STUDIES ON THE COAGULATION AND FLOCCULATION OF COAL WASHERY EFFLUENT: A KINETIC APPROACH.

By

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ABSTRACT

The effect of coagulant type, coagulant dosage and pH variation on the coagulation of coal washery effluent has been investigated at room temperature using various coagulants. Turbidity measurement was employed using the nephelometric standard method. In addition, the coagulation reaction rate constant, K, the order of reaction, α and the distribution of particles were also determined.

The results show that for coagulant mixture containing $FeCl_3$ and lime, the maximum turbidity removal occurred at pH of 4 and 2 for the $FeCl_3$/lime ratio of 30:400 and 500:1000 respectively. The least and highest values for order of reaction (α) recorded for the dosage variations are 2.0 and 3.0 respectively. With the exception of α value computed for 50 mgl^{-1} $FeCl_3$+1000 mgl^{-1} lime, there is no regular pattern in the variation of α in response to the increment of pH from 2 to 10. The over all results show that with the exception of few blends, the computed order of reaction, α, and rate constants, K, agree with previous works reported in the literature.

It is concluded that jar test and nephelometric method still provide the convenient and routine means of flocculation studies. The results obtained confirmed that the theory of fast coagulation holds for the coagulation of coal washery effluent using the coagulants investigated and at the conditions of the experiment.

INTRODUCTION

Coagulation and flocculation are of immense importance in waste water management. They are employed to separate suspended solids from water. Finely dispersed solids (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)

Except under idealized laboratory conditions, colloids stability is a very complex issue. Several factors can operate between the colloids; some attractive others repulsive. These forces may react in different ways upon variation in the conditions (pH, temperature, salt concentration, etc) surrounding them. One must also consider the rate at which two particles approach each other. Both static and dynamic properties are of significance. (Sudan, 1988)

The most frequently occurring forces between colloids are: Vander Waal's forces, electrostatic forces, and forces due to adsorbed macro molecules. In addition, specific forces may act in special cases. For instance, magnetic colloids particles may attract each other magnetically or chemical bond may be found between the colloids (O' Melia, 1978). Some of these forces, such as Vander Waal's and electrostatic repulsion are active at long range such that their impacts are felt over several tens of nanometers. It is on this phenomenon that the fundamental picture of colloids stability is based. Chemical bonds are short range and therefore can only come into effect in the absence of long range repulsion.

The flocculation of particles in a liquid depends on collision between particles, caused by their relative motion. This relative motion may be caused by Brownian movement, by fluid movement giving rise to velocity gradient or by particle motion due to an external force (e.g. gravity). The rate of flocculation is determined by the collision frequency induced by the relative motion. When this collision is by Brownian movement, it is called perikinetic flocculation. That which is caused by velocity gradient is called Orthokinetic flocculation. 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 includes two separate and sequential steps, a collision step followed by attachment step (WST, 2005). The collision steps could be product of Brownian motion, fluid shear or differential sedimentation.

Brownian motion, only affecting the movement of particles (<1μm), is the random motion of particles caused by the thermal energy of surrounding liquids. Fluids sheer, either laminar or turbulent, is caused by velocity gradients that occur in all real flow fluids. Differential sedimentation is produced at a rate associated with the gravity and buoyancy forces. In this process, aggregated, dense and large particles can settle faster than smaller or less dense ones. (Lentech, 2005, Thomas & Judd, 1999)

The kinetic coagulation was first systematically described by Von Smoluchowski (1917) and his research still serves as the foundation for modeling the coagulation process. He proposed collision frequency theory based on Brownian motion and fluid shear. These studies were based on a rectilinear collision model, assuming that the particle motion is linear until collision occurs. This conventional model is known to over predict particle collision frequencies to a great extent since it neglects hydrodynamic interactions and short range forces between approaching particles (Han & Lawler 1992, O' Melia 1978). One of the on going corrective measures against the problem of over prediction is the use of Hi-Tech particle counter.

The application of coagulation/flocculation is very evident in the level of success attained in water treatment technology. While various works have examined coal effluents in different parts of the world, little or none has been done in Nigeria in spite of the abundance of coal. In this work, attempt is made to use coagulation/flocculation as a tool to investigate the aggregation process while varying the pH, dosage and type of coagulants.

THEORETICAL BACKGROUND AND PRINCIPLES DEVELOPMENT.

Turbidity provides an estimate of the muddiness or cloudiness of water due to clay, silt, finely divided organic and inorganic matter, soluble colored organic compounds, plankton, colloids and microscopic organism (Greenberg et al, 1992, Jin, 2005).

Based on the work of Metcalf & Eddy (2003), the relationship is as follows:

TSS (mg/l) = (TSS_f). (T)

where TSS = total suspended solid, mg/l

(TSS_f) = factor used to convert turbidity reading to total suspended solids (mg/l)

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 light absorbing properties of suspended materials. In spite of this limitation, 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 (Ma, 2001, Van Zanten, 1992).

The particle concentration during early stages of coagulation can be determined directly, by visual particle counting or indirectly, from turbidity (spectrophotometer or light scattering) measurement (Metcalf & 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 the 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 (Van Zanten et al, 1992).

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

$$\frac{dC_n}{dt} = \frac{1}{2}\sum_{i+i} k_{in} C_i C_j - C_n \sum_{i=1} k_{in} C_i \quad \text{.....(1)}$$

Where $C_n(t)$ is the time-dependent number concentration of n-fold cluster, t is the time, and K_{ij} 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 diffusion and initially having monodispersed suspension. The implication of this is that the analysis attempts to quantitatively interpret the kinetics of rapid coagulation on the basis of diffusional (Brownian) motion of which is best studied during the early parts (say $t <$ 30 min) of coagulation process. (Fridriskhberg et al, 1984; Van Zanten,

1992, Holthof et al, 1996; Ma et al, 2001; Maiti et al, 2004; Suidan, 1998; WST, 2003).

According to the works of Fridriskhsberg (1984) and Danov et al, (2001), it was shown that the rate of depletion of particle count (TSS or turbidity removal) can generally be represented as

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

Based on the Brownian controlled (diffusion controlled) rapid coagulation.

Along this line, the generalized case of equation 2 can be used to determined the aggregation constant K_f and order of the reaction, α by taking [Ln] of both sides of equation 2. Mathematically, it translates to:

$$\ln\left(-\frac{dc}{dt}\right) = \ln k + \alpha \ln C \text{.....} \text{.....(3)}$$

A plot of *ln* (-γ) versus *ln C* gives a slope of α and intercept of *Ink,* from which *K* is determined.

For simple monodispered aggregation model, the rate of coagulation can be found using equation (1) or (2). The implication is that for Brownian controlled coagulation, equation 1 and 2 are equal (Danov et al, 2001, Smoluchowski, 1916, Fridriskhberg, 1984).

