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Research Article

Evaluation of Cacao Husk Ash Extract as Coagulant Aid in the Removal of Turbidity in Low Alkalinity Aqua Medium

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Abstract

The need to ameliorate some of the inherent limitations in the use of alum in water purification engendered these studies. Synthetic water of varying turbidities (50, 100, 300 NTU) and varying pHs (2, 3, and 4), but low alkalinity were prepared. The results from the different studies showed that water of lower residual turbidity could be got from the use of 50% of optimum alum dose when combined with CHAE as coagulant aid. The depression in the pH of the treated, usually experienced with alum use, could be avoided with the use of CHAE as coagulant aid. Studies on the effect of using CHAE, as coagulant aid, on the kinetics of flocculation showed that the removal rate of the CHAE/alum combination was faster than that of the alum alone and the redistribution and redispersion of the flocs, observed with the use of alum alone was not noticed when the coagulant aid was used. The sludge volume was also greatly reduced with the use of CHAE as coagulant aid.

Keywords: Coagulant aid; Cacao; Ash; Extract; Alum; Turbidity; Water treatment

1. Introduction

In water and wastewater treatment, using coagulation and flocculation unit processes, the use of metal salts such as lime, alum and ferric salts are reliable and well established processes. Aluminum salts are the most commonly used coagulants but a number of drawbacks synonymous with its use have been identified and delineated by researchers viz: Alzheimer's disease and similar-health related problems have been associated with residual aluminum in treated water; large sludge volume production; reaction with natural alkalinity present in the water, leading to pH reduction; exhibition of low coagulation efficiency in cold waters and ecotoxicological impacts when introduced into the environment as post-treatment sludge. In order to obviate these inherent inadequacies, several coagulants such as ferric salts, polyaluminum chloride, polyferric chloride,

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and synthetic organic polymers, have been proffered as alternatives to aluminum salts. Although these materials enhanced coagulation processes, health and environmental safety is still not guaranteed.

Myriads of materials have been studied as an aid to improve the process of coagulation and flocculation. Some of the materials that have been studied were classified thus: oxidants (e.g. Cl, ClO_2, $KMnO_4$, and O_3); adsorbent weighting agents (e.g. clay, powdered silica, limestone, activated carbon); activated silica and; polyelectrolytes (anionic, cationic, non-ionic and anfolitic). Some biological based materials that have also been investigated include aqueous extracts of seed of *moringa* Oleifera (Ndabingesere, and Narasiah, 1996, 1998a 1998b) , tannin (Ozacar, and Sengil, 2000, 2002a and b, 2003a and b) extracts of okra and nimali seeds (Al-Samawi, and Shokralla, 1996) , extracts of *prosopis julifora* and *cactus Latifaria* (Diaz et al., 1999) , chitosan and modified chitosan biopolymers (Pan et al, 1999, Roussy, et al., 2005, Chen, et al., 2003, Strand, 2003, Tripathy, 2001) and snail shell (Oladoja, N.A., Aliu, 2009) .

The choice of a material as coagulant aid is usually premised on the particular physical or chemical property of the colloidal particulates or the aqua medium to be modified. In water industry the four different kinds of colloidal suspensions commonly found (Weber, 1972) are: suspension with high colloid concentration and low alkalinity; suspension with high colloid concentration and high alkalinity; suspension having low colloid concentration but with high alkalinity and low colloid concentration with low alkalinity suspension. In situations where low alkalinity prevail, irrespective of the colloid concentration, the use of any of the inorganic coagulant alone were found to be ineffective as the pH of the aqua medium will be too low to effect rapid flocculation of colloidal particles. Addition of slaked lime [Ca (OH_2)] furnishes necessary alkalinity which provides the much needed effect (Gray, 1999; Ademoroti, 1996). Lime is an undesirable coagulant/coagulant aid because of the high sludge production and handling difficulties. The optimum dosing pH of 11 is also undesirable for use prior to or during biological treatment and would require a very high dosage if water/wastewater with low pH is encountered. Sequel to the aforementioned facts, the need to improve on the process economy and ameliorate the inherent drawbacks in the use of alum for water and wastewater treatment is expedient. Consequently, the present study aimed at the use of extract of cacao husk ash as coagulant aid in the treatment of water with medium and low colloidal particles but having low pH (i.e. low natural alkalinity water e.g. acid mine drainage and sulphuric acid plant effluent).

Cacao (*Theobroma Cacao*) is the plant from which the husk of the fruit produced was ashed and the ash was extracted with water to obtain the water extract. Cacao trees belong to the family *Stersuliaceae*. The common cacao tree is classified as *Theobroma cacao*. The seeds are surrounded by a yellow or reddish brown pod (about 28cm long). It has been estimated that an annual availability of over 30,000 tonnes of KOH could be derived from cacao-pod waste alone in Nigeria which more than met the importation requirements of KOH and NaOH of 26,000 tonnes in 1985 (Edewor, 1984). Onifade, 1994), posited that the dumping of cocoa pod wastes in concentrated heaps on the farms (the usual practice in Nigeria) was adverse to soil fertility and that hogs and other livestock could not completely remove the total wastes available, as fodder. Thus, this agricultural waste needed to be removed from the farms and the potentially viable resources should be harnessed.

In the present study, the ash of the cacao husk was obtained, the alkali extracted and characterized. Its application, as coagulant aid, in the removal of colloidal particles from simulated low alkalinity (pH= 2, 3 and 4) but medium and low turbid water (50,100 & 300NTU) was evaluated. The effects of the CHAE use on the kinetics of flocculation, pH of the treated water and sludge volume was also determined.

