Flocculation of Kaolinite Clay using Natural Polymer.

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ABSTRACT

The flocculation of kaolinite using natural polymer was investigated between pH range of 3.5–10.71 using causticised cassava starch as the natural polymer. The sample was characterized using X-ray Diffraction (XRD). Results revealed that the settling rates increased as a function of flocculant dosage up to a maximum settling rate before decreasing at high flocculant dosages. Settling rates produced by natural polymer decreased with increasing pH. The flocculant, displayed an initial increase in floc size up to the optimum dosage before decreasing with increasing flocculant dosages while the bed height decreased with increasing pH.

(Keywords: causticised cassava starch, kaolinite, settling rate, floc size, bed height)

INTRODUCTION

In many industrial waste tailings systems, kaolinite is a major component (Rey, 1989). Karadi et al., 2007 reported that flocculation can remove more than 80 percent of suspended solids in some industrial waste-treatment operations. Polymeric flocculants are added to tailings systems to enhance the settling rate of the suspended solids. For instance in coal mining operation, on removing the desired ores from a soil system, the kaolinite-rich waste tailings stream is passed into the feed-well of thickening vessels in the form of slurry.

Because of little electrostatic destabilization, kaolinite particles exists as aggregate which will flocculate together and settle into the thickening vessel upon the addition of flocculants under shear conditions. A lot of studies have been performed examining the performance of different flocculant types (Taylor, 2002; Nwafor, 1986); however there has been little focus on the use of natural polymer as flocculant.

Flocculant or Flocculating Agent

Reagents that are use to promote flocculation are called flocculants. They work by causing colloids and other suspended particles in liquid to aggregate, forming a floc. Flocculants are used to increase adhesion and consequently optimize the separation of the solid phase from the liquid phase in aqueous suspension.

Flocculants can either be inorganic or organic in their composition. Organic flocculants are either natural or synthetic water soluble polymers. Natural organic flocculants include water soluble starch, guar gum, etc.

Starch

Starch is a white, granular, organic chemical that is produced by all green plants. It is a soft, white, tasteless powder that is insoluble in cold water, alcohol, or other solvents (Britannica, 2008). The basic chemical formula of starch molecule is $(C_6H_{10}O_5)_n$. The molecular weight of starch ranges from 15,000 to 100,000g/mol. Starch is a polysaccharide (meaning “many sugars”), comprising glucose monomers joined in *α* 1,4 linkages. The simplest form of starch is the linear polymer amylose; amylopectin is the branched form.

Adsorption Mechanisms

The type of contact that does occur between the polymeric flocculant and the particle surface is described by this mechanism. Adsorption mechanisms are comprised of electrostatic and chemical interactions, hydrogen bonding, hydrophobic bonding, or a combination of these.

Flocculation Mechanism

The stability of a suspension depends on the number, size, and surface properties of the solid particles and on the dispersion medium. Flocculation can occur through these mechanisms-double layer compression, specific ion adsorption, polymer bridging (Hunter, 1995) and depletion flocculation. During flocculation process, many of these mechanisms may be occurring simultaneously.

Double Layer Compression

Double layer compression involves increasing the ionic strength of a system to decrease the thickness of the double layer (Atkins et al., 2006). Compression of the electrical double layer means that the particles can get close enough to another for the attractive van der Waals forces to dominate over the electrostatic repulsions, therefore rendering the suspension unstable.

Specific Ion Adsorption

The mechanism of specific ion adsorption applies when cations such as aluminum is bound chemically to the particles surface (e.g. by forming complexes with the surface atoms). As a result, the particle charge may be partially or completely neutralized, thereby reducing the component of electrostatic repulsive forces, hence flocculation is enhanced.

Flocculant Properties

Improved flocculating power can be seen with an increase in molecular weight (Clark et al., 1990). When a negatively charge flocculant is adsorbed on a negatively charged surface, a low adsorption capacity at the surface is observed because of electrostatic repulsion (Pradip et al., 1991).

