ZETA POTENTIAL MEASUREMENT FOR WATER TREATMENT COAGULATION CONTROL
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ABSTRACT
Zeta potential was assessed as a tool to optimise pre-chlorination and coagulation at Happy Valley WTP. Samples were obtained from jar tests using raw water spiked with green algal cells. Treatments including pre-chlorination, polyelectrolyte addition and alum dose were investigated. Results indicate that: pre chlorination of algal spiked raw water had a negative effect on zeta potential; alum dose was the most important factor in determining zeta potential; and, the alum dose that achieved the point of neutral charge was equivalent to the alum dose predicted using a predictive algorithm (WTC-coag) which used raw water UV254, colour and turbidity as input parameters. Results obtained from full scale trials did not reproduce jar test results.

INTRODUCTION
Raw water for Happy Valley water treatment plant (WTP) is indirectly supplied from the River Murray and natural catchment and includes open reservoir storage prior to treatment. Raw water quality typically contains elevated concentrations of natural organic matter (NOM) and is generally low in turbidity (<10 NTU). Happy Valley reservoir is subject to algal and cyanobacterial blooms and Cryptosporidium oocysts are detected at the inlet to the WTP. Physical treatment including alum coagulation, cationic (positively charged) polyelectrolyte addition as a flocculant aid, flocculation, sedimentation and granular media filtration are employed. These physical treatment processes rely upon modification of size, surface charge and density of particulate and colloidal contaminants in raw water by coagulation (Jefferson et al., 2004).

Zeta potential provides a measure of the overall surface charge of all the particles and colloids in a water sample. Most particles and colloids, including NOM, algal cells, microorganisms, clay and silt, that are found in natural water at normal pH conditions (pH 6 to 9) are negatively charged possessing a zeta potential in the range -14 to -30 mV (Jefferson et al., 2004). These surface charges give rise to repulsive forces which prevents aggregation and results in a stable system.

NOM has a great influence over the fate of colloids and particles in surface waters. NOM is a diverse group of chemicals including algogenic organic matter (AOM). The chemical properties of NOM is an important factor in determining whether colloids will be stabilised or destabilized (Wilkinson et al., 1997; Walker and Bob, 2001). In typical raw water conditions, fulvic acids will coat and impart a negative charge to colloids and prevent agglomeration while organic compounds with chain like structures can aggregate inorganic colloids through the formation of bridges (Wilkinson, 1997).

Zeta potential is determined by measuring the velocity of particles and colloids while they are subject to an electric field (Jefferson et al., 2004). Charged particles and colloids migrate towards an electrode of the opposite polarity in proportion to the field strength and zeta potential (Jefferson et al., 2004). Recently developed, commercially available instrumentation enables automatic measurement of zeta potential within water samples; the Zetasizer™ is one such instrument.

Edzwald and Tobiason (1999) described two mechanisms for alum coagulation of NOM. The first involves reactions with positively charged aluminium hydrolysis species and negatively charged NOM to form a complex. The second mechanism enables additional NOM removal as colloids and particles adsorb to the complex-metal hydroxide precipitate.

The surface charge of particulate and colloidal contaminants in water are strongly influenced by pH and in most cases the zeta potential increases with increasing pH (Jefferson et al., 2004). Similarly the positive charge of aluminium hydrolysis species is also pH dependent, within the pH range that is required to minimize aluminium solubility. The minimum pH of solubility is about 6.0 and 6.8 at 25°C and 4°C respectively (Edzwald and Tobiason, 1999). Interestingly the surface charge of the aluminium species is greatest at low pH and decreases as pH increases. This explains why alum coagulation at low pH can be achieved with lower doses than at high coagulation pH (Edzwald and Tobiason, 1999).

Reports in the literature indicate that a range of optimum zeta potential conditions are required in order to achieve treatment objectives and site specific testing is recommended (Jefferson et al., 2004). Henderson (2008) claimed an operational zeta potential window between -10 to +2 mV is required in order to achieve optimum removal of
both algal cells and extracellular organic matter. The author claimed that this can be achieved through a combination of coagulant dose and/or pH adjustment. Similarly Sharp et al., (2005) reported an operational window in the range -10 to +5 mv for the optimal removal of dissolved organic carbon (DOC).

