COAGULATION-SETTLING OF NATURAL ORGANIC MATTER FROM SOFT TROPICAL WATER USING ALUMINIUM AND IRON(III) SULPHATE

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ABSTRACT

High natural organic matter (NOM) containing tropical forest river waters are very difficult to treat for drinking because of their low values of alkalinity, mineralization and turbidity. In addition, owing to cost of chemicals, coagulation of these waters is performed under variable pH conditions. We report studies on such high NOM water, using synthetic water containing NOM extract from a tropical forest river and natural raw water from the same river, by Jar test and column settling experiments. Two coagulants were tested, aluminium and iron (III) sulphate, in order to determine, firstly, the pH range at which the initial water pH should be set for best coagulation and minimisation of residual NOM, and secondly, the influence of each coagulant on NOM removal and floc sedimentation. Jar test results showed that minimum coagulant consumption for maximum NOM removal attended by minimum NOM residuals obtained for initial pH in the range 5.5 – 6.5 for both coagulants. The amount of Al sulphate required was at least 2 times that of Fe (III) sulphate. In column settling of metal-NOM flocs, Al was generally better than Fe but both gave comparable results at hydraulic loading rates \( \leq 1.0 \) m/hr.

Keywords: Coagulation, humic substances, sedimentation, soft water, water treatment.

1. INTRODUCTION

In the hot humid tropical regions, surface waters, especially river waters constitute the principal source of raw water for drinking water production for cities. The river waters are soft with slightly acidic to neutral pH, have low levels of alkalinity and mineralization. In the
dense luxuriant rainforest zones, river waters have low turbidity and medium to high values of dissolved natural organic matter (NOM), generally called humic substances [1, 2, 3]. Aquatic humic substances represent at least 50% of the dissolved organic matter (DOM) in natural surface waters, and in the tropical rainforest, they are essentially, the water extractable fraction of soil humus that derives from biogeochemical processes such as the decay of plant residues [1,4]. The yellow to brown colour of medium to high NOM containing waters can at least in part be attributed to the presence of dissolved coloured humic substances. At typical natural surface water pH, the humic substances present are a mixture of fulvic and humic acids, which account for about 80% of DOM; with fulvic acids predominating in most waters especially non-coloured waters and humic acids can be of greater proportion in highly coloured waters [4,5]. Fulvic and humic acids possess phenolic and carboxylic groups whose dissociation increases with pH so that in the pH conditions of natural surface waters, they have negative charges making them more soluble and stable, and enabling them to contribute to the stabilisation of aquatic inorganic colloids [2].

Several water quality problems are posed by the presence of humics, necessitating their complete removal or at least minimization. First, aesthetically, colour, taste and odour make these waters unfit for drinking. The presence of humic substances in natural waters renders these waters difficult to treat, causing higher coagulant demand [6, 7]. Indeed, membrane fouling, trihalomethanes formation during chlorine desinfection, or biological regrowth in the distribution network, have all been linked to the presence of residual humic substances in clarified water [8,9,10]. Humics substances form complex with hazardous inorganic and organic contaminants such as trace (heavy) metals and pesticides, thus probably facilitating their transport through treatment systems [11,12].

Chemical coagulation by hydrolysing metal salts is the major technique used around the world for removal of NOM from water, with Al salts most widely used and iron (III) salts to a lesser extent [13,14, 15, 16]. For the purpose of improving dissolved NOM removal, considerable research efforts have been made in recent years towards investigating the mechanism of destabilisation of aquatic NOM by Al and Fe salts [17, 18, 19, 20]. Three main mechanisms are generally invoked to explain the removal of humic substances by coagulation: charge neutralization/complexation preferentially applies at acidic pH and finds experimental support from stoichiometric relationships between coagulant demand and dissolved organic matter concentration, and from suspension restabilization upon overdosing [21, 22, 23]. On the other hand, under conditions favoring metal hydroxide precipitation, physical ensmeshment and/or adsorption onto the freshly formed precipitate are assumed to play a major role in humic substances elimination [24].

