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THE COAGULATION PERFORMANCE OF OKRA MUCILAGE IN AN INDUSTRIAL EFFLUENT BY TURBIDIMETRY

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ABSTRACT

The determination of coagulation rate constants was achieved by monitoring changes in the concentration of the coagulating suspension with time. These coagulation rate constants were obtained by turbidimetric studies on fibre-cement industry effluent (FCIE). The gravimetric method of measuring the concentration of suspended particles is tedious and thus not suitable for routine evaluations of coagulation kinetics. The coagulation rate constants were obtained from the slopes of first and second order plots of the coagulation reactions using aluminum sulphate and okra mucilage (OMUC) as coagulants. The work further examined the suitability of OMUC as a novel coagulant for the removal of colloids from FCIE.

Key words: Nephelometric, Coagulation rate constant, Colloids, Fibre-cement, Orthokinetic.

INTRODUCTION

In the process design and manufacture of industrial products such as electronic, ceramic, optic and magnetic materials, the kinetics of coagulation of colloidal particles in liquids is of immense importance. This is also applied in the removal of colloidal impurities in wastewater treatment and in the manufacturing of pharmaceutical and biomedical products. The study of coagulation kinetics is also of fundamental interest in the field of colloid science; it can be used as a means of investigating the colloidal and hydrodynamic interactions involved in particle-particle interaction phenomena[1]. Coagulation is the destabilsation of colloids causing the particles in suspension to aggregate and form settle able flocs.

A wide variety of techniques have been proposed for the evaluation of coagulation kinetics. The ultramicroscope[2] can be used for the direct counting of the coagulating

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colloids.There is also the method whereby the use of a particle counter[2-4] is employed and the approach of using gravimetry to measure the concentration of the suspension. However, the latter technique is very tedious and thus not suitable for routine determination of coagulation kinetics. In this study, the turbidimeter is used to monitor changes in the turbidity of the coagulating suspension of a fibre-cement industry effluent, with time and the results obtained used to estimate the coagulation rate constants using aluminum sulphate and okra mucilage as coagulants.

Turbidity is described as an expression of the optical property that causes light to be scattered and absorbed rather than transmitted in straight lines through the sample[5]. Modern turbidimeters use the technique of nephelometry, which measures the amount of light scattered at right angles to an incident light beam by particles present in a fluid sample. As light passes through distilled water, the light beams travel along relatively undisturbed paths. However, when light passes through a fluid containing suspended solids, the light beam interacts with the particles, and the particles absorb the light energy and reradiate light in all directions. The basic turbidimeter instrument contains a light source, sample container or cell, and photodetectors to sense the scattered light. The most common light source used is the tungsten filament lamp.

Grab samples are typically introduced into bench top turbidimeter instruments through a transparent sample cell made of glass. These samples cells, or cuvettes, are usually about 30 mm. in capacity. Some on-line turbidimeters utilize the glass sample cell, but most designs use a flow-through chamber with the light source located outside the sample. Sample chambers in on-line instruments range from 30 mm. to over 2 Litres.

In turbidimeters, photodetectors detect the light produced from the interaction of the incident light and the sample volume and produce an electronic signal that is then converted to a turbidity value. These detectors can be located in a variety of configurations depending on the design of the instrument.

Gravimetric analysis describes a set of methods in analytical chemistry for the quantitative determination of an analyte based on the mass of a solid. A simple example is the measurement of solids suspended in water sample. To obtain the concentration a known volume of water is filtered and the collected solids are weighed.

Theoretical expressions

The first major attempt at modeling the coagulation process was made by Smoluchowski[6]. Hence, the equations in Smoluchowski's model have formed the core of almost all subsequent research into coagulation – flocculation modeling.

The mathematical representation of flocculation, the process whereby destabilized suspended particles are aggregated has conventionally been based on the relationship between size of particles j and k[7]:

$$\text{Rate of flocculation} = \alpha\beta\ (i, j)\ n_i\ n_j \qquad \ldots(1)$$

Where α is the collision efficiency, β (i,j) is the collision frequency between particles of size i and j and n_i, n_j, are the particle concentrations for particles of size i and j respectively.

Almost all flocculation models are based upon this one fundamental equation.

