was much lower than the 8 mg $L^{-1}$ of cationic Catfloc required to produce a positively charged bubble (17). Similarly, in the same study the dose range used for treatment of humic acid and clay by chemical dosing to the saturator was higher than that required in the current study, at 0.8–6 mg $L^{-1}$ depending on the relative concentrations of humic acid and clay present. However, a direct comparison of the dosages was not possible as Catfloc charge density was not reported and the % of active polymer was not stated. The residual DOC for PosiDAF experiments with polymer addition did not vary significantly in the case of PEI, chitosan, Magnafloc LT31, Agefloc A50, or polyDADMAC, such that levels of $0.66 \pm 0.17$, $0.9 \pm 0.3$, $1.12 \pm 0.24$, $1.13 \pm 0.14$, and $1.34 \pm 0.45$ mg $L^{-1}$ were obtained respectively.

Magnafloc LT31 and Agefloc A50 had similar patterns of removal and optimum dose ranges of 0.0019–0.0023 meq $L^{-1}$, despite the differing removal efficiencies. In the case of Magnafloc LT31, the ZP changed relative to the initial value for the optimum dose range, decreasing to $-16.4 \pm 0.2$ mV, while that of Agefloc A50 remained stable. Structurally, these polyamines only differ in terms of their intrinsic viscosities (Table 1), which can be related to molecular weight and thus indicates that the MW of Agefloc A50 is greater than that of Magnafloc LT31. Hence, differences arising in PosiDAF performance for these polyamines can be related to MW. PEI required a much greater dose of 0.004 meq $L^{-1}$ for optimum removal which remained constant for the dose range tested – up to 0.01 meq $L^{-1}$. The ZP changed with increasing removal, decreasing to $-16.8 \pm 1.0$ mV at the onset of optimum removal and reversing the charge to $+2.7 \pm 1.2$ mV at the maximum dose and microflocs were visible to the naked eye during optimum removal. Chitosan experiments that were conducted at both pH 5 demonstrated improved removal at 82% in comparison to pH 7 results, at a dosage of 0.0012 meq $L^{-1}$, 2.5 times lower



(a)

(b)

***Figure 3.*** Comparison of A. % cell removal and B. zeta potential, of PosiDAF and conventional coagulation and flotation using cationic polymer (polyDADMAC) at pH 7.

than at pH 7. However, at pH 5, the ZP changed from $-16.5 \pm 0.9$ mV to $-13.3 \pm 2.4$ mV at the onset of optimum removal and microflocs were observed. In comparison, the ZP values of chitosan experiments undertaken at pH 7 remained stable at $-21.8 \pm 0.2$ mV for the optimum dose range.

A comparison of cell removal achieved by PosiDAF and conventional coagulation and flotation was conducted for polyDADMAC (Fig. 3) and Agefloc A50 (not illustrated here). It was observed that although similar removal efficiencies were obtained using both procedures, the onset of removal by conventional methods was achieved at slightly higher doses of 0.0028 meq L$^{-1}$ and 0.0027 meq L$^{-1}$ for polyDADMAC and Agefloc A50 respectively compared to 0.0020 and 0.0019 meq L$^{-1}$ as observed using PosiDAF. When using PosiDAF, optimum removal was obtained for a relatively constant ZP of $-20.1 \pm 3$ mV and $-20.2 \pm 2.8$ mV for the same chemicals and decreases in removal efficiency were concurrent with decreases in the magnitude of the zeta potential of the bulk solution when using PosiDAF. Similarly, at the onset of removal by conventional methods the ZP in the case of polyDADMAC remained constant, although it increased slightly in the case of Agefloc A50 to $-16.0 \pm 0.7$ mV. In contrast to PosiDAF, good removal continued to be achieved for conventional treatment when the ZP decreased to $-3.5$ mV and 6.5 mV for polyDADMAC and Agefloc respectively. Notably, for polyDADMAC, the removal efficiency achieved by conventional means then decreased when charge reversal occurred. Importantly, when using PosiDAF, no microflocs were observed at optimum removal for either system. However, flocs were formed when treating by conventional methods.

