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Factors affecting the coagulation of seawater by ferric chloride

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ABSTRACT

The combination of chemical coagulation and membrane filtration (e.g. micro- or ultra-filtration) represents an effective pretreatment for seawater desalination by reverse osmosis (RO). The removal of dissolved organic substances requires optimization in order to enhance treatment performance and minimize the risk of membrane fouling. For this reason a detailed understanding of the performance of hydrolyzing metal salts during coagulation is essential. In this study, coagulation experiments with ferric chloride were carried out using a standard jar test technique, and microfiltration (MF) was simulated using a 0.45-µm membrane filter. Factors affecting the coagulation behaviour in terms of the removal of humic acids (HA) in seawater were investigated, namely the pH, coagulant dose, saline strength, HA concentration and presence of oil. Experimental evidence concerning the chemical bonding of high valence metal ions (Fe^{+3}, Ca^{+2}, Mg^{+2}) were provided by fluorescence spectroscopy and its theoretical relevance to the coagulation processes has been discussed. Laboratory experiments were carried out over a wide range of iron dosage (16–2,500 µmol/L) and pH (4–9) and a coagulation diagram (iron dosage versus pH) defining domains of HA removal has been established with corresponding values for the electrical surface potential of aggregates. The maximum removal of HA (~95%) in samples of Singapore seawater was found to occur at pH 5 and at a coagulant dose ≥150 µmol Fe/L. For water quality comparable to that of offshore seawater the coagulation performance in terms of HA removal was not strongly influenced by seawater strength, the presence of oil or the initial HA concentration within practical ranges of these parameters.

Keywords: Coagulation; Seawater; Water treatment; Ferric chloride; Humic acid; Oil

1. Introduction

The rapid development in membrane technologies in the last few decades has made reverse osmosis (RO) a more affordable process to produce drinking water from seawater or estuarine sources [1]. However, membrane fouling, especially irreversible fouling remains an important limiting factor in the process. Irreversible fouling normally refers to the phenomenon of the long-term decrease of membrane permeability in the course of module operation due to the accumulation of various materials on surfaces and within inter-segmental spaces of the membranes. With the accumulation of such fouling materials, the capability of salt rejection of the membrane will eventually decrease and cannot be recovered [2]. Despite recent improvements in the performance of the membranes arising from advances in membrane material science and the increased tolerance towards foulants, the feed water quality remains one of the most critical factors in designing a reliable RO plant [3]. Pretreatment is usually required to remove the potential membrane foulants, and the extent of pretreatment depends on the membrane configuration and

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feed seawater quality. It has been considered better to over-design the pretreatment system in order to protect the membranes [1,4]. Although playing a complementary role, the pretreatment of raw seawater for desalination by RO is of great importance in order to obtain efficient operational conditions and a high operational economy [5].

An effective pretreatment arrangement is to combine chemical coagulation with a membrane module, such as microfiltration (MF) and/or ultrafiltration (UF), as well as nanofiltration (NF) [6]. Compared with the conventional coagulation-sedimentation-media filtration process sequence, pre-treatment involving UF/MF possesses many merits and is a more energy friendly option for RO desalination [7]. Most dissolved or soluble natural organic compounds, such as humic and fulvic acids, can penetrate MF and UF membranes, so removal of these substances relies largely on the effectiveness of the coagulation process prior to membrane. A full and detailed study of coagulation as a pretreatment step in the desalination of seawater is therefore important in order to evaluate and optimize the performance in practice. The purpose of coagulation is two-fold: (1) to precipitate as much colloidal and soluble natural organic matter as possible; and (2) to create such precipitates or flocs with advantageous physicochemical properties that avoid adverse effects on the subsequent membrane processes in respect of the intrinsic cake filtration mechanisms [8] and membrane fouling. It has been reported that the electrical charges of organic compounds affect membrane flux and fouling [9], and potentially the electrical properties of co-precipitates, plus aggregate size or density, may be important [10] also. Thus, information about the surface charge or potential of the co-precipitated aggregates should be useful in identifying the optimal coagulation conditions.

Coagulation by hydrolyzing metal salts is a well-researched topic and a comprehensive review of this has been published recently [11]. However, while the general mechanisms of coagulation are well-established there are some aspects that still require further investigation. In our previous studies [12,13], we have confirmed that humic acids are much less electrically charged in seawater conditions than in non-saline and de-ionised waters, and that competition for hydroxyl ions in solution in co-precipitation processes may be responsible for the optimal removal of humic acids in water. Also, the nature of the interaction of divalent metal ions, such as Ca^{+2} and Mg^{2+}, in seawater and natural organic substances during coagulation is complex. Chemical interactions between humic substances and metal ions can be detected using fluorescence spectroscopy [14] and this analytical method may be beneficial in providing an insight into the nature of the interactions.

