

Polymer-coated bubbles in dissolved air flotation for processing algae-laden water

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POLYMER-COATED BUBBLES IN DISSOLVED AIR FLOTATION FOR PROCESSING ALGAE-LADEN WATER

by

Russell Yap

A thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy



School of Civil and Environmental Engineering The University of New South Wales

September 2013

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The contamination of waterways with algae and cyanobacteria is a challenging problem for water treatment plants in many parts of the world. Dissolved air flotation (DAF) is a popular method for the clarification of algae-laden water. Pre-treatment by coagulation-flocculation (C-F) is necessary for effective flotation; however, as raw water characteristics can vary rapidly during an algae bloom, coagulation can be difficult to optimise. Hence, eliminating the dependence of DAF on C-F is desirable.

An alternative to C-F prior to DAF is the chemical modification of microbubble surfaces generated during flotation. This adaptation has been effective in floating various laboratory cultured algae and cyanobacteria cells; however, research has been limited to laboratory studies using commercially available polymers. The purpose of this work was to synthesise purpose-designed cationic polymers to closely adhere to a microbubble surface and test the use of these modified microbubbles in DAF at both at bench-and pilot-scale.

A collection of hydrophobically-associating cationic polymers was synthesised. Selected polymers were then used to modify microbubble surfaces in bench-scale flotation experiments to treat two strains of Microcystis aeruginosa without pretreatment with C-F. Results obtained using the synthesised polymers were compared with a commercially available flocculant aid. Greater than 95% cell removal was obtained for one strain of *M. aeruginosa* with all polymers tested. Polymer performance was differentiated via charge residuals, where more negative zeta potentials indicated lower polymer residual, suggesting stronger bubble adherence. While the removal efficiency achieved for the second strain was only 37%, this was improved to >95% by adding extracellular organic matter extracted from the original strain. Subsequently, polyDADMAC and the best-performing synthesised polymer were trialled using a purpose built DAF pilot plant where they were used to treat algal blooms in a waste stabilisation pond. It was found that the use of polyDADMAC-modified bubbles resulted in contaminant removal, similar to that of conventional DAF. However, 46 % lower removal efficiencies were obtained for the synthesised polymer, contrasting with bench-scale results of 98% turbidity removal. For the first time, modified-bubble flotation has been demonstrated in field experiments, proving to be an alternative for conventional DAF.

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Publications and Presentations

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<u>Yap R.</u>, Holmes M., Peirson W., Whittaker M., Stuetz R., Jefferson B., Henderson R. (2012) *Optimising dissolved air flotation/filtration treatment of algae-laden lagoon effluent using surface charge: a Bolivar treatment plant case study*, <u>Water Science and Technology</u>, 66 (8), 1684-1690

<u>Yap R.</u>, Whittaker M., Duong H., Marquis C., Bulmuş V., Peirson W., Stuetz R., Henderson R. (2013) *Solution, self-association and antibacterial properties of partially quaternised poly[2-(N,N-dimethylamino)ethyl methacrylate]* prepared manuscript for submission to Polymer Science

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<u>Yap R.</u>, Holmes M, Peirson W, Whittaker M, Stuetz R, Newcombe G, Jefferson B, Henderson R. (2012), *The selectivity of pH regulated alum coagulation in dissolved air flotation of algae laden stabilisation pond effluent – a case study*, <u>OzWater12</u>, Sydney, Australia, 7th - 10th of May, 2012

<u>Yap R.</u>, Holmes M., Peirson W., Whittaker M., Stuetz R., Jefferson B., Henderson R. (2011) *Optimising dissolved air flotation/filtration treatment of algae-laden lagoon effluent using surface charge: a Bolivar treatment plant case study*, 9th IWA Specialist Conference on Waste Stabilisation Ponds, Adelaide, 1st - 3rd August, 2011

Other Conference Presentations

Yap R., Whittaker M., Bulmuş V., Peirson W., Stuetz R., Henderson R. (2012) *The use of cationic polymers at bubble interfaces for water reclamation*, <u>33rd Australasian</u> Polymer Symposium, Hobart, Australia, 12-15th February, 2012

Abstract

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List of Abbreviations

AFM	Atomic force microscopy
ANACC	Australian National Algae Culture Collection
AOM	Algogenic organic matter
ASR	Activated sludge reactor
ATR	Attenuated total reflectance
AWQC	Australian Water Quality Centre
BASF	Badische Anilin- und Soda-Fabrik
BCP	Biopolymer cluster
BHT	Butylated hydroxytoluene
BLAST	Basic Local Alignment Search Tool
BSA	Bovine serum albumin
CCAP	Culture Collection of Algae and Protozoa
CCD	Charge-coupled device
CDA	Charge demand analyser
C-F	Coagulation and flocculation
CGA	Colloidal gas aphron
CSIRO	Commonwealth Scientific and Industrial Research Organisation
CTAB	Cetyl trimethylammonium bromide
DAF	Dissolved air flotation
DAF/F	Dissolved air flotation over filtration
DLS	Dynamic light scattering
DLVO	Derjaguin, Landau, Verwey and Overbeek
DMAc	N,N-dimethylacetamide
DMAEMA	2-(N,N-dimethylamino)ethyl methacrylate
DOC	Dissolved organic carbon
DTGS	Deuterated triglycine sulphate
EDL	Electrical double layer
GPC	Gel permeation chromatography
GSE	Generalised Sutherland equation
IAF	Induced air flotation
LC-OCD	Liquid chromatography with organic carbon detection

LT510	Cationic Polymer from BASF, Australia (polyDADMAC)
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- MW Molecular weight
- MWCO Molecular weight cut-off
- NHMRC National Health and Medical Research Council
 - NIR Near infrared
 - NMR Nuclear magnetic resonance
 - NOM Natural organic matter
 - NSW New South Wales
 - NTU Nephelometric turbidity unit
 - PCC Pasteur Culture Collection
 - PDI Polydispersity index
 - PES Polyethersulphone
- PES-Na Sodium polyethylene sulphonate
- polyDADMAC Poly(diallyldimethylammonium chloride)
- polyDMAEMA Poly[2-(N,N-dimethylamino)ethyl methacrylate]
 - SA South Australia
 - SCADA Supervisory Control and Data Acquisition
 - SDS Sodium dodecyl sulfate
 - SUVA Specific UV absorbance
 - TEM Transmission electron microscopy
 - TOC Total organic carbon
 - UK United Kingdom
 - UNSW The University of New South Wales
 - USA United States of America
 - UV-vis Ultra Violet-Visible
 - VIC Victoria
 - WRC Water Research Centre
 - WSP Waste stabilisation pond
 - WTP Water treatment plant
 - WWTP Wastewater treatment plant

Chapter 1

1 INTRODUCTION

1.1 Background

Dissolved air flotation (DAF) is a solid-liquid separation process used in water and wastewater treatment plants (WTPs and WWTPs, respectively) in which microbubbles are used to float contaminants from influent water, separating solids from water. This is typically applied to either improve the quality of the water or remove excess water from sludge. Microbubbles are produced by the dissolution of air into water under pressure, which is then depressurised in a contact zone, where microbubbles are generated and introduced to the influent water. Subsequent to bubble generation, the collision and attachment to influent contaminants is critical for successful flotation. However. influent particles are generally negatively charged at pH values normally observed in WTPs and WWTPs and experience an electrostatic repulsion force with the negatively charged bubbles that are generated in DAF (Han and Dockko 1999). To prepare influent water for flotation, influent particles, colloids and dissolved organic matter (DOM) are thus initially treated, or coagulated, typically with cationic hydrolysing metal salts. The hydrolysing metal salts facilitate coagulation via direct absorption of the dissolved macromolecules onto hydroxide surfaces or complexation with cationic hydrolysis products (Duan and Gregory 2003). The flocculation of particles is encouraged by slow mixing, which increases interparticle collisions. After coagulation and flocculation (C-F) repulsion force that a bubble would experience upon approaching a paricle is reduced (Haarhoff and Edzwald 2004) and therefore the likelihood of adhesion after collision is increased. The attachment of bubbles and particles in DAF create low density bubble-particle agglomerates which then rise to the surface to form a float layer for subsequent removal via mechanical or hydraulic means. Investigations into the operation of numerous water treatment plants have demonstrated that reducing

the charge in influent waters to zeta potentials of -10 to 0 mV is desirable for effective C-F (Jefferson *et al.* 2004).

The presence of algae and cyanobacteria in raw water can present a significant challenge for water treatment operators. Cyanobacteria are frequently referred to as "blue-green algae" and this terminology has been used in this thesis. C-F in particular can be difficult to optimise due to highly variable population densities, morphologies and cell motility as well as interferences by algogenic organic matter (AOM), and, downstream flotation can be potentially rendered ineffective (Henderson et al. 2008c, Henderson et al. 2008d, 2010a, Pieterse and Cloot 1997, Takaara et al. 2004). For example, turbidity breakthrough and filter clogging have been principal consequences of the presence of algae and cyanobacteria in raw water (Buisine and Oemcke 2003). Moreover, when removal of algae or cyanobacteria is unsuccessful, toxins can be released due to the treatment process damaging cell integrity or harmful disinfection byproducts can form from reactions of cell matter with disinfectants (Al-Tebrineh et al. 2010, NHMRC 2011). DAF is currently considered one of the most effective treatment processes for algae and cyanobacteria treatment (Edzwald 2010, Teixeira and Rosa 2006, Vlaški et al. 1996); however, it remains highly reliant on successful C-F. Hence, to avoid treatment issues faced during algae and cyanobacteria blooms in water treatment plants, the optimisation of DAF beyond current capabilities and the development of a DAF process that does not rely on preceding C-F is desirable.

Poor contaminant flotation arising from the poor coagulation of influent particles in DAF may be alleviated by the use of bubbles that can adhere to uncoagulated particles. The modification of bubble surfaces has the potential to facilitate bubble adherence to particle surfaces. Specifically, positively charged bubbles have an electrostatic attraction to anionic contaminants. The modification of bubble surfaces in place of particle surface modification has the advantage of predictable bubble properties, such that bubble surface coverage with modifying agents can be controlled. In practice, the modification of bubble surfaces has been demonstrated by the adsorption of various chemicals. Using salt solutions, the preferable adsorption of cationic species can yield cationic bubbles from pH 2 to 7 (Dockko and Han 2004, Han *et al.* 2006b, Li and Somasundaran 1991). Cationic bubbles have also been generated by forming bubbles in the presence of surfactants. This has been practiced by adding cationic surfactant to water in the saturator (Féris and Rubio 1999, Henderson *et al.* 2008e). The advantage

of using a surfactant is the presence of a hydrophobic component, which encourages the chemicals to concentrate at the air-liquid interface. However, in the removal of contaminants, the use of surfactant modified bubbles alone has not resulted in contaminant removal comparable to conventional C-F dependant DAF (Henderson et al. 2008e). By using cationic polymers in saturator water, bubbles have been shown to be cationic at pH 7 (Malley 1995, Oliveira and Rubio 2011, Oliveira and Rubio 2012). In application, polymer coated bubbles have shown promise in clarifying water containing cyanobacteria, specifically a UK strain of Microcystis aeruginosa strain CCAP 1450/3 (Henderson et al. 2010b). In other laboratory simulated DAF influent waters, using polymer modified bubbles was found not to be as effective: Henderson et al. (2010b) attributed this to the presence of AOM interacting with polymer, removing it from bubble surfaces. Flocs were observed to form during flotation despite the absence of C-F, indicating that polymers were not remaining at the bubble surface (Henderson et al. 2010b). Thus, the addition of hydrophobic functionality to polymers was identified as a potential method to increase adherence to bubble surfaces. This also has the advantage of increasing polymer removal from water resulting in lower chemical residuals in DAF treated water.

1.2 Research Objectives

The overall aims of this present research was to develop hydrophobically functionalised polymers to adhere to bubble surfaces for use in DAF, and test these polymers in modified-bubble DAF for the treatment of algae-laden water. Modified-bubble DAF tests with a conventional water treatment polymer (polyDADMAC) are to be compared with the performance of the hydrophobically functionalised polymers. In past studies, modified-bubble DAF has been demonstrated to be an alternative to conventional DAF that is preceded by DAF; however, investigations have been limited to conventional flotation chemicals and laboratory synthesised DAF influent waters. This research extends the completed laboratory trials by investigating the application of modified-bubble DAF on environmentally relevant water at pilot scale. To achieve the aims, the following objectives were identified:

- 1. To review the state of flotation technology in the literature as a solid liquid separation method
- 2. To synthesise and characterise specifically designed treatment polymers for modifying the bubble surface in DAF
- 3. To establish the performance of the synthesised polymers compared to polyDADMAC in modified-bubble DAF under laboratory conditions, *M. aeruginosa*, strain CS-564/01, as a model algal contaminant
- 4. To investigate the robustness of the process to an alternate strain of *M*. *aeruginosa* and examine the influence of organic matter character
- 5. To construct, install and commission a pilot DAF plant in the field
- 6. To trial modified-bubble DAF at pilot-scale on real-world DAF influent comprising algae blooms using both conventional polymers and purpose-designed polymers

1.3 Synopsis

This thesis focuses on the development of a novel DAF process that operates through the use of modified bubbles rather than relying on upstream C-F for successful flotation. To achieve this, modified-bubble DAF is investigated, progressing to commencing with polymers design and synthesis, laboratory-scale tests and concluding with tests at pilotscale.

Initially, a literature review was conducted on the mechanisms of flotation (Chapter 2), focusing on DAF practices for water treatment in comparison with those used in mineral flotation to identify potential areas for knowledge transfer. In this chapter, the physical characteristics of bubbles and particles in water were reviewed. The mathematical models that are applied to lend insight into underlying process mechanisms in both mineral flotation and DAF were analysed to establish similarities and differences between the processes. In the review of chemical types used and interaction forces facilitating bubble-particle collision and flotation, it was found that the use of hydrophobic reagents for the association of bubbles, though common in mineral flotation, is not utilised in DAF for water treatment. The use of modified bubbles in

DAF has demonstrated potential in increasing their adherence to particle surfaces without the requirement for upstream C-F with success in clarifying water with low colour and turbidity and *M. aeruginosa*. Currently, application of chemically modified bubbles was found to be limited, using only commercially available chemicals, laboratory synthesised influent water and bench-scale equipment.

In Chapter 3, specifically designed polymers were developed for use in modifying To achieve this, the monomer dimethylaminoethyl methacrylate bubble surfaces. (DMAEMA) was used to synthesise three polymer scaffolds of different molecular weight from which hydrophobic pendant groups could be attached via quaternisation. This effectively increased both hydrophobic association and cationic nature of the polymers. Hydrophobic carbon chains of a range of lengths were attached at three different concentrations, such that an archive of polymers was established for characterisation. The base polymer length was determined by gel permeation chromatography (GPC) and structures of the polymers were confirmed by proton nuclear magnetic resonance (¹H NMR). The water properties were investigated using surface tension and charge demand, which indicated that the archive of polymers had a range of different properties, from which nine samples were identified for further investigation. With the nine samples, polymer self-association was conducted by forming nano-objects, which were subsequently analysed via transmission electron microscopy (TEM). The presence of the larger hydrophobic groups was apparent by nano-object geometry.

Chapter 4.1 presents the outcomes of modified-bubble DAF jar testing using *M. aeruginosa* as a model algal contaminant. The process was successfully demonstrated using all polymers synthesised in Chapter 3 and polyDADMAC, a polymer commonly used in water treatment. Polymer performance was further differentiated by examination of residual charge in the DAF treated water; greater negative charge suggests a lower polymer residual concentration and therefore better bubble attachment. It was found that the polymer with the greatest quantity of highly hydrophobic groups associated to the largest polymer backbone resulted in more negative modified-bubble DAF treated water charge, indicating strong adherence to bubble surfaces. This polymer was therefore selected for pilot scale tests reported in Chapter 5.2. In Chapter 4.2, an additional strain of *M. aeruginosa* of similar morphological characteristics but different organic character was tested to investigate the effect of associated algogenic

organic matter (AOM) on the success of modified bubble DAF. The maximum cell removal achieved with polymers in modified-bubble DAF did not match that of Chapter 4.1; however, the cell removal did match that predicted by performance models. From this investigation, it was found that the AOM released was critical in the success of modified-bubble DAF; AOM enhanced rather than hindered the process.

A pilot DAF plant was constructed, installed and commissioned for experiments treating waste stabilisation pond (WSP) effluent reported in Chapter 5.1. Initial tests of the plant demonstrated its operation as a conventional DAF plant was comparable to the performance of the full scale DAF plant already present onsite. Further tests with coagulant and cationic polymer were conducted to assess potential process optimisations that could be made to further improve the performance of conventional DAF. Using a charge demand analyser, it was found that the onsite operation could be safeguarded by using a minimum charge set point in coagulation of -46×10^{-3} meg L⁻¹, corresponding to a zeta potential of -15 mV. Furthermore, when using more acidic conditions during coagulation, a linear dose response curve for charge was determined, which could be applied for process automation. Chapter 5.2 presents experiments in which the pilot plant was operated to conduct modified-bubble DAF experiments. It was found that highly effective clarification could be achieved with performance comparable to optimised conventional DAF employing C-F. In contrast to jar testing, the hydrophobically modified polymer was found not to be as successful in clarification as the highly charged, conventional polymer. This was attributed to poor organic matter removal during flotation, resulting in the complexation of polymer and organic matter in the saturator feed water. Some improvements were observed with increasing the hydrophobic polymer charge; however, highly charged polyDADMAC was found to be most suitable for modified-bubble DAF without influent water pretreatment.

The body of work in this thesis has demonstrated modified-bubble DAF as a feasible process for the clarification of waste stabilisation pond effluent subject to algae blooms. The use of hydrophobically modified polymer was demonstrated to enhance the polymer-bubble attachment; however, it was the interaction between AOM in influent waters and the polymer that was found to be critically important in process success. While the hydrophobically functionalised polymer was found not to be effective in modified-bubble DAF at pilot scale, bench scale tests suggest that appropriate conditions can result in highly effective clarification while minimising polymer

residual. Therefore further development of specifically designed polymers has potential to increase process robustness and decrease polymer residuals. In comparison with conventional DAF, modified-bubble DAF has two major advantages: a smaller footprint since coagulation-flocculation is not required and reduced chemical consumption resulting in up to 41% cost savings while meeting turbidity targets. Overall, this thesis demonstrates modified-bubble DAF to be an effective alternative to conventional DAF and represents a step change in DAF technology.

2 BUBBLE-PARTICLE INTERACTIONS AND THE INFLUENCE OF CHEMICALS IN FLOTATION: A REVIEW

2.1 Introduction

Flotation is a solid-liquid separation process whereby microbubbles are introduced into a particle suspension where they then interact with the particles and float them to the liquid surface. The typical applications of flotation include selective mineral ore flotation (Kitchener 1984, Nguyen and Evans 2004) and water clarification (Kiuru 2001, Rubio et al. 2002). As the process can be used to selectively float particles from solution, flotation is also applied in applications such as ink removal from recycled paper (Borchardt 1994, Costa and Rubio 2005) and the separation of plastics (Drelich et al. 1999). The methods of introducing bubbles into water can depend on the application. For example, mechanical bubble generation is typically applied in froth flotation (Tao 2004) whereas in dissolved air flotation (DAF) air super-saturated water is subjected to a drop in pressure, resulting in the formation of microbubbles (Kiuru 2001). The methods of bubble generation are generally varied to accommodate the type of particles that are present; for example, high shear conditions would break flocculated particles, therefore, for the flotation of flocs, DAF is more appropriate. The interaction of bubbles and particles is highly dependent on particle pretreatment which is often employed to increase the effectiveness of the process.

The application of chemicals to facilitate effective bubble-particle attachment, via the modification of particle surfaces, is typical pretreatment for successful particle separation. In selective particle flotation, specific chemical-particle interactions are targeted to facilitate particles specific adherence to bubbles. In the clarification of water, particles are coagulated and flocculated so that particle numbers and surface charge are reduced while the relative size of particle aggregates and hydrophobic sites
are both increased (Edzwald 1995), allowing particle collection by bubbles to be non-specific and effective.

The purpose of this review is to investigate the interaction mechanisms that take place in flotation and the use of chemicals to aid these interactions. Specifically, bubbleparticle interactions and the influence of flotation reagents on interactions will be examined for process improvements which can be applied to DAF. With the most significant quantity of theory and research originating from mineral ore flotation and water clarification, the majority of reference will be from these two fields; however, some advancements in colloid theory will also be reviewed.

2.2 Physical Properties and Interactions of Particles and Bubbles in Water

2.2.1 The Electrical Double Layer

The surfaces of all particles have a charge in solution, attracting oppositely charged ions and repelling like charges. This is described in the electrical double layer (EDL) theory, in which surface charge results in an electrical double layer (Figure 2-1). The magnitude of the double layer can be quantified by measuring zeta potential which can be used to determine particle stability in water (O'Brien and White 1978).



Figure 2-1. The depiction of a surface in an ion-containing solution (adapted from Metcalf & Eddy. et al., 2003)

Manipulation of the EDL can depress or elevate electrostatic interactions between surfaces. In the case of water clarification, the EDL is suppressed by applying oppositely charged chemical reagents (Edzwald 1993b). This results in the dominance of other interparticle forces such as van der Waals forces, allowing particles to coagulate (Section 2.2.3). The same principles can be applied to the interaction of bubbles. The adherence of bubble to particle surface may be hydrophobically driven due to the hydrophobic nature of the air-water interface (see Section 2.2.4).

As the EDL depends on the ions in the solution, the pH can greatly affect the magnitude and even polarity of the EDL. As an example, hematite (Carlson and Kawatra 2013), natural organic matter (NOM) (Sharp *et al.* 2006a) and algae (Henderson *et al.* 2008b), can switch between being positively charged to negatively charged in water simply by altering pH to low values or high values respectively. When applying this principle in a chemical system used to float these particles, the attachment of a surface modifying chemical can be specifically optimised. For example, in the pH range 7-8, above 80% haematite recovery can be achieved; however, outside of this pH range, recovery is severely hindered, dropping to recovery rates of <10% at pH 4 and <40% at pH 9 (Kulkarni and Somasundaran 1980, Uwadiale 1992). The principle behind this is that adsorption of a cationic chemical can be increased by rendering a surface anionic, and vice versa (Fuerstenau and Pradip 2005). In the context of flotation, the adsorption of these chemicals is essential for particle flotation.

2.2.2 Bubble Properties in Water

There have been a range of studies into the mechanics and surface properties of bubbles. On the approach to a bubble surface, three zones have been described: 1) a bulk solution zone whereby hydrodynamic forces dominate; 2) a "diffusiophoretic" zone in which particle diffusion and electrostatic interaction becomes significant in determining bubble collisions and 3) the wetting perimeter (Figure 2-2) (Derjaguin and Dukhin 1993). In the wetting perimeter, electrostatic, van der Waals and structural forces are exerted by a bubble on a foreign particle. Successful particle attachment and flotation for dense particles (such as in mineral flotation) occurs when a particle overcomes these forces and ruptures the bubble surface (Yoon 2000).



Figure 2-2. Zones surrounding a bubble, influencing bubble interactions with other objects in water (adapted from Derjaguin and Dukhin, 1993)

In multiple studies, it has been shown that bubbles carry a negative charge at pH values above 4 in both distilled water (Han and Dockko 1999, Okada *et al.* 1990) and in sodium chloride solutions of ionic strength of 0.01 M (Kubota and Jameson 1993, Li and Somasundaran 1991, Oliveira and Rubio 2011, Yang *et al.* 2001). A plot summarising bubble zeta potential results from multiple studies is presented in Figure 2-3. The origin of bubble surface charge has been speculated to be due to either preferential adsorption of OH⁻ or desorption H⁺ ions yielding negative charges, resulting in pH sensitivity (Yang *et al.* 2001). As such, the background electrolytes and the gas used in bubble formation can influence the measured charge (Uddin *et al.* 2013). This was demonstrated by Han *et al.* (2006b) using magnesium and aluminium compounds, resulting in bubbles with positive zeta potentials under acidic conditions.



Figure 2-3. Plot of zeta potential results of bubbles in distilled water (Han and Dockko 1999, Okada et al. 1990) and water containing 0.01 M NaCl (Li and Somasundaran 1991, Yang et al. 2001, Oliveira and Rubio 2011, Kubota and Jameson 1993)

In addition to ionic conditions in solution, bubble size can influence bubble surface charge. Larger bubbles have been found to be less negative due to larger distortions of the electrical double layer (Usui et al. 1981). Furthermore in much larger bubbles, 1 mm and above, bubble shapes become altered changing the topography and therefore charge distribution on the bubble surface (Edzwald 1995, Wesselingh and Bollen 1999). Bubble size can vary significantly with the method of generation. Rodrigues and Rubio (2003) compiled an example list of bubble size ranges with associated bubble generation and measurement methods, which has been expanded upon in Table 2-1. DAF or electrolysis generally produce smaller bubbles than mechanical methods at 13 - 96 µm (Han 2002) compared to 300 - 3600 µm (Rodrigues and Rubio 2003), respectively. To produce smaller bubbles using mechanical methods, surfactants can be introduced to a solution and vigorously agitated, producing colloidal gas aphrons (CGAs) with a size range of 32.4 - 66.5 µm (Jauregi et al. 2000). As per modeling, smaller bubbles have the potential to improve DAF performance (Haarhoff and Edzwald 2004). The presence of nanobubbles (sub-micron in size) in DAF has been observed (Liu *et al.* 2013); however, their low rise rates may inhibit flotation ability upon attachment to particles.

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Bubble generation method	Bubble size	Measurement method	References
Induced air flotation (IAF) / mechanical agitation	1500 - 3600 μm	Image analysis	(Chen <i>et al.</i> 2002)
Dissolved air flotation (DAF)	13 - 96 µm	Particle counter	(Han 2002)
Electrolysis	30 - 50 μm		(Sarkar <i>et al.</i> 2010)
Nucleation at a hydrophobic surface	40 - 220 nm†	Atomic force microscopy (AFM)	(Simonsen <i>et al.</i> 2004)
Residual from dissolved air	182 - 249 nm ‡	Dynamic light scattering (DLS)	(Liu <i>et al.</i> 2013)
Colloidal gas aphrons / mechanical agitation	32.4 - 66.5 μm	Image analysis	(Jauregi <i>et al.</i> 2000)
Porous plate	75 - 655 μm	Image analysis	(Rodrigues and Rubio 2003)
DAF	29 - 77 μm‡	Image analysis	(Rodrigues and Rubio 2003)
IAF	350 - 1750 μm‡	Image analysis	(Rodrigues and Rubio 2003)
Synthetic filter cloth	300 - 2000 μm	Optical sensor	(Rodrigues and Rubio 2003)
Perforated plate	3700 - 4100 μm‡	Optical sensor	(Rodrigues and Rubio 2003)
Venturi	420 - 900 μm‡	Drift flux analysis	(Rodrigues and Rubio 2003)
Static mixer	350 - 1100 μm‡	Drift flux analysis	(Rodrigues and Rubio 2003)

Table 2-1.Bubble sizes from a range of bubble generation methods

[†] Diameter on solid surface

[‡] Average values

The use of nanobubbles is a much more recent field of research with initial reports of their existence in 1994 (Parker *et al.* 1994), though their formation and properties have yet to be fully explained (Craig 2011). It has been found that the presence of nanobubbles can be beneficial to flotation. Nanobubbles which form at a hydrophobic particle surface can cause the rupture of the wetting perimeter of a conventional-sized bubble (Simonsen *et al.* 2004, Stöckelhuber *et al.* 2004). The benefits of this are apparent in coal flotation, with reported increased recovery in laboratory scale tests (Sobhy and Tao 2013, Tao *et al.* 2008). The zeta potentials of nanobubbles in water have been reported to be negative (Liu *et al.* 2013). However, the specific nanobubble-particle interaction mechanisms have yet to be thoroughly investigated, as research of bubble generation methods remains in early stages (Park *et al.* 2012, Sobhy and Tao 2013).

2.2.3 Bubble-Particle Interaction Models

The collision and attachment of bubbles and particles are the driving factors of flotation. With excessive forces on bubbles with attached particles, or particles themselves, detachment can occur decreasing flotation effectiveness (Tao 2004); however, this is of greater consideration with higher density particles in flotation, and thus is negligible in typical water treatment scenarios in which contaminants (such as algae) have densities similar to that of water, for example, the specific density of *Chlorella vulgaris* has been reported to be 1.07 (Henderson *et al.* 2008a). Accordingly, three events or processes can be used to express the efficiency of bubble-particle attachment and subsequent flotation: collision predominated by forces in bulk solution (E_c), bubble-particle attachment efficiency (E_a) and the efficiency of the bubble-particle stability (E_s , Eqn. 1, Table 2-2) (Dai *et al.* 1998). Of greatest consideration is the collision term (E_c) which is the dominant factor in flotation models. In this review, models developed for mineral ore flotation and DAF for water treatment are considered. All equations are summarised with parameters in Table 2-2.

Of the various models for E_c in mineral flotation, the generalised Sutherland equation (GSE) is recognised as the most accurate in fitting experimental data (Eqns. 2, 3, 4, Table 2-2) (Min *et al.* 2008). In the derivation of the GSE, only internal forces on the near part of trajectory were considered and is applied only when Stokes number is equal to or larger than the critical Stokes number value (1/12), in which particle motion is similar to that of its suspending fluid (Dai *et al.* 1998). The approach and collision of a bubble and a particle is therefore governed mostly by the physical parameters of bubbles, particles and the suspending fluid, in which streamlines can dictate collision (Dai *et al.* 2000). In initial modelling of mineral flotation using the GSE, attachment and detachment efficiencies (E_a and E_s , respectively) were largely dismissed. Despite being a comprehensive model for particle with a density much greater than that of water, Nguyen and Nguyen (2009) found that for the flotation of non-ultrafine particles (>10µm), the GSE model differed significantly from computational data, due to effects of particle density.

Table 2	2-2. Co	ommon e	quat	ions used	in mi	neral floi	tatio	on and	DAF				
References	(Dai <i>et al.</i> 1998)	(Dai <i>et al.</i> 2000) (Kitchener and Gochin 1981)	(Min <i>et al.</i> 2008)		(Chau 2009) (Tao 2004)		(Haarhoff and	Edzwald 2004) (Edzwald 2010)		(Edzwald 1995)			
Parameters	Bubble collision efficiency (E) , collision predominated by forces in bulk solution (E_c) , attachment efficiency (E_a) , bubble-particle stability term (E_s)	Generalised Sutherland equation (E_{csE}), Sutherland equation (E_{csU}), particle diameter (d_{o}), bubble diameter (d_{o}).	intersection angel or the angle of tangency (θ_i) , contact angle measured at the	solid/gas/liquid interface (θ), bubble velocity (U_b), difference in bubble and particle density ($\Delta \rho$), dynamic viscosity of the fluid (μ)	Maximum floatable particle diameter (d_p $_{max}$), the gas liquid interfacial tension ($\gamma_{g/l}$),	energy dissipation rate in the turbulent field of a flotation (ϵ), liquid density ($ ho$)	Ratio between floc or particle number	concentration in the treated water and influent $(N_{p,out} \mid N_{p,in}),$ the bubble-particle	attachment efficiency (α_{pb}) , the collision efficiency (η_{7}) , the bubble volume concentration (ϕ_{p}) , the rise velocity of bubble–particle aggregates $(v_{f(p)})$, residence	Brownian diffusion (η_D) , flow interception	(η_l) , differential settling (η_{S}) , inertia (η_{M}) , Boltzmann's constant (k) , absolute temperature (T)	-	
Field of Application	General flotation equation	Mineral flotation, bubble-particle attachment force	generalised Sutherland	equation (GSE)	Detachment terms		DAF contact zone	efficiency: the <i>white water</i> model		Collision terms	in DAF modelling		
Equation Number	(1)	(2)	(3)	(4)	(2)	(9)		(2)	(8)	(6)	(10)	(11)	(12)
Equation	$E = E_c \times E_a \times E_s$	$E_{GSE} = E_{c-Su} \cdot sin^2 \theta_t \cdot exp\left(3K_3 \left[cos\theta_t \left\{ln \frac{3}{E_{c-Su}} - 1.8\right\} - \frac{2+cos^3\theta_t + 3cos\theta_t}{E_{c-Su} \cdot sin^2\theta_t}\right]\right),$	$E_{c-Su} = \frac{3u_p}{d_b},$	$K_3 = \frac{2U_b \cdot \Delta \rho \cdot d_p^2}{9\mu \cdot d_b^2}$	$E_s = 1 - exp\left\{1 - \left(rac{d_{p\ max}}{d_p} ight)^2 ight\},$	$d_{p \ max} = 1.53 igg(rac{\gamma_{g/l}^{6/5}(1-cos heta)}{\Delta ho \cdot arepsilon^{4/5} \cdot ho_{l}^{1/5}} igg)$		$igg(1-rac{N_{p,out}}{N_{niir}}igg)=1-expigg(rac{-3}{2}rac{lpha_{pb}\cdot\eta_T\cdot \Phi_b\cdot v_{f(t)}\cdot t}{d_h}igg)$	$\eta_T = \eta_D + \eta_I + \eta_S + \eta_{IN}$	$\eta_D = 0.9 \left(rac{k \cdot T}{\mu} \cdot d_p \cdot d_b \cdot U_b ight).$	$\eta_I = \frac{3}{2} \left(\frac{d_p}{d_b} \right)^2,$	$\eta_S = \frac{\Delta p \cdot g \cdot d_p^2}{18\mu \cdot U_b},$	$\eta_{IN} = \frac{g \cdot d_b \cdot d_p^2}{324^2}$

At the particle surface, van der Waals interaction energy, electrostatic forces from the EDL and hydrophobic forces predominate. In experimental determination and verification of the GSE, solutions and particles were selected such that $E_a \cdot E_s$ could be assumed to be unity but, in practice, this is not the case. Expressions for forces occurring at the particle surface are functions of bubble and particle radius, bubbleparticle separation, bubble and particle zeta potential and various constants (Nguyen and Attachment efficiency (E_a) has predominantly been derived from Evans 2004). experimental data as an empirical constant and been used to describe the difference between E and E_c (Dai *et al.* 2000); however, modelling of specific systems has been achieved for flotation of a quartz particles (Hewitt et al. 1994). In DAF research, Han (2002) investigated the effect of bubble and particle size and zeta potentials, as well as particle density and solution ionic strength, demonstrating the importance of bubble and particle electrostatic nature. However, beyond these systems with precisely controlled particle systems, the modelling of the attachment efficiency for general systems has yet to be achieved.

