Impacts of salt type and concentration on coagulation of humic acid and silica

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ABSTRACT

Zeta potential distributions of model waters containing silica, humic acid, and differing ionic composition were evaluated. These distributions showed that under high ionic strength and in the presence of divalent cations, positive colloids exist in suspension with neutral and negative colloids. Positive colloids do not form at lower ionic strength or when polyvalent cations are absent. The existence of the positive colloids in suspension with the negative colloids suggests that, while electrodynamically unstable, some stabilizing factor is preventing coagulation. This stabilizing factor is likely adsorbed humic acid causing steric hindrance. Further tests indicated that under the conditions that lead to the existence of positive colloids, removal of humic acid by ferric chloride coagulation is diminished as compared to coagulation in lower ionic strength water or water containing just sodium chloride as the ionic matrix. As positively calcium–humic complexes can increase fouling of desalting membranes through the formation of densely packed fouling layers, understanding the mechanisms of coagulation in high ionic strength waters is crucial to improving performance of desalination operations.

Key words | coagulation, desalination, organic matter, water treatment, zeta potential

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BACKGROUND

Fouling of reverse osmosis (RO) membranes is one of the major concerns in the desalination industry. High fouling rates lead to either increased pressure to maintain a permeate flux set-point or decreased specific flux, which in turn lead to higher capital and operations and maintenance costs. To reduce fouling, many desalination facilities include coagulation as a pretreatment step designed to remove particulates and organic matter and limit biological growth in the membrane systems. However, little literature exists regarding how these pretreatment processes are optimized for reducing foulants. At present, the main tool that is used for evaluation of RO membrane fouling is the silt density index (SDI) or its close relative, the modified fouling index (MFI). However, SDI (or MFI) is not truly representative of RO membranes' characteristics and properties; nor do the SDI or MFI tests account for biological growth on

membranes or membrane systems, or take adsorption of organic matter onto membrane surfaces into account.

The main causes of membrane fouling on surfaces or inside pores are biological growth, deposition of naturally occurring or precipitated particles, and adsorption of organic matter. Although micro/ultrafiltration membranes are being used more commonly as pretreatment for RO and nanofiltration membranes, submicron particles and dissolved organic matter can still pass through the pretreatment membranes and act as foulants on the RO membranes. Removal of the foulants can be improved by optimization of coagulation as a pretreatment. For surface waters, tools such as streaming current monitors or zeta potential analyzers have been developed to optimize coagulation and have been used for design and treatment optimization in many places. However, for technical and economic reasons, the desalination industry

has not been able to integrate these same diagnostic approaches into design/operations of desalination facilities. Therefore, reliable operation of coagulation resulting in stable, high quality feed water quality for RO membranes has been very difficult to achieve, especially for desalination plants using open water intakes.

As part of a larger project examining the fate of organic matter in desalination pretreatment (Schneider et al. 2012), zeta potential measurements were made on two natural seawaters from Monterey Bay (Pacific Ocean) and Tampa Bay (Gulf of Mexico). These measurements consistently showed that positively charged colloids were found in the seawaters. In high ionic strength solution, coagulation theory suggests that particles should rapidly coagulate because of electric double layer compression (Edzwald et al. 1974). The fact that these positively charged particles exist in suspension with neutral and negatively charged particles suggests that a stabilizing force is preventing coagulation of the particles. This stabilizing factor is likely adsorbed organic matter that causes steric hindrance preventing the particles from approaching close enough to coagulate and subsequently settle. Figure 1 shows zeta potential distributions of a river water with low ionic strength along with a raw seawater. The plot clearly illustrates that the fresh water has no particles with positive charges while the raw seawater has a significant fraction of particles in the positive range.

The objective of this portion of the larger project was to evaluate particle charge in high conductivity model waters and examine the impacts of mono- and divalent cations on coagulation of organic matter. The particle charge distribution of high conductivity waters was explored using a series of model waters with varying conductivity and ionic make-up. The impacts of mono- and divalent cations on removal of organic matter by coagulation was examined through jar testing of model waters with ferric chloride.
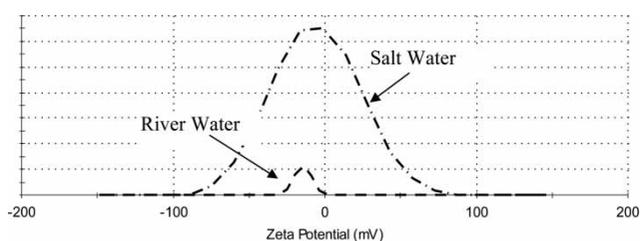

Figure 1 | Comparison of zeta potential distributions of fresh and salt water.

