Coagulation-Flocculation Performance Of Snail Shell Biomass For Waste Water Purification

J.U. Ani[1], M.C.Menkiti*[2], O.D. Onukwuli[2]

[1]Department of Pure and Industrial Chemistry, University of Nigeria, Nsukka.

[2]Department of Chemical Engineering, Nnamdi Azikiwe University, Awka, Nigeria.

*Corresponding author: M.C.Menkiti. E-mail : cmenkiti@yahoo.com

Abstract: Coagulation and flocculation treatment of fibre-cement effluent was studied in respect of pH and dosage variation at room temperature using snail shell biomass as a precursor to coagulant .Coagulation kinetics parameters such as order of reaction, α, and rate constant, K. .Coagulation performance was measured in nephelometric jar test while coagulant preparation was based on work reported by Fernandez-Kim. Maximum parameter values are recorded at K of 4.5 x 10^{-3} l/mg.min, α of 2 and total solid of 2028mg/l. Parameters obtained lie within acceptable range while it can be concluded that the coagulation performance of snail shell biomass is adequate.

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Introduction

Water is very essential for human survival and existence. Among man's major survival needs, water is next to air in hierarchy. It is therefore necessary that water conservation is given the proper attention it deserves.About 75% of the present world population live in the developing countries of planet earth. About 1.2 billion people still lack safe drinking water and more than 6 million children die from diarrhea in developing countries every year (Eman *et al*; 2009).Water is mainly sourced from rivers, aquifers and rainfall for both industrial and municipal uses.

Coagulation – flocculation followed by sedimentation, filtration and disinfection, often by chlorine, is used worldwide in the water treatment industry before distribution to consumers (Ndabigengesere *et al*;1995).Effluents that are generated as a result of industrial and municipal activities are normally disposed into the surroundings and also into the nearby river thus causing pollution. The pollution menace can reach some disturbing proportions as crops on the land; aquatic and human lives are in serious danger. Most of the rivers in the metropolis of the developing world are the end points of effluents from industries. Industrial effluents if not treated adequately and properly controlled could also pollute ground water. As a result, both boreholes and rivers generally have poor quality water in the affected areas leading to diseases such as cholera, bilharzias, and diarrhea.

Inorganic coagulants such as $A1(SO_4)_3$ $18H_2O$ and $Ca(OH)_2$ are widely used for the removal of raw water turbidity because they are cost effective and easy to handle. However, the sludge obtained from such treatment poses disposal problems due to its aluminum content and the residual aluminum concentration in treated water has raised public health concerns (Driscoll and Lettermon; 1995). It has been reported that extensive intake of alum causes Alzheimer's disease (Mclachlan;1995, Divakaran and Pillai,2001).

The search for a better alternative for conventional coagulants has become an important challenge in the water treatment process with the aim of minimizing the detrimental effects associated with the use of such coagulants. The use of coagulants of biological origin has become imperative. Some of the coagulants and flocculants of biological origin that have been used include chitosan (Ozacar and Sengli A,2002), tannins ((Ndabigengesere and Narasiah,1998).), aqueous extract of the seed of *Moringa oleifera* (Oladoja and Aliu, 2008), extracts of okra , nirmali seed (Roberts,1997) and snail shell , which is the subject of the study.

Snails belong to the phylum molluscs and to the class gastropods; this class includes the gastropods, slugs and snails. Snail shell is being suggested as a low cost material to remediate the turbidity of a fibre - cement plant effluent (FCE) in the present studies. The group of snails that is common in this part of the world belongs to the family of the achatinadae, also known as the achatina snails. The main constituent of the shell is calcium carbonate which are either of two crystalline forms calcite and aragonite. The remainder is organic matrixes which constitute a protein known as conchiolin that usually make up to 5% of the shell. The fine structure of molluscs shells has been studied by using various techniques including scanning electron microscope of broken surfaces. In each of them, blocks or stripe of calcium carbonate are separated by a thin layer of conchiolin.

