Coagulation-Flocculation Treatment of a Tropical Surface Water with Alum for Dissolved Organic Matter (DOM) Removal: Influence of Alum Dose and pH Adjustment

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Abstract: Effective removal of turbidity and soluble dissolved organic matter (DOM) from the Agbo reservoir water was investigated, since DOM can lead to the formation of potential carcinogens compounds during water disinfection. An enhanced coagulation with alum was then conducted by standard jar test to optimize coagulation pH and alum dose. Optimum removal of turbidity (98%) and dissolved organic carbon (DOC) (70%) was achieved for 100 mg alum L^{-1} at pH 5. Alum dose and pH control of coagulation were found to be important factors governing DOM removal. It was also showed that humic substances are rather more removed by alum than the other DOC compounds.
Keywords: *alum; coagulation; DOM; Turbidity; removal.*

Introduction

Dissolved organic matter (DOM), defined as the complex matrix of organic material present in waters, affects significantly many aspects of water treatment, including the performance of unit processes, application of disinfectants, and biological stability. DOM has become increasingly important with regard to water supplies, because it reacts with chlorine during the disinfection process in drinking water treatment and produces disinfection by-products (DBPs) such as trihalomethanes (THMs) (Lee *et al*., 2006; Sharp *et al.* ,2006). The formation of THMs is of much concern because of their carcinogenic effects on humans (Tardiff, 1977, Krasner *et al.,* 1994). Aquatic humic substances, comprising fulvic and humic acids are the most common precursors of THMs. Organic matter in natural water can also cause bad odour, taste, colour, and bacterial regrowth problems (Yan et al., 2006) in water distribution systems.

Of these DOMs, coloured humic substances (mainly humic and fulvic acids) generally predominate, and a large proportion of these substances are soluble. Generally, there are in colloids systems, *i.e,* the dispersed phase is about the particles of small sizes, about a few microns (Franceschi *et al.,* 2002). The very significant specific surface area of the particles and the existence of a surface charge on these colloids explain the prevalence of surface forces over volumes forces, which stabilise the systems and remove any possibility of elimination by spontaneous settling (Masschlein, 1996).

In Agboville, water in the distribution system is yellow/orange coloured with slit odour, giving evidence of the presence of humic substances and insufficiency of treatment. This bad quality of drinking water leads to frequent complaint of consumers.

One of the most commonly used methods for the removal of these colloids in drinking water is the addition of coagulant and flocculation aids, such as alum and ferric chloride (AWWA, 1997). The coagulation/flocculation process neutralizes or reduces the negative

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charge on particles. This allows the van der Waals force of attraction to encourage initial aggregation of colloidal and fine suspended materials to form microfloc (Ebeling *et al*., 2003). Improper coagulation causes poor filter performance, as compared to the results attained when coagulation is done correctly, and removal of colloids is erratic.

The most widely used coagulant is aluminium sulphate. Its efficacy depends on the physical and chemical characteristics of the raw water and the operating conditions (Gregor *at al.,* 1997). pH and coagulant dose control of coagulation are the most important factors governing natural organic matter (NOM) removal (Volk *et al*., 2000).The role of the pH is particularly significant insofar as it determines at the same time the electrical charge of organic and inorganic colloids and it is a major factor in the hydrolysis of aluminium salts (Changqing at al., 2006). For many authors, aluminium sulphate is most effective over a limited pH range of 6.5-7.5, and that seems to be its primary disadvantage (Ebeling *et al.,* 2003).

For others, several mechanisms are referred to when describing the removal of NOM, and each mechanism is favoured by a particular set of operational conditions depending on the water pH. In practice, it is likely that these operational conditions will overlap and that more than one mechanism will be responsible for NOM removal. The three mechanisms of NOM removal most commonly referred to are charge neutralisation, entrapment, and adsorption. Charge neutralisation is the mechanism used to explain the precipitation of NOM in operational regions where aluminium hydroxide precipitation is minimal (pH 4.5-6). In operational regions where insoluble aluminium hydroxide forms (pH 6-8), NOM can be removed by entrapment or surface adsorption (Gregor et al., 1997). The mechanism involve for each water treatment (and therefore the coagulation pH) depends on the water characteristics.