2. Materials and Methods

2.1 Cacao Husk Ash Extract (CHAE)

Cacao husks were obtained from Cacao Research Institute of Nigeria. They were dried in the oven at 103 -105^{0}C. The dried cacao husks were placed in a furnace and heated at 550 - 600^{0}C to obtain the cacao husk ash. The ashed sample was homogenized and sieved to remove large particle size fractions. Cacao husk ash (150 g) was placed in 2.5 L of deionised water and kept at 60^{0}C in thernostated water bath for 8 h. Subsequently, the slurry was filtered to obtain the extract. The Molarity of the CHAE was determined by titration against 0.1 M HCl using phenolphthalein indicator. Metallic ions content of the extract was determined using Atomic Absorption Spectrophotometer (AAS) (AAS 200A Buck Scientific Model).

2.2 Synthetic Turbid Water

A stock of the synthetic turbid water sample was prepared by adding 10g of pulverized clay to a litre of deionised water. The mineralogy and geochemistry of the clay sample were studied using a Diano 2100*E-X-ray diffractometer and AAS respectively. Synthetic water, of different turbidities (50,100 and 300NTU), were prepared from the stock by dilution with deionised water. The pH of the turbid water was adjusted with dilute HCl and NaOH to give the desired pHs (2, 3 and 4).

2.3 Alum Solution

Accurately weighed quantity of alum ($Al_2(SO_4)_3$) was dissolved in distilled-deionised water to obtain a final alum concentration of 0.1g of alum per ml.

2.4 Jar Test Experiment

The different studies, concerning the coagulation and flocculation of the synthetic turbid water, were conducted using the jar test method. The experiment was conducted in a system containing six rectangular pales (75 X 25mm). A typical experiment involves the addition of the coagulants to the turbid water (500ml) of a particular pH. This was followed by rapid mixing of the mixture (i.e. coagulant + turbid water) for 2 mins at 200rpm and the slow stirring for 20min at 45rpm. The mixture was allowed to settle and samples were withdrawn from 3cm depth after 20min for turbidity and pH determinations. Premised on the results obtained from these studies the flocculation time was optimized by method of continuous variation.

3. Result and Discussion

3.1 CHAE Characterization

The results presented in Table 1 are the physicochemical characteristics of the CHAE. The value of the pH (10.06) shows the alkaline nature of the extract. The molarity of the CHAE, obtained from the titration of the extract against 0.1M HCl was 0.45M. The turbidity of the extract, determined with the aid of turbidimeter was 6.0NTU. The results of the spectrometric analysis showed that the predominant metallic ions present in the CHAE were potassium (86.52%). Other metallic ions, found within the detectable limit of the AAS were present in relatively small quantities (Table 1).

Table 1 Physicochemical characteristics of the CHAE

Parameters	Values
K_2O	86.52%
Na_2O	12.25%
CaO	0.82%
CrO	0.06%
ZnO	0.05%
Fe_2O_3	0.08%
PbO	0.06%
NiO	0.06%
pH	10.06
Molarity	0.45M
Turbidity	6.0NTU

3.2 Clay Characteristics

An X- Ray diffractometer (Diano 2100*E) was used for the clay mineralogical analysis. A copper anticathode (λ = 1.54A^o) was used. XSPEX version 5.41 software was used in the interpretation of the diffractograms. Geochemical analysis of the different clay samples was performed using Atomic Absorption Spectrophotometer after the clay samples were digested in a polypropylene bottle using a mixture of HF, HCI and $HCIO_4$.Ten major elements were determined. The interpretation of the diffractogram obtained from the X-Ray Diffraction analysis revealed the presence of the following clay minerals: Kaolinite; Smectite; Illite; Mixed Layer (i.e. smectite/illite mixed layer); Quartz. The geochemical analysis showed the abundance of the presence of SiO_2 (50.11%); Al_2O_3 (17.00%) and structural water H_2O^+ (15.01%). This revealed the hydrated aluminosilicate nature of this material. The percentage oxide compositions of the other elements present are: Fe_2O_3 (1.42%); MgO (78%); CaO (6.01%); Na_2O (1.61%); K_2O (1.02%); TiO_2 (0.21%); MnO (0.001%); P_2O_5 (0.01%).

3.3 Determination of Optimum Alum Dose

The optimum Alum (Al_2 $(SO_4)_3$) dose for the coagulation of the synthetic water of different turbidities (50,100 and 300NTU) at different pHs (2, 3 and 4) were conducted in a jar test apparatus. The results obtained are presented in Fig.1a, b and c. The results obtained when synthetic water of 300NTU of varying pHs (2, 3 and 4) were used showed that the turbidities of the water reduced with increasing alum dose. When the experiment was conducted using water of different turbidities (i.e. 300, 100 and 50NTU), the optimum alum dose was obtained at 3.2ml/l for 300 NTU, 2.8ml/l for 100NTU and 2.0ml/l for 50 NTU. It was noted that the residual turbidities of the treated water reduced with increase in the initial turbidity values of the raw water (Fig. 1a, b, c). The higher residual turbidities of water with low initial turbidities could be ascribed to the low level of colloids to bridge between particles and the low rate of interparticle contacts in such systems. Gregor et al., (1997) opined that natural turbidity of water provides a ready source of nucleating sites for flocs development. Sequel to this, when a relatively low turbid water was treated with alum, lower nucleating sites are provided, hence despite the optimization of micro-flocs formation, macro flocs development and flocs settling may limit the overall turbidity removal. Therefore, when relatively low turbid waters were used (i.e. 50 and 100NTU) the effectiveness of coagulation may not be as high as when water of high turbidity was used. This possibly account for the observed disparity in the value of the percentage turbidity removal in the different turbid waters.