## Overall Comparison

The average removal at optimum dosage was continually greater than that obtained when no chemical was added to the saturator (Fig. 4). Specifically, an average of 9% cell removal was obtained without

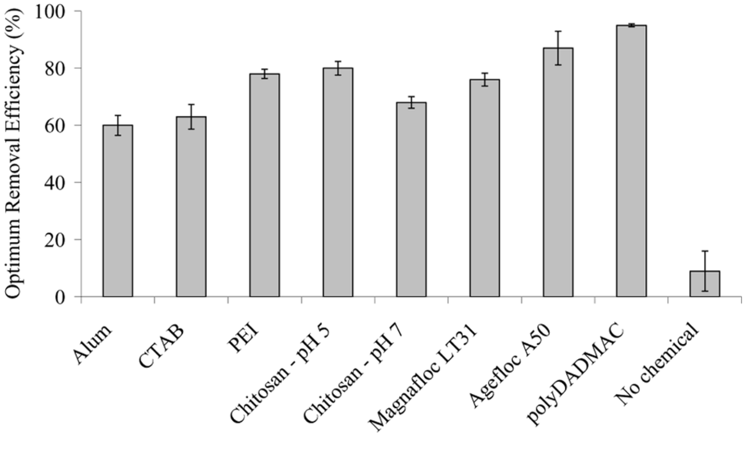


***Figure 4.*** Optimum removal efficiencies obtained using PosiDAF for all chemicals trialled.

PosiDAF, which increased in the range of 60–95% for the chemicals trialled thus demonstrating that a certain degree of removal was possible without upstream coagulation. Removal efficiency was lowest for aluminium and highest for PolyDADMAC. The best removal was achieved for polymers as opposed to surfactant or metal coagulant. Overall, the dose range of the chemicals was most comparable in terms of charge added. For example, a dose of 0.0023–0.0024 meq $L^{-1}$ ensured optimum removal for most chemicals, excepting aluminium, PEI and chitosan (pH 5). This indicates that a charge dependent mechanism is important in achieving removal. The charge concentration of the system was $-0.0014$ meq $L^{-1}$ (22) and is therefore approximately 1.6 times smaller than the charge required for optimum removal.

## DISCUSSION

Each chemical trialled demonstrated that improved removal could be achieved by adding a positively charged chemical to the saturator compared to no chemical addition. However, different degrees of removal occurred depending on the characteristics of the chemical utilized. Furthermore, corresponding residual zeta potential values also differed, thus indicating that different removal mechanisms were responsible for the overall cell removal achieved.

While no direct measurements of bubble charge were possible in the investigation, the associated data strongly suggests that the modifying chemicals, particularly CTAB, chitosan (pH 7), polyDADMAC and Agefloc A50, are predominantly associated with the bubble surface and hence with the generation of a positive bubble. In each case, the removal increases to an optimum without the zeta potential of the algae increasing or the observation of microflocculation. In parallel studies, where the chemical was added directly to the jar, removal proceeded by flocculation and, with the exception of polyDADMAC, an associated decrease in zeta potential was observed. Moreover, when compared with conventional methods, a lower dose overall was required for removal using PosiDAF, particularly in the case of CTAB where the dose was 100 times less. In contrast, the observation of microflocculation in the instances of aluminium sulphate, PEI and chitosan (pH 5), in addition to the concurrent decreases in ZP relative to initial values for the same chemicals, suggest that chemical was more closely associated with the cell. While no microflocculation was observed when using Magnafloc LT31, the decrease in ZP observed relative to the initial value again suggests that in contrast to the similar chemical Agefloc, a certain amount of chemical is associated with the cells as opposed to the bubbles. Hence, the character of CTAB, chitosan (pH 7), Agefloc A50 and polyDADMAC allows them to associate more closely with the bubble, whilst the character of aluminium sulphate, PEI, and chitosan (pH 5), and to an extent Magnafloc LT31, means these chemicals will preferentially bind to the cells.