In all water treatment plants in Côte d'Ivoire, the pH of coagulation – flocculation is the consequence of aluminium sulphate addition responding to variable water turbidity and organic matter contain, rather than the result of deliberate pH adjustment. This practice leads to variable coagulation pH and consequently variable removal efficiency of colloids and fine suspended materials. The aim of this study is to optimise the natural organic matter removal by alum dose and pH control during coagulation flocculation.

Materials and Methods

Water used for this study comes from the water reservoir Agbo, located in Agboville town (Côte d'Ivoire) under tropical climate. The water reservoir is colonized by aquatic plants. The raw water characteristics are summarized in Table 1.

Table 1. Characteristics of raw water submitted to the coagulation-flocculation process

Parameters	Values
TOC (mg L^{-1})	20.85
DOC (mg L^{-1})	20.32
Turbidity (NTU)	15.10
SUVA (m^{-1} L mg^{-1})	3.55
pH	6.61

Jar test procedure

The coagulation-flocculation tests were carried out following the standard practice for coagulation-flocculation testing of drinking water to evaluate the chemicals dosages and conditions required to achieve optimum results (ASTM, 1995). A standard jar test apparatus, the Phipps & Bird six-paddle Stirrer with illuminated base was operated for the tests, with six 2-1 squareB-Ker Plexiglas jars. The jars are provided with a sampling port, 10 cm below the water line, which allows for repetitive sampling with minimal impact on the test. The six flat paddles

are all driven by a single variable speed motor from 0 to 300 rpm. An illuminated base helps observation of the flock formation and settling characteristics.

The coagulant solution [10 g L^{-1} aluminium sulphate $Al_2(SO_4)_3$] were prepared before the experiment. Each jar was filled with 2 L of raw water measured with a graduate cylinder. The coagulant dose added to each jar was carefully measured with a burette. The solutions were stirred rapidly at 150 rpm for 1 min, followed by slow stirring at 20 rpm for 15 min. After this period, the paddles were withdrawn and the flocks allowed settling for 30 min. Samples were then withdrawn from the sampling ports for analysis. For all the jar tests, UV_{254}, DOC, turbidity and soluble aluminium residual were measured after water filtration through Whatman glass fiber filters membranes (0.45μm) previously pre-combusted at 500 °C overnight.

A wide range of alum dosage and pH were explored to achieve optimum removal of turbidity and DOC. The coagulation pH was adjusted with sulphuric acid (H_2SO_4, 1 M) or sodium hydroxide (NaOH, 1M) or saturated solution of lime (filtered through 0.45 μm filter) to obtain values between pH 3.5 and 7.5.Optimization of parameters was determined by high turbidity and DOC removal, low residual aluminium and low specific ultraviolet absorbance (SUVA).

Analysis

Dissolved organic carbon analysis

Dissolved organic matter (DOM) is analyzed as Dissolved organic carbon (DOC). A total carbon analyser Shimadzu TOC-VCSH was used to analyse organic carbon in raw and treated waters by combustion at 680 °C. Samples to measure organic carbon concentration were collected using amber glass bottles previously rinsed with nitric acidic solution (20%) and copious amounts of analytical grade water (Milli-Q) from a laboratory system (Millipore Milli-Q academic) and then grilled (500 °C overnight). Each sample was determined thrice, the average value was considered as the DOC data.

Aluminium residual, Turbidity and UV absorbance

UV_{254} absorbance was measured by spectrophotometer Hitachi U – 2001. The specific ultraviolet absorbance (SUVA) was calculated as the UV absorbance at 254 nm (cm^{-1}) per mass of carbon (DOC in mg L^{-1}). Differences in SUVA for water samples collected at different locations or times reflect inherent structural differences in the material containing the DOC. According to Imai et al. (2001) and Weishaar *et al.* (2003), the SUVA is a very useful parameter for evaluating the characteristics of DOM in waters.

Soluble aluminium residual has been measured by Hach colorimetric method with a spectrophotometer Hach 2010. Soluble aluminium has been measured instead of total aluminium since soluble aluminium is more concerned with Human Health (Alzheimer's disease) than total aluminium residual (Schintu *et al.*, 2000). Turbidity was measured with a turbidimeter Hach 2100 P.

Results

Different doses of alum were submitted at different pH to determine both the optimal flocculation pH and alum dose. It is supposed that improvement of flocculation pH may reduce the alum dose needs for the optimization of the process. It was also necessary to know the effect of pH beyond the optimal dose of coagulant. The experiment was then carried out in a range of alum doses from 80 to 125 mg L^{-1} and a range of pH 4-6. To evaluate the process efficiency, turbidity, UV_{254}, DOC, aluminium residual and SUVA were analysed.