The studies undertaken so far on NOM removal from natural waters have been essentially concerned with hard, high alkalinity waters. However, Eikebrokk [25, 26], has investigated NOM removal by Al salts from low alkalinity soft Norwegian waters at constant pH and found that minimisation of NOM residuals occurred at pH 5 – 6 and Al metal residuals at pH 5 - 7. The case of tropical soft humic waters with low alkalinity, mineralization and turbidity, has hardly received any attention. Removal of NOM from these waters by water suppliers notably in tropical Africa is based on turbidity and colour reduction with Al sulphate. Insufficient importance is accorded to process improvement with respect to minimisation of DOM residuals, despite the risks associated with the presence of humics in water as indicated earlier above.

In addition, although it has been established that pH is one of the most crucial factors regulating NOM removal and metal ion speciation [19, 27, 28, 29, 30], coagulation of
tropical soft humic waters is carried out under conditions of variable pH. Coagulant is added to the water at its natural pH or after raising pH to a desired value by liming, depending on in-plant experience. The pH is then allowed to drift downwards, towards, it is expected, the optimum pH for NOM destabilisation. Unfortunately, the coagulation process often fails in this case, causing coloured water to arrive at the tap. Even though the high cost of treatment chemicals is at the root of this practice in developing tropical Africa of allowing pH drift during coagulation. The operative mechanisms have been inferred from the discussions by Duan and Gregory [31]. There are no studies available to indicate the optimum initial pH range for coagulation of these soft waters under conditions of variable pH, where pH is not adjusted after adding coagulant.

Al is preferred over Fe III sulphate as coagulant for treating humic surface waters in the tropics because of the corrosiveness of Fe III salts and the risk of staining of clothes by these salts. However, research is giving greater consideration to the use of Fe III salts because the aluminium is non essential metal. Also, it is claimed that Fe III forms stronger and denser flocs with NOM than does Al and it should thus be expected that Fe-NOM flocs should settle faster than Al-NOM flocs. Yet, no pilot scale study has been performed to test the settling properties of the two types of metal-NOM flocs. Deductions are made based on small scale Jar tests [32].

The settling characteristics of flocs can be evaluated by column settling pilot scale tests in the laboratory [33,34]. Zanoni et al. [35] have shown that for columns of height equal to or greater than 2.0 meters and internal diameter of 100 mm or above, the results of the column settling tests were similar. Most studies by column settling of aqueous flocculent suspensions have been performed on inorganic colloids and waste water systems.

This study was therefore directed at the investigation of the removal of NOM with freshly prepared Al and Fe III sulphate from soft, low alkalinity and mineralization tropical river water in a treatment situation involving pH drop from a preset initial value. It had two aims, namely, determining the initial pH range for optimum coagulation with minimum NOM residuals and evaluating on pilot scale the settling of metal-NOM flocs formed by the two coagulants and hence appreciate their relative effects on clarification. The study was performed by Jar test and column settling tests and involved synthetic waters and natural river water.

2. MATERIALS AND METHODS

2.1. Water sources

Feedstock waters used in this study were from two sources, distilled water and raw river water. Distilled water from a borosilicate glass still (JENCONS, UK), was used for extraction of natural organic matter (NOM) and preparation of synthetic waters containing NOM for Jar test experiments and column settling tests. Raw river water was from River Nyong in the Cameroon rainforest south of Yaounde (Latitude 4°N), on which is located the water treatment plant supplying Yaounde, Cameroon’s capital. The river water was used for Jar test and column settling experiments.

2.2. Chemicals

All chemicals were analytical grade reagents. Aluminium sulphate \((\text{Al}_2(\text{SO}_4)_{3.18}\text{H}_2\text{O})\) coagulant, sulphuric acid \((\text{H}_2\text{SO}_4)\) and sodium hydroxide \((\text{NaOH})\) used for pH adjustment, were obtained from PROLABO France, now MERCK-Eurolab. Ferric sulphate, \(\text{Fe}_2(\text{SO}_4)_{3.x}\text{H}_2\text{O}\) coagulant was from RIEDEL DEN HAEN, Germany. Since the number of molecules of
water in the ferric sulphate was unknown, this chemical was dried to constant weight at 105°C and cooled in a desiccators before being used to prepare solutions based on the formula weight of 399.88 g/mol.