Since humic acid (HA) represents a prominent cause of membrane fouling in RO desalination, HA was selected in our work as the target contaminant material for laboratory tests investigating seawater coagulation. In a previous study [12] we evaluated the performance of aluminium sulphate (alum) in the coagulation of seawater. Based on the coagulation properties of aluminium and iron coagulants in freshwater, it was expected that iron coagulants would perform better than aluminium in the removal of HA from seawater. A preliminary study of HA removal by ferric chloride indicated a satisfactory treatment performance could be achieved at pH 6 at a particular dose (200 μmol/L), and suggested the important role of hydroxyl ions and thus a strong pH dependence on coagulation performance [13]. In this paper we present further information regarding the removal of HA from seawater by ferric chloride. A coagulation diagram of Fe dose versus pH with reference to the electrostatic charge potential of the aggregates is presented indicating the optimal conditions for HA removal. We also provide experimental information from fluorescence spectroscopy measurements concerning the chemical binding of high valence ions with HA in a series of complex solution systems in order to interpret in more detail the coagulation mechanisms. In addition, the influence of seawater strength and the presence of oil have been examined given that offshore seawaters can be diluted by runoff and contaminated by oils.

2. Materials and methods

2.1. Experimental procedure

The coagulation experiments were carried out using a typical jar test technique [13]. The procedure was as follows: An 800-mL test sample (see below) was put into a 1-L glass beaker and the pH was adjusted by adding alkalinity to achieve the required conditions. The coagulant was dosed with the simultaneous application of flash mixing for 2 min at 250 rpm. Slow mixing was subsequently applied for 20 min at 50 rpm, and then the test sample was allowed to stand to enable the coagulated flocs to settle quiescently.

2.2. Sample collection

At the end of the flash mixing, a 50-mL sample of the test solution was collected from the supernatant and analyzed for zeta potential. After the test solution had settled for 30 min, another 50-mL sample was collected from the supernatant and analyzed for pH, and a further 50-mL sample was collected at the end of the settling period and analyzed for turbidity. A final 250-mL sample was collected from the supernatant at the end of the settling period, filtered through a 0.45-µm filter, and analyzed for HA concentration to represent the separation efficiency of microfiltration (MF).

2.3. Materials and reagents

Ferric chloride ($FeCl_3·6H_2O$, Extra pure grade, Merck Germany) was used as coagulant. HCl and NaOH were used for pH adjustment, and $NaHCO_3$ was used for alkalinity addition. Humic acids were obtained as a commercial reagent grade solid (Aldrich Inc., USA). One gram of humic acids was dissolved in 80 mL of 0.1 M NaOH solution. The resulting solution was kept overnight, diluted to 100 mL with 0.1 M NaOH solution, further diluted to 900 mL with de-ionized water, kept overnight, diluted to 1 L with de-ionized water, and filtered through a 1.5-µm filter and a 0.45-µm filter in succession. The filtrate was used as the HA stock. Approximately 5% of HA were removed by the filtration processes. The concentration of the HA stock was therefore approximately 950 mg/L.

Raw seawater was collected from Raffles Marina in Northwestern Singapore and filtered through a 0.2-µm filter (details of the water quality of typical Singapore seawater can be found in a previous paper [13]). Selected water quality parameters of the raw and filtered seawater from the laboratory analyses are shown in Table 1. It can be seen that the TDS was in the range of 31–32 g/L, indicating that the seawater strength was approximately 85–88% that of 'standard' seawater, the total salinity of which is 36.4 g/L [15].

Test waters (or HA solutions) with different ionic strengths were prepared, and the details of these are shown in Table 2. "Full seawater" refers to filtered seawater without any dilution. "Half seawater" and "1/4 seawater" refer to solutions obtained by diluting 500 mL of filtered seawater to 1 L and 2 L, respectively, with de-ionized water. The values of HA concentration shown in Table 2 were calculated accordingly and were taken as the initial, or reference values, for assessing the removal of HA by coagulation and subsequent filtration separation.

Table 1
Water quality of raw and filtered seawater samples.

	Parameter	Range	Average
Raw seawater	pH	8.1–8.3	8.2
	Zeta potential (mV)	–12 to –14	–12.6
	Turbidity (NTU)	2.0–5.5	2.75
Filtered seawater	HA (mg/L)	0.8–2.3	1.3
	TDS (g/L)	31–32	31.9
	Turbidity (NTU)	0.07–0.90	0.30

2.4. Equipment

The equipment used for the jar tests was a commercially available, multiple paddle scientific flocculator unit (Stuart, SWI). It consists of six stainless steel paddles, each having a height of 2.5 cm and a width of 6.4 cm. Zeta potential measurements were made using a zetasizer instrument (Malvern, 3000). Turbidity and UV absorbance measurements were made using a proprietary nephelometric instrument and UV/Visible spectrophotometer (Perkin Elmer, Lambda Bio 20), respectively.

2.5. HA analysis

UV-absorbing organic substances in a water sample absorb UV in proportion to their concentration, and 253.7 nm (often approximated to 254 nm) has been used as the standard absorbance wavelength for its quantification [16]. The relationship between UV_{254} (UV absorbance at 254 nm) and HA concentration was obtained by analyzing UV_{254} of 40 standard HA solutions made by diluting the HA stock with distilled water. The HA concentrations of water samples, including seawater and coagulated test samples, were all translated from values of UV_{254}.