Turbidity, UV_{254} and DOC removal

As shown in Figure 1, for a same pH value, the efficiency of turbidity removal increases with increasing alum doses. For the same value of alum dose, the removal efficiency decreases

with pH increasing. The removal is optimal between pH 4-5 and there is no significant difference in alum doses efficiency in the range of 80 to 125 mg/L for pH 4-4.5.

Both UV_{254} (Figure 2) and DOC (Figure 3) removal is pH dependant. These two parameters exhibit very similar coagulation behaviours in term of pH dependence. The optimal pH value for UV_{254} and DOC removal is pH 5. Removal of the two parameters increases with increasing of pH values until pH 5. High values of pH beyond pH 5 exhibit an inefficiency of UV_{254} and DOC removal. These high values of pH lead to a decreasing of UV_{254} and DOC removal with increasing of pH. However the UV_{254} removal is much higher than the DOC one.
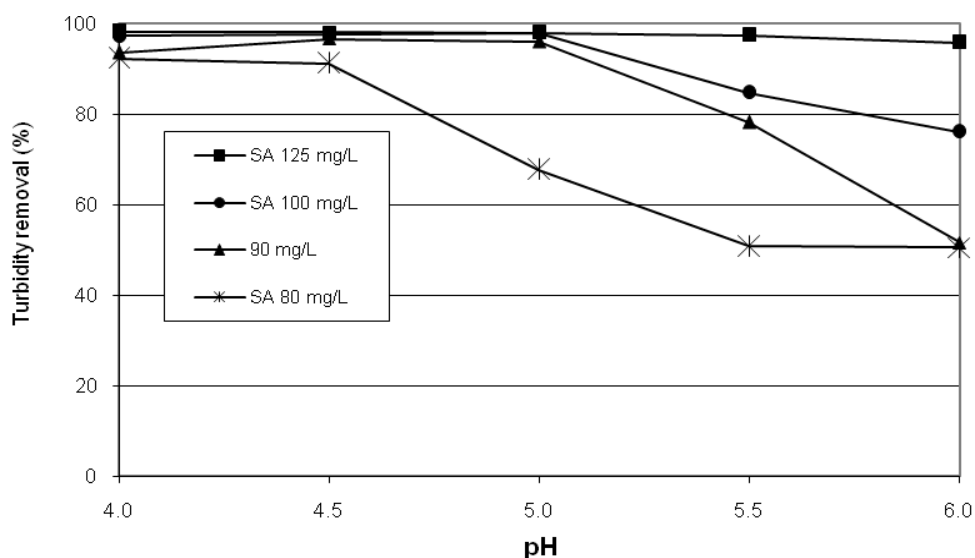
Figure 1. Effect of pH on the percent removal turbidity for different doses of alum using standard jar test with 150 rpm rapid mixing for 1 min, low mixing for 15 min at 20 rpm and 30 min settling time

Soluble aluminium residual

Measurement of soluble aluminium residual content in clarified water after the coagulation-flocculation process is one way of ascertaining the efficiency of the process. Figure 4 depicts the concentrations of aluminium residual as a function of pH. Aluminium concentration decreases with increasing pH values. A coagulation-flocculation pH ≥ 5 is required to ensure relatively low soluble aluminium concentration. The minimum of aluminium residual (0.05 mg Al L^{-1}) is obtained at pH 5 for a 100 mg L^{-1} alum dose.

