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Coagulation and flocculation behaviour of snail shell coagulant in fibre-cement plant effluent

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Abstract

The ability of a coagulant prepared from snail shell (SS) to carry out removal of suspended solid (TSS) in a fibre-cement plant effluent was evaluated at bench scale using a standard jar test apparatus operated at room temperature. In order to verify the results obtained from the study, alum was used in the control experiment. The effects of variation of coagulant dosage and flocculation reaction kinetics at the pH of the waste water were investigated. The optimum coagulant dosage for turbidity removal was found to range between 400 and 500mg/l at the end of 30 minutes of coagulation. The highest values of K recorded are $4.5x10^{-3}$ and $7.6x10^{-3}$ l/mg. min for SS and alum at dosage of 400mg/l. From the results obtained it is suggested that SS is an efficient coagulation agent and a potential alterative for the treatment of waste water at the conditions of the experiment.

INTRODUCTION

Coagulation study, first systematically proposed by Von Smoluchowski in 1917, can be used to model the coagulation process. He proposed collision frequency theory based on Brownian motion and fluid shear stress. These studies are based on a rectilinear collision model, assuming that the particle motion is linear until collision occurs.

Coagulation which is a unit process, includes two separate and sequential steps; a collision step followed by attachment step.

In the unit process, finely dispersed solid (colloids) suspended in waste water are stabilized by electric charges on their surface, causing them to repel each other. These charges prevent the particles from colliding to form large masses called flocs. Coagulation is the destabilization of colloids by neutralizing the forces that keep them apart. These colloids may include organic and inorganic particles (O Melia, 1978; Edzwald, 1987).

The flocculation of particles in a liquid depends on collisions between particles caused by their relative motion. This relative motion may be caused by Brownian motion, by fluid movement giving rise to velocity gradient or by particle motion which may be gravitational.

The rate of flocculation is determined by the collision frequency induced by the relative motion. If there is no surface repulsion between the particles, then every collision leads to aggregation and the process is called rapid flocculation. If a significant repulsion exists, then only a fraction of the collision results in aggregation. This is called slow flocculation.

Coagulation and flocculation as a unit process, in water and waste water treatment entails the use of metal salts ($Al^{3+}$and Fe^{3+} salts) (Xu *et al*, 2009 and Menkiti *et al*, 2007). However, studies have discovered a number of drawbacks concerning the use of these conventional coagulants. For example, Alzheimer's disease and other related problems are associated with residual alum in treated water (Divakaran *et al*, 2001).

Against this back drop, the use of coagulants of biological origin becomes imperative. Some of the coagulants and flocculants of biological origin that have been used include chitosan (Roussy *et al*, 2005), tannins (Ozacar *et al*, 2002) ; aqueous extract of the seed of moringa oleifera (Narasiah *et al*, 1998); extract of plantain peelings ash (Oladoja, 2008); and extracts of okra and nirmali seed (Shokralta *et al*, 1996).

Snail shell is being proposed as a low-cost material to remediate the turbidity of a fibre-cement plant effluent in the present studies.

Fibre-cement is commonly used in the construction of houses and commercial buildings, for internal and external wall cladding and floor underlays. Fibre-cement is produced from four main raw materials- silica (sand), cement, cellulose, paper and water. These materials are mixed together to form a slurry. This is then 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 8 hours.

The effluent from the production process flows into a drainage that channels it into a nearby river.

The present study is aimed at investigating the potential application of SS as a coagulant in the treatment of fibre-cement effluent.

THEORETICAL BACKGROUND AND PRINCIPLES DEVELOPMENT

Turbidity produces an estimate of the muddiness or cloudiness of water due to clay, silt, finely divided organic and inorganic matter, soluble coloured organic compounds, plankton, colloids and microscopic organism. Based on the work of Metcalf and Eddy (2003), the relationship is as follows:

$$\text{TSS (mg/l)} = (\text{TSS}_f)\ .\ \text{T}$$

Where TSS = total suspended solid (mg/l)

TSS_f = factor used to convert turbidity (T) to TSS.