The process of aggregation is very complex one, and for the complicated particles, equation 1 can be solved exactly to give for a generalized case of particle of any i^{th} order, the following general exact solutions:

$$\frac{C_i}{C_0} = \frac{(t/\tau^t)^{i-1}}{(1+t/\tau^{ti})^{i+1}} \text{.....} \quad \text{.....(4)}$$

where $\tau^t = 2/KC_0$

$\tau = 1/KC_0$ (*Coagulatio n* time)

C_i = *particle* distributi on Concentrat ion

The values of $i = 1, 2, 3$

Hence when,

i=1 (Primary particle/singlet)

i= 2 (Secondary particle/doublet)

i= 3 (Tertiary particle/triplet)

Therefore, for generalized equation (4):

When *i*=1 $C_1 = \frac{C_0}{(1+t/\tau^t)^2}$ .....(5)

when *i*=2 (twins) $C_2 = \frac{(t/\tau^t)C_0}{(1+t/\tau^t)^3}$ .....(6)

when *I* = 3 (triplets) $C_3 = \frac{(t/\tau^t)^2 C_0}{(1+t/\tau^t)^5}$ .....(7)

MATERIALS AND METHODS

MATERIALS

The coal washery effluent was collected from now moribund Coal Washery Unit situated at Akwuke in Enugu, Enugu State, Nigeria. Turbidimeter (Model no: WZS-

185) was calibrated with solution of known turbidity. The effluent was measured using Delta 320 pH meter. The coagulants: Iron III chloride, Alum, Lime and Starch used were of analytical grade. Other materials utilized are six place laboratory stirrer, beakers, magnetic stirrer, alkalinity measurement kits, two aluminum rods/electrodes, 12 volts transformer, digital multimeter and connecting wires.

METHODS

JAR-TEST PROCEDURE

Coagulation and flocculation was performed using bench scale jar test. Suspension were subjected to 20 minutes of rapid mixing, 15 minutes of slow mixing and followed by 30 minutes of settling. Coagulants ($FeCl_3$, Alum, Lime, and Starch) were added at the beginning of the rapid mix. During settling, samples were withdrawn using pipette from 2 cm depth and analyzed for turbidity. Coagulation pH was not adjusted during the jar test. At the end of 30 minutes settling, the remaining samples were analyzed for pH and alkalinity. All jar tests were performed at a temperature of 28 $^{o}C \pm 2\ ^{o}C$. Two types of measurement were performed. The first type was to determine the effect of coagulant dosage and coagulant mix on the coagulation and flocculation of the coal washery effluent. The second was to determine the effect of pH variation on the coagulation process.

The minimum turbidity selected for calibration was 3 NTU and the maximum at 10,000 NTU. After calibration, the sample was measured by inserting the tube containing the sample in the space provided for it on the turbidometer.

Effluent pH was measured by Delta 320 pH meter. The instrument was first calibrated with solution of known pH. Two point calibration methods was adopted in which two buffers of pH 4.01 at 25-30 ^{o}C and 7.0 at 25-30 ^{o}C was selected for calibration. After calibration, the pH of samples was measured by dipping the probe into the sample. The sample was constantly stirred until a stable pH was obtained. The pH of the sample was varied between 2 and 10 using caustic soda and sulphuric acid.

The turbidity was measured using the nephelometric standard method. This method is based on the comparison of the intensity of light scattered by a standard reference suspension under the same conditions (Greenberg et al, 1992).

The experimental parameters of bench-scale tests were determined based on laboratory

manual of simplified procedures for water examination (AWWA, 1977) and handbook of public water systems (Bagwell et al. 2001).

RESULTS AND DISCUSSION

Jar Test Results for Variable Dosage

The results obtained in the unit of turbidity (NTU) were converted to concentrations (mg/l) by multiplying by a factor of 2.35 (Metcalf & Eddy, 2003). These results (Concentration units only) are presented in fig 1 to fig 8.

The general trend in all the results is that the turbidity decreases with time. The highest degree of coagulation is witnessed within the first five minutes. Indeed, for most of the runs, more than half of the coagulation takes place within the first five minutes. The decrease of turbidity with time reflects the fact that as the reaction proceeds, the amount of particle available for the coagulation decreases. The sharp decrease in the turbidity between 0 to 5 minutes is a product of either floc mechanism or combination of entrapment-bridging mechanism (WST, 2005).

Fig. 1 shows that as the dosage of alum increases, the rate of particle removal increases also. A particle concentration of note is the 500 mg/l of alum. The decrease in turbidity is almost constant. This simply reveals that the dosage is large enough for total destabilization and sweeping almost instantly.

In fig 2, the concentration of 1000 mg/l lime has the highest TSS removal while the concentration of 200 mg/l has the least turbidity removal. In essence, the gentle curve of 200 mg/l alum in fig 2 is an indication of destabilization controlled by bridging. Interestingly, the curves of concentration of 400 mg/l to 1000 mg/l alum indicate the domination of sweep floc. This is a very common phenomenon in lime and alum. The implication for the concentration ranges (400 mg/l – 1000 mg/l lime) is that starting from 400 mg/l lime the coagulation mechanism transform from bridging to floccing. This is supported by the closeness of the curves of the stated range which practically remain constant from the 5^{th} minutes (WST, 2005). Meanwhile it is important to note that the prevalence of bridging in fig 1 is common to $FeCl_3$ during coagulation.

Figs 3 and 4 are products of coagulation process involving lime and starch respectively. Both figs 3 and 4 show curves

that steep gently. These are expected for unblended coagulation. The curves depict the situation in which destabilization and aggregation dominate. Generally, aggregation dominated mechanism are associated with unblended coagulants; and have been known to be associated with lime and starch (Teilizzi,1994).

Generally, for the figures 1 to 8, the general trend is the reduction of concentration of particulate with time and the mechanisms dominating can fall into any of the ones discussed above (Greenberg, et al, 1992). The sharp reduction in TSS observed in figs 1 to 8 is in accordance with theory of fast coagulation proposed by Smoluchowski in 1917. In short, in real life application of coagulation, 90% TSS removal is usually achieved within first 5 minutes (WSR, 2005).

This rapid coagulation and settling is facilitated based on the energy acquired during the rapid stirring in which two particles on collision course must have sufficient kinetic energy to agglomerate into flocs for rapid settling (Holthof, et al, 1996). Once this energy barrier is cleared, the net interaction energy is all attractive. No further repulsive areas are encountered and as a result the particle agglomerate leading to fast turbidity removal as observed in figs 1 to 8.

Also observing from figs 1 to 8 shows that the turbidity reduces slowly between 5 minutes and 30 minutes. This is expected and can be accounted for due to very small sizes of the particle remaining after the initial 5 minutes of coagulation. Of course, to a large extent, the rate of settling reduces with the reduction in concentration of the suspended particles. Hence, both the size and concentration of the particle contribute to the slow decrease in values of turbidity between 5 and 30 minutes (Fridriskhberg et al, 1984).