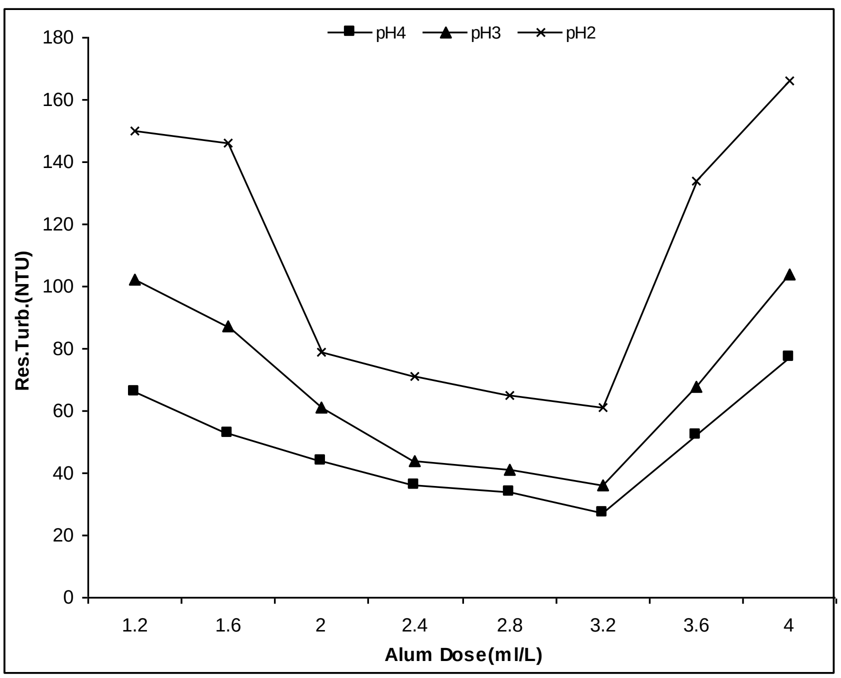

Fig.1a. Determination of optimum alum dose at 300NTU

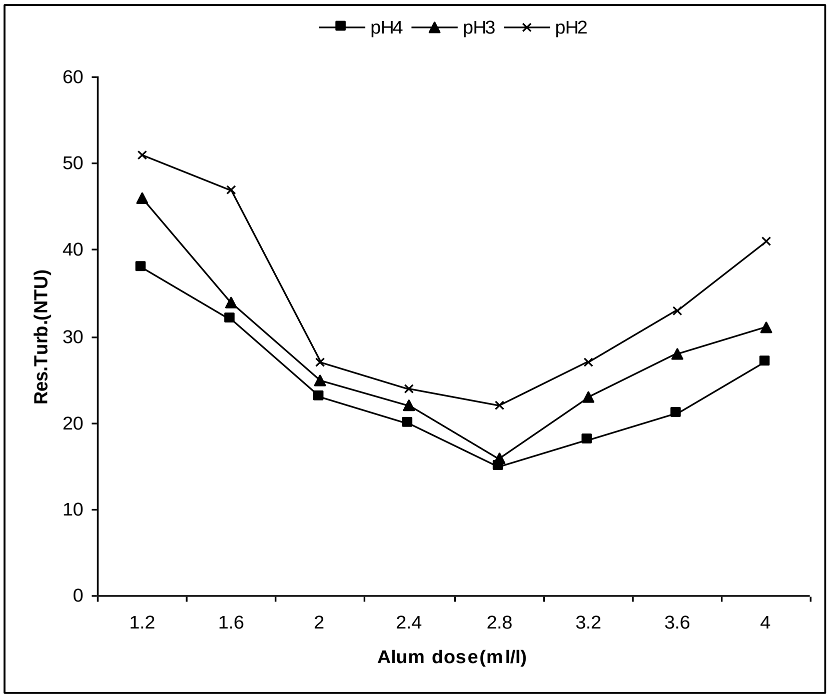

Fig.1b. Determination of optimum alum dose at 100NTU

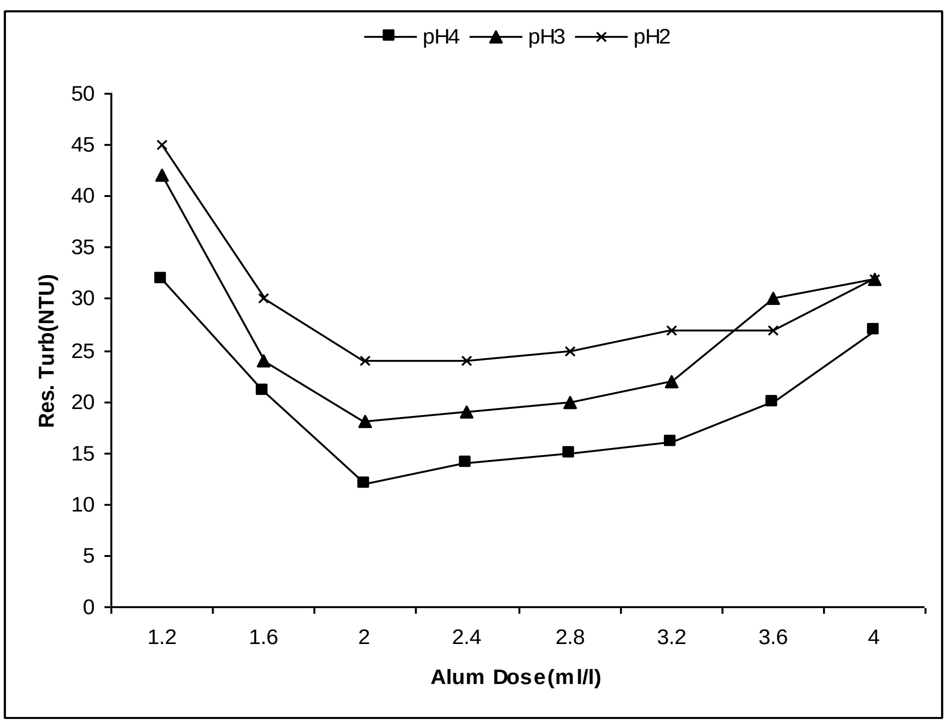

Fig.1c. Determination of optimum alum dose at 50NTU

The values of the optimum alum dose obtained when the initial solution pH was varied were similar but the residual turbidity values varied with the initial solution pH. Synthetic turbid waters of higher initial pH value had lower residual turbidity values than those of lower initial pH values. The initial solution pH is one of the pertinent factors that is given higher consideration in the use of coagulation/flocculation as a method of treatment in the water industry. This could be understood, possibly, from the reported speciation of alum in water. Alum dissociate in water to give Al^{3+}, SO_4^{2-} and various alum complexes such as $Al(OH)^{2+}$, $Al(OH)_3$, Al $(OH)_4^-$ depending on the pH of the medium. The various positive charged species which are formed may combine with negatively charged colloids to neutralize part of the charge on the colloid particles, if charge neutralization is the controlling mechanism of coagulation, thus:

$$Al^{3+} + [\text{colloid}]^{n-} = [Al\ (\text{colloid})]^{3-n}$$

The colloidal materials then come together and become incorporated into masses that can be readily precipitated. It is noteworthy that the pH of the water plays a prominent role in the determination of the hydrolysis species that is predominant in the aqueous medium. Lower pH favors the species with higher positive charge on them. At pH below 5.0, the (OH) is insufficient to precipitate Al^{3+} completely, so that [Al $(OH)^{2+}$] and Al $(OH)_2{}^+$ occur. These positively charged Al ion attracts the colloidal particles and form loose flocs which are not dense enough for easy macro floc formation and subsequent sedimentation.