SUVA evolution during coagulation/flocculation

Dissolved organic matter (DOM) is a highly heterogeneous mixture of organic compounds. In order to investigate a possible specific affinity of aluminium to certain compounds, the evolution of SUVA was determinated during coagulation-flocculation process. It is generally supposed that the increasing of SUVA indicates an increasing aromatically. Figure 5 shows the SUVA values as a function of pH. It can be seen that aluminium has more affinity to aromatic compounds and that increase with increasing pH in the range pH 4-5. Over pH 5, an increasing pH values leads to the remaining of these compounds in solution.
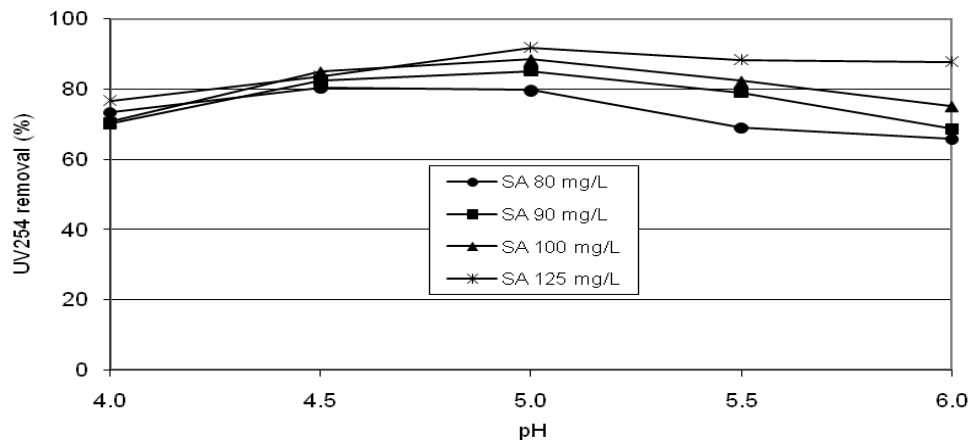
Figure 2. Effect of pH on percent Absorbance UV_{254} removal for different doses of alum using standard jar test with 150 rpm rapid mixing for 1 min, low mixing for 15 min at 20 rpm and 30 min settling time
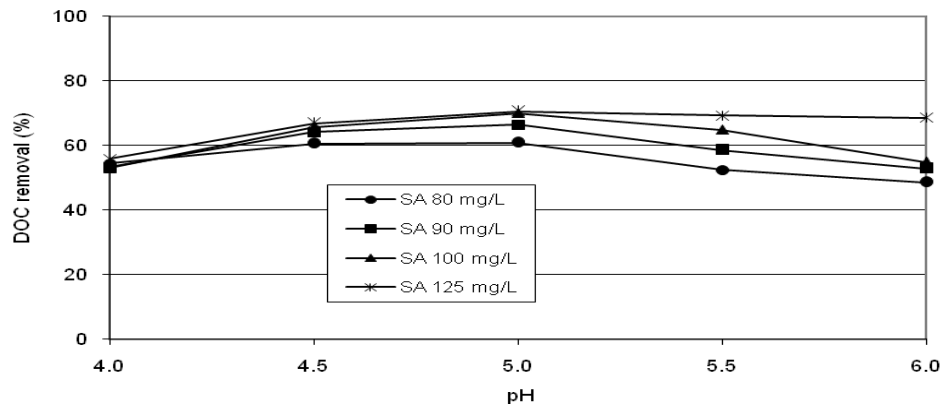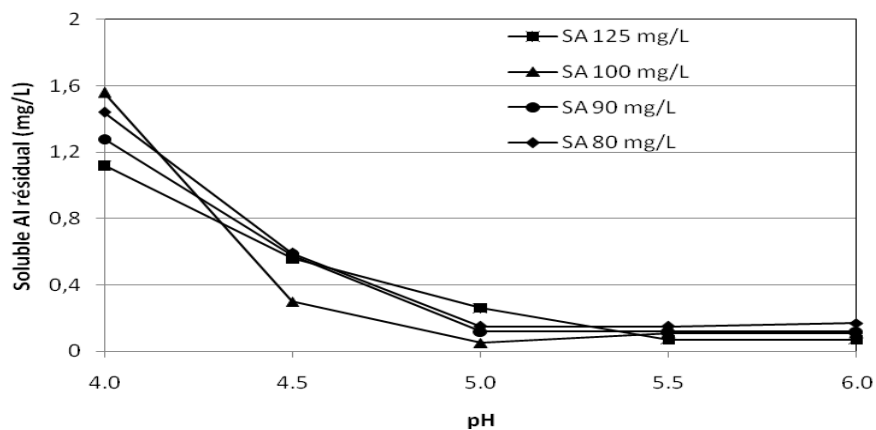

Figure 3. Effect of pH on percent DOC removal for different doses of alum using standard jar test with 150 rpm rapid mixing for 1 min, low mixing for 15 min at 20 rpm and 30 min settling time