2.6. Fluorescence spectroscopy

Fluorescence spectra for solutions of HA with and without the presence of high valence ions (e.g. Fe^{3+}, Ca^{2+}) were measured using a JASCO FP-6500 (Japan) fluorescence spectrometer. HA solutions (DOC approximately 2 mg/L) were prepared at pH 3 and pH 6 and a small quantity of 0.1 mM ferric chloride was added by pipette. Care was taken to ensure that there was no observable turbidity after addition of ferric chloride to the HA solutions (precipitation was not expected under the given conditions). For tests involving Ca^{2+} addition, quantities of 1 mM $CaCl_2$ were added to HA solutions. Using excitation (EX) wavelengths in the range of 300–500 nm and emission (EM) wavelengths in the range of 300–600 nm, two dimensional fluorescence spectroscopic matrices (EEMs) were established under specified experimental conditions in order to assist in interpreting the coagulation mechanisms. Fluorescence spectroscopy can provide useful information on the chemical nature of humic substances and chemical reactions or bonding with metal ions. Fluorescence spectra are extremely sensitive and can be affected by solution chemistry, such as pH, ionic strength, and temperature. The fluorescence emission

Table 2
Description of test water samples.

Sample	Preparation	HA (mg/L)
No. 1	The HA stock mixed with **full seawater** with a volume ratio of **1/49**, i.e., 20 mLof the HA stock making 1 L of the test sample.	20.3
No. 2	The HA stock mixed with **half seawater** with a volume ratio of **1/49**, i.e., 20 mL of the HA stock to making 1 L of the test sample.	19.6
No. 3	The HA stock mixed with **1/4 seawater** with a volume ratio of **1/49**, i.e., 20 mL of the HA stock to making 1 L of the test sample.	19.3
No. 4	The HA stock mixed with **de-ionized water** with a volume ratio of **1/49**, i.e., 20 mL of the HA stock to making 1 L of the test sample.	19.0
No. 5	The HA stock mixed with **full seawater** with a volume ratio of **1/99**, i.e., 10 mL of the HA stock to making 1 L of the test sample.	10.8

of HA is due to the aromatic moieties, or aromatic rings and conjugated unsaturated (double and triple) bonds in the molecules. When humic acids interact with metal ions the fluorescence intensity may shift or decrease (fluorescence quenching) [14].

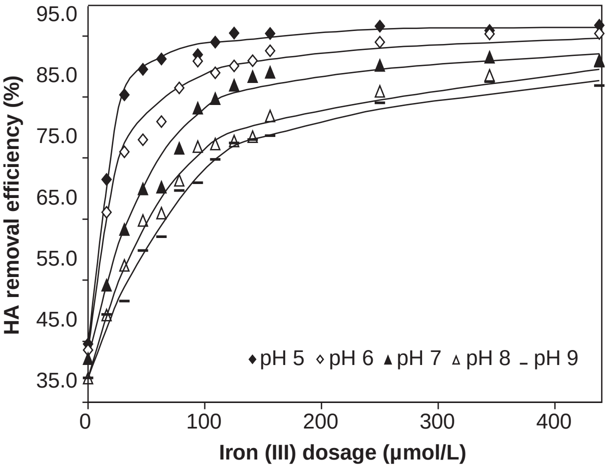

Fig. 1. HA removal vs iron dosage at different pH.

3. Results and discussion

3.1. Coagulation of seawater at different pH

Jar tests were performed over a wide range of $FeCl_3$ dosage (16–2500 μmol Fe/L) and pH (4–10) using test sample No. 1 (see Table 2). The pH of the experiments was maintained within ± 0.1 of the target pH. Duplicate experiments were performed and the results presented are the mean values. The standard deviations for the duplicate experiments are less than 5% of the HA removal efficiency and 2 mV of the zeta potential.

The variation of HA removal with $FeCl_3$ dosage for pH 5–9 and [Fe] = 0–450 μmol/L, is shown in Fig. 1. For each pH, an iron dosage of approximately 125 μmol/L resulted in a HA removal equivalent to 90% of the respective highest HA removal achieved, and HA removal increased only slightly with further increase in iron dosage to the maximum of 450 μmol/L. Thus, the iron dosage of 125 μmol/L (7 mg/L Fe) may be considered a '*threshold*' value for the 'practical' optimal dosage and the practical dosage may be considered approximately 150 μmol/L (8.4 mg/L Fe). As expected the pH has an important influence on the degree of HA removal and particularly at iron dosages below 150 μmol/L. The degree of HA removal was greatest at pH 5, where a strong charge neutralisation effect was evident at high dosages of the coagulant (see later). At the threshold dosage or above, coagulation may proceed in the conventionally named 'sweep flocculation' region for colloidal particulate removal since the concentration of the metal ion exceeded greatly its solubility and large volumes of precipitation were produced. It is noted that 'sweep' coagulation refers to the effect of enmeshment of particles (e.g. clay particles) or particulate impurities (e.g. bacteria, protozoa) by voluminous metal salt precipitates (e.g. $Fe(OH)_3$) giving rise to a significant removal of these suspended particles [11]. However, for coagulating HA or other dissolved substances co-precipitation may be the more preferred term in describing the intrinsic coagulation mechanism, or more appropriately *co-precipitation and charge neutralization* [11,17,18]. Under these conditions the optimum coagulation of HA was at pH 5, with an iron dosage of approximately 150 μmol/L.