In coagulation process involving large doses of Alum and $FeCl_3$, colloidal entrapment dominates. This is fairly represented in figs 1 and 2. In the mechanism, aluminum and iron salts precipitate a hydrous metal oxide which initiates some charge neutralization of the colloids. Most of the colloids are then literally swept from the bulk of the water by becoming enmeshed in the settling hydrous oxide floc

In the case of combination of inorganic primary coagulants and organic polyelectrolytes as represented in the blends of [$FeCl_3$ and starch (fig 6)] and [Alum and Lime (fig 7)], two mechanism are involved. The mechanisms are bridging and charge neutralization. For this phenomenon, the inorganic and organic salts initiate the process of bridging which is complimented by the charge neutralization contributed by inorganic salts (Jin, 2006). At over dose concentration of any of the coagulants, it can lead to sweep floc.

One important fact is that the species of ions, the blends of the coagulants and competing mechanism are among the factors that determine the final observable behavior of the coagulation process.

Jar Test Results for Variable pH

The jar test results for the variable pH are graphically shown in figs 5, 6, 7 and 8 for the various blends investigated. Each of the blends was subjected to jar test at the following pH: 2, 4, 6, 8 and 10. The readings were taken at intervals of 3, 5, 10, 15, 20, 25, 30, 35, 40 and 45 minutes.

The trends in figs 5 to 8 show that the concentration (turbidity) of TSS reduces with time. A close comparison between figs 1 to 4 and figs 5 to 8 show a similar trend among the plots. This is a strong indication that similar coagulation mechanisms are responsible for the coagulation behavior.

In fig 5, there is no particular trend developed by the curves in response to pH variation. However, the fact remains that the best coagulation is achieved under acidic conditions (pH = 4). One can argue that the blend dosage (especially the dose of lime) can cause a major shift in the response of coagulation to pH.

In fig 6, it is observed that process developed a definite response with respect to the pH of the effluent. The highest TSS removal (best coagulation) was achieved at pH of 2; followed by pH of 4, 8 and finally 10. In effect, as the pH increases, the coagulation efficiency decreases. This is in agreement with previous works considering that $FeCl_3$ are known to perform better in acidic medium (Terilizzi, 1994).

A look at fig 7 simply shows that the best coagulation is observed at pH of 6. This is expected considering that lime has been known to perform better under alkaline medium. This explains why lime is usually

used to tone the pH of acidic coagulants or acidic medium (Suidan, 1988). The combination of lime and alum is usually employed because the lime provides for alum the alkaline medium needed for optimum performance of alum. Alum performs best under alkaline medium (Lentech, 2005). Observe that at low pH of 2, the blend of fig 7 performed poorly. In short, the least coagulation was obtained at the pH of 2, showing that alum cannot function efficiently under acidic medium. A look at fig 8 simply shows it follows a similar pattern as fig 7. The best coagulation is achieved at pH of 6 and the least at pH of 2. Similar explanation offered for the behavior of fig 7 holds for fig 8. For all the figures shown for the pH variation, the turbidity reduces with time.

Coagulation Reaction Constants

The values obtained for the reaction constants are shown in tables 1 to 3. Table 1 presents the values of K and α for variable dosage while Tables 2 and 3 present same for the variable pH. Generally, both K and α are determined from model equation $(-\gamma) = KC^{\alpha}$. Linearized forms of the equation give a slope of α and intercept of K when produced graphically.

Reaction Constants for Variable Dosages

A look at the value of K shows that the least values of K is 7.49×10^{-8} $ml^2.min^{-1}$ while the highest is 04.53×10^{-5} $ml.mg^{-1}.min^{-1}$. Observation shows that the blends with very high values of α maintain low values of K. As the values of α decrease, the value of K tends to increase. The relationship observed between α and K is expected. Since, K is basically rate per concentration, and K is associated with energy barrier, (KT), it is understandable that for higher α to be obtained, a lower K is a necessary condition for that (Fridriskhsberg, 1984).

The values of K and α obtained in this work are consistent with previous studies of Brownian coagulation (Van Zanten et al, 1992, Jin, 2005). The ranges of α are between 2 and 3. This is expected and is consistent with the theory of Smoluchowski, which is the foundation of Brownian controlled coagulation, (Holthof et al, 1996), Fridriskhberg, 1984). However, any discrepancy in the expected corresponding behavior between α and K could be

attributed to the retarding effect of hydrodynamic interaction (Jin, 2005, Nicholls, 1979).

Reaction Constants for Variable pH

The values of α and K for variable pH are shown in tables 2 and 3. Form table 2, the least and highest values of α are 0.497 and 3 respectively while those of K are 1.02×10^{-8} $ml^2.mg.^{-2}.min^{-1}$ and 0.34 $mg^{0.5}l^{-0.5}$ min^{-1} respectively. With the exception of α equal to 0.612, 0.518 and 0.497, the rest lie between 1 and 3. The values of α between 1 and 3 are within the range of expected order of reaction in coagulation process. However, it is important to note that majority of works in coagulation process have shown the order of reaction to be mainly 2. It is pertinent to point out that for 50 mg/l $FeCl_3$ +1000 mg/l lime, there is increase in the α as the pH increases from 4 to 8. Equally, there is increase in the rate of reaction. This trend is not true for 30 $mgl^{-1}/FeCl_3/400$ mgl^{-1} lime. This regular trend for the former can be explained by the prevalence of internal ionic quasi-equilibrium among alum, lime and water ions such that it partially balances out the common hydrodynamic interference responsible for most deviation in coagulation processes such that only pH is having controlling influence on the process (Stochi, 1990, Hawley & Hampel, 1973, Anderson, 1979, Fridriskhberg, 1984).

From table 3, the least and highest values of α are 0.5 and 2 respectively while that of K are 4.63×10^{-4} l/mg.min and 0.324 min^{-1} respectively. With the exception 0.5, 0.67 and 0.7, the other values of α ranges from 1 to 2. Generally, there is no consistent pattern in the variation of α and K as the pH increases.

Particle Distribution Behaviour

The particle distribution behaviour of the coagulation process is presented here. The distribution behaviour is presented in the graphical form of concentration versus time. The particle distribution in coagulation can be denoted by C_i, where C stands for concentration and subscript i stand for 1, 2, or 3. For primary (singlets) particles, $i=1$, and for secondary (doublets) particles, $i=2$. Finally, for triplets, $i=3$. The singlets are composed of monomers while doublets are composed of double monomers. Finally, the triplet is composed of three monomers.