Fibre - cement is commonly used in the construction of houses and commercial buildings for internal and external wall claddings and floor underlays. Fibre - cement is produced from four main raw materials – silica, cement, cellulose, paper and water. These materials are mixed together to form a slurry. The slurry is often filtered and fed into a press roller where it produces a layer of fibre – cement ranging from 4mm to 15mm in thickness. It then enters into a pressure vessel where it is processed for about 3 hours. The effluent from the productive process flows into a drainage that channels it into a nearby river.

In the present investigation, conditioning of snail shell was carried out with different additives prior to its use as a coagulant for the removal of colloids in a fibre-cement effluent. The optimum dosage of the snail shell was determined. The influence of p^H of the effluent on the coagulation process was studied. The results obtained could be used to estimate the performance of snail shell coagulant (SSC) in the treatment of fibre-cement effluent when compared with $Al_2 (SO_4)_3$. $18H_2O$ in the control experiments.

THEORY

Coagulant aggregation chemistry.

Calcium the main composition of snail shell when in solution dissociates into Ca^{2+} and various calcium complexes such as $Ca(OH)^{2+}$, the various positive species of which are formed may combine with negative charges leading to the formation of flocs:

$$Ca^{2+} + 2Colloid \longrightarrow \boxed{Ca\ (colloid)_2}$$

During coagulation, the colloidal materials will come together and become incorporated or adhere into the mass that can readily be precipitated. When alum is added to water it undergoes the reaction below. The alum reacts with bicarbonate to form aluminum hydroxide, a precipitate.

$$Al_2\ (SO_4)_3\ 18H_2O + 3Ca(HCO_3)_2 \longrightarrow \boxed{2Al(OH)_3 + 6CO_2 + 3CaSO_4 + 18H_2O}$$

The above equation can also be written as shown below which recognizes that calcium bicarbonate and calcium sulphate are soluble and do not necessarily exist as distinct molecules but only as ions.

$$Al_2(SO_4)_3 .\ 18H_2O + 3Ca^{+2} + 6HCO_3^- \longrightarrow \boxed{2Al(OH)_3 + Ca^{+2} + 3SO_4 + 18H_2O}$$

Alum reacts with the bicarbonate molecule. In the reaction above bicarbonate is shown associated with Ca^{+2} in order to preserve charge neutrality. For most water with P^H of 6 - 8 the bicarbonate is measured as alkalinity.The aluminium hydroxide adsorbs onto the colloids,aggregating into visible flocs that settle under gravity.

Coagulation kinetics

The time evolution of the clusters –size distribution for colloidal particles is usually described by the smoluchowski equation (Smoluchowski, 1917):

$$\frac{dc_n}{dt} = \frac{1}{2}\sum_{1+1} K_{in} C_i C_j - C_n \sum K_{in} C_i \qquad \ldots 1$$

Where $C_n^{(t)}$ is the time –dependent number concentration of n – fold cluster, t is the time, and ki; are the elements of the rate kernel which control the rate of the coagulation between an i –fold and j-folder cluster. In the smoluchoaski analysis, the coagulation process is approximated to be controlled by Brownian motion and monodispersed suspension. So the analysis attempts to interpret the kinetics of rapid coagulation on the basis of diffusion (Brownian) motion which is best studied during the early parts (t <30 min.) of the coagulation process (Menkiti et al ,2010;Holthof *et al*,1996; Fridriskhberg, 1984; VanZanten and Elimelech ,1992; Suidan ,1998; Ma *et a*l,2001; WST,2005)

According to the works carried out by Fridriskinsberg (1984), it was shown that the rate of depletion of particle count (TSS or turbidity removal) can generally be represented as

$$-\frac{dc}{dt} = KC^{\alpha} \quad \text{...2}$$

based on the Brownian controlled, rapid coagulation.