Decrease in removal that was observed beyond the point of optimum removal for all polymers, with the exception of PEI, is likely to be due to a combination of positive patches on the algae surface forming through the adsorption of the polymer and also steric repulsion between polymer chains at these higher concentrations, as commonly described when using cationic polymers for coagulation by polymer bridging (23). In the case of surfactants, the chains are expected to be orientated such that the hydrophilic head faces the bulk solution, and hence the decrease is principally attributed to electrostatic patch repulsion (24). For example, when a previous study investigated the interactions between particles and bubbles in surfactant solutions, it was observed that the energy change due to steric repulsion was not significant compared to hydrophobic and electrostatic forces (25), imporved removal with surfactants may also be attributed in part to a decrease in bubble size. Couto et al. (26) determined that a decrease in size of approximately 10% could be anticipated on the addition of the surfactant at concentrations and critical micelle concentrations relevant to this study. The removal efficiency plateau that was achieved when using aluminium sulphate and PEI, in addition to the observed microflocculation, suggests that repulsive effects of the type previously described are not occurring. Firstly, there will be no steric hindrance from long chain polymers, particularly for PEI, which is 50–60 kDa in comparison to 100–300 kDa for polyDADMAC. Secondly, if there is no or very little chemical associated with the bubble, as implicated in an earlier discussion then electrostic patch repulsion between bubble and particle is unlikely to occur.

The variation in removal efficiencies from $63 < 68 < 87 < 95\,\%$ (Fig. 2) for CTAB, chitosan (pH 7), Agefloc A50, and polyDADMAC respectively, indicate that although the underlying mechanism in terms of removal by positive bubble remain the same, differences in the specific chemical characteristics affect overall removal efficiencies. This can be attributed to the way in which the chemical interacts at the interface. Figure 5 demonstrates how modification of the bubble surface may be envisaged in the case of surfactant and polymers (24,27). The surfactant is likely to lie relatively close to the bubble surface as a result of both the low MW of the chemical, $365\,\mathrm{g\ mol^{-1}}$, and the hydrophobic tail adsorbing tightly at the air-liquid interface. The hydrophilic head will lie on the outer edge of the bubble, thus generating positively charged regions in the current example of CTAB. In contrast, the polymers will be more loosely associated as they are more hydrophilic than the

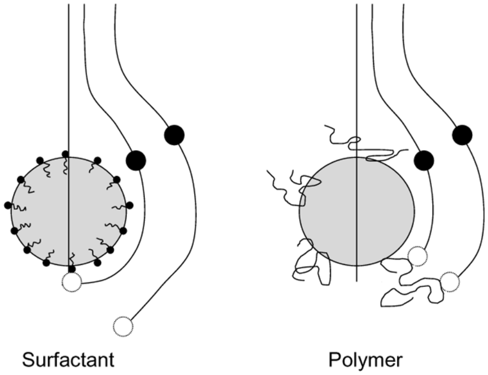


***Figure 5.*** Modification of bubble surface using surfactants and polymers leading to differences in removal efficiencies.

surfactants. Consequently, it is likely that the polymer will project from the bubble into the bulk solution, thus intercepting the commonly described trajectory of a particle around its collector (28). The extent to which the polymer reaches into solution will depend on the relative hydrophilic/hydrophobic portions and also on the molecular weight. For example, shorter chain polymers have lower affinity isotherms (24). Overall, there are two implications. First, that the "swept volume" will increase for polymers with larger molecular weights increasing cell-bubble collision and attachment efficiency (Fig. 5) and second, that longer chain polymers will more strongly adsorb to the interface. Long chain polymers could therefore act as bridges between cells and bubbles. Comparison of the removal exhibited by Magnafloc LT31 to that of Agefloc A50 supports this suggestion as the only difference between them is associated with there MW. The lack of association of PEI with the bubble surface can be attributed to both its relatively low molecular weight of 50–60 kDa and also to its highly hydrophilic nature. Hence, although CTAB will be most tightly adsorbed to the bubble surface, the swept volume will be smallest (Fig. 5) and thus the removal efficiency will be low in comparison to the long chain polymers.