The particle distribution plots principally show the pattern and distribution of aggregation ions/particles as they floc into

visible blobs. The discussion is presented in three cases as follows:

Case I

One major observation is the case in which the values of [C_3 and $\sum C_i$] are so close such that their variation with time is almost the same. Also in the same vain, the values of C_2 and C_1 are also so close such that their variation with time is same. This situation is represented in fig 9. Another major observation is that there exist wide margin of difference in concentration values between pair of [C_3 and $\sum C_i$] and pair of [C_2 and C_1]. This phenomenon can be accounted for by the flocs greater ability to withstand shear forces and greater resistance. The graph shows that the value of C_1 practically remained constant, an indication of mainly charge neutralization dominated mechanism (Nicholls 1979, Ø degaard,1979) with high energy and resistance barrier.

Case II

Fig. 10 shows the particle distribution for 500 mg/l Alum + 800 mg/l lime. There is apparent sharp decrease in C_1 between time zero and five minutes. This is an indication of coagulation process controlled by mechanism of colloidal entrapment. The mechanism is prevalent in system in which the coagulants added are relatively of large doses ensuring near complete floc sweep within the first five minutes of the coagulation.

Case III

The distribution of particle expected in typical coagulation process is shown in fig 11 and 12. It represents a normal curve ideally generated in theoretical coagulation process. The curves are for 400 mg/l lime unblended and 250 mg/l starch unblended. These curves are expected in coagulation where there is absence of colloidal entrapment and high shear resistances. Mainly, the dominant mechanism in the graphs is the charge neutralization combined with low bridging to ensure moderate speed of coagulation as represented by both graphs (Fridriskhberg, 1984, Suidan, 1988). The discrete nature of formation of C_1, C_2, and C_3 is also associated with low energy barrier which is prevalent in alum (Lentech, 2005).

CONCLUSION

Jar test in conjunction with nephelometric method (turbidimetry) still provide routine and convenient means of carrying out flocculation and coagulation studies; in the absence of high tech particle counters. Once the measurement on the change of turbidity

with time is taken, the aggregation process will be analyzed.

The experimental result in this research, with reference to K and α agreed with the result for flocculation kinetics given by Jin(2005) Holthof *et al*(1996) and Van Zanten *et al*(1992). The fact is that there is no common regular pattern in the variation of K and α as the blends, types and pH of the coagulant varied. However, the α and K vary in inverse form.

The pH is an important factor in coagulation process. It is observed that a coagulant known to perform optimally under acidic conditions (e.g. $FeCl_3$) and alkaline conditions (e.g. lime) conforms to that fact. The response of the turbidity changes to dosage variations does not follow a definite trend.

The amount of reduction of TSS from the initial value to its value at 5 minutes mark apparently indicates a process of rapid coagulants. This justifies the measurement time of 30 minutes and confirms the theory of rapid coagulation.

Table 1: Representative results of *K*, α and rate equations for variable blends

Blends	K-values	α	Rate equation (mg/l min)
1000mgl^{-1} Alum+500mgl^{-1} lime	7.49x10^{-8} l.^{2}mg.$^{-2}$min^{-1}	3.0	$-\gamma = 7.49 \times C^3$
500 mg/l Alum+800mgl^{-1} lime	4.53x10^{-5} l.mg^{-1}.min^{-1}	2.0	$-\gamma = 4.53 \times C^2$
400 mgl^{-1} lime only	5.64x10^{-6} l.mg.$^{-1}$.min^{-1}	2.0	$-\gamma = 5.64 \times C^2$
250 mgl^{-1} Starch only	3.85x10^{-5} l.mg^{-1}min	2.0	$-\gamma = 3.85 \times C^2$

Table 2: Representative results of *K*, α and rate equations for variable pH

	50 mgl^{-1} $FeCl_3$ + 1000 mg*l*$^{-1}$ Lime			30mg*l*$^{-1}$$FeCl_3$ + 400mg*l*$^{-1}$ lime		
pH	k-values	α	Rate equation (mg/l min)	k-values	A	Rate equation (mg/l min)
2	0.19 mg$^{0.4}$/*l*$^{0.4}$min	0.612	$-\gamma = 0.19xC^{0.612}$	1.02x10^{-8} l.^{2}mg.$^{-2}$min^{-1}	3.0	$-\gamma$=1.02x10^{-8}C^3
4	0.34 mg$^{0.6}$/*l*$^{0.5}$min	0.518	$-\gamma = 0.34xC^{0.518}$	0.337 mg$^{0.5}$l$^{-0.5}$ min^{1}	0.497	$-\gamma$= $0.33xC^{0.497}$
6	1.37x10^{-3} min^{-1}	1.000	$-\gamma$ = 1.37x10^{-3} C min^{-1}	8.56x10^{-3} min^{-1}	1.0	$-\gamma = 8.5x10^{-3}C$
8	7.20x10^{-6} *l*/mg min	2.00	$-\gamma = 7.20x10^{-6}C^{2.0}$			
10				4.26x10^{-3} min^{-1}	1.0	$-\gamma$= 4.26x10^{-3}C

Table 3: Representative results of *k*, α and rate equations for variable pH

	500 mg*l*$^{-1}$ Alum + 1000mg *l* $^{-1}$ Lime			200 mg*l*$^{-1}$ Alum + 1000 mg/*l* Lime		
pH	k-values	α	Rate equation (mg/l min)	k-values	α	Rate equation (mg/l min)
2	0.013 min^{-1}	1.0	$-\gamma = 0.01_3 \times C$	0.324 min^{-1}	1.0	$-\gamma = 0.32$ C
4	0.015 min^{-1}	1.0	$-\gamma = 0.015$ C	4.63x10^{-4}l/mg.min	2.0	$-\gamma$ = 4.63x10^{-4}C^2
6	0.241mg$^{0.5}$/l$^{0.5}$min	0.500	$-\gamma = 0.241$ C$^{0.5}$	0.385mg$^{0.5}$l$^{-0.5}$ min	0.5	$-\gamma = 0.385$ C$^{0.5}$
8	0.0702 mg$^{0.4}$/l$^{0.4}$min	0.670	$-\gamma_0$=0.0702xC$^{0.67}$	0.07 min^{-1}	1.0	$-\gamma = 0.070$ C
10	0.201 mg$^{0.3}$/l$^{0.3}$.min	0.700	$-\gamma = 0.201xC^{0.7}$	1.68 x 10^{-3} min^{-1}	1.0	$-\gamma$ =1.68x10^{-3} C