The generalized form of equation (2) can be used to determine the aggregation constant K if **α = 2**. Hence:

$$\frac{1}{C} = Kt + \frac{1}{C_0} \quad \text{...3}$$

MATERIALS AND METHOD

Collection of Effluent Samples

The fibre-cement effluent was collected from the effluent channels of the factory located in Enugu, Nigeria. Effluent sample was placed into thoroughly cleaned 20-litre polyethylene bottle and tightly closed. Bottle was rinsed with effluent sample before the final sample collection.

Effluent Analysis

The temperature was measured using calibrated mercury-in-glass thermometer (0-100^{o}c) to the nearest ± 0.05^{o}c. A DELTA 320 pH meter was used for pH determination. Determinations of dissolved oxygen, biological oxygen demand (BOD), total dissolved solid; total suspended solid (TSS), Cl^-, PO_4^{3-}, $S0_4^{2-}$ were carried out according to the standard methods for the examination of water and waste water. A UNICAM 919 model atomic absorption spectrophotometer was used for the determination of the heavy metals including copper (Cu), iron (Fe), arsenic, chromium, cadmium (Cd) and manganese (Mn). The characteristics of the waste water collected from the outlet of the fibre-cement industry are given in table1.

Snail Shell (SS) Preparation

The SS was obtained after the snail has been removed in boiled water. The snail shell was first washed with tap water and then rinsed thoroughly with distilled water. It was ground in a wooden mortar and pestle. The ground SS was made into powder using a grinding machine and sieved with a laboratory sieve of known mesh size. The ground SS was then processed into a coagulant using standard methods(Fernandez-Kim,2004).

Coagulation Experiment(Jar Test)

Coagulation and flocculation was performed using bench scale jar test. Suspensions were subjected to 2 minutes of slow mixing and 20 minutes of rapid mixing, followed by 30 minutes of settling. SSC coagulant was added at the beginning of the rapid mixing. During settling, samples were withdrawn using pipette from 2cm depth and analyzed for turbidity. Coagulation $_P{}^H$ was adjusted using sulphuric acid and sodium hydroxide during the jar test. All the tests were performed at a temperature of 28^{o}c ± 2^{o}c. The above procedure was repeated using alum in a control experiment.

RESULTS AND DISCUSSION

The Effect of pH variation on Turbidity Removal

The pH influences polymeric metal species which are formed when the metal coagulants are dissolved in water (Stamm and Morgan,1996). Figures 1 and 2 show that the percentage turbidity removal was appreciable in all the pH values studied, the optimum turbidity removal occurring at pH of 6. The average percentage turbidity removal was recorded at 92%.

For alum coagulation whose performance profile was plotted in figure 2, the best turbidity removed occurred at pH 12.The results obtained are in agreement with the work done by Oladoja and Aliu (2008).The appreciable values of the turbidity removal observed could be ascribed to the alkaline nature (pH = 8.01) and the neutralizing ability of the snail shell used. It should also be noted that snail shell has large surface areas. Owing to the predominance of $CaCO_3$ in SSC the hydrolysis reaction of calcite could be used to elucidate the surface reaction of the SSC at different pH values. Considering the hydrolysis reaction of calcite, it derives that cation species such as Ca^{2+}, $CaHCO_3^+$ and $CaOH^+$ prevail for pH less than 8, rendering the mineral surface positively charged (Karageorgwu *et al*, 2007).Alum is said to perform best under alkaline medium (Lentech,2005)

Good coagulation at a lower pH could be attributed to a higher degree of protonation of amine groups of the SSC. Coagulation of turbidity particles was enhanced by the increase in charged groups of SSC, which increased electrostatic interaction with anionic surface of total suspended solid (TSS).