Flocculant of a slight anionic nature actually help the flocculation and subsequent settling process. This behavior could be attributed to the fact that for polymer with low anionic charge, the ionisable groups on the polymer chain cause repulsion between them, hence extending the polymer into solution, promoting bridging between the particles.

Ionic Strength

Rapid settling rate and low bed height occurs when particles are aggregated by the addition of electrolyte before flocculant addition (Hogg, 1999).

Substrate surface area decreases with the formation of aggregates, hence less flocculant is required to produce the maximum settling rate.

Mixing

Settling behavior of a flocculated system is significantly influenced by the intensity and magnitude of agitation imparted to it (Keys and Hogg, 1978). It is understood that some degree of agitation is essential to optimize the particle-particle and particle-flocculant interactions to achieve optimum flocculation. But too much agitation is known to fragment flocs, causing poor flocculation and slow settling.

MATERIALS AND EXPERIMENTAL METHODS

Kaolinite Sample

The kaolinite clay use in this work was collected from Agbahara-Nsu, Ehime-Mbano Local Government, of Imo State. The clay lumps were crushed, ground, and sieved to obtain a 100% passing 75μm, executed at Institute for Erosion Studies, Federal University of Technology, Owerri.

Materials Preparation

The flocculant used in this work is natural polymer. Cassava starch $(C_6H_{10}O_5)n$ was extracted locally from cassava tuber, dried and processed into flocculant reagent by causticizing it with sodium hydroxide (NaOH) at ambient conditions at a ratio of 2:1 as recommended by Osborne, 1974.The caustic starch was then diluted to the required concentration with cold water. Osborne, suggested three methods of processing cassava into flocculant reagent, however, one of his suggestions was adopted in this work.

It was carried out in the Chemistry Laboratory of Federal University of Technology, Owerri.

Molecular Weight Determination

The molecular weight of cassava starch was determined at the chemistry laboratory of Federal University of Technology, Owerri, and using Analar grade of starch with a known molar mass.

General Reagents

Distilled water was used in all experiments. Other chemicals used in this experiment include: potassium chloride, hydrogen chloride, potassium dihydrogen citrate, acetic acid, sodium acetate, etc.

X-ray diffraction (XRD)

Mineralogical phase analysis/composition of Nsu clay mineral was done with Philip, PW 3710 mode diffractometer using CuKα radiation and a graphite monochromator (λ=1.5418 Å). X-ray patterns were collected on powdered samples in $\theta/2\theta$ mode with a starting analysis angle of 5deg. and a finishing analysis angle of 70deg, and a data interval of 0.01deg. This was carried out at Alfa Research Laboratory Lagos.

Settling Test

Settling rate of the kaolinite was measured using a 50ml measuring cylinder. Cylinder volumes greater than 50ml displayed no difference in the initial settling rate (Farrow et al., 1996).

Kaolinite samples was conditioned in 0.01MKCL in a beaker for 2 hours at the desired pH. A strip of graph paper was stuck along the length of the measuring cylinder and numbered in an increasing order from its bottom. After conditioning of the sample, a known mass of the kaolinite was poured into the measuring cylinder followed by the addition of a known volume of flocculant.

The cylinder was then covered and shaken for 8 times. Settling was taken to commence as the cylinder was placed upon the bench top and a stop watch was used to time the settling of the suspended solids. The height of fall in (cm) for each test under consideration-pH, was recorded against time in (sec) .

The linear regions of the settling curves (plots of height of fall in (cm) versus time in (sec)) display the initial settling region, where the individual aggregates are able to settle without hinderance of others. The settling rates were obtained by taking the slope of the linear regions of the settling curves.

- **Bed height, BH (%)-** Is the percent of the initial interface height prior to settling and it was used in calculating the final bed height. The final heights of the settled beds were obtained after 24 hours. Bed height (%) was calculated using the relation:

$$BH, (\%) = \frac{h_f}{h_i} \times 100 \tag{1}$$

Where hi and h_f are initial and final bed height respectively.