Gregor et al., (1997) reported that charge neutralization is the mechanism used to explain the precipitation of natural organic matter in operational regions where aluminum hydroxide precipitation of natural organic matter is minimal (i.e. low pH). Greenwood and Earnshaw, (1989) posited that the ionic mobility of H^+ ion is extremely faster than any metallic ion in solution. The extremely fast ionic mobility of the H^+ cum its abundance at low pH could interfere with the ability of the positively charged alum species in charge neutralization, if it is the domineering mechanism.

3.4 CHAE as Coagulant Aid

Aside the need to overcome coagulation problems, there has also been a continuing desire to improve the process by forming flocs with such desirable characteristics as rapid settling and toughness. With improved settling or toughness of flocs, plants have been able to increase water production with the existing physical plant, in some cases avoiding the construction of additional plant capacity (Jessey, and Sydney, 1971).

The results obtained from the determination of the optimum doses of alum for different turbidity values (50,100 and 300 NTU) at pH 4, 3 and 2 were used as a premise for the present studies. Half (50%) of the quantities of the optimum alum doses for the different turbid waters at different pH's were used with varying quantities (mL) of the CHAE (0.36, 0.4, 0.8, 1.2, 1.6 and 2.0). The results presented in Fig. 2a, b and c showed the effect of the addition of CHAE on the residual turbidities of the treated waters. The values of the residual turbidities of the treated synthetic waters were lower, with the addition of CHAE, than when alum was used alone. The water with the initial highest turbidity value (i.e. 300NTU) produced water with the highest value of percentage turbidity removal (92.67% at pH 4). This could be ascribed to the high colloidal concentration in the medium which promotes interparticle bridging and macro floc formation. At relatively, low colloid concentration (i.e. 100 and 50NTU), an improvement in the value of the residual turbidity was also recorded; when the results obtained from these studies were compared with studies where alum alone was used.

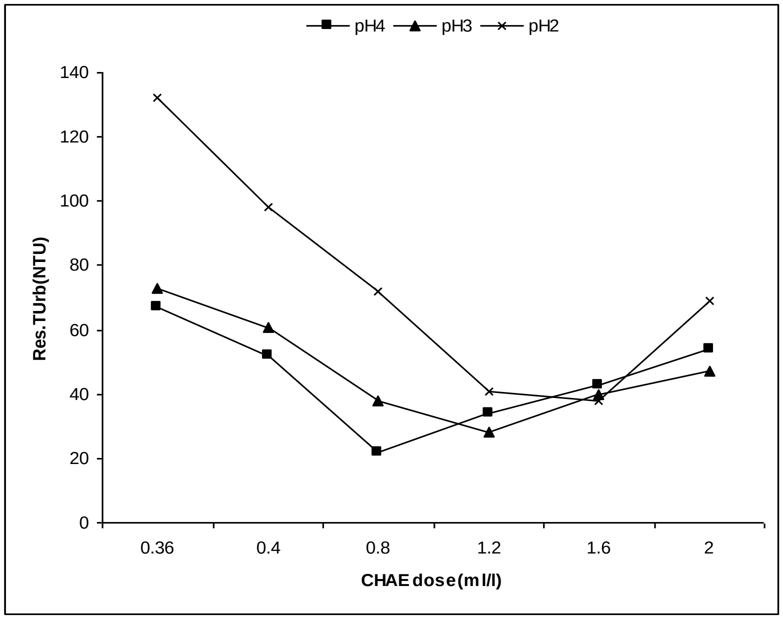

Fig. 2a. Effect of CHAE as coagulant aid at 300NTU (alum dose used = 1.6mL/L)

