Evaluation of Plantain Peelings Ash Extract as Coagulant Aid in the Coagulation of Colloidal Particles in Low pH Aqua System

Nurudeen A. Oladoja* and Yekini D. Aliu

Department of Chemistry, Adekunle Ajasin University, Akungba-Akoko, Nigeria

The use of plantain peelings ash extract (PPAE) as a coagulant aid in a low pH water was evaluated in the present studies. Plantain peelings were collected, washed, dried, and ashed in a furnace. The ash was extracted using deionized water, and the chemical composition was examined using an atomic absorption spectrophotometer. Synthetic turbid water of varying turbidities (50, 100, 300 NTU) and varying pHs (2, 3, 4) were prepared by clay dispersion in deionized water. The optimum alum dosages for the coagulation of colloidal particles in different turbid waters of varying pHs were determined by method of continuous variation using the jar test procedure. The residual turbidities of the treated waters were determined, and the alum doses that gave the minimum residual turbidities were taken as the optimum dosage for the removal of colloidal particles. The use of PPAE as a coagulant aid with alum showed an improvement in the value of residual turbidities of the treated waters. Results obtained from the different studies showed that treated waters of lower residual turbidities were obtained from synthetic waters of higher initial turbidities and pHs. The pH of the treated water decreased with an increase in alum dosage, whereas an increase in the pH value was observed with the addition of PPAE as a coagulant aid. High correlation coefficient values ($r^2$) were obtained when the changes in pH (i.e., $\Delta$PH = pHf –pHi) of the treated waters were correlated with alum and PPAE additions, and mathematical relationships were derived from the linear graph. Studies on the effect of flocculation time on residual turbidity showed that an optimum flocculation time of 30 minutes was attained, when alum was used alone, before redistribution and redispersion of the flocs was noticed. This phenomenon did not occur when PPAE was used as a coagulant aid.

Key words: plantain peel extract, ash, turbidity, alum, coagulant

Introduction

A large number of human settlements have developed along watercourses. The demand on these watercourses as a source of potable water and a means of disposing the waste generated by the community has greatly depleted the natural quality that such splendid water resources possessed. The indispensable and foremost position of water in man's daily operations has left him with no option other than to recycle such waters for reuse. This has culminated in the development of varying sophisticated water and wastewater treatment processes to cater for his water needs (Oladoja 2003).

Coagulation-flocculation is one of the simplest and most cost effective unit operations in the treatment of water and wastewater. This process, which is operational in most treatment plants, usually entails the use of a coagulant for the removal of dissolved and suspended colloidal particles from the system. In performing this operation, the reaction conditions are optimized for optimum process performance. The efficiency of the coagulation-flocculation process varies based on the physical and chemical characteristics of the water and the operating conditions. Aluminum salts are the chemicals most commonly used together with synthetic polymers (Diaz et al. 1999). However, different studies have discussed several serious drawbacks of using the alum salts. For example, Alzheimer's disease and other related problems have been associated with residual aluminum in treated waters (Pan et al. 1999; Schintu et al. 2000; Divakaran and Pillai 2001). Synthetic organic polymers have been used as effective coagulant aids in drinking water purification systems (Bratby 1980). However, organic polymers have potential limitations. Polymer formulations contain contaminants (such as residual monomers and other reactant and reaction by-products) from the manufacturing process that could potentially negatively impact human health. Polymers and product contaminants can react with other chemicals added to the water treatment process to form undesirable secondary products (Kawamura 1991; Bolto 1995; Lee et al. 1998; Ozaric and Sengil 2003a). Consequent upon this, the need to develop coagulant and coagulant aids from natural sources is a necessity.

Coagulant aids are used in coagulation-flocculation operations, mainly to improve the efficiency of the primary coagulant and reduce costs. The choice of a material as a coagulant aid is premised on the particular physical or chemical property of the colloidal particulates or the water on which the operation is to be performed. In recent time, a surfeit of naturally derived substances have been reported as coagulant aids in water and wastewater treatment. Aqueous extracts of the seed of *Moringa oleifera* has been investigated as a coagulant...
aid in water and wastewater treatment (Ndabigengesere 1995, Ndabigengesere et al. 1995; Ndabigengesere and Narasiah 1998). Other materials of plant origin that have been studied include tannin (Ozacak and Sengil 2000, 2002, 2003a, 2003b, 2003c); extracts of okra and nimali seeds (Al-Samawi and Shokralla 1996); extracts of Prosopis julifora and Cactus latifaria (Diaz et al. 1999); and chitosan and modified chitosan biopolymers (Pan et al. 1999; Ashmore and Hearn 2000; Huang et al. 2000; Divakaran and Pillai 2001; Bratskaya et al. 2002; Strand et al. 2003; Roussy et al. 2005).