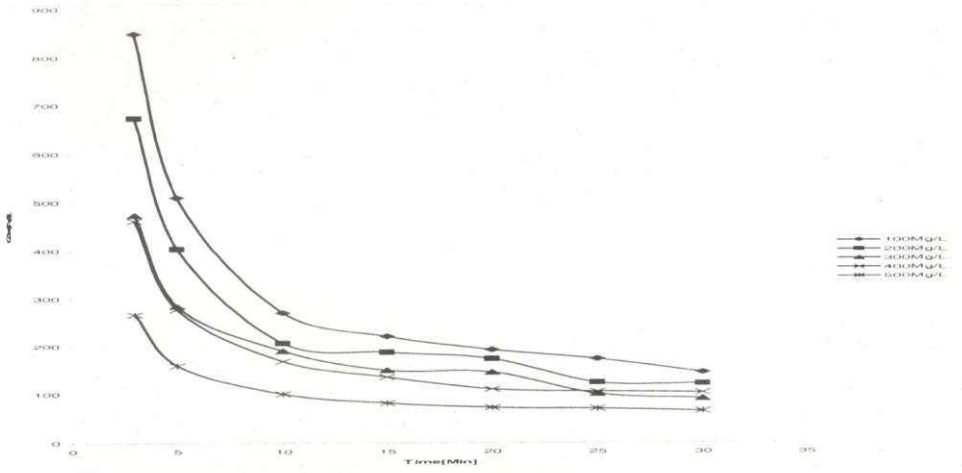

Fig 1: Tss Removal at 1000Mg/L $FeCl_3$ and Varying Alum

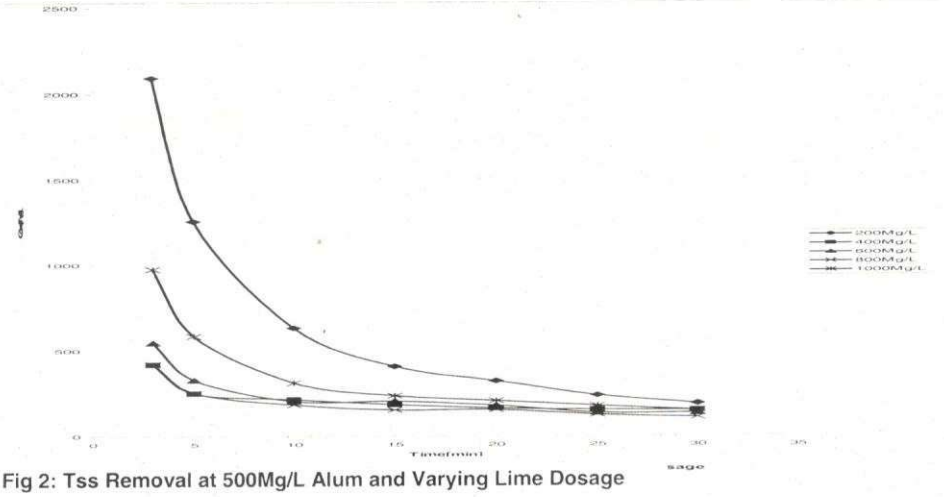

Fig 2: Tss Removal at 500Mg/L Alum and Varying Lime Dosage

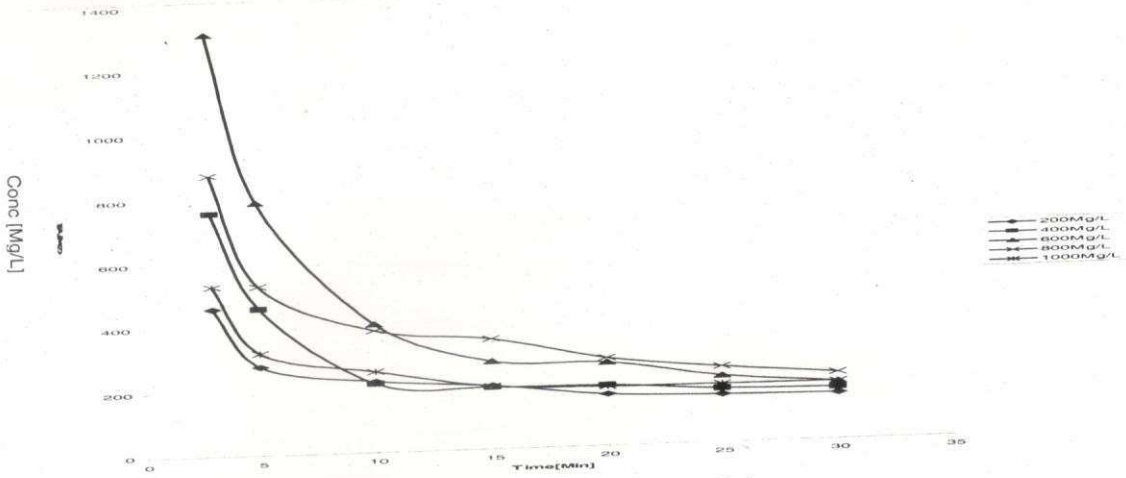

Fig 3: Tss Removal at Varying doses of Lime Only

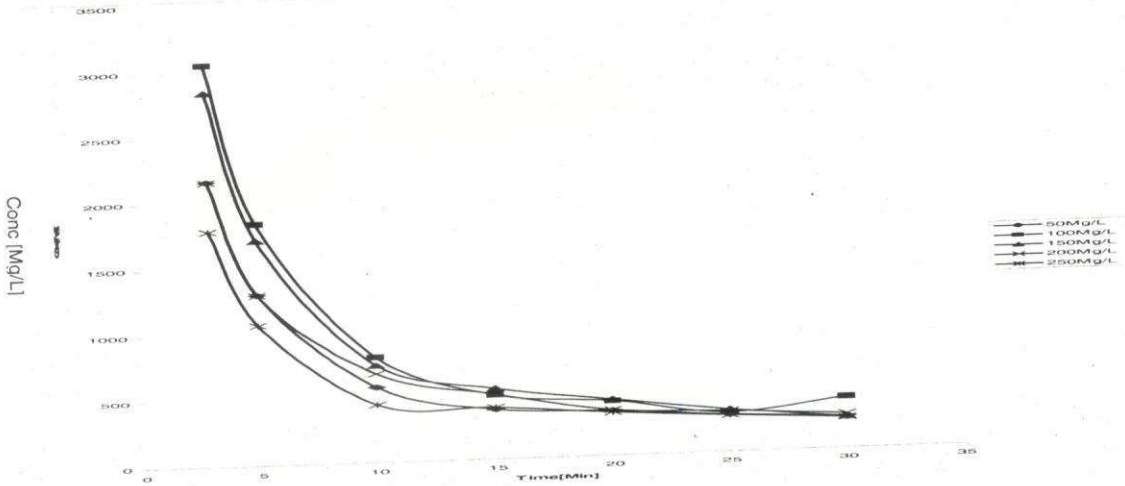