Predominant in mineral separation flotation, deinking and other selective flotation processes, is the use of surfactants to modify particle surfaces. The surfactants attach to the surface of particles and induce hydrophobicity (Chau 2009). The resultant attractive force increases the attachment efficiency and aggregate stability. By measuring contact angle, the effect of particle surface modification in terms of the bubble-particle stability (E_s) can be quantified (Eqns. 5, 6, Table 2-2). This model is valid for cases where the difference of maximum and minimum contact angles are smaller than the minimum contact angle (insignificant contact angle hysteresis) (Chau 2009).

From observation of the contact zone in DAF where microbubbles are formed, the GSE method is not applicable, as the effect of internal force is substantial (Dai *et al.* 1998). In water clarification, it has been observed that the dominant mechanism for bubble-particle attachment is that of collision as opposed to bubble entrapment or nucleation inside a floc (Kitchener and Gochin 1981). As flocs are formed and aggregated with bubbles, the use of a contact angle measurement does not appear in the DAF *white water* bubble blanket model performance equation (Eqn. 7, Table 2-2) (Haarhoff and Edzwald 2004). Instead, the bubble-particle agglomerate stability appears as an empirical factor, termed the attachment efficiency (α_{pb}) (Haarhoff and Edzwald 2004). This variable depends on upstream treatment and is typically 0.35 to 0.55 for good

coagulation conditions (Edzwald 2010). The term for collision efficiency (η_T) can be further segregated into terms of Brownian diffusion (η_D , Eqn. 9), flow interception (η_L , Eqn. 10), differential settling (η_S , Eqn. 11), and inertia (η_{IN} , Eqn. 12), all of which were combined in the GSE for froth flotation. By expanding the values for η_T , single bubble collection efficiency curves can be generated. Assuming a bubble diameter of 40 µm (average bubble size in DAF) and particle densities of 1.01 g cm⁻³, Edzwald (1995) demonstrated that particle diameters less than or greater than 1 µm have greater collision efficiencies due to dominance of diffusion (η_D) or interception (η_I), respectively and thus recommended a particle size of 10 – 30 µm.

A decrease in bubble size leads to an increase in the flotation efficiency for both the GSE and *white water* models. Absent from the flotation of particles or flocs in water treatment are the hydrophobic particle modifiers that are employed in selective flotation. As a result of this, the contact angle measurement cannot be used as a parameter to determine the stability of bubble-particle aggregates. Although attachment efficiency can be measured (Beaussart *et al.* 2009), it is not a function of variables that can be optimised. Similarly, in water clarification, the attachment efficiency term is dependent on the electrostatic nature of bubbles and particles and therefore the flocculation ability of the particles and response to chemical treatment (Han 2002).

2.2.4 Attraction and Repulsion Forces in Flotation

The attachment of a particle to a bubble is reliant on forces in what has been considered to be the diffusiophoretic zone (Derjaguin and Dukhin 1993), whereby numerous physicochemical factors can affect the success of bubble-particle collision. The interaction forces that occur between bubbles and particles in flotation have roots in the DLVO theory, named after its developers Derjaguin, Landau, Verwey and Overbeek (Liang *et al.* 2007). This theory considers the interactions of particles as a result of van der Waal forces and electrostatic interactions from the EDL.

In measurement practice, numerous non-DLVO forces have been observed (Table 2-3). Some examples of non-DLVO forces include repulsive hydration forces (Liang *et al.* 2007) and long-range attractive hydrophobic forces (Hammer *et al.* 2010). In addition to this, forces can originate from interactions with polymeric material, in which steric

interaction forces or bridging forces can result in repulsive and attractive forces, respectively (Cappella and Dietler 1999). Steric repulsion forces take place in particle suspensions with polymer covered surfaces (Liang *et al.* 2007). The interaction between the polymers saturating particle surfaces in a suspension yields a repulsive osmotic pressure (Liang *et al.* 2007). If the polymer concentration is sufficiently low and polymer size is sufficiently large, an attractive force can result due to single polymer chains spanning two or more particles in a mechanism known as bridging. The action of polymers in a particle suspension will depend not only on the nature of the polymer but also the conditions of the solution. Steric hindrance between particles with adsorbed polymer layers occurs when the liquid phase is a good solvent for the polymer, and elevated concentrations on particle surfaces result in polymer-polymer interactions (Kleshchanok and Lang 2007).

Table 2-3. Typical forces that exist in the diffusiophoretic zone and examples of interaction distances

inter action	aistances			
Force	Repulsive / Attractive	Distance (nm)	Notes	References
Electrical	Repulsive	≤150	Typical length in pure water	(Hammer <i>et al.</i> 2010)
van der Waals	Attractive	32.6 - 44	Distance before a "jump" to contact of a silica particle to a bubble surface	(Ducker <i>et al.</i> 1994)
van der Waals	Attractive	<2.5	Existent at long ranges, dominant at very short range	(Liang <i>et al.</i> 2007)
Hydration	Repulsive	<1.2	Measured between (sodium dodecylsulfate) SDS layers	(Faraudo and Bresme 2005)
Hydrophobic	Attractive	1 - 15	Three separate forces were identified at a range of distances	(Hammer <i>et al.</i> 2010)
Steric	Repulsive	20 - 180†	For poly(acrylic acid), M _w =750kDa, R _g =56nm	(Cappella and Dietler 1999)
Bridging	Attractive	400 - 1300 [†]	For anionic dextran and extracellular polysaccharides	(Cappella and Dietler 1999)

† Distances in different systems are dependent on polymer and solution

Upon the approach of a bubble and a particle, the longer range forces are overcome, hydrophobic forces become predominant. When considering the interaction between bubbles and hydrophobic or flocculated particles, it was observed that rupturing of the bubble surfaces facilitated particle adherence (Ralston *et al.* 1999). In flocs, charge

neutralisation gives way to the dominance of hydrophobic regions through hydrophobic-hydrophobic interactions (Ducker *et al.* 1994). It is possible for flocs not only to encapsulate bubbles, but also to act as sites for nucleation in supersaturated water in DAF (Oliveira and Rubio 2012). However, due to the availability of long-range hydrophobic forces, contactless flotation can occur, facilitating successful bubble-particle attachment without the need for particle penetration of the wetting perimeter (Derjaguin *et al.* 1984). Recently, Jiang *et al.* (2010) was able to demonstrate this, by observing the collection of Al_2O_3 with nitrogen bubbles.

2.3 Chemicals in Flotation

2.3.1 Basic Chemical Structures

A range of chemicals are used in flotation to modify surfaces and solution properties, promote stable floats and regulate the pH of the process (Bulatovic 2007). These chemicals can be segregated into basic categories based on their molecular configuration. In the selective flotation of particles, surfaces are rendered hydrophobic by the use of collectors for attachment to bubbles (Leja 1982). The foam or froth of the flotation process is maintained by the use of frothing chemicals. To control chemistry in collector interactions, flotation modifiers are used. Finally, flocculants and dispersants are used for viscosity modification and to promote constructive and destructive particle-particle interactions, respectively. For water treatment, electrostatic interactions are taken advantage of whereby metal coagulants are used to neutralise surface charge to promote particle-particle interactions (Edzwald and Haarhoff 2012). Metal coagulants complex with dissolved organic matter (DOM) or directly adsorb DOM onto hydroxide surfaces, resulting in particles (Duan and Gregory 2003). To facilitate removal, the use of coagulants and flocculants are optimised to create floatable agglomerates. Figure 2-4 depicts a pictorial representation of chemicals used in flotation. With similar chemical configurations, the roles of many flotation reagents are multifunctional.



Figure 2-4. Pictorial representation of chemical reagents applied in flotation

2.3.2 Collectors

The role of collectors is to react with a particle surface such that it more readily interacts with bubbles in flotation. Collectors can adsorb onto particle surfaces via a number of interactions including covalent bonding, electrostatic interactions, hydrogen bonding, hydrophobic and van der Waals forces (Moudgil *et al.* 1988). Though these chemicals are typically surfactants, numerous chemicals can be used to facilitate these interactions, with more specific interactions resulting in specific surface functionalisation and in turn, specific flotation.

The use of xanthate (Efrima and Pradhan 2003, Sawant *et al.* 2001), dithiophosphate (Grano *et al.* 1997) and other sulfhydryl based collectors have the ability to chemically bond specifically to metals and metal ions facilitating selective modification of ores (Crozier 1991). Selectivity can be improved by the use of a combination of these chemicals, demonstrated on pyrite and copper pyrite flotation by Ignatkina *et al.* (2010). The specific interaction of these chemicals to particle surfaces ensure selectivity; however, charged collectors, such as xanthates, can result in non-selective flotation (Herrera Urbina 2003).

2.3.3 Coagulants

In the application of removing contaminants from water non-selective interactions are targeted. For example, in the treatment of surface water, bulk anionic charge of particles, colloids and DOC is neutralised with cationic chemicals during coagulation and flocculation (C-F) (Henderson *et al.* 2008d, Jefferson *et al.* 2004). In DAF, bubbles are applied directly to the flocculated particles (Crossley and Valade 2006), without the application of additional chemicals to increase hydrophobicity of the particles and thereby their association to bubbles. There has been research into applying surfactants to activate flocs for the remediation of algae laden water (Phoochinda *et al.* 2013). Aside from surfactants, other hydrophobically-associating chemicals have been investigated for their use in water treatment. In the treatment of oily water the use of a hydrophobic flocculant and flotation has been shown to be beneficial, however the focus of the research was in interactions of the polymer with contaminants rather than direct interactions with bubble surfaces (Bratskaya *et al.* 2006).

2.3.4 Modifiers

The use of modifying reagents can facilitate specific interactions between particles and collectors. These chemicals are often used for altering the pH or the manipulation of the EDL, such as with coagulants. However, the use of various ions can facilitate the specific interactions of collectors at particle surfaces. For example, in the flotation of ink particles from recycled paper pulps, calcium (Ca^{2+}) is used to form fatty acid soaps which then interact with the ink particles, allowing them to adhere to bubbles via hydrophobic interactions (Rutland and Pugh 1997). In more complex systems, copper sulphate can be used for sphalerite modification facilitating more specific interactions with the present zinc ions and xanthates (Finkelstein and Allison 1976, Fuerstenau 1982). In both cases the use of specific ions directs collector interactions by conditioning particles.

In using trivalent metal salts as modifiers, coagulation mechanisms can be beneficial for the removal of dissolved species. In semiconductor waste, these metal coagulants act as modifying reagents such that dissolved ionic species are precipitated for interaction with surfactants preceding flotation (Tsai *et al.* 2007). A similar system has been applied to algae removal from water, using a cationic flocculant to provide sites in which anionic surfactant can attach to, in froth flotation (dispersed air flotation) (Phoochinda *et al.* 2004). However, in conventional surface water treatment (via DAF), surfactants are not typically used in flocculation-flotation (Edzwald 2007b), nor do they feature on the recommended chemicals list for drinking water treatment in the Australian Drinking Water Guidelines (NHMRC 2011).

In terms of metal oxide minerals, the alteration of pH can significantly change the surface chemistry, creating metal complexes (de Bruyn 1984). At low pH values, mineral solubility increases, making collection impossible (Fuerstenau and Urbina 1988). This control of soluble metal species has been advantageous in water treatment. The presence of hydrolysing metal salts can be used to coagulate negatively charged particles in water (Duan and Gregory 2003). The presence of insoluble metal hydroxides can also aid flocculation by increasing particle numbers (Montgomery 2005). Flocs that are produced can then interact with bubbles for their removal from water. This may occur through contactless hydrophobic interaction (Rubio *et al.* 2002), or physical entrapment of bubbles in flocs (Da Rosa and Rubio 2005), though as microbubbles carry a negative charge (Dockko and Han 2004), electrostatic interactions may occur with positively charged sites.

2.3.5 Flocculants and Organic Polymers

The attachment of polymers to a particle surface in water can result in a large number of adsorption conformations and configurations. The theory for this has been discussed at length by Netz and Andelman (2003). The addition of polymer in a solution can provide attractive forces via patch charge neutralisation or bridging, whereby electrostatic forces or physical tethering attract particles together, illustrated in Figure 2-5 (Bolto 1995, Bolto and Gregory 2007). However, at sufficient concentration, the presence of polymers on surfaces can result in repulsion due to increased steric interactions resulting in particle stabilisation (Liang *et al.* 2007).



Figure 2-5. Depiction of inter-particle forces resulting from polymer interaction: Steric hindrance (left) polymer bridging (middle) and patch charge neutralisation (right).

The use of cationic polymers for water clarification is typically in combination with coagulants to aid in flocculation, though it is possible to use highly charged cationic polymers on their own to coagulate particles in water (Bolto 1995, Bolto and Gregory 2007). Where DAF is applied to clarify these waters, influent particles are typically low in density (Edzwald 2010). In contrast, mineral ores have a much greater density and therefore flocculation would depress flotation. Taking advantage of the selectivity of flocculation, flotation of various mineral ores can be depressed, such that unwanted materials selectively collect in the froth. The pre-conditioning of particles to exclude them from flocculation has been found to be a critical step in this process (Ding and Laskowski 2007, Mathur *et al.* 2000). Specifically, anionic, non-ionic and cationic polymers have been reported for flotation of coal (Ding and Laskowski 2007), iron ores (El-Midany and Ahmed 2008), quartz (Forbes 2011) and copper ores (Attia and Yu 1991).

2.3.6 Frothers

Frothers are often used in froth flotation to stabilise triple phase interfaces, allowing the formation of a stable layer from which particles can be collected. In stabilising bubble froths, or bubble foams, particles can be subsequently removed from the top of a flotation cell. Frothers are a group of chemicals used to establish desirable hydrodynamics, stabilise and dewater the froth in froth flotation (Cappluccitti and Finch 2008, Farrokhpay 2011). An ideal frother will act solely to fulfil this function; however, in general non-sulphide flotation, the collectors are sufficiently surface-active

to carry out the function of frothers as well (Klimpel and Hansen 1988). The primary mechanism of frothers is to reduce the surface tension at the gas/liquid interface to form fine bubbles (Farrokhpay 2011). In addition to this, frothing agents can also adsorb at the mineral liquid interface (Pearse 2005) leading to non-specific bubble-particle attachment and thus non-specific flotation. The maintenance of the froth is critical to achieve sufficient ore grades, though it is dependent on particle size, density and hydrophobicity (Ata *et al.* 2004). In water and waste water flotation, bubbles are entrapped in the float layer, providing float stability, eliminating the necessity for frothing agents.

2.4 Bubble Surface Modification with Chemical Reagents

A recent trend in flotation research has seen the use of chemicals to modify bubble surfaces rather than particle surfaces. Bubbles that have a cationic charge can be used to improve bubble-particle interactions and has the potential to increase the robustness of DAF (Edzwald 2010, Haarhoff and Edzwald 2004, Han and Dockko 1999, Henderson *et al.* 2009b). Using a modified bubble has the potential to alleviate the process dependency on particle pretreatment, which is crucial for the success of conventional DAF (Edzwald 2010). In particular, the alteration of bubble charge has been demonstrated on several occasions, conducted by the adsorption of various reagents including; metal salts, (Dockko and Han 2004, Han *et al.* 2006b, Li and Somasundaran 1991), surfactants (Cho *et al.* 2015, Féris and Rubio 1999, Henderson *et al.* 2008e), and polymers (Henderson *et al.* 2010b, Malley 1995, Oliveira and Rubio 2011, Oliveira and Rubio 2012). The maximum zeta potentials found for various modified bubbles can be found in Table 2-4.

Chemical Used	pH Range for Cationic Bubbles	Concentration for Maximum Zeta Potential	Maximum Zeta Potential (mV)	References
AlCl ₃	3 - 8.2	10 ⁻² M in 0.01 M NaCl	+30	(Dockko and Han 2004) (Han <i>et al.</i> 2006b)
MgCl ₂	9.2 - 10.6	10 ⁻² M in 0.01 M NaCl	+25	(Li and Somasundaran 1991)
MgCl ₂	9 - 10.2	10 ⁻³ M in 0.01 M NaCl	+10	(Dockko and Han 2004) (Han <i>et al.</i> 2006b)
C10TAB [†] cationic surfactant	-	>8 × 10 ⁻² M in 0.01 M KBr	+26	(Cho <i>et al.</i> 2005)
C ₁₂ TAB [†] cationic surfactant	-	>3 × 10 ⁻² M in 0.01 M KBr	+28	(Cho <i>et al.</i> 2005)
C ₁₄ TAB [†] cationic surfactant	-	>2 × 10 ⁻³ M in 0.01 M KBr	+28	(Cho <i>et al.</i> 2005)
C ₁₆ TAB [†] cationic surfactant	-	>2 × 10 ⁻⁴ M in 0.01 M KBr	+28	(Cho <i>et al.</i> 2005)
Calgon® Catfloc LS cationic polymer	7.0*	14 mg L ⁻¹ in Milli-Q	+10	(Malley 1995)
Cytec® C448 cationic polymer	2-8	10 ⁻³ M in 0.01 M NaCl	+40	(Oliveira and Rubio 2011)

Table 2-4. A summary of bubble charge measurements made on bubbles modified with various metal salts, surfactants and cationic polymers – "-" indicates data not shown

 $+ \overline{C_n}$ indicates the length of the surfactant hydrocarbon chain and TAB, trimethylammonium bromide + Investigation of samples was only conducted at pH 7

In the presence of metal ions, bubbles can be modified by the preferable adsorption of the cationic ions (Han *et al.* 2006b). This is known to be specific to some ions over others. For example, sodium ions (Li and Somasundaran 1991) or potassium ions (Han *et al.* 2006b) were found not to adsorb on bubble surfaces. Han *et al.* (2006a) found that using positively charge bubbles, generated by electrocoagulation with aluminium electrodes, enhanced removal of negatively charged kaolin particles without the use of C-F could be achieved, with a maximum removal efficiency of 12%. In a different approach, Henderson *et al.* (2009b) added aluminium sulphate to the saturator, such that bubbles were formed in the presence of the reagent. When applied to a *Microcystis aeruginosa* laden solution, up to 60% cell removal was obtained without C-F pretreatment. However, microflocculation was observed during flotation, indicating that the significant desorption of coagulant from the bubble surface occurs (Henderson *et al.* 2009b).

Using surfactants has the benefit of adding hydrophobic components (via the hydrophobic tail), such that a physical interaction occurs with a bubble's gas phase. By applying surfactants for modifying bubbles in DAF, (Henderson *et al.* 2008e) found that up to 65% cell removal could be obtained. Upon testing a range of algae and cyanobacteria strains, it was found that the use of surfactants as bubble modifiers could result in robust cell removals, with performance comparable to maximum removals predicted by the *white water* model for the associated cell size (Eqn. 7, Table 2-2) (Henderson *et al.* 2008e).

In much higher concentrations of surfactants, it is possible to generate stable microfoams consisting of bubbles with multiple layers of surfactant (Sebba 1971). Compared to research on surfactant modified bubbles in DAF, the concentration of surfactants used is approximately 240 times greater, at 350 mg L⁻¹ (comparing experiments from Henderson et al. (2008e) to those of Roy et al. (1992). These bubbles are commonly known as colloidal gas aphrons (CGAs) and are accepted to consist of surfactant stabilized bubbles surrounded by a layer of water or aqueous solution, encapsulated by a surfactant vesicle (Hashim et al. 2012). Despite their name, CGAs are not colloidal in nature with sizes up to 100 µm (Jauregi and Varley 1999). In terms of contaminant removal, the use of CGAs has been shown to be useful in the collection of dyes (Roy et al. 1992), proteins (Jauregi et al. 1997, Jauregi and Varley 1999, Noble et al. 1998) and microorganisms (Jackson et al. 1998). This can be attributed not only to charge interactions that can occur with surfactant hydrophilic groups, but also with the hydrophobic regions, provided by surfactant solutions (Save and Pangarkar 1994). The success of CGAs to recover specific materials from a solution is extensive (Hashim et al. 2012). The use of CGAs in clarification has been demonstrated, with promise to reduce the requirement for pretreatment (Subramaniam et al. 1990); however, vast quantities of chemicals are required which would result in large masses of sludge, specifically in water treatment.

The application of polymers in modifying bubble surfaces in DAF has by far demonstrated the greatest contaminant removal, with performance comparable to conventional DAF using low doses of chemical (Henderson *et al.* 2010b). The specific systems in which polymer modified-bubble DAF performed well was in treating turbidity and colour contaminated water (Malley 1995), and *M. aeruginosa* laden water (Henderson *et al.* 2009a, Henderson *et al.* 2010b). In work by Henderson *et al.* (2010b),

several polymers were trialed; however, it was only low molecular weight polyDADAMAC that resulted in consistently high cell removals, tested from pH 7 to 9. Additionally, three other species of algae were tested, including *Chlorella vulgaris*, *Asterionella formosa*, and *Melosira* sp. For all species, cell removal was greater than that predicted by the *white water* model, except for *A. formosa* in which poorer than expected removal was obtained. From these results, it was determined that in samples with poorer cell removal, the associated organic matter preferentially interacted with polymers, removing them from bubble surfaces (Henderson *et al.* 2010b). To improve the process, Henderson *et al.* (2010b) suggested that the presence of hydrophobic functionalisation in the polymer backbone could anchor the polymer to the bubble surface and potentially increase robustness to varying algae conditions.

The application of DAF to treat water and flotation for mineral recovery are similar in that both rely on the pretreatment of particles such that bubble attachment can occur during flotation. A fundamental discrepancy in the chemical systems used in water treatment is the lack of hydrophobic reagents that are common to mineral flotation. It has been identified that C-F ahead of DAF facilitates strengthened interactions between bubbles and existing hydrophobic sites on contaminants (Edzwald 2010). However, the use of hydrophobically associating chemicals in DAF has been limited to the use of surfactant at laboratory scale for modifying bubble surface properties (Henderson *et al.* 2008e). To further this research the development of specifically designed hydrophobically associating reagents is essential.

Up to now, the understanding of the factors and mechanisms that result in successful modified-bubble DAF is limited, with tests confined to well-defined laboratory conditions. Furthermore, the performance of modified-bubble DAF on environmentally relevant samples is unknown and represents a critical gap in the knowledge for advancing the technology. Fundamental process differences exist between laboratory-scale and full-scale operations, such as contact zone hydrodynamics and recycle water quality. Testing the process in continuous operation is thus critical to determine its practical feasibility.

2.5 Summary

In this review, an overview of the forces and mechanisms in flotation has been provided. From this review the following gaps in research have been found:

- 1) The use of nanobubbles for practical flotation has yet to be comprehensively investigated
- 2) Modelling of the attachment efficiency in flotation outside of laboratory conditions has yet to be established
- 3) Though non-DLVO forces have been identified, dominant forces between bubbles and particles at close range have yet to be fully investigated, particularly for floc-bubble interactions and when rupturing of the bubble surface does not occur
- The design application of hydrophobically functionalised reagents for specific bubble adherence has yet to be investigated
- 5) Though process success was demonstrated in modified-bubble DAF on synthetic influent water prepared with various algal species, testing on environmentally relevant samples has yet to be conducted

3 PARTIALLY QUATERNISED, HYDROPHOBICALLY-ASSOCIATING POLYMERS

3.1 Introduction

In dissolved air flotation (DAF) used in water treatment applications, coagulation and flocculation (C-F) of influent particles, colloids and dissolved organic matter (DOM) is critical for the effective collection and flotation of influent contaminants (Edzwald 1995). As the bulk charge in influent water is anionic, C-F employs cationic chemicals to reduce electrostatic repulsion by neutralising the negative charge of DOM through complexation and adsorption mechanisms, as discussed in Chapter 2. Cationic chemicals such as hydrolysing metal coagulants (Duan and Gregory 2003) and cationic polymers (Bolto and Gregory 2007) or a combination of both are commonly used to facilitate C-F. The interaction of bubbles and flocs is reliant on appropriate floc charge, such that any electrostatic repulsion forces are reduced sufficiently to allow bubble attachment to hydrophobic sites within flocs (Edzwald 2010).

The use of chemical reagents in DAF to specifically interact with bubbles is not conventionally employed in water treatment (Chapter 2). Hydrophobically-associating cationic polymers are known to have interpolymer interactions (Bolto 1995), but also have the potential to adsorb strongly onto bubble surfaces. The application of hydrophobically-functionalised chitosan has been shown to be of benefit in the flocculation of oily contaminants in water ahead of DAF (Zhao *et al.* 2002). However, the use of hydrophobic polymers to adhere to microbubble surfaces for water treatment has not currently been investigated.

The generation of microbubbles in the presence of polymer rich solutions is known to result in polymer adsorbed to bubbles (Oliveira and Rubio 2011). When applied in

DAF, the use of the common water treatment polymer, cationic poly (N,Ndiallyldimethyl-ammonium chloride) (polyDADMAC) of molecular weight 100-200 kDa, has been shown to result in bubbles that can be used to effectively remove algae and cyanobacteria (Henderson et al. 2010b) and turbidity and colour (Malley 1995) without the requirement for prior C-F. Aside from these specific conditions, modifiedbubble DAF has been shown not to be as effective, potentially attributed to poor microbubble-polymer attachment. It was therefore apparent that the incorporation of hydrophobic character to anchor a cationic polymer to a bubble surface was worthy of further investigation (Henderson et al. 2010b). However, the chemical modification of polyDADMAC to incorporate additional hydrophobic moieties is not easily achieved as the quaternary amine groups must be prepared under harsh conditions ahead of further reaction (Bazito et al. 2005). Instead, a similar cationic polymer, poly[2-(N,Ndimethylamino)ethyl methacrylate] (polyDMAEMA), that has tertiary side-chain amines which can be easily manipulated to increase the number of hydrophobic groups (Bütün *et al.* 2001), has been investigated in this chatper for its potential to act as a backbone for the development of hydrophobically-associating polymers to be used as bubble modifiers in DAF.

Poly[2-(N,N-dimethylamino)ethyl methacrylate] (polyDMAEMA) has an extended range of applications including stabilisers in emulsion based processes (Jaeger *et al.* 2010, Ni *et al.* 2006), cationic carriers for non-viral gene delivery (Sevimli *et al.* 2012, van de Wetering *et al.* 1999, van de Wetering *et al.* 2000, van de Wetering *et al.* 1998), nano-scale applications (Xu *et al.* 2008) and flocculant aids in water treatment (Bolto 1995). As a homopolymer, with a pKa value of approximately 7.5 (for a 100 kDa polymer), polyDMAEMA can be protonated to varying degrees by changing the pH (van de Wetering *et al.* 1998); at pH 7.5, polyDMAEMA is cationic with approximately 50% protonation of amine groups (van de Wetering *et al.* 1999). With quaternisation of the tertiary amine side-groups in combination with pH changes, polyDMAEMA cationic concentration can be adjusted.

The use of haloalkanes, such as 1-bromodecane, to quaternise tertiary amine groups on a polymer can result in graft, brush-like amphiphilic random copolymers which have the ability to hydrophobically associate (Laschewsky 1995). This modification can lead to a range of intermolecular interactions resulting in advanced architectures (Jaeger *et al.* 2010, Laschewsky 2003) and elevated solution viscosity (Taylor and Nasr-El-Din 1998). Hydrophobic pendant groups can also alter exhibited multi-responsive behaviour. For example, high concentrations of permanent charge associated to the polymer backbone can lower the limiting surface tension (Ni *et al.* 2006, Vamvakaki *et al.* 2001). A consequence of this is the production of internal electrostatic repulsive forces which can have effects on the unimer conformation in solution (Xu *et al.* 2008).

Aside from self-association, the hydrophobic regions can also interact with hydrophobic surfaces. This ability has been used to modify a range of inorganic surfaces (Yap et al. 2012, Zhang et al. 2013). In solution, the use of both charged and hydrophobic groups have been demonstrated to be advantageous in flocculating emulsified oil in water (Bratskaya et al. 2006, Zhao et al. 2002). Bratskaya et al. (2006) used chitosan modified with dodecane side chains, demonstrating superior flocculation performance compared to unmodified chitosan and cationic polyacrylamide. In the context of DAF, microbubbles can be greatly influenced by the presence of aggregated hydrophobic regions and the presence of cationic components: microbubble nucleation may be influenced by the catalytic effect of hydrophobic zones (Lubetkin 2003) and bubble size may be influenced by the presence of surfactants (Féris and Rubio 1999). Furthermore, the surfaces of microbubbles are negatively charged (Dockko and Han 2004) and can experience electrostatic attraction to cationic charged surfaces or polymers. The use of amphiphilic, cationic polymers to attach to microbubble surfaces in DAF and result in charge inversion might result in cationic microbubbles that can then readily adhere to negatively charged water contaminants such as algae. The aim of this work was to synthesise a 'library' of graft-amphiphilic polymers with a range of solution properties. This was achieved using polyDMAEMA as a starting scaffold, and through functionalisation via quaternisation with a collection of alkyl halides. Overall, 39 polymers with a range of properties were systematically generated. The solution properties of the synthesised iterations of the fully characterised quaternised polyDMAEMA were subsequently investigated.

3.2 Materials and Methods

3.2.1 Chemicals

2-(N,N-dimethylamino)ethyl methacrylate (DMAEMA, Aldrich, 98%) was passed through a basic alumina column to remove inhibitor prior to use. 2,2'-

Azobisisobutyronitrile (AIBN, Wako Chemicals, 98%) was re-crystallised twice from methanol. Iodomethane (Aldrich, 99%), 1-bromopentane (Aldrich, 98%), 1-bromodecane (Aldrich, 98%) and 1-bromopentadecane (Aldrich, 97%) was used as received.

3.2.2 Free Radical Polymerisation of DMAEMA

DMAEMA was polymerised using simple bulk free radical polymerisation. The molecular weight of the polymer was broadly manipulated by the monomer to initiator ratio used in the reaction. An example of a polymerisation is as follows: 10 g (6.36 \times 10^{-2} mol) of purified DMAEMA was added to a 25 ml reaction vial, followed by 32.8 mg (2 \times 10⁻⁴ mol) of AIBN. The reaction vial was then purged with nitrogen at 0°C for 30 minutes to remove any dissolved oxygen. The mixture was then placed in an oil bath at 65°C for 12 hours and left to react. Three samples of increasing molecular weight were synthesised using 3.28 mg (2×10^{-5} mol) 1.64 mg (1×10^{-5} mol) and 1.64 mg 0.82 mg (1 \times 10⁻⁵ mol) of AIBN per gram of DMAEMA for low, medium and high molecular weight polymers respectively, and will herewith be referred to as L-0, M-0 and H-0 respectively. The polymer molecular weight was assessed by gel permeation chromatography with a N,N-dimethylacetamide mobile phase (DMAc GPC). The sample was then dissolved in ethanol and dialysed against water in a 25 kDa MWCO membrane to remove any unreacted monomer. After freeze drying, the polymer was assessed for purity via NMR analysis. Typical analysis via ¹H NMR at 300 MHz in deuterated chloroform (CDCl₃) are as follows (all x-axis shifts (δ) are quoted in ppm): 4.08 (triplet signal, 2 hydrogen atoms, from a CH₂ group), 2.58 (t, 2H; CH₂), 2.31 (singlet signal, 6H; CH₃), 1.86 (s, 2H, CH₂), 0.98 (s, 3H, CH₃).

3.2.3 Quaternisation of the Tertiary Amine

Quaternisation of the homopolymer was carried out with iodomethane and a selection of 1-bromo alkanes at room temperature. As an example, 300 mg of purified polymer was first dissolved in 3 mL of methanol, followed by adding 211 mg of 1-bromodecane to the reaction mixture. The solution was stirred vigorously for 36 hours, before being dried by vacuum oven at 40°C. The molar ratio of the alkyl halide was selected to be 10%, 50% and 75%. The homopolymer was dissolved in methanol prior to the addition of alkyl halide. The reaction mixture was allowed to react for 48 hours before drying in a vacuum oven for 24 hours. Purity and degree of quaternisation were assessed with ¹H

NMR spectroscopy and excess alkyl halide was removed via dialysis against methanol in a 25 kDa MWCO membrane if required. Typical analysis via ¹H NMR (300 MHz, CDCl₃, δ in ppm) is as follows: 4.51 (t, 2H; CH₂), 4.08 (t, 2H; CH₂), 3.67 (t, 2H; CH₂), 3.51 (s, 6H; CH₃), 2.58 (t, 2H; CH₂), 2.31 (s, 6H; CH₃), 2.06 (multiplet, 2H, CH₂), 1.86 (s, 2H, CH₂), 1.31 (m, 16H, CH₂), 0.98 (s, 3H, CH₃), 0.89 (m, 3H, CH₃).