The Effect of Coagulation Concentration on Turbidity Removal

The results obtained for turbidity of sample in NTU were converted to concentrations (mg/l) by multiplying with a factor of 2.20 (Ozacar and Sengli, 2002). These results are shown in figures 3 and 4. The observable pattern in most of the results is the decrease of concentration from initial value of 2028mg/l. The decrease of turbidity with time reflects the fact that as the reaction progressed the amount of particle available for the coagulation decreases. The decrease in turbidity from 0-5 minutes is a product of either floc mechanism or combination of entrapment bridging mechanism. Figure 3 illustrates that as the concentration of SSC increases, the rate of particle removal increases also. At 400 mg/l the ability of SSC to remove turbidity from the fibre-cement waste water is at the optimum. Figure 4 shows the performance plots of the TSS removal by use of alum coagulant. The experiment served as the control. For most of the coagulant dosages, the concentration values in Figure 3 compare favourably with those in Figure 4 indicating that the SSC coagulant can be used for TSS removal in fibre-cement effluent. Meanwhile , figure 7 indicates that with exception of 400 mg/l dose, snail shell coagulant performed better than alum.

Table 1. Physiochemical properties of fibre cement plant effluent

Parameter	Fibre Cement effluent
Odour	Alkalinic
Appearance	Pale yellow
Colour (Oxygen disc)	0.08
Ph	>11
Conductivity (µs/cm)	4 x 105
Temperature (oC)	30
Acidity (mg/l)	ND
Alkalinity (mg/l)	1350
Total solids (mg/l)	2028
Dissolved solid (mg/l)	1578
Suspended solid (mg/l)	450
Nitrate (mg/l)	20.20
Calcium (mg/l)	9418.8
Magnesium (mg/l)	4226.85
Total Hardness (mg/l)	13645.65
Dissolved Oxygen (mg/l)	4.40
Biochemical Oxygen Demand (mg/l)	66.20
Chemical Oxygen Demand (mg/l)	58.70
Phosphate (mg/l)	ND
Copper (mg/l)	0.01
Iron (mg/l)	36.3
Chloride (mg/l)	106.38
Manganese (mg/l)	0.016
Arsenic (mg/l)	ND
Chromium (mg/l)	4.33

Sulphate (mg/l)	951.2
Cadmium (mg/l)	0.05
Calcium (mg/l)	9418.8
Magnesium (mg/l)	4226.85

Coagulation Reaction Constants for Variable Dosages

Representative figures 5 and 6 shows the pseudo second order model plots for TSS removal using SSC. From these plots the K and C_0 values can be deduced. The K values obtained from the linearized equations from the figure were then used to formulate the rate equations for the removal of TSS from the waste water as contained in tables 2 and 3. Meanwhile, table 1 shows the characterization results of the fibre – cement effluent. The results posted from tables 2 and 3 shows that high values of R^2 indicate a high measure of agreement to the second order model common to coagulation process. It is also observed that high values of K indicating faster raste of coagulation. This is expected since sweep floc may be in force.

Table 2: Coagulation Kinetics of SSC for a second order system

Coagulant dosage (mg/l)	*K-values(l/mg min)*	*Rate equation (mg/l min)*	*R^2*	α	*Co(mg/L)*
100	$1.4x10^{-3}$	$-r=1.4x10^{-3}C^2$	0.28	2	149.25
200	$1.1x10^{-3}$	$-r=1.1x10^{-3}C^2$	0.65	2	138.89
300	$1.9x10^{-3}$	$-r=1.9x10^{-3}C^2$	0.88	2	138.89
400	$4.5x10^{-3}$	$-r=4.5x10^{-3}C^2$	0.92	2	222.22
500	$0.5x10^{-3}$	$-r=0.5x10^{-3}C^2$	0.79	2	10.53

Table 3: Coagulation Kinetics of alum for a second order system

Coagulant dosage (mg/l)	*K-values(l/mg min)*	*Rate equation (mg/l min)*	*R^2*	α	*Co(mg/L)*
100	$3.2x10^{-3}$	$-r=3.2x10^{-3}C^2$	0.95	2	222.22
200	$4.5x10^{-3}$	$-r=4.5x10^{-3}C^2$	0.94	2	200.00
300	$4.6x10^{-3}$	$-r=4.6x10^{-3}C^2$	0.95	2	88.50
500	$4.7x10^{-3}$	$-r=4.7x10^{-3}C^2$	0.99	2	256.41