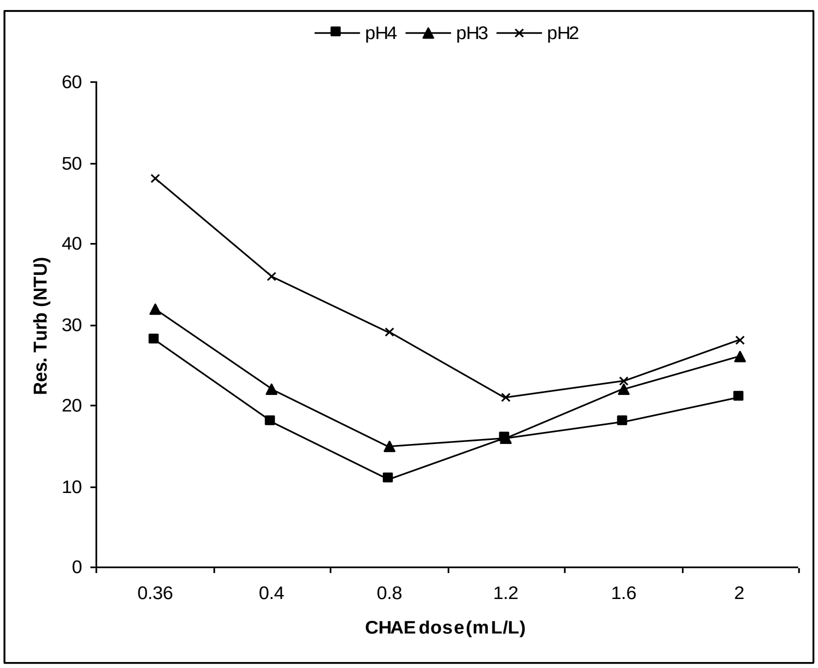

Fig. 2b. Effect of CHAE as coagulant aid at 100NTU (alum dose used = 1.4mL/L)

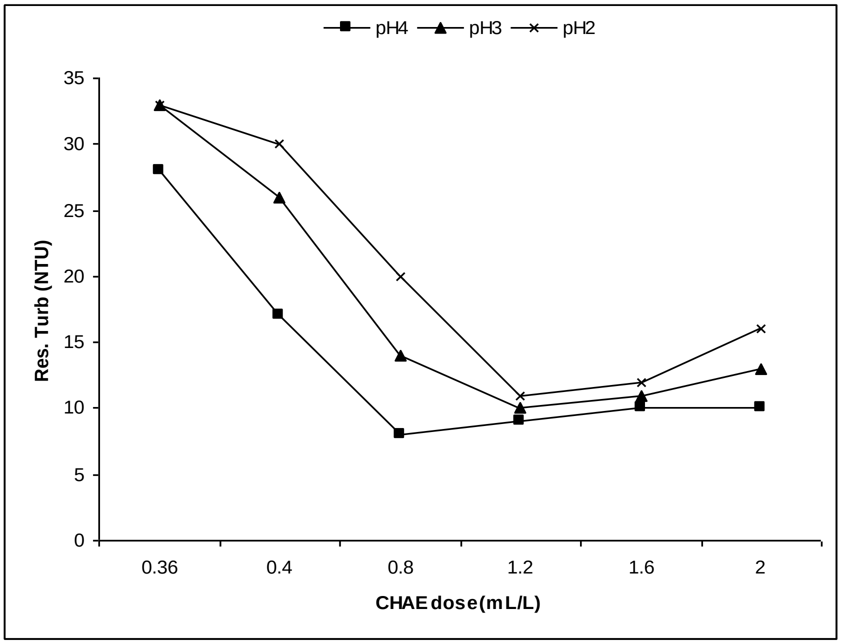

Fig. 2c. Effect of CHAE as coagulant aid at 50NTU (alum dose used = 1.0ml/L)

The importance of natural alkalinity of water, in the efficacy of coagulation and flocculation, as a method of water and wastewater treatment is a fact that has been recognized in the water industry. This is because at pH levels below 5.0, the OH^- is insufficient to precipitate Al^{3+} completely so that Al $(OH)^{2+}$ and Al $(OH)^{+}_{2}$ occur. Ademoroti, (1996) surmised that the residual alkalinity serves to buffer the systems at pH levels above 5.0 for Al^{3+} and above 4.0 for Fe^{3+} to ensure complete precipitation of the coagulation ions. Packham, (1965) surmised that, in many cases, optimal removal of particles from water is achieved under conditions of rapid hydroxide precipitation. In the case of aluminum coagulants, optimum pH conditions are close to the point of minimum solubility. Although precise mechanisms are still not fully understood, it is clear that impurity particles are enmeshed in the growing precipitate and hence can be removed from water by sedimentation. This process has become known as sweep flocculation, since particles are "swept out" of water by an amorphous hydroxide precipitate. Sweep flocculation generally improves particle removal compared to particle destabilization by charge neutralization alone. At least part of the reason is the greatly improved rate of aggregation, owing to the increased solids concentration. Hydroxide precipitates tend to have a rather open structure, so that even a small mass can give a large effective volume concentration and hence a high probability of capturing other particles. It is also possible that binding of particles by precipitated hydroxide may give stronger aggregates (Gregory, and Duan, 2001).

Beer and Gibbs (1975) pointed out that iron (III) chloride added to a slightly alkaline effluent dissociates into iron (III) hydroxide ions and chloride ions. The iron (III) hydroxide ion having a positive charge attracts the colloidal particles and form loose floc. On the addition of a suspension of slaked lime the more alkaline conditions cause the loose floc to form into dense flocs which settle out rapidly. If this scenario is applied to the application of CHAE, which is alkaline (pH=10.06) and predominantly, KOH, the mechanism of the changes, occasioned by the addition of the CHAE could be represented thus.