The variation of the zeta potential of the co-precipitates at pH 5, 6, 8, 9 and 10 is shown in Fig. 2. From this it is evident that pH had no significant influence on charge neutralization at iron dosages lower than 150 μmol/L, with the exception of pH 10. At higher iron dosages (greater than 150 μmol/L), within the acidic and neutral

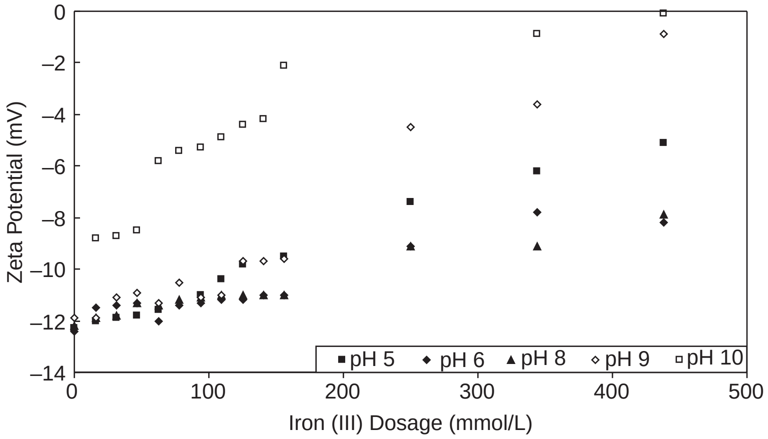

Fig. 2. Zeta potential vs iron (III) dosage at different pH.

pH range, a stronger charge neutralization effect was evident at pH 5; however, across the whole pH range from acidic to alkaline, charge neutralization was observed to be strongest at pH 10. Therefore, it can be summarized that within the acidic to neutral pH range, the greatest coagulation efficiency was observed at the pH that had the strongest charge neutralizing effect (pH 5), while in contrast at high pH, although strong charge neutralization effects were seen, the coagulation efficiency was relatively low and not comparable to that at low pH. It is clear that the relatively minor difference in precipitate charge with pH in the acidic to neutral pH range did not correspond to the more substantial difference in HA removal efficiency (Fig. 1), nor explain the existence of a threshold iron dosage of 125 μmol/L. Consequently, it can be concluded that charge neutralization alone was not the predominant mechanism in the coagulation process.

It is interesting to compare these results with those of our previous study with alum in similar seawater experiments [12]. In the acidic to neutral pH region, the strongest charge neutralization effects were observed at pH 5 for both alum and ferric chloride within the practical pH range for water treatment. However, the optimal removal of HA occurs at pH 6 for alum coagulation, in contrast to pH 5 for ferric chloride as observed in this study. Since the minimum solubility of ferric ions typically occurs at a much higher pH (~8) than that of aluminium (~6.5), the difference in the optimal pH cannot be explained solely by the degree of metal ion hydroxide precipitation. Thus, the optimal coagulation conditions are likely to involve a combination of effects, including both charge neutralization and metal ion hydroxide precipitation. In addition, charge reversal was observed with alum coagulation at pH 6, whereas no charge reversal was observed with ferric chloride in this study under the given conditions (Fig. 2). This may be important since charge reversal is potentially undesirable and may enhance fouling effects on the subsequent membrane process.

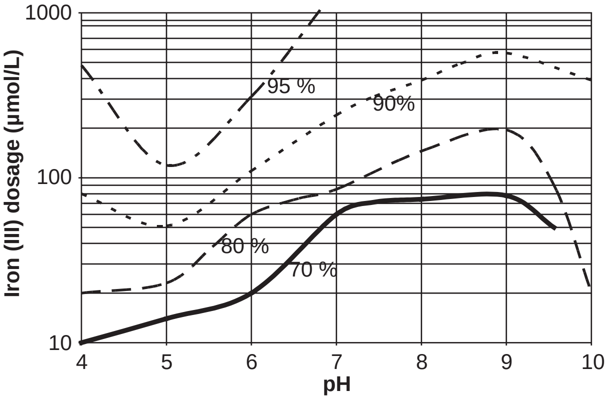

Fig. 3. Coagulation diagram for HA removal.

In the pH range of neutral to alkaline, the zeta potential of aluminium-HA precipitates was a minimum at pH 9, in contrast to pH 10 for ferric chloride-HA precipitates as observed in this study. However, the corresponding degree of HA removal was relatively poor under such charge neutralizing conditions. Since metal ion hydroxide precipitation is weak at these alkaline pH conditions, the coagulation performance again is likely to involve a combination of effects, including both charge neutralization and metal ion hydroxide precipitation. Thus, 'co-precipitation' may be a better term to describe the coagulation mechanism at or above the optimal dosage in this study as some previous studies have suggested [19]. In addition, other mechanisms apart from co-precipitation and charge neutralization may be involved depending on the pH and metal ion dosages, including the influence of highly charged polymeric hydrolyzing species, as speculated elsewhere [12,20].