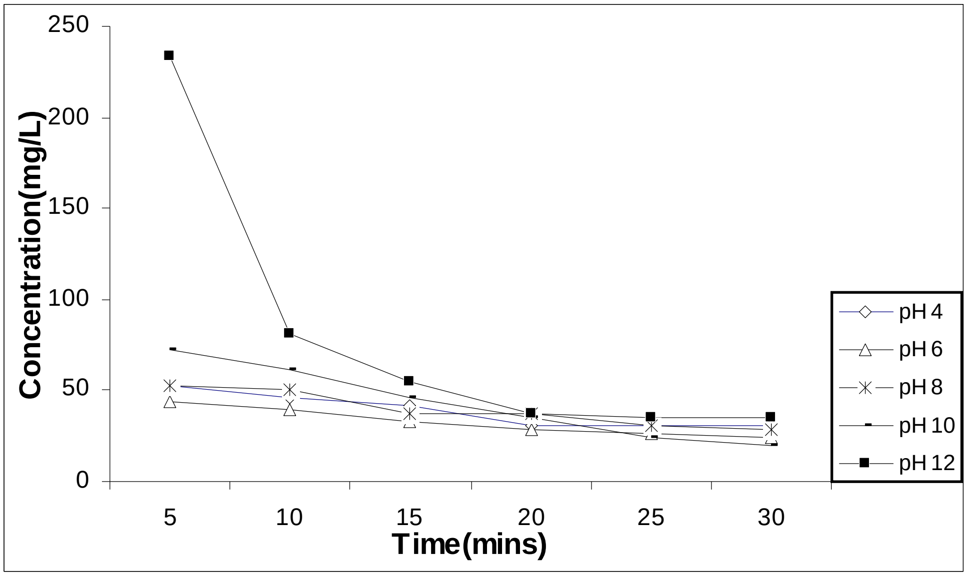

Fig 1 : TSS Removal at varying pH of effluent for 400mg/L SSC dosage.

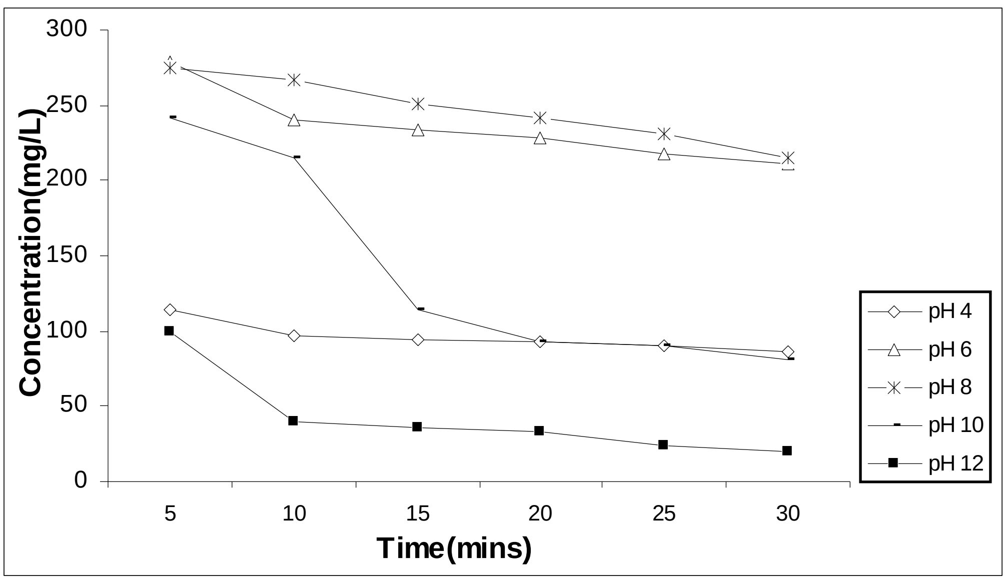

Fig 2 : TSS Removal at varying pH of effluent for 300mg/L Alum dosage.