Figure 3-1 Schematic of the reaction of DMAEMA homo polymer and modification to 1alkylhalide

3.2.4 Polymer Characterisation

3.2.4.1 Gel Permeation Chromatography

GPC analysis of the polymers was performed in DMAc [DMAc; 0.03% w/v LiBr, 0.05% 2, 6-dibutyl-4-methylphenol (BHT)] at 50°C (flow rate $\frac{1}{4}$ 1 mL min⁻¹) using a Shimadzu modular system comprised of an SIL-10AD auto-injector, a PL 5.0-mm bead-size guard column (50 × 7.8 mm) followed by four linear PL (Styragel) columns (10⁵, 10⁴, 10³, and 500 Å) and an RID-10A differential refractive-index detector. Calibration was achieved with commercial polystyrene standards ranging from 500 to 10⁶ g/mol.

3.2.4.2 ATR-FTIR

Samples were analysed via fourier transform infrared spectroscopy (FTIR) using a Bruker IFS66/S High End FT-NIR/IR Spectrometer system equipped with a tungsten halogen lamp, a KBr beam splitter, and a DTGS detector (Bruker, Germany). Infrared

spectra were obtained between 4000 and 400 cm⁻¹ by 32 scans and with a scanning resolution of 4 cm⁻¹, using attenuated total reflectance (ATR) as the sampling technique.

3.2.4.3 Nuclear Magnetic Resonance

¹H NMR spectra were recorded using a Bruker ACF300 (300 MHz) (Bruker, Germany) spectrometer employing CDCl₃ as solvent. Quaternisation conversions were determined via the signal areas of the ethyl and methyl protons, adjacent to the amine group.

3.2.4.4 Surface Tension

A NIMA Surface Tensiometer equipped with a Du Nuoy ring was used to assess the surface tension (γ). Polymer samples were dissolved in buffer solution consisting of 1.8 mM NaCl and 0.5 mM NaHCO₃, adjusted to pH 7 as monitored by a Hanna Instruments pH210 Microprocessor pH Meter (Hanna Instruments, Nusfalau, Romania), at a concentration of 1 mg mL⁻¹. Samples were allowed to dissolve for 24 hours at room temperature (approximately 25°C) before assessing γ at 25°C ± 0.1°C. To determine the comparative hydrophobic nature of the cationic polymers, the surface activity was measured by assessing the surface tension using a tensiometer equipped with a Du Nuoy ring. Physical measurements of the surface tension, such as with a tensiometer and Du Nuoy ring, can result in inaccuracies due to the extended times it takes for the polymer solutions to come to equilibrium (Riess 2003). For this reason, samples were left at 25°C on a plate stirrer for exactly 24 hours before measurement.

3.2.4.5 Charge Density Analysis

Following the procedure used by Schwarz *et al.* (2007), the charge density was assessed using a particle charge detector (PCD-04 Travel; Mütek BTG, Eclépens, Switzerland). Measurements were conducted on 1 mg of polymer in 10 mL of pH 7 buffer. The PCD-04 measures the charge density of a sample by titrating it with oppositely charged polyelectrolyte standard. To determine the charge polarity, streaming current detection is employed in which counter ions are segregated from their respective colloids via a reciprocating piston, resulting in a measurable current (Dentel *et al.* 1989). Solutions of low molecular weight poly(N, N-diallyl-N,N-dimethylammonium chloride)(polyDADMAC) and sodium polyethylene sulphonate (PES-Na) were used as titrants for anionic and cationic systems, respectively, at a concentration of 0.001 N. Charge density was calculated using the following formula:

Charge Density =
$$\frac{C_t V_t}{M}$$

In which C_t is the titrant concentration (0.001 N), V_t is the volume of titrant used (L) and *M* is the mass of the polymer in solution (g).

3.2.4.6 Dynamic Light Scattering

Dynamic light scattering (DLS) studies to determine hydrodynamic diameter were performed using a Malvern Zetasizer Nano ZS Instrument (Malvern, UK) equipped with a 4 mV He-Ne laser operating at $\lambda = 633$ nm, an avalanche photodiode detector with high quantum efficiency and an ALV/LSE-5003 multiple tau digital correlator electronics system. Size measurements were performed in Disposable Solvent Resistant Micro Cuvettes ZEN0040 (Malvern Instruments) recorded in nanometers (nm). The dispersant parameters used for the analyses were RI: 1.330, Abs: 0.01 and diluent (water) viscosity: 0.88 cP. The polymer sample solutions were prepared with 1.8 M NaCl and 0.5 NaHCO₃ buffer, adjusted to pH 7, at a concentration of 0.1% w/v. All samples were measured by scanning 5 times with using automatic measurement settings. Assays were done in triplicate.

3.2.4.7 Transmission Electron Microscopy Imaging

Samples for Transmission Electron Microscopy (TEM) imaging were prepared with a micellisation procedure as described in (Zhang and Eisenberg 1996). Briefly, dry polymer sample was dissolved in DMF to a concentration of 6 mg ml⁻¹. 200 μ L aliquots were put into separate vials and made up to 2 mL using Milli-Q water. Water was added drop wise at a rate of 1 drop every 10 seconds under vigorous stirring. Samples were then dialysed against water for 5 days and allowed to stand at room temperature for 7 days to ensure stability before allowing a 5 μ L aliquot of sample to dry on a TEM grid.

3.2.5 Micellisation procedure

A solvent switch micellisation procedure was conducted to induce tertiary structure formation. 0.6 mg of polymer sample was dissolved in 200 μ L of DMF. Water was

then added to the sample at a rate of 1 drop every 10 seconds until a final volume of 2 mL was obtained. The resulting solution was then dialysed against water using a 25 kDa MWCO membrane for 2 days before collection and further analysis.

3.3 Results

3.3.1 Synthesis and quaternisation of polyDMAEMA

Three base homopolymers, L-0, M-0 and H-0, were synthesised yielding weight average molecular weights (MW) of 81 kDa, 161 kDa and 404 kDa, respectively. This was done to generate polymers that were in the range of previously used polyDADMAC in work reported in Henderson *et al.* (2010b), in which low MW polyDADMAC had a weight average MW of 100-200 kDa. Having used "classical" free radical polymerisation, broad polydispersity indices (*PDI*) resulted, ranging from 2.01 to 4.83, as determined by DMAc GPC. DMAEMA homopolymer characteristics are outlined in Table 3-1 and GPC traces shown in Figure 3-2.

Table 3-1.Molecular weights of synthesised homopolymers after free radicalpolymerisation - nomenclature indicates high (H) medium (M) and low (L) molecular weights

Sample Name	M_w (g mol ⁻¹)	M_n (g mol ⁻¹)	PDI
L-0	80880	40280	2.01
M-0	160500	59520	2.70
H-0	403700	83660	4.83



Figure 3-2. GPC trace of the low, medium and high molecular weight DMAEMA homopolymers

Homopolymer samples were quaternised with alkyl halides to result in polymer samples with 3 concentrations of each alkyl halide used. Naming of the polymers was based on the backbone chain length (L, M or H), the alkyl halide carbon chain length used (1, 2, 3 or 4 for C1, C5, C10 or C15, respectively) and the concentration of alkyl halide used in the reaction (1, 2 or 3 for stoichiometric concentrations 10%, 50% and 75%, respectively). Successful quaternisation reactions of the amino groups were initially confirmed via ATR-FTIR. For example, peaks in the range of 2922-2852 cm⁻¹ identified the additional C–H stretching from $-CH_2-$ and $-CH_3-$ groups confirming alkyl side-chain additions (Figure 3-3). The conversion of the amino group to the quaternary amine was assessed by ¹H NMR, with shifts of the ethyl and methyl hydrogens adjacent to the nitrogen group. Using H32 as an example (from Table 3-2), the ¹H NMR in Figure 3-4 shows that peaks 'a' (4.08 ppm), 'b' (2.58 ppm) and 'c' (2.31 ppm) were observed to shift to 'f' (4.51 ppm), 'g' (3.67 ppm) and 'h' (3.51 ppm). The reaction of quaternised groups along the polymer chain.



Figure 3-3. FT-IR results of DMAEMA homopolymer (A) before and (B) after quaternisation with 1-bromodecane

The reaction conversions for all polymers can be found in Table 2.2. From these results, it can be seen that obtaining high degrees of functionalisation was difficult as alkyl chain lengths increased. With increasing alkyl chain length, self-association would be expected to increase as the quaternisation and association of alkyl chains result in a surfactant like structure, or more specifically, "head-type" polysurfactant (Laschewsky 1995).



Figure 3-4. ¹H NMR spectra of purified polyDMAEMA (A) before and (B) after quaternisation with 1-bromodecane - arrows indicate shifts in DMAEMA peaks to quaternised residuals

3.3.2 Polymer properties in water

Polymers functionalised via quaternisation with alkylhalides will result in hydrophobic carbon chains attached to cationic quaternary amines. A total library of 39 polymers was produced; however, samples that were quaternised with 1-bromopentadecane with stoichiometric concentrations 50 and 75% (namely H42, H43, M42, M43, L42 and L43) resulted in highly swollen gels and were thus unable to be analysed further. Surface tension and charge demand data are detailed in Table 3-2.

Polymer	Quaternisation	Charge Contribution	Charge	Surface Tension at
Name	(mol 0/)	(mag gr1)	(mog g:1)	1 IIIg IIII - (mN m:1)
		(med g -)	(med g -)	
H-0	0%	0	1.21	44.0
H11	10%	0.59	1.32	44.4
H12	35%	1.7	3.01	56.8
H13	43%	1.98	3.23	57.4
H21	7%	0.4	1.66	48.5
H22	37%	1.74	3.16	59.8
H23	75%	2.84	3.56	58.8
H31	7%	0.43	1.62	49.7
H32	37%	1.54	2.49	61.6
H33	49%	1.85	2.76	69.0
H41	8%	0.45	1.38	41.1
M-0	0%	0	1.54	46.2
M11	8%	0.48	1.79	52.2
M12	42%	1.94	3.44	66.2
M13	66%	2.63	3.49	65.3
M21	2%	0.14	1.91	44.1
M22	19%	1.02	2.54	58.3
M23	56%	2.31	2.94	58.6
M31	10%	0.56	1.74	47.9
M32	29%	1.32	2.52	59.5
M33	34%	1.46	2.45	56.8
M41	9%	0.49	1.83	50.9
L-0	0%	0	1.26	43.2
L11	10%	0.59	1.58	51.0
L12	46%	2.07	3.37	60.6
L13	69%	2.7	3.9	68.4
L21	5%	0.3	1.2	45.6
L22	21%	1.11	2.41	54.3
L23	30%	1.48	2.87	58.7
L31	9%	0.5	1.94	49.8
L32	35%	1.49	2.7	65.5
L33	40%	1.64	2,88	69.5
L41	11%	0.57	1 78	48.4

Table 3-2. Polymer quaternisation, calculated charge density, measured charge density and surface tension in buffered water at 1 mg ml⁻¹ - Nomenclature indicates the molecular weight of the unfunctionalised homopolymer used in the reaction (H = high, M = medium, L = low molecular weight)

The charge density results revealed that all polymers were cationic at pH 7, with greater degrees of quaternisation resulting in greater charge densities (Table 3-2). Measured charge densities were observed to be greater than charge densities calculated theoretically from quaternisation. This is because while charge density can be calculated from the ¹H NMR conversions (Appendix 1), actual charge density is also dependent on protonation of unreacted DMAEMA units. The quaternised polymers with the minimum and maximum charge densities were found to be polymers L21 (1.20 meq g⁻¹) and L13 (3.90 meq g⁻¹), respectively. This was not reflected in the calculated

charge densities with the maximum and minimum being H23 (2.84 meq g⁻¹) and M21 (0.14 meq g⁻¹), respectively, indicating that self-association behaviour and backbone protonation could be influencing available charge. The total monomer units that were protonated can be calculated using the difference between the measured charge density and the theoretical charge contribution from quaternary amines. The average amount of protonated repeating units was found to be 19% (Figure 3-5). At pH 7, polyDMAEMA is known to be cationic as a result of protonation (van de Wetering *et al.* 1998), though these results suggest that, within the experimental error, the amount of protonation of the unmodified amines is not influenced by the degree of quaternisation.



Figure 3-5. The concentration of protonation of repeating units versus the quaternisation percentage for high molecular weight (\circ), medium molecular weight (\times) and low molecular weight (+) samples at pH 7

Plots of the variation of surface tension versus degree of quaternisation for different structural parameters (the scaffold molecular weight and alkane chain length) can be found in Figure 3-6. There was no clear dependence of the measured surface tension on the molecular weight of the polyDMAEMA backbone or the length of the hydrocarbon chain. Instead, it was found that polymer solutions had increasing surface tensions, and thus lower surface activity, as the degree of quaternisation was increased. With increased degree of quaternisation, an increase in the surface tension was observed, regardless of the side chain length, similar to observation has been made by Ni *et al.*

(2006) and Vamvakaki *et al.* (2001). As such, the homopolymers generally demonstrated the greatest surface activity with surface tensions at 43.2, 46.2 and 44.0 mN m⁻¹ for polymers L-0, M-0 and H-0, respectively, compared to the functionalised materials (Figure 3-6) or pure water (71.2 mN m⁻¹).



Figure 3-6. Surface tension versus mole per cent for (A) iodomethane, (B) 1-bromopentane and (C) 1-bromodecane functionalised polymers

The increase of charge density was correlated to the increase of surface tension (and decrease of surface activity) linearly, with an r-squared value of 0.76 (Figure 3-7). As

the CMC for polyDMAEMA was found to be approximately 1.7×10^{-3} mg mL⁻¹ (Appendix 3), the concentration used to generate the results in Figure 3-7 was three orders of magnitude larger than the CMC values of the polymers. Thus if any reduction in the surface tension were to occur it would be apparent at the concentrations used. In comparison, solutions of commonly used surfactants; Tween 20, sodium dodecyl sulphate (SDS) and cetyl trimethylammonium bromide (CTAB); were found to have depressed surface tensions, regardless of their absolute charge density. In surfactants, the influence of the salt groups and alky chain length on surface tension can be significant (Guo *et al.* 2006, Verdinelli *et al.* 2008); however, as observed in Figure 3-7, the influence of side chain properties is not as significant for polymers. Despite the surfactant-like structures of the polymers, an increase of surface tension was observed for increasing quaternisation degrees regardless of the length of the alkyl side chain.

Though polymers are not adsorbed at the bulk air-liquid interface, the hydrophobic regions can influence bubble association or formation in DAF. For example, it is known that hydrophobic zones can act as a catalyst for bubble nucleation (Lubetkin 2003), indicating that bubble surface association can occur by *in situ* bubble formation. The surface activity alone of the various polymers alone was not completely representative of the full range of hydrophobic activity of the polymers particularly those with larger alkyl side chains (C10 and C15). For this reason, self-association studies were required. To further investigate the effects of hydrophobic regions, the self-association of the polymers was conducted. The polymers selected for this work were, L33, L21, L22, L33, M12, M33, M21, H33, H41 and H12, yielded the highest, lowest and median surface tension results (and thus roughly the charge density results) for each subset (L, M and H), respectively.


Figure 3-7. The relationship of surface tension at 1 mg ml⁻¹ and charge density of the DMAEMA polymer library

3.3.3 Self-association

From TEM images, a range of morphologies were found to occur after polymer micellisation (Figure 3-8, TEMs for all nano-objects analysed can be found in Appendix 4). As revealed in Figure 3-8, the molecular structure of these graft amphiphilic polymers, i.e., molecular weight of back bone, degree of quaternisation and the chain length of the hydrophobic chain, have important influences on the morphology of the nano-objects assembled in solution. These nano-objects range from micelles, large compound-micelles, "star anise" like structures and crystal-like assemblies. Careful analysis of the images revealed that spherical micelles or compound micelles formed for polymers L21, L22, M12 and M21 (Figure 3-8). These polymers had low and medium molecular weight polyDMAEMA backbones, and were modified with alkyl chains of less than length C10 with quaternisation concentrations ranging from 2 to 42%. However, when either of these materials was modified with C10, higher order structures become evident in the TEM image: including "petals"/"leaves" and "star anise" like assembles on the micron scale, present with micelles (Figure 3-8, L33 and M33).



Increasing carbon chain length

Figure 3-8. An example of nano-object morphologies of assembled materials (polymer sample number in the top right corner for pictures - all TEMs are shown in Appendix 4)

The aggregates that formed in Figure 3-8 demonstrated a progression of self-association behaviour. This verified affirmative interpolymer interactions, influenced by the hydrophobic group associated to the polymers. In samples with high molecular weight backbones and in samples with side chains of C10 or C15, crystalline structures appeared. Chen *et al.* (2012) observed similarly complex micelle architectures, using crystalline-coil block co-polymers. The formation of the "star anise"-like structures was attributed to branched architectures (Chen *et al.* 2012, Chen *et al.* 2011), whereas in the polyDMAEMA-based amphiphilic polymers used in this study, the large polydispersity has led to a range of aggregate architecture and multi modal distributions (select DLS data shown in Appendix 5).

3.4 Discussion

3.4.1 Hydrophobic association

The polymers that have been synthesised in this work have demonstrated a range of hydrophobic activity as evident in self-association ability which was not demonstrated in the surface tension studies alone. It has been observed that associated side chains of C8 and above better facilitate hydrophobic domain formation (Yang and Engberts 1991), so it is unsurprising that a change in the geometric shapes of the aggregates can be observed between C5 and C10 functionalised polymers.

To obtain a sufficient response from the polymers in analysis, the concentration of the polymers was 0.3 or 1.0 mg mL⁻¹ for micellisation and surface tension studies respectively. For use in water treatment, it would be expected that the concentration of polymer would not exceed 0.01 mg mL⁻¹ (Bolto and Gregory 2007), or 0.001 mg mL⁻¹ for bubble modification (Henderson *et al.* 2010b), and the behaviour of the polymers would be heavily influenced by the immediate matrix, for example, with oppositely charged colloids (Bolto 1995). As such, the coulombic forces that the polymers experience internally and from polymer-polymer interactions are much more influential during self-association studies. However, interpolymer interactions are evident at concentrations as low as 0.0005 mg mL⁻¹ as observed by surface tension (Appendix 3). This indicates that hydrophobic forces exerted by unimers on particles, bubbles and other unimers in DAF can take effect at very low concentrations.

Crystalline structures were observed to form with polymers with larger, and thus more hydrophobic, side chains. In the context of surfactant-water systems, the formation of cubic phases is well documented, with bicontinuous layers forming in supra structures (Pevzner and Regev 2000, Tiddy 1980). This presents a rationale for the large geometric aggregates that form in the partially-quaternised polyDMAEMA samples, but more importantly it demonstrates a progression in the hydrophobic behaviour of the polymers. Though surface tension measurements did not indicate surfactant-like properties, the association to bubble surfaces in DAF may behave in a different manner. In comparison to the air-liquid interface in surface tension measurements, in DAF, the interfacial area is much greater and microbubbles can be generated in the presence of a polymer solution. The latter of these points could further influence bubble formation,

with the catalytic effects of hydrophobic zones, facilitating bubble formation (Lubetkin 2003).

3.4.2 Hydrophilic behaviour

The observation that surface tension increased with quaternisation was supported by recent reports of non-surfactant, "non-surface activity" observed in cationic- and anionic-amphiphilic diblock-copolymers. The effect of image charge repulsion at the air-liquid interface is attributed to this behaviour (Ghosh *et al.* 2011). Zhao *et al.* (2013) could reproduce this "non-surface activity" in a non-quaternised polyDMAEMA block system by simply lowering the pH and therefore introducing cationic charge to the polyDMAEMA block. In an similar system, Bütün *et al.* (2001) found that diblock copolymer consisting of DMAEMA and di(ethylaminoethyl) methacrylate (DEAMEA) had a diminished surface activity with an increase of cationic functionality, analogous to "non-surface activity": lower surface activity was observed at concentrations greater than the CMC after quaternising the DMAEMA block. In the results displayed in Figure 3-7, there was no clear dependence of the molecular weight of the base polyDMAEMA or the length of the hydrocarbon chain on the measured surface tension, indicating that the observed decrease in surface activity can be attributed to image charge repulsion at the air-water interface (Zhao *et al.* 2013).

With large alkyl side-chains, hydrophobic interaction and thus intra- and intermolecular forces can still dictate the behaviour of the polymers, as previously discussed and shown in Figure 3-8. The surface tensions for polymers with greater concentrations of quaternary amine groups demonstrated lower surface activity, indicating an overall greater affinity for the water phase and thus a shift in the hydrophile-lipophile balance (HLB). The HLB is a measure of the polar character of surfactants and though it does not directly apply to polymers the same principals can apply (Perrin *et al.* 1999). Cationic surfactants do not often feature in HLB literature, the associated HLB has been derived experimentally (Ho 1998). It is known that the influence of associated ionic groups have much greater influences over the HLB of a molecule compared to alkyl chains, particularly at the length used in this present work. In the case of quaternary amine, the HLB groups number was determined to be 22.0 (Ho 1998) compared to -0.475 for $-CH_2-$ or $-CH_3$ groups (Becher 1984, Guo *et al.* 2006). However, in the case of these polymers, hydrophobic activity can be demonstrated, regardless of the HLB and apparent hydrophilic nature by surface tension studies. With microbubbles, electrostatic attraction to the cationic polymers can take place when free in solution. However, as there is a dominance of hydrophobic regions, as evident by self-association, the formation of bubbles can be strongly influenced in DAF; aggregated hydrophobic regions provide ideal nucleation points for the formation of bubbles.

3.5 Summary

DMAEMA homopolymer was synthesised at three different molecular weights using free radical polymerisation. Via quaternisation of the tertiary amines, hydrophobic alkyl chains were associated to the polymers, simultaneously increasing the cation concentration of the polymers. Outcomes of this work are:

- 1) A range of polymers of differing charge and hydrobicity were successfully synthesised and characterised
- Polymers that were modified to contain random hydrophobic pendant groups displayed limited surface activity
- 3) With increasing modification of the polymer, the overall polymer charge and surface tension, and thus water affinity, increased regardless of the length of the pendant alkyl chain
- 4) Self-association of the polymers was apparent after micellisation of the quaternised polymers, with partially quaternised polymers with alkyl chains of C10 and C15 resulted in geometrically shaped aggregates, indicating a shift in the mode of self-association
- 5) The mechanisms of association to hydrophobic surfaces can vary depending on pendant hydrophobe size and concentration on the polymer
- 6) For microbubble coating, it is suggested that hydrophobic regions of the polymers provide zones for bubble nucleation, resulting in bubble formation on polymers as opposed to polymers adsorbing onto bubbles after formation.

4.1 HYDROPHOBICALLY-ASSOCIATING CATIONIC POLYMERS AS MICRO-BUBBLE SURFACE MODIFIERS IN DISSOLVED AIR FLOTATION

4.1.1 Introduction

Over the last 20 years, understanding of the underlying flotation mechanisms in DAF has improved, particularly with respect to the interaction of microbubbles and particles within the contact zone. For example, it is now accepted that both the majority of contaminants in natural waters and microbubbles generated in DAF carry a negative surface charge (Dockko and Han 2004, Han 2002). As such, repulsive forces exist between microbubbles and particles, minimising attachment and therefore flotation, unless particle surfaces have been appropriately modified, for example, by coagulation (Edzwald 2007a, Haarhoff and Edzwald 2001). Furthermore, from the development of DAF models, such as the white water model performance equation (Haarhoff and Edzwald 2004), it is now understood that process adjustments such as increasing particle size, bubble numbers, bubble velocity, bubble-particle attachment efficiency and decreasing bubble size can result in elevated particle separations. Without changing process parameters, Han (2002) demonstrated the effect of particle charge and size on the collision efficiency of bubbles; the attachment efficiency of bubbles and particles could effectively be increased by neutralising or reversing charge and increasing the size of the particles. Such advancement of knowledge has led to innovation in DAF optimisation studies whereby less conventional properties have been altered during operation, for example, bubble properties (Han et al. 2006b, Henderson et al. 2009b).

The modification of bubble surface properties, as opposed to those of particles, has received attention as an alternative to C-F via the minimisation of repulsive forces

between microbubbles and particles in the contact zone. Specifically, controlling the bubble surface charge in DAF has been investigated via two methods: 1) Altering the ion content or pH of water in which bubbles are introduced (Han et al. 2006b), or 2) by using a chemical additive dosed into the air saturated water stream (Henderson et al. 2009b, 2010b, Malley 1995, Oliveira and Rubio 2012, Van Le et al. 2012). The latter has shown promise in algae separation applications. For example, Henderson et al. (2008e), (2010b) tested a range of surfactants and water treatment polymers for their ability to modify bubble surfaces and thus treat algae-laden water by dosing the chemical into the recycle stream. For the use of surfactants (Henderson et al. 2008e), it was found that cell removal without C-F matched modelled data, assuming a maximum attachment efficiency of 1. However, overall cell removal remained relatively low due to size dependency, such that Microcystis aeruginosa of approximately 5.4 µm were removed by a maximum of 64%. This result was improved upon by using polyDADMAC where cell removals for M. aeruginosa reached 98 %, therefore exceeding that which would be anticipated by modelling (Henderson et al. 2010b). The success of chemically modified bubbles in DAF, however, was specific to low molecular weight polyDADMAC and the treatment of *M. aeruginosa* cells. High molecular weight polymers resulted in heavy flocs that were prone to settling and removal of other species of algae and cyanobacteria was poor, attributed to variable surface organic character. It was concluded that polymer interactions with organic matter resulted in polymer being readily stripped from bubbles in preference for more anionic surfaces (Henderson et al. 2008e, 2010b). Based on these tests, it was suggested that the addition of a hydrophobic component to a cationic polymer would facilitate greater adherence to bubbles and thus more robust flotation of contaminants (Henderson *et al.* 2010b). Though the integration of hydrophobic regions in polymers has been investigated for oily water treatment (Zhao et al. 2002), the development of water treatment polymers has generally targeted higher molecular weight, branched water soluble polymers with minimal hydrophobicity (Bolto and Gregory 2007). Hence, to the best of my knowledge, there have not been any polymers designed specifically for bubble modification in DAF.

For the first time, this chapter reports the investigation of the use of polymers that have been specifically designed for the alteration of bubble surface properties in DAF (Chapter 3) and the resultant separation effectiveness for an algae system. This process, without the use of C-F, will be hereafter referred to as modified-bubble DAF. Polymer modified bubbles were initially characterised via bubble charge measurements. An Australian strain of *M. aeruginosa* was used as a model contaminant for these tests due to its small size and interest to industry and to facilitate comparison with previous studies that have also used this model contaminant. The chapter focuses on the mechanisms of interaction between the bubbles, functionalised polymers and cells, to assess the ideal polymer functionalisation for the modification of bubble surfaces.

4.1.2 Materials and Methods

4.1.2.1 Hydrophobically Functionalised Polymers

Polymers used in this current chapter are the same polymers that were synthesised and characterised in Chapter 3. Briefly, homopolymers of 2-(N,N-dimethylamino)ethyl methacrylate (polyDMAEMA) (Aldrich) were first synthesised as a cationic backbone, controlling the polymer molecular weight by varying the concentration of free radical initiator AIBN in a classical free radical polymerisation. In total, three base polymers were synthesised at three molecular weights, yielding high, medium and low molecular weight polymers. The homopolymers were then functionalised by quaternising the tertiary amines with iodomethane, 1-bromopentane, 1-bromodecane or 1bromopentadecane at a range of concentrations, increasing the cationic charge and associated hydrophobic moieties. The synthesised polymers were named according to their molecular weight (L: Low; M: Medium and H: High), the hydrocarbon chain length of quaternising alkyl halide (1, 2, 3 and 4 for C1, C5, C10 and C15 respectively) and the concentration of alkylhalide used in quarterisation reaction (1, 2 and 3 for low, medium and high conversions). For example, a low molecular weight polymer with a high concentration of 1-bromopentane was designated L23.

Initially a library of 39 polymers were synthesised (discussed in Chapter 3). In this study, nine of these functionalised polymers that carry a range of surface activity and hydrophobic side chains were chosen based on surface tension and charge density measurements for use in bench test experiments. For example, high molecular weight functionalised homopolymers, H41, H12 and H33, were found to have a surface tension of 41.1 mN m⁻¹, 56.8 mN m⁻¹ and 69.0 mN m¹, representing low, median and high surface tensions, respectively. Those selected for investigation included: L21, L22,

L33, M12, M21, M33, H12, H33 and H41. A table of these selected polymers and properties as determined in Chapter 3 can be found in Table 4.1-1.

Table 4.1-1.Table of halo alkane modified polymers identified for use in modified-bubbleDAF and properties including polymer stoichiometric quaternisation percentages (asdetermined by NMR), charge density and surface tension

Sample Name	Stoichiometric Quaternisation	Charge Density (meq g ^{.1})	Surface Tension (mN m ⁻¹ at 1 mg L ⁻¹)
L21	5%	1.20	45.6
L22	21%	2.41	54.3
L33	40%	2.88	69.5
M12	42%	3.44	66.2
M21	2%	1.91	44.1
M33	34%	2.45	56.8
H12	35%	3.01	56.8
H33	49%	2.76	69.0
H41	8%	1.38	41.1

4.1.2.2 Commercially Available Chemicals

Cetyl trimethylammonium bromide (CTAB) (Sigma Aldrich, Australia) and low molecular weight (weigh average molecular weight = 100-200 kDa) poly(diallyldimethylammonium chloride) (polyDADMAC) (Sigma Aldrich, Australia) were used as standard commercially available chemicals to compare the performance of the synthesised polymers. In conventional coagulation-flocculation-DAF experiments, aluminium sulphate (Sigma Aldrich, Australia) was used.

4.1.2.3 Cyanobacteria

M. aeruginosa (CS-564/01) was obtained from the Commonwealth Scientific and Industrial Research Organisation (CSIRO) Australian National Algae Culture Collection (ANACC), Hobart, Australia, and recultured in MLA media (Bolch and Blackburn 1996). Cultures were subjected to a 16/8 hour light/dark cycle, with temperature controlled to 21°C, in a 500 L, PG50 incubator with a photosynthetic photon flux output of $600 \pm 60 \mu mol m^{-2} s^{-1}$ (Labec, Australia). Cultures were grown in 100 mL batches in 250 mL conical flasks. At the end of the exponential growth phase, as determined by cell counting via microscope and a haemocytometer, cells were harvested for bench testing. An example of a growth curve can be found in Appendix 6. Cells were characterised by measuring size with a Mastersizer 2000 (Malvern, UK), charge demand with a Mütek PCD-04 particle charge detector (BTG, Switzerland), zeta potential using a Zetasizer Nano NZ (Malvern, UK) and dissolved organic carbon (DOC) using a TOC–Vsch Analyser (Shimadzu, Australia). To prepare synthetic DAF influent water, cultured cells were diluted to 7.5×10^5 cells mL⁻¹ with Milli-Q water buffered with 0.5 mM NaHCO₃ and brought to an ionic strength of 1.8 mM using NaCl to ensure comparability with previous studies (Henderson *et al.* 2008e, 2009b, 2010b).

4.1.2.4 Conventional Flotation Bench Testing

A DAF Batch Tester, Model DBT6 (EC Engineering, Alberta, Canada), was used for modified-bubble DAF bench testing. The recycle flow consisted of Milli-Q water also containing 0.5 mM NaHCO₃ and made up to an ionic strength of 1.8 mM with NaCl and adjusted to pH 7 using 1 M HCl and 1 M NaOH prior to bench testing. Industrial grade air was used to pressurise the saturator to 450 kPa which was subsequently shaken until water was completely saturated. Jar tests were conducted in 1 L aliquots, with synthetic DAF influent water. Aluminium sulphate was added the jar with rapid mixing which was conducted for 180 seconds at 200rpm. Immediately following the addition of coagulant, the pH was adjusted to the desired value using 1 M HCl and 1 M NaOH solutions. A pH210 Microprocessor pH Meter (Hanna Instruments, USA) was used to monitor the pH during rapid mixing. The samples were then flocculated for 10 minutes at 30 rpm followed by flotation for 10 minutes with a recycle ratio of 10% to match that of modified-bubble flotation testing. Residual analysis included cyanobacteria cell concentration achieved by cell counting using a haemocytometer or Sedgwick Rafter counting chamber and Leica DM500 light microscope (Leica Microsystems Ltd, Switzerland), and zeta potential and hydrodynamic size analysis using a Zetasizer Nano ZS (Malvern, UK), using a 175° backscatter to measure Brownian motion via scattering intensity fluctuations; this instrument is capable of measuring materials of sizes as low as 0.3 nm (Malvern 2013). Each analysis was conducted in triplicate.