One of the problems with measurement of turbidity (especially low values in the filtered effluent) is the high degree of variability observed, depending on the light source (incandescent versus light emitting bodies) and the methods of measurement (reflected versus transmitted light). Another problem often encountered is the absorbing properties of suspended materials. In spite of these limitations, turbidity measurement still offers the commonest method to study coagulation. In experimental tests of stability theories, it is usual to restrict measurements to the early stages of coagulation (where the early aggregation mechanism is most straight forward), using moderately dilute solutions. The particle concentration during early stages of coagulation can be determined directly, by visual particle counting or indirectly, from turbidity (spectrophotmetric or light scattering) measurement (Metcalf and Eddy, 2003).

In most colloid stability studies, coagulation rates are measured, as far as possible, under perikinetic (non-agitated) conditions where particle-particle encounters are solely the result of Brownian motion.

In the work of Holthof *et al* (1996), it was shown that coagulation rate constants could be determined by monitoring the changes in the turbidity of the coagulation liquid with time. While this method is rapid, there are difficulties inherent in interpreting the turbidity changes.

The time evolution of the cluster size distribution for colloidal particles is usually described by the Smoluchowski equation:

$$\frac{dc_n}{dt} = \frac{1}{2}\sum_{\text{i+1}} \text{K}_{\text{in}}\ \text{C}_\text{i}\text{C}_\text{j} \quad - \quad \text{C}_\text{n} \quad \sum_{i=j} \text{K}_{\text{in}}\ \text{C}_\text{i}$$

(1)

Where $c_n(t)$ is the dependent number concentration of n-fold cluster, t is the time and kij are the elements of the rate kernel which control the rate of the coagulation between an i -fold and j – fold cluster. In the Smoluchowski analysis, the coagulation process is approximated to be entirely controlled by Brownian motion and initially having mono dispersed suspension. The implication of this is that the analysis attempts to quantitatively interpret the kinetics of rapid coagulation on the basis of diffusion (Brownian motion) which is best studied during the early parts (say $t < 30$ min) of coagulation process (Fridriskhberg et al, 1984, Holthof *et al*, 1996). According to the work of Fridriskhberg (1984), it was shown that the rate of depletion of particle count (TSS or turbidity removal) can generally be represented as

$$-\frac{dc}{dt} = \text{kC}^{\alpha} \tag{2}$$

where C = concentration of effluent at time t,

K = coagulation rate constant,

α = order of reaction.

For coagulation process of this type, the reaction order, α, can be assumed to be second order (Menkiti *et al,* 2007). Hence,

$$\int_{C_o}^{C} \frac{dC}{C^2} = K\int_{o}^{t} dt$$

By integrating equation 3, we obtain

$$\frac{1}{C} = kt + \frac{1}{C_o} \tag{4}$$

Where Co = initial concentration of the effluent.

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 (Ademoroti, 1996). 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 table 1.

Snail Shell 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.

Coagulation Experiment

Coagulation and flocculation was performed using bench scale jar test. Suspensions were subjected to 20 minutes of slow mixing, followed by 30 minutes of settling. SS 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 not adjusted 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 Coagulation Dosage 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 (Metcalf and Eddy, 2003). These results are shown in figures 1 and 2. The observable pattern in most of the results is the decrease of turbidity with time. 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 1 illustrates that as the dose of SS increases the rate of particle removal increases also. At 400 mg/l the ability of SS to remove turbidity from the fibre-cement waste water is at the optimum and this is confirmed by a comparatively high value of R^2 for this column.

Figure 2 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 1 compare favorably with those in Figure 2 indicating that the SS coagulant can be used for TSS removal in fibre-cement effluent.

Figure 3 shows the pseudo second order model for TSS removal using SS coagulant. From these plots the K and I 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 table 2.

Figure 4 was used to generate the coagulation reaction constants for variable dosages of alum. With the exception of the 300mg/l dosage, the values of R^2 confirm that the majority of the plots are second order.

Coagulation Reaction Constants for Variable Dosages

Tables 2 and 3 show reaction constants obtained for SS and alum-coagulated water respectively. Both K and α are determined from the general equation, $-r = KC^{\alpha}$.