A coagulation diagram for HA removal based on the experimental results is shown in Fig. 3. It can be seen that a HA removal of 95% could be achieved at an iron dosage of 120 μmol/L at pH 5, or at an iron dosage of 500 and 300 μmol/L at pH 4 and 6, respectively. However, a HA removal of 95% was not achieved at pH 7–9 over the whole iron dosage range examined (0–2,500 μmol/L). An evident improvement in coagulation performance at high pH (~pH 9) was also reported in an earlier study of the removal of HA by an iron coagulant for a non-saline water, although no explanation was proposed for this [21]. The reason why the lowest iron dose for 70% and 80% HA removal was at pH 4 is unclear, but this is thought to relate to the heterogeneous nature of the humic compounds and that at pH 4 the ferric coagulant acts principally by charge interaction, while at pH 5 and above some additional coagulation effects arise from adsorption on insoluble Fe hydrolysis products.

3.2. Fluorescence spectroscopy measurements

The results of fluorescence spectroscopy measurements are presented in Fig. 4. Two-dimensional spectra of excitation (250–400 nm) and emission (300–600 nm) matrices (EEMs) were established for the given conditions. Fig. 4(A) is the fluorescence spectrum for Milli-Q water, which can be used as a reference for comparison with those for the test solutions. Figs. 4(B) and (C) are the spectra for Milli-Q water containing humic acid at pH 4 and 6, respectively. Fig. 4(D) is the fluorescence spectrum of Milli-Q water containing humic acid and $CaCl_2$, and Figs. 4(E) and (F) are the spectra of Milli-Q water containing humic acid and a small quantity of $FeCl_3$ at pH 4 and 6, respectively.

By comparing the fluorescence spectra for the various solutions with the spectrum for the high purity water, several fundamental aspects can be inferred, as follows: (1) The basic pattern of the spectra for HA solutions at pH 4 and 6 (B and C) was almost the same, while the EX-EM spectroscopic intensity increased significantly as the pH increased from 4 to 6. This phenomenon may be expected from the theory of fluorescence, but the difference in intensity observed at these two pH values was substantial; (2) With the addition of calcium ions to the HA solution the general pattern and intensity of the spectra was very similar, and only at a small region around the interception point of EX 270 nm–EM 450 nm, was a slight fluorescence quenching evident (D cf. B). The low level of fluorescence quenching suggested a minor degree of chemical bonding between the

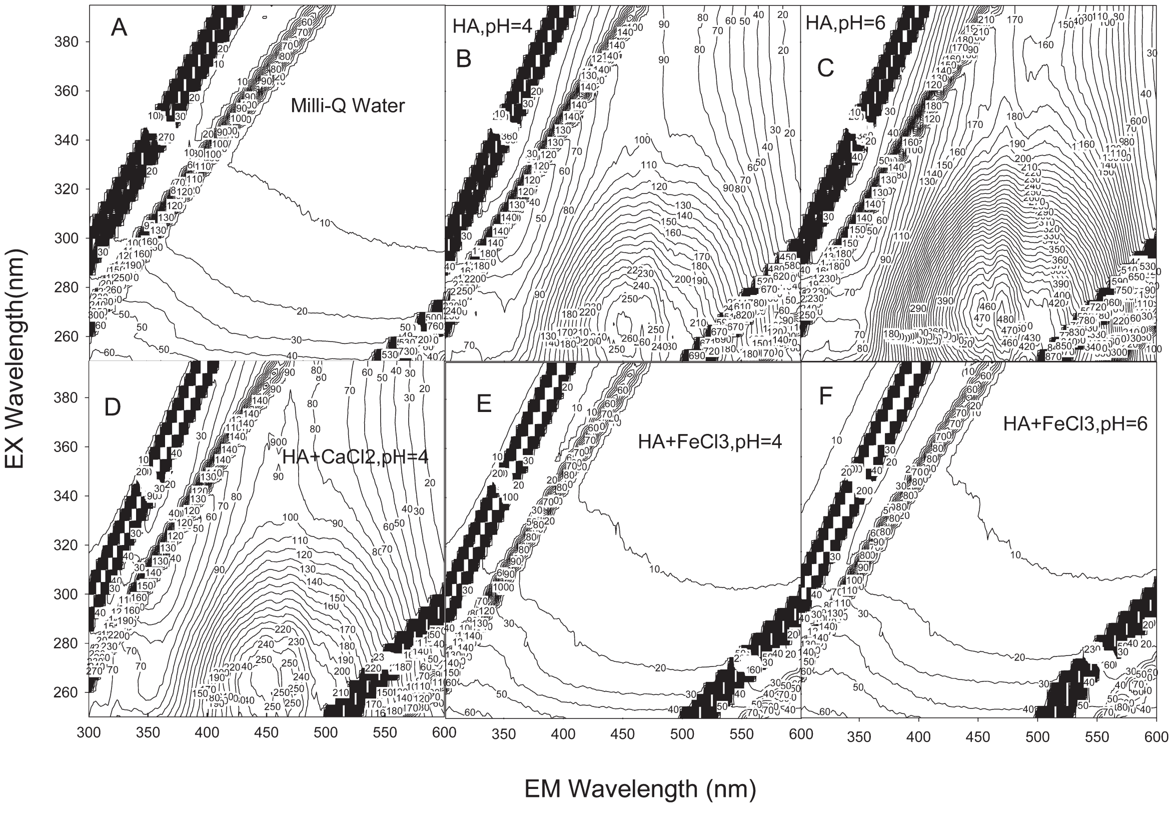

Fig. 4. EX-EM Fluorescence spectra of (A) Milli-Q water only, (B) Milli-Q water containing HA at pH 4, (C) Milli-Q water containing HA at pH 6, (D) Milli-Q water containing HA and $CaCl_2$, (E) Milli-Q water containing HA and $FeCl_3$ at pH 4, (F) Milli-Q water containing HA and $FeCl_3$ at pH 6.