4.1.2.5 Bubble Charge Measurements

Bubble surface charge measurements were measured to determine whether the polymers were able to effectively modify the surface properties of the bubbles. Measurements were contracted to the School of Chemical Engineering at the University of Queensland, whereby a Micoelectrophoresis Apparatus Mk II (Rank Brothers Ltd., UK), consisting of a rectangular cell (10 mm \times 1 mm) and platinum electrodes was used in the measurement of microbubbles. The generation of microbubbles and measurement was similar to that described by Qu *et al.* (2009) whereby nitrogen or air was dissolved into Milli-Q water at 500 kPa by allowing to sit overnight, and measurements were made on surfactant solutions made up using the gas saturated water. The modifications used in this experiment included pressurisation of Milli-Q water to 450 kPa with nitrogen and solutions for measurement were made up to 1.8 mM of NaCl and 0.5 mM of NaHCO₃, corrected to pH 7 with 1.6 mg L⁻¹ of polymer prior to zeta potential measurements. This polymer concentration was based on saturator concentrations typical for bench testing. About 100 mL of the oversaturated solution was introduced to the glass cell of the microelectrophoretic unit. At room pressure, microbubbles formed and floated through the cell in which they were subject to an electrical field. The motion of the bubbles were then recorded with a CCD camera and their electrophoretic mobilities and zeta potentials were calculated using the Von Smoluchowski equation (Hunter 1981), for which 60 to 100 bubble measurements were taken per polymer tested.

4.1.2.6 Modified-Bubble DAF Jar Testing

Jar testing was conducted using the same equipment, described in Section 4.1.2.4. The synthetic DAF influent water used was corrected to pH 7 ahead of testing. Aliquots of buffered solution were dosed with various polymer concentrations up to 3 mg L^{-1} and added to the saturator before pressurisation. Low molecular weight polyDADMAC was used as a standard water treatment polymer to compare performance of the synthesised polymers as per Henderson *et al.* (2010b). Industrial grade air was used to pressurise the saturator to 450 kPa. A recycle ratio of 20% was selected for all tests to ensure a high bubble to particle ratio was maintained given that C-F of cells was not undertaken to lower particle number. Residual analysis was conducted as per Section 4.1.2.4.

Given that cell removal obtained with synthesised polymers and polyDADMAC did not vary significantly with polymer character, polymer performance was further evaluated by examination of the treated water charge. To do this, zeta potential measurements obtained using a Zetasizer Nano ZS (Malvern, UK) were used to qualitatively determine the presence of the polymer in solution. The assumption was made that the cationic polymers are likely to complex or adsorb onto oppositely charged colloids and particles and thus reduce the negative charge of these as measured by zeta potential measurements. However, given that the minimum size required for zeta potential detection using this instrument is 3.8 nm, in the event that free polymer remains in solution, the cationic charge will still be measurable as the size of the polymers in solution range from 12.2 – 1129.0 nm (Appendix 9).

4.1.3 **Results**

M. aeruginosa Characterisation 4.1.3.1

On microscopic evaluation at the end of the exponential growth phase, the M. aeruginosa cultures were found to be spherical and unicellular with an average diameter of $3.0 \pm 0.7 \,\mu\text{m}$ as measured using the Mastersizer 2000. The charge density and zeta potential of the cell system (cells and associated organic material) were determined to be $-1.51 \times 10^{-9} \pm 7 \times 10^{-11}$ meg cell⁻¹ (-31.7 ± 1.5 meg L⁻¹) and -31.6 ± 1.6 mV, respectively. Average cell concentration and DOC at this phase of growth was found to be $2.1 \times 10^7 \pm 2 \times 10^6$ cells mL⁻¹ and $8.04 \times 10^{-10} \pm 4.4 \times 10^{-11}$ mg cell⁻¹ (16.9 ± 0.9 mg L^{-1}), respectively (Table 4.1-1). Compared to the UK strain of *M. aeruginosa* (CCAP) 1450/3), used in previous modified bubble DAF research, Henderson et al. (2008d) found cell sizes were larger (5.4 μ m) and had a greater charge density per cell at 1.9 \times 10^{-9} meg cell⁻¹. However, with much smaller cells the Australian strain (CS-564/01) had a greater cell surface charge density, at -57 meg m^{-2} compared to -40 meg m^{-2} for CCAP 1450/3 (Henderson et al. 2008d), assuming all extracellular matter was attached or associated to cell surfaces. Similar to the surface charge density, the zeta potential obtained was greater in magnitude, found to be -20.2 mV for CCAP 1450/3 reported by (Henderson et al. 2008e). In summary, cells were found to be smaller with a greater cell charge compared to the UK strain.

<i>Table 4.1-2.</i>	M. aeruginosa cell	properties
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Attribute	CS-564/01	CCAP 1450/3		
Morphology	Spherical	Spherical		
Diameter (µm)	3.0 ± 0.7	5.4 †		
Cell Concentration (cells mL ⁻¹)	$2.1 \times 10^7 \pm 2 \times 10^6$	-		
DOC (mg cell ⁻¹)	$8.04 \times 10^{-10} \pm 4.4 \times 10^{-11}$	10 × 10 ⁻¹⁰ †		
Zeta Potential (mV)	-31.6 ± 1.6	-20 †		
Charge Density (meq cell-1)	$-1.51 \times 10^{-9} \pm 7 \times 10^{-11}$	-0.002× 10 ⁻⁹ †		
[†] Data obtained from Henderson <i>et al.</i> (2010a)				

Data obtained from Henderson *et al.* (2010a)

4.1.3.2 Cell Removal with Conventional DAF

Conventional DAF with C-F pre-treatment upstream of flotation resulted in high cell removal efficiencies (Figure 4.1-1) that were dependent on effective coagulation. For example, it was observed that a dose of 1 mg L⁻¹ as Al (or 12.4 mg L⁻¹ Al₂(SO₄)₃) was required to achieve cell removals greater than 95%, coinciding with charge neutralisation (Figure 4.1-1). At a dose of 5 mg L⁻¹, a maximum cell removal of 99% was obtained. For doses above 1 mg L⁻¹ at pH 7, sweep flocculation would be expected to occur (Amirtharajah and Mills 1982), explaining the lack of particle restabilisation despite charge reversal, as observed by zeta potential.



Figure 4.1-1. Conventional DAF with C-F ahead of flotation - dose is quoted as concentration of aluminium ions

Interestingly, during flocculation, aggregates formed large fibrous structures (Figure 4.1-2), as opposed to being more commonly observed uniformly-distributed roughly spherical agglomerates (Gregory 1997, Jun *et al.* 2009, Zhao *et al.* 2012). This indicates that extracellular organic matter may be aiding the conventional, spherical-particle flocculation for this particular strain of *M. aeruginosa*.



Figure 4.1-2. Observation of floc formed after coagulation of M. aeruginosa with alum at a dose of $l mg L^{-l}$ as Al.

4.1.3.3 Modified Bubble Character

Bubbles coated with hydrophobically modified polyDMAEMA were confirmed to be cationic at pH 7, with zeta potentials ranging from between +38.6 mV to +63.8 mV (Figure 4.1-3). These values were comparable with the charge of bubbles modified with polyDADMAC and CTAB of +44 \pm 9 mV and +44 \pm 7 mV, respectively. In comparison to other studies, the zeta potentials observed in the current study were consistently slightly higher; for example, Cho *et al.* (2005) used a range of cationic surfactants to modify nanobubbles, resulting in bubbles with a maximum zeta potential of +30 mV at pH 7. Similarly, Han *et al.* (2006b) generated bubbles with a zeta potential of +30 mV using aluminium hydroxide, although high standard deviations were observed.

Overall, bubble zeta potential did not vary to the same extent as polymer charge density. It was observed that the modification of bubbles with polymers quaternised with a high concentration of C10 groups resulted in bubbles with less positive zeta potentials for each of the molecular weight ranges (specifically, polymers L33, M33 and H33). Applying a two-tailed t-test taking a null hypothesis of $H_0 = 0$ (distribution means are significantly different) for L33as compared to L21 or L22, the P-value obtained was found to be less than 0.05 in both circumstances, suggesting that L33 had a significantly different mean. In contrast, the P-value for the comparison of L21 and L22 was found to be 0.16, demonstrating statistical similarity. Similar to L33 with respect to the other low molecular weight polymers, corresponding observations can be made for M33 and H33 in the medium and high molecular weight polymer groups respectively. The less positive zeta potentials for L33, M33 and H33 modified bubbles suggest that less charge

and thus polymer was adsorbed per bubble. An explanation for the less positive zeta potentials is that the highly hydrophobic polymers had a flatter conformation upon bubble adsorption, occupying a larger area on the bubble surface, thereby preventing further polymer adsorption.

On examining the average zeta potential for each of the molecular weight groups, it was revealed that lower molecular weight polymers resulted in more positive bubble zeta potentials. For example, using polymers with backbones of low, medium and high molecular weights yielded average bubble zeta potential results of $+60 \pm 13$ mV, $+47 \pm 10$ mV and $+42 \pm 12$ mV, respectively. A possible explanation for this decrease in charge with increased polymer molecular weight is that electrostatic polymer-polymer interactions limit the adsorbance of polymers on the surface of the bubbles. In contrast to this, Aoki and Adachi (2006) observed that electrophoretic mobility was constant regardless of the polymer molecular weight by observing polystyrene latex particles with adsorbed fully quaternised polyDMAEMA.



Figure 4.1-3. Average bubble zeta potentials for the selection of polymers, polyDADMAC and CTAB (×) and respective charge density of the polymer used in the test (\circ); zeta potential measurement were conducted on solutions made up to 1.8 mM of NaCl and 0.5 mM of NaHCO₃, corrected to pH 7 with 1.6 mg L⁻¹ of polymer

Similar to bubbles modified with synthesised polymers, those modified with CTAB and polyDADMAC resulted in positive bubbles with little variation in the magnitude of

their zeta potentials at pH 7. This is in agreement with literature for CTAB (Collins *et al.* 1978, Yoon and Yordan 1986); however, the study of the effect of various cationic polymers is limited. Oliveira and Rubio (2011) measured the zeta potential of cationic polyacrylamide modified bubbles, confirming that positively charged bubbles were obtained from pH 2 to pH 8; however, adsorption decreased above this range, most likely due to polymer hydrolysis (Bolto and Gregory 2007, Holmberg *et al.* 2003, Oliveira and Rubio 2011).

4.1.3.4 Cell Removal Using Modified-Bubble DAF

Results from jar tests that were conducted using the nine synthesised polymers to modify bubble surfaces demonstrated that cell removals in excess of 93% were achievable for each polymer tested when applying doses of 0.3 mg L⁻¹, without coagulation. With a maximum cell removal of 99%, modified-bubble DAF has the same cell removal effectiveness as conventional DAF, with C-F followed by flotation, demonstrated in Section 4.1.3.2. Figure 4.1-4A shows cell removal of modified-bubble flotation when applying L21, L22 and H33 as examples of low, medium and highly quaternised polymers. The resultant dose response curves for all polymers can be found in Appendix 8. Overall, the dose response curves increased to greater than 90% cell removal, with no decrease of cell removal observed even at the highest doses of polymer used in this test. All dose response curves were similar despite variations of polymer charge densities and associated hydrophobic groups as indicated in Table 4.1-1. Comparing the polymers in terms of their charge dose demonstrated similarity in the removal efficiencies for polyDADMAC and polyDMAEMA samples with medium and high concentrations of quaternised residuals, specifically L22, L33, M12, M33, H12 and H33 (Figure 4.1-4B). However, polymers with low concentrations of quaternised residuals (L21, M21 and H41) resulted in greater removal efficiencies at low charge concentrations. To exemplify this, the charge dose response curve for L21 is compared to the curves for L22, H33, polyDADMAC and CTAB in Figure 4.1-4 B. It can be seen that for a polymer dose of approximately 3×10^{-3} meg L⁻¹, cell removal achieved by modified-bubble DAF with L22 and H33 was $66 \pm 6\%$, whereas with L21 $97 \pm 4\%$ was achieved. This could be an artefact of polymer bridging in which elevated charge may not be necessary in establishing polymer-particle attachments. However, it is known

that low charge density polymers have different neutralisation effects in water: Kam and Gregory (2001) showed that polymers with a charge density of greater than 3 meq g^{-1} exhibited a stoichiometric neutralisation of anionic humic substances whereas this was not true for polymers of charge densities less than 3 meq g^{-1} , showing that less charge was required to neutralise the humic substances.



Figure 4.1-4. Dose response curves for 3 of the 9 polymers and CTAB in comparison to polyDADMAC and CTAB - graphs show cell removal versus dose as (A) polymer mass and (B) dose as charge - the results for all polymers can be found in Appendix 8

Similar to the modified-bubble tests undertaken with the hydrophobically functionalised polymer, jar tests conducted with polyDADMAC revealed that cell removal effectiveness was again high, with up to 99% removal achieved at doses above 1.0×10^{-3} meq L⁻¹. Using a UK strain of *M. aeruginosa* (CCAP 1450/3), Henderson *et al.* (2009b) found that 95% removal could be achieved at a dose of 2.4×10^{-3} meq L⁻¹,

indicating the required polymer dose was strain dependent. To demonstrate this the dose was normalised to charge dose per cell charge; in this work the optimal dose was found to be 0.9 meq polyDADMAC per meq *M. aeruginosa* whereas Henderson *et al.* (2009b) reported the optimal dose to be 1.7 meq polyDADMAC per meq *M. aeruginosa* for CCAP 1450/3. A major difference between these strains was the cell size, where CS-564/01 was nearly half the diameter of CCAP 1450/3 (3.0 μ m versus 5.4 μ m, respectively). Considering this, the relative dose per cell surface area is 67% less than for CCAP 1450/3. From previous analysis (Section 4.1.3.1), the charge density per m² is 42% greater for CS-564/01. This elevated charge density may be responsible for more effective interactions with polymer, however other factors in the system must be considered. The presence of bubbles in the system is an additional surface for polymer adsorption, influencing polymer demand; however, the difference in the algogenic organic matter (AOM) between the strains may also have an impact on the process as suggested by Henderson *et al.* (2010b).

The highest cell removal obtained using CTAB as the bubble modifier was found to be much lower than those obtained for polymers at $33 \pm 7\%$ using a dose of 1.18×10^{-3} meq L⁻¹ (Figure 4.1-4). This was found to be much less than results obtained by (Henderson *et al.* 2008e) who obtained 64 % removal using 2.2×10^{-3} meq L⁻¹. However, both the results obtained in the current study and those obtained by (Henderson *et al.* 2008e) are comparable with modeled results obtained using the *white water* model performance equation (Haarhoff and Edzwald 2004) (Appendix 7). For example, assuming an attachment efficiency of 1, it was determined that the modeled cell removal was 30% for a particle size of 3.0 µm, and 64% for a particle size of 5.4 µm.

During flotation, large bubble networks were observed to develop during the 10 minute flotation period (Figure 4.1-5A), creating a voluminous, cell rich float layer (Figure 4.1-5B). The large web-like bubble-cell networks formed rapidly after the introduction of the recycle stream and were clearly visible to the naked eye, which may be responsible for extending bridging and aiding cell removal. The formation of such structures can be attributed to AOM present in algae systems which can influence the action of the polymers in flotation with modified bubbles. For example, it has been demonstrated that polymer preferentially interacts with AOM over cells (Haarhoff and Cleasby 1989) and dissolved matter over other particles (Lurie and Rebhun 1997).

Furthermore, in the case of CCAP1450/3 (Henderson *et al.* 2010b), polymers-AOM interaction were suggested to create favourable flotation conditions for cells.



Figure 4.1-5. Visual observations from modified-bubble DAF using 2×10^{-10} mg cell⁻¹ of polyDADMAC – (A) a photograph of rising bubble networks beneath the float layer, observed from the side of the jar after the introduction of saturated water (26mm lens) and (B) A microscope image of the float after a jar test (10× magnification)

Overall, as demonstrated in this study and in previous research, the use of polymer for removal of cells in modified-bubble flotation was much more effective than surfactants. Using synthesised polymers that were modified with surfactant-like pendant groups, a high cell removal was obtained, achieving process performance comparable to that obtained using commercial polyDADMAC. Furthermore, cell removal with this process was comparable to conventional DAF with C-F ahead of flotation. Given that cell removal obtained with synthesised polymers and polyDADMAC did not vary significantly with polymer character, polymer performance was further evaluated by examination of the residual charge. This can be used to indicate likely polymer residuals and therefore determine whether the inclusion of hydrophobic pendant groups were encouraging better adsorption to the bubble as hypothesised.

4.1.3.5 Residual Charge in Modified-Bubble DAF Treated Water

The residual charge obtained on jar tests on application of the nine synthesised polymers was highly variable, ranging from -44.6 mV to +12.7 mV. Zeta potential dose response curves for L21, L22 and H33 are displayed in Figure 4.1-6, as examples of polymers yielding low, medium and high residual zeta potentials in DAF treated water.

For all polymers, increased doses resulted in more positive residual zeta potentials (Figure 4.1-6; see Appendix 8 for the entire dataset). Of the polymers tested, those modified with high concentrations of highly hydrophobic groups, specifically, L33, M33 and H33, resulted in the most negative resultant zeta potentials and, retained negative zeta potentials over the range of doses applied despite a high concentration of cationic polymer. Conversely, polymers with the fewest quaternised groups resulted in positive residual zeta potentials at lower charge doses than the other polymers. For example, polymer L21, with the lowest charge density of the polymers, had the greatest increase in residual zeta potential for the lowest dose of charge. At a polymer dose of only 0.50 meq L⁻¹, the zeta potential became positive; however, the optimal dose for cell removal was obtained at 0.27 meq L⁻¹, in which 96 \pm 6% cell removal was achieved. Similar observations were made for polymers H41 and M21 in Appendix 8.



Figure 4.1-6. Dose response of H33, L21, L22, polyDADMAC and CTAB in terms of zeta potential

In comparison to the synthesised polymers, the resultant zeta potential values obtained for polyDADMAC were similar to that obtained for L22. For both polyDADMAC and L22, a sharp change to less negative zeta potentials occurred for doses greater than 1.0 meq L⁻¹, corresponding to the dose at which greater than 90% cell removal was obtained. The similarity between polyDADMAC and L22 can be attributed to the high charge density of the polymer. The change in zeta potential to less negative values or

charge reversal suggests increased concentrations of detected cations in the solution. Assuming that the cationic products in water will be attracted to or complex with negative particles and AOM, the measured zeta potential is representative of the average balance of cationic and anionic components. After a jar test, the remaining cells, AOM and cationic polymer contribute to the zeta potential which can therefore indicate treated water polymer concentration relative to other polymers with similar cell removals. The presence of AOM can also influence the zeta potential; however, the removal of natural organic matter with polyDADMAC and methacrylate based water treatment polymers have been demonstrated to be similar (Bolto et al. 1999) and thus significant difference in AOM removal would not be expected. Similar to L22 in Figure 4.1-6, polymers H12 and M12 followed the same dose response trend. H12, unlike M12 and L22, retained a negative zeta potential at doses much greater than the dose for optimal cell removal (Appendix 8). The requirement for a larger dose of high molecular weight polymer to achieve charge reversal has been observed previously, both in modified-bubble flotation (Henderson et al. 2010b) and in conventional DAF (Gehr and Henry 1982). This observation is in line with established polymer theory, whereby long chain polymers can adsorb more favourably than shorter chain polymers (Cosgrove 2005).

For all tests with CTAB, zeta potential remained low, regardless of cell removal. This suggests that the CTAB had low residuals in the DAF treated water after flotation which can be attributed to its ability to congregate at air-water interfaces, for example, bubble surfaces or water surface. Similar in structure to surfactants, polymers H41, H33, M33 and L33, all have long pendant carbon groups on the polymer backbone. The implications of this functionalisation on the hydrophobic activity has been discussed in Chapter 3; however, in the case of these experiments, polymers with high concentrations of hydrophobic pendant groups (H33, M33 and L33), resulted in more negative zeta potentials in modified-bubble DAF treated water than in other polymers. Similar to cationic charge indicating the presence of polymer, the lack of cationic charge indicates low residual cationic polymers. Of these polymers, H33 tests resulted in the lowest zeta potential residuals, close to that of CTAB (Figure 4.1-6 and Appendix 8). Thus, with H33, the beneficial properties of polymer and surfactant modified bubbles was obtained, with superior cell removal and low charge residuals, indicative of close bubble adhesion.

4.1.4 Discussion

4.1.4.1 Bubble Coating with Hydrophobically Modified Polymers

The surface of microbubbles in water have been found to be negatively charged under a range of pH conditions (Elmallidy *et al.* 2008, Han and Dockko 1999), which yields the opportunity for cationic chemicals to adhere to their surfaces. At pH 7, the zeta potential of a micro-bubble in water is approximately -25 to -60 mV (Chapter 2, Section 2.2.2), though the value can be altered depending on background ionic conditions (Dockko and Han 2004, Li and Somasundaran 1991, Oliveira and Rubio 2011, Yang *et al.* 2001). With all polymers used in this work, positively charged bubbles were generated. It is postulated that cationic chemicals are likely to be attracted initially to the bubble surfaces by an electrostatic interaction, though the actual mechanism of adsorption at the bubble surface may be a result of hydrogen bonding (Yang *et al.* 2001). As both OH⁻ and H⁺ can exist at the bubble surface, both cationic and anionic polymers can adhere to the bubble surface, as demonstrated by Oliveira and Rubio (2011).

From observing the shifting distributions of disperse bubble charge results for the synthesised polymers, some deductions can be made about their interaction with bubble surfaces. By increasing the polymer molecular weight or by elevating the concentration of hydrophobic functionalisation, bubble zeta potentials decrease, indicating a comparatively diminished electrical double layer (EDL) length. This can arise from lower concentrations of charge at the bubble surface. With the presence of hydrophobic pendant groups associated to cationic polyDMAEMA, it is considered that functionalised polymer interaction at the bubble surfaces would be enhanced by hydrophobic association (Figure 4.1-7A). With larger hydrophobic groups, the attachment to bubble surfaces would be expected to be greater. In practice, polymers with large hydrophobic groups (L33, M33 and H33) were observed to have a slightly less cationic bubble zeta potential in comparison to polymers of similar molecular weight. The addition of alkyl side chains facilitates stronger association to the bubble surface by providing sites for which hydrophobic association can occur. The hydrophobic regions also provide a nucleation point for the bubble formation upon the depressurisation of air-saturated water (Figure 4.1-7B). The formation of bubbles with polymer in situ at the bubble surface cannot be quantified by direct measurement, but evidence of polymer-bubble association was apparent by monitoring modified-bubble DAF treated water charge. For a hydrophobically modified polymer at the bubble surface, flatter conformations may occur, occupying more space on the bubble surfaces. This would result in an overall lower concentration of cations on a given bubble surface.



Figure 4.1-7. Possible mechanism for polymer-bubble attachment – (A) polymer adoption after electrostatic attraction and (B) bubble nucleation within hydrophobic groups

Overall, it was found that the low molecular weight polymers resulted in the most cationic bubble zeta potential. This indicates that the packing of cationic sites at the surface of the bubble is greater, resulting in larger electrical double layers. As the extension of a low molecular weight polymer from the surface of a bubble is less than that of high molecular weight polymers (Henderson *et al.* 2010b, Napper 1983), less steric interaction would be encountered and more polymer and charge could occupy the same area on a microbubble surface.

Complicating modified-bubble measurements, Oliveira and Rubio (2011) noted that randomly measured bubbles do not carry the same charge in a given system. Furthermore polymer molecular weight is highly dispersed due to synthesis methods. In the investigation of well-defied polymers (with low polydispersity) at an air-water interface, (Matsuoka *et al.* 2004) found that charged polymers exhibited "non-surface activity". This was observed for highly cationic polymers in Chapter 3, with physical measurements of the air liquid interface. From these observations it was suggested that

polymers do not adsorb on the interface surface, which was found to be in line with dielectric theory (Greiner and Walter 1998). However, measurements of the air-liquid interface with X-ray reflectance established that solutions of either hydrophilic-hydrophobic random copolymers or homopolymers containing styrenesulfonate did in fact adsorb at the air-liquid interface (Matsuoka *et al.* 2012). The demonstration of bubble charge reversal using cationic polymers further indicates that adsorption does occur in at air-liquid interfaces in bubble systems. This was theorised to occur as hydrogen bonding with OH^- or H^+ groups at the air-liquid interface (Oliveira and Rubio 2011). However, an understanding of the mechanisms of adsorption of polymer to the air-liquid interface on bubbles is yet to be developed. To achieve this, advanced physical measurements must be made with polymers at bubble or air liquid interfaces, such as atomic force microscopy with polymer coated probes in water.

On consideration of the flotation mechanisms when using polymer-coated bubbles in DAF, the interactions between bubbles and particles are significantly different to those in conventional DAF: Firstly, the presence of the macromolecules at the bubble surface can affect bubble-surface rupturing when attaching to particle surfaces and, secondly, electrostatic interactions are reversed by reversing bubble charge. Surface tension measurements could indicate the resistance to rupturing, however with hydrophobically modified polymers; this was not quantifiable due to alterations in the bubble surface association mechanisms (i.e. bubbles could form with polymers *in situ* rather than relying on adsorption). The presence of polymer at the bubble surface could also alter the contact angle of a bubble attached to a particle; however, in DAF for water treatment, contact angle is not incorporated into the *white water* performance efficiency term, which is known to most greatly affected by electrostatic interaction (Han 2002). With the reversal of bubble charge, attachment efficiency to anionic particles is likely to improve, theoretically improving flotation of anionic particles.

4.1.4.2 Mechanisms of Cell Removal in Modified-Bubble DAF

When chemicals are applied to bubble surfaces as opposed to particles and colloids, the collection of particles from water is dependent on their effective interaction with bubbles. In this work and previous research (Henderson *et al.* 2008e), the use of CTAB

resulted in cell removals comparable to that predicted by theory and were thus dependent on cell size (Haarhoff and Edzwald 2004). The use of polymers in this system has been able to exceed this theoretical particle removal efficiency, demonstrated not only in this research, but on other algae and cyanobacteria (Henderson et al. 2009a, Henderson et al. 2010b) and other synthetic raw water (Malley 1995). Current theories, as discussed by Henderson et al. (2010b), is the occurrence of an increased "swept volume", whereby the effective surface area of a polymer modified bubble, is greater than an unmodified bubble, facilitating further cell attachments. As the bridging distances of the polymers used are insignificant compared to cell sizes (200 nm (Henderson et al. 2010b) versus 3.0 µm, respectively), additional components would be required to increase bridging lengths. This may be enhanced by the presence of AOM, particularly that of high molecular weight, as suggested by Henderson et al. (2010b). During conventional DAF tests, evidence of high molecular weight AOM was apparent with large, fibrous flocs. Similarly, during modified-bubble DAF jar tests, large bubble-particle networks could be observed. This indicates that there are structures in the AOM that aid in extended bridging lengths. As it is known that polymer preferentially interacts with AOM over cells (Haarhoff and Cleasby 1989), hence suprastructures arising from polymer and AOM interactions may be forming, facilitating considerable bridging lengths.

The association of polymers containing large quantities of hydrophobic pendant groups, particularly H33, may further strengthen interaction with bubbles. The large hydrophobic regions can also be responsible for a degree of inter- and intrapolymer interactions. This was evident from results in Chapter 3 in which a micellisation procedure was used to encourage existing hydrophobic interactions. The grouping of the hydrophobic regions can facilitate bubble nucleation via catalytic effects offered by the hydrophobic zones (Lubetkin 2003). When bubbles are formed in the presence of the polymer little to no diffusion is required to associate a polymer to its surface. Though the hydrophobically functionalised polymer may not project into solution as readily as a cationic polymer without hydrophobic pendant groups, it is evident that AOM-polymer suprastructures still form. The result of this is enhanced bubble and contaminant interactions such that both contaminants and polymer are effectively floated, minimising undesirable polymer residuals.

4.1.5 Summary

The principal finding of this phase of the investigation were:

- CTAB, polyDADMAC and all synthesised polymers resulted in positively charged bubbles with only subtle differences in zeta potentials and charge characteristics
- 2) All synthesised polymers resulted in cell removals in excess of 90% and up to 99% and as such comparable removal efficiencies to that obtained when using commercial polyDADMAC as a bubble modifier and conventional coagulation-DAF were attained
- 3) Highly negative zeta potentials in modified-bubble DAF treated water were achieved with synthesised polymer H33, indicating low polymer residuals and therefore stronger bubble attachment. Therefore, higher polyDMAEMA quaternisation / hydrophobic functionality led to enhanced bubble attachment and subsequently less polymer in the DAF treated water
- 4) Synergistic effects might be occurring between polymers and AOM leading to enhanced particle-particle and bubble-particle bridging distance, aiding in both flocculation and flotation

4.2 THE INFLUENCE OF AOM ON MODIFIED-BUBBLE DISSOLVED AIR FLOTATION

4.2.1 Introduction

The presence of algogenic organic matter (AOM) in modified-bubble DAF has been hypothesised to reduce cell removal (Henderson et al. 2010b). From investigating the effectiveness of modified-bubble DAF on a range of algae and cyanobacteria species, a large variation of removal efficiency was detected (Henderson et al. 2010b). This was attributed to differing AOM character and concentration between algae and cyanobacteria species. Though some AOM from algae and cyanobacteria can inhibit flocculation (Vandamme et al. 2012), the high molecular weight components can aid flocculation (Bernhardt et al. 1989, Bernhardt et al. 1985). In modified-bubble DAF such components associated to *M. aeruginosa* have also been suggested to aid cell removal, not observed for other species (Henderson et al. 2010a). As the variability of AOM can impact water treatment of different species of algae and cyanobacteria, it may be that the same is true for different strains of *M. aeruginosa*. It is known that a range of *M. aeruginosa* strains can have significantly different toxicities (D'Ors *et al.* 2012). Consequently, other cell by-products can be subject to variation: Mancuso Nichols et al. (2009) demonstrated that Australian strains of *M. aeruginosa* have AOM of varying viscosity, implying changes in AOM molecular weight or self-associative behaviour.

In Chapter 4.1, a difference in the removal of an Australian strain of *M. aeruginosa*, CS-564/01, and UK strain (CCAP 1450/3) (Henderson *et al.* 2010b), using bubbles modified with cationic polymer (modified-bubble DAF) was observed. Using polyDADMAC, the Australian strain required less polymer in modified-bubble DAF to obtain greater than 90% cell removal. Dose response curves from flotation jar testing in Chapter 4.1 differed to those generated by Henderson *et al.* (2010b) in that cell removal did not lessen at very high doses of polymer despite reversal of the treated water zeta potential. This demonstrates that the two strains used had a different response to treatment, despite being the same species.

As AOM has as considerable impact on the removal of cells from water, an additional Australian strain of *M. aeruginosa* was obtained for investigation of the effect of AOM. As per the tests in Chapter 4.1, a selection of the hydrophobically modified polymers synthesised in Chapter 3 were tested to assess any improvements that can be made via strengthened polymer-bubble attachment. The specific aims of this chapter were to investigate the influence of AOM on modified-bubble DAF. AOM that was known to be beneficial to cell removal in Chapter 4.1 was extracted and used as an aid to modified-bubble DAF. This investigation was furthered by filtering the AOM to assess the importance of AOM size for bubble-polymer-cell interactions in modified-bubble DAF.

4.2.2 Materials and Methods

4.2.2.1 Cyanobacteria

Two strains of *Microcystis aeruginosa*, CS-555/01 and CS-564/01, were obtained from the Commonwealth Scientific and Industrial Research Organisation (CSIRO) Australian National Algae Culture Collection (ANACC) (Hobart, Australia), and recultured in MLA media (Bolch and Blackburn 1996). Cultures were grown in 100 mL batches in 250 mL conical flasks and harvested at the end of the exponential growth phase, typically occurring after 10-12 days of growth. A haemocytometer and microscope were utilized for cell counting. The cyanobacteria was subjected to a 16/8 hour light/dark cycle, with temperature controlled to 21°C, in a 500 L, PG50 incubator with a photosynthetic photon flux output of $600 \pm 60 \,\mu\text{mol}\,\text{m}^{-2}\,\text{s}^{-1}$ (Labec, Australia).

4.2.2.2 Algogenic Organic Matter

AOM was separated from cells via centrifugation at $10,000 \times \text{g}$ for 15 minutes with an Allegra[®] X-15R Centrifuge (Beckman Coulter, Australia) as described by Henderson *et al.* (2008b). To remove any additional tightly bound AOM, each aliquot of pelleted cells were resuspended in MLA media without micronutrients by vortexing for 20 seconds, followed by another cycle of centrifugation. The AOM containing supernatants were further treated by filtration using 934-AH glass microfiber filters (1.50 µm nominal pore size) (Whatman, USA) to remove cell debris. In order to investigate organic carbon properties, the AOM solutions were subjected to further

filtration using a 0.45 μ m polyethersulphone (PES) syringe filter. AOM from the three stages of AOM extraction were used in an investigation of the impact of AOM size on treatment performance, to include unfiltered, 1.50 μ m filtered and 0.45 μ m filtered AOM.

4.2.2.3 Chemicals

PolyDADMAC (Sigma Aldrich, Australia), aluminium sulphate (Sigma Aldrich, Australia) and the nine polymers synthesised (details in Chapter 3, Section 3.2.2 and 3.2.3) were used in bench tests, as per Chapter 4.1. The full list of synthesised polymers with charge density that were used in these tests can be found in Table 4.1-1 in Chapter 4.1.