The WTC-coag™ software model (previously referred to as mEnCo™) is employed at metropolitan Adelaide WTPs to predict the required alum dose for an operator set point removal of dissolved organic carbon (DOC). The model has been described previously (van Leeuwen et al., 2005 and 2009). Inputs to the model are raw water colour, turbidity and absorbance at 254 nm (UV254).

In recent years operators at Happy Valley WTP have reported that nuisance algal blooms have upset filter performance resulting in increased filtered water turbidity and reduced backwash intervals as well as increasing the required alum demand. The preferred operational response to nuisance algal blooms is pre chlorination where a chlorine dose in the range 1 to 2 mg L⁻¹ is applied prior to coagulant (alum) addition. Jar tests have been undertaken by operators at Happy Valley WTP in an attempt to optimize the pre chlorine dose using conventional endpoints such as colour, turbidity and UV254. However, results obtained to date have been inconclusive. This, together with the instability of algae populations in the raw water, presents a challenge when attempting to select the optimum pre chlorine and alum dose required to achieve water quality requirements cost effectively. Zeta potential measurement was identified as a possible way to optimize treatment at Happy Valley WTP.

This paper presents results from a trial undertaken to assess zeta potential as a tool to assist operators optimize pre chlorine and alum dose at Happy Valley WTP.

**EXPERIMENT**

**Algal cultures and water preparation**

Green algae (Ankistrodesmus) cells were cultivated in ASM-1 media (Gorham et al., 1964), sparged with air, in an incubation cabinet under constant cool-fluorescent light intensity 50 mmol m⁻² s⁻¹ (measured with a scalar quantum sensor (LI-COR LI-190)) on a 12 h: 12 h light-dark cycle at a constant temperature of 20 ± 1 ºC. Bulk raw water samples were collected from Happy Valley reservoir (South Australia) and stored at 4 ºC. Raw water aliquots were spiked with green algae cells and left overnight at 4 ºC prior to use. Cells were counted on a compound microscope (Nikon 50i, Japan) in a Sedgewick Rafter counting chamber after preservation in Lugol's iodine.

Cell concentrations described as low had a cell count of 7,500 cells mL⁻¹, medium 37,500 cells mL⁻¹ and high 75,000 cells mL⁻¹.

**Jar testing**

A PB-900 programmable 6-paddle gang stirrer and B-Ker2 gator jars (Phipps & Bird, USA) containing 2 L of cell spiked raw water was used. Aluminium sulphate (alum; Al₂(SO₄)₃.18H₂O) was added as the coagulant at the WTP concentration (75 mg L⁻¹) unless otherwise indicated. The coagulant was applied during the flash mix period, 2 min at 200 rpm. For experiments with coagulant aid (Magnafloc LT22, BASF Australia (LT22)), the polyelectrolyte was added in the final minute of the flash mix at the water treatment plant dose (0.09 mg L⁻¹). The water was then flocculated for 15 min at 20 rpm and left 20 min for settling. The settled water qualities were assessed by monitoring turbidity and pH. Filtered water was achieved through gravity filtration using 11 µm paper filters (Whatman, UK). The filtered water qualities were assessed by monitoring UV254, colour, and filtered turbidity. All experiments were run at room temperature 22 ± 2 ºC.

For pre-chlorination experiments, a chlorine stock solution was generated by 2, 4, 6-trichloroisocyanuric acid (TCCA) and concentrated hydrochloric acid in an amber Schott bottle. The bottle was then sealed and stored at 4ºC in darkness. Typical chlorine stock solution concentrations ranged from 3-5 g L⁻¹ as free chlorine. The pre chlorination doses were added at a concentration of 2 or 5 mg L⁻¹ prior to alum addition in flash mix. Samples (100 mL) were withdrawn and measured for residual chlorine after the sedimentation period. The DPD-FAS titration method was used to determine the chlorine stock concentrations and free chlorine residuals as described in Standard Methods (APHA et al., 1998).