2.3. Glassware
All glassware used was of borosilicate glass.

2.4. Apparatus
The pH of solutions and suspensions was measured by means of a HANNA HI 931000 pH-meter (Hanna Instruments, Portugal) with a precision of 0.05 pH units.

A SPECTRONIC GENESYS 2PC model 336003 single beam UV-Visible spectrophotometer (Spectronic Instruments Co, USA) equipped with a quartz cuvette (10 mm optical path) was used to determine the absorption peak of dissolved NOM and also for establishing the calibration graph for determining NOM concentration in waters tested. The absorption peak was confirmed on a double beam UV-visible spectrophotometer.

Coagulation - flocculation of NOM in water was performed on a VITTADINI Jar test apparatus (PROLABO, France) equipped with 6 paddle stirrers.

Column settling experiments to determine removal rates of coagulated NOM were carried out with the system shown in Figure 1. It consists of a rapid mixing tank, a pump and transparent acrylic polymer (Polymethylmethacrylate) Column of height 2m and internal diameter 100mm. Both the mixing tank and the column are equipped with paddle stirrers as shown. Sampling ports on the column were fitted with short silicone tubing tightly sealed with screw valves at 0.5m, 1.0m and 1.5m depths. A syringe fitted with a small hypodermic needle was used to withdraw samples the column were fitted with short silicone tubing tightly sealed with screw valves at 0.5m, 1.0m, and at each port.

![Figure 1 Schematic diagram of gravity sedimentation apparatus](image-url)
2.5. Procedures

NOM extract for coagulation-flocculation studies was obtained by alkaline extraction from river sediment (soil) knowing that aquatic NOM and soil humus have the same chemical behaviour (Stevenson 1994). The extraction was done by the Jackson [36] method as follows. Fresh sediment was dug out during the rainy season from Nyong river bed upstream from the water treatment plant. The sediment was allowed to dry in air at room temperature (24±2°C) inside a vacuum cupboard. The dried sediment, hereafter called soil, was then ground to fine powder in an agate mortar. Aliquots (100g) of powder soil were placed in glass beakers (2L) to each of which was then added 1L of NaOH solution (0.25M). The mixture in each beaker was agitated for 20 minutes with a HB502 magnetic stirrer (Bibby Sterilin, UK). After stopping agitation, the beakers were covered with parafilm and the suspensions formed were allowed to settle for 12 hours. The supernatant (pH 12) was carefully poured into other 2L glass beakers, pH adjusted to 7 by adding drops of H₂SO₄ (0.5M) and the resultant suspension allowed to stand from 12 h. The supernatant solutions containing NOM extract were then carefully transferred to 1L screw capped glass bottles.

The aqueous NOM extract so obtained was filtered by means of a CARBOSEP (TECH-SEP, France) tubular membrane module having a membrane pore size of 0.14 μm. The clear filtrate, also called permeate, containing dissolved NOM was stored in 1L screw capped glass bottles at 4°C until required for experiments.

Before use, the concentration of the stock NOM extract was determined gravimetrically after drying the extract solution. A sample of the NOM extract solution was placed in a Spectra/Por membrane dialysis tube (Spectrum Medical Industries, USA) and dialysed exhaustively against distilled water (conductivity 3 μS/cm) under agitation in a glass tank. Water was changed every 12 hours until the conductivity of the dialysing water was constant and close to that of distilled water. Conductivity was measured with a TACUSSEL CD 60 Resistimeter (TACUSSEL Electronique, France). The concentration of the dialysed stock NOM extract solution was then determined gravimetrically by drying a sample (200 mL) to constant weight at 105°C. Triplicate determinations were made and the average taken to calculate the concentration of the stock NOM solution.