In the treatment of wastewater with low alkalinity (e.g., acid mine drainage), irrespective of the colloid concentration, the use of a primary coagulant alone has been found to be ineffective since the pH of the medium will be too low to effect rapid flocculation of colloidal particles. Addition of slaked lime (CaOH) as a coagulant aid furnishes necessary alkalinity which provides the much needed effect. Lime is an undesirable coagulant aid because of the problems associated with the sludge produced from its use (i.e., high sludge production and handling difficulties). Its optimum dosing (pH 11) is also undesirable for use, prior to or during biological treatment, and would require a very high dosage if wastewater with a low pH is encountered. Owing to these facts and the need to improve on the economy of water and wastewater treatment operations, the present studies examined the use of the water extracts of plantain peelings ash as a coagulant aid in the treatment of water of low pH values (e.g., acid mine drainage, sulphuric acid plant effluent).

The plantain peel ash extracts (PPAE) come from the peelings of the plantain fruit. The plantain, also known as cooking banana, is classified as Musa paradisiaca. Banana is a common name for any of a genus of tropical, tree-like herbs, and their fruits. Bananas make up the genus Musa of the family Musaceae. Species of the genus are native to Southeast Asia, but are now grown extensively in all tropical countries for their fruits, fiber, or foliage. The banana is a large, herbaceous plant with a perennial root or rhizome from which the plant is perpetuated by sprouts or suckers. The fruit vary in length from about 10 to 30 cm. The fruit of the plantain is larger, coarser, and less sweet than the banana that is generally eaten raw. The edible part of the banana contains, on the average, 75% water, 26% carbohydrate, and about 1% each of fat, protein, fiber, and ash. Other parts of the plant abound in fiber which can be used in the manufacture of paper and cordage. Owing to the rich concentration of alkali in the water extracts of plantain peelings ash, the making of soap from the ash-derived alkali is an age-old craft in most West African countries. In the present studies, water extracts from plantain peelings ash were examined for use as a coagulant aid in the coagulation of colloidal particles in water with low alkalinity.

### Materials and Methods

#### Extraction of Plantain Peelings Ash

Plantain peelings were obtained from a commercial farm in Nigeria. They were dried in the oven at 103 to 105°C. The dried peelings were placed in a furnace and heated at 550 to 600°C to obtain the plantain peelings ash. The ashed sample was homogenized and sieved to remove large particle size fractions. Plantain peelings ash (150 g) was placed in 2.5 L of deionized water and kept at 60°C in a thermostated water bath for 8 h. Subsequently, the slurry was filtered to obtain the extract. The molarity of the PPAE was determined by titration against 0.1 M HCl using a phenolphthalein indicator. Metallic ion content of the extracts was determined using an atomic absorption spectrophotometer (AAS).

#### Synthetic Turbid Water

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

#### Alum Solution

An accurately weighed quantity of alum $\text{Al}_2\left(\text{SO}_4\right)_3\cdot18\text{H}_2\text{O}$ (Merck) was dissolved in distilled-deionized water to obtain a final alum concentration of 0.1 g of alum per mL. A fresh alum solution was prepared daily for reliability of results.

#### Jar Test Experiment

The different studies, concerning the coagulation and flocculation of the synthetic turbid water, were conducted using the jar test method. The optimum alum dosages for the coagulation of different turbid waters (50, 100, and 300 NTU) at different pHs (2, 3, and 4) was determined. The ability of PPAE to act as a coagulant aid in the treatment of water with low alkalinity was also assessed. Each experiment was conducted in duplicate and the results were reproducible within values of 0.1 to 0.5 NTU. The experiment was conducted in a system containing six rectangular pales (75 x 25 cm). A typical experiment involved the addition of the coagulants to turbid water (500 mL) of a particular pH. This was followed by rapid mixing of the mixture (i.e., coagulant plus turbid water) for 2 minutes at 200 rpm, and slow stirring for 20 minutes at 45 rpm. The mixture was allowed to settle and samples were withdrawn from a 3-cm depth after 20 minutes for turbidity and pH determinations.
effects of flocculation time on the residual turbidities of the different turbid waters at different pHs were studied at the optimum dosage of alum and alum/PPAE combination ratio.