The collision frequency β is a function of one mode of flocculation, i.e. perikinetc, orthokinetic or differential sedimentation. The collision efficiency α is a function of the degree of particle destabilization; the greater the degree of destabilization the greater the value of α[12].

Thus, in effect, β is a measure of the transport efficiency leading to collisions, whilst α represents the percentage of those collisions leading to attachment. The value of the parameters α and β are dependent upon a large number of factors ranging from the nature of the particles to the method of destabilization (whether charge neutralization or bridging mechanism) and the prevailing flow regime during flocculation. Much of the research in flocculation modeling has been directed at establishing equations and specific values for these two parameters, α and β.

The basic equation developed by Smoluchowski is given by[8,9] -

$$\frac{dN}{dt} = \frac{1}{2}\sum_{i+j=n} k_{ij}\, N_i\, N_j - Nn\sum_{i=l}^{\infty} k_{in}\ N_i \qquad \ldots(2)$$

Where Nn (t) is the time-dependent numbers concentration of n-fold clusters, t is the time, and Kij are the elements of the rate kernel which control the rate of coagulation between an i-fold and an j-fold cluster.

In the Smoluchowski analysis, the coagulation is entirely controlled by Brownian diffusion (peri kinetic, laminar) and the coagulation rate constant for dimmer formation of an initially mono dispersed suspension is then given by[10] -

$$K_{11} = \frac{8k_B T}{3\eta} \qquad \ldots(3)$$

Where K_B is the Boltzmann constant, T is the temperature, and η is the viscosity of the medium

By assuming a constant kernel, ie., Kij = K_{11}, the Smoluchowski equations can be solved exactly, resulting in the expression[6,8-11]

$$\frac{N_n(t)}{N_O} = \frac{(K_{11}N_O t/2)^{n-1}}{(1+K_{11}N_0 t/2)^{n+1}} \quad \ldots(4)$$

Where N_o is the initial particle concentration. For n = 1, the following linear function in time for the inverse square root of the monomer concentration N_1 is obtained

$$N_n(t) = \frac{N_0}{(1+K_{11}\ N_0\ t/2)^2} \quad \ldots(5)$$

$$\frac{1}{N_n(t)} = \frac{(1+K_{11}N_0 t/2)^2}{N_0}$$

$$= \frac{1}{No} + \frac{(K_{11}\ N_o\ t/2)^2}{N_0} \quad \ldots(6)$$

$$\frac{1}{\sqrt{Nn(t)}} = \frac{1}{\sqrt{N_0}} + \frac{K_{11}N_0 t}{\sqrt[2]{N_0}} \quad \ldots(7)$$

$$\frac{1}{\sqrt{N_1}} = \frac{1}{\sqrt{N_0}} + \frac{K_{11}N_0 t}{\sqrt[2]{N_0}} \quad \ldots(8)$$

Therefore a graphical representation of the inverse square root of monomer concentration N_1 versus time should give a straight line and the coagulation rate constant can be measured from the slope of this function once the initial particle concentration N_0 is known. Based on the work of Tchnobanglous et al.,[12] a relation exists as follows:

$$TSS\ (mg/L) = (TSS_f).\ T \quad \ldots(9)$$

Where TSS = Total suspended solid, mg/L = 2.20

The kinetics of Brownian coagulation of monodispersed particles at the early stage can be described as[13] -

$$\frac{dN}{dt} = -KN^{\alpha} \quad \ldots(10)$$

Where N is the total number concentration of particles, t is the time, and K is a α^{th} order coagulation rate constant. This rate constant is a product of the collision frequency, β and the Smoluchowski rate constant for rapid coagulation, K_{11}:

$K = Bij\ K_{11}$

For α = 2 (second order)

$$\frac{dN}{dt} = -KN^2 \quad \ldots(11)$$

$$-\int_{No}^{N} \frac{dN}{N^2} = K\int_{o}^{t} dt = Kt$$

$$-\left(\frac{1}{N}\right)_{N0}^{N} = Kt\ ; \quad \frac{1}{N} - \frac{1}{No} = Kt \quad \ldots(12)$$

Hence a plot of $\frac{1}{N}$ against t yields a straight line whose slope equals the second order rate constant, k.