HA and calcium ions in solution; (3) With the addition of small quantities of ferric ions to the HA solution, a major degree of fluorescence quenching was evident at pH 4 (E), such that the fluorescence spectrum was almost the same as for blank Milli-Q water (A). This indicates a strong chemical bonding between Fe^{3+} ions and HA in solution, whereby nearly all the chemical bonding sites, or the functional groups, of the HA which can fluoresce were bonded to Fe^{3+} ions in solution; (4) the degree of fluorescence quenching at pH 6 (F) was almost identical to that at pH 4 (E). At pH 6, the metal ion species $Fe(OH)^{2+}$ and/or $Fe(OH)_2^+$ may predominate rather than the simple Fe^{3+} ions which is likely to be the most prevalent species at pH 4 [22]. The similarity in the results at both pH values suggests that the chemical bonding of these different ferric species with HA is equally strong.

It has been speculated that compression of the electrical double layer is the dominant coagulation mechanism for divalent ions, principally Ca^{2+} and Mg^{2+}, in the normal pH range of water treatment [12]. As the fluorescence spectrum suggested only a weak chemical bonding between calcium ions and humic acids, the assumption of a double layer compression mechanism is probably valid, especially considering the high concentration of these ions in seawater. In this and our previous studies, it was noted that seawater alone could produce some degree of HA aggregation (as retained on a 0.45 micron pore membrane), and this aggregation is believed to occur principally by the double layer compression mechanism.

It is generally assumed that metal ion precipitation and charge neutralization are the predominant coagulation mechanisms but these do not always account for the observed behaviour in certain coagulating conditions. In our tests the fluorescence spectra showed a strong chemical bonding or interaction between HA and various mono- or polymeric cationic iron species, suggested to be mainly Fe^{3+} at pH 4 and $Fe(OH)^{2+}$ and/or $Fe(OH)_2^+$ at pH 6. These interactions may play a significant role in coagulating humic substances which is distinct from metal ion precipitation and charge neutralization. Such effects may explain why alum-HA coagulation is relatively poor at high pH ≥ 9 in seawater conditions, compared to pH 6, even though alum solubility is relatively low compared with pH 6 (thus, a high degree of metal ion precipitation) and the charge-neutralizing effect is equally strong [12]. It may be speculated that under high pH conditions the chemical bonding between the HA and iron species is weak due to the large concentration of hydroxyl ions in solution and metal ion precipitates. We have discussed in a precious study that competition between hydroxyl ions and aluminium ions for HA play an important role in the coagulation mechanisms [13]. In view of this, a more complete description of the mechanisms of coagulation would be that they include the combination of charge neutralization, co-precipitation, and specific chemical bonding between HA and the metal ion hydrolysis species and precipitates.

3.3. Coagulation in seawater in the presence of oil

Owing to the intensity of marine traffic around the coast of Singapore and other coastal areas around the world, seawaters are likely to be contaminated by oil. Thus, a series of jar tests was performed at pH 5 with the iron dosage ranging from 0 to 440 µmol/L, using test sample No. 1 (Table 2), with 20 µL of *crude oil* added to each test sample. The results of the coagulation experiments were compared with those of the control experiments in the absence of oil. Fig. 5 shows the degree of HA removal and residual turbidity for the

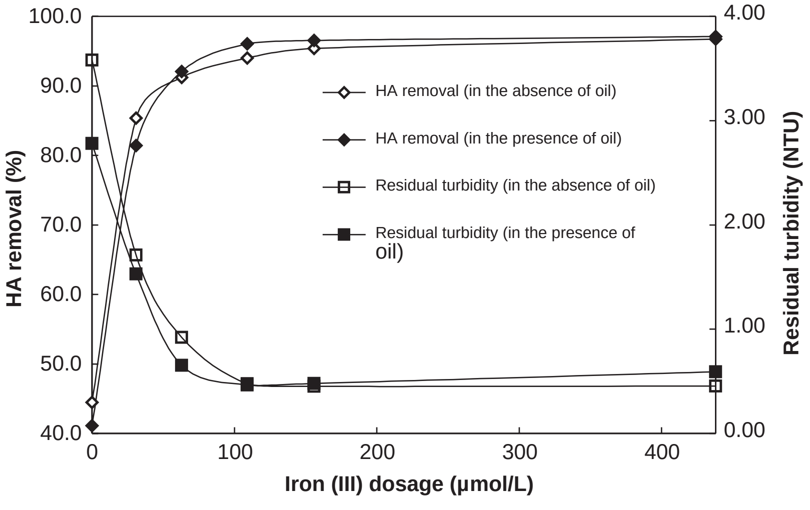

Fig. 5. Influence of the presence of oil on coagulation.

two sets of experiments. The presence of oil resulted in slightly different coagulation performances. At iron dosages below 50 μmol/L, the presence of oil resulted in lower HA removal and lower residual turbidity. For the iron dosage range of 50–150 μmol/L, the presence of oil resulted in higher HA removal and lower residual turbidity. At iron dosages higher than 150 μmol/L, the presence of oil resulted in higher HA removal and higher residual turbidity. Thus, at the suggested optimal iron dosage (150 μmol/L), the presence of oil was found to be slightly beneficial rather than detrimental in terms of both HA removal and residual turbidity.