- **Floc size -** Stoke's equation was used in calculating floc size (Nyle, et al., 1999).

$$V_t = \frac{d^2 g(d_s - d_f)}{18\eta} \tag{2}$$

Where g=gravitational force (N/kg)
η=viscosity of water at 25˚C (K/m^3)
d_s=density of the solid particles,(kg/m^3)
df = density of the fluid (water)kg/m^3
V_t=terminal velocity of particle (settling rate)
d=particle diameter; floc size (µm)

RESULTS AND DISCUSSION

XRD

XRD pattern for the clay is presented in Figure 1. The pattern acquired proved that the clay is very ordered going by its narrow and intense diffraction peaks which is in tandem with suggestion made by Raftery, 2006. The clay is poorly crystalline. Using Braggs equation, (ʎ = 2dsin□), the first order spacing (001) of the XRD, yielded about 7.3Ǻ, which agreed with Grim, 1968, who reported that the first order spacing for poorly crystalline clay do occur around 10 degrees theta.

XRD Result

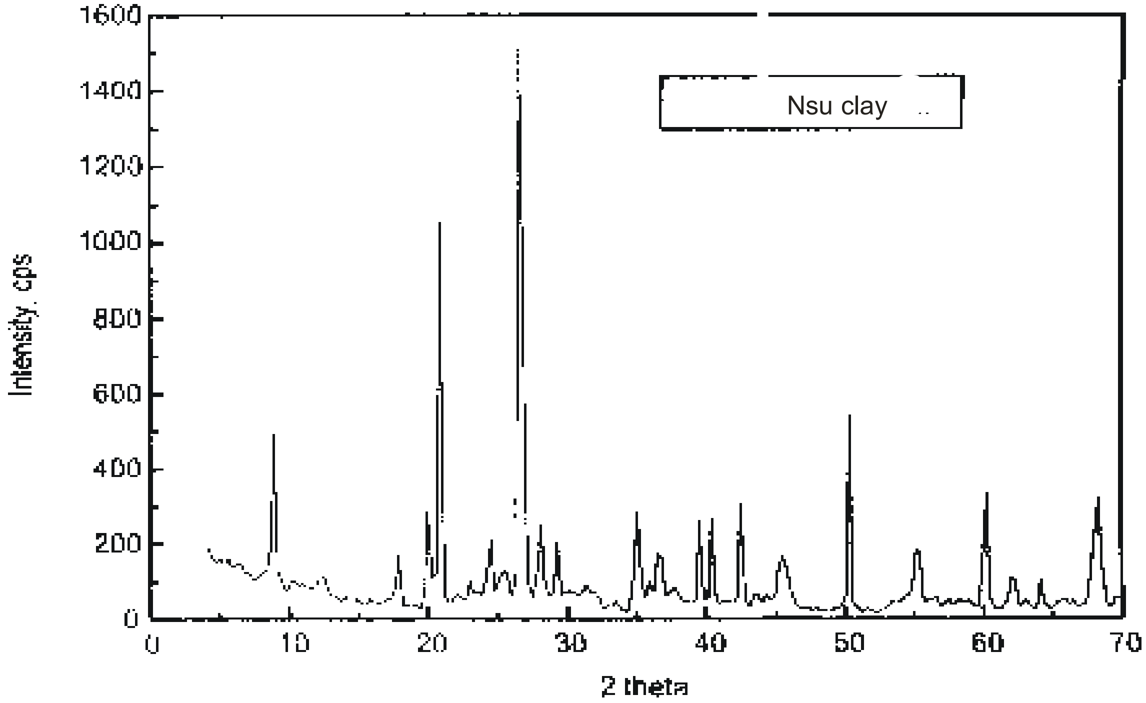

Figure 1: XRD Pattern of Nsu Clay.

A mineralogical composition as determined by XRD, showed that kaolinite is the major constituent (69%). Others include Haemitite (Fe_2O_3), Quartz (SiO_2), Calcite ($CaCO_3$), etc.