For α = 1 (first order)

$$\frac{dN}{dt} = -KN \quad \ldots(13)$$

$$\frac{dN}{N} = -Kdt$$

Integration` yields (assuming $N = N_O$ at t = 0)

$$\ln \frac{N}{N_0} = -Kt \quad \ldots(14)$$

Hence a plot of $\ln \frac{No}{N}$ vs t yields a straight line whose slope equals the coagulation reaction rate constant, k.

EXPERIMENTAL

Materials and method

Collection of effluent samples

The fibre-cement effluent was collected from the effluent channels of a Fibre-cement industry 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.

Preparation of okra mucilage

The okra (Hibiscus esculentus) used in this study was bought from Ogige market in Nsukka, Enugu state. Preparation was carried out based on the work of Anastasakis et al.,[14] 2 Kg of the okra seed pods were washed thoroughly with water to remove impurities, dried at 110^{o}C in an oven for about 14 hours. It was then ground with a micro hammer mill and sieved to about 0.25 mm particle size and stored in a desiccator to preserve the integrity of the sample. The proximate analysis of sample was also carried out and the results shown in Table 1. The H. esculentus used in this study is the same species used in Agarwal et al.,[15,16] and Mishra et al.,[17] where the substances and properties of okra mucilage are discussed in detail.

Effluent analysis

The parameters selected for analyses were based on the processes responsible for generating the waste. Much of the effluent is obtained from the resulting filtrate after passing the fibre-cement effluent through a pressure vessel. 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^{-}, SO_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 iron (Fe), chromium (Cr), cadmium (Cd) and manganese (Mn). The characteristics of the wastewater collected from the outlet of the fibre-cement industry are given in Table 2.

Coagulation experiment (Jar test)

Coagulation and flocculation was performed using bench scale jar test. Suspensions were subjected to 2 minutes of rapid mixing and 20 minutes of slow mixing, followed by 30

minutes of settling. Aluminum sulphate coagulant was added at the beginning of the rapid mixing. During settling, samples were withdrawn using pipette from 2 cm depth and analyzed for turbidity using a turbidimeter. Coagulation pH was adjusted using NaOH and HCl. All the tests were performed at a temperature of 28^{o}C ± 2^{o}C. Coagulation with okra mucilage was applied using same procedure.

RESULTS AND DISCUSSION

FTIR Studies

The FTIR spectrum of OMUC is shown in Fig. 1.

The wide peak in the 3000-3600 cm^{-1} range is characteristic of –OH groups. The results from proximate analyses support this because of the –OH signals of moisture (water) oil and carbohydrate (glycerides). The peak range that centres at 3281 cm^{-1} has about 17% transmittance (0.770 absorbance), therefore, is characteristic of N-H stretching signals. This also agrees with our proximate analyses results that show the presence of proteins. The peak range that centres around 1629 cm characterize: C = C, C = N and N-H bonds. The peak centered at 1418 cm^{-1} and 1059 cm^{-1} are characteristic of C-H and C-O groups respectively. The wide signal around 632 cm^{-1} characterise aromatic substitutions. The FTIR spectrum of okra and the proximate analyses presented in Table 1 suggest the presence of glycosides, proteins and esters, which are known to be very medicinal and also justify the use of okra as potential source of coagulant in this present work.