Fig 4: Tss Removal at Varying Starch dosages

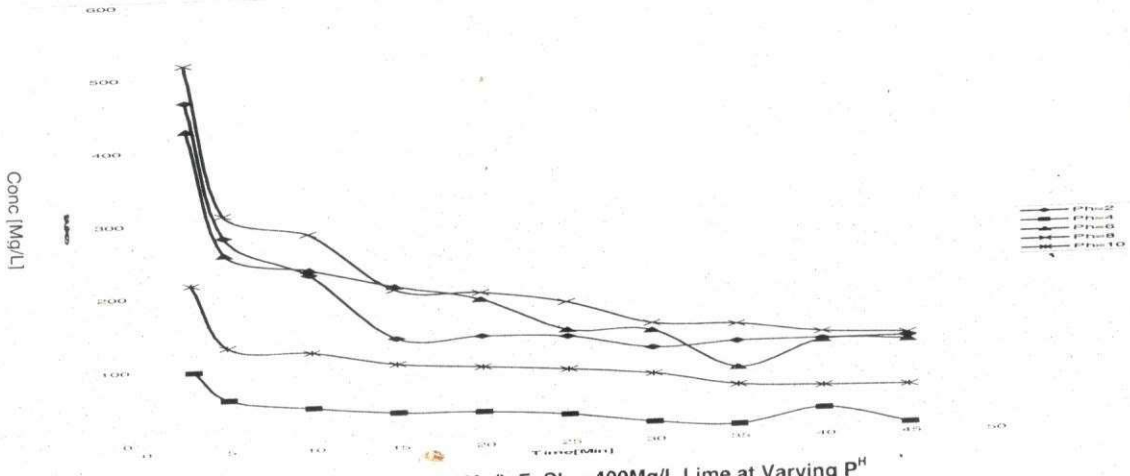

Fig 5: Tss Removal of 30Mg/L $FeCl_3$ + 400Mg/L Lime at Varying P^H

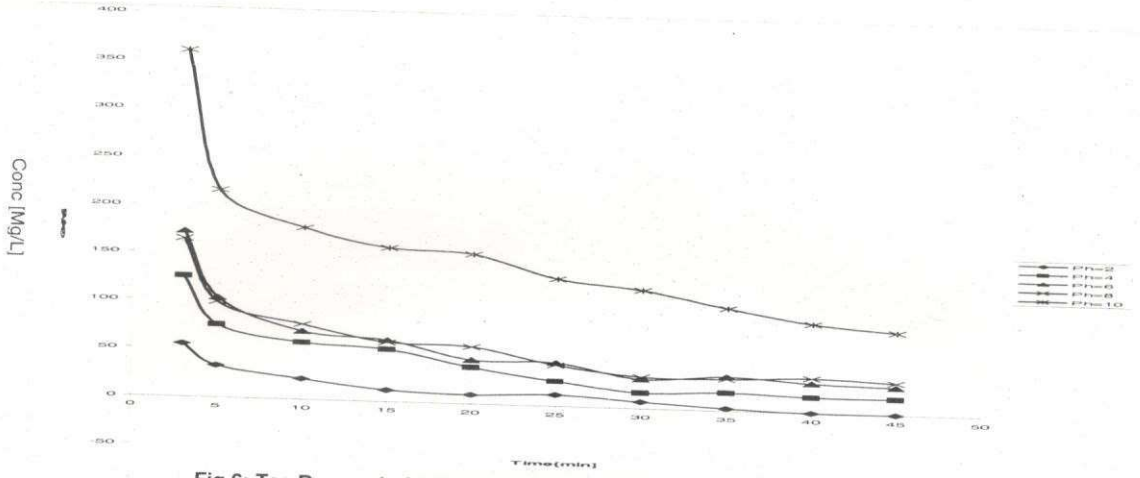

Fig 6: Tss Removal of 50Mg/L $FeCl_3$ + 1000Mg/L Lime at Varying P^H

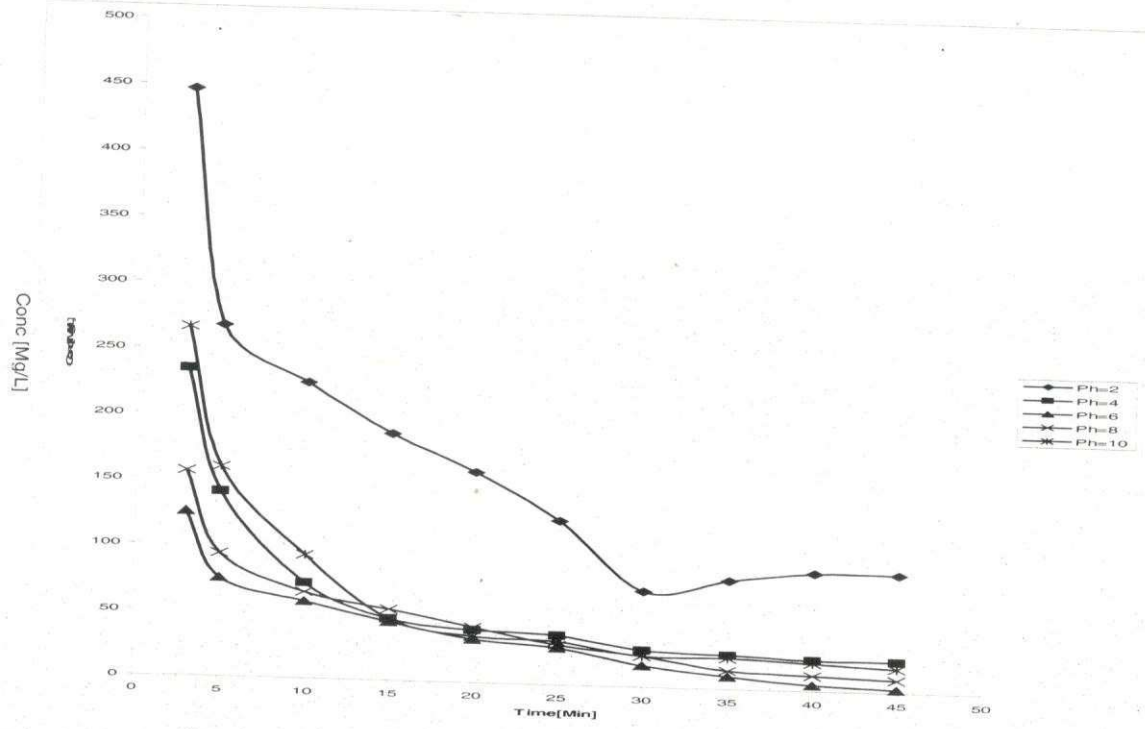