For pH adjustment experiments a series of pH titrations were performed, where the respective alum dose (75, 90, 100 set point WTC-coag™ i.e. 44, 75, 103 mg L⁻¹ respectively) was added prior to a stepwise addition (200 µL) of 0.2 M sulphuric acid (H₂SO₄) to achieve the target pH (6.8, 6.5, 6.2). The jar tests were conducted as described above with the exception that immediately prior to the commencement of the flash mixing, appropriate amounts of 0.2 M H₂SO₄ were added to achieve the targeted pH during coagulation.

**Water quality testing**

Turbidity measurements were carried out on a 2100AN Turbidimeter (Hach, USA). Colour (true) measurements (456 nm) were made on an Evolution 60 spectrometer (Thermo Scientific, Australia). UV254 measurements were carried out on an Evolution 60 UV/VIS Spectrophotometer (Thermo Scientific, Australia). Prior to UV254 analyses, samples were passed through pre-rinsed 0.45 µm cellulose nitrate filters (Schleicher and Schuell, Germany). Prior to colour analysis,
samples were passed through pre-rinsed 0.22 µm cellulose nitrate filters (Schleicher and Schuell, Germany). The pH of the waters was measured on a WTW 3110 pH meter (WTW GmbH, Germany) which was calibrated with pH 4, 7 and 9 standard buffers (BDH, Australia).

**Measurement of zeta potential (ζ)**
Zeta potential samples were taken from the middle of the jar using a 5 cc/mL syringe (Terumo, Philippines). Disposable folded capillary cells (DTS1070) were pre rinsed with pure ethanol (15 mL) and MilliQ water (15 mL) prior to their use. After pre rinsing, water samples were flushed through the capillary cell which was then filled with 750 µL of sample ensuring no bubbles were formed. The zeta potential of each sample was analysed at 22.5 °C and measured with a Zetasizer™ Nano ZSP (Malvern, UK) using the Zetasizer™ software (v7.03 Malvern, UK). The values presented represent the average of three measurements and the error is one standard deviation.

**Statistical analysis**
The statistical relevance of the differences between the samples was tested using Student’s t-test.

**DISCUSSION AND RESULT ANALYSIS**

**Raw water quality**
The mean and standard deviation (S.D.) values for Happy Valley WTP raw water samples obtained for this trial are presented in Table 1.

**Table 1: Happy Valley WTP raw water quality**

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>Turbidity</th>
<th>Colour</th>
<th>UV254 cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
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<td>3.1</td>
<td>48</td>
<td>0.33</td>
</tr>
<tr>
<td>S.D.</td>
<td>0.12</td>
<td>0.3</td>
<td>2.0</td>
<td>0.01</td>
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</tbody>
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The Zetasizer™
The Nano ZSP zeta potential analyser was rigorously tested over the time span of five weeks in the laboratory using samples obtained from simulated treatment (jar test) and from the full scale WTP. Results from this trial confirm that the performance of the instrument was within the manufacturer’s claimed range for error (± 2.5 mV). Zeta potential gives an estimate of the average surface charge of the particles and colloids in a mixture. The instrument was easy to set up requiring bench space and a laptop or desktop computer to operate the analysis software supplied with the instrument. The software includes analyser and measurement diagnostic checks and allows export of results to MS Excel and other file formats. Pure ethanol is required to wet cells prior to use and to rinse between samples as well as ultra pure water. The sample cells used to analyse zeta potential are reusable/disposable and in excess of 200 single measurements were completed without signal quality impairment. Sample size is small (5 mL), the majority of this is used for cell flushing prior to analysis. No sample preparation is required. The time required for sample analysis is short, ranging from 40 seconds to two minutes. Little difference to zeta potential measurement was found if samples were stored prior to analysis for durations of ~3 hours at ambient temperature. While further site specific testing is required to confirm this observation, it provides the opportunity to locate the analyser at a central location and transport samples from the WTP for measurement.