4.2.2.4 Algal System Characterisation

Cell Properties

Cell counting and visual observations were conducted using a Leica DM500 light microscope equipped with a Leica ICC50 camera (Leica Microsystems Ltd, Switzerland). Cell size measurements were made using a Mastersizer 2000 (Malvern, UK). Cultures were adjusted to pH 7 with 1 M hydrochloric acid for charge analysis as follows: zeta potential measurements were conducted with a Zetasizer Nano ZS (Malvern, UK) and charge demand analysis with a PCD-04 particle charge detector (Mütek BTG, Switzerland). To confirm both cultures were in fact species of *M. aeruginosa* as stated by supplier, 16S ribosomal RNA sequences were obtained and compared to the Basic Local Alignment Search Tool (BLAST) database (http://blast.ncbi.nlm.nih.gov), conducted by the Neilan Laboratory of Microbial and Molecular Diversity, at the University of New South Wales.

Analysis of Algogenic Organic Matter

Samples were analysed immediately after extraction. To analyse unfiltered, 1.50 μ m filtered and 0.45 μ m filtered AOM, a TOC–Vsch Analyser (Shimadzu, Sydney, Australia) was used to determine organic carbon (OC). Protein and carbohydrates were analysed for each sample using a modified Lowry method (Frølund *et al.* 1995) and phenol-sulphuric acid method (Zhang *et al.* 1999), respectively. Bovine serum albumin (BSA) and d-glucose were used for calibration at 750 nm and 480 nm, respectively.

Each measurement was conducted on triplicate samples. Charge measurements were conducted on 0.45 µm filtered samples corrected to pH 7 with 1 M hydrochloric acid such that measurements can be made in terms of dissolved organic carbon (DOC) and compared to previous research (Henderson et al. 2008b). As with the unprocessed cultures, zeta potential were conducted with a Zetasizer Nano ZS (Malvern, UK), using a 175° backscatter to measure Brownian motion via scattering intensity fluctuations; this instrument is capable of measuring materials of sizes as low as 0.3 nm (Malvern 2013). Charge demand analysis was conducted with a PCD-04 particle charge detector (Mütek BTG, Switzerland). The AOM was further analysed using size exclusion liquid chromatography with organic carbon, UV₂₅₄ and organic nitrogen detection (LC-OCD) (DOC Labor, Germany). A Toyopearl TSK HW-50S column was used that has a particle size of 30mm, length of 250 mm and internal diameter of 20 mm. The mobile phase employed was phosphate buffer at pH 6.37 (2.5 g L^{-1} KH₂PO₄ and 1.5 g L^{-1} $Na_2(HPO_4)_2 \cdot H_2O)$ at a flow rate of 1.1 mL min⁻¹. An injection volume of 1 mL was used to analyse samples. From this analysis, the apparent molecular weight of DOC and UV absorbing compounds could be analysed, as described extensively in Huber et al. (2011).

4.2.2.5 Conventional Flotation Jar Tests

Synthetic DAF influent and saturator water were prepared using Milli-Q water (18.2 M Ω ·cm) with 0.5 mM NaHCO₃ and brought to an ionic concentration of 1.8 mM with NaCl. The DAF influent contained cultured cells, diluted to a cell concentration of 7.5 $\times 10^5$ cells mL⁻¹. The procedures used for conventional DAF jar testing were the same as described in Chapter 4.1, Section 4.1.2.4. Briefly, rapid mixing was conducted for 180 seconds at 200 rpm, during which, alum addition and pH was corrected to pH 7, using 1 M HCl and 1 M NaOH solutions and monitored with a pH210 Microprocessor pH Meter (Hanna Instruments, USA). Slow mixing was conducted for 10 minutes at 30 rpm followed by flotation for 10 minutes. A recycle ratio of 10% was used as a typical set point applied in DAF (Edzwald 1995). Residual analysis for all tests included counting 100 cells using a haemocytometer or Sedgwick Rafter counting cell for cyanobacteria cell concentration as per Henderson *et al.* (2008b). Zeta potential

analysis was conducted using a Zetasizer Nano ZS (Malvern, UK). All measurements were made in triplicate.

4.2.2.6 Modified-Bubble DAF Jar Tests

Modified bubble flotation jar testing was carried out by adding polymer or chemicals to the saturator, as described in detail in Chapter 4.1, Section 4.1.2.6. Influent and saturator water were prepared as described for conventional DAF. A recycle ratio of 20% was selected for all tests, with a saturator pressure of 450 kPa. Aliquots of buffered Milli-Q water were dosed with polymer to give a range of final concentrations in the jar of 0 to 3×10^{-3} meq L⁻¹. Residual analysis was conducted via cell counting and zeta potential analysis according to the methods outlined in Section 4.2.2.5.

4.2.2.7 Modified-Bubble DAF Jar Tests with Altered AOM Conditions

Using the procedures for standard modified bubble flotation jar testing and a fixed polyDADMAC dose of 0.3 mg L⁻¹, synthetic DAF influent preparation was conducted such that the amount of AOM in solution was altered to explore the influence of AOM on treatment performance. These experiments can be split into two separate tests:

Experiment 1

With both CS-555/01 and CS-564/01, AOM and cells were separated and collected via the extraction method described in Section 4.2.2.2. AOM was recombined with the cells to give the desired AOM concentration using buffer consisting of 0.5 mM NaHCO₃ and made up to an ionic strength of 1.8 mM with NaCl. These solutions were corrected to pH 7 and mixed at 50 rpm for 60 seconds ahead of flotation to ensure complete mixing. The final cell concentration in the jars were $7.5 \times 10^5 \pm 5 \times 10^4$ cells mL⁻¹ with AOM of various concentrations between 0 and 1 mg L⁻¹ as measured by a TOC–Vsch Analyser (Shimadzu, Australia). As per previous modified-bubble DAF tests, a recycle ratio of 20% was used followed by a flotation time of 10 minutes.

Experiment 2

AOM from CS-564/01 was extracted as per the method described in Section 4.2.2.2. Isolated cell pellets were discarded. CS-555/01 was used to make up synthetic DAF influent as per initial modified-bubble DAF with no AOM adjustments. AOM extracted from CS-564/01 was added to the synthetic influent water solutions containing CS-555/01 cells, such that the desired AOM concentration was achieved, with a final CS-555/01 cell concentration of $7.5 \times 10^5 \pm 5 \times 10^4$ cells mL⁻¹. Due to experiment variability, a final test was conducted with the three AOM samples described in Section 4.2.2.2; namely, unfiltered, 1.50 µm filtered and 0.45 µm filtered AOM

4.2.3 Results

4.2.3.1 Microcystis aeruginosa Strain Characterisation

With 16S ribosomal RNA sequencing for both cultures, CS-564/01 and CS-555/01, the BLAST database was queried for matching species. The top 5 matches returned were *Microcystis aeruginosa* confirming that the cyanobacteria species in cultures CS-564/01 and CS-555/01 was indeed *M. aeruginosa*. Visually, the cells were similar, existing with spherical, unicellular morphology when grown in the laboratory (Figure 4.2-1). Physicochemical characteristics of the cells were measured (Table 4.2-1). The physical diameter of the spherical cells was found to be the similar at $3.0 \pm 0.7 \mu m$ and $3.1 \pm 0.6 \mu m$ for CS-555/01 and CS-564/01, respectively. Cell diameter distribution plots can be found in Appendix 11.



Figure 4.2-1. Photo of a (A) CS-555/01 cell and a (B) CS-564/01 cell at 100x magnification using a light microscope

nom exitatica from CS 555701 and CS 507701						
Properties	Units	CS-555/01	CS-564/01	CCAP 1450/3		
Diameter	μm	3.0 ± 0.7	3.1 ± 0.6	5.4 [‡]		
Cell Count	$\times 10^7$ cells mL ⁻¹	1.79 ± 0.08	2.01 ± 0.12	0.06 *		
Zeta Potential (culture)	mV	-9.3 ± 0.7	-32.8 ± 0.6	-19.8 [‡]		
Charge Density (culture)	$\times 10^{-7}$ meg cell ⁻¹	-9.3 ± 0.6	-15.8 ± 0.8	-0.00002‡		
AOM (0.45 μ m filtered)	$\times 10^{-10}$ mg cell ⁻¹	9.6 ± 0.1	8.5 ± 0.5	10 *		
Charge Density (1.50 µm filtered)	$\times 10^{-3} \text{ meq } \text{L}^{-1}$	-12 ± 1	-17 ± 3	-1.2 ‡		
Zeta Potential (1.50 um filtered)	mV	-12.5 ± 1.9	-28.2 ± 1.8	-20 ‡		

Table 4.2-1. Physicochemical properties of the CS-5555/01 and CS-564/01 cultures, and AOM extracted from CS-555/01 and CS-564/01

[†]Data obtained or calculated from Henderson *et al.* (2010a)

[‡] Data obtained from Henderson *et al.* (2010b)

The 0.45 µm filtered AOM from CS-555/01 was observed to have more concentrated organic carbon than CS-564/01, at 9.6×10^{-10} mg cell⁻¹ versus 8.5×10^{-10} mg cell⁻¹, respectively (Table 4.2-1). These concentrations were found to be in agreement with that of the UK strain investigated by Henderson *et al.* (2010a). Both Australian strains were found to have smaller concentrations of AOM with higher overall charge compared to the UK strain used in previous research. For example, the anionic charge density associated with CS-564/01 AOM was found to be 1.75 times that per gram of DOC than that of CS-555/01. In contrast, AOM of the UK strain of *M. aeruginosa* was found to have a much less negative charge density at -0.2 meq g⁻¹. It is unknown whether this disparity is a reflection of the natural variability in AOM charge between strains or as result of the application of a different technique implemented for charge measurement; back titration with *ortho*-Toluidine blue (Henderson *et al.* 2008b).

Additional analysis of the 0.45 μ m filtered AOM with LC-OCD showed slight variations in the size fractions between strain CS-555/01 and strain CS-564/01 (Figure 4.2-2). Both strains showed that there were similar components as fractionated by the LC-OCD, with the most obvious difference in the strains occurring at peaks typically identified as humics and low molecular weight neutrals (Huber *et al.* 2011). Strain CS-564/01 had a larger fraction of building blocks at 45% versus 23% for CS-555/01 whilst the LMW neutrals fractions were 21% and 31% for strains CS-564/01 and CS-555/01, respectively.


Figure 4.2-2. LC-OCD and UV results for (A) CS-555/01 and (B) CS-564/01; organic matter class definitions are those described by Huber et al. (2011)

4.2.3.2 Conventional DAF of CS-555/01

After coagulation and flocculation of model algal influent water containing *M. aeruginosa* strain CS-564/01, optimal cell removal of 96 \pm 3% was obtained (Figure 4.2-3). This removal was obtained at an aluminium dose of 2.0 mg L⁻¹, although to obtain a cell removal of greater than 90%, only 1.0 mg L⁻¹ was required. As outlined in Table 4.2-2, these results were comparable to those obtained with model algal influent water containing CS-564/01: The same dose of aluminium was required to achieve the equivalent removal. However, the maximum cell removal in CS-564/01 samples was greater, at 99% and, furthermore, a higher dose of alum was required for charge neutralisation; 1.5 mg L⁻¹ compared to 1.0 mg L⁻¹ for CS-555/01 and CS-564/01, respectively. This was surprising as the charge demand of CS-564/01 is 1.7 times greater than that of CS-555/01, on a cell to cell basis.

Table 4.2-2. A comparison of the key data for conventional DAF jar testing of model algal influent water containing either CS-555/01 or CS-564/01

ijiueni waler containing either CB-5.	JJ/01 01 CD-J04/0	/1		
Properties	Units	CS-555/01	CS-564/01	
Highest cell removal	%	96 ± 3	99 ± 1	
Firs dose for >90% cell removal	mg L ⁻¹ as Al	1.0	1.0	
Charge neutralisation dose	mg L ⁻¹ as Al	1.5	1.0	



Figure 4.2-3. Cell removal and zeta potential dose response curves for conventional DAF using alum as a coagulant and M. aeruginosa (strain CS-564/01) as an algal contaminant

The flocs that formed were visually observed to have a more uniform shape in comparison to those observed for CS-564/01 (Chapter 4.1, Figure 4.1-1), with closely packed morphology (Figure 4.2-4). With similar cell physical dimensions, this suggested that CS-564/01 AOM components, that are absent in CS-555/01 AOM, alter flocculation mechanisms and resultant floc properties.



Figure 4.2-4. Observation of flocs formed after coagulation of M. aeruginosa (strain CS-555/01) with alum at a dose of $l mg L^{-l}$ of Al

4.2.3.3 Modified-Bubble Flotation of CS-555/01

The initial tests with polyDADMAC demonstrated a significantly lower removal of CS-555/01 in comparison to CS-564/01. The maximum cell removal obtained was only 31 \pm 1%, requiring a polymer dose of 1.0 \times 10⁻³ meg L⁻¹ (Figure 4.2-5A), above which, the cell removal decreased. Comparing these tests to results generated by Henderson et al. (2010b), the optimum cell removal (94%) was obtained at a dose of 2.4×10^{-3} meg L⁻¹ with polyDADMAC. A similar decrease in cell removal was observed at doses above this. In Chapter 4.1, higher cell removal was obtained (99% at a dose of 1.9×10^{-3} , Chapter 4.1, Figure 4.1-4); however, application of doses above that required for optimal removal did not result in poorer cell removal. When using CTAB, lower cell removals were obtained, similar to Chapter 4.1 and work by Henderson et al. (2008e). A maximum cell removal of $11 \pm 4\%$ was achieved at a dose of 2.4×10^{-3} meg L⁻¹. However, unlike previous research, this did not coincide with the maximum cell removal predicted by the white water model. This may be because of the lack of essential bridging mechanisms offered by the presence of polymer in this system implying that cell removal in CS-564/01 modified-bubble DAF jar tests was a consequence of the presence of specific AOM.

The zeta potential of the DAF treated water was reversed at a dose of approximately 0.5 $\times 10^{-3}$ meq L⁻¹ of polyDADMAC (Figure 4.2-5B). This was much lower than previous

work observing charge reversal at a polyDADMAC dose of 3.0×10^{-3} meq L⁻¹ and 1.5×10^{-3} meq L⁻¹ in Chapter 4.1 and in work by Henderson *et al.* (2010b), respectively. When CTAB was applied, up to the highest doses applied, the DAF treated water retained a negative zeta potential, also observed in previous studies (Chapter 4.1, Henderson *et al.* (2008e)). As discussed in Chapter 4.1 (Section 4.1.3.5), the highly negative zeta potentials demonstrate low cationic availability, indicating that fewer cations reside in solution.



Figure 4.2-5. PolyDADMAC, hydrophobically functionalised polymers and CTAB used in bubble modification for flotation of CS-555/01 - plots display (A) cell removal and (B) zeta potential - H41, H33 and H12 are displayed in this plot representing highest cell removals, lowest zeta potentials and a polymer of moderate charge - graphs of the entire dataset are presented in Appendix 12 and Appendix 13

The maximum removal of $37 \pm 8\%$ was obtained using H41, a polymer with low levels of quaternisation with large alkyl chains (C15) (Chapter 3, Table 3-2), at a dose of 0.70 $\times 10^{-3}$ meq L⁻¹ (Figure 4.2-5A); approximately a third of what could be achieved when treating the strain CS-564/01. This removal was a slight improvement compared to that

achieved with polyDADMAC in the removal of CS-555/01. As the maximum cell removal for all hydrophobically functionalised polymers ranged from 21 to 37%, the overall improvement was only marginal, and cell removal was still not comparable to work done in Chapter 4.1, or by Henderson *et al.* (2010b). The addition of the hydrophobic pendant group did not improve cell removal efficiency; however, the effect of the hydrophobic groups was apparent from observing modified-bubble DAF treated water charge.

In terms of the DAF treated water charge, polymer H33 demonstrated much more negative zeta potentials, similar to that of CTAB modified-bubble DAF (Appendix 13), indicating lower cationic availability and therefore lower concentrations of cationic polymer in the DAF treated water. As observed in Chapter 4.1, the polymers of the lowest charge density, namely L21, M21 and H41, resulted in cationic treated water at lesser doses of polymer charge compared to the other polymers tested. When comparing all polymers by mass, it was observed that the zeta potential dose responses were similar for all polymers (Appendix 13), with the exception of H33, which remained more negative at any given dose below 0.64 mg L⁻¹, corresponding to a charge dose of 1.77×10^{-3} meq L⁻¹. This indicated that H33 had superior bubble attachment compared to all other polymers used and, similar to Chapter 4.1, demonstrates similarity in bubble adherence to a surfactant, below a dose of 1.5×10^{-3} meq L⁻¹.

The more negative zeta potentials exhibited in Figure 4.2-5B when using polymer H33 as a bubble modifier indicates good bubble adherence, in agreement with tests in Chapter 4.1 (Section 4.1.3.5). Hence, the polymer is less likely to be removed from the bubble surface through interactions with AOM. This is in contrast to the hypothesis presented by Henderson *et al.* (2010b), in which polymer in the liquid phase binds with cell surfaces resulting in steric repulsion with polymer modified-bubbles. As the characteristics of CS-564/01 and CS-555/01 cells are similar (Section 4.2.3.1) the AOM in strain CS-564/01 may be responsible for enhancing cell removal.

4.2.3.4 The AOM Effect on Modified-Bubble DAF

Experiment 1

On performing modified-bubble DAF experiments after stripping AOM from the system, poor cell removal was obtained when AOM was controlled to 0 mg L⁻¹, using 0.3 mg L^{-1} of polyDADMAC for both CS-555/01 and CS-564/01 (Figure 4.2-6 A and B, respectively), demonstrating the key role AOM plays in enhancing cell removal. Upon increasing the AOM concentrations in the jar tests, CS-555/01 cell removal remained low with maximum values of $18 \pm 4\%$ and therefore removal efficiencies observed in Figure 4.2-5 were not able to be emulated. However, in contrast, increasing the AOM concentration of CS-564/01 samples showed a significant improvement in modifiedbubble DAF. The highest cell removal that was obtained was 95 ± 3 % at the highest AOM concentration used, which is 3% lower than cell removals observed in Chapter 4.1 (Figure 4.1-4). For these strains, the original concentration of AOM for the jar tests was 0.72 and 0.64 mg L^{-1} for CS-555/01 and CS-564/01, respectively. It was observed that the substitution of the AOM back into cell solutions did not completely replicate cell removals obtained with unprocessed cell cultures. On examination of zeta potential results, both strains demonstrated similar dose responses: An initial dose of AOM in the synthetic DAF influent changed the zeta potential of the DAF treated water from negative to positive (Figure 4.2-6) and as the concentration of AOM was increased further, the treated water zeta potential can be observed to decrease. This initial negative zeta potential is surprising and indicates that little cationic polyDADMAC remains in the DAF treated water. After adding AOM, the zeta potential of the DAF treated water changed from negative to positive, indicating that there was a greater concentration of polyDADMAC in the treated water. This suggests that AOM is responsible for stripping polymer from bubble surfaces in both CS-555/01 and CS-564/01 samples. However, the removal of the polymer from bubble surfaces has little impact on cell removal, as up to 95% cell removal was obtained for CS-564/01.



Figure 4.2-6. Bench test outcomes for (A) CS-555/01 and (B) CS-564/01 cells with AOM added to jars at various concentrations, quoted as mg L^{-1} as C with a corrected cell concentration of 7.5 × 10⁵ cells mL⁻¹ and a constant polymer dose at 0.3 mg L^{-1} polyDADMAC

Experiment 2

With the beneficial effects of CS-564/01 AOM in modified-bubble DAF jar testing clearly demonstrated, the CS-564/01 AOM was further tested as an additive for enhancing CS-555/01cell removal effectiveness. In initial experiments, an AOM dose of 0.58 mg L⁻¹ (as measured by OC analysis) resulted in a cell removal of 96 \pm 3% which is comparable to that obtained in conventional C-F based DAF jar tests (Figure 4.2-7). Upon repetition of the initial round of experimentation with a different batch of algae, much greater AOM concentrations were required to remove cells. For example, in round 2 tests, up to 2.61 mg L⁻¹ of AOM was required to obtain 80% cell removal, whereas in round 1 tests, only 0.43 mg L⁻¹ was required. In repeat 3 of tests, 80% cell removal was obtained at an AOM dose of 0.75 mg L⁻¹; however, a maximum removal of only 82 \pm 4% was achieved in this test. Despite very high doses of AOM, positive

zeta potentials were obtained, over all tests. Throughout these tests, filtration of the AOM resulted in the formation of a gelatinous layer on $1.50 \mu m$ filter paper. This indicates that large complexes in the AOM exist.



Figure 4.2-7. Jar tests of CS-555/01, using CS-564/01 AOM as a flotation enhancer for polyDADMAC modified bubble flotation with plots displaying (A) cell removal and (B) zeta potential – the data were generated over 3 separate tests repeats

Upon analysis of protein and carbohydrates in the AOM, it was found that both protein and carbohydrate concentrations were variable. For example, over the course of the three repeats of tests, there was a decrease in the concentration in carbohydrates, and variable protein concentrations (Figure 4.2-8). In repeat 1 of the tests, the protein and carbohydrate concentrations were found to be 1.3 ± 0.4 mg L⁻¹ and 16.4 ± 1.2 mg L⁻¹, respectively. In repeat 2, where very high concentrations of AOM were required to remove cells, protein was undetectable, whereas the carbohydrate concentration was reduced to 13.3 ± 9 mg L⁻¹. In repeat 3 of the tests, the AOM had a protein concentration of 1.9 ± 0.4 mg L⁻¹ and carbohydrate concentration of 9.2 ± 0.3 mg L⁻¹. Hence, over the three testing periods, it was found that there was significant variability in biopolymer concentrations. Interestingly, in experiments with detectable protein, it was found that the concentration of AOM required to remove cells was much less. This indicates that the presence of protein may be responsible for enhanced cell removal, and furthermore that very low protein concentrations may be required for the success of the process.



Figure 4.2-8. Protein and carbohydrate measurements made on the AOM used in Figure 4.2-7 - protein and carbohydrate samples were calibrated against BSA and d-glucose respectively

Given the very high concentrations of AOM required to improve cell removal in repeat 2 tests, the following repeat 3 of tests were conducted using unfiltered AOM, AOM filtered to 1.50 μ m and AOM filtered to 0.45 μ m, in order to determine the effect of AOM size in aiding modified-bubble DAF (Figure 4.2-9). The unfiltered AOM yielded the best CS-555/01 cell removal with a maximum of 98 ± 2%. This result exceeded maximum cell removals obtained in both repeat 1 of the initial Experiment 2 jar tests and conventional DAF jar testing. Filtration of the AOM resulted in lower cell removals with a higher concentration of AOM required; for example, 0.45 μ m filtered AOM yielded a maximum removal of 86 ± 7%. Similar to initial tests, all zeta potentials remained positive.



Figure 4.2-9. Jar tests of CS-555/01, using CS-564/01 AOM as a flotation enhancer for polyDADMAC modified bubble flotation with plots displaying (A) cell removal and (B) zeta potential – AOM for this experiment was unfiltered during the extraction process, filtered with a 1.50 μ m filter (from round 3 test) and 0.45 μ m filter

As per the previous tests, the protein concentrations were found to be just above the detection limit for the assay (1 mg L⁻¹) (Figure 4.2-10). Protein and carbohydrate concentration for 0.45 μ m filtered AOM was found to be similar to that of 1.50 μ m filtered AOM at 7.7 ± 1.0 mg L⁻¹ and 1.6 ± 0.9 mg L⁻¹, respectively. With unfiltered AOM, it was found that the protein and carbohydrate concentrations were much higher at 2.6 ± 0.5 mg L⁻¹ and 22.3 ± 0.8 mg L⁻¹, respectively. With unfiltered AOM, there is the possibility that remaining cell debris could artificially increase the absorbance readings. However, it is apparent that the presence of proteins in the AOM samples correlates to higher cell removals below AOM doses of 1 mg L⁻¹ in jar testing.



Figure 4.2-10. Protein and carbohydrate analysis conducted on centrifuged and filtered AOM samples obtained from CS-564/01 - protein and carbohydrate samples were calibrated against BSA and d-glucose respectively

4.2.4 Discussion

This chapter clearly demonstrates that in modified-bubble flotation, the presence of AOM is critical for cell removal. This deduction can be made from polyDADMAC modified-bubble DAF jar tests in the absence of AOM for both CS-555/01 and CS-564/01: Negative zeta potentials in the DAF treated water after flotation indicated that bubbles produced interacted with polymer in preference to the bulk solution or contents and fewer detectable cations, and thus cationic polymer, reside in treated water. The increase of the DAF treated water zeta potential after adding AOM was surprising as AOM has a negative charge (Haarhoff and Cleasby 1989, Henderson et al. 2010a). This suggests that AOM interactions are responsible for stripping polyDADMAC from bubble surfaces. However, the absence of AOM resulted in poor cell removal indicating that the presence of AOM was crucial for effective attachment of a bubble to In this current research, the complexing of polymers with AOM therefore a cell. played two vital roles in cell removal: 1) adherence to or complexation with polymers and 2) attachment to the cell surface. This implies that the AOM in CS-555/01 has a much lower cell adherence than AOM in CS-564/01.

Without filtration, CS-564/01 AOM resulted in very high cell removals, indicating that very large AOM constituents are responsible for enhanced cell removal in modifiedbubble DAF. In a separate study of modified-bubble DAF, Henderson *et al.* (2010b) attributed high cell removals of *M. aeruginosa* to high molecular weight compounds found in its AOM (Henderson *et al.* 2008b). This may be attributed complexation of proteins and quaternary amine similar to that observed for coagulant and proteins (Pivokonsky *et al.* 2006, Takaara *et al.* 2004). Furthermore, Bernhardt *et al.* (1985) demonstrated that extracellular organic matter was able to attach to turbidity causing particles despite similar electric charge. The observation of very large web structures during flotation was evidence of large bridging structures in solution. It is therefore AOM-polymer complexes that can assist bubble and cell interactions by bridging large distance. Given that modified-bubble DAF is ineffective without the presence AOM, it is AOM (and cells) to bubble surfaces (Figure 4.2-11).



Figure 4.2-11. Interactions of bubbles, polymers, AOM and M. aeruginosa cells during modified-bubble DAF (polymer and AOM not to scale)

Extracellular material from *M. aeruginosa* has been observed to further aggregate and self-associate to produce supra-macromolecular structures such as fibrils (Leppard 1995) or biopolymer clusters (Wang and Li 2008). Specific investigations into the extracellular organic matter in CS-564/01 cultures has also shown that bacteria that coexist with the *M. aeruginosa* cells produce high molecular weight substances,

consisting of both polysaccharides and proteins, are effective wood adhesive (Mancuso Nichols *et al.* 2009). Furthermore the observation of gelatinous material on glass microfiber filters indicates that very large AOM structures are present in CS-564/01. In combination with cationic polyelectrolytes it is possible that the bridging lengths would be visible to the naked eye, which may already be the case given the web-like networks visible in CS-564/01 modified bubble flotation (Chapter 4.1, Figure 4.1-5).

The very large AOM complexes observed could be formed according to a couple of theories. For example, biopolymer complexes have been observed to create clusters in membrane bioreactors. These biopolymer clusters (BCPs) were found to be a combination of proteins, polysaccharides and humic substances (Wang and Li 2008), forming agglomerates of tens of microns in diameter, and it is possible that similar structures could be forming in these algae systems. An alternative and more probable theory due to the elevated carbohydrate concentration and lack of humic substances observed in the AOM samples, is that the large gelatinous structures that are forming are similar to fibrils, as observed by Leppard (1995) and further described by Harel et al. (2012). These fibrils were found to be associated to the surface of M. aeruginosa strains PCC 7806 (from the Netherlands) and were determined to consist of polysaccarides. Protein was aslo identified in these samples; however, it was not confirmed whether or not the proteins formed a part of the fibril structure (Harel et al. 2012). A much more detailed analysis of the CS-564/01 AOM would be required to determine if such structures or building blocks for fibrils exist, and furthermore, whether they are likely to occur in environmentally relevant waters.

Reviewing the literature on CS-564/01 and CS-555/01 reveals that the isolation sites for each of these strains is significantly different: CS-564/01 is a non-axenic strain isolated from a waste stabilisation pond St. Marys WWTP in Tasmania whereas CS-555/01 is an axenic strain, isolated from Lake Burley Griffin in the ACT (Bolch and Blackburn 1996). The mix of associated bacteria organic matter may be influencing the mucilage production (Worm and Søndergaard 1998) and thus contributing to the AOM. Hence, waste stabilisation ponds are more likely to have organic matter with similar characteristics to that found in CS-564/01 and thus are ideal for further investigation of modified-bubble DAF in the field.

4.2.5 Summary

The principal finding of this phase of the investigation were:

- 1) The use of modified bubble flotation for the removal of CS-555/01 cells was shown to be less effective than previously tested strains of *M. aeruginosa*
- 2) The success of modified-bubble DAF heavily relied on the presence of AOM and the formation of AOM-polymer complexes
- 3) The presence of high molecular weight AOM components facilitate higher cell removals. In CS-564/01 these compounds have been found to be carbohydrate rich and may be similar to those observed in fibrils, observed in other strains of *M. aeruginosa*
- 4) It is conjectured that associated bacteria may encourage the production of high molecular weight AOM as CS-564/01 was obtained from a waste stabilisation pond. Hence it is considered that a WSP may provide suitable character of DAF influent for cell removal with modified-bubble DAF

Chapter 5

5.1 OPTIMISATION OF WASTE STABILISATION POND EFFLUENT TREATMENT USING A PILOT DISSOLVED AIR FLOTATION PLANT

5.1.1 Introduction

The investigation of modified-bubble dissolved air flotation (DAF) has currently been limited to bench-scale jar tests using synthetic water samples (Chapter 4.1, (Henderson et al. 2008e, 2009b, 2010b, Malley 1995). Though the results of jar testing for modified-bubble DAF can yield insights to the process performance and operational requirements, there are fundamental differences between a DAF jar tester and a continuous flow DAF plant. As an example, Lundh et al. (2002) investigated the effect of contact zone construction on flow in a DAF reactor at pilot-scale. It was found that the removal of contaminants can be impacted greatly depending on the depth and shape of the contact zone; variables that cannot be changed in jar tests. In addition to this, the DAF recycle flow is diverted from the clarified water; thus any contaminants that carry over from DAF are recycled back into the process via the saturator. Furthermore, if a pilot plant is installed on the site of the source water, the plant is subject to the natural variable water quality and any processes that are applied can be directly translated to full-scale operation. Though environmental samples can be moved to a laboratory, any potential character change from sample transport can be avoided from onsite work. Hence, the investigation of modified-bubble DAF at pilot-scale is critical to assess the feasibility of the process outside of laboratory conditions.

Algae and cyanobacterial blooms are more prevalent at waste stabilisation ponds (WSPs) than other waterways such as reservoirs (personal communication, Michael Holmes, Researcher, United Water). This is because WSPs have naturally nutrient rich

feed waters, often being fed with wastewater or WWTP effluent. Due to the presence of algae and cyanobacteria in WSP effluent, DAF is suited for clarification and thus there is a trend in installing DAF plants for further treatment at this stage (Edzwald 1993a, Edzwald 2010, Plummer *et al.* 1995); though C-F pretreatment remains challenging due to highly variable algae species populations and concentrations (Bernhardt and Clasen 1991, Buisine and Oemcke 2003). In Chapter 4.2, it was identified that effective modified-bubble DAF was dependent on organic matter produced by the strain of *Microcystis aeruginosa*, which originated from a WSP rather than naturally occurring surface water. Thus the operation of a pilot modified-bubble DAF plant at a WSP would have the benefit of increased exposure to algae and cyanobacteria as well as testing of waters suggested to be suitable for process effectiveness. It was therefore decided to commission a pilot DAF plant on site at a WSP for modified-bubble DAF testing. The WSP at the Bolivar WWTP was selected for this purpose.

The WSPs at the Bolivar WWTP (Adelaide, Australia) feed the St Kilda dissolved air flotation/filtration (DAF/F) plant, treating up to 120 ML day⁻¹. Recycled water from the DAF/F plant is used for a range of applications, including horticultural irrigation in the Virginia Pipeline Scheme, irrigation of gardens/parks, and car washing/toilet flushing in the Mawson Lakes Reclaimed Water Scheme (Rinck-Pfeiffer 2007). During algae and cyanobacteria blooms at the Bolivar WSPs, cell concentrations can reach greater than 1 million cells mL⁻¹ and are typically rich in *Microcystis flos aquae* (Buisine and Oemcke 2003). Ideal conditions for algal blooms often coincide with periods of high product demand, typically in warmer, sunnier times of year. Such conditions impose increased peak loads on the DAF/F plant operation, both in terms of greater throughput and overall contaminant loads, resulting in increased chemical usage during these periods. Thus the application of a pilot DAF plant during a bloom would be ideal to assess process performance and facilitate optimisation studies of modified-bubble DAF. The typical approach to optimising coagulant dosing at DAF plants is by operator experience and laboratory jar testing. DAF jar testing is often used to indicate the appropriate chemical dosing to be used at full-scale operation (Montgomery 2005); however, it is an offline tool. In real time, indicators that are used to determine if there are changes in the coagulant demand include influent turbidity and operator experience. By installing the pilot DAF plant adjacent to the St Kilda DAF/F plant, its conventional operation can be benchmarked against the full scale plant and, furthermore, there is a high probability of high algae loading during trial periods.