Figure 4. Effect of pH on soluble aluminium residual for different doses of alum using standard jar test with 150 rpm rapid mixing for 1 min, low mixing for 15 min at 20 rpm and 30 min settling time
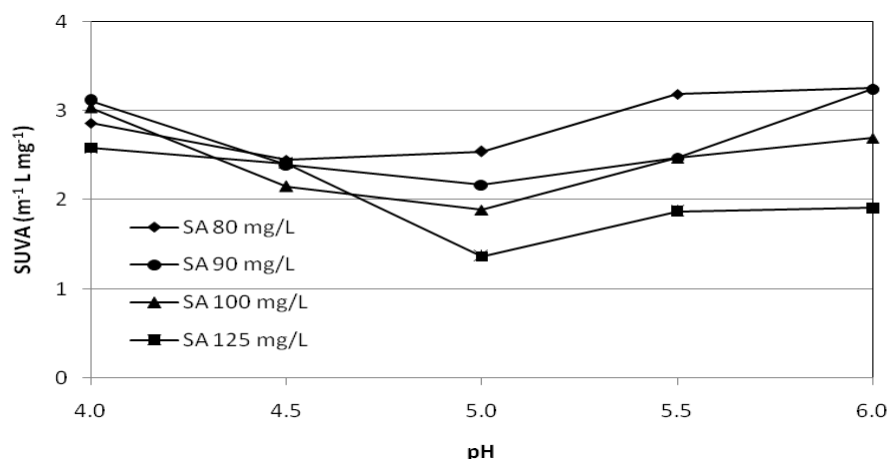
Figure 5. Effect of pH on SUVA for different doses of alum using standard jar test with 150 rpm rapid mixing for 1 min, low mixing for 15 min at 20 rpm and 30 min settling time

pH adjustment option

Having established that pH adjustment and control are necessary for effective coagulation and flocculation of soluble DOM, the option for pH adjustment was studied to determine which base to use. Lime and sodium hydroxide are the most common bases used to raise pH and carbon dioxide and alum will decrease the pH. Figures 6, 7, 8 and 9 show the impact of lime or sodium hydroxide respectively on turbidity and DOC removal, on SUVA and on the soluble aluminium. Coagulation and flocculation are carried out for an alum dose of 100 mg L^{-1}, rapid mix at 150 rpm for 1 min, flocculation at 20 rpm for 15 min and 30 min settling time. Lime addition lead to more efficiency of the turbidity removal and low soluble aluminium residual than does sodium hydroxide. Dissolved organic carbon or SUVA removal exhibit no difference effect of these two bases.
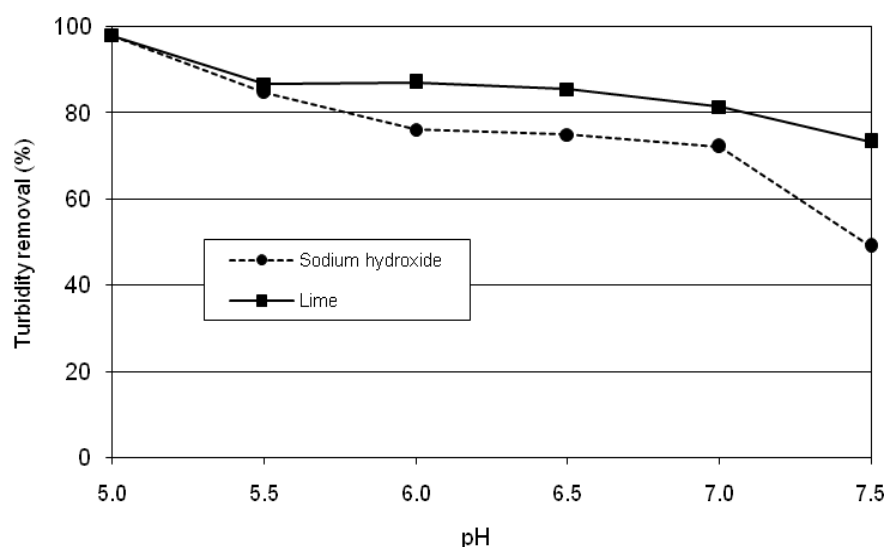