Molecular Weight Result

Natural polymer (cassava starch) = 39,000g/mol.

Effect of Flocculant Dosage

Settling rate as a function of flocculant dosage is displayed in Figure 2. The flocculant showed increasing kaolinite settling rate at low flocculant dosages prior to a settling rate decrease. Taylor, (2002), observed similar effect using synthetic polymer with Koilinite.

The magnitude of the settling rate is shown in Table 1. In the presence of flocculant, kaolinite showed an increase in the settling rate with increasing flocculant dosage until an optimum dosage is reached. Table 2 shows optimum dosage that produced the maximum settling rates.

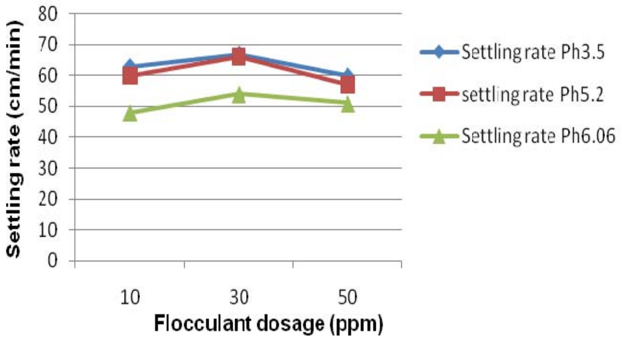

Figure 2: Settling Rate of Kaolinite as a Function of Flocculant Dosage.

After the optimum dosage has been reached, the settling rate decreased. It is understood that as polymer adsorption takes place, and thus flocculation occurs, there is continuous reduction in the available surface area which prevent further adsorption.

The decrease in the settling rates above the optimum flocculant dosages could be attributed to steric stabilization.

Table 1: Settling Rate with Natural Polymer (NP)*.

pH 3.5		**pH 5.2**		**pH 6.06**	
Dosage(ppm)	Settling Rate(cm/min)	Dosage(ppm)	Settling Rate(cm/min)	Dosage(ppm)	Settling Rate(cm/min)
10	63	10	60	10	48
30	67	30	66	30	54
50	60	50	57	50	51

****Natural Polymer***

Table 2: Optimum Dosage and Maximum Settling Rate with Natural Polymer.

Flocculant type: (NP)	**pH**	**Optimum dosage (ppm)**	**Maximum Settling rate (cm/min)**
NP	3.5	29.3	67
NP	5.2	30	66
NP	6.06	30	51

Beyond the optimum flocculant dosages, there is a reduction in the settling rate, as the polymer chains surrounding the particles cannot interpenetrate and tend to repel one another causing steric stabilization.

Influence of pH

Figure 3 displays the settling rate of kaolinite versus pH. The figure shows that the settling rate of kaolinite flocculated with natural polymer decreases with increasing pH. This could be as a result of increasing electrostatic repulsion which encourages low adsorption capacity at the surface, with pH 6.06 producing the slowest settling rate. Nwafor (1986), had made similar observation using caustic starch with coal effluent. However flocculation of kaolinite using natural polymer (causticised cassava starch) was not possible at higher pH values (alkaline pH) examined in this work. This may be due to its low molecular weight and its inability to bridge as many kaolinite aggregates as possible.

Floc Size

Floc size at pH 5.2 is presented in Table 3. Figure 4 shows floc size versus flocculant dosage at pH5.2.

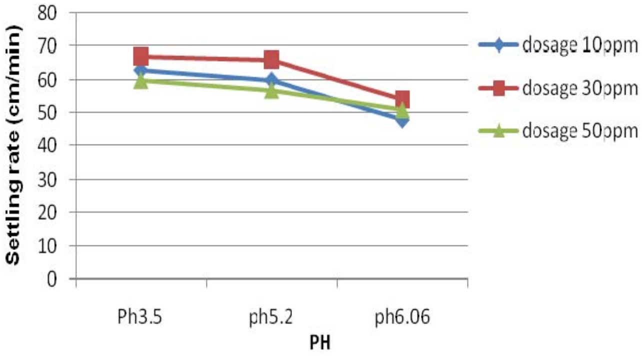

Figure 3: Settling Rate of Kaolinite as a Function of pH.