The residual concentration of NOM after Jar test coagulation-flocculation and settling experiments was determined as follows. The UV-Visible absorption peak of dialysed stock NOM solution at several pH values was found by measuring absorbance versus wavelength after diluting the NOM solution to give an absorbance value in the range 0.1 to 0.9 [37]. The absorption peak was at 280 nm was quite independent of pH as can be seen in Figure 2 Korshin et al. [38] in their work show that the presence of coagulant species doesn’t modify the spectrum of NOM. Knowing the concentration of the dialysed stock NOM solution and the dilution factor used, a calibration graph of NOM concentration, C (mg/L) versus absorbance at 280 nm was established and shows a linear graph. This graph of equation, Absorbance = 0.0230°C + 0.0364, has a correlation coefficient of 0.994.
Coagulation-flocculation experiments were performed on synthetic waters and Nyong River water by means of a Jar test bench with 6 glass beakers of 1L each filled with 800 mL of water. Nyong River water was tested as such, the average dissolved NOM concentration being 20±0.6 mg/L and pH 5.9±0.2 during the period of investigation. The synthetic waters were obtained by diluting stock NOM extract solutions with distilled water down to a desired concentration (10, 25 or 40 mg/L), and the pH was then adjusted under agitation to a predetermined value with sulphuric acid or NaOH (0.05M). The Jar test procedure involved adding coagulant from a freshly prepared stock solution of 10g/L not more than 6 hours old to the NOM containing water under rapid agitation at 260 rpm, after which, stirring was continued for 2 minutes at 260 rpm followed by 10 minutes at 50 rpm. Agitation was then stopped and the resultant suspension was allowed to settle for 20 minutes. The final pH was measured, the ccc ascertained and residual NOM at ccc determined by absorbance at 280 nm on a small sample prefiltered on a 0.45 µm porosity disc membrane. The sample analysed for residual NOM was withdrawn each time at the same level (5cm) below the water surface in the beaker using a syringe fitted with a small hypodermic needle. The values of ccc, final pH, as well as residual NOM concentrations, were established on the basis of triplicate coagulation-flocculation tests.

Column settling studies were carried out with the set-up shown in Figure 1 on synthetic waters (25mg/L NOM) at initial pH 5.0±0.05 and 6.0±0.05 and on Nyong river
water (20.0±0.6mg/L NOM) at pH 5.9±0.2. For this purpose, the predetermined volume of coagulant solution to attain the ccc was added to water in the mixing tank under high speed agitation and stirring continued for 2 minutes at the same speed then stopped. The pump was then used to rapidly transfer enough suspension (15.7L) to fill the settling column to the zero mark. The suspension in the column was agitated for 15 minutes at slow speed (velocity gradient 40/s). Agitation was stopped and samples were withdrawn from the indicated ports (0.5m, 1.0m, 1.5m) at predetermined times. Sample withdrawal was staggered and alternated between column sides in order to avoid channelling effects. Removal rate of flocculent NOM particles was determined by measuring turbidity of withdrawn samples with a HACH RatioXR turbidimeter (HACH Co., Loveland, USA). The column settling tests were conducted in duplicate in each case studied. At the end of each run, the percentage removal at the three selected depths for each settling time was calculated [39]. Then, following the method of Krishnan [33] the average percentage removal in the column and the corresponding settling velocity also called hydraulic loading rate (HLR) was evaluated for each of the chosen settling times. HLR was given by the height of the column divided by the settling time. In literature, sometimes surface overflow rate (SOR) is also used but that is simply obtained by dividing the HLR values by the cross-sectional area of the settling tank.

3. RESULTS AND DISCUSSION

3.1. Coagulant Demand and NOM Residuals
The influence of initial pH of water (pH_i) on the critical coagulation concentration (ccc) and thus on coagulant demand on the one hand and on NOM residuals on the other hand after coagulation and settling in Jar tests are shown in Figure 3 for synthetic water containing 25mg/L NOM. Table 1 presents the results for experiments carried out on Nyong River water containing 20mg/L NOM.