LITERATURE REVIEW

When particles are placed in water, they develop a surface charge (typically negative) due to one or more factors including imperfections in crystal lattices (isomorphic substitution), ionization of functional surface groups, and adsorption of organic matter (Stumm 1992). Surface charges, in combination with fluid flow fields, govern the transport and attachment of particles to other particles as well as to surfaces (Hunter 1981). When surfaces have low charge, there is little repulsion and the surfaces can stick together due to attractive van der Waals forces (Hunter 1981). As surface charges increase on particles, interparticle repulsion increases preventing particle attachment and making particle removal more difficult. While the dynamics of particle transport and accumulation are complex, the role of coagulation is to decrease the repulsive forces between particles to allow them to approach close enough that attractive forces predominate. To evaluate and minimize the surface charges in an efficient and scientific way, it is necessary to be able to examine particles' surfaces.

One method of doing this utilizes measurements of the electrostatic potential on particles; this is known as the zeta potential. Zeta potentials are measured by passing an electrical current between two electrodes in a cell containing a sample. Negatively charged particles move towards the positively charged electrode. The movement response of these moving particles is then analyzed. The speed of the particles' movement is directly proportional to the zeta potential, or surface charge of the particles (Hunter 1981; Hiemenz 1986). To increase the accuracy of measurement, applied voltages of greater than 100 volts are often used. However, in high conductivity media, e.g., seawater, even relatively low applied voltages lead to deposition of salts or evolution of gases on electrodes that can cause inaccuracies in the measurement (Hunter 1980) and invalidate the results.

Newer generations of zeta potential instruments rely on the use of lasers and Phase Analysis Light Scattering (PALS) to enable measurements of zeta potential in high conductivity environments (up to a conductivity of 200,000 μS/cm), well within the limits of seawater and unlike conventional zeta potential instruments which are limited to

conductivity below 25,000 µS/cm (Tscharnuter 2001). Additionally, these newer instruments measure the zeta potential of all particles (from as low as 3 nm to >10 µm in diameter, depending on the instrument and configuration) in their sensing zones. Because the charges on all of the particles are analyzed, a more statistically significant result is gained as compared to conventional zeta potential monitoring systems where fewer than 50 particles are commonly analyzed.

Because of the difficult nature of measuring particle charge in seawater, relatively few studies have been performed that measure particle charge. Particle charge in seawater is important, however, because of the nature of membrane surfaces. In a United States Bureau of Reclamation report (Elimelech & Childress 1996), the authors found that all of the RO membranes tested were negatively charged at normal pH operating conditions. Furthermore, the authors state that in high ionic strength waters, when deposited particles and membrane surfaces are of opposite charge, deposition of particles results in a thick fouling layer and extensive fouling. Thus, understanding the nature of particles entering the membrane cartridges is important if fouling is to be minimized.

Despite these difficulties, several studies have been performed that examined particle surface charge in seawater. An early study on the charge characteristics of particles in seawater (Hunter 1980) explored the surface charge of synthetic particles coated with natural organic matter (NOM) extracted from coastal seawater under high ionic strength conditions. The surface charge of these particles showed responses to changes in pH and metal ion concentrations. The author concludes that 'macromolecular species and hydrophobic humic material are important contributors to ambient organic films [on particles in seawater] and that these results suggest that an important fraction of seawater DOM [dissolved organic matter] displays a systematic uniformity of behavior'. From this statement it can be surmised that this 'systematic behavior' might be exploited by the use of coagulants to neutralize these particles and dissolved organic matter for removal by pretreatment processes.

In the neutral pH range, most suspended particles typically encountered in natural waters are negatively charged (Stumm 1992). A literature review has shown that there are relatively few functional groups that are positively charged at pH 7 and above in seawater. In a 1980 paper on electrophoretic properties of seawater, Hunter states that:

'… widely different surfaces freshly exposed to seawater become covered by a tenacious film of natural surface-active organic material which dominates their subsequent surface chemistry. The mobility variation with pH and metal ion concentration point to carboxylic acid and phenolic groups as the major ionizable functions … The studies provide no evidence for functional groups capable of positive charge such as –NH, guanidyl, and imidizole groups' (Hunter 1980).