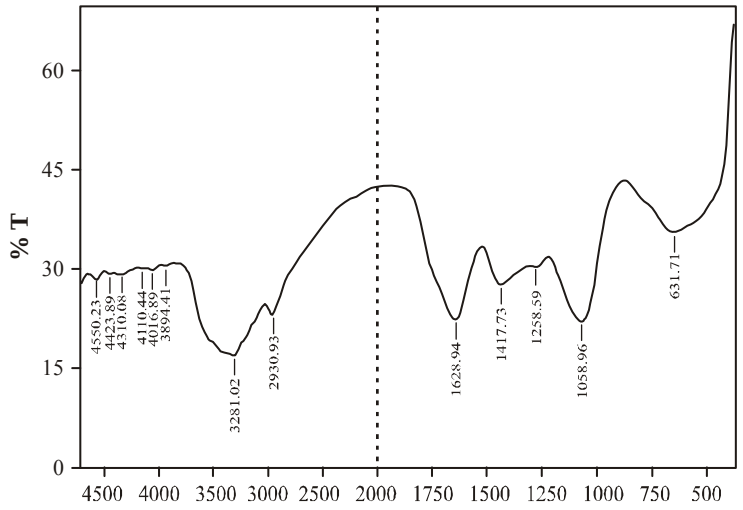

Fig. 1: FTIR spectra of OMUC

Table 1: Analysis of Okra mucilage

Parameter	Value
Moisture content (%)	10
Ash content (%)	2.69
Protein content (%wt)	0.376
Carbohydrate (%)	78
Oil content (%)	7
Fibre (%)	1.89
Calcium (mg/g)	77.9
Magnesium (mg/g)	1.62
Phosphorus (mg/g)	3.26
Potassium (mg/g)	0.019

Physico-chemical properties of fibre-cement industry effluent (FCIE)

Table 2 shows the values of the physico-chemical parameters obtained for FCIE. There were significant variations in values of the hydrogen ion concentration, electrical conductivity, hardness, turbidity, and total dissolved solids. These values were above the WHO standard limits. The foregoing results tell much about the toxicity levels of the effluent. The pH value of the effluent, 6-9, was fairly higher than the WHO limits[18,19]. pH is understood to have indirect effect on health since it affects the removal of viruses, bacteria and other harmful microorganisms. The alkaline nature of the effluent could be attributed to the type of raw materials used in the processing of the products. Silica, cement, cellulose and water were the major materials for the formulation of fibre-cement products. The high conductivity in the effluent may be due to the relatively low dissolved oxygen in it.

The principal ions causing hardness in natural waters are calcium and magnesium. Others which may be present though in much smaller quantities are iron, manganese, strontium and aluminium[16]. The prevalence of some of these ions in the formulation of fibre-cement may be the cause of high concentration for hardness in the effluent. The results obtained from the analysis of FCIE was a pointer to its pollution load. Calcium content was recorded as 9418.8 mg/L and magnesium, 4226.85 mg/L compared to their WHO limits of 75-200 mg/L and 30-150 mg/L respectively. High concentrations of calcium and magnesium

ions can lead to scale forming in some industrial plants and difficulty of soap to foam during cleaning activities.

Table 2: Physio-chemical properties of fibre-cement plant effluent

Parameter	Fibre-Cement effluent	WHO Limits
pH	>11	6-9
Conductivity (Ωs/cm)	4 x 105	1.2-1.4
Temperature (^{o}C)	30	<40
Alkalinity (mg/L)	1350	100-500
Dissolved solid (mg/L)	1578	500-1500
Suspended solid (mg/L)	450	30
Nitrate (mg/L)	20.20	45
Calcium (mg/L)	418.8	75-200
Magnesium (mg/L)	4226.85	30-150
Dissolved oxygen (mg/L)	4.40	5.0
Chemical oxygen demand (mg/L)	58.70	250
Iron (mg/L)	36.3	0.1-1.0
Chloride (mg/L)	106.38	600
Manganese (mg/L)	0.016	5.0
Chromium (mg/L)	4.33	0.05
Sulphate (mg/L)	951.2	200-600

The total suspended solids (TSS) refers to the suspended insoluble materials occurring in surface or wastewater, which makes them objectionable for almost all uses. The measured value of the turbidity of FCIE was 450 mg/L much higher than the WHO recommended limit of 30 mg/L showing that the wastewater was polluted prior to treatment. TSS may be due to the presence of colloidal particles arising from discharges of sewage and industrial waste or the presence of large number of microorganisms.

The biochemical oxygen demand (BOD) value was recorded to be above the limit. The BOD test provides a measure of the total quantity of microorganisms in the sample and

of the nutrients available to them. It does this by monitoring the amount of O_2 needed by microorganisms to decompose complex organic molecules present in the water in their aerobic metabolic processes. This is also an indication of organic load in the effluent as indicated by values of TSS, dissolved solids etc.[17,18]

Furthermore, for the FCIE, the levels of chloride, copper, manganese and calcium were within limits whereas sulphate, magnesium, chromium and iron were above limits. Excessive intake of iron and chromium may increase susceptibility to infection and cancer.