Results and Discussion

PPAE Composition

The physicochemical characteristics of the PPAE are presented in Table 1. The alkaline nature of the water extracts of the plantain peelings could be seen in the pH value of the extract (11.08). The molarity of the extract, determined by the titration of the extracts against 0.1 M HCl, using a phenolphthalein indicator, was 0.654. The turbidity of the water extract, determined with the aid of a turbidimeter, was 6.0 NTU. The results of the AAS analysis revealed that the principal metallic ions were potassium (87.32%) and sodium (11.08%). Other metallic ions, found within the detectable limits of the AAS, were present in relatively small quantities.

Clay Characteristics

An X-ray diffractometer (Diagno 2100*E) was used for the clay mineralogical analysis. A copper anticathode (\(\lambda = 1.54\AA\)) was used. XSPEX version 5.41 software was used in the interpretation of the diffractogram. The interpretation of the diffractogram obtained from the X-ray diffraction analysis revealed the presence of the following clay minerals: kaolinite (27.68%); smectite (7.55%); illite (16.43%); mixed layer (i.e., smectite/illite mixed layer) (8.48%); and quartz (39.86%). Geochemical analysis of the different clay samples was performed using AAS after the clay samples were digested in a polypropylene bottle using a mixture of HF, HCl, and HClO\(_4\). Ten major elements were determined. The geochemical analysis showed the abundance of the presence of SiO\(_2\) (50.11%), Al\(_2\)O\(_3\) (17.00), and structural water (H\(_2\)O\(^+\)) (15.01%). This revealed the hydrated

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>K(_2)O</td>
<td>87.32%</td>
</tr>
<tr>
<td>Na(_2)O</td>
<td>11.08%</td>
</tr>
<tr>
<td>CaO</td>
<td>1.35%</td>
</tr>
<tr>
<td>CrO</td>
<td>0.08%</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.01%</td>
</tr>
<tr>
<td>Fe(_2)O(_3)</td>
<td>0.06%</td>
</tr>
<tr>
<td>PbO</td>
<td>0.04%</td>
</tr>
<tr>
<td>NaO</td>
<td>0.06%</td>
</tr>
<tr>
<td>pH</td>
<td>11.08</td>
</tr>
<tr>
<td>Molarity</td>
<td>0.65 M</td>
</tr>
<tr>
<td>Turbidity</td>
<td>6.0 NTU</td>
</tr>
</tbody>
</table>

Fig. 1. Determination of optimum alum dose at (a) 300 NTU, (b) 100 NTU, and (c) 50 NTU.
alumino-silicate nature of this material. The percentage oxide compositions of the other elements present was:

Fe₂O₃ (1.42%); MgO (78%); CaO (6.01%); Na₂O (1.61%); K₂O (1.02%); TiO₂ (0.21%); MnO (0.001%); and P₂O₅ (0.01%).

**Optimum Alum Dose Determinations**

The optimum alum doses, which are the smallest doses giving the best turbidity removal, were determined for each of the turbid waters (50, 100, and 300 NTU) at different pHs (2, 3, and 4). The experiments were conducted in a jar test apparatus. Figure 1 shows the results of the different experimental runs. The turbidities of the different turbid waters reduced with increasing alum dosages. The reduction in the turbidity values continued until a minimum turbidity value was obtained, thereafter an increase in the turbidity value was observed. The smallest doses that gave optimum turbidity removal for the different turbid waters varied with the initial turbidity of the water. The higher the initial turbidity, the higher the value of the optimum alum dose used (3.2 mL/L for 300 NTU, 2.8 mL/L for 100 NTU, and 2.0 mL/L for 50 NTU). The residual turbidities, at lower initial turbidities, were higher than when water of higher turbidity of identical pH was used in the experimental runs.

The observed difference in the value of the percentage turbidity removal in the different turbid waters could be ascribed to the different mechanisms of coagulation, as proposed by Ozacar and Sengil (2002). At higher turbidities, the predominant mechanism for coagulation of colloidal particles was “sweep coagulation.” The large quantity of Al(OH)₃ precipitate was capable of sweeping the fine colloidal particles from the water. The Al(OH)₃ adsorbed on the surface of the particles and reduced the negative charge with its slightly positive charge. When relatively low turbid water was used (i.e., 50 and 100 NTU), the effectiveness of this coagulation may not have been as high as when water of high turbidity was used.