![Figure 3](image-url)
Table 1: Coagulation of Nyong River water, Cameroon

<table>
<thead>
<tr>
<th>Raw water characteristics (in rainy season)</th>
<th>pH initial</th>
<th>Al sulphate coagulation</th>
<th>Fe sulphate coagulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 5.9±0.2</td>
<td>5.0±0.1</td>
<td>44.59</td>
<td>29.98</td>
</tr>
<tr>
<td>Alkalinity 9.1±0.5 (mg/L)</td>
<td>5.5±0.1</td>
<td>59.31</td>
<td>38.73</td>
</tr>
<tr>
<td>NOM 20.0±0.6 (mg/L)</td>
<td>6.0±0.1</td>
<td>59.82</td>
<td>37.67</td>
</tr>
<tr>
<td>Turbidity 3.8±0.4 (NTU)</td>
<td>6.5±0.1</td>
<td>57.80</td>
<td>39.05</td>
</tr>
<tr>
<td>Colour 180±20 Pt/Co (mg/L)</td>
<td>7.0±0.1</td>
<td>89.19</td>
<td>59.90</td>
</tr>
<tr>
<td>Temperature 24±0.5°C</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

It can be seen that the graph of figure 3a, ccc vs pH, has three segments defined by pH_i for both Al and Fe(III) sulphate coagulation. First, when pH_i is in the range 4.5 – 5.5, coagulant demand rises gently with increase in pH, 54.33mg/L per pH unit for Al and 29.63mg/L per pH unit for Fe(III). Then for pH_i between 5.5 and 6.5, coagulant demand roughly stabilizes, with a difference per pH unit of only 11.38 mg/L for Al and 5.88 mg/L for Fe (III). Finally, for pH_i in the range 6.5 – 7.5, coagulant demand rises rapidly with increase in pH, being per pH unit, 128.00 mg/L for Al and 78.45mg/L for Fe (III). The trends seen in figure 3a were also observed in coagulation experiments on other synthetic waters containing NOM at concentrations of 15mg/L and 40mg/L except that the values of ccc were lower for 15mg/L NOM and higher for 40mg/L NOM. The results shown in table 1 for raw river water confirm the stabilization of ccc for pH_i in the range 5.5 – 6.5. Throughout the pH_i range investigated in figure 3a, coagulant demand is much higher for Al than for Fe (III), and on average 100% higher; the ccc value for Al sulphate is at least two times that of Fe (III) sulphate. The higher coagulant demand involved in using Al sulphate is confirmed in table 1 even though the difference between the two coagulants is around 50% only for the coagulation of raw Nyong River water. Figure 3b also presents the variation of NOM residuals against pH_i for synthetic water containing 25mg/L NOM. The curves shows three segments for Al sulphate coagulation whereas Fe (III) sulphate coagulation has only two segments for NOM residuals vs pH_i. Both coagulants show the same trend for NOM residuals vs pH_i below 5.5. Above this value of pH_i, the curve for Al has two segments, one with almost constant (4.0 ± 0.5 mg/L) but slightly increasing NOM residuals for pH_i between 5.5 and 6.5, and one with falling NOM residuals at pH_i above 6.5; whereas for Fe (III), at pH_i above 5.5, there is only one segment, with roughly constant NOM residuals generally less than 1mg/L. In general, Al sulphate coagulation leaves higher NOM residuals than does Fe (III) sulphate coagulation. This is corroborated by the results shown in table 1 on raw river water but the difference in NOM residuals arising from the use of the two coagulants is much smaller. Furthermore, table 1 also confirms the stabilization of NOM residuals for the two coagulants for the condition, 5.5 < pH_i > 6.5.

The trends shown by the results displayed in Figure 3 for synthetic water as well as those in table 1 for raw Nyong river water, when considered together, enable establishment of
an optimum pH region for minimization of both coagulant demand and NOM residuals during coagulation of soft, low alkalinity, low mineralization and low turbidity water under variable pH conditions where, pH is preset but allowed to vary by dropping after coagulant addition. The optimum value of pH$_i$ is between 5.5 and 6.5. Both coagulant demand (ccc) and NOM residuals are roughly constant in this pH$_i$ range. This corresponds to a final pH in solution (pH$_f$) of 4.5 – 5.0 for Al sulphate and 4.5 – 5.5 for Fe (III) sulphate. For pH$_i$ below 5.5, NOM residuals are high and for pH$_i$ above 6.5, NOM residuals are minimized but at the expense of steeply increasing coagulant demand. The optimum pH range is not affected by the presence of particulate turbidity as shown by the results on raw river water (table 1). This is in agreement with Edwards and Amirtharajah [40], who studied removal of colour caused by humic acids using alum and found that added turbidity had no effect on the optimum coagulation domain for medium to high humic acid water. Eikebrokk[25], Cheng et al, [41] studied the removal of humic substances from soft, low alkalinity and low turbidity waters by Al coagulants and stated that Al was minimized at pH 5 – 7 while NOM residuals were minimized at pH 5 – 6.