Coagulation kinetics

The results obtained for turbidity of sample in NTU, by use of the turbiditimeter, were converted to concentrations (mg/L) by multiplying with factor of 2.20[20]. A summary of the coag-flocculation functional parameters at optimum conditions as obtained in this study is shown in Tables 3, 4, 5 and 6 where the results of the kinetics of coagulation and flocculation on the FCIE using aluminium sulphate and okra mucilage are shown for first and second order reactions respectively.

Table 3: Coagulation kinetics of alum for a first order system

Coagulant dosage (mg/L)	10^3 K values (L/mg min)	R^2	C_0 (mg/L)
100	2.2	0.94	164.37
200	2.9	0.98	136.95
300	2.8	0.88	123.17
400	0.04	0.01	135.612
500	2.5	0.97	106.41

Table 4: Coagulation Kinetics of alum for a second order system

Coagulant dosage (mg/L)	10^3 K values (L/mg min)	R^2	C_0 (mg/L)
100	7.0	0.95	101.01
200	11.0	0.94	909.09
300	16.3	0.96	99.01
400	10.7	0.96	60.40
500	9.8	0.99	117.65

Table 5: Coagulation kinetics of OMUC for first order system

Coagulant dosage (mg/L)	10^3 K values (L/mg min)	R^2	C_0 (mg/L)
100	132.1	0.81	138.32
200	230.5	0.88	371.15
300	45.1	0.36	294.95
400	30.0	0.85	420.94
500	419.0	0.92	448.9

Table 6: Coagulation kinetics of OMUC for second order system

Coagulant dosage (mg/L)	10^3 K values (L/mg min)	R^2	C_0 (mg/L)
100	1.6	0.89	153.85
200	1.7	0.95	215.11
300	0.2	0.35	294.12
400	0.09	0.84	454.55
500	0.1	0.95	434.78

The accuracy of fit of the studied model (Equation 8) with the experimental data (with $R^2 > 0.90$) were significantly described by the linearised form of Equation 8. The k values are determined from the slopes of Equations 12 and 14 on plotting I/N vs time (second order) and ln N vs time (first order) respectively. The results presented in the aforementioned tables indicate that k values as deduced from respective kinetic plots (Fig. 2-5) are invariant with dosage variation. This may be attributed to the equal aggregation rate achieved by the varying coagulant dosages. Also, the variation of $k = f(T,\eta)$ is minimal, following insignificant changes in the values of temperature and viscosity of the effluent medium. In addition, the coagulation rate constant generally decreases with a decrease in the initial effluent concentration due to increase in repulsive double layer interactions.

These results are shown in Fig. 6 and 7. The observable pattern in most of the results is the decrease in concentration from initial value of 2028 mg/L. The decrease of turbidity with time reflects the fact that as the reaction progressed the amount of particle available for coagulation decreases. This behaviour reflects the complete dependence of turbidity on particle number (dropping) and particle size (increasing) over time[21].

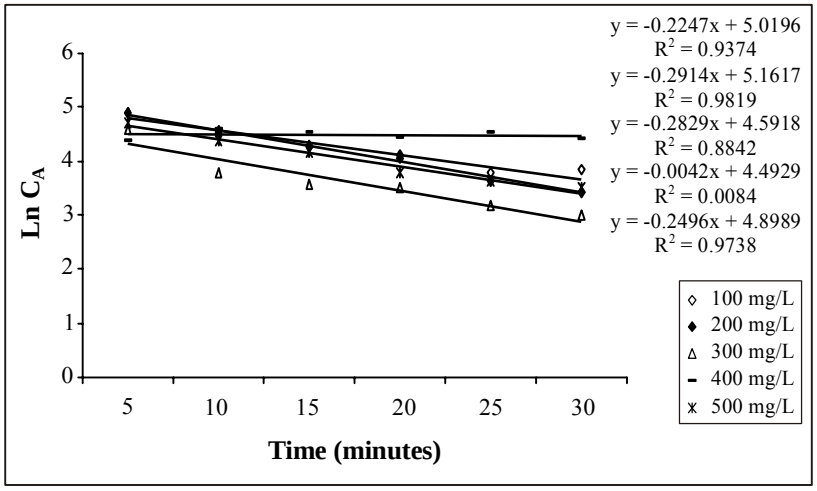

Fig. 2: Plot of ln C vs time for the coagulation of FCIE using aluminium sulphate