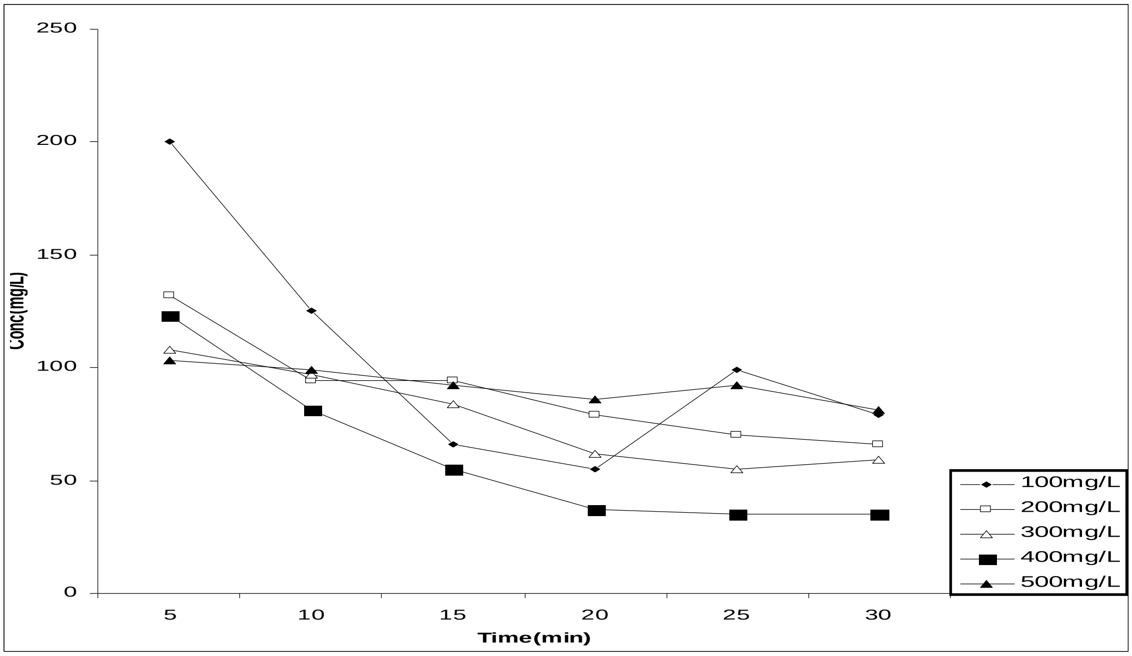

Fig 3: TSS removal at varying doses of SSC coagulant

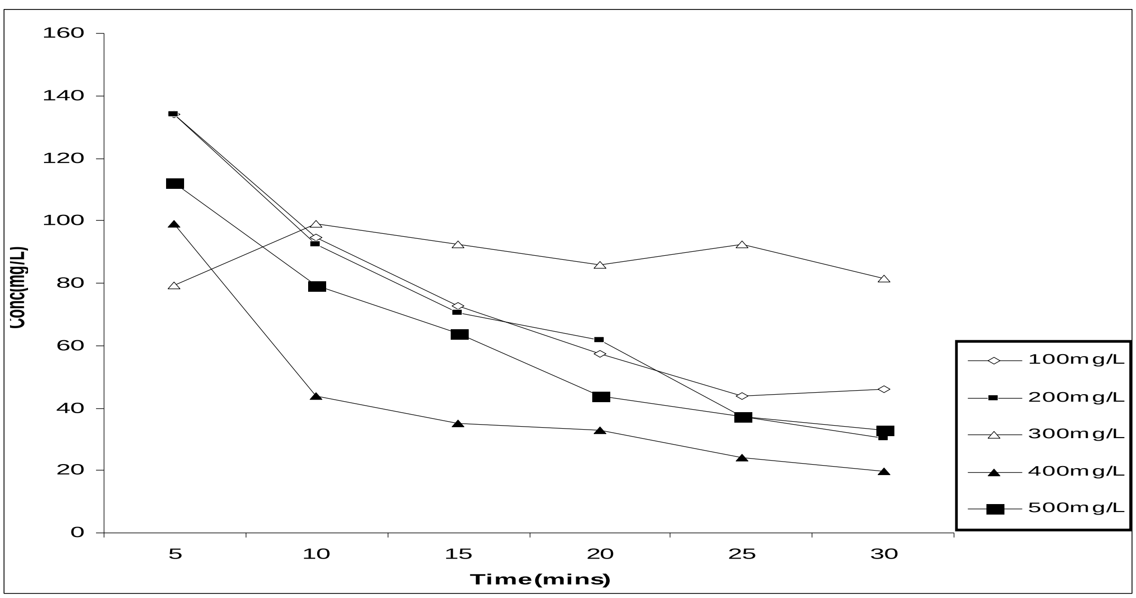

Fig 4: TSS Removal at Varying doses of Aluminum Sulphate

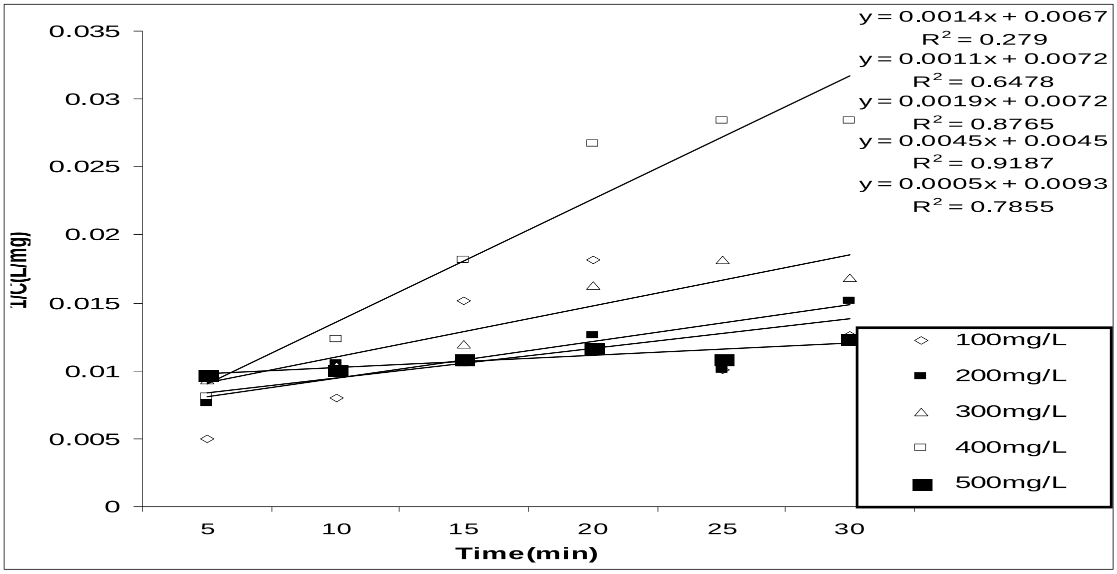

Fig 5: Plots of 1/C Vs Time for TSS Removal at Varying doses of SSC Coagulant

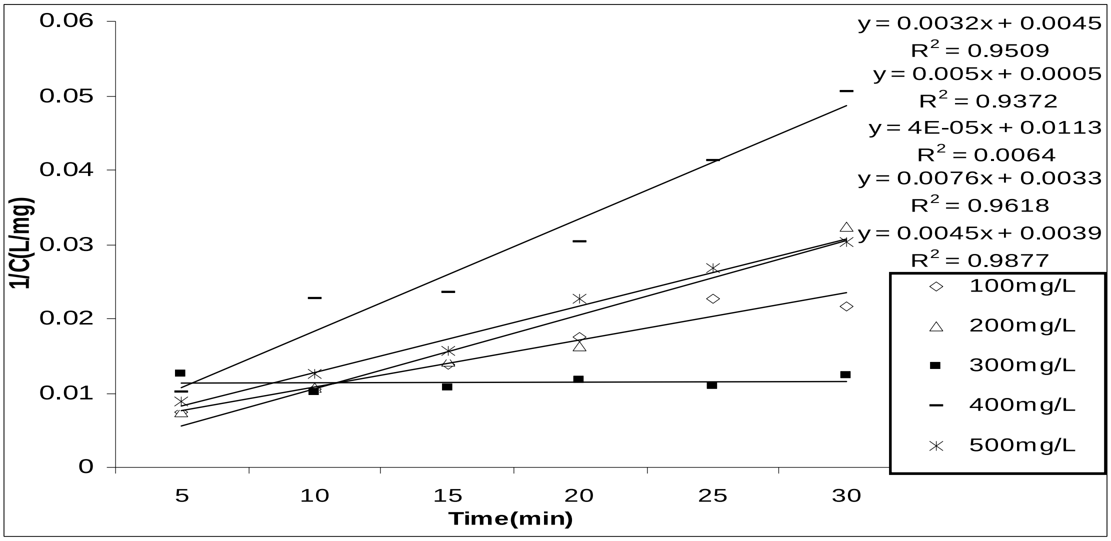