**Jar tests**
A series of jar tests to simulate treatment processes used at Happy Valley WTP were undertaken. Happy Valley raw water was spiked with laboratory cultivated green algae at low (7,500 cell mL⁻¹), medium (37,500 cell mL⁻¹) and high (75,000 cell mL⁻¹) cell densities. Trends are presented in the following sections to illustrate the response in zeta potential to a range of treatments including pre chlorination, polyelectrolyte addition and alum dose applied to Happy Valley raw water (natural and spiked with algae). Error bars for figures represent standard deviation, n=3.

**Effect of Pre chlorination**
Figure 1, 2, 3 and 4 present the response in zeta potential (ζ) to treatment including pre chlorination and alum coagulation. For these tests pre chlorine was dosed at 0, 2 and 5 mg L⁻¹. Similarly, the alum dose used was equivalent to the alum dose employed at Happy Valley WTP at the time of sampling (75 mg L⁻¹ alum, WTC-coag™ set point 91).

![Figure 1: The effect of (●) no Cl, (▲) 2 mg L⁻¹ Cl, and (■) 5 mg L⁻¹ Cl, in the presence of no algal cell spike.](image-url)
The addition of alum in the absence of pre chlorine reduced the magnitude of zeta potential to a mean of -8.6 ± 0.1 mV for non-algal spiked water. Interestingly zeta potential remained stable following alum addition through flocculation and sedimentation. This observation was demonstrated for all subsequent tests including pre chlorination tests. Similar results have been reported by Sharp et al. (2005). This indicates that the effectiveness of the coagulation process can be monitored very rapidly, within minutes following alum addition using zeta potential. Treatments with pre chlorination at 2 and 5 mg/L increased the zeta potential compared to raw water at zero, low and medium spiked algal density conditions. Combined treatment using pre chlorination and alum coagulation was less effective than alum alone in neutralising zeta potential and measured values were -10.2 and -10.1 mV respectively for comparable dose rates. This increased zeta potential suggests increased colloid and particle stability resulting in impaired removal of NOM, colloids and particles by sedimentation and filtration processes. This trend was also demonstrated in Figures 2 and 3 which presents results for jar tests using raw water spiked with low and medium algae cell densities respectively. Treatment without pre chlorination (alum only) resulted in zeta potential values closer to neutrality than that achieved with pre chlorination. However, for raw water spiked with high algal cell density (Figure 4), there was no significant difference between zeta potential following treatment using alum only and pre chlorination and alum (p> 0.05). These results indicate that pre chlorination was not beneficial in reducing zeta potential at all spiked algal cell densities. In fact pre chlorination increased zeta potential at low and medium spiked algal cell densities. Pre treatment using chlorine has been reported to be beneficial for the removal of algae from water using treatment processes as a result of algal inactivation (Henderson et al., 2008). Mechanisms for this include modification of cell structures, impairment of mobility, and modification of DOC to decrease alum demand and to enable auto flocculation (Henderson et al., 2008). There are several drawbacks to pre chlorination including the formation of disinfection by products such as trihalomethanes (THMs) while overdosing can lead to cell lysis with the release of taste and odour compounds (MIB and geosmin), toxins, and extracellular DOC (Henderson et al., 2008). According to Henderson et al., (2008) the optimum pre chlorine dose is that which causes cell modification but not lysis. The author reported that pre oxidation studies are inconclusive and some species have responded better to this treatment than others.