Fig 7: Tss Removal of 200Mg/L Alum + 1000Mg/L Lime at Varying P^H

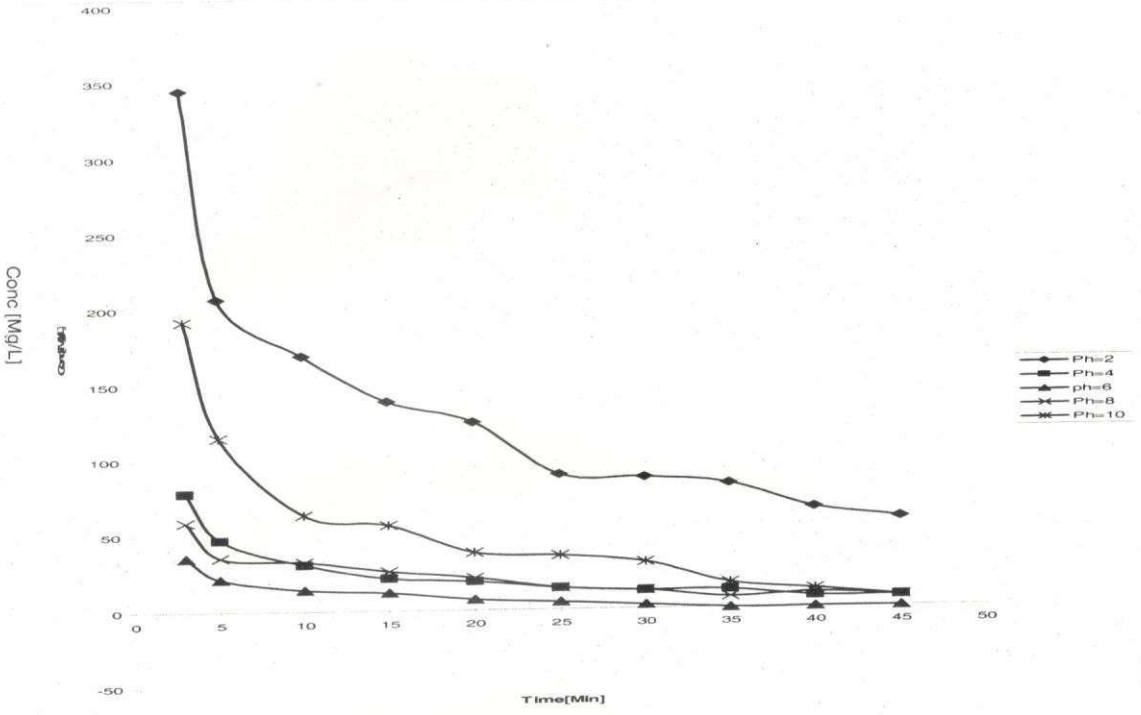

Fig 8: Tss Removal of 500Mg/L Alum + 1000Mg/L Lime at Varying P^H

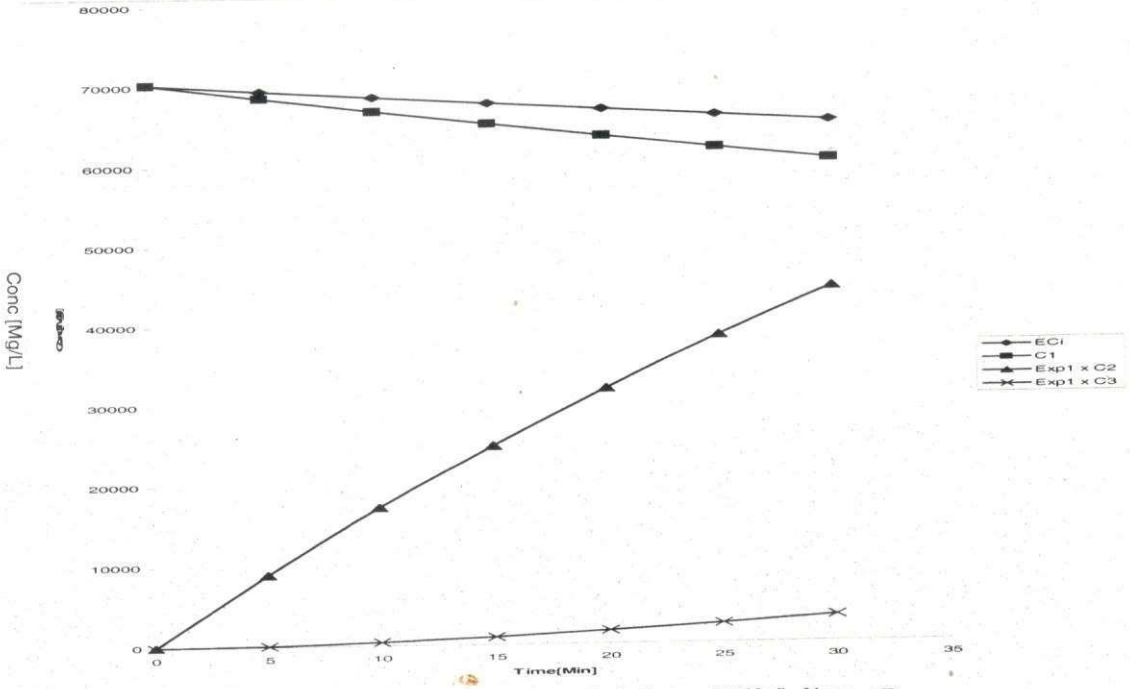

Fig 9: Particle distribution plot for 1000Mg/L Lime + 500Mg/L Alum

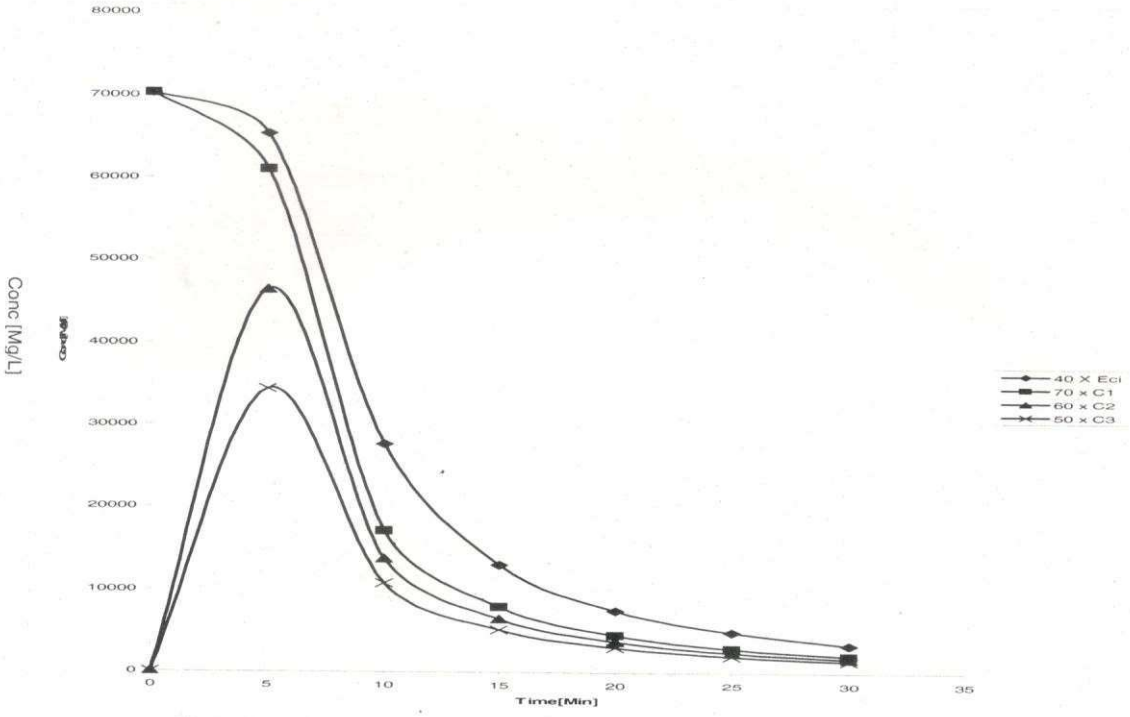