However, there have been reports of positively charged particles in marine environments when measured by streaming current (Pravdić 1970); other papers (Edzwald *et al*. 1974; Hunter 1980; Hunter & Liss 1982) clearly report the reduction in negative charge (but not a charge reversal). These reports have typically suggested that calcium and/or magnesium complexation is the cause (Pravdić 1970; Newton & Liss 1989). Several of these papers (Hunter & Liss 1979; Newton & Liss 1987, 1989; Hong & Elimelech 1997) suggest that divalent cations complex with monovalent negatively charged groups leading to the formation of monovalent positive carboxyl–calcium complexes ($\equiv RCOO\text{-}Ca^+$). If enough of these complexes form on a particle, a net positive charge may be observed. With a net positive charge, several outcomes could occur:

- If steric hindrance is low, the calcium may act as a bridge bond and complex two carboxyl groups on one or more particles ($\equiv RCOO\text{-}Ca\text{-}OOCR\equiv$) leading to particle growth.
- The calcium may act as a bridge bond between a carboxyl group adsorbed to a particle and a carboxyl group adsorbed to a membrane surface (Yoon *et al*. 1998).
- Dissolved humic molecules may form a cross-linked fouling layer in the presence of divalent calcium ions via calcium binding with humic carboxylic groups and bridging among adjacent humic molecules (Lee & Elimelech 2006).
- The now positively charged particle may be transported to the negatively charged membrane surface and interact directly with it (Elimelech & Childress 1996).

A more recent paper (Furukawa *et al.* 2009) examined aggregation of clay and organic matter in artificial seawater. This study showed that increasing salinity resulted in less negative zeta potential, and that when even a small amount of electrolyte (salt) was present, the zeta potential becomes insensitive to pH. The authors conclude, based on surface energy interaction calculations, that organic macromolecules prevent clay mineral aggregation primarily through the introduction of steric repulsion. While this study only reports average zeta potentials, at higher salinities average zeta potentials >0 mV were reported at pH ranges between 7 and 8.

MATERIALS AND METHODS

Approach

In an effort to understand under what conditions positively charged colloids form and how the presence of these colloids may affect treatment, a series of model waters were created and tested. To examine the factors that can lead to the formation of positive colloids, solutions of silica, Aldrich humic acid (AHA), and various ionic matrices were used. The ionic matrices consisted of sodium chloride, sodium chloride plus magnesium chloride, sodium chloride plus calcium chloride, or a commercially available seawater mix, Instant Ocean®. The salt concentrations were varied to represent 'fresh' water (no salts), 500 mg/L (mildly salty), 3,000–5,000 mg/L (brackish), and approximately 25,000 mg/L (saline or estuarine water).

The components of the model waters were chosen for specific purposes. Silica is a natural particle and the surface charge has been well characterized (Kim & Lawler 2005). AHA was selected as the organic matter specifically for its terrestrial origin and is more representative of surface runoff with low residence time in the marine environment than organics of marine origin; it has also been used in other studies investigating coagulation in seawater (Duan *et al.* 2002a, b). The salts used (sodium, magnesium, calcium, and chloride) are major ionic components of seawater. The combination of these components, while still a model system, allows insights into the factors that inhibit coagulation of organic matter in real seawaters.

For the model waters, magnesium concentrations up to 1,500 mg/L as Mg and calcium concentrations up to 400 mg/L as Ca were selected as these somewhat exceed the concentrations of these ions in several seawaters analyzed (Tampa Bay, FL and Monterey Bay, CA).

The first group of tests involved measurements of zeta potential distributions and was performed to examine what conditions (salt type and concentration, organic type and concentration) led to the formation of positively charged colloids. The second group of tests involved jar testing and was designed to determine whether the presence of positively charged colloids had an impact on organic removal by coagulation.

Model waters

Model waters were created using laboratory-grade total organic carbon (TOC)-free deionized water. All chemicals added to the water were laboratory grade. Prior to use, all model waters were allowed to equilibrate at room temperature for at least 24 hours while being continuously mixed on a stir plate.

Silica

All particulate matter used in the model water were 5-μm silica Min-U-Sil® 5 supplied by the US Silica Company. According to the certificate of analysis supplied, the particles were 99.2% silicon dioxide (SiO_2) with 97% of the particles ≤ 5 μm in size.

A stock solution of these particles was made by placing 2.0 g into 100 mL of deionized water. Prior to use in experiments, this stock solution was sonicated for 15 min to ensure dispersion of the solids. A constant silica concentration of 20 mg/L was used for all experiments.

Aldrich humic acid

AHA was purchased from Sigma-Aldrich Inc. According to the accompanying assay, the material is 55.2% by weight carbon. A stock solution of the humic acid was made by dissolving 0.55 g of the solid material into 100 mL of TOC-free water. AHA was chosen as the source of organic matter specifically because of its terrestrial origins as this would

be more representative of surface runoff with low residence time in the seawater than lower molecular weight organic matter that had been subject to marine biodegradation or organic matter of marine origin, e.g., algal by-products.