$Al_2(SO_4)_3 + 6H_2O$ === $2Al(OH)_3 . 2H_3^+ + 3(SO_4)^{2-}$
$2Al(OH)_3 . 2H_3^+$ + colloidal particle == loose floc
$2Al(OH)_3 . 2H_3^+ + 6KOH$ === $2Al(OH)_3 + 6H_2O + 6K^+$
$Al(OH)_3$ + colloidal particle === dense floc

3.5 Effect of using CHAE on the Treated Water pH

The pH of the different treated waters was determined and a comparison was made between the pH of the treated water, using alum alone for the treatment of water of different turbidities and when the CHAE was used as coagulant aid with alum. It was noted that with alum alone, the pH of the treated water was lower than the initial pH of the turbid water. This same trend was observed in all the studies carried out using alum alone (i.e. water of different turbidities and pH's). When alum was used with the coagulant aid (i.e. CHAE), the pH values of the treated waters were higher than the respective initial pHs. The observed pH elevation increased with increase in CHAE dosage. The dissolution of alum in water furnishes the aqua medium with H^+, which depresses the pH of the medium. Owing to the paucity of OH^- ion in a low alkalinity water, the neutralization of the H^+ ion produced is hindered hence acidity prevails. When alum is used with the CHAE, the CHAE used acts as a reservoir of OH^- ions, thereby reducing the effect of the H^+ ion, generated by the dissolution of alum, and the acidity effect is suppressed. This account for the observed pH elevation, when alum was used with the CHAE. The changes in the pH of the treated water at different alum dosages and alum and coagulant aid (CHAE) dosages were correlated. This was achieved by plotting the change in pH i.e. $\Delta pH = pH_f - pH_i$ versus alum and CHAE dosages. A linear graph was obtained with high correlation coefficients (Fig. 3a and b and Table 2).

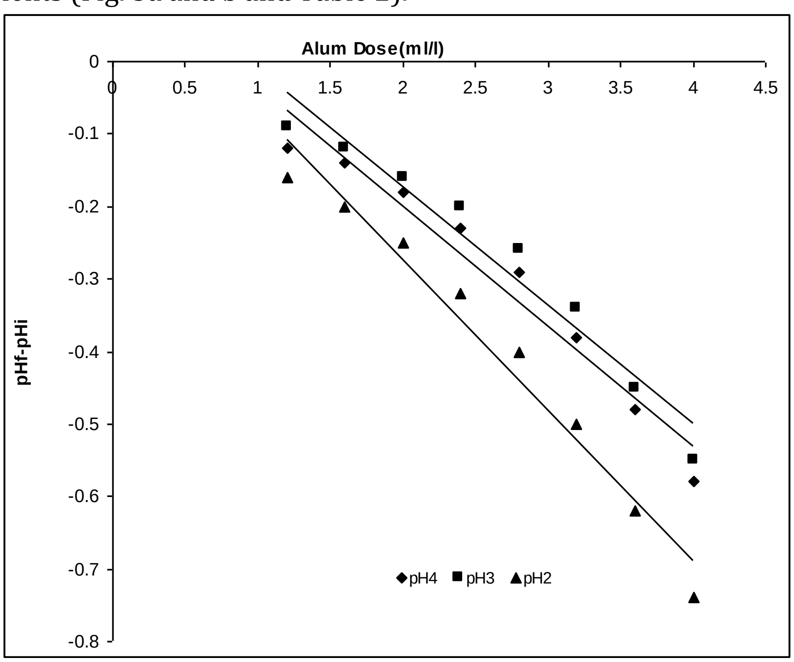

Fig. 3a. Linear correlation of $\Delta pH = pH_f - pH_i$ versus alum dosage

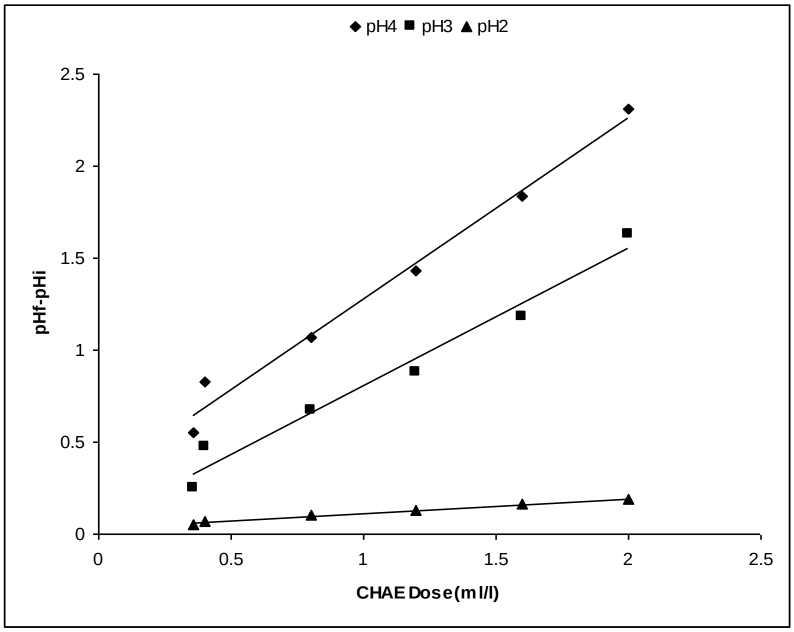

Fig. 3b. Linear correlation of $\Delta pH = pH_f - pH_i$ versus CHAE dosage

Table 2 Linear correlation values of the change in pH ($\Delta pH = pH_f - pH_i$) versus alum and CHAE dosages

Initial pH	CHAE	Alum
pH4	0.9837	0.9524
pH3	0.9714	0.9489
pH2	0.9877	0.9679

3.6 Effect of using CHAE on the Flocculation Kinetics

The time- concentration profile of the coagulation process (Figure 4), using alum alone and alum and CHAE as coagulant aid was determined to evaluate the detention/ residence time of water to be treated in a coagulation/flocculation basin in a water treatment plant. The effect of flocculation time on the residual turbidities of the treated water was studied, at the optimum dosage of alum and alum/ CHAE combination ratio, initial turbidity of 300NTU and pH 4, 3, 2. The data obtained (Figure 5) were fitted to the kinetic equation proposed by Pan et al., (2006) to obtain the flocculation rate constant, k, and removal rates, R_t at different pHs.