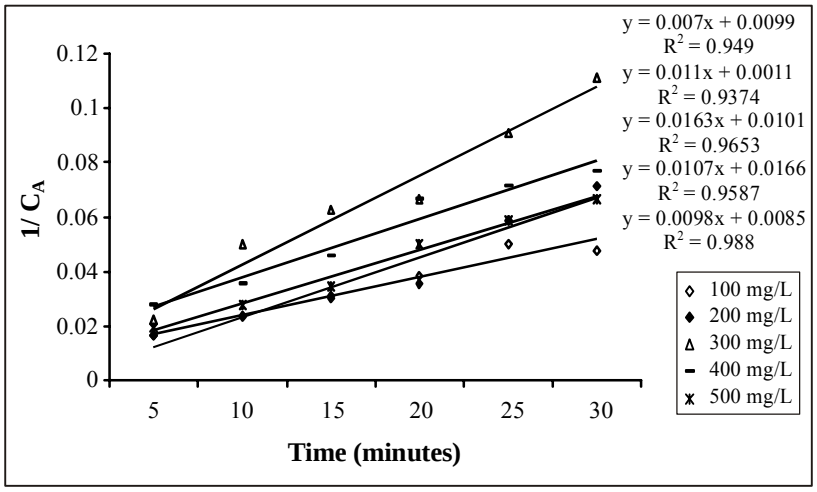

Fig. 3: Plot of 1/C vs time for coagulation of FCIE using aluminium sulphate

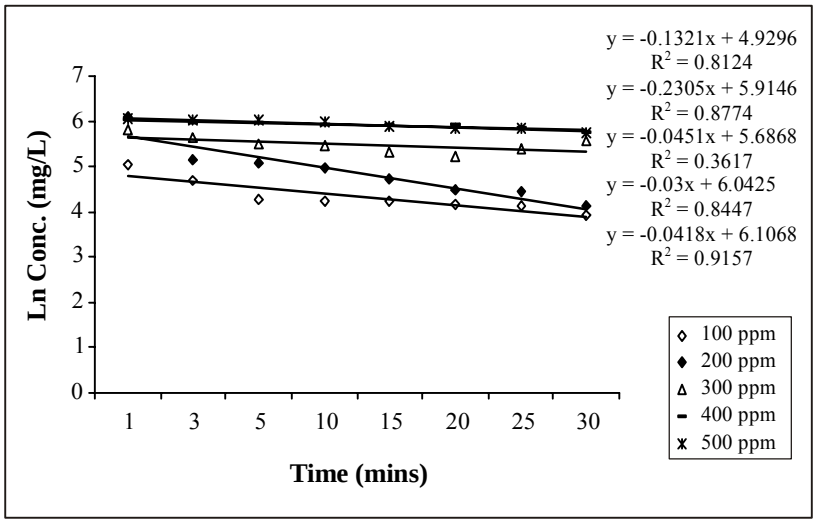

Fig. 4: Plot of ln C vs time for the coagulation of FCIE using OMUC

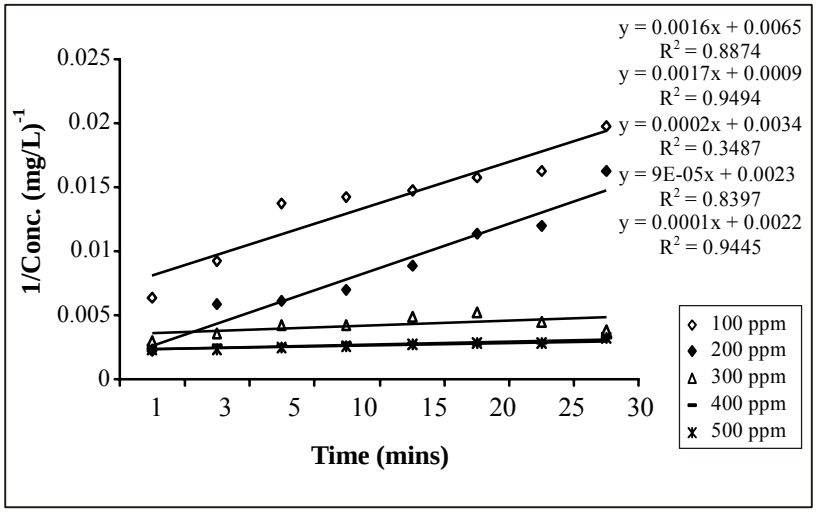

Fig. 5: Plot of 1/C vs time for the coagulation of FCIE using OMUC

The sharp decrease in turbidity from 0-5 minutes is in agreement with previous works and may be a product of either floc mechanism or combination of entrapment bridging mechanism[22]. At 100 and 400 mg/L respectively the ability of OMC and alum to remove turbidity from the fibre-cement effluent was at the optimum. For most of the coagulant dosages the concentration values in Fig. 6 and 7 are comparable indicating that the OMUC can be used for turbidity removal in FCIE.