Salts

Sodium chloride, sodium bicarbonate, calcium chloride, and magnesium chloride were all used as part of various ionic matrices for the model waters. The salts were purchased as analytical grade from either Sigma-Aldrich or JT Baker Chemical Company. These salts were added as solid crystals to TOC-free deionized water to achieve desired concentrations.

Artificial seawater

The commercially available artificial seawater mix, Instant Ocean, was used for the artificial seawater. This salt mix is representative of seawater and contains both the major constituents (chloride, sodium) and minor constituents including sulfate, magnesium, potassium, calcium, carbonates, bromide, strontium, boron, fluoride, lithium, iodide, and barium. This seawater mix was added to TOC-free deionized water to achieve a total mass concentration up to 30,000 mg/L.

Jar testing

The model waters for the jar tests contained 20 mg/L silica and approximately 2 mg/L (as C) AHA with varying amounts of sodium chloride or Instant Ocean. All test waters contained 1 mM sodium bicarbonate. For the jar tests, 500-mL aliquots of the model waters were measured using a graduated cylinder, and placed in 1-L round beakers.

Jar tests were conducted using a Phipps and Bird model PB-700 jar test apparatus equipped with 2.5 cm × 7.5 cm stainless steel paddles. The mixing speeds were set and changed manually at each time interval.

Mixing

The waters were mixed at a G of 500 s^{-1} for 1 min. This step was followed by two steps of slow mixing for 12 min ($G = 50$ and 25 s^{-1}) and then settling for 30 min.

Analyses

Turbidity: Turbidity measurements were performed using a Hach model 2100N bench top turbidimeter according to Standard Method 2130 B (APHA 2005).

Total organic carbon: TOC was measured using a Shimadzu TOC-V$_{csh}$ TOC analyzer with autosampler according to Standard Method 5310 B (APHA 2005). Samples were acidified using sulfuric acid to pH < 2 prior to analysis. Results shown are the average of triplicate injections.

Zeta potential distribution: Zeta potential distributions were measured on samples using a Malvern Instruments ZetaSizer Nano ZS-90. Samples were placed in the glass cuvette using the dip cell and a standard operating procedure run. The standard operating procedure was manually set to equilibrate the sample for 2 min at 20 °C and then run 100 subruns. The subruns were conducted with automatic voltage and attenuation settings. Despite the high conductivity, the data were processed using the General Purpose analysis to provide the distribution data instead of a Monomodal analysis that would provide an average reading.

RESULTS

Zeta potential investigations

The zeta potential investigations were designed to examine the different factors that contribute to the existence of positively charged colloids. The suspensions were created and examined in a step-wise fashion that would enable pair-wise comparison between independent variables. The variables that were examined included salt type (sodium chloride, artificial seawater, calcium chloride, and magnesium chloride), salt concentration (reported as conductivity), and the presence of organic matter (0 or 5 mg/L AHA).

For the first set of water, the impact of salt type and concentration on the charge distribution of 20 mg/L of silica was examined without the presence of organic matter as shown in Figure 2. As seen in this figure, as the salt concentration increased, the negative charge on the particles decreased. This effect has previously been reported in the literature (Hunter & Liss 1979; Kim & Lawler 2005). It is
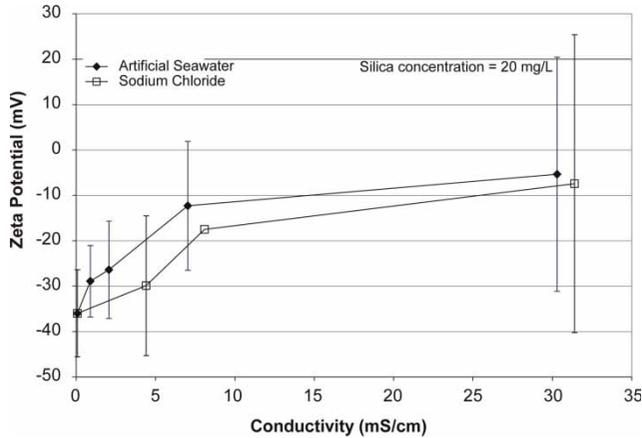
Figure 2 │ Impact of salt on silica zeta potential.

notable that the waters with the Instant Ocean had average zeta potential less negative than for sodium chloride given the same conductivity. This was likely due to the presence of polyvalent cations (notably magnesium and calcium) in the ionic mix.