**Effect of Polyelectrolyte**

Figure 5 presents the response in zeta potential following treatment including the addition of polyelectrolyte for raw water spiked with algae with and without pre chlorination at 5 mg/L.
In this test alum and polyelectrolyte were dosed at equivalent concentrations to that dosed at the full scale WTP. Results indicate that polyelectrolyte addition had no significant difference on zeta potential as compared to alum only treatment (p>0.05). This may be explained as the polyelectrolyte used is a copolymer of quaternary acrylate salt and acrylamide and possesses a low degree of cationic charge with medium molecular weight (BASF, 2015). Given the relatively low dose of the polyelectrolyte used and its low charge density minimal reduction in zeta potential is expected. Higher molecular weight polymers are generally used to promote bridging flocculation (Bolto and Gregory, 2007). The long chain polymers attach at a few sites on the particles, leaving long loops and tails which stretch out into the surrounding water (Bolto and Gregory, 2007). In order for the bridging flocculants to work, the distance between the particles must be small enough for the loops and tails to connect with particles. The polymer molecule thus attaches itself to another particle forming a bridge. If too much polymer is used however, the entire particle surface can become coated with polymer, such that no sites are available to “bridge” with other particles (Bolto and Gregory, 2007). Bridging flocculation can produce very strong flocs but broken flocs are not easy to regrow (Bolto and Gregory, 2007).

Effect of alum dose
The software model WTC-coag™ described previously (van Leeuwen et al., 2005 and 2009) was used to predict the alum dose required to remove an operator set percentage (set point) of DOC through the use of alum coagulation (coagulable DOC). Alum doses were predicted using four standard removal set points (50, 70, 90 and 100) together with measured UV254, colour and turbidity values for the raw water sample obtained for jar testing. These predicted doses were used for subsequent jar tests to investigate the impact of alum dose on zeta potential. The relationship between WTC-coag™ set point and UV254 residual following jar testing with the alum dose (applied and predicted) is presented in Figure 5. It can be seen that the residual UV254 value is reduced as the applied alum dose is increased. The residual UV254 then plateaus as the WTC-coag™ predicted alum dose reaches the set point value equivalent to 100.

Figure 5: The effect of polyelectrolyte LT22 (0.09 mg L⁻¹) addition on the zeta potential with (■) no chlorine, and (●) 5 mg L⁻¹ chlorine, in the presence of medium density algal cell spike.

Figure 6 presents results from a preliminary test which was undertaken to investigate the effect of different alum doses on zeta potential using non algal spiked Happy Valley raw water. The alum doses applied were equivalent to the WTC-coag™ standard set point doses previously described, where 90 represents the standard set point used at Happy Valley WTP (70 mg L⁻¹ alum). It can be seen that the zeta potential was approximately -10 mV at an alum dose equivalent to that applied at full scale. Interestingly, the alum dose equivalent to WTC-coag™ set point 100 (106 mg L⁻¹) which aims to predict maximal removal of coagulable DOC achieved near neutral zeta potential. Further, there was no significant difference in zeta potential at alum doses equivalent to WTC-coag™ set points of 50 and 70 (25 and 44 mg L⁻¹ respectively).

Figure 6: The effect of varying the coagulation dose based on WTC-coag model parameters set at (■) 100, (♦) 90, (▲) 70, and (●) 50.

The impact of alum dose was then assessed in the presence of varying green algae densities. As with the non-algal spiked test, preliminary results
indicated no significant difference between alum doses equivalent to WTC-coag™ set points 50 and 70. For this reason a single alum dose equivalent to a WTC-coag™ set point 75 (44 mg L⁻¹) was used in this test. Results for this test are presented in Figure 7 and a similar trend to that found in Figure 6 can be seen. This illustrates that under the conditions used, coagulant dose impacted zeta potential and the presence of green algae did not.

**Happy Valley WTP field trial**
At the completion of the laboratory experiments the Zetasizer™ was relocated and set up at Happy Valley WTP to investigate zeta potential through the treatment process. Treatment included pre chlorination, however it was not possible to obtain a sample between pre chlorination and alum addition. The respective alum and pre chlorine doses applied at the WTP were 78 and 1 mg L⁻¹ (approximately). The nominal hydraulic retention time for each process was calculated and samples were taken for zeta potential analysis to time match the flow through the process. Results for this investigation are presented in Figure 8. It can be seen that raw water zeta potential was -15.7 ± 0.9 mV. In the absence of chlorine, the addition of alum (78 mg L⁻¹) reduced the zeta potential to -12.9 ± 0.9 mV (p= 0.01).