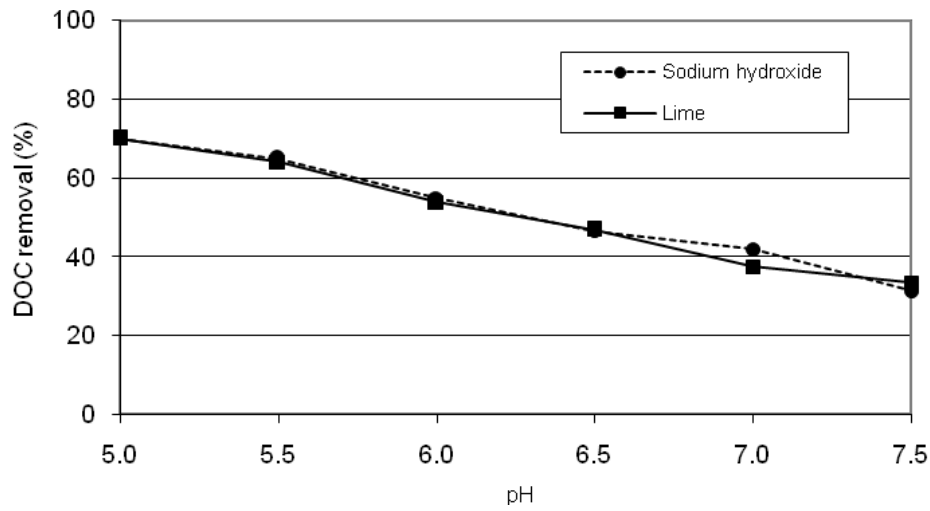**Figure 6.** Effect of lime or sodium hydroxide use for pH adjustment on turbidity removal

Figure 7. Effect of lime or sodium hydroxide use for pH adjustment on DOC removal
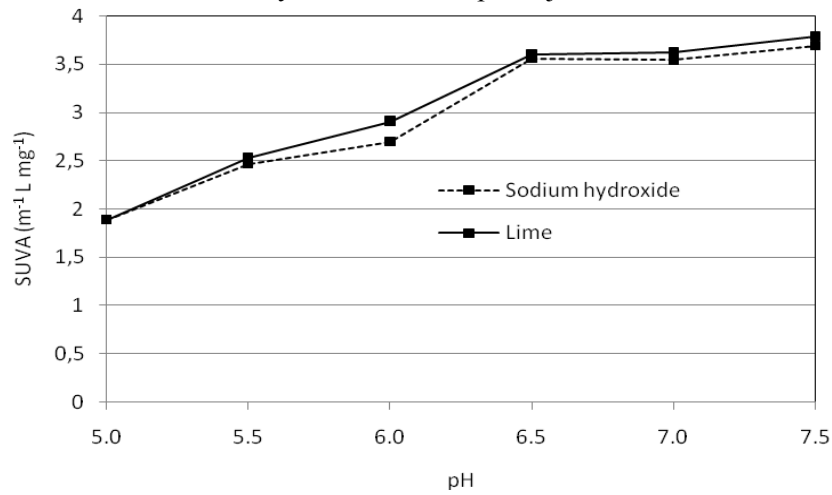

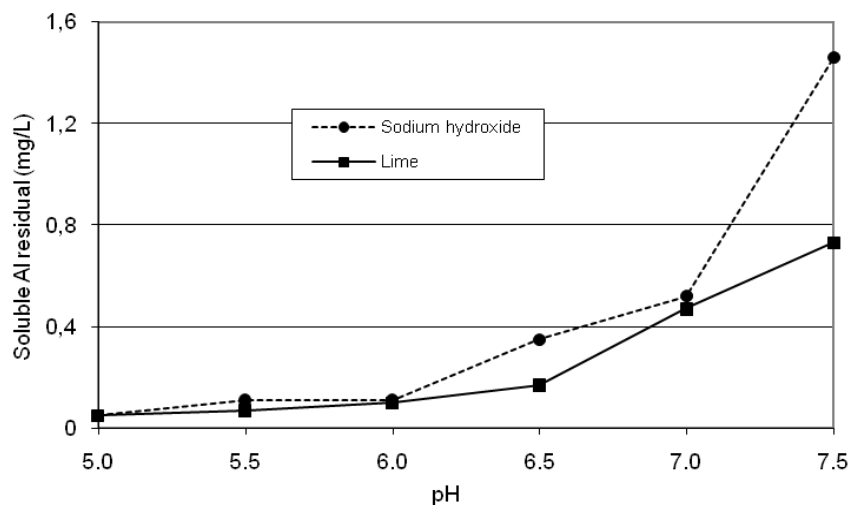**Figure 8.** Effect of lime or sodium hydroxide use for pH adjustment on SUVA