For the second set of experiments, organic matter was included in the water matrix. Figure 3 shows the impact of salt concentration on the silica zeta potential with 5 mg/L AHA present. Again, as the salt concentration increased, the average zeta potential became less negative.

The average zeta potential values for the suspension with AHA were more negative than the silica without AHA indicating that the organic matter adsorbed to the silica and imparted additional negative charge. Even at the highest concentrations of sodium chloride, the average

zeta potential for all samples was negative. It is interesting to note in this figure that positively charged particles were not observed in the waters with sodium chloride and only observed in the Instant Ocean when the conductivity approached 30 mS/cm. Because no positive charges were observed when the monovalent sodium was added, it was inferred that polyvalent cations (primarily magnesium and calcium) cause this phenomenon. It is well known that calcium can complex humic acid and, furthermore, these calcium–humate complexes are known to lead to fouling of microfiltration and nanofiltration membranes through the formation of intra- or intermolecular bridges (Yoon *et al.* 1998; Yuan & Zydney 1999).

Based on several reports and laboratory measurements, seawater contains (on a mass basis) approximately five times more magnesium than calcium (up to 300 mg/L as Ca and 1,500 mg/L as Mg). For the next set of analyses, instead of using the Instant Ocean mixture (which contains both magnesium and calcium), magnesium chloride, or calcium chloride was used in the water matrix to try to determine whether one of these ions had a bigger impact on surface charge of the silica particles (with humic acid present) than the other. The calcium concentrations were 100, 200, 300, and 400 mg/L as Ca; the magnesium concentrations were 250, 500, 1,000 and 1,500 mg/L as Mg. These results are combined and shown in Figure 4.

When comparing the relative impacts of calcium and magnesium, one interesting feature stands out, as shown in Figure 4. At low sodium chloride concentrations
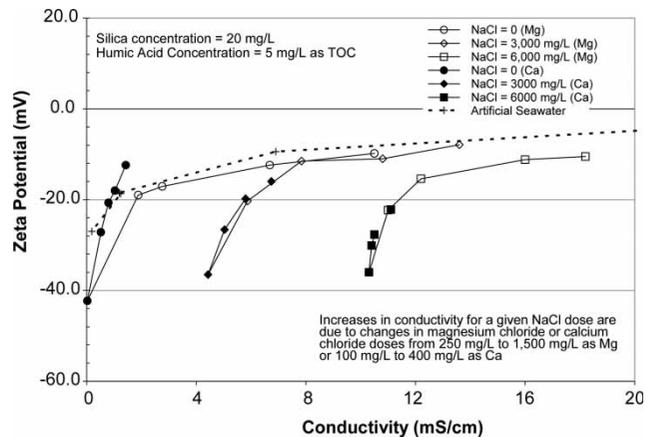

Figure 3 │ Impact of salt on silica zeta potential with NOM.

Figure 4 │ Comparison of impact of calcium, magnesium, and Instant Ocean on zeta potential.

(conductivity), the impact of calcium on charge was much stronger than the impact of magnesium, possibly due to specific complexation of calcium. However, at higher background sodium chloride concentrations (3,000 and 6,000 mg/L) there was essentially no difference in the impact of calcium versus magnesium suggesting that complexation by calcium was equivalent to complexation by magnesium. When the impacts of calcium and magnesium are compared to the artificial seawater (Figure 4), it was apparent that the artificial seawater had much the same impact on surface charge as sodium/calcium or sodium/magnesium combinations. This would seem to indicate that the Instant Ocean is a good model for salts in natural seawaters, as shown in Figure 5.

Jar test results

Once it was determined that positively charged colloids could be produced in the laboratory under salt and organic carbon concentrations that are similar to real seawater, the next step was to examine if organic removal by coagulation is affected by salt type and concentration.

The purpose of these tests was to examine the impact of the salt type and concentration on treatment performance. As shown in the zeta potential investigations above, increasing salt concentration resulted in a decreased negative charge; however, at high concentrations of Instant Ocean, positive colloids were formed. These jar tests were designed to see whether the high concentrations of polyvalent cations resulted in poor coagulation performance.

Sodium chloride

The first set of jar tests examined the impact of sodium chloride on coagulation performance alone. As shown in
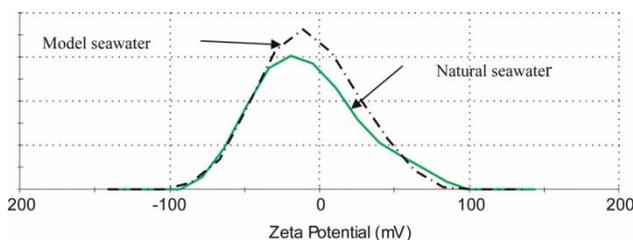
Figure 3, increasing the sodium chloride concentrations up to 25,000 mg/L resulted in increasing zeta potential (less negative) but no positive colloids were observed. Based on these observations, it was hypothesized that increasing sodium chloride concentrations up to a conductivity of 26 mS/cm (approximately 25,000 mg/L) would result in increased coagulation performance.