The results obtained, when the effect of initial pH of the turbid water was taken into consideration, showed that the values of the optimum alum dose were similar, but the residual turbidity values varied with the initial solution pH. Synthetic turbid water 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 important factors that is given higher consideration in the use of coagulation-floculation in the water industry. This could be understood from the reported speciation of alum in water. Alum dissociates in water to give Al³⁺, SO₄⁻² and various alum complexes such as Al(OH)²⁺, Al(OH)₃⁺, and Al(OH)₄⁻, depending on the pH of the medium. The various positively charged species that are formed may combine with negatively charged colloids to neutralize part of the charge on the colloid particles (Ademoroti 1996). 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 hydrosolysis species that is predominant in the aqueous medium. Lower pH favours the species with higher positive charge on them. At pH below 5.0, the OH is insufficient to precipitate Al³⁺ completely, so that [Al(OH)³⁺] and Al(OH)⁴⁻ occur. The positively charged Al attracts the colloidal particles and forms loose flocs which are not dense enough for easy macrofloc 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⁺ ions is much faster than any metallic ion in solution. The authors were of the opinion that the extremely fast ionic mobility of the H⁺ ions, cum its abundance at the operational pHs in the present studies (i.e., low pH), could be a source of interference in the potency of the positively charged alum species in charge neutralization, which could be the domineering mechanism, of the negatively charged colloidal particles.

**Studies on the Use of PPAE as a Coagulant Aid**

Metal salt coagulants react with the alkalinity in water to produce insoluble metal hydroxide precipitates that enmesh the colloidal particles in water and adsorb other materials including dissolved organic matter present (Gray 1999). Where the natural alkalinity of the water is insufficient, lime in the form of calcium hydroxide is added to aid the formation of flocs. In order to assess the ability of PPAE to function as a coagulant aid in the treatment of low alkalinity water, half of the quantities of the optimum alum doses obtained from the previous studies (see section above: Optimum Alum Dose Determinations) were used with varying quantities (in millilitres) of the PPAE (0.15, 0.20, 0.25, 0.50, 1.00, and 1.20). The results presented in Fig. 2 show the effect of the addition of PPAE, as a coagulant aid, 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 PPAE than when alum was used alone. The water with the initial highest turbidity value (i.e., 300 NTU) produced water with the highest value of percentage turbidity removal (93.33% at pH 4; Table 2). This could be ascribed to the high colloid concentration in the medium, which promotes interparticle bridging and macrofloc formation. At relatively low colloid concentrations (i.e., 100 and 50 NTU), 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.

The importance of the natural alkalinity of water to be treated, in the efficacy of coagulation-floculation operations, is a fact that has been recognized in the water industry. This is because at pH levels below 5.0, OH⁻ is insufficient to precipitate Al³⁺ completely so that
Plantain Peeling Ash Extract as Coagulant Aid

Al(OH)\(_2^+\) and Al(OH)\(_3^+\) 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.

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 colloidal particles and forms loose flocs. On the addition of a suspension of slaked lime, the more alkaline conditions cause the loose flocs to form into dense flocs which settle out rapidly. If this scenario is applied to the application of PPAE, which is alkaline (pH=11.08) and predominantly KOH, the changes occasioned by the addition of the extract could be represented thus:

\[
\begin{align*}
\text{Al}_2(SO_4)_3 + 6H_2O & \rightarrow 2Al(OH)_3 + 3SO_4^{2-} \\
2Al(OH)_3 & \rightarrow 2Al(OH)_2 + 2H_2O + 3OH^- \\
2Al(OH)_2 + 2H_3O^+ + \text{colloidal particle} & \rightarrow \text{loose flocs} \\
2Al(OH)_3 + 6KOH & \rightarrow 2Al(OH)_2 + 6H_2O + 6K^+ \\
Al(OH)_3 + \text{colloidal particle} & \rightarrow \text{dense flocs}
\end{align*}
\]

Despite the observed improvement in percentage turbidity removal at 100 and 50 NTU when the PPAE was used, the percentage turbidity removal was relatively low when the results were compared with synthetic water of 300 NTU. The relatively low initial turbidities of the waters could inhibit the rapid formation of flocs as the rate of interparticle contact is too slow to utilize destabilization by charge neutralization.