The impact of alum coagulation at full scale was not as noticeable as that seen when treatment was simulated in the laboratory (jar test). As previously described, simulated treatment using alum addition at a slightly lower dose (75 mg L⁻¹), to that employed at full scale without pre chlorination, achieved a zeta potential closer to neutrality (-5.56 ± 0.1 mV). Jar testing under the conditions employed represents ideal conditions for coagulation. The reduced impact of coagulation at full scale may be explained by deficiencies in plant hydraulic performance such as mixing. Unlike results obtained from jar tests, the addition of pre chlorination and alum reduced the zeta potential to -13.8 ± 1.2 mV (p= 0.003) which was not significantly different to the values obtained without pre chlorine addition (p=0.005). Interestingly lime addition for pH correction, as a slaked-slurry, to settled water increased zeta potential to approximately -15 mV. However, the zeta potential post sand filtration was approximately -10 mV.

**Figure 7: Effects of WTC-coag™ coagulation set point at 100 (black filled symbols), 90 (grey open symbols), and 70 (black open symbols) in the presence of (●) No cells, (♦) low, (▲) medium, and (▲) high algal cells.**

**Figure 8: Happy Valley WTP with (●) no chlorine and (▲) approximately 1 mg L⁻¹ chlorine. Black symbols represent zeta potential readings. Grey symbols represent pH.**

**CONCLUSION**
The performance of the Zetasizer™ Nano ZSP was evaluated under different aspects of the conventional water treatment process. It was demonstrated that the addition of chlorine, at a low (2 mg L⁻¹) and at a high (5 mg L⁻¹) dose, as pre-oxidant had a significant impact on the zeta potential of Happy Valley reservoir raw water with spiked green algae in the range 0 to 37,500 cells m⁻³. Pre chlorination, when applied to raw water, increased the zeta potential and was not beneficial when combined with alum coagulation in reducing the magnitude of zeta potential at low and medium spiked algal cell densities. This trend was not observed at high spiked cell density; it is proposed that the pre chlorine dose was not sufficiently high to overcome the chlorine demand at the high cell concentration.

The polyelectrolyte employed at Happy Valley has medium molecular weight and serves as a coagulant/flocculant aid to improve floc size and strength. The polyelectrolyte did not significantly impact on zeta potential; this is expected given its low charge density.

The WTC-coag™ predictive model does not include specific input data for algae. Similarly zeta potential was found to be largely insensitive to algal cell density based upon results obtained from this study. Results from this investigation indicate that alum dose was the most important factor in controlling zeta potential.

The impact of alum coagulation on zeta potential under at jar test conditions was greater than that observed at full scale. Differences may be
explained as jar tests employed ideal mixing and hydraulic conditions which may not be achievable at the full scale WTP. Jar tests indicate alum doses that achieved neutral zeta potential were equivalent to the alum dose predicted using WTC-coag™ to achieve maximum removal of coagulable DOC using raw water turbidity colour and UV254 input data. This investigation demonstrated that samples can be collected and analysed with at least a three hour delay without loss of sensitivity. Furthermore, the Zetasizer™ is easily operated and transportable. It requires little specialised equipment or chemicals. The analysis cells are reusable/disposable, but allow at least 300 separate measurements before replacement is required. The acquisition of an autosampler, would enable more rapid and time saving analysis.

This trial demonstrates that zeta potential measurement using the Zetasizer™ Nano is relatively easy to perform. Results obtained are reliable, reproducible and easy to interpret. Zeta potential complements the evaluation criteria currently applied to determine the coagulation requirements for the WTC-coag™ coagulant prediction model. Samples can be obtained immediately after alum flash mixing and zeta potential measured within minutes. Zeta potential can be used to provide rapid, consistent and reliable feedback to optimise and control the coagulation process.

REFERENCES

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