A theoretical evaluation determined using the white water model described in detail by Haarhoff and Edzwald (1) and assuming an average bubble size of 40 µm and saturator efficiency of 0.7, suggests that optimum removal for a cell of this diameter should be 40–70% for attachment efficiencies of 0.5–1.0 respectively. This compares well with removal efficiencies obtained for CTAB and chitosan (pH 7); however, it is considerably less than those achieved for Agefloc A50 and polyDADMAC. The increased swept volume of the polymer explains this discrepancy. It is suggested that these polymers bridge between cells and bubbles, forming an effective mesh, entrapping cells that fall into it as the bubble and associated polymer rise. Hence, 95% removals can be obtained.

Overall, it was revealed that metal coagulants were not suitable for modifying the bubble surface as they preferred to associate with the cell surfaces. Similarly, small, hydrophilic chemicals were also shown not to be suitable as again they associated preferentially with the cell surface. In contrast, when using chemicals with a defined hydrophobic component, such as that exhibited by the surfactant, the strong suggestion was that only minor interactions with the cell surface were occurring when applying doses in the range 0.0022–0.0040 mM; however, removal was reduced as a result of its tight adsorption and small molecular weight. When the chemical was more loosely associated with the bubble and furthermore was of a significant MW, projection into the bulk phase could occur, increasing the swept volume of the bubble. The ideal chemical character for PosiDAF would therefore be a chemical that had a strong hydrophobic component to allow tight adsorption to the bubble surface as it rises vertically, but additionally a hydrophilic charged component with long chain length that would project far into solution to collect cells on its upward path. For example, a co-polymer containing strongly hydrophobic and hydrophilic blocks, such as that synthesised and characterised by Lieske and Jaeger (29) which incorporates both hydrophobic poly(ethylene glycol) and more hydrophilic polyDADMAC, contains these attributes.

In order to gain further insight into the use of surfactants in the saturator of a DAF process, further tests have been conducted on a range of surfactants with differing characteristics and these are presented elsewhere (30). During this subsequent study, algae removal was observed to improve with an increase in the hydrophobicity of the positively charged surfactant. Further research is also required in order to confirm that results obtained using a batch, bench-scale DAF unit at 20% recycle ratio can be emulated on a larger scale and thus future work must include pilot and full-scale studies. The optimum recycle ratio for posiDAF also requires investigated. This would additionally present an opportunity to conduct experiments to investigate a) the volume and character of sludge produced, allowing a thorough evaluation of the cost of PosiDAF in comparison to conventional DAF and b) the fate of the PosiDAF chemical. The latter point is important as while the cationic polymer may be removed by downstream filters, chemicals such as surfactants may require more advanced treatment, for example ozone followed by granular activated carbon filtration, and the fate of the residual chemical requires full investigation prior to use. Finally, the impact of NOM, particularly that characterized by hydrophobic, high-charged material, on the removal of particles also needs to be researched.

## CONCLUSIONS

1. Greater than 60% removal of un-coagulated cells can be obtained by adding a cationic chemical to the saturator of a batch, bench-scale DAF unit operated with a 20 % recycle ratio, although removal occurs by different mechanisms dependent on the chemical characteristics.
2. Removal obtained by small, hydrophilic polymers and metal coagulants was the result of microflocculation occurring during the turbulent flotation regime rather than by the production of positive bubbles.
3. It was possible to obtain 95% removal efficiencies for algae cells using polyDADMAC, a cationic polymer, despite theoretical removal efficiencies of only 48–70% being calculated for the cell diameter. This was attributed to the polymer projecting into the bulk phase from the bubble surface, capturing increased cell numbers as a result of increased swept volume.
4. Overall, three criteria are required for the chemical utilized to generate a positively charged bubble for successful cell removal: 1) positively charged region; 2) a hydrophobic component to encourage adsorbance at the bubble surface; and 3) high molecular weight both to increase the swept volume or enmeshment area.

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