The experimental results indicate that the presence of oil at this concentration is not very significant in affecting the general coagulation performance, but can be either beneficial or detrimental on the HA coagulation depending on the coagulant dosage applied. The coagulation mechanisms causing this behaviour can be speculated from both the interfacial interactions between the colloids and the coagulant species, and the kinetics of the coagulation. When oil is dispersed in aqueous solution an emulsion may co-exist with the soluble or colloidal HA, thereby creating a 'binary' colloidal system. It might be expected that the oil emulsion colloids are negatively charged and their surface is hydrophobic. Thus, the effect of this may be that more coagulant is required to neutralize the additional (negative) surface charges present from the combined colloidal mass. In contrast, the presence of the oil may induce some advantageous hydrophobic interactions between the emulsion colloids and the HA or coagulated HA precipitates; that is, the HA precipitates may migrate towards, and adhere to, the oil emulsion surface through hydrophobic interactions arising from the high molecular weight aromatic nature of the organic colloids. The latter might lead to kinetically favourable conditions for the coagulation of the HA. However, at the present time there is little information in the literature regarding such interactions.

In addition to the mechanisms mentioned previously, some physical aspects may also play a part. Firstly, the viscosity of crude oil is much higher than that of water, and the presence of oil might therefore hinder Brownian motion and perikinetic coagulation of colloids. However, since the content of oil in this case is very small such effects may be insignificant. Secondly, the density of oil is lower than that of water, and therefore the coating of flocs by oil may reduce their settling velocities, causing less separation through settling processes. This helps to explain the reason why turbidity is higher with the presence of oil after coagulation and subsequent settling. In this study, at low dosages of coagulant, the detrimental effects on coagulation may be due to the increased colloid surfaces with the presence of oil. At high coagulant dosages, the enhanced coagulation may be due to the favourable hydrophobic interactions, and thus a greater, more efficient, floc aggregation. Overall, the effects are observed to be small but this may be dependent on the prevailing oil concentration.

3.4. Influence of seawater strength on coagulation

The influence of seawater strength on the coagulation performance was investigated at pH 5 with an iron dosage range from 0 to 440 mol/L, using solution test samples No. 2, No. 3 and No. 4 (Table 2). The results of the experiments were compared with those of the experiments using test sample No. 1 (Table 2). The observed degree of HA removal (%) in the tests is shown in Fig. 6. In the absence of any added coagulant, there was some degree of HA coagulation and separation in the saline waters, where the extent of the coagulation increased with saline strength. This is expected since the presence of dissolved salts and counter-ions reduces charge

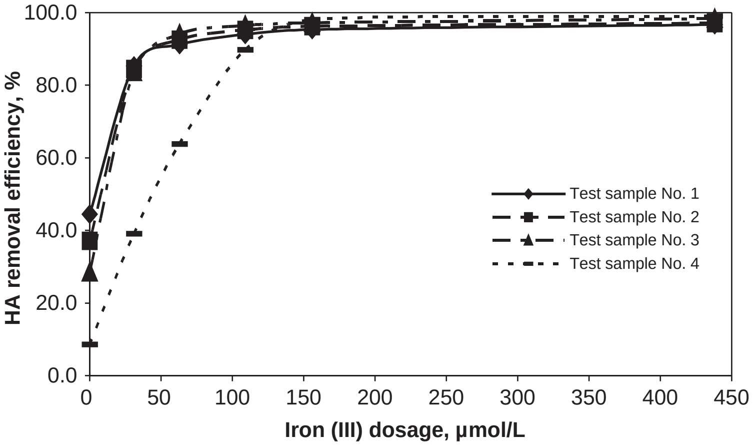

Fig. 6. Influence of seawater strength on HA removal.

repulsion between the HA molecules (compresses the electrical double layers thickness), and thus their solubility. The fluorescence spectroscopy measurements indicated only a weak chemical association/bonding between HA and Ca^{2+} ions. Considering the high concentration of divalent cations in seawater (principally Ca^{2+} and Mg^{2+}), it is likely that chemical bonding interactions would be easily saturated leaving an excess of the cations and other counter-ions available to achieve electrical double layer compression.

With the addition of the iron coagulant, and for Fe doses up to 150 μmol/L, the coagulation performance in de-ionized water (test sample No. 4) was clearly inferior to that achieved in the saline waters (test samples No. 1–3). However, at iron dosages greater than 150 μmol/L, the coagulation performances in de-ionized water, quarter-strength seawater, half-strength seawater, and full-strength seawater were virtually identical and corresponded to a very high HA removal (>95%). As stated above the associated presence of divalent cations causes humic acids to be less negatively charged and of increased size. This is probably the reason that at low dosages of metal ion coagulants the coagulation performance is superior in saline water than in deionised water. In addition, it has been reported that divalent cations can influence the kinetics of Fe(III) complexation by organic ligands in natural waters [23]. In contrast, at high dosages of metal ions coagulant, chemical interactions between HA and cationic metal ion hydrolysis species and precipitates become predominant and the effects of divalent ions on the coagulation process are much less important or negligible. As expected, for the whole iron dosage range examined, the HA removal increased with increasing iron dosage, regardless of the seawater strength of the test samples. Since the coagulation performance of the saline waters was very similar, irrespective of the salinity, it is speculated that seawaters in general, in different locations and with different ionic strengths will produce similar coagulation results at similar dissolved organic carbon levels.