In addition to the determination of the turbidity of the treated water, the pH value was also determined and the results obtained are presented in Fig. 3. The pH values of the treated water, when alum was used alone and when PPAE was used as a coagulant aid, were compared. It was noted that when alum was used 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 pHs). When alum was used with the coagulant aid (i.e., PPAE), the pH values of the treated waters were higher than the respective initial pHs. The observed pH elevation increased with an increase in PPAE 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

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**TABLE 2. Percentage (%) turbidity removal in the use of PPAE as coagulant aid with 0.5 optimum alum doses**

<table>
<thead>
<tr>
<th>PPAE dose (mL/L)</th>
<th>300 NTU</th>
<th>100 NTU</th>
<th>50 NTU</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH 4</td>
<td>pH 3</td>
<td>pH 2</td>
</tr>
<tr>
<td>0.15</td>
<td>78.33</td>
<td>76.67</td>
<td>64.33</td>
</tr>
<tr>
<td>0.20</td>
<td>84.00</td>
<td>80.33</td>
<td>73.33</td>
</tr>
<tr>
<td>0.25</td>
<td>90.00</td>
<td>86.67</td>
<td>78.67</td>
</tr>
<tr>
<td>0.50</td>
<td>93.33</td>
<td>91.67</td>
<td>86.67</td>
</tr>
<tr>
<td>1.00</td>
<td>84.00</td>
<td>84.67</td>
<td>89.33</td>
</tr>
<tr>
<td>1.20</td>
<td>80.33</td>
<td>83.33</td>
<td>77.67</td>
</tr>
</tbody>
</table>

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Fig. 2. Effect of PPAE as a coagulant aid at (a) 300 NTU, (b) 100 NTU, and (c) 50 NTU.
is used with the PPAE, the PPAE 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 accounts for the observed pH elevation when alum was used with the PPAE.

The changes in the pH (Δ pH) of the treated water at different alum dosages, and alum and coagulant aid (PPAE) dosages, were regressed (Fig. 3a and b) to derive a mathematical relationship with high coefficients of determination (r² > 0.940). Therefore, Δ pH can be expressed as a function of alum and PPAE dosage at different pHs as follows:

**Alum:**
- pH4: \( \Delta \text{pH} = 0.1661A^{0.1318} \)
- pH3: \( \Delta \text{pH} = 0.1628A^{0.132} \)
- pH2: \( \Delta \text{pH} = 0.208A^{0.1421} \)

**PPAE:**
- pH4: \( \Delta \text{pH} = 2.9715P^{0.3773} \)
- pH3: \( \Delta \text{pH} = 1.4535P^{0.2206} \)
- pH2: \( \Delta \text{pH} = 0.6975P^{0.1264} \)

**Effect of Flocculation Time**

The time of macrofloc formation (flocculation time) is one of the operating parameters that is given great consideration in any water treatment plant that involves coagulation-flocculation operations. Consequent upon this, the effect of flocculation time on the residual turbidities of the treated water was studied at the optimum dosage of alum and alum/PPAE combination ratio. The flocculation time was varied between 10 and 90 minutes. The results obtained are presented in Fig. 4. When only alum was used, the residual turbidity of the treated water reduced, with time, until after 30 minutes when
a minimal increase in the value of residual turbidity was noticed. Nozaki et al. (1993), Sengil (1995), and Ozacar and Sengil (2002) have reported an optimum flocculation time of 30 minutes when natural polyelectrolyte, alunite, and tannin were used, respectively, as a coagulant and coagulant aid in water treatment. Sengil (1995) ascribed the increase in the residual turbidity after the optimum time to the possibility of redispersion and restabilization of flocs at higher flocculation time. This problem of redispersion and restabilization did not arise when the PPAE was used as a coagulant aid with alum; instead, a reduction in the value of the residual turbidities was recorded over the entire period of study (90 minutes).

**Conclusion**

The efficacy of PPAE as a coagulant aid in a low pH aqua system was examined. Water extract of the plantain peeling ash was prepared, and the physicochemical characteristics were studied. The results of the characterization showed that the PPAE was alkaline (pH 11.08) and the molarity was 0.65 M. The principal metallic ions in the extract were potassium (87.32%) and sodium (11.087%). The ability of PPAE to function as a coagulant aid was shown by the higher percentage of turbidity removal observed when waters of same characteristics (i.e., initial turbidity concentration and initial pH) were subjected to the same treatment procedure. The percentage turbidity removal varied with the initial pH and turbidity. The higher the initial turbidity of the synthetic water, the higher the percentage turbidity removal observed. The lower the pH, the higher the residual turbidity of the treated water observed.

When the pH values of the treated waters were compared, a diminution in the value of the initial pH was observed in the water treated with alum alone. The use of PPAE as a coagulant aid produced waters with pHs higher than the initial pHs. The observed changes in pH (i.e., ΔpH = pH – pPH) was plotted against the alum and PPAE dosages, and the results obtained were correlated and high correlation coefficients were recorded.

The effect of flocculation time on the residual turbidities of the treated waters revealed that an optimum residual turbidity was attained at 30 minutes when alum was used alone. When the PPAE was used as a coagulant aid, the values of the residual turbidities reduced with an increase in flocculation time.

**References**


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