As shown in Figures 6 and 7, increasing the background sodium chloride concentration reduced the ferric chloride dose required for both turbidity and organic removal. When no sodium chloride was present, the required ferric chloride dose for turbidity removal exceeded 30 mg/L. At 500 mg/L NaCl, the required ferric chloride dose was 30 mg/L, with some turbidity removal occurring at 20 mg/L. When the NaCl was 5,000 mg/L, the required ferric chloride dose was
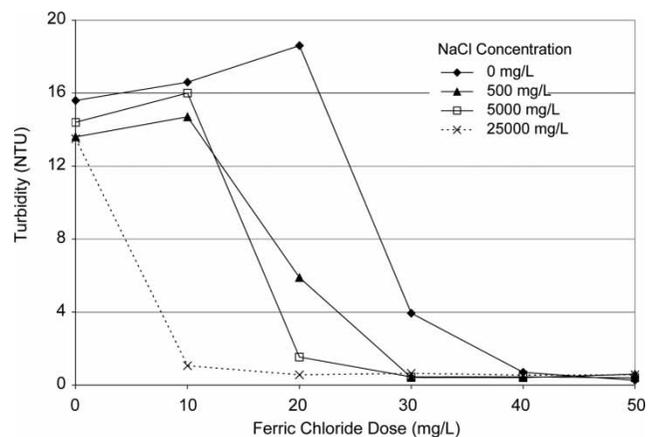

Figure 6 │ Impact of sodium chloride on coagulation performance – turbidity.

Figure 5 │ Comparison of natural seawater and model seawater.
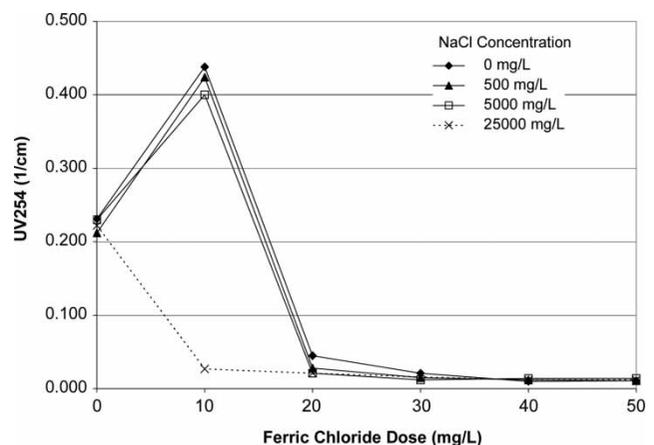

Figure 7 │ Impact of sodium chloride on coagulation performance – UV254.

20 mg/L; at 25,000 mg/L, the required dose was only 10 mg/L. For organic removal, the same trends existed, although the required dose for TOC removal was 30 mg/L at the lower NaCl values (0–5,000 mg/L) and only 10 mg/L at 25,000 mg/L.

Artificial seawater

The second set of jar tests examined the impact of the Instant Ocean on coagulation performance. As shown in Figure 3, increasing the seawater concentration increased the zeta potential (less negative); at conductivity less than 6 mS/cm (approximately a mass concentration of 5,000 mg/L), no positive colloids were observed. However, at some point between 6 and 28 mS/cm (mass concentration approximately 25,000 mg/L), positive colloids began to form. Thus, based on these observations, it was hypothesized that at low and moderate Instant Ocean concentrations, the salt would improve coagulation performance but at the highest salt concentrations tested, coagulation performance might be degraded.

Figures 8–10 show the results from jar tests when Instant Ocean was used as the ionic matrix. As shown in Figure 8, increasing the salt concentration improved coagulation performance for removal of turbidity. Higher levels of salt also lowered the required ferric chloride dose from 40 to 10 mg/L.