Figure 9. Effect of lime or sodium hydroxide use on soluble aluminium residual

Discussion

Results obtained in this study indicate pH and alum dose effect on turbidity and DOM removal during coagulation/flocculation process. For Dominguez *et al.* (2007), within all the factors involved in coagulation-flocculation process, those that most affect the process efficiency are pH and coagulant dose, since influence in the hydrolysis equilibria of coagulant species. Aluminium sulphate dose and pH are linked. An increasing of the alum dose lead to a decreasing in pH values

The role of pH is particularly significant insofar as it determines at the same time the electrical charge of organic and inorganic colloids and it is a major factor in the hydrolysis of aluminium salts.

The results of the experiment indicate that DOM removal increases with pH increasing for values ranged from pH 4-5. Similar results have been already published (Lu *et al.*, 1999; Kim *et al.*, 2001; Guida *et al.*, 2007). Above pH 5, the coagulation flocculation leads to a decreasing of DOM removal for alum dose below 100 mg/L. However, for higher dose of alum (125 mg/L), no significant decrease of DOM removal was observed over pH 5 and the optimum DOM removal obtained at acidic conditions was unchanged. The mechanism involved in DOM removal with aluminium sulphate is strongly pH dependent. In natural water, DOM and nearly all colloidal impurities are negatively charged. These DOM and particularly humic substances can be regarded as natural anionic polyelectrolytes (Figure 10), of rather indeterminate structure. They have various functional groups, including carboxylic and phenolic, and a framework of randomly condensed aromatic rings. Because of the ionisation of carboxylic groups, humic substances will have anionic charge at pH values higher than 4 and are generally soluble under these conditions (Duan & Gregory, 2003). Hence, these negative charges can be neutralized by aluminium sulphate hydrolysis products positively charged at pH below pH 6 (Kim *et al.*, 2001).

As shown by Exall and vanLoon (2003) and Duan and Gregor, (2003), in acidic conditions, numerous monomeric and many possible polynuclear forms positively charged of sulphate aluminium hydrolysis products are formed. The hydrolysis products include Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al_2(OH)_2^{4+}$, $Al_3(OH)_4^{5+}$ and $Al_{13}O_4(OH)_{24}^{7+}$ (Figure 11). It is found that these compounds are responsible of the removal of turbidity and humic substances by binding to anionic sites, thus neutralising their charge and giving a reduced solubility. This leads to the precipitation of a metal-humic complex that can be removed by filtration. As can be seen in Figures 5, 6 and 7, at pH below 5, no significant difference is observed between removal of DOM or turbidity either at low or higher coagulant dose for the same pH value. The implication is that charge neutralisation can occur at low concentration of coagulant as already shown by Letterman and Vanderbrook, (1983). But at pH above 5, high dose of coagulant (125 mg/L) is required to enhance the turbidity and DOM removal. It is very likely that the removal of DOM under these conditions is predominant by sweep flocculation. Sweep flocculation requires high dose of coagulant to promote aluminium hydroxide $(Al(OH)_3)$ formation at pH range 5.5-7.5 (Gregor *et al.*, 1997; Kim *et al.*, 2001). Although details are not fully understood, it seems clear that impurity particles are enmeshed in a growing hydroxide precipitate and are effectively removed from suspension (Shi *et al.*, 2007). This process has become known as "sweep flocculation" since particles are "swept out" from water by an amorphous hydroxide precipitate. As regard to the residual soluble aluminium (Figure 8), the coagulation-flocculation at pH below 5 leads to high concentration of residual aluminium remained in solution after filtration compared to that obtained at pH range 5-6. But at pH above 6, the residual soluble aluminium increases again (Figure 9). This sequence of evolution of residual aluminium means that the hydroxide precipitate occurs effectively at pH range 5-6. Probably, the two mechanisms occur simultaneous at pH 5. Adjusting pH with lime or sodium hydroxide showed no difference in DOC removal, but lime is more effective in turbidity removal and leads to low level of soluble aluminium residual. Similar result has been obtained by Gregor et al. (1997) and can probably be explained by the fact that Ca^{2+} is more positively charged than Na^+. The difference between the percent removal of UV_{254} (90%) and DOC (70%) can be attributed to a greater affinity of