Table 1. Physiochemical properties of fibre cement plant effluent

Parameter	*Fibre Cement effluent*	*WHO standard limits*
Odour	Alkalinic	Unobjectionable
Appearance	Pale yellow	Clear
Colour (Oxygen disc)	0.08	15

pH	>11	6.5 – 8.5
Conductivity (µs/cm)	4 x 10^5	1000
Temperature (^{o}C)	30	25
Acidity (mg/l)	ND	NS
Alkalinity (mg/l)	1350	NS
Total solids (mg/l)	2028	1000
Dissolved solid (mg/l)	1578	1000
Suspended solid (mg/l)	450	25
Nitrate (mg/l)	20.20	30
Calcium (mg/l)	9418.8	200
Magnesium (mg/l)	4226.85	50-125
Total Hardness (mg/l)	13645.65	500
Dissolved Oxygen (mg/l)	4.40	5
Biochemical Oxygen Demand (mg/l)	66.20	50
Chemical Oxygen Demand (mg/l)	58.70	NS
Phosphate (mg/l)	ND	NS
Copper (mg/l)	0.01	NS
Iron (mg/l)	36.3	0.1
Chloride (mg/l)	106.38	250
Manganese (mg/l)	0.016	0.05
Arsenic (mg/l)	ND	NS
Chromium (mg/l)	4.33	NS
Sulphate (mg/l)	951.2	400
Cadmium (mg/l)	0.05	NS
Calcium (mg/l)	9418.8	200
Magnesium (mg/l)	4226.85	50-125

Key:

NS = Not Stated
ND = Not detected

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

Coagulant dosage (mg/l)	***K-values(l/mg min)***	***Rate equation (mg/l min)***	***R^2***	***Co(mg/L)***
100	$1.4x10^{-3}$	$-r=1.4x10^{-3}C^2$	0.28	149.25
200	$1.1x10^{-3}$	$-r=1.1x10^{-3}C^2$	0.65	138.89
300	$1.9x10^{-3}$	$-r=1.9x10^{-3}C^2$	0.88	138.89
400	$4.5x10^{-3}$	$-r=4.5x10^{-3}C^2$	0.92	222.22
500	$0.5x10^{-3}$	$-r=0.5x10^{-3}C^2$	0.79	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***	***Co(mg/L)***
100	$3.2x10^{-3}$	$-r=3.2x10^{-3}C^2$	0.95	222.22
200	$5.0x10^{-3}$	$-r=5.0x10^{-3}C^2$	0.94	200.00
300	$4.0x10^{-3}$	$-r=4.0x10^{-3}C^2$	0.01	88.50
400	$7.6x10^{-3}$	$-r=.7.6x10^{-3}C^2$	0.96	303.03
500	$4.5x10^{-3}$	$-r=4.5x10^{-3}C^2$	0.99	256.41