The impact of Instant Ocean concentration on organic carbon removal is shown in Figure 9. Clear effects of salt
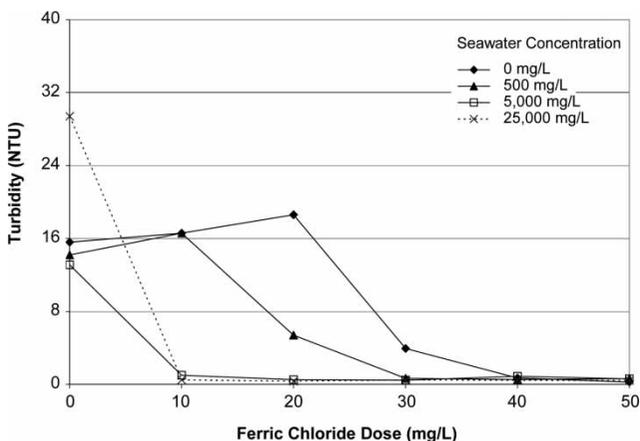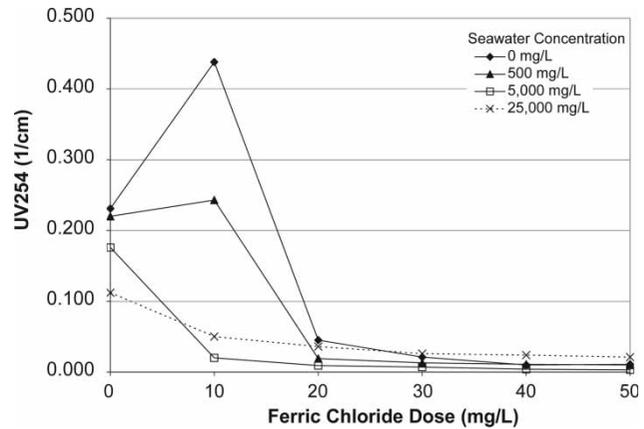
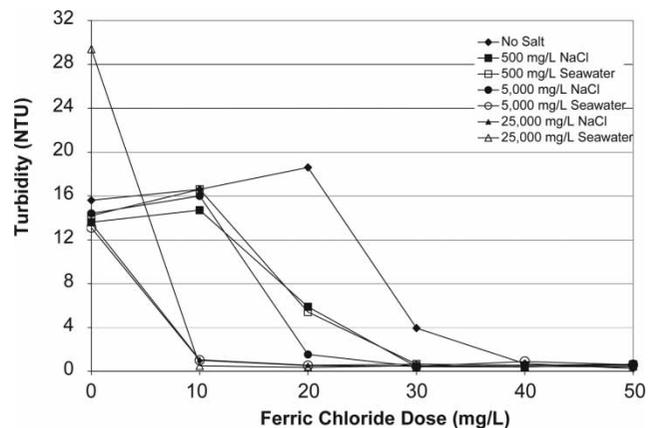**Figure 9** | Impact of Instant Ocean on coagulation performance – UV254.

Figure 10 | Impacts of salt type and concentration on turbidity removal.

are seen for UV254 removal. Low (500 mg/L) and moderate (5,000 mg/L) background salt concentrations resulted in improved coagulation performance. However, at the highest salt levels (25,000 mg/L), the UV254 levels were higher than at 5,000 mg/L.

Comparison of sodium chloride and artificial seawater

Figures 10 and 11 show comparisons of the impact of sodium chloride and Instant Ocean on the removal of turbidity and UV254. As shown in these figures, at low salt concentration, both the sodium chloride and Instant Ocean increased removal of both turbidity and UV254 versus the no salt condition; there was essentially no difference in impact of salt type. At moderate salt concentrations
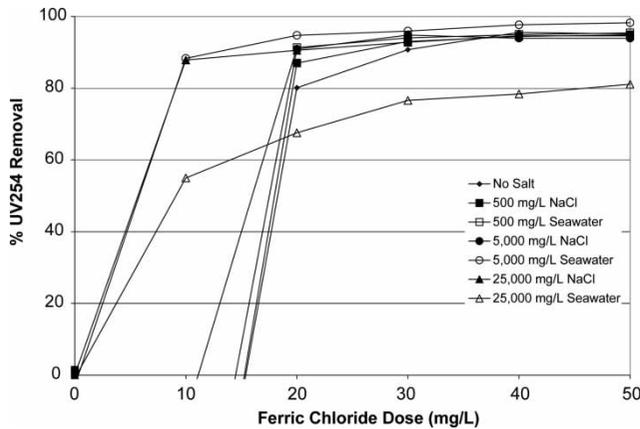
Figure 8 | Impact of Instant Ocean on coagulation performance – turbidity.

Figure 11 │ Impacts of salt type and concentration on UV254 removal.