The flocculant displayed increase in the floc size up to the optimum dosage before it started to decrease with increasing dosage.

It was observed that floc size increased up to the optimum dosage, producing a rapid settling rate, associated with large floc size. Above the optimum flocculant dosage, the floc size was observed to decrease due to stabilization and compaction.

Table 3: Floc Size with Natural Polymer at pH 5.2.

Flocculant Dosage (ppm)	Settling Rate (cm/min)	Floc Size (µm)
10	60	99.5
30	66	104
50	57	97

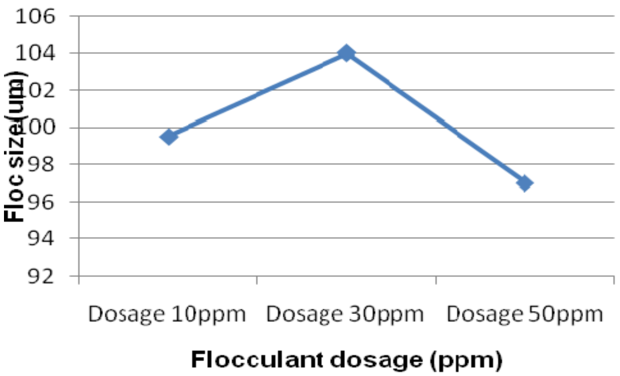

Figure 4: Floc Size as a Function of Flocculant Dosage, at pH 5.2.

Table 4: Showing the Final Bed Height (%) of Kaolinite (4%w/w) at different pH .

pH	Natural polymer Bed ht (%)
3.5	16.5
5.2	16
6.06	13

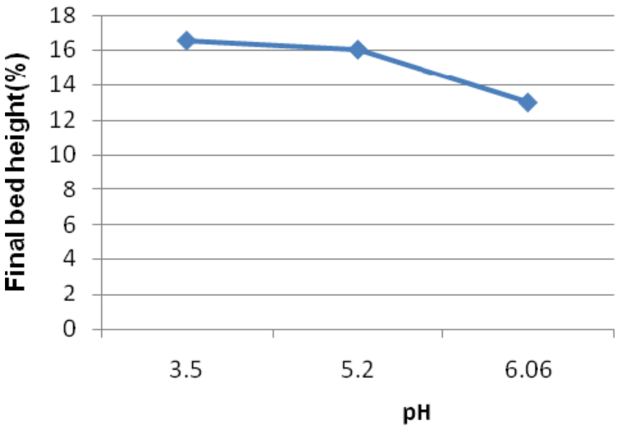

Figure 5: Final Bed height of Kaolinite versus pH.

Bed Height

The bed heights achieved from the settling test is shown in Table 4 and Figure 5 shows the plot of bed height as a function of pH. However, the figure showed that the kaolinite bed height (BH) decreased with increasing pH. This may be due to increased packing efficiency and particle orientation, an observation previously established by (Taylor, 2002; Michaels et al., 1962). Smaller flocs naturally, will pack more effectively therefore reducing the void volume in the bed. Observations made also revealed that the bed height is dictated mostly by the kaolinite pH-dependent structural properties.

CONCLUSION

The addition of the investigated flocculant to the kaolinite suspension forcefully increased the settling rate of the suspended solids. Causticised cassava starch is good as a flocculant at low pH; hence it had its maximum settling rate at pH 3.5 and at a dosage of 30ppm. From results obtained, it can be concluded that causticised cassava starch is not too sensitive to over dosage.

Therefore in developing countries with poor analytical instruments, this flocculant may be useful in practical conditions where control of flocculant dosage is not good enough.

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