The results of ccc vs pH and NOM residuals vs pH as seen above show that Fe (III) is a better coagulant than Al both in terms of coagulant demand and NOM residuals. This result is in accord with Black et al. [42] who pointed out that Fe (III) sulphate was more than two times as effective as Al sulphate in the coagulation of colour causing organic compounds in water. In the optimum pH$_i$ domain (5.5 – 6.5) where ccc is stabilized in our studies, consideration of coagulant demand in terms of metal ion to NOM mass ratio (mg metal ion / mg NOM) gives for Al, 0.27± 0.01, and for Fe (III), 0.46 ± 0.02 for synthetic water; but for raw river water, 0.24 mg Al / mg NOM and 0.50 mg Fe (III) / mg NOM. Outside the optimum pH domain for ccc, it is found that NOM residuals increase below 0.22 mg Al/ mg NOM and 0.4 mg Fe (III) / mg NOM; also, at pH$_i$ = 6.5 – 7.5, mg Al / mg NOM rises from 0.27 to 0.49 and mg Fe (III) / mg NOM rises from 0.46 to 0.91 but NOM is still minimized. Thus, NOM residuals are minimized at mg Al /mg NOM values of 0.27 – 0.49 and at mg Fe (III) / mg NOM values of 0.46 – 0.91. These results are in general agreement with those in the literature. In the case of Al, Eikebrokk [25] for soft, low alkalinity Norwegian waters reported dosage requirements of 0.29 – 0.56 mg Al / mg NOM to minimize NOM and metal residuals and Jekel [43] suggest a minimum dosage 0.4 – 0.5 mg Al/mg NOM for low Al residuals and best removal of NOM. As regards Fe (III), the results of Cheng [44], recalculated along these lines give mg Fe / mg NOM values of 0.34 – 0.57 for good NOM removal with minimization of residuals.

In fact in the optimum range of initial pH of water, pH$_i$ 5.5 – 6.5, determination of NOM residuals after Jar Test coagulation experiments show that NOM removal was as high as 97.58% for Fe (III) as against 86.69% for Al. The difference in behaviour of Al and Fe (III) sulphate with respect to pH depression during coagulation, coagulant demand and NOM residuals, points to the possibility that in at least part of the pH range explored in these studies, some of the types of species involved in NOM coagulation by the two metals are different.

3.2. Column Settling of Metal-NOM Flocs

Figure 4 represent the column settling results obtained on the humic synthetic water tested and Figure 5 shows those obtained on raw natural humic water (Nyong River). The values of pH$_i$ at which experiments were performed on synthetic waters were selected on the
basis of the results obtained for NOM residuals, with pH 5 (Fig. 3b) being in the zone of high NOM residuals and pH 6 (Fig. 3b) in the zone of minimum NOM residuals.