aromatic humic substances to aluminium species compared with other dissolved organic carbon compounds (Uyak et al., 2007). Edzwald and Van Benschoten (1990) demonstrated that the SUVA relate closely to the among of removable dissolved aromatic organic matter in raw water. That is confirmed by the decreasing of SUVA in the region where an efficiency removal of DOC is observed.
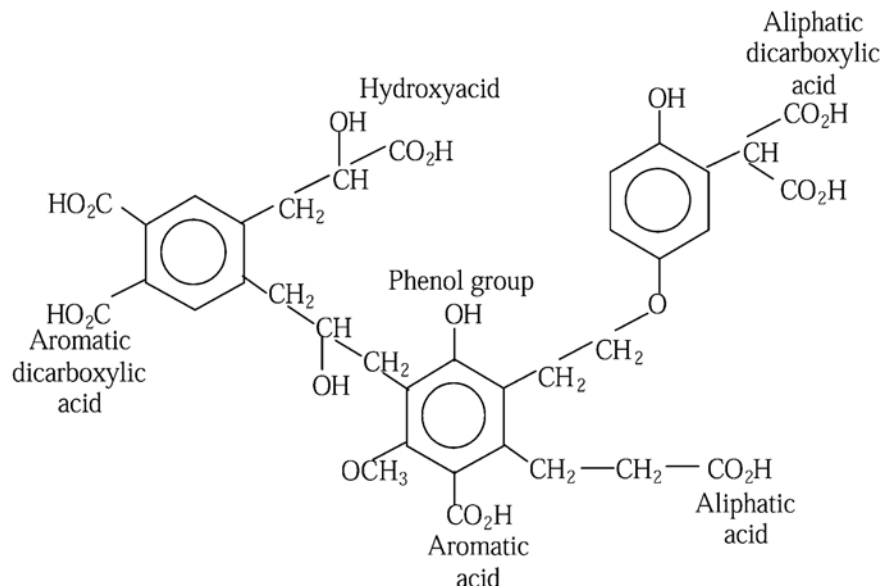

Figure 10. Hypothetical molecular structure of humic acid, showing important functional groups (Duan & Gregor, 2003)
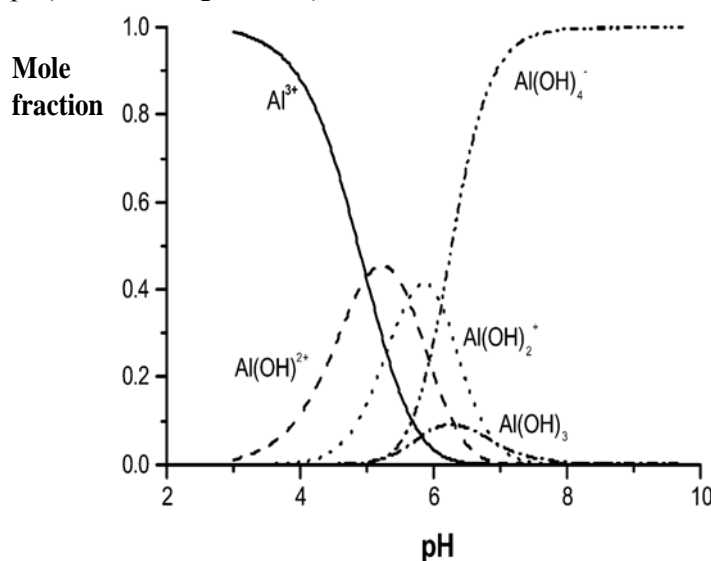

Figure 11. Proportions (mole fractions) of aluminium dissolved hydrolysis products in equilibrium with amorphous hydroxides (Duan & Gregor, 2003)

Conclusion

For Agbo reservoir water, enhanced coagulation jar test results showed that aluminium sulphate could remove about 70% DOC, 90% UV_{254} and 98% turbidity. The optimum removal of both DOC and turbidity were obtained for 100 mg/L alum at pH 5. It is very clear from the literature and this work that pH and coagulant dose control of coagulation-flocculation are the most important parameters governing DOM removal. The results also showed that coagulation

with alum removes preferentially aromatic humic substances and thus for our next works we will try to remove non humic fractions of DOC by another process such using activated carbon.

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