In optimising DAF, effective coagulation and flocculation (C-F) is critical. Currently, the St Kilda DAF/F plant doses aluminium sulphate to achieve turbidity targets within a pH range (6.5 - 8.5) and adds a fixed dose of flocculant aid. However, as C-F is dependant on making influent particle surface charge less negative (discussed in Chapter 2), the use of a charge measurement has potential to automate coagulant demand. This has been investigationed by numerous authors (Adgar et al. 2005, Bernhardt and Schell 1993, Byun et al. 2007, Henderson et al. 2008d, Mayer 2007, Morfesis et al. 2009, Sharp et al. 2005, Sharp et al. 2006b). In practice, the nature of the DAF plant influent water can greatly impact the effectiveness of the measurement in determining coagulant dose. Charge neutralisation is often not required for effective C-F, attributed to non-electrostatic forces for organic matter, enhancing flocculation (Sharp et al. 2005). With different concentrations and types of organic matter, the zeta potential at which effective C-F occurs varies between water sources. When using C-F, the charge of amorphous hydroxide precipitates and dissolved species of hydrolysing metal coagulant vary with pH (Duan and Gregory 2003, Palmer and Wesolowski 1992). By maintaining a constant pH value during coagulation, the dose of cations may be more predictable, facilitating coagulation monitoring via charge measurements.

Hence, in this research, a custom built pilot DAF plant was constructed, installed and commissioned for operation at the Bolivar WWTP. The experiments described in this chapter were a precursor to modified-bubble DAF experiments which are described in Chapter 5.2. It was determined to be necessary to initially compare the performance of the pilot-scale DAF plant versus the full-scale plant. Furthermore, the pilot DAF plant was also used to assess the optimal C-F operating conditions at the St Kilda DAF/F to ensure that fully optimised conditions were compared against modified-bubble DAF (Chapter 5.2). This therefore enabled investigation of the potential to optimise current operations at the St Kilda DAF/F plant at the Bolivar WWTP. Finally, courtesy of BTG Australia, an online charge demand analyser was installed at the pilot plant to monitor charge and therefore examine the potential for using charge measurements as a method of coagulation control. Hence, overall, the objectives of this chapter were to: a) establish the operation of the pilot DAF plant using standard St Kilda DAF/F operating

protocol and compare the performance of the two plants; b) investigate the performance of pH regulated coagulation of aluminium sulphate in DAF for clarification of Bolivar WSP effluent; c) investigate the use of cationic polymer to assess its ability to improve process performance; and, d) investigate charge demand analysis as a potential tool for automating C-F at the St Kilda DAF/F plant.

5.1.2 Materials and Methods

5.1.2.1 Treatment Chemicals

Aluminium sulphate (Orica, Australia) and a low molecular weight polyDADMAC (LT510, BASF, Australia, nominal manufacturer molecular weight = 500 kDa) were diluted with distilled water to 1.6 mg mL⁻¹ as Al (20 mg mL⁻¹ as Al₂(SO₄)₃·18H₂O) and 1 mg L⁻¹, respectively, prior to use. In all instances in this chapter, doses of aluminium sulphate are quoted as aluminium (Al) equivalent. For pH correction, 10% w/w solutions of sodium hydroxide (Recochem Inc., Australia) and hydrochloric acid (Recochem Inc., Australia) were used.

5.1.2.2 WSP Effluent

The Bolivar WSPs are located north of Adelaide, SA, Australia, and consist of three ponds in series, with a total residence time of 14 days (Figure 5.1-1). The WSPs are fed with clarified effluent from activated sludge reactors (ASRs), treating municipal wastewater from Adelaide city. With nutrient rich conditions, the WSPs are often subject to seasonal algae and cyanobacteria blooms, typically occurring between October and May. This, makes the site ideal for the investigation of algae and cyanobacteria laden water treatment. The installation of the pilot DAF plant conducted in January 2011 with operation of the plant commencing in mid-February. Optimisation tests then took place at the start of March. All tests were concluded in early April 2011, such that pilot plant operation was conducted while the WSP effluent was rich in algae and cyanobacteria.



Figure 5.1-1. Satellite image of the Bolivar WWTP, Adelaide - the ASR and DAF/F plants are indicated by red and blue boxes respectively (satellite image of Bolivar WWTP retrieved on 12-Sep-2011 from the website www.maps.google.com.au)

5.1.2.3 DAF Processes Employed

Jar Tester

Jar tests were conducted in the St Kilda DAF/F water quality laboratory using an Aztec Flotation Jar Tester (Aztec Environmental, Henley-on-Thames, UK) (Figure 5.1-2), prior to running tests at pilot-scale.

Jar tests were conducted with 1L of DAF influent water while water used for the recycle stream was obtained directly from the St Kilda DAF/F saturators. Rapid mixing was conducted for 60 seconds at 300 rpm, during which time the coagulant was added at doses of between 3 to 12 mg L^{-1} as Al and the pH was adjusted to the desired pH as monitored by a pH210 Microprocessor pH Meter (Hanna Instruments, Australia). The samples were then flocculated for 10 minutes at 30 rpm, followed by flotation for 10 minutes with a 15% recycle ratio, as per the operation of the St Kilda DAF/F plant at

the time of the tests. After flotation samples were taken for cell counting and turbidity analysis.



Figure 5.1-2. Aztec Flotation Jar Tester

Pilot DAF Plant

Pilot Plant Construction

A pilot DAF plant was constructed at the Water Research Laboratory at the University of New South Wales (UNSW) (Sydney, NSW, Australia) (Figure 5.1-3 and Figure 5.1-4). The main construction of the pilot plant consisted of an in-line rapid mixer, a single stage up-flow flocculator, flotation tank and a saturator built from marine grade aluminium by Aquagenics, Australia. These components were installed inside an insulated 20 ft shipping container with air conditioning unit such that ambient temperature could be regulated. An external sand filter was used to further polish DAF treated water, which was then collected in a balance tank to feed the saturator. The flotation loading of the pilot plant was 9.0 m h⁻¹, operating at 103 kL d⁻¹, with a hydraulic retention time of 36 minutes.



Figure 5.1-3. Photographs of the pilot DAF plant, installed at the Bolivar WSPs



Figure 5.1-4. Schematic of the pilot DAF plant

Installation

At the end of January 2011, over a three week period, the pilot DAF plant was installed on site at the Bolivar WWTP (Adelaide, SA, Australia). The pilot plant was situated in proximity to the St Kilda DAF/F plant such that feed water was obtained from the same WSP effluent channel (Figure 5.1-5). The influent water was pumped through a primary screen and into the pilot plant at 103 kL d⁻¹. Process waste and overflow was gravity fed to a near-by waste ditch.

Two additional balance tanks were installed on site to collect DAF treated water and filtered water from the plant (Figure 5.1-6). The DAF treated water was used to minimise interruptions of the filter operation, maintaining levels in the internal filtered water balance tank. The additional filtered water balance tank was used as a contingency to the internal filtered water balance tank, and for line flushing and cleaning.



Figure 5.1-5. Diagram of the pilot DAF plant layout as installed at Bolivar WWTP



Figure 5.1-6. A photograph of the two balance tanks for DAF treated water and filtered water, located outside of the pilot plant

Operation

Aluminium sulphate and polymer (LT510) were obtained from the full-scale DAF/F plant and used during coagulation-flocculation at the pilot plant where they were dosed into the pilot plant before static mixing and before flocculation, respectively (Figure 5.1-4). The pilot plant was operated for 7 hours per day. The acid or base was dosed ahead of static mixing using a pH meter-pump (Etatron, Canada), to adjust the pH to 6.5, 7.0 or 7.5. Flotation was conducted with a 15% recycle ratio, as per the operation

of the St Kilda DAF/F plant at the time. Collected float was removed hydraulically every 20 minutes. The set point for chemical dosing was established from jar testing, the day prior to commencing pilot plant tests.

Full-scale Bolivar Dissolved Air Flotation/Filtration Plant

The St Kilda DAF/F plant consisted of a rapid mixing weir, dual stage flocculators, followed by flotation over filtration, shown in Figure 5.1-7 and as a schematic, depicted in Figure 5.1-8. Aluminium sulphate was added before weir rapid mixing and LT510, before dual stage flocculation. Aluminium sulphate was used both as a coagulant and to adjust the pH of the raw water. LT510 was used as a flocculant aid at a fixed dose of 0.6 mg L⁻¹ for the course of the experiments in 2011. Flotation was conducted with a 15% recycle ratio and design loading and filtration rates of 9.0 m h⁻¹ and 9.9 m h⁻¹, respectively (Buisine and Oemcke 2003). The filtration media consisted of sand and anthracite. The treated water quality requirements during the study were: DAF treated water turbidity less than 2 NTU, process product pH in the range 6.5-8.5 and pathogens (*Cryptosporidium* oocysts) less than 1 mL⁻¹.



Figure 5.1-7. Photographs of the (A) rapid mixing weir, (B) flocculators and (C) flotation tank



Figure 5.1-8. Schematic of the St Kilda DAF/F plant

5.1.2.4 Sample Analysis

Jar Tests

Upon the completion of a jar test, sample lines were flushed with 2 mL of DAF jar testing treated water, ahead of sample collection. Using 350 mL collection bottles, 200 mL samples were collected in for further analysis. In the laboratory, turbidity was measured with a 2100N Turbidimeter (Hach, Germany) and cell counting was conducted by microscope (Olympus, Japan) and haemocytometer. All measurements were conducted in triplicate or greater.

Pilot DAF Plant Tests

For each parameter adjustment made, the pilot plant was operated for 2.5 hydraulic retention times (1.5 hours) before measurements and samples were taken. Turbidity and charge demand were recorded as 5 minute averages and samples taken for algae cell counting, conducted in triplicate. Pilot plant DAF treated water was monitored using an online Low Range Turbidimeter (AquaClear, Thermofisher Scientific, Australia), which was taken offline when required to measure grab samples of influent water turbidity. Online charge demand analysis (CDA) was conducted with a Mütek PCT-20 (BTG, Switzerland). A sample line fed the instrument such that there was a reservoir of continuous sample for the instrument to draw upon. During a measurement, a 20 mL aliquot was drawn from the reservoir and titrated with a 0.001N poly(diallyldimethyl ammonium chloride) (polyDADMAC) solution, measuring streaming current until the isoelectric point was found. This measurement in the field (Yap *et al.* 2012). Selected

samples were also subjected to zeta potential measurements were made with a Malvern Zetasizer Nano ZS (Malvern, UK) at the Water Research Centre (WRC), at UNSW, to establish the empirical relationship between zeta potential and charge demand. As with jar testing, cell counting was conducted via microscope and haemocytometer with formal algae and cyanobacteria counts and speciation data obtained from SA Water. To compare dose response results, all results obtained were normalised to an influent charge demand value of -60 μ eq L⁻¹, which represents the average influent charge demand obtained from all influent water samples points during experiments, over the course of the pilot plant operation in 2011.

Samples collected for further analysis were filtered upon collection using a 0.45 μ m polyethersulphone (PES) syringe filter (Millipore, Australia) and refrigerated. Samples were analysed by the Australian Water Quality Centre (SA Water, Adelaide) for UV-visible 254 nm measurements with a UV-vis spectrophotometer, Model 918 (GBC, Australia), and dissolved organic carbon (DOC) analysis with a total organic carbon (TOC) analyser, Model 820 (Sievers Instruments Inc., USA).

Full-Scale Operation

At the St Kilda DAF/F plant, water quality data was recorded via a Supervisory Control and Data Acquisition (SCADA) system. Turbidity and pH was recorded from online instruments installed on the plant influent line. Similarly, DAF treated water turbidity (before filtration) was measured by a continuous turbidimeter, with sample intake located above the filtration bed on a DAF/F unit.

5.1.2.5 Experiments Conducted

Experiment 1: Performance Comparison of the Pilot- and Full-Scale DAF Plants

Initially, the pilot plant was operated using the same dosing parameters applied at the full-scale plant (9.7 to 14.5 mg L^{-1} as Al with 0.6 mg L^{-1} of cationic polymer, LT510) in order to obtain a baseline that could be used to compare the performance against the full scale plant. In total, four days of data was collected from late February to early March, 2011, to compare the operation of the pilot plant with the St Kilda DAF/F plant.

Turbidity, charge demand, UV-vis and DOC of DAF influent and treated water were monitored over this period.

Experiment 2: Impact of pH Control on Process Performance

Pilot-scale DAF coagulation was conducted at pH 6.5, 7.0 and 7.5 to determine the optimal aluminium sulphate dose and pH. This experiment was conducted from early to late March, 2011. Jar testing was conducted initially to determine the appropriate dosing range. Turbidity measurements from the pilot plant were taken from continuous data for the DAF treated water and grab samples from the DAF influent. Triplicate measurements were obtained for cell counting and single samples were filtered for UV-vis and DOC analysis.

Experiment 3: Process Optimisation using Cationic Polymer

In addition to coagulation with aluminium sulphate at pH 6.5 and 7.0, cationic polymer LT510 was tested to evaluate whether its use improved DAF performance, with experiments spanning from late March to early April, 2011. Both aluminium sulphate and LT510 doses were varied to determine optimal doses. Jar testing was conducted to inform pilot plant operation as per previous tests. Turbidity, charge demand, cell counting, UV-vis and DOC samples were obtained for analysis as per Experiment 2.

Experiment 4: The Use of Charge Demand Analysis for Process Optimisation

This experiment was conducted alongside Experiments 1, 2 and 3. During pilot plant operation, the charge demand of DAF influent and treated water at the pilot plant was monitored, to assess the use of charge demand analysis (CDA) as a metric to quantify coagulation effectiveness and potential as a tool for feedback control. During Experiment 1, CDA was compared to zeta potential using DAF influent and treated water at the pilot plant. This was used to put CDA results in context of previous research using zeta potential (Henderson *et al.* 2008d, Jefferson *et al.* 2004, Sharp *et al.* 2006b). Over the duration of Experiments 1, 2 and 3, CDA was used on both the DAF influent and pre-flocculation, post rapid mixing, coagulated water to assess its use as a monitoring tool for Bolivar WSP effluent clarification.

5.1 Results

5.1.2 Influent Water Quality

Table 5.1-1 displays the WSP effluent quality over the February to March, 2011, trial period and is compared against data obtained by the operators of the full scale plant, United Water, during a previous study undertaken in 2010. The average turbidity was observed to be greater in 2011 at 41 NTU compared to 28 NTU in 2010. This was found to correspond to an elevated concentration of algae, with an average of 3.03×10^5 cells mL⁻¹ compared to 5.12×10^4 cells mL⁻¹ in 2010. The average concentration of DOC in 2011 was found to be 13.9 mg L⁻¹ with an average specific UV absorbance (SUVA) of 2.4 m⁻¹ mg⁻¹ L. The low SUVA suggests that that low DOC removals are likely to occur (Edzwald 1993b).

Dominant microbiological species present over during the pilot plant setup and the trial period were *Aphenocapsa* in January, 2011, followed by a combination of *M. aeruginosa* and *M. flos aquae* in February and March, 2011. During pilot plant operation, *Microcystis sp.* dominated the algae population comprising of up to 99.6% of the cells counted. The full breakdown of major species detected can be found in Appendix 14. This contrasted with work undertaken over the same period in 2010 whereby there was no dominant species present and fewer total cells.

In terms of treatability, the average dose of aluminium sulphate was much greater in 2011 compared to 2010 with averages of 11.7 mg L⁻¹ and 5.3 mg L⁻¹, respectively. The maximum aluminium sulphate dose applied over the course of the trial period was 15.4 mg L⁻¹; however, coagulant demand at the DAF/F plant can exceed 16 mg L⁻¹ when the WSPs are subject to severe algal blooms. This did not occur over the monitoring periods of 2010 and 2011.

		Feb-Mar 2011			Jan-Mar 2010†				
	Units	Min	Max	Ave	Min	Max	Ave		
Turbidity	NTU	10	221	41	11	65	28		
Charge Demand	ìeq L-1	-93	-27	-62	-93	-28	-60		
Total Algae	cells mL-1	1.66×103	1.05×10^{6}	3.03×10 ⁵	5.52×10 ³	1.89×10^{5}	5.12×104		
Dominant species		Microcystis sp.			-				
рН		7.7	9.7	8.7	7.5	8.9	8.2		
Water temperature	°C	14.6	26.9	20.6	-	-	-		
Influent DOC	mg L-1	9.6	15.2	13.9	-	-	-		
Specific UV Absorbance	m ⁻¹ mg ⁻¹ L	2.1	4.2	2.4	-	-	-		
Aluminium sulnhate dose	$ma L^{-1} (as Al)$	64	154	117	3.6	10	53		

Table 5.1-1. DAF/F influent water analysis (and dose of aluminium sulphate) over the experiment period in 2011 compared to data obtained during 2010 and 2009, courtesy of United Water - "-" indicates measurements that were not available

† Data courtesy of United Water

The influent water quality at the St Kilda DAF/F plant was highly variable with the turbidity subject to rapid changes over the course of 24 hours. In an extreme example, the turbidity increased 800% over the course of 5 hours on the 27th of February (Figure 5.1-9). The large spikes in turbidity were attributed to varying cell populations of associated algae blooms.



Figure 5.1-9. DAF/F influent turbidity and total cell counts obtained form the SCADA system and official reccords courtesy of SA Water

The current response during plant operation to elevated turbidity events relies on operator experience and jar testing. However, in past extreme events, water treatment has been halted due to coagulant demands resulting in process pH values lower than minimum acceptable value (personal communication, Barry Walsh, DAFF Plant Manager, United Water). Over the pilot plant operation in 2011, the St Kilda DAF/F did not experience any events that jeopardised water treatment.

5.1.2.6 Experiment 1: Performance Comparison of Pilot- and Full-Scale DAF

It was found that both pilot- and full-scale plants had comparable DAF treated water turbidities at 1.0 ± 0.2 NTU and 1.5 ± 0.2 NTU, respectively, equating to average turbidity removals of $98.6\% \pm 1.5\%$ and $98.0\% \pm 2.2\%$, respectively (Figure 5.1-10). Over this monitoring period, the average dose of aluminium sulphate applied was 12.1 mg L⁻¹. The DAF treated water turbidity of the pilot plant was generally observed to be lower than that of the St Kilda DAF/F plant, with the exception of a period over the afternoon of the 2nd and the morning of the 3rd of March. This could be an artefact of both varying flow rates and thus varying loading rates and recycle ratios on the particular DAF/F unit monitored.



Figure 5.1-10. Residual turbidity for the DAF/F plant and pilot DAF plant – data was taken form 4 consecutive running days in which the plant was run during onsite working hours only

It was found that DAF treated water DOC over this period remained relatively stable at $8.1 \pm 0.3 \text{ mg L}^{-1}$, regardless of influent DOC concentrations (Figure 5.1-11). This resulted in DOC removals between 16–43% over the course of the monitoring period. Over this period, SUVA was found to be $3.4 \pm 0.5 \text{ m}^{-1} \text{ mg}^{-1} \text{ L}$ and thus removal less than 50% can be expected (Edzwald 1993b), which therefore corresponds with results obtained.



Figure 5.1-11. DAF treated water and influent concentrations of DOC during conventional DAF operation

5.1.2.7 Experiment 2: Impact of pH Control on Process Performance

Jar Testing

Jar testing using aluminium sulphate without LT510 revealed that lower DAF treated water turbidities could be obtained with coagulation carried out at pH 6.5 and 7.0 in comparison to pH 7.5 (Figure 5.1-12). Despite the deterioration of turbidity removal at lower doses, particularly at pH 7.5, cell removal remained high: greater than 90% removal for all jar tests, with no distinct trend in removal. To obtain DAF treated water turbidity removal above 95%, aluminium sulphate doses of 8.1, 9.7 and 9.7 mg L^{-1} were required for coagulation conducted at pH 6.5, 7.0 and 7.5, respectively.



Figure 5.1-12. Jar testing turbidity (shapes) and cell removal (crosses) results for various pH values

With an Al dose of 3.2 mg L⁻¹, it was observed that pH 7.5 coagulation resulted in poorer turbidity removal. Reducing the pH from 7.5 to 6.5 during coagulation resulted in a turbidity residual of 4.2 NTU or 14% improvement in turbidity removal at an alum dose of 3.2 mg L⁻¹ (Figure 5.1-12). Compared to standard operation at the full scale plant, 98% cell removal was obtained at lower doses; 9.7 mg L⁻¹ and 10.5 mg L⁻¹ for pH 6.5 and 7.0, respectively, compared to 12.1 for standard operation. Over the course of these experiments, a dose of 11.3 mg L⁻¹ at pH 6.5 and 7.0 resulted in comparable removal to that obtained in baseline tests (Experiment 1), at 98.6% \pm 0.4%. Adjusting the coagulation pH to 6.5 yielded more cationic hydrolysis products than pH 7.5 (Martin 1991) which in this case was observed to be beneficial to turbidity removal.

Pilot Plant Tests

Pilot plant observations were similar to those obtained by jar testing, such that coagulation at lower pH values resulted in more effective clarification (Figure 5.1-13). A turbidity removal of 95% or greater was obtained at an Al dose of 6.5 and 8.9 mg L⁻¹ for coagulation at pH 6.5 and 7.0, respectively. Maximum removals of 97.8% \pm 0.3% and 97.0% \pm 0.2% were obtained for pH 6.5 and 7.0, respectively, which was 0.8% to

1.6% less than that obtained during baseline tests (Experiment 1). In all tests, cell removals obtained were all in excess of 90%, again with no distinct trend in removal. Unlike coagulation at pH 6.5 and 7.0, coagulation at pH 7.5 resulted in a maximum turbidity removal of $93.5\% \pm 0.6\%$ at a dose of 8.1 mg L⁻¹.



Figure 5.1-13. Turbidity (solid shapes) and cell removal (hollow squares) of DAF treated water at various pH values from pilot plant trials – the pH values of the points without pH regulation are 8.0, 7.8, 7.6, 7.4 and 7.4 from low to high dose of aluminium sulphate

At the St Kilda DAF/F plant, the coagulation pH is governed by the concentration of aluminium sulphate used. These conditions were employed briefly at the pilot plant, whereby coagulation without acid and base to adjust pH was conducted. It was found that an Al dose of 10.5 mg L^{-1} was required to achieve turbidity removals above 95% (Figure 5.1-13). Thus to maintain turbidity targets, without regulating the pH of coagulation, 30 to 61% more aluminium sulphate would be required, compared to pH 7.5 and pH 6.5 regulated coagulation, respectively.

When observing the removal of DOC, it was found that increasing the dose of aluminium sulphate increased removal. The removal of DOC did not follow the same trends as turbidity. In tests with coagulation pH controlled to 7.5, DOC removal remained lower than for more acidic coagulation conditions; however, for all doses tested, coagulation at pH 7.0 outperformed coagulation at pH 6.5. The influent water

quality has the potential to impact DOC removal, however over the course of these experiments, SUVA remained stable at $2.4 \pm 0.1 \text{ m}^{-1} \text{ mg}^{-1} \text{ L}$. The lowest residual DOC was 8.7 mg L⁻¹ obtained at pH 7.0, with a dose of 11.3 mg L⁻¹ as Al (Figure 5.1-14). This equated to a removal of 38% which was also the highest DOC removal of all tests. The % removal of DOC was found to be comparable to that obtained in the pilot-scale/full-scale performance comparison (Section 5.1.2.6). In terms of residual DOC, coagulation at pH 7.0 resulted in slightly higher removals, with a maximum of $8.7 \pm 0.1 \text{ mg L}^{-1}$, compared to $8.1 \pm 0.3 \text{ mg L}^{-1}$, detailed in Section 5.1.2.6. From these tests it can be seen that coagulation at pH 7.5 was found to be detrimental to the removal of DOC, though increasing the dose of aluminium sulphate could lower the residual DOC. These results suggest that the optimum DOC removal was obtained when coagulating at pH 7.0, however without the use of polymer, turbidity removal was poorer than that obtained in baseline tests (Experiment 1).



Figure 5.1-14. DOC observed in the DAF treated water at pilot-scale

5.1.2.8 Experiment 3: Process Optimisation using Cationic Polymer

Jar Testing

With the addition of polymer to the jar tests, it was revealed that turbidity removal above 95% was obtained with all combinations of aluminium sulphate and LT510 investigated (Figure 5.1-15). In all cases, the cell removal remained above 90% over the dosing range tested, with no distinct trend in removal. The highest turbidity removal, 98.1 \pm 0.3%, was obtained at pH 6.5 with the highest dose of aluminium sulphate and lowest dose of LT510; 4.9 mg L⁻¹ and 0.4 mg L⁻¹, respectively (Figure 5.1-15A). This is comparable to turbidity removal obtained at full-scale, using 60% less aluminium sulphate and 33% less polymer. With LT510 concentrations of 0.6 or 0.8 mg L⁻¹, 3.2 mg L⁻¹ as Al was found to result in better turbidity removal than higher or lower doses at pH 6.5. Increased residual turbidity at higher coagulant doses indicated charge overdose. This also occurred at lower doses, indicating a coagulant under-dose. This demonstrates that an optimal dosing point was obtained in this set of experiments.



Figure 5.1-15. Jar testing dose response of combinations of aluminium sulphate (as Al) and LT510 for (A) pH 6.5 and (B) pH 7.0 - average error on all tar testing results is 0.4%

For jar tests at pH 7.0, the same LT510 dosing range was used as tests at pH 6.5 and the dosing range for Al was increased to 3.2-6.5 mg L⁻¹ from 1.6-4.9 mg L⁻¹ for pH 6.5 tests (Figure 5.1-15B). Within this elevated aluminium sulphate dosing range, coagulation at pH 7.0 resulted in similar overall DAF treated water turbidities for all tests, averaging 97.1% \pm 0.8% removal in comparison to 97.0% \pm 0.9% removal at pH 6.5. At an Al dose of 6.5 mg L⁻¹ and an LT510 dose of 0.6 mg L⁻¹ the optimal dosing point was found, resulting in a turbidity removal of 98% \pm 0.6%. Upon increasing or decreasing the dose of LT510 from the optimum level, the DAF treated water turbidity was observed to deteriorate.

At both pH 6.5 and pH 7.0 and at the concentrations of aluminium sulphate used in these jar tests, it is likely that sweep flocculation is the dominant coagulation mechanism (Amirtharajah and Mills 1982). Deterioration in the jar tests are therefore due to insufficient treatment chemical or polymer overdosing, the latter resulting in particle restabilisation in the bulk solution. Overall, the addition of LT510 to the jar tests improved the removal of turbidity for the same aluminium sulphate dosing range.

Pilot Plant Tests

Similar to observations in jar testing, the turbidity of the DAF treated water using both aluminium sulphate and LT510 to treat the water was observed to be much lower than when using aluminium sulphate alone. Cell removal in all cases was again found not to have a distinct trend, remaining above 90% for all tests. Turbidity removal from pilot plant tests was observed to be poorer than those obtained in jar tests, with average treated water of 95.2% \pm 2.2% and 96.6% \pm 1.3% for the whole range of tests carried out at pH 6.5 and 7.0, respectively (Figure 5.1-16). At both pH ranges, the greatest dose of aluminium sulphate and LT510 was required to obtain the greatest turbidity removal. Explicitly, 4.9 mg L^{-1} Al and 0.8 mg L^{-1} LT510 at pH 6.5; and 6.5 mg L^{-1} Al and 0.8 mg L^{-1} LT510 at pH 7.0. This resulted in turbidity removals of 97.5% ± 0.9% and 98.2% ± 0.4%, respectively. In these tests, the addition of LT510 to flocculation in DAF reduced the consumption of aluminium sulphate, as observed previous research (Bolto et al. 2001). The turbidity removal of DAF with pH regulated coagulation remained 0.4% to 1.1% lower than baseline tests (Experiment 1). Coagulation using the greatest concentration of aluminium sulphate in these tests yielded results comparable to baseline tests (Experiment 1) with a 43% reduction of aluminium sulphate used. This
indicates that the regulation of pH during coagulation at the full-scale plant can result in much less coagulant consumption.



Figure 5.1-16. Pilot plant dose response of combinations of aluminium sulphate and LT510 for (A) pH 6.5 and (B) pH 7.0 - average error on all results in this figure is 0.3%

There was no apparent improvement of DOC removal attributed the addition of LT510 from Experiment 2 results. Little variation in the residual DOC was observed between the tests conducted at pH 7.0 and 6.5, with averages of 11.4 ± 0.4 and 11.1 ± 0.9 mg L⁻¹, respectively (Figure 5.1-17). The average DOC removal that was obtained in these tests was 9% \pm 5% at pH 7.0 and 6% \pm 2% at pH 6.5. Over this period, influent DOC concentration did not vary drastically with an average of 13.0 ± 0.9 mg L⁻¹ and SUVA 2.5 ± 0.4 m⁻¹ mg⁻¹ L. With these values, a maximum removal of 30% would be expected (Edzwald 1993b), therefore all residual DOC would be expected to be above 9.1 mg L⁻¹. From extrapolating residual DOC results from Experiment 2, residual DOC would be expected to be 11.9 to 12.6 mg L⁻¹ and 9.2 to 9.5 mg L⁻¹ for coagulation at pH



6.5 and 7.0, respectively. This suggests that the process out performed expectations at pH 6.5 and underperformed at pH 7.0.

Figure 5.1-17. Removal of DOC by flotation at (A) pH 6.5 and (B) 7.0 using combinations of aluminium sulphate and LT510 - average standard deviation on all measurements was 0.1 mg L^{-1}

With these results, it can be seen that the addition of polymer can significantly improve the performance of aluminium sulphate in C-F, upstream of DAF. By regulating the pH to more acidic values, the performance of aluminium sulphate can be improved in regard to turbidity removal. However, to achieve higher removal of DOC, much greater doses of aluminium sulphate would be required, particularly in the absence of further treatment methods such as the addition of activated carbon.

5.1.2.9 Experiment 4: The Use of Charge Demand Analysis for Process Optimisation

Charge as a Process Monitoring Tool during Standard Operation

Over the monitoring period for standard site operation, a decrease in the anionic charge was consistently observed between influent water and coagulated water. The charge demand of water before and after aluminium sulphate addition was found to be -79 ± 8 and $-46 \pm 6 \times 10^{-3}$ meq L⁻¹, respectively (Figure 5.1-18). On the 1st, 2nd and 3rd of March, DAF influent was found to have a greater anionic charge later in the day. This was mirrored in the aluminium sulphate dosed water charge density, with less negative charge demand in the morning than the afternoon (Figure 5.1-18). Similar trends were observed in 2010 at the full-scale DAF/F plant (Appendix 15, and described in Yap *et al.* (2012)). From monitoring the charge demand at full scale, 24 hour measurements indicated that the fluctuations represented a diurnal trend. For both full-scale and pilot-scale operation, the anionic charge demand was decreased to an average coagulant dosed value of -46 to -40×10^{-3} meq L⁻¹. With this range, it may be possible to use a charge demand set point for feedback control over the coagulation stage.



Figure 5.1-18. Charge demand of raw water and aluminium sulphate coagulated water over a 4 day monitoring period, during conventional DAF operation in 2011 - chemical dosing rates were determined by the full-scale operation

From measuring both the zeta potential and charge demand for samples collected during Experiment 1, zeta potential was found to be correlated with charge demand (Figure 5.1-19). A simple linear correlation was established with an R^2 value of 0.64. This is not unexpected as the zeta potential indirectly reflects charged sites on a particle or colloid surface (Fuerstenau and Pradip 2005). As these measurements represent different manifestations resulting from the presence of charged groups, this correlation cannot be used universally across all water types; however, the correlation developed here can be used to compare the zeta potential for this particular system. Over the duration of Experiment 1, it was found that the average charge demand in the DAF treated water was $-46 \times 10^{-3} \pm 5 \times 10^{-3}$ meq L⁻¹. Using the correlation, this equates to a zeta potential of -15 ± 3 mV. To put this into context, a survey of 12 UK water treatment plants showed that typical operational zeta potentials were from -15 to -10 mV, though zeta potentials as negative as -22 mV has been reported to result in low treated water turbidities (Jefferson et al. 2004, Sharp et al. 2005). Therefore, over this monitoring period, charge demand analysis can be used as an analogue for zeta potential, and furthermore, optimal charge ranges can be determined.



Figure 5.1-19. Charge density versus zeta potential for a collection of samples over a short sampling period

Charge as a Process Monitoring Tool with pH Control

During pilot plant tests with pH regulated coagulation (Experiment 2), linear dose response trends could be observed for low coagulant doses (Figure 5.1-20). At coagulant doses in which DAF treated water turbidities were below 95%, the charge demand was found to be more positive than -45×10^{-3} meq L⁻¹, or -15 mV (Figure 5.1-20). This result is in agreement with those obtained from Experiment 1 (Section 5.1.2.6). During coagulation at pH 7.0, 7.5 and without pH regulation, higher doses of coagulant resulted in a stabilised charge demand. In contrast, when the coagulation pH was maintained at 6.5, charge density showed a near linear dose response over the dose range examined.



Figure 5.1-20. Charge demand of chemically treated water in aluminium sulphate only dosing tests - error for the online charge measurement was found to be 2×10^{-3} meq L^{-1} determined from continuous measurement

As coagulation at pH 6.5 contains more cationic products than other coagulation conditions used in this research (Duan and Gregory 2003), it is understandable why the effect on the charge demand is more apparent. Thus at pH 6.5, charge demand set points can be used to alter aluminium sulphate dose, critical for dose automation. From tests at other pH values, the stabilisation of charge demand that occurs at higher doses

of aluminium sulphate limits its capability for process automation. This would not allow such fine adjustments in the charge demand.