It can be seen from Figure 4 for synthetic waters that, for both coagulants, the graphs show the same trends generally. Metal - NOM floc removal is low (< 20%) and independent of HLR at HLR higher than 5 m/hr. For HLR less than 2 m/hr, NOM removal increases rapidly with decreasing HLR. Comparison of Figure 4a and b shows Metal – NOM floc removal is generally higher for Al coagulated NOM than for Fe (III) coagulated NOM. This implies that Al – NOM flocs have higher settling rates compared to Fe (III) – NOM flocs. At all values of HLR investigated, Fe (III) – NOM flocs seem to have the same settling rates at pH 5 and pH 6, as indicated by results of NOM removal. The absence of a pH effect on floc settling points to the possibility that in the conditions prevailing in these studies, the structuring of aggregates, Fe (III) – NOM flocs, deriving from Fe (III) coagulation of NOM in these waters occurs by the same mechanism at both pH values. This situation is similar to that applicable in the mechanism of coagulation which is complexation – charge neutralization at both pH values, as suggested earlier. However, Vilgé – Ritter et al. [45] stated that floc structuring in Fe (III) coagulation of NOM in natural waters (Lake Ribou and Seine River) was pH dependent as indicated by the fractal dimensions of aggregates and was controlled by the nature of the organic matter. It is suggested that the nature of the tropical river organic matter may be responsible for the absence of a pH effect in our case. Regarding Al –NOM flocs, settling rates are similar at both pH values for HLR less than 2 m/hr, but at higher HLR, pH has a small but weak effect with pH 6 giving slightly higher floc settling (removal) rates than pH 5. This could be due to a small difference in coagulating species present, in view of the suggestion made earlier that at pH 5, Al coagulates NOM purely by complexation – charge neutralization while at pH 6, although complexation – charge neutralization is predominant. At higher HLR shearing would tend to reduce floc aggregate sizes and hence cause slower settling rates.

The results presented in Figure 5, pertaining to Nyong River water (pH 5.9), confirm the metal cation effect on settling rates. At all HLR values greater than 2m/hr, the percent removal of Al-NOM flocs is higher than that of Fe(III)-NOM flocs, indicating that Al-NOM flocs have a higher settling rate compared to Fe(III)-NOM flocs for HLR above 2m/hr. But for HLR below 2m/hr, the difference between the two coagulants reduces rapidly so that percent removal and hence settling rates are comparable at HLR below 1m/hr. As in Figure 4, the percent removal of NOM, for both coagulants and for HLR greater than 5m/hr, is quite low (< 30%). Interestingly, for greater than 50% NOM removal, it is necessary to operate at HLR values less than 2m/hr, that is, at quite low HLR as observed in practice at the Nyong River water treatment plant. NOM removal values of 80% or more can be achieved at HLR values of 1m/hr or less. The need for very low HLR values to achieve high percent removal of NOM points to low density of metal – NOM flocs in the absence of significant turbidity in these waters. It has been observed from the results presented above that, Al – NOM flocs generally settle faster than Fe (III) – NOM flocs, the difference being more evident for Nyong River water.
Figure 4 Effect of hydraulic loading on the removal of NOM from 25 mg/L NOM water coagulated at pH 5 (a) and pH (6.5) (b) with Al sulphate (●) and Fe (III) sulphate (○)

Figure 5 Effect of hydraulic loading on NOM removal from Nyong river raw water (20 mg/L NOM) coagulated at pH 5.9 with Al sulphate (●) and Fe (III) sulphate (○)
3.3. Coagulation Mechanisms

Reaction of NOM with Al and Fe (III) depends on the metal hydrolysis species present and the degree of dissociation of carboxyl and phenolic groups of the NOM. The hydrolysis of Al and Fe (III) in the presence of humic acids and NOM is limited by the presence of the latter but still dependent on solution pH. Masion et al. [46] studied the hydrolysis of Al in the presence of small organic acid ligands using small angle X-ray scattering and found that speciation of Al in the pH range of 3 – 8 was limited to monomers, dimers and small oligomers (trimers). Further, Vilgé-Ritter et al. [45] found that Fe (III) hydrolysis in the presence of lake and river NOM at pH 5.5 and 7.5 was limited to small oligomers (trimers) due to hindrance of the hydrolysis of Fe (III) by NOM. Rose et al. [47] who studied Fe speciation in NSIMI river water from the same tropical forest zone as Nyong River in Cameroon, stated that NOM hindered Fe hydrolysis even at pH 6, Fe was poorly polymerized due to complexation with NOM which blocks the Fe growth sites. Hence the presence of NOM prevents formation of polymers and oxyhydroxides of Fe at pH below 7.5. In view of the foregoing, it can be inferred that the mechanisms of coagulation of Al and Fe (III) sulphate with NOM as suggested by the trends in Fig. 3 are as follows.