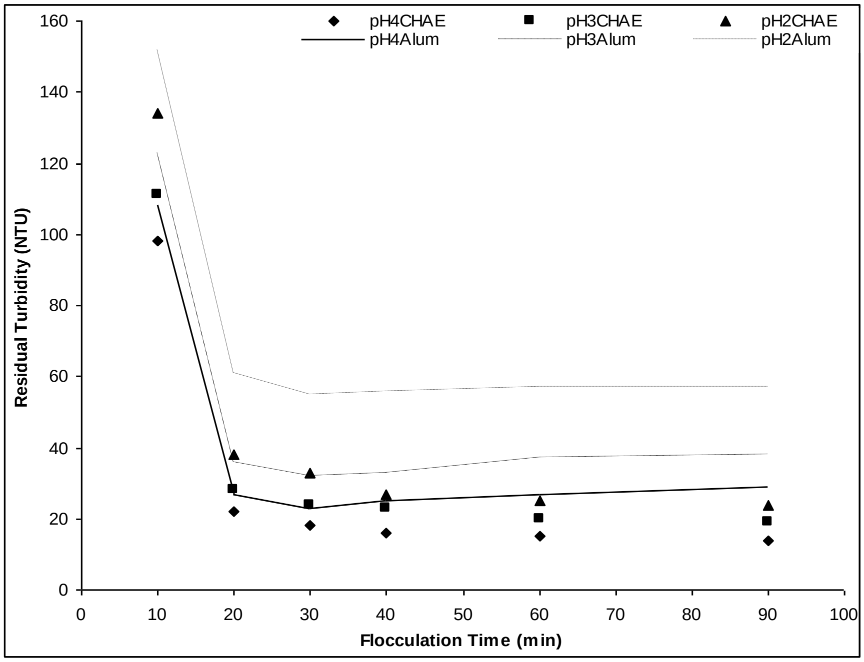

Fig. 4. Effect of flocculation time on residual turbidity at 300NTU

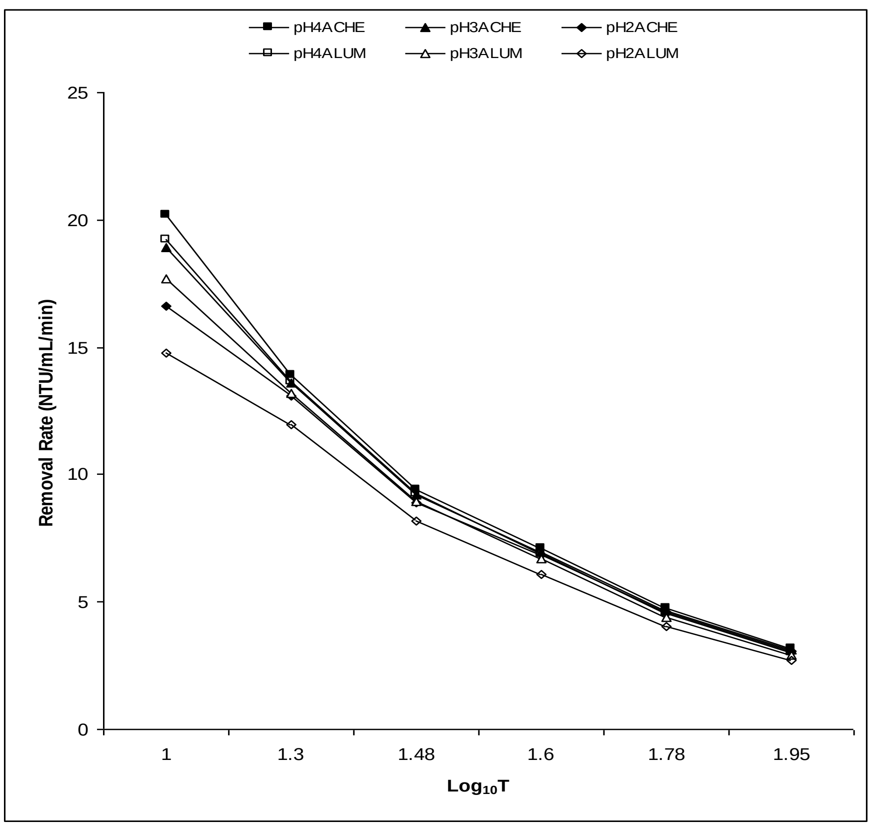

Fig. 5. Turbidity Removal Rates

The residual turbidities of the treated water reduced, with time, until after 30 min when a minimal increase in the value of residual turbidity was noticed with the use of alum alone but this increase in value of the residual turbidity was not observed with the use of CHAE as coagulant aid, instead a continuous reduction in the residual turbidity was noted. Sengil, (1995) ascribed the increase in the residual turbidity after the optimum time to the possibility of redispersion and restabilisation of flocs at higher flocculation time.

The flocculation kinetic equation, proposed by Pan et al. (1999), used, is presented below:

$$Q_t = Q_0 \, [1- \exp (kt^{1/2})]$$

The removal rate, R_t (NTU/mL/min) can therefore be described as follow:

$$R_t = \frac{dQt}{dt} = -0.5Q_0kt^{-1/2}\exp (kt^{1/2})$$

where: Q_t (NTU/mL/min) is the amount of turbidity removed at time, t, Q_0 is the initial turbidity (NTU), k, is the flocculation rate constant.