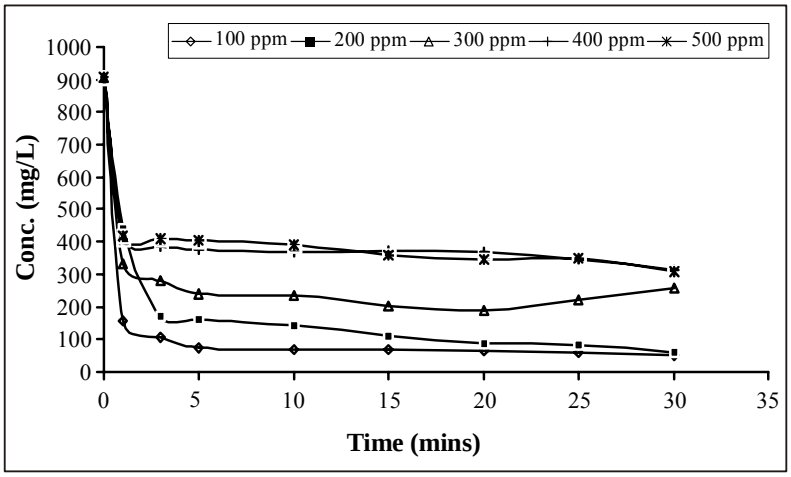

Fig. 6: Concentration versus time for varying dosage of OMUC coagulant at pH 12.2

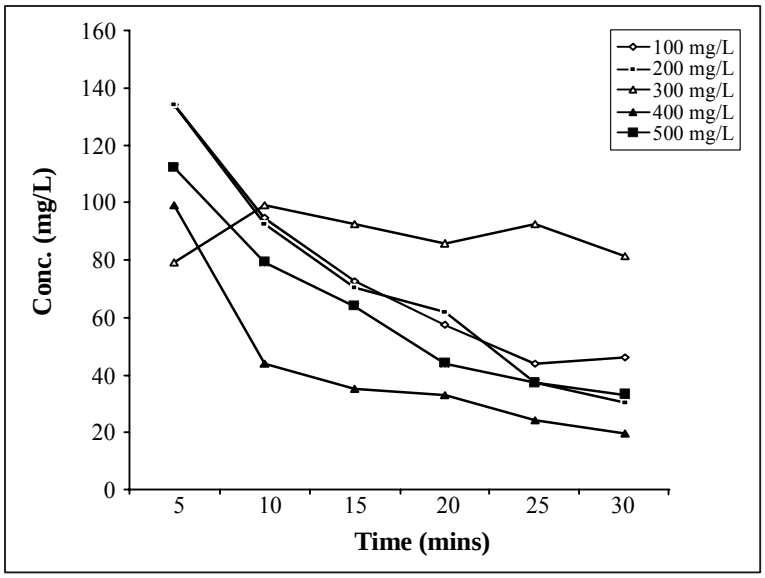

Fig. 7: TSS Removal at Varying doses of Aluminium Sulphate

CONCLUSION

The coagulation rate constants for the alum and okra mucilage removal of particulate matter from a fibre-cement effluent have been evaluated by using the turbidimeter to monitor the changes in the turbidity of the suspension with time. The concentration values were derived from the turbidity readings and then used to prepare the first and second order plots and the slopes determined to obtain the coagulation rate constants.

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