In the case of Al sulphate, there are three segments. For pH$_i$ 5.5 – 4.5 corresponding to final pH (pH$_f$) 4.3 – 4.5, reaction between positively charge Al ionic species (monomers, dimers and trimers) and ionized carboxyl of NOM occurs by electrostatic attraction followed by complexation –charge neutralization. The effective pH (4.3 – 4.5) is too low for the formation of a significant amount of Al hydroxide and it is also known that at least 80 % of the carboxyl groups are ionized in this pH$_f$ range [19,48]. The high level of residuals in this pH range is probably due to soluble metal NOM complexes and non-complexed NOM. In the range of pH$_i$ 5.5 – 6.5 (pH$_f$ 4.5 – 5.0), the amount of NOM residuals roughly stabilizes as does the ccc. This could be due to the fact that most of the NOM carboxyl groups are ionized. However, in this pH$_f$ range, dimer and trimer, aluminum species with different numbers of sulfate ions also forms [48-50] and so there is formation of Al – NOM complexes by reaction of NOM with various Al ionic species. Coagulation probably occurs by complexation charge neutralization. At pH$_i$ 6.5 – 7.7 (pH$_f$ 5.0 – 5.4) all the carboxyl groups of NOM and some of the phenolic groups have ionized and dimeric and trimeric aluminium species has become predominant. In this region, coagulation also occurs principally by complexation-charge neutralization. The fall in NOM residuals as pH$_i$ increases above 6.5 in Figure 3 is consistent with the total ionization of carboxyl and partial ionization of phenolic groups of NOM. As regards removal of NOM by Fe (III) sulphate, Figure 3b shows only two segments. NOM residuals increase as pH falls (pH$_i$ 5.5 – 4.5, pH$_f$ 4.5 – 3.9). In this pH zone, coagulation occurs by complexation – charge neutralization, similar to the case of Al sulphate. Increase in NOM residuals as pH falls in this zone is probably due to the formation of soluble Fe (III) – NOM species. Indeed, from studies of coagulation of humic acid by Fe (III) salts using fluorescence quenching, Cheng [44] stated that under low pH conditions, dissolved complexes of Fe (III) – organic matter were found in solution. For pH$_i$ 5.5 – 7.5, that is at pH$_f$ 4.5 – 6.3, the amount of NOM residuals is constant and independent of pH, thus suggesting strongly that in this pH range, the mechanism of NOM removal by Fe is independent of pH. Since, as stated above, there is no evidence of Fe (III) hydroxide in the presence of NOM [45, 47], coagulation occurs by complexation – charge neutralization. It is clear that throughout the pH range (pH$_i$ 4.5 – 7.5, pH$_f$ 3.9 – 6.3) explored in our studies, removal of NOM by Fe (III) takes place by complexation – charge neutralization. The size of humic substances is also known to depend on pH: a stretched configuration occurs at alkaline pH.
due to intramolecular electrostatic repulsions, whereas small humic aggregates can be formed below pH 5 [51, 52]. Thus the aggregation of humic acid with hydrolyzed-Fe species can be ascribed as the restructuration of flexible humic network during association with coagulant species. As shown in recent electron energy loss spectroscopy and pyrene fluorescence experiments [29, 22], conformational rearrangements can also be evidenced during the coagulation of negatively charged humic colloids with cationic hydrolyzed metal species.

4. CONCLUSIONS

Studies of NOM coagulation by Al and Fe (III) sulphate in soft, low alkalinity, low turbidity high NOM containing tropical water using Jar test show that coagulant demand is much higher (twice or more) for Al compared to Fe (III) salt. Whereas, column settling experiments show that Al gives better floc settling rates than Fe (III) except at very low hydraulic loading rates. The difference between Al and Fe (III) sulphate in terms of coagulant demand (ccc) and removal of NOM from soft, low alkalinity and low turbidity humic water observed is due to differences in metal hydrolysis species present in the pH range concerned. In the pH zone where NOM residuals are minimized (pH > 5.5) Al and Fe (III) coagulates NOM by complexation – charge neutralization.

REFERENCE