Fig 10: Particle distribution plot for 500Mg/L Alum + 500Mg/L Lime

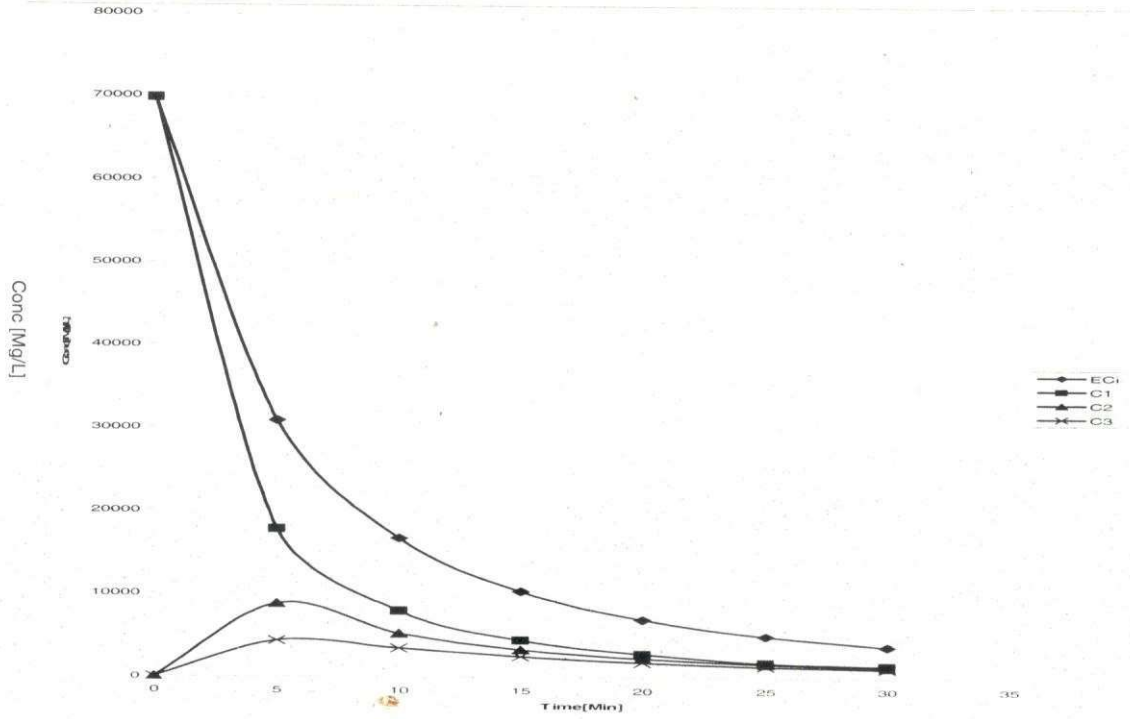

Fig 11: Particle distribution plot for 400Mg/L Lime Only

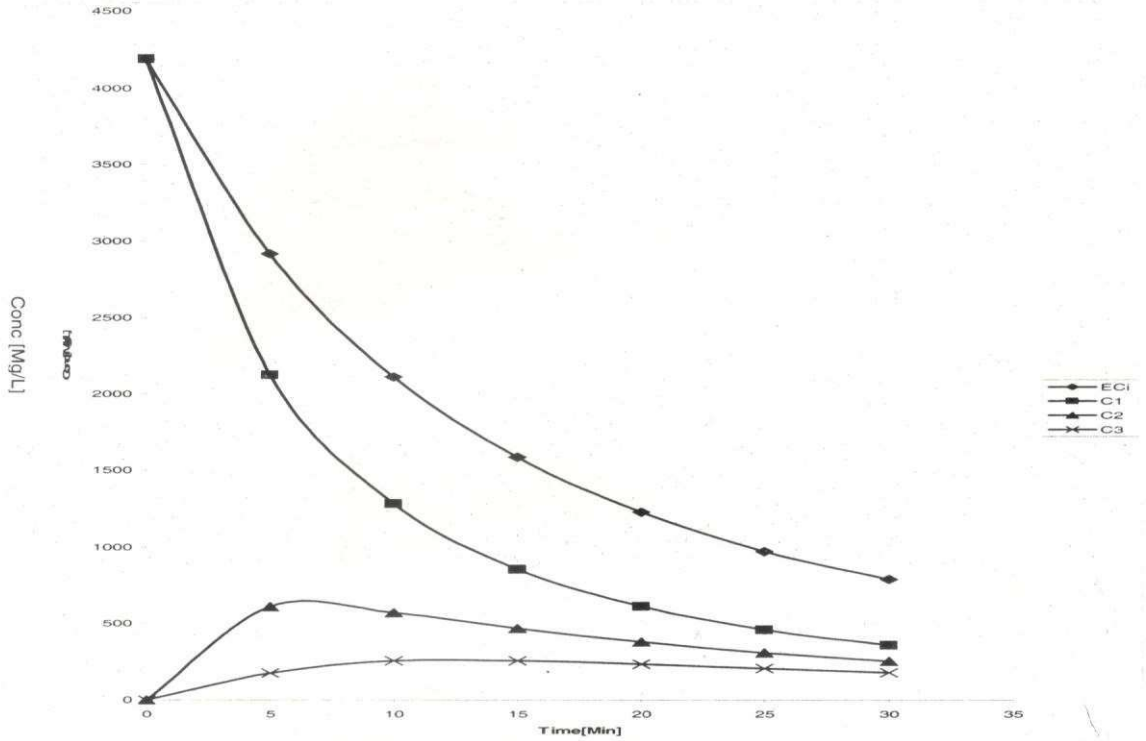

Fig 12: Particle distribution plot for 250Mg/L Starch Only

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