The kinetic evaluation showed that the flocculation rate constant, k, increased with increase in pH and varied between 2.675 and 3.146 for alum alone and 2.5351 and 3.028 for CHAE/alum combination, as the pH increases from 2 to 4. The values of the removal rate, R_t,, obtained with the use of CHAE as coagulant aid, at all the studied pH values were higher than that of the use of alum alone and these values also varied with time. At the inception (i.e. the first 10min) of the flocculation process, R_t, value ranged between 16.6NTU/mL/min and 20.2NTU/mL/min for the use of CHAE as coagulant aid while a range of 14.8NTU/mL/min and 19.2NTU/mL/min was obtained for the use of alum alone. The optimum removal rate reduced significantly and approached zero with time

3.7 Effect of using CHAE on the Sludge Volume

Large sludge volume generation is one of the limitations of the use of alum in water treatment hence the sludge volume index (SVI) was used to determine the effect of the use of CHAE as coagulant aid in the process sludge generation. SVI was measured over time for the two modes of treatment processes and the results obtained are presented in Fig. 6. An overview of the results obtained from the two processes showed that the SVI of the sludge produced from the use of CHAE as coagulant aid was lower than the SVI of the sludge produced from the alum alone for the entire period of study. The SVI of the sludge from the use of CHAE was below 80mL/g after the first 10min while that of alum alone was above 100mL/g. At the time considered as the optimum coagulation time, (90min), the SVI of the CHAE was below 20mL/g while that of Alum was above 60mL/g. Premised on the assumption of Gray,(1999) a good sludge should have an SVI less than 80mg/g and a very good one around 50mg/g. An SVI greater than 120 mg/g indicates poor settling characteristics. It could be taken that the settleability and volume of the sludge got from the use of CHAE was better than that of only alum.

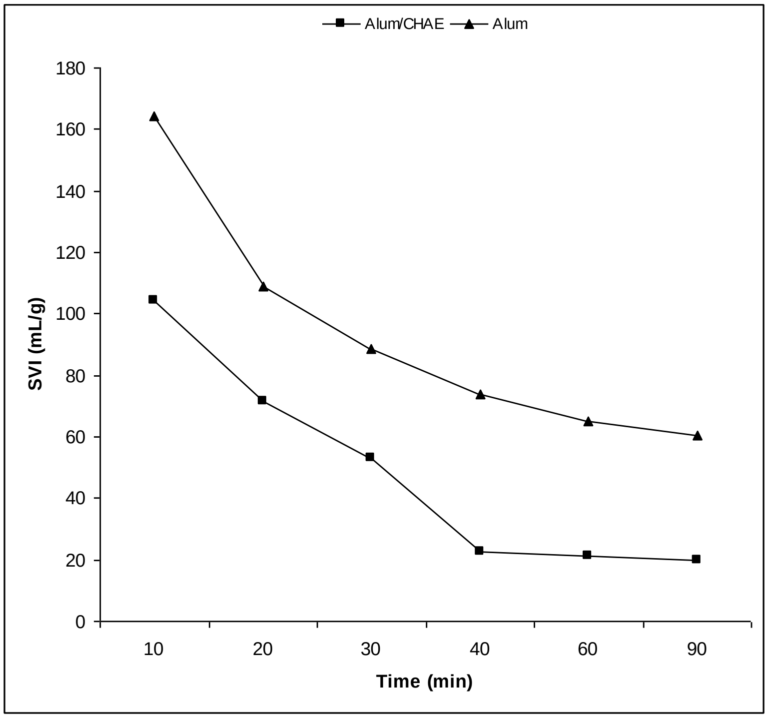

Fig. 6. Determination of sludge volume index

3.8 Simple Economic Evaluation

In the developing world, the use of alum as coagulant for water treatment is the standard practice because of the simplicity of the process. In effect, tonnes of alums are imported, in most developing countries, for this purpose from the developed world. Considering the high cost and other economic needs these countries have to grapple with adequate investment in this salient item of water purification is being jettisoned. Contending with the ecotoxicological effect of the use of alum is also an issue being relegated to the background because of lack of adequate data and mechanisms for monitoring this effect. CHAE, obtained from the husk of cacao, could be got from the cacao processing mills at no cost. It's an abundant waste material that has got no use at present, in most countries. However, the handling charges for the collection, transportation and extraction shall be the only cost to be incurred if its use is to be explored. Despite this, the total cost of CHAE will be extremely low in comparison with alum cost. If this resource could be explored as a coagulant aid in alum coagulation it has the potential of reducing the cost of alum by 50% for any volume of water treated. In addition savings could be made from the use of lime, for pH correction of the treated water. The task of processing and handling of sludge would also be reduced since a lower sludge volume can be better handled.

4. Conclusion

The potential of CHAE, as coagulant aid to alum, to improve the water treatment potential and reduce some of the dangers associated with the use of alum was exhibited by the higher percentage turbidity removal and improved characteristics of the treated water and the sludge obtained from the process. Greater turbidity removal was achieved with the use of half the optimum dose, obtained with the use of alum alone, when combined with CHAE as coagulant aid which would eventually reduce the cost of water treatment. The pH depression, usually experienced with the use of alum alone, was not observed when the CHAE was used as coagulant aid which made the additional cost of pH correction evitable. The problem of redispersion and restabilisation was suppressed with the use of CHAE as coagulant aid with alum. A reduction in the sludge volume generation was also achieved via the use of CHAE as coagulant aid.

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