3.5. Influence of HA concentration on coagulation

In order to study the relationship between the coagulation performance and the initial HA concentration, a series of jar tests was performed with iron dosages in the range from 0 to 440 μmol/L at pH 5, using solution test sample No. 5 (HA 10.8 mg/L; see Table 2). The results of the coagulation experiments were compared with those of test sample No. 1 which contained twice the HA concentration (HA 20.3 mg/L; see Table 2). Fig. 7 summarizes the variation of HA removal with coagulant dose at the two HA concentrations. It can be seen that in the absence of iron coagulant there was an observable increase in the proportion of HA precipitated with the higher HA concentration. This was also observed with the addition of coagulant for the entire range of iron coagulant dose studied.

For non-saline waters a coagulant-HA dose stoichiometry is frequently observed under optimum conditions [11], reflecting the predominance of charge neutralization as the mechanism of coagulation. In marked contrast, a different behavior was evident from the results obtained with the saline waters in these tests (Fig. 7) whereby to achieve the same degree of HA removal a much greater coagulant dose was required for the lower HA concentration than at the higher HA concentration. This provides further evidence that coagulation is the result of a combination of mechanisms rather than solely charge neutralization. Overall, the treatment performance for both HA concentrations was substantial corresponding to >85% HA removal for iron dosages greater than approximately 70 μmol/L (4 mg/L Fe). The 'practical' optimal iron dosage appeared to be the same

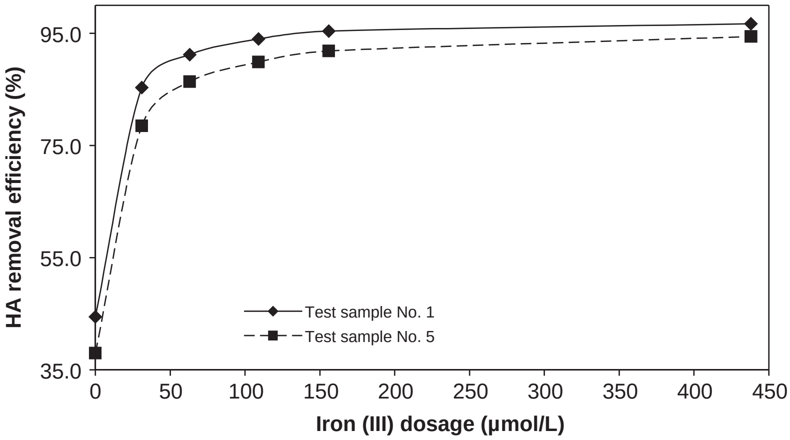

Fig. 7. Influence of original HA concentration on HA removal.

for both HA concentrations and equal to approximately 150 μmol/L. This suggests that in practice the optimal coagulant dose may not be sensitive to the prevailing HA concentration, or to temporal changes in HA concentration.

4. Conclusion

Chemical bonding between ferric species, either as free ions or especially hydrolysis products, is one of the major coagulation mechanisms of humic substances by metal ion salts, in addition to co-precipitation and charge-neutralization. While calcium (and magnesium) ions can chemically bond with humic acids, the intensity and extent of this is much weaker compared to ferric ion species as indicated by EX-EM fluorescence spectroscopy. For seawaters, while high concentrations of these divalent ions can cause compression of electrical double layers on humic substances, the effects are not strong enough to cause significant coagulation and humic acid removal by these divalent ions alone. Thus, the addition of a metal ion coagulant is required to achieve this and bring about the required degree of pretreatment.

In this study a coagulation diagram has been established for the removal of HA in seawater by $FeCl_3$, and the optimal pH was shown to be approximately pH 5; in comparison the optimal pH for alum was 6 [12]. The zeta potential of coagulated particles diminished with iron dose but was relatively unchanging for [Fe] ≤ 150 μmol/L. However, at higher dosages, a strong charge neutralizing effect was observed at this pH. The maximum removal of humic acids reached a limit of approximately 95% with increase of the ferric concentration, and the maximum removal limit was attained at a dosage of 150 μmol/L; further increase of coagulant dosage gave no further increase in HA removal.

The existence of relatively small quantities of oil was found to have no detrimental impact on the extent of HA and turbidity removal at high iron dosages (e.g. greater than 100 μmol/L). The colloidal emulsion of oil may consume some of the coagulant since a slight reduction of HA removal was observed at low dosages of the coagulant. These findings may suggest that there are no direct chemical reactions between the colloidal oil and humic acids (e.g. electrostatic repulsive and hydrophobic interactions) that might cause the humic material to be more difficult to coagulate by the ferric chloride.

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