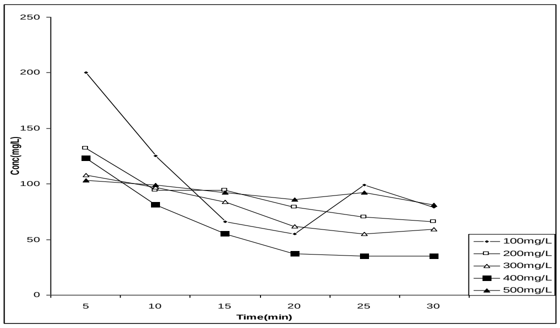

Fig 1: TSS removal at varying doses of SS coagulant

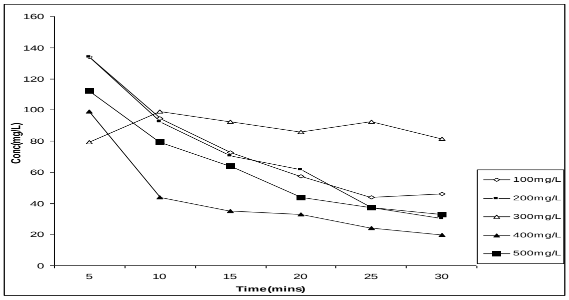

Fig 2: TSS Removal at Varying doses of Aluminum Sulphate

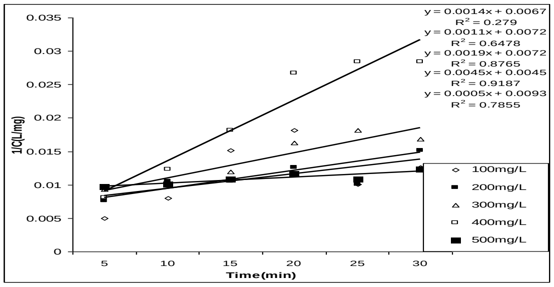

Fig 3: Plots of 1/C Vs Time for TSS Removal at Varying doses of SS Coagulant

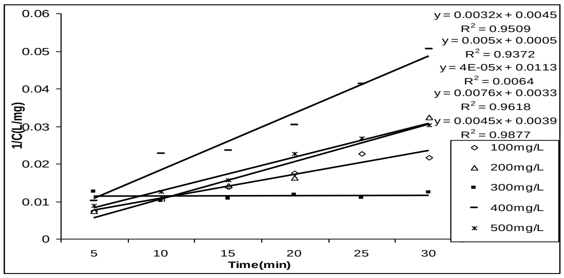

Fig 4: Plots of 1/C vs Time for TSS removal at varying doses of aluminium sulphate

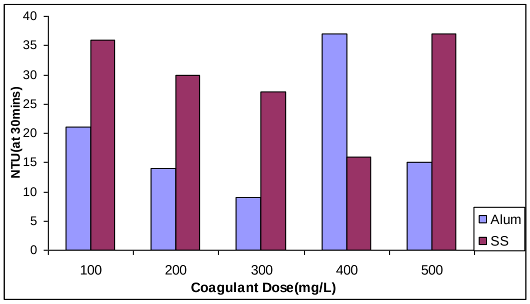

Fig 5: Particle reduction profile for alum and SS coagulants

CONCLUSION

Snail shell has been identified as a potential source of coagulation agent for the removal of turbidity from waste water. Some of the parameters that control coagulation were found to include coagulation dosage, reaction time, rate constant, order of the reaction and pH of effluent.

It was observed that the percentage turbidity removal increased with increase of the flocculation time and coagulant dosage. With the exception of the alum dose of 300mg/l, the coagulation behaviours of the various samples were found to follow second order kinetics.

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REFERENCES

Ademoroti C.M.A. (1996); Standard methods for water and effluent analysis, Marchprints and consultancy, Benin, Nigeria pp75-145.

Al-Samawi A. and Shokralla E. M. (1996); An investigation into an indigeneous natural coagulant, J. Environ. Sc. Health vol. 31 pp1881-1897.

Divakaran R. and Pillai V.N.S. (2001); Flocculation of koalinite suspension in water by chitosan, Water Res. 35, pp 3904-3908.

Edzwald, J.K. (1987); Coagulation-sedimentation-filtration processes for removing organic substances from drinking water; control of organic substances in water and waste water, Noyes Data Corporation, Park Ridge, New Jersey.

Fridriskhberg O.A. (1984; A course in colloid chemistry, Mir Pubishers, Moscow, Russia.

Holthof, H. *et al* (1996); Coagulation rate measurements of colloidal particles by simultaneous static and dynamic light scattering; Langmuir, switzerland 12, pp 5541-5549.

Menkiti M.C, Ugodulunwa F.X.O. and Onukwuli O.D. (2007); Studies on the coagulation and flocculation of coal washery effluent; Nigerian Society of Chemical Engineers proceedings, 37, pp 169-184

Ndabingesere A. and Narasiah K.S. (1998); Quality of water treated by coagulation using moringa oleifera seeds, Water Res. 32, pp 781-791.

O' Melia C.R. (1978); Coagulation in waste water treatment. The scientific basis of flocculation. (NATO Advanced Study Inst. Series E, Appl. Sci. No 27).

Oladoja N.A. and Aliu Y.D. (2008); Evaluation of plantain peelings ash extract as coagulant aid in the coagulation of colloidal particles in low $_P{}^H$ aqua system, Water Quality Research Journal, Canada.

Ozacar M. and Sengil A.(2002); The use of tannins from Turkish, J. Eng. Environ. Sci. 26, pp 255-263.

Roussy J., Chastellan P., Vooren M. and Guibal E. (2005); Treatment of ink-containing waste water by coagulation/flocculation using biopolymers, Water SA 31 (3), pp 369-376.

WST (2005); About coagulation and flocculation, Information Bulletin, USA.

Xu C.R.,Yan Z.C. and Wang Y.C. (2009); Recycle of alum recovered from water treatment studies in chemically enhanced water treatment; Journal of hazardous materials 161 pp 663-669.