With the addition of LT510 in Experiment 3, decreases similar to Experiment 2 in charge demand were observed for lower doses of LT510 (Figure 5.1-21). The greatest reduction of anionic charge occurred at the highest doses of aluminium sulphate and lowest doses of LT510; specifically, 4.9 mg L⁻¹ and 0.4 mg L⁻¹ as Al and LT510, respectively, at pH 6.5 and 6.5 mg L⁻¹ and 0.4 mg L⁻¹ as Al and LT510, respectively, at pH 7.0. Using 0.8 mg L⁻¹ of LT510 under both pH conditions resulted in less sensitive charge demand dose responses. This is surprising as the charge density of LT510 is insensitive to pH, with a theoretical value of 6.19 meq g⁻¹ (Bolto 1995).



Figure 5.1-21. Charge demand of chemically treated water after LT510 and aluminium sulphate doses at (A) pH 6.5 and (B) pH 7.0 - error for the online charge measurement was found to be 2×10^{-3} meq L⁻¹ determined from continuous measurement (note: aluminium sulphate axis is in reverse for clarity of the data)

5.1.3 Discussion

5.1.3.1 pH Regulation and the Removal of Turbidity and DOC

As evident in Experiment 2, decreasing the pH of coagulation was beneficial for the removal of turbidity with DAF treatment of WSP effluent. With lower pH, the concentration of cationic hydrolysis products increases (Amirtharajah and Mills 1982, Duan and Gregory 2003). This indicates that more effective coagulation for DAF can be achieved with a greater concentration of cations. This was further demonstrated in Experiment 3, in which cations were added via the use of cationic polymer, resulting in a further decrease of coagulant demand. With algae and cyanobacteria WSP effluent making up the DAF influent water, turbidity has historically been caused largely by the presence of cells in water (Buisine and Oemcke 2003). This was confirmed in 2013, with a correlation occurring between turbidity and cell concentration (Appendix 18). By closely controlling the addition of cationic components in C-F, the removal of algae and cyanobacteria can be optimised (Henderson et al. 2008d). For other turbidity causing particles, such as kaolin, removal is more effective under more basic, sweep flocculation coagulation conditions (Duan and Gregory 2003). This implies that the effective removal of algae and cyanobacteria contributes significantly to the observed reductions in turbitity for the treatment of WSP effluent.

In this research, DAF with coagulation at pH 7.0 resulted in lower DOC in the treated water than at pH 6.5 or 7.5. This is surprising as DOC removal is typically dependant on complexation reactions between dissolved hydrolysed metal species that tend to dominate at lower pH values; hence, it would have been expected that lower pH result would result in better DOC removal (Edwards 1997). Over this period, the DAF influent SUVA was found to fluctuate, indicative of the variable nature of the WSP effluent. It is important to note that the site water quality was subject to a number of factors, including WWTP feed character, and therefore the DOC removal may be an artefact of changes in the WSP effluent character. Over this period, no correlation could be made between SUVA and DOC removal. To optimise the treatment to remove DOC, longer term studies would be required.

5.1.3.2 The Use of Charge Demand for Treating WSP Effluent

Over the course of the initial monitoring period (Experiment 1) and previous work conducted by United Water (Yap et al. 2012), charge demands from -46 to -40×10^{-3} meq L^{-1} were identified as a good minimum operating set point for coagulation in DAF. Using a set point from a coagulated water measurement is particularly beneficial during periods of rapid influent water quality changes. Currently, the most rapid indicator of changes in the coagulant demand is turbidity of the influent water. Jar testing can also be applied to determine appropriate coagulant dose; however, these tests require an experienced operator and time (usually 20-30 minutes). In extreme cases at the St Kilda DAF/F plant, influent water quality can change over the time taken to complete a jar test. With an additional metric to assess coagulation, the reliance on operator experience and jar tests can be reduced. Furthermore, a variable coagulant dose from an automated measurement has the potential to reduce chemical consumption. The fluctuations in the treated water charge demand is an indicator of periodic coagulant over dosing. For example, on the 28th of February, a coagulated water charge demand of -51×10^{-3} meg L⁻¹ resulted in the same treatment outcomes as a charge demand of -43 $\times 10^{-3}$ meq L⁻¹ earlier in the day. If contaminant removal is dependent on the coagulated water charge demand, it may be possible to automate the coagulant dose to reduce periods of overdosing. From other research, there is evidence that effective water treatment occurs within a specific coagulated water charge range: Jefferson et al. (2004) surveyed 12 treatment plants in the UK and found that typical coagulation zeta potentials were between -15 and -10 mV, with a recommended zeta potentials range of -10 to 0 mV. From measurements at the pilot plant, this equates to charge demand values of -37×10^{-3} meg L⁻¹ to 0×10^{-3} meg L⁻¹.

To achieve full automation of coagulation using charge demand analysis, a linear dose response curve should be able to be generated. Explicitly, with an increase in coagulant dose, anionic charge demand should decrease at all operational coagulant doses. Results from Experiment 2 suggest that full automation using charge demand analysis could be achieved at pH 6.5. However, ideal contaminant removal may be dependant on the hydrolysis products at more basic pH values. This was demonstrated in Experiment 2, in which coagulation at pH 7.0 outperformed coagulation at both pH 6.5 and 7.5 in regards to removing DOC. Without a linear dose response curve, the use of charge demand analysis is best suited to detecting periods of under-dosing, as a security

measure. The detection of poor coagulation conditions can minimise non-productive time.

Aside from the use of charge demand, other commercially available charge detectors have been tested at the St Kilda DAF/F plant: Yap *et al.* (2012) compared the use of a charge demand analyser to streaming current detectors as charge measurements for influent and coagulated water and found that streaming current instruments were prone to fouling. The success of the charge demand analyser was attributed to the advanced automated cleaning system that the instrument employed. However, all instruments used required the movement of fluid with coagulated particles around a piston (Yap *et al.* 2012). The application of zeta potential for the clarification of water is currently well established (Henderson *et al.* 2008d, Jefferson *et al.* 2004, Sharp *et al.* 2005, Sharp *et al.* 2006a); however, the application of an online zeta potential measuring system for regulating C-F has yet to be reported in the literature.

5.1.3.3 Control in Contaminant Removal

As algae and cyanobacteria have low densities, the use of DAF to remove cells has been demonstrated to be more effective than sedimentation on numerous accounts (Gregory 2010, Henderson *et al.* 2008c, Teixeira and Rosa 2006). In this present research, the removal of cells in all cases was found to be greater than 90%, regardless of the removal of other contaminants. This is the most obvious in coagulation with aluminium sulphate and without LT510, whereby the removal of turbidity could be reduced with little effect on the removal of algae cells. Furthermore, at pH 7.5, the removal of DOC was found to be the lowest, yielding a float layer further enriched with algae cells. This demonstrates that the process can be applied for the collection of biomass, potentially improving downstream sludge digestion by reducing aluminium products in the sludge.

With occurrence of seasonal algae blooms, applying a system to selectively remove algae cells ahead of water clarification can have two benefits: 1) A biomass rich sludge can be recovered and 2) the loading of the clarification plant is reduced. The drawbacks of applying aluminium sulphate are that the actual consumption of chemicals is not reduced and metal coagulant remains in the sludge. The use of modified-bubble DAF for this application is ideal. As detailed in Chapter 4, modified-bubble DAF has comparatively low chemical consumption and can treat water without altering pH or charge. By operating and optimising the pilot DAF plant onsite at Bolivar WWTP, a clarification target has been established for comparison to modified-bubble DAF.

5.1.4 Summary

The principal finding of this phase of the investigation were:

- 1) A dissolved air flotation pilot plant was successfully constructed and commissioned at the Bolivar WSPs.
- 2) The operation of the pilot plant was found to be comparable to the full-scale DAF/F plant onsite with an average turbidity removal of 98.6% (Experiment 1).
- 3) Within the pilot plant, the consumption of aluminium sulphate can be reduced by adjusting the pH to more acidic values (Experiment 2):
 - a) A maximum turbidity removal of 98.6% was obtained, matching that of Experiment 1, with all cell removals remaining above 90% with no distinct trend.
 - b) Selective removal of cells from the WSP effluent it was found to be possible: With low doses of aluminium sulphate at low pH values, less DOC and turbidity causing compounds were removed.
- Within the pilot plant, the use of polymer with pH regulation enabled enhanced coagulation (Experiment 3):
 - a) Compared to Experiment 2, lower doses of aluminium sulphate could be used while retaining high turbidity removal, reaching a maximum of 98.2%.
 - b) DOC and charge demand was not impacted significantly by polymer dosing.
- 5) The use of an online charge demand analyser could be beneficial at the St Kilda DAF/F plant (Experiment 4):
 - a) Coagulation with current on-site operation was found to result in an average charge density -46×10^{-3} meq L⁻¹ over this period, indicating a charge set point that can be used for automation.

- b) At pH 6.5, a linear dose response curve for charge demand, ideal for process automation.
- 6) A turbidity removal of 98.6% and a cell removal of >90% is the standard treatment goals for future modified-bubble DAF work. Within the pilot plant, residual DOC ranged from 16 to 45% in these tests with effective removal dependant on the presence of aluminium sulphate.

5.2 THE TREATMENT OF WASTE STABILISATION POND EFFLUENT WITH MODIFIED-BUBBLE DISSOLVED AIR FLOTATION

5.2.1 Introduction

Conventional DAF remains highly dependent on effective coagulation and flocculation (C-F) for elevated contaminant removal (Edzwald 2010). C-F can be difficult to control when influent water quality fluctuates rapidly, such as during an algal bloom, although it is possible that charge monitoring can be used to determine appropriate coagulant doses on-line, as demonstrated in Chapter 5.1. With appropriate charge neutralisation, bubble-particle interactions can be optimised to result in effective flotation (Haarhoff and Edzwald 2004). However, as an alternate approach, polymers can be used to modify bubble surfaces in dissolved air flotation (DAF). This was demonstrated firstly by Malley (1995), followed by Henderson *et al.* (2010b) and then in this study as reported in Chapter 4 using in jar tests. However, up to now, investigation of this process has not progressed past laboratory scale tests.

The effective removal of *Microcystis aeruginosa* cells from water using modifiedbubble DAF was demonstrated in Chapter 4.1 and by Henderson *et al.* (2010b). The influence of the influence of algogenic organic matter (AOM) on modified-bubble DAF was further explored in Chapter 4.2, in which the process success was found to be enhanced by AOM, particularly that from CS-564/01, originally tested in Chapter 4.1. This strain was found to have been isolated from a waste stabilisation pond (WSP) (Bolch and Blackburn 1996), suggesting that a WSP may host algae with similar characteristics that also enhance the performance of modified-bubble DAF.

To further research on modified-bubble DAF from Chapter 4, tests on environmentally relevant samples at pilot scale are required as fundamental differences exist between bench-scale jar tests and pilot-scale tests, discussed in Chapter 5.1 and demonstrated by Lundh *et al.* (2002). With the construction of a pilot DAF plant that is comparable in operation to a full-scale facility (Chapter 5.1), modified-bubble DAF can be applied on environmentally relevant water whilst using a process indicative operation performance

at full scale. With the pilot DAF plant installed onsite at the Bolivar WWTP in 2011 to obtain feed water from the WSPs, the plant was recommissioned for further use in 2013. Reconfiguration of the pilot DAF plant to apply modified-bubbles in DAF requires simple readjustment of dosing lines and appropriate polymer solutions.

In Chapter 3, hydrophobically-associating polymers were synthesised for attachment to a bubble surface. Upon testing the polymers samples in modified-bubble DAF using a jar tester in Chapter 4, it was found that polymer sample H33 was the best performing polymer for modified bubble-flotation. Jar tests with H33 resulted in the most negative modified-bubble DAF treated water zeta potential, indicative of low concentrations of residual cationic polymer in comparison to other polymers tested. PolyDADMAC was used to compare the success of synthesised polymers in bubble modification, given the success in previous research (Henderson et al. 2010b, Malley 1995), and thus both polyDADMAC and H33 were identified for pilot-scale studies. To do this, a large batch of polyDADMAC could be obtained from a supplier however, it was necessary to scale-up production of H33 to provide sufficient polymer. Pilot plant operation was conducted from February to April of 2013, with initial conventional operation to reassess the performance of the pilot plant. The specific aims of this chapter were to a) assess modified-bubble DAF at bench-scale using environmentally relevant water, b) determine the feasibility of applying modified-bubble DAF for treating WSP effluent and c) compare the performance of polyDADMAC and H33 in pilot-scale modifiedbubble DAF.

5.2.2 Materials and Methods

5.2.2.1 WSP Effluent

The Bolivar WSPs are part of a wastewater treatment plant, treating municipal wastewater from Adelaide, SA, Australia, using activated sludge reactors (ASRs). Secondary effluent is further treated using waste stabilisation ponds WSPs with a residence time of 14 days. From a WSP effluent channel, water is passed through a primary screen and fed into the St Kilda DAF/F plant. The WSP effluent used for jar tests was obtained at a sample point located past the primary screen. For pilot plant

tests, WSP effluent was passed through an independent primary screen at the location of the pilot plant.

5.2.2.2 WSP Effluent Matrix for Preliminary Jar Testing

WSP effluent was shipped to the University of New South Wales via overnight shipment for preliminary testing via jar tests. To obtain a background WSP matrix, unwanted cells and other particulate contaminants were removed via filtration with a 100 μ m nylon mesh (SEFAR, Australia), followed by a GF-C glass microfiber filter (Whatman, USA) and finally with a 0.45 μ m filter (Millipore, USA). The filtration of WSP effluent was conducted within 2 days of collection and stored at 4°C for use within 5 days of filtration.

5.2.2.3 Microcystis aeruginosa for Preliminary Jar Testing

As per Chapter 4, *M. aeruginosa* strains CS-564/01 and CS-555/01 were obtained from the Commonwealth Scientific and Industrial Research Organisation (CSIRO) Australian National Algae Culture Collection (ANACC), Hobart, Australia. The strains of *M. aeruginosa* were recultured in MLA media (Bolch and Blackburn 1996) for use as a model contaminant. As per Chapter 4, cultures were subject to a 16/8 hour light/dark cycle, with temperature controlled to 21°C, in a 500 L, PG50 incubator with a photosynthetic photon flux output of $600 \pm 60 \mu mol m^{-2} s^{-1}$ (Labec, Australia). Cultures were grown in 100 mL batches in 250 mL conical flasks and were observed to be unicellular cultures. For jar testing, cultures were harvested at the end of the exponential growth phase, occurring after 10 to 12 days of growth.

5.2.2.4 Polymers

Low molecular weight polyDADMAC (Sigma Aldrich, Australia) was first diluted to 5% by weight in Milli-Q (18.2 M Ω ·cm) water before use in jar testing and distilled water before use at pilot scale. The polymer charge density was found to be 6.82 meq g⁻¹, as determined by charge demand analysis with a Mütek PCD-04 laboratory charge demand analyser (BTG, Australia), described in full in Chapter 3.

A total of 500 g of H33 was synthesised in bulk using the procedure described in Chapter 3, at 10 times the scale, with changes to the quaternisation procedure: 2-(N,N-

dimethylamino)ethyl methacrylate monomer (Sigma Aldrich, Australia) was purified by passing it though a basic alumina column. Following purification, 100 g of monomer was added to a 500 mL vial. The sample temperature was lowered to 0°C before 328 mg of azobisisobutyronitrile was added to the vial. While at 0°C, the reaction mixture was then purged with nitrogen for 45 minutes to remove dissolved oxygen. The mixture was then placed in an oil bath at 65°C for 12 hours and left to react. The resultant polymer was then dissolved into methanol, without purification, such that the final volume was 1 L before mixing 1.5 mL of 1-bromodecane (Sigma Aldrich, Australia) and allowed to react at room temperature for 3 days. Samples were dried by exposure to air before placing in a vacuum oven at 40°C for 24 hours. The resulting polymer was dissolved into distilled water to result in a 5% by weight polymer solution for use in the pilot plant. The charge density of the polymer was found to be 2.97 meq g⁻¹, using charge demand analysis as described in Chapter 3.

In later tests, the charge demand of H33 was manipulated by acidification. For this experiment 1 L of 5% w/w H33 solution was mixed with 35 mL if 10% w/w HCl to protonate any unreacted DMAEMA groups. After acidification, the charge density of H33 increased from 2.97 meq g⁻¹ to 3.48 meq g⁻¹.

5.2.2.5 Jar Testing

DAF Influent Water Characterisation

In October 2012, effluent from the Bolivar WSPs, and saturator feed from the St Kilda DAF/F plant was collected and sent to the Water Research Centre (WRC) at the University of New South Wales (UNSW) for jar testing. WSP matrix was prepared as per Section 5.2.2.2. WSP matrix was subject to analysis including dissolved organic carbon (DOC) analysis with a total organic carbon (TOC) analyser, model TOC–Vsch (Shimadzu, Japan), zeta potential analysis with a Zetasizer Nano ZS (Malvern, UK) and charge demand analysis with a Mütek PCD-04 laboratory charge demand analyser (BTG, Australia). For jar tests, cultured *M. aeruginosa* cells were diluted to 7.5×10^5 cells mL⁻¹ with WSP matrix and counted by haemocytometer and light microscope (Leica Microsystems Ltd, Australia).

Modified Bubble DAF Jar Tests

Modified-bubble DAF jar testing was conducted using both polyDADMAC and synthesised polymer H33, primarily to establish the dosing range required during pilot scale experiments. A DAF Batch Tester, Model DBT6 (EC Engineering, Canada) was used, with procedures as described in Chapter 4, Section 4.2.2.6. Saturator feed water obtained from the St Kilda DAF/F plant at Bolivar WWTP was used in the jar tester saturator. All solutions were adjusted to pH 7 using 1 M HCl and 1 M NaOH prior to Aliquots of saturator feed water were dosed with polymer up to a jar testing. concentration of 300×10^{-3} meg L⁻¹ (or 30 mg L⁻¹) and added to the saturator before pressurisation. Both polyDADMAC and H33 were used as bubble modifiers in jar testing. Industrial grade air was used to pressurise the saturator to 450 kPa. A recycle ratio of 20% was used for all tests. After a 10 minute flotation period, a 50 mL sample was collected. Residual analysis from jar testing included cell counting using a haemocytometer or Sedgwick Rafter counting chamber and a DM500 light microscope (Leica Microsystems Ltd, Australia), and zeta potential analysis using a Zetasizer Nano ZS (Malvern, UK) with each analysis was conducted in triplicate.

AOM Aided Modified-Bubble DAF Jar Tests

As results from Chapter 4.2 suggested that AOM from CS-564/01 could be used to enhance cell removal of CS-555/01 in modified-bubble flotation, the same experiment was repeated in WSP matrix. This experiment was conducted with the method described in Chapter 4.2, with a variation in the polymer dose used. Briefly, CS-555/01 cells were combined with CS-564/01 AOM in WSP matrix. The solution was corrected to pH 7 and mixed at 50 rpm for 60 seconds ahead of flotation for 10 minutes with a recycle ratio of 20%, applying a polyDADMAC dose of 40×10^{-3} meq L⁻¹. This dose was selected as the highest cell removal for CS-555/01 was obtained at this point in prior experiments. After flotation, a sample was collected for cell counting and zeta potential measurements.

5.2.2.6 Influent Water and Conventional DAF at the Bolivar WSPs

Pilot DAF Plant Influent Water Characterisation

Water turbidity data at the St Kilda DAF/F plant was recorded via a Supervisory Control and Data Acquisition (SCADA) system for DAF influent and unfiltered treated water. Measurements were made with continuous turbidimeters located on the plant influent line and sample line located above the filtration bed on a DAF/F unit. Over the course of the pilot plant operation, samples were obtained yielding results for DOC measured with a TOC analyser, Model 820 (Sievers Instruments Inc., USA). Algae and cyanobacteria counts and speciation data were obtained from SA Water.

Performance Comparison of the Pilot- and Full-Scale DAF Plants

Conventional operation of the DAF pilot plant was carried out as per Chapter 5.1. Briefly, aluminium sulphate (Orica, Australia) and cationic polymer LT510 (BASF, Australia) were obtained from the St Kilda DAF/F plant and used for chemical pretreatment at the pilot plant. The aluminium sulphate and LT510 were dosed into the influent before static mixing and before flocculation respectively. Flotation was conducted using a 15% recycle ratio as per the full scale plant at the time of operation (mid to late February, 2013). Turbidity monitoring of the pilot plant DAF treated water was conducted with a Low Range Turbidimeter (AquaClear, Thermofisher Scientific, Australia) for comparison to the St Kilda DAF/F plant, acquired from the SCADA system.

5.2.2.7 Pilot-Scale Modified-Bubble DAF

Modified-Bubble DAF at Pilot-Scale

The DAF pilot plant described in Chapter 5.1 was reconfigured such that modified bubbles could be generated by dosing polymer into the saturator. To conduct modified bubble tests, flow was diverted past the flocculator with no chemical pre-treatment. A separation baffle was inserted to prevent free flow of process water from the raw water source to the flocculator bay (Figure 5.2-1). The plant was fed with WSP effluent at a rate of 5 m³ h⁻¹.



Figure 5.2-1. A depiction of the modification on the flocculator – DAF unit - 'C' denotes the location of separation baffle, installed for modified bubble experiments

Polymer addition was conducted with a DDI 209 digital dosing pump (Grundfos Alldos, Australia) after the recycle feed pump but upstream of the saturator such that sufficient chemical mixing occurred ahead of the release of bubbles in the DAF contact zone. Polymers used in these tests were polyDADMAC, H33 and an acidified sample of H33. All polymer doses were normalised to an equivalent influent water charge demand of - 30×10^{-3} meq L⁻¹ (the average influent water charge demand observed). Influent water pH was not corrected in this study as the difference in polymer performance was found to be marginal (Appendix 16). DAF treated water from the flotation tank was filtered via depth filtration with a sand filter and collected in a balance tank to feed the saturator. A recycle ratio of 20% was used unless otherwise stated. After adjustment to any polymer dosing set point, the plant was allowed to run for 30 minutes to allow the plant to reach steady state. Grab samples of DAF influent and treated water were then taken at 3 minute intervals over the course of 15 minutes in 375 mL sample bottles, creating influent and treated water sample sets. Each sample collected was subject to turbidity analysis, with a 2100N Laboratory Turbidimeter (Hach, Australia) to assure sample stability. A composite sample was then created from each sample set by combining 20 mL from the each of the 5 grab samples such that combined treated water and combined influent samples were obtained.

The composite samples were subject to charge demand analysis with a Mütek PCD-04 laboratory charge demand analyser (BTG, Australia) and cell counting with a haemocytometer and CH Series light microscope (Olympus, Tokyo, Japan). For off-site

analysis, composite samples were filtered with a 0.45 μ m polyethersulphone (PES) syringe filter (Millipore, Australia) and were sent to the Australian Water Quality Centre (AWQC) at SA Water for UV-visible 254 nm measurements with a UV-vis spectrophotometer, Model 918 (GBC, Australia) and DOC analysis with a TOC analyser, Model 820 (Sievers Instruments Inc., USA).

Modified-Bubble DAF Jar Testing with Unprocessed with DAF Influent

Three jar tests were conducted to assess the performance of polyDADMAC, H33 and acidified H33 in the latter stages of pilot plant operation. Sample influent water was obtained from the pilot plant feed pump and saturator feed water was obtained from the St Kilda DAF/F plant and shipped to the WRC at UNSW for testing on the following day. The jar tests were conducted as per the Section 5.2.2.6 using dose of 30×10^{-3} meq L⁻¹; using influent and saturator feed water as received. DAF treated water samples from these tests were analysed via cell counting and zeta potential measurements.

5.2.3 Results

5.2.3.1 Jar Testing

Characterisation of WSP Matrix

Generated from WSP effluent in October 2012, the WSP matrix was found to carry a negative charge, with a zeta potential of -6.5 ± 0.9 mV and a charge density of $-25 \pm 1 \times 10^{-3}$ meq L⁻¹ (Table 5. 2-1). Upon combination with cells, the zeta potential became more negative; however, surprisingly, the charge demand for WSP matrix combined with CS-555/01 became less negative. Specifically, the dilution of the WSP matrix was less than 5% upon the addition of cells but resulted in a 12% decrease in the charge demand. The decrease in anionic charge when mixing WSP matrix with CS-555/01 may indicate that CS-555/01 is responsible for anionic charge adsorption. When CS-564/01 was added to the WSP effluent, the charge demand remained unchanged. With the addition of both CS-555/01 and CS-564/01 to WSP matrix, the change in the DOC was not measurable, remaining at a concentration of approximately 18 ± 1 mg L⁻¹. Saturator feed water was WSP effluent, treated by the St Kilda DAF/F plant at Bolivar

WWTP. As the water used for the DAF recycle line is treated by C-F, DAF and filtration, the residual DOC of $11.5 \pm 0.3 \text{ mg L}^{-1}$ in the saturator feed water indicated that there was a non-sorbable DOC fraction of 64% in the WSP matrix. In comparison to unfiltered WSP effluent in Chapter 5.1, it can be seen that DOC was 23% lower with an average of 13.9 mg L⁻¹. Charge demand of unfiltered WSP effluent was also found to be much greater in 2011 with an average of $-62 \times 10^{-3} \text{ meq L}^{-1}$; however, the presence of particles in the unfiltered DAF treated water may have influenced this result.

Zeta potential **Charge demand Dissolved organic** (mV) (×10⁻³ meq L⁻¹) carbon (mg L⁻¹) **Saturator Feed Water** 11.5 ± 0.3 18.1 ± 0.5 WSP Matrix -6.5 ± 0.9 -25 ± 1 WSP Matrix + CS-555/01 -11 ± 1 -22 ± 1 17.8 ± 0.4 WSP Matrix + CS-564/01 -21 ± 2 -25 ± 1 18.2 ± 0.5

Table 5. 2-1.WSP matrix measurements ahead of jar tests

Modified Bubble DAF Jar Tests

Jar testing of lab grown *M. aeruginosa* in WSP matrix demonstrated that maximum cell removals of $95 \pm 2\%$ and $92 \pm 1\%$ for strain CS-564/01 could be achieved, using polyDADMAC and polymer H33, respectively (Figure 5.2-2). The cell removal of CS-555/01 in modified-bubble DAF was less effective, reaching a maximum cell removal of $41 \pm 3\%$ and $48 \pm 2\%$ for polyDADMAC and H33, respectively. However, the cell removal of CS-555/01 was much greater in with the presence of WSP matrix in comparison with results generated in Chapter 4.2, where a maximum cell removal of only 36% was obtained using a sodium chloride and sodium bicarbonate buffered background matrix.

In addition to differences in cell removal, the doses required to achieve maximum cell removals were found to be much greater when filtered WSP effluent was used as a background matrix as opposed to using a buffer as background matrix. In polyDADMAC modified-bubble DAF with CS-564/01 as a model contaminant, the first point with cell removals above 95% was found to be 17×10^{-3} meq L⁻¹ compared to tests using a buffer matrix where a dose of only 0.7×10^{-3} meq L⁻¹ was required

(Chapter 4.1, Figure 4.1-4) demonstrating the extra polymer demand generated by the matrix. These polymer dosing values were used to determine an appropriate dosing range for pilot-scale experiments of $0 - 40 \times 10^{-3}$ meq L⁻¹.



Figure 5.2-2. Modified bubble flotation at bench scale, using (A) polyDADMAC and (B) H33 - tests were conducted on lab grown strains, CS-564/01 (squares) and CS-555/01 (diamonds) and matrix obtained from Bolivar WSP effluent

It was observed that applying modified-bubble DAF with H33 resulted in more negative DAF treated water residual charge than with polyDADMAC for the same charge dose. As an example, comparing polyDADMAC and H33 at a dose of 20×10^{-3} meq L⁻¹ (via extrapolation of the results), equivalent zeta potentials are -12.5 and -17.8 mV, respectively, for CS-564/01; and -10.8 and -15.2 mV, respectively, for CS-555/01. These observations were also made in Chapter 4.1, Figure 4.1-6, with much greater differences in the zeta potential of up to 45 mV. In contrast to previous results, and despite doses up to 50×10^{-3} meq L⁻¹ of polyDADMAC, DAF treated water remained negatively charged.

The improved cell removal of CS-555/01 compared to work in Chapter 4.2 (Figure 4.2-5) indicated that the presence of organic matter enhanced cell removal in modifiedbubble DAF. As demonstrated in Chapter 4.2 (Section 4.2.3.4) and suggested by Henderson *et al.* (2010b), organic matter has a large influence on the effectiveness of flotation. In Chapter 4.2 (Figure 4.2-7), the large AOM structures or complexes was essential for the effective flotation of cells.

5.2.3.2 Influent Water and Conventional DAF at the Bolivar WSPs

Influent Water Quality

The WSP effluent at Bolivar had much greater variability in 2013 when compared to 2011. Greater average turbidity, cell concentrations, pH, influent temperature and DOC were observed in the DAF/F influent (Table 5.2-2). The average turbidity of the WSP effluent was skewed by occasional turbidity spikes, leading to saturation of the sensor and saturation of the records on the Supervisory Control and Data Acquisition (SCADA) system. Using 2 hour sample points, it was found that there was an average raw water turbidity of 134 NTU over the pilot scale trial in 2013 compared to an average of 41 NTU in 2011 (Figure 5.2-3). Over the duration of the pilot plant trial, algae population densities remained high with total cell concentrations ranging from 4.60 x 10^5 to 5.23×10^6 cells mL⁻¹ and concentrations of *Microcystis flos aquae* contributing between 46 and 97% of total cells as determined via analysis obtained from SA Water. Other dominant species over this period include *Stichococcus, Planktolyngbya, Aphanocapsa, Chlorella, Dimorphococcus* and *Planctonema*, details of which can be found in Appendix 17.

	,							
		I	eb-Apr 201	3	Feb-Apr 2011			
	Units	Min	Max	Ave	Min	Max	Ave	
Turbidity	NTU	26	899	134	10	153	40.6	
Charge demand	meq L-1	-36	-24	-30	-93	-27	-62	
Total cell count ^b	cells mL-1	4.60x10 ⁵	5.23x10 ⁶	1.18×10^{6}	1.66x10 ³	1.05×10^{6}	3.03x10 ⁵	
Dominant Species		Mici	ocystis flos a	quae	Microcystis sp.			
рН		7.7	10.3	9.4	7.7	9.7	8.7	
Temperature	°C	17	27.2	21.5	14.6	26.9	20.6	
Dissolved organic carbon	mg L-1	13.2	15.2	14.4	9.6	15.2	13.1	
Specific UV Absorbance	m ⁻¹ mg ⁻¹ L	2.13	2.58	2.29	2.1	4.2	2.4	
Aluminium sulphate dose ^a	mg L-1	8.9	18.8	13	6.4	15.4	11.7	

Table 5.2-2. Selected influent water quality indicators and aluminium sulphate dose measured at the St. Kilda DAF/F plant, fed from the WSP system. Results were obtained from pilot plant operation, unless otherwise stated

¹ Dose quoted as Al,^b Biological records from analysis of weekly samples at the AQWC, SA Water



Figure 5.2-3. DAF/F influent turbidity as measured at the Bolivar DAF/F plant, with 1 point taken every 2 hours – algae cell counts

It was found that the effective coagulant dose at the St Kilda DAF/F plant was often not significantly affected by the very large variability in influent cell concentration or turbidity. However, these measurements may be closely related and may not be the most appropriate measurements to normalise the required coagulant dose at the St Kilda DAF/F plant. Given that the Bolivar WSPs are facultative ponds (with no mechanical agitators to stir up sediment), the cause of turbidity in the WSP effluent turbity was primarily from low density algae and cyanobacteria. As a result, the relationship between turbidity and the cell concentration was roughly linear (Appendix 18),

suggesting that turbidity may be used to a degree as a surrogate for cell concentration. Using the charge demand can indicate the required coagulant required for charge neutralisation, shown by Bernhardt and Schell (1993). To compensate for the highly variable DAF influent water quality, the influent water charge demand was therefore the most appropriate measurement to normalise the data.

Performance Comparison of the Pilot- and Full-Scale DAF Plants

Over a baseline period to compare the conventional operation of the pilot plant with the St-Kilda DAF/F plant, it was found that the performance of the pilot plant was better than that of the full-scale plant, with average DAF treated water turbidities of 1.7 ± 1.2 NTU and 6.1 ± 1.8 NTU, respectively. In both plants, similar fluctuations in DAF treated water quality were observed. The average turbidity and cell removal at the pilot plant was 97.9% ± 1.3 % and 88.5% ± 4.5 %, respectively. With sudden deterioration of the influent water quality, an increase of the DAF treated water turbidity was observed at both the pilot plant and the St Kilda DAF/F plant. On the 19th of February, a poor influent water quality lead to filter fouling and turbidimeter measurement saturation at the pilot plant despite using the same coagulant dose as the full-scale plant. The stability of the St Kilda DAF/F plant can be attributed to its buffering capacity, whereby sufficient particle coagulation can be maintained in the flocculators given a longer hydraulic retention time. Over the course of these experiments, DOC removal was observed to fluctuate from 12% to 22%.