(5,000 mg/L), the Instant Ocean had a greater beneficial impact on performance than the sodium chloride. With sodium chloride, the optimal ferric chloride dose was 20 mg/L, but with the Instant Ocean, the optimal ferric chloride dose was 10 mg/L. In terms of performance, the 5,000 mg/L Instant Ocean resulted in performance similar to the performance of 25,000 mg/L NaCl. This was likely due to the charge neutralization effects of the polyvalent cations as well as compression of the electric double layer at higher ionic strength. This improved performance with increasing salt concentration agrees with findings by Edzwald *et al*. (1974) for clay minerals.

At the highest salt concentrations, both the sodium chloride and Instant Ocean had optimal ferric chloride doses of 10 mg/L for turbidity removal. However, for UV254 removal, the Instant Ocean had a negative impact
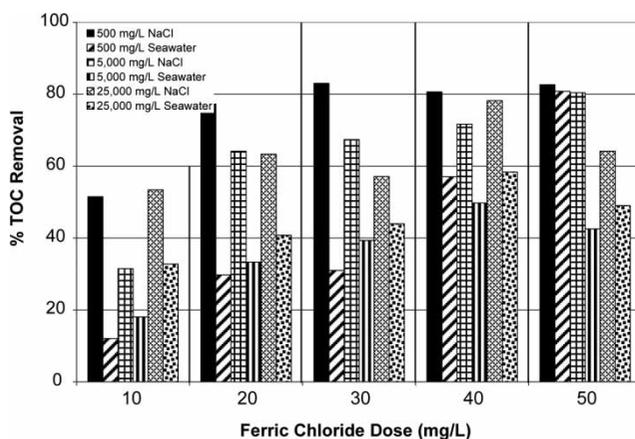

Figure 12 │ Impacts of salt type and concentration on percent TOC removal.

on removal, while the NaCl had a positive impact. This disparity in performance was possibly due to the formation of positively charged colloids at high Instant Ocean concentrations as shown in Figure 2.

Figure 12 shows the impact of salt type and concentration on percent TOC removal. As shown in this figure, for every ferric chloride dose tested, the percent removal of TOC was lower when the Instant Ocean was used as the ionic matrix as compared to when sodium chloride was used. Again, this poorer removal may be due to the presence of polyvalent cations complexing organic matter and preventing subsequent removal by coagulation.

SUMMARY

Zeta potential investigations

When sodium chloride was used as the ionic matrix, no positive colloids were observed up to a total dissolved solids (TDS) of 25,000 mg/L (Figure 3). When the artificial seawater matrix was used, positive colloids were observed when the salt concentration was increased to a TDS of approximately 25,000 mg/L (Figure 3). When experiments were conducted to compare the impacts of magnesium and calcium on the presence of positive charged particles, there was no difference seen between these two divalent cations at moderate and high sodium levels (Figure 4). These results are similar to the conclusions in Hong & Elimelech (1997) who found that there was no difference in the zeta potential of nanofiltration membranes that had been used to treat calcium complexed NOM and magnesium complexed NOM.

Jar tests

When sodium chloride was used as the background matrix, coagulation by ferric chloride was improved, with increasing performance at higher salt concentration (Figures 6 and 7). However, when the artificial seawater mix was used, coagulation performance improved at low and moderate salt concentrations, but was harmed at the highest salt concentration (Figures 8 and 9). When combined with the data regarding the causative factors for positively charged colloids,

this would seem to indicate that the presence of positively charged colloids appears to inhibit coagulation performance.

One implication for this is that desalination plants using open water intakes may require more extreme pretreatment methods that alter the complexation and charge characteristics of the humic acid–coagulant interactions for removing organic matter from the water prior to membrane treatment. These methods may include but are not limited to coagulation at high doses, very low (≤ 5) or high (≥ 11) pH, or oxidation.

Conclusions

Zeta potential measurements clearly indicate the existence of positively charged colloids in waters containing NOM and high levels of divalent cations (notably calcium and magnesium). Increasing salt levels initially aids the coagulation of organic matter by ferric chloride, probably due to the charge neutralizing effects of the divalent cations. However, increasing divalent ion concentrations beyond some critical level (a TDS between 5,000 and 30,000 mg/L for this water, but likely dependent on the type and concentration of NOM) results in decreased performance of coagulation.

Conventional coagulation theory suggests that increasing ionic strength results in improved coagulation due to electric double layer compression. However, the presence of NOM in high ionic strength solutions inhibits coagulation due to the formation of calcium or magnesium–carboxylate complexes and steric stabilization.

The presence of positively charged colloids may result in increased fouling of negatively charged desalting membranes. Thus, there is a need to understand the basic coagulation mechanisms involved and how to improve organic matter removal through desalination pretreatment processes.

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