Fig 6: Plots of 1/C vs Time for TSS removal at varying doses of aluminium sulphate

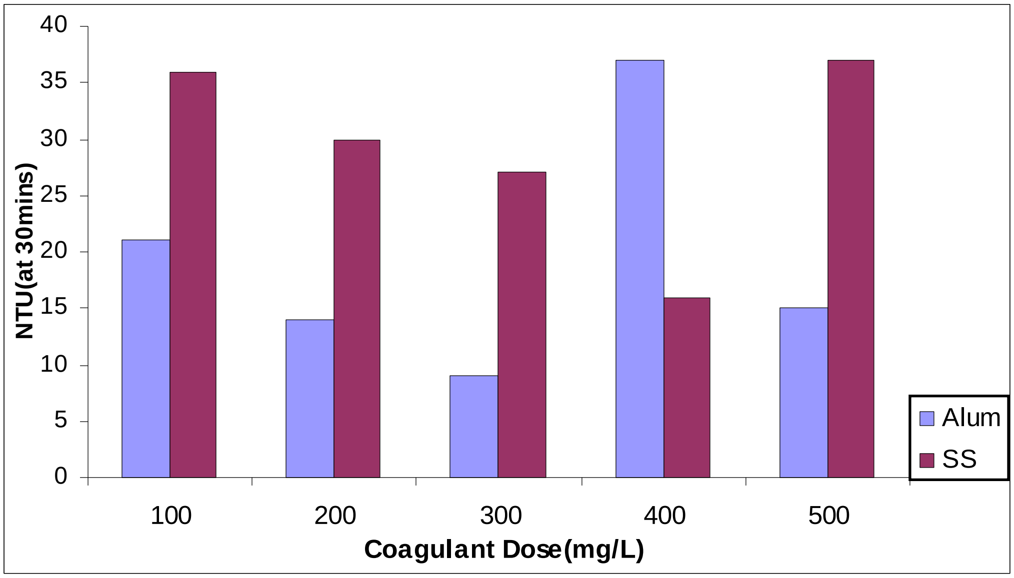

Fig 7: Particle reduction profile for alum and SSC coagulants at optimum conditions.

CONCLUSION

Studies on the physicochemical treatment of fibre – cement effluent has been carried out using coagulant prepared from snail shell. The results obtained showed that for SSC treatment optimum turbidity removal occurred at 400mg/l and effluent pH 6 while in the alum control experiment, optimum concentration was 300mg/l at effluent pH of 12. The kinetics of the coagulation reaction also revealed K range that agrees with results reported to conform with theory of perikinetic coagulation (Menkiti *et a*l,2010;Ani *et al*,2010)

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