Figure 5.2-4. DAF treated water turbidity for the St Kilda DAF/F plant and pilot DAF plant - data was taken form 4 consecutive operating days for 7 hours per day – influent water was measured using the St Kilda DAF/F plant instrumentation and SCADA system

5.2.3.3 Pilot-Scale Modified-Bubble DAF

Modified-Bubble DAF at Pilot-Scale

A sample of any specific dose at the pilot plant was taken over 15 minutes to ensure water quality stability, as observed by turbidity, during sample collection. An example of a turbidity measurement for a single sample can be found in Figure 5.2-5 which shows no change in water quality over the period of the collection of the data point. For all of the experiments conducted, it was found that neither DAF influent nor treated water water quality fluctuated significantly, showing that conditions remained stable (Appendix 19). The doses applied ranged up to a maximum of 6.0 mg L⁻¹ (0.041 meq L⁻¹) for polyDADMAC and up to 10 mg L⁻¹ (0.034 meq L⁻¹) for H33.



Figure 5.2-5. An example of a polyDADMAC dosing point - the concentration of polymer used was 33×10^3 meq L⁻¹

For modified bubble experiments at pilot-scale, greater than 95% cell removal was obtained at a dose of 12×10^{-3} meq L⁻¹ using polyDADMAC (Figure 5.2-6). Over the course of the experiments, an average cell removal of $98 \pm 1\%$ was achieved for all doses greater than 12×10^{-3} meq L⁻¹, with a maximum cell removal of $99 \pm 1\%$. In comparison, jar tests resulted in similarly high cell removals were attained, reaching a maximum of 96.3%, but required 56% more polymer to achieve this cell removal. Both results from jar testing and pilot plant tests exceeded that obtained from conventional DAF by 7.8% and 9.5%, respectively. The optimal removal of turbidity in modified-bubble DAF with polyDADMAC occurred at doses of 19.5×10^{-3} meq L⁻¹ or greater averaging $95 \pm 2\%$, reaching a maximum of $98 \pm 2\%$. This was found to be comparable to the conventional DAF conducted over the performance comparison for which the average cell removal over 4 days and 142 data points was $98 \pm 1\%$.

Unlike experiments with polyDADMAC, modified-bubble DAF with H33 resulted in much poorer performance. A maximum turbidity removal of $43 \pm 3\%$ was achieved at a dose of 30×10^{-3} meq L⁻¹. This was in contrast to laboratory results whereby modified-bubble DAF using H33 was comparable to polyDADMAC. Cell removals over this trial period were generally below 50%; however, cell removal did reach as high as $81 \pm 6\%$ at a dose of 6.8×10^{-3} meq L⁻¹. This was found not to be reproducible in later experiments.

The charge of the DAF treated water from the pilot plant was found to be negative for all doses of polymer, as it was in jar testing (Figure 5.2-6). It can be seen that at doses above 10×10^{-3} meq L⁻¹ the charge of the DAF treated water was more anionic for H33

than polyDADMAC. For both polymers, a plateau in the charge was apparent above 23 $\times 10^{-3}$ meq L⁻¹ and 11 $\times 10^{-3}$ meq L⁻¹ for polyDADMAC and H33, respectively. In experiments with H33, the least negative charge of $-20 \pm 2 \times 10^{-3}$ meq L⁻¹ was obtained at a dose of 30 $\times 10^{-3}$ meq L⁻¹, whereas least negative charge for polyDADMAC was to $-7 \pm 1 \times 10^{-3}$ meq L⁻¹ at a dose of 33 $\times 10^{-3}$ meq L⁻¹. Though the measurement in this case uses a titrant rather than relying on electrophoretic mobility, the charge observations in Figure 5.2-6 are comparable to those obtained in jar tests conducted in this Section (5.2.3.1) and in Chapter 4.1 and 4.2 (Sections 4.1.3.3 and 4.2.3.3, respectively). In both charge measurements, a more negative charge was obtained for H33 than polyDADMAC, demonstrating a comparatively lower availability of cationic charge in solution, suggesting polymer concentrations were lower in the DAF treated water when using polymer H33.



Figure 5.2-6. The removal of cells and turbidity in polyDADMAC (A) and H33 (B) modified bubble flotation tests at pilot scale - polymer dose is normalised to an influent water charge demand of -30×10^{-3} meq L⁻¹

Unlike turbidity, which was stable in polyDADMAC test, the removal of DOC did not remain at a steady level (Figure 5.2-7). For the dosing range tested, a maximum of 23.9

 \pm 0.5% DOC removal was obtained using 33 × 10⁻³ meq L⁻¹ polyDADMAC while when using H33, a maximum of 8.8 \pm 0.9% DOC removal was obtained. This was slightly lower than that obtained during conventional tests with removals ranging between 12 and 22%. Over the course of the pilot plant operation, DAF influent SUVA remained low, ranging between 2.12 m⁻¹ mg⁻¹ L and 2.58 m⁻¹ mg⁻¹ L, indicating that the concentration of removable DOC is low in regard processes using metal coagulants (Edwards 1997, Edzwald 1993b). This was demonstrated in conventional performance comparison tests with the pilot plant in which a maximum DOC removal of only 22% was achieved. For conventional water treatment with C-F, it is known that highly cationic polymers are more effective for the removal of DOC (Bolto *et al.* 1999). This was demonstrated in modified-bubble DAF, with highly cationic polyDADMAC outperforming moderately charged H33.



Figure 5.2-7. Removal of DOC at pilot scale for modified bubble flotation with polyDADMAC (grey circles) and H33 (white circles)

Modified-Bubble DAF at Pilot-Scale with Acidified of H33

In an attempt to improve the performance of H33, the H33 was acidified to increase the cationic nature of H33 and thus its attraction to anionic contaminants and pilot plant experiments were repeated. These pilot plant tests revealed that turbidity removal

improved marginally from $43 \pm 3\%$ to $47 \pm 4\%$ (Figure 5.2-8); however, turbidity and cell removal remained significantly less than that achieved when using polyDADMAC.



Figure 5.2-8. The removal of cells and turbidity in H33 (hollow shapes) and acidified H33 (solid shapes) modified bubble flotation tests at pilot scale - polymer dose is normalised to an influent water charge demand of -30×10^{-3} meq L⁻¹

Modified-Bubble DAF Jar Testing with DAF Influent

Due to the discrepancy between results obtained for cell removal in jar testing H33 on *M. aeruginosa* in WSP effluent matrix, a further sample of WSP effluent was subjected to additional jar testing experiments at the WRC at UNSW. To cross check turbidity and cell removal, polyDADMAC, H33 and acidified H33 were tested at a dose of 30×10^{-3} meq L⁻¹ directly on WSP effluent. In comparison to pilot plant operation, the modified bubble jar test results for polyDADMAC, H33 and acidified H33 resulted in turbidity removals of $93 \pm 7\%$, $89 \pm 3\%$ and $92 \pm 2\%$, respectively, with corresponding cell removals of >90% (Figure 5.2-9). Interestingly, polyDADMAC modified-bubble DAF jar tests in Chapter 4 had positive zeta potentials in the treated water (Section 4.1.3.5 and 4.2.3.3), unlike that observed in pilot scale tests and in preliminary jar tests (Section 5.2.3.1). Similar to results obtained in other modified-bubble DAF jar tests, H33 was found to have low charge remaining in the treated water, which was found to be the same for previous bench scale tests (Chapter 4, Section 4.1.3.5 and 4.2.3.3). One important difference between pilot and bench scale modified-bubble DAF experiments

was the quality of the recycle water. For example, in jar testing, recycle water was obtained from the St Kilda DAF/F plant. However, unlike the jar tests, the pilot plant generates recycle water using the sand filters, with measurements being taken only once steady state has been achieved. The poor quality for the DAF treated water produced when poor polymer-reactive DOC is not completely removed is not used to generate recycle water. Without the presence of polymer reactive DOC in the saturator, H33 remains active for the removal of cells and turbidity in jar testing.



Figure 5.2-9. Cell removal, turbidity removal and residual charge of modified bubble flotation tests at lab scale using polyDADMAC, synthesised polymer, H33, and an acidified H33 - errors represent standard deviation measurements on a single sample

Float Condition

An interesting feature of modified-bubble DAF is the nature of the float which was very different to that observed when operating under conventional DAF. Images of the modified-bubble float at pilot scale revealed that the float developed as a foamy layer (Figure 5.2-10). During hydraulic float removal, the float behaved as a single agglomerated sheet as opposed to discrete agglomerated clusters observed with conventional C-F/flotation. This was evident in float removal, whereby the shear forces during float removal easily separate floc-clusters (Appendix 20) whereas the float generated in modified-bubble DAF was removed in a single sheet. In the development of a float using modified-bubble DAF, particles and polymer were concentrated on the surface of the DAF tank whereby further inter-particle bridging can take place, resulting in a single uniform, foamy float. Upon the coalescence of bubbles, the available anionic

surface area would reduce, increasing the polymer to contaminant ratio. In H33 modified-bubble DAF, much greater coalescence can be observed, with much larger bubbles in the float. With much lower contaminant removal, the concentration of polymer with respect to contaminants was very high, which could lead to *in situ* sludge dewatering.



Figure 5.2-10. Images of the float that occurs during pilot scale modified bubble flotation with polyDADMAC (A) and H33 (B) at 30×10^3 meq L⁻¹, compared to conventional coagulation / flocculation / flotation (C).

5.2.4 Discussion

5.2.4.1 Dissolved Organic Matter in Modified-Bubble DAF

In this work it was demonstrated that the removal of cells from water in modifiedbubble DAF was aided by the presence of organic matter in the WSP effluent. From Chapter 4.2 it is known that the presence of certain organic matter can result in enhanced cell removal in modified-bubble DAF, likely to be forming very large structures. Compared to filtered initial jar tests (Section 5.2.3.1), pilot plant tests on WSP effluent resulted in greater cell removals. This indicates that the *in situ* organic matter on cells and particles in WSP effluent result in better turbidity and cell removal outcomes compared to added organic matter in jar testing. These materials may also be responsible for enhancements in coagulation and flocculation (C-F). With the observation that that complete charge neutralisation is not necessary for optimised C-F, Sharp *et al.* (2005) suggested that organic matter can enhance flocculation processes via non-DVLO forces present. The identification of such materials and the exact forces responsible requires investigation.

The results of CS-555/01 interactions with WSP matrix components were apparent: Firstly, the charge demand of WSP matrix decreased when combined with CS-555/01 and, secondly, cell removal was improved in comparison to tests without the matrix in Chapter 4.2 (Section 4.2.3.3). Given that the removal of CS-555/01 cells was improved by the addition of AOM from CS-564/01 (Section 4.2.3.4), it may be that the complexation of organic matter from WSP effluent could be contributing to enhance cell removal. However this assumes that the water chemistry of the WSP may be different to that used in the jar tests undertaken in Chapter 4 in terms of pH, ionic strength and other constituents. Further work would be required to determine the influence of water chemistry. In addition it was shown in Chapter 4.2, Section 4.2.3.4 that no cell removal could be achieved in modified-bubble DAF without the presence of AOM. As CS-555/01 cell removal was improved in filtered WSP effluent (Section 5.2.3.1), the organic matter present also aids modified-bubble DAF. It has been noted that the adsorption, complexation and entrapment by precipitating metal coagulants is a dominant mechanism in the removal of organic matter which can interfere with the removal of other contaminants (Matilainen et al. 2010, Wei et al. 2009). Hence, in the case of modified-bubble DAF, both adsorption of the organic matter to particles and later complexation with polymers was essential for the elevated cell and particle removal.

5.2.4.2 Mechanism of Cell Removal for Pilot-Scale Modified-Bubble DAF

There was a significant difference in cell removal achieved at pilot scale compared to jar testing when using H33. While pilot-scale modified-bubble DAF using

polyDADMAC resulted in cell removals similar to those observed in jar tests using filtered WSP effluent as the background matrix, the use of H33 was much less effective than previously demonstrated. The key difference between the bench- and pilot-scale processes is that the saturator water used in the jar tester has already been treated by C-F, DAF and filtration, in which the adsorbable DOC is likely to be removed (Duan and Gregory 2003, Edwards 1997). The presence of organic matter in modified-bubble DAF influent that is adsorbed on particle surfaces is essential, with the complexation of polymers on bubble surfaces during flotation required for particle flotation. Thus any organic matter or adsorbable DOC that flows through to the saturator would be detrimental to the effective modified bubble DAF. Poorer removal of adsorbable DOC in modified-bubble DAF with H33 than polyDADMAC was likely to occur, given that H33 has a much lower charge density than that of polyDADMAC at 6.82 meg g^{-1} and 2.07 meg g⁻¹, respectively (Bolto and Gregory 2007). Thus, it is suggested that the complexation of the residual, adsorbable DOC in the saturator reduced its effectiveness in modified-bubble DAF, causing poorer removal at pilot-scale than at bench-scale when using synthesised polymer H33.

With elevated cationic charge, it is known that polymer-organic matter interactions can result in better organic matter removal (Bolto *et al.* 1999). In modified-bubble DAF this was demonstrated in DOC removal using polyDADMAC and H33: Though low removals was obtained in all cases, polyDADMAC was able to remove more DOC than H33 in modified-bubble DAF. The protonation of the tertiary amines in H33 was conducted by acidification to increase the charge density of the polymer and therefore strengthen interactions with organic matter. This resulted in a slight improvement of the turbidity removal, demonstrating that cationic polymers with greater charge densities are better suited for clarification with modified-bubble DAF.

Despite poor cell and turbidity removal, the adherence of H33 to bubbles in modifiedbubble DAF is apparent. With the same dose of cations to influent anions, charge demand in the DAF treated water was significantly less negative for H33 compared to polyDADMAC. Though the interaction of the H33 coated bubbles with anionic contaminants are limited due to interaction with organic matter in the saturator, the hydrophobic zones of the polymer can still lead to catalytic effects whereby bubbles can nucleate (Lubetkin 2003) facilitating good polymer-bubble adhesion. Further investigation of other synthesised polymers in modified-bubble DAF is necessary in order to retain both high cell removal and low polymer residuals.

5.2.4.3 Process Economics

The overall cost of chemical consumption was found to be lower in modified-bubble DAF in comparison to conventional DAFF at Bolivar (Table 5.2-3). Over the trial period in 2013, the use of alum (as $Al_2(SO_4)_3 \cdot 18H_2O$) was 110-230 mg L⁻¹, with an average dosing rate of 161 mg L⁻¹. The polymer used at site was BASF LT510, which is a low molecular weight polyDADMAC, suitable for bubble modification. Polymer dosing is usually set at 0.6 mg L⁻¹, but is sometimes varied to as low as 0.4 mg L⁻¹ and as high as 1.2 mg L⁻¹. Using the chemical prices AUD 240 tonne⁻¹ for alum from Orica and AUD 1,800 tonne⁻¹ for bulk polymer from BASF, the alum cost ranges from 5.05 to 10.55 cents kL⁻¹ and polymer 0.27 to 0.80 cents kL⁻¹. Based on average the chemical consumption over the trial period, the price of polymer used in modified-bubble DAF was 3.67 cents kL⁻¹.

Chemical consumption at the modified-bubble flotation plant did not include alum. As the operation was found to be compatible with the polymer used on site (BASF's Magnafloc LT 510), calculations were based around the price of this chemical. The dosing range tested and found to be effective was 3 mg L⁻¹ to 8 mg L⁻¹, equating to a price of 2.00 to 5.33 cents kL⁻¹. Comparing this price to average chemical consumption costs of conventional DAFF, chemical savings can range from 32% to 74%.

Table 5.2-3. Chemical cost (cents kL^{-1}) and consumption (mg L^{-1}) at the Bolivar DAFF plant and modified-bubble flotation pilot plant fed with WSP effluent over the course of the 2013 trial period (February – April). For the full scale plant, average doses were calculated from alum and polymer dose values every 10 minutes over this period as recorded on the SCADA system. For the pilot plant, average doses were determined based on experimental data

Conventional Treatment								Modified-Bubble Flotation	
Chemical	Alum		LT 510		Combination		LT 510		
Unit	$mg L^{-1}$	Cents	$mg L^{-1}$	Cents	$mg L^{-1}$	Cents	$mg L^{-1}$	Cents kL ⁻¹	
	used	kL ⁻¹	used	kL ⁻¹	used	kL^{-1}	used		
Lowest	110	5.05	0.4	0.27	110.4	4.27	3	2.00	
Highest	230	10.55	1.2	0.80	231.2	9.16	8	5.33	
Average	161	7.39	0.6	0.40	161.6	6.25	5.5	3.67	
5.2.4.4 Downstream Process Benefits

In addition to chemical savings, process products from WSP effluent treatment will have a different character. With the absence of metal coagulants and much lower masses of treatment chemical used, the waste stream produced in modified-bubble DAF is richer in organic materials. This has the potential to improve biomass quality and sludge digestion due to the reduction of alum content in the sludge (Sukias and Craggs 2011). Furthermore, the presence of polymers in anaerobic digestion can improve methane production though at high concentrations (>15 g kg⁻¹ as dry solids) their presence can inhibit digestion performance (Chu *et al.* 2003). Also with dissolved nitrogen and phosphorus removal dependent on coagulating metal salts (Arnaldos and Pagilla 2010), these nutrients would remain in product water, which would be of great benefit for agricultural and horticultural use which currently uses the product water. Further research is required to fully elucidate the impact on sludge character, for example dewaterability.

5.2.5 Summary

The principal finding of this phase of the investigation were:

- In modified-bubble DAF jar testing using filtered WSP effluent as background matrix, 95% and 92% CS-564/01 cell removal was obtained using polyDADMAC and polymer H33, respectively
- CS-555/01 cell removal was improved by flotation in the WSP matrix compared to the buffer matrix for both polymers suggesting that process enhancing organic matter was present
- At pilot-scale, modified-bubble DAF was effective in removing both algae cells and turbidity using polyDADMAC but not when using polymer H33
- Residual charge obtained when using polymer H33 remained more anionic than when using polyDADMAC with the same charge dose
- 5) Decreased performance of polymer H33 may be attributed to build up of organic matter in the recycle stream and low polymer charge density

- 6) Strong polymer-organic matter interaction is critical for the effective clarification of WSP effluent with modified-bubble DAF
- 7) Over the course of the trial period, it was found that a cost saving of 32% to 74% could made by implementing modified-bubble DAF for the clarification of WSP effluent

Chapter 6

6 CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The development and application of modified bubbles in dissolved air flotation (DAF) has been investigated. The major outcome of this work was that modified-bubble DAF can be used as an alternative to conventional coagulation and flocculation (C-F) based DAF. This was found to be specific to water with the appropriate organic matter content such as waste stabilisation pond (WSP) effluent. It was also found that chemical costs in conventional DAF could be significantly reduced by implementing modified-bubble DAF. With extended investigation of modified-bubble DAF, year-round application has the potential to replace current practice. Modified-bubble DAF has the potential to increase the waste stream quality for sludge digestion and provide nitrogen and phosphorus rich treated water which can increase the productivity of agricultural and horticultural end users. Further tuning and investigation of other specifically-designed polymers might further enhance the process outcomes, resulting in further optimisation of this modified DAF process.

Addressing the objectives outlined in Section 1.2, specific outcomes of this research are:

1. To review the state of flotation technology for solid liquid separation

• In a review of the mechanisms in flotation, it was found that the founding principles of flotation are the association of bubbles to hydrophobic regions. In many cases the interaction between bubbles and particles has been shown to be greatly influenced by non-DVLO forces such as hydrophobic attraction. Though the use of chemicals to create hydrophobic surfaces in mineral flotation is commonplace, chemical systems for flotation in water treatment lacks the use of hydrophobic components to exploit hydrophobic forces.

- The use of cationically modified bubbles can reduce or potentially eliminate the dependence of DAF on particle pretreatment. The use of a hydrophobically-associating cationic polymer can increase the robustness of the process by strong interaction with both bubble surfaces and particles.
- 2. To synthesise and characterise specifically designed treatment polymers for modifying the bubble surface in DAF
 - In developing hydrophobically functionalised polymers containing quaternary amines, it was found that hydrophobic activity manifests in self-association properties; however, surface tension was a poor indicator. From images of nano-objects formed by these polymers, it was found that the size of pendant hydrophobic groups has the greatest effect on the resulting conformations.
 - Upon testing samples of cationic polymers and a cationic surfactant in bubble modification, it was found that the use of all samples resulted in positively charged bubbles.
 - Polymer adherence to bubble surfaces has been observed. This has been postulated to occur by both hydrogen bonding of the polymers to the bubble surface and bubble nucleation in hydrophobic regions in the case of hydrophobically functionalised polymers.
- 3. To establish the performance of the synthesised polymers compared to polyDADMAC in modified-bubble DAF under laboratory conditions, using Microcystis aeruginosa as a model algal contaminant
 - In modified-bubble DAF, it was found that polymer functionalised bubbles resulted in the highly effective treatment of *M. aeruginosa* contaminated water (specifically for strain CS-564/01). Cell removals were found to be comparable to conventional processes and required a significantly smaller mass of chemical.
 - Of the hydrophobically functionalised polymers, it was found that a polymer of high molecular weight containing high concentrations of more hydrophobic pendant groups (specifically decane) resulted in the most negative zeta potentials in modified-bubble DAF treated water. This translates to lower concentrations of polymer in the DAF treated water and stronger bubble-surface adherence,

confirming the hypothesis that hydrophobic functionalisation of a polymer can result in stronger bubble adherence.

- 4. To investigate the robustness of the process to an alternate strains of M. aeruginosa and examine the influence of organic matter character
 - The presence of organic matter was found to be essential for the success of modified-bubble DAF. Modified-bubble DAF jar testing of model algae laden water using a specific strain of *M. aeruginosa* cells (CS-564/01) resulted in cell removals of up to 99%. In the absence of AOM, however, modified-bubble DAF resulted in no cell removal.
 - In tests on an alternative strain of *M. aeruginosa*, modified bubble DAF consistently resulted 35% cell removal or less. Interestingly, the addition of high molecular weight AOM extracted from a different strain to the samples improved cell removal to 96%. Hence, it was demonstrated that AOM not only enhanced the process when present naturally but could be extracted and applied as an additive to enhance modified-bubble DAF.

5. To construct, install and commission a pilot DAF plant in the field

- A pilot DAF plant was successfully constructed and operated as a conventional C-F based DAF plant, using WSP effluent to feed the plant. Pilot plant performance was comparable to full-scale operation. Optimisation tests with aluminium sulphate and a highly cationic polymer demonstrated that both coagulation at lower pH values and the use of cationic polymer could reduce required coagulant dose for effective treatment in conventional DAF.
- 6. To trial modified-bubble DAF at pilot-scale on real-world DAF influent comprising algae blooms using both conventional polymers and purposedesigned polymers
 - The use of filtered WSP effluent as a background matrix to prepare influent cell samples for treatment by modified-bubble DAF at bench-scale improved the removal of strain CS-555/01 cells in comparison to that achieved in previous jar tests, indicating that suitable organic matter for process enhancement was present in WSP effluent. The removal of CS-564/01 remained high during parallel tests.

- Pilot-scale modified-bubble DAF revealed that highly charged cationic polyDADMAC could be used successfully to treat WSP effluent, eliminating the need for influent pretreatment via C-F. It is acknowledged that the results obtained and conclusions drawn are specific to the WSP effluent at Bolivar WWTP. The organic matter character and cell composition may be expected to be different at other treatment plants; however, the robustness of the operation of this modified process over 3 months suggests that it may be applicable to other WSP effluents. The less cationic, hydrophobically functionalised polymer was unable to result in high cell and turbidity removal; however, turbidity removal could be improved be increasing the cationic charge density of the polymer. It was concluded that poor organic matter removal in flotation resulted in polymer-organic matter complexing in the saturator and subsequent poor cell and turbidity removal.
- Modified-bubble DAF improved cell removal while achieving comparable to turbidity and DOC removal to conventional DAF and has the potential to reduce treatment costs.

6.2 Recommendations for Further Work

Over the course of this investigation, a number of priority issues for further work have been identified. These include:

- a) The short range forces between bubbles and flocs in DAF are largely unexplored. The interactive forces between bubbles and flocs have been postulated to proceed via interactions with hydrophobic regions; however, the presence of these interactions has yet to be confirmed via physical measurements.
- b) With the investigation of the charge of polymer-coated bubbles, results were found to have large standard deviation and data were handled as *t*-distributions. To make firmer conclusions about exact alteration of a polymer-coated bubble charge, well defined bubble and polymer sizes and charges are necessary. The fine control of bubble properties may not be achievable; however, the use of

polymers of well-defined molecular weight can be produced at small scale and may yield more accurate insights to the effect of polymer composition (such as hydrophobic and cationic concentrations).

- c) The mechanism for the adsorption of materials to bubble surfaces has been postulated in this thesis, but has yet to be proven. Advanced physical measurements, such as atomic force microscopy, at bubble surfaces with a range of polymers have the potential to give insights to the mechanisms of polymerbubble attachment.
- d) The organic matter responsible for enhancing flotation requires further investigation and identification. It is known that these AOM components are high molecular weight and can interact with cell surfaces and cationic polymers in water. Furthermore, only a single site has been tested thus far. The isolation of these materials and their molecular characterisation is necessary to determine more specific interaction mechanisms. This could enable the development of a synthetic biopolymer with similar attributes.
- e) Testing of modified-bubble DAF at other WTPs is required. Currently only one site has been investigated, thus the application of modified-bubble DAF at any other site cannot be guaranteed. The testing of other WSP effluents may also be an initial step in determining the exact organics that are required in influent water for the success of modified-bubble DAF.
- f) The kinetics of the interactions of modified bubbles with contaminants in flotation requires further investigation. The contact time of chemicals with contaminants in modified-bubble DAF is significantly shorter than in C-F and thus, very rapid interactions are required for successful modified-bubble DAF. However, it may be possible to improve contaminant adsorption to modified bubbles with extended contact time, such as mixing in a plug flow reactor.
- g) Current research on modified-bubble DAF has been confined to simulated surface waters with laboratory cultured cyanobacteria and WSP effluent. The application of modified-bubble DAF in other solid liquid separation processes has yet to be considered, a good example of this would be the application of modified-bubble DAF for biomass harvesting.

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Appendix

Chapter 3

Charge Density =
$$\frac{Q}{(1-Q)M_D + QM_Q} = \frac{Q}{M_D} + \frac{1}{M_Q - M_D}$$

Appendix 1. Calculation for charge density as a result of quaternisation: Q is the stoichiometric percentage of quaternised repeating units, MD is the mass of the unreacted DMAEMA repeating units and MQ is the mass of the quaternised repeating units



Appendix 2. Surface tension versus mole per cent for (A) iodomethane, (B) 1-bromopentane and (C) 1-bromodecane functionalised polymers



Appendix 3. Surface tension measurements to calculate the CMC of polyDMAEMA homopolymer (H-0)

Material*	Zeta	A	B	C
L21	+27			
L22	+28			
L33	+39	Zo (1)	***	
M12	+28			
M21	+37	_		
M33	+29			***
H12	+54			
Н33	+17			
H41	+45	· · ·		

Appendix 4. TEM images of assembled quaternised polyDMAEMA samples



Appendix 5. TEM images with corresponding DLS data for (a) HC1-50, (b) HC10-75 and (c) HC15-10 after micellisation - highlighted in (b) is individual aggregates in contact - DLS revealed that bi- or tri-modal size distributions were present in the samples in solution. Larger particles that formed were found to have diameters of 229, 356 and 266 nm for polymers H12, HC33 and HC41

Chapter 4.1



Appendix 6. An example of growth curves obtained for M. aeruginosa strains CS-555/01 and CS-564/01 – the end of the exponential growth phase in this instance was found at day 10

$$\left(1 - \frac{n_{p,e}}{n_{p,i}}\right) = \left\{1 - \exp\left(\frac{-\frac{3}{2} \alpha_{pb} \eta_{T} \phi_{b} v_{b} t_{cz}}{d_{b}}\right)\right\}$$

Appendix 7. White water model performance equation as developed by Haarhoff and Edzwald (2004). $n_{p,e}$ and $n_{p,i}$ = number of particles in the treated water and influent water respectively; a_{pb} = the attachment efficiency; η_T = the dimensionless particle transport coefficient; φ_b = the bubble volume concentration; v_b = the bubble rise velocity; t_{cz} = the time the bubble spends in the contact zone; d_b = the bubble diameter


Appendix 8. All dose response curves for functionalised polymers compared to results from polyDADMAC and CTAB

Sample	Zeta Pote	ential (mV)	Hydrodynai	nic Diameter
			(D _h , nm)) and PDI
L21	+26.7	± 1.7	18.7	PDI: 0.55
L22	+27.6	± 2.0	90.5	PDI: 0.46
L33	+38.6	± 0.9	110.9	PDI: 0.53
M12	+27.8	± 2.2	12.2	PDI: 0.46
M21	+37.9	± 1.8	17.3	PDI: 0.18
M33	+29.1	± 2.0	66.1	PDI: 0.23
H12	+54.4	± 1.4	235.9	PDI: 0.44
H33	+17.2	± 1.8	244.0	PDI: 0.30
H41	+44.7	± 2.6	1129.0	PDI: 0.43

Appendix 9. Zeta potential and hydrodynamic diameter (with polydispersity index (PDI)) of polymers in buffer solution at pH 7 and a concentration of $Img mL^{-1}$



Appendix 10. All zeta potential results as plotted against mass dose of polymer

Chapter 4.2



Appendix 11. Cell diameter distribution plots obtained via Mastersizer measurement



Appendix 12. All results for modified bubble flotation of CS-555/01 using hydrophobicallyassociating polymers



Appendix 13. Dose response of all polymers as a function of polymer mass. H33 is indicated with filled boxes and line

Chapter 5.1

is (large) 00cystis	E+04 2.92)E+04 5.35	3.29	1.00	E+04 1.10							
nus Oocysti	5 3.05	4 1.90	3	3	3 1.04							
Scenedesn	2.10E+0	7.50E+0	1.78E+0	4.00E+0	2.45E+0							
a Chlorella	4.45E+03	2.02E+04			2.08E+03		4	4	4 5.25E+03	5 1.26E+04		1
e Nitzschie							1.45E+0 ⁴	1.36E+0 ⁴	5.15E+0 ⁴	1.68E+05		7.50E+0
M. flos aqua				8.60E+03	4.70E+04	2.78E+04	1.96E+05	7.85E+04	4.41E+05	1.63E+05		7.60E+02
M. Aeruginosa				1.67E+04		3.00E+04	8.53E+05	2.31E+05				6.67E+03
t Aphenocapsa	2.16E+04	4.00E+04	3.58E+05									
Total Cell Coun	2.32E+05	1.15E+05	4.90E+05	4.09E+05	6.30E+04	5.78E+04	1.05E+06	3.10E+05	4.94E+05	3.32E+05	1.66E+03	7.63E+03
ate	0-Jan	7-Jan	1-Jan	r-Feb	4-Feb	1-Feb	8-Feb	-Mar	5-Mar	1-Mar	3-Mar	Apr

Appendix 14. Break down of major algae and cyanobacteria present in the WSP effluent over the trial period, courtesy of SA Water



Appendix 15. 2010 charge demand monitoring for 24 hours per day over a 4 day period. Raw water charge demand (squares), aluminium sulphate treated water charge demand (circles) and pH (line) can be observed to fluctuate in day-long cycles.

Chapter 5.2



Appendix 16. DAF treated water turbidity with and without acid additions to correct the pH - pilot plant raw feed water pH was from 9.8 to 10.1 over this period

Date	Total Algae	Stichococcus	Planktolyngbya	Aphanocapsa	Microcystis flos-aquae	Chlorella	Dimorphococcus	Planctonema
7-Feb	9.69E+05	,	·	I	4.40E+05		ı	4.57E+05
14-Feb	2.10E+06	ı	ı	ı	1.97E+06	·	ı	1.11E+05
21-Feb	4.60E+05			ı	3.80E+05		ı	6.20E+04
28-Feb	1.73E+06		·	ı	1.65E+06	2.80E+03	ı	7.75E+04
7-Mar	5.23E+06	1.05E+03	ı	1.25E+05	5.06E+06	·	ı	2.90E+04
14-Mar	1.77E+06	·	ı	6.80E+04	1.69E+06		ı	1.21E+04
21-Mar	1.22E+06	1.78E+04		4.85E+05	6.78E+05	9.00E+03	3.45E+03	1.01E+04
28-Mar	1.78E+06	2.10E+05	6.18E+05	ı	9.22E+05	6.40E+03	5.30E+03	5.55E+03
4-Apr	2.77E+06	4.24E+05	ı	1.04E+06	1.28E+06	4.90E+03	1.12E+04	1.40E+03
11-Apr	9.83E+05	1.00E+05	ı	ı	8.16E+05	5.10E+04	3.85E+03	1.70E+03
18-Apr	8.30E+05	9.20E+04	·	ı	6.58E+05	7.70E+04	1.90E+03	9.25E+02
26-Apr	9.94E+05	2.47E+05	·	ı	6.36E+05	6.50E+04	2.57E+04	6.00E+02

Appendix 17. Formal cell counting records from SA Water - all counting data quoted as cells mL^{-1} , "-" indicates no cell counted or no data



Appendix 18. Relationship between turbidity and total cell count measured in the DAF influent



Appendix 19. Plots for all sample points for (A) polyDADMAC and (B) H33 experiments - Results displayed here are raw results with no normalisation



Appendix 20. Float removal for polyDADMAC modified-bubble DAF (A) and conventional DAF (B). In modified-bubble DAF, float is removed in sheets, whereas in conventional DAF the float can be seen to less strenght to shear forces