Effect of Coag-Flocculation Kinetics on Telfairia Occidentalis Seed Coagulant (TOC) in Pharmaceutical Wastewater

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***Abstract*– The effect of coag-flocculation kinetics on Telfairia occidentalis seed coagulant in pharmaceutical wastewater has been investigated at room temperature. Various dosages of the coagulant at different wastewater medium was used in evaluating how coag-flocculation kinetic parameters affected Telfairia occidentalis seed coagulant in pharmaceutical wastewater. Such kinetics parameters determined were coagulation reaction rate constant K, the order of reaction α, τ^1 and R^2. Turbidity measurement was employed in line with turbidimetric standard method. The highest and least values for K, are 1.1282E – 01Lg min^{-1} and 4.1402E-03Lgmin^{-1}; α, are 1.5 and 1.1; τ^1, are 0.35 and 2.4E-04; R^2 are 0.997 and 0.972, respectively. The best turbidity percentage removed is recorded at 88% for 0.6g coagulant dosage and pH of 13. Conclusively, Telfairia occidentalis is an effective bio-coagulant which can reduce the level of turbidity in pharmaceutical wastewater.**

***Keywords*–** Effect, Kinetics, Pharmaceutical Wastewater, Telfairia Occidentalis Seed and Coagulation/Flocculation

I. INTRODUCTION

Pharmaceutical processes are accompanied by the generation of waste water commonly referred to as pharmaceutical wastewater. Generally, raw pharmaceutical wastewater contains biochemical oxygen demand (BOD) in the range 1,200 – 1,700 mg/l, chemical oxygen demand (COD) in the range 2,000 – 3,000 mg/l, total alkalinity (as $CaCO_3$) in the range 50 – 100 mg/l, suspended solids in the range 300 – 400 mg/l, pH in the range 6.5 – 7.0, phenols in the range 65 – 72 mg/l (Mayadhate, et al, 1988), The wastewater characteristics vary greatly upon the manufacturing process and raw materials used (Anderson, 1980).

The pharmaceutical industry employs a wide array of wastewater treatment and disposal methods (Struzeski, 1980). Such methods includes; neutralization/pH adjustment, coagulation/flocculation, sedimentation, adsorption etc. It was reported that treatment of pharmaceutical wastewater with inorganic coagulants (Salts of Fe, and Alum.) at pharmaceutical plant in Bombay was less effective (Mayabhate, et al, 1988). Therefore, it becomes necessary to develop new technologies, practices and bio-raw materials for the treatment of pharmaceutical wastewater or the optimization of the existing ones for efficient growth of the industry while minimizing impacts to the environment (Menkiti, et al, 2011). Coag-flocculation technique with bio-raw materials can be applied for these purposes.

Coagulation and flocculation are important unit processes used in water and wastewater treatment. Although used inter-changeable but there are two distinct terms coagulation step proceeds flocculation (Diterlizzi, 1994). Coagulation involves the addition of chemical Coagulants during relatively intense mixing to destabilize colloidal particles (Ma, et al, 1993).

The addition of chemical agents in water provides positive electric charges to reduce negative charge (potential) of the colloids. As a result, it will overcome the repulsive forces of the particles (WST, 2003., Lenntech, 2005). Flocculation is the aggregation of destabilized particles into larger flocs that can be removed subsequently by sedimentation and or filtration (Suidan, 1988., Koohestanian, et al, 2008). This aggregation is influenced by interparticle interaction forces, volume fraction of the suspension, pH etc (Glover, et al, 2000).

Number of aggregating agents used in water treatment processes include, inorganic coagulants (salts of Fe and Al) and natural organic polymers. (Faust and Aly, 1998., Gregor, et al, 1997). Alumunium Salt is widely used as coagulants but its usage are associated with the following problems; influences the pH value of the water, increases the soluble residues metal content of the sludge, and infection of Alzheimer's disease (Crapper, et al, 1973., Miller, et al, 1984).

For developing economies, the use of renewable bio-raw materials as an alternative coagulant to inorganic salts will help conserve the nations foreign earnings. In this regard, natural materials of plant origin, which are non toxic, biodegradable, eco-friendly, cheap and locally abundant can be introduced as a viable alternative coagulant for the treatment of waste water. Among such natural coagulant is Telfairia occidentalis seed. Telfairia occidentalis is a pod herbs of family cucurbitaceae. It is grown in southern part of Nigeria .The seed kernel when expressed on dry weight basis contains 33.92% crude protein, 3.97% fibre, 31.57%fats and oil, 8.46% moisture, 21.9% ash, 0.11% total sugars respectively(Rezig, et al.,2012).

Apparently, no major studies have been done to treat pharmaceutical wastewater by Telfairia occidentalis in coagulation and flocculation process. Therefore, this study was carried to analyze the effects of Telfairia occidentalis in treating pharmaceutical wastewater in different experimental

conditions. The optimum pH, dosage and settling time needed to achieve the best performance of Telfairia Occentalis in flocculation process were determined.

II. THEORETICAL PRINCIPLES AND COAG-FLOCCULATION KINETICS

The kinetics of Brownain Coagulation of particles can be described by:

$$\frac{dN_z}{dt} = \frac{1}{2}\sum_{i+j} K_{ij}\ N_i\ N_j - N_z \sum_{i=1}^{\infty} K_{iz}\ N_i \qquad (1)$$

Where K_{ij} is a second order coagulation rate constant, t is the time, and N_z is the total particle concentration of z - fold aggregates. It has been shown that the kinetics of coagulation process being controlled by Brownian motion have best performance at the early stage (t > 30 mins) (Smoluchowski, 1917; Menkiti, et al, 2010; Van Zanten, 1992; Suidan, 1998; Fridriskhberg, 1984). However, for the kinetics of Brownian Coagulation of mondispersed particles at the early stage is described generally by (Smoluchowski, 1917., Menkiti, et al, 2008)

$$\frac{dN_t}{dt} = -KN_t^{\alpha} \qquad (2)$$

Linearizing equation 2 yields

$$\ln\left(-\frac{dN_t}{dt}\right) = \ln K + \alpha \ln N_t \qquad (3)$$

From graphical illustration of equaton 3 i.e.,

$$\ln\left(-\frac{dN_t}{dt}\right) = VS \ln N_t,$$ K and α can be determined.

Where, K = Coagulation rate constant/Collision frequency/Absolute coagulation rate constant

α = The order of coagulation reaction.

N_t = The concentration of the particles (TDSP) at time, t.

Previous works has shown that for the conditions described above (Menkiti, et al, 2008., Fridrikhsberg, 1984., Van – Zanten and Elimelech, 1992., Smoluchowski, 1917).

$$K = 8R_1\pi D_1 \qquad (4)$$

$$\alpha = 2$$

$$R_1 = 2a \qquad (5)$$

Where, a = particle radius,

D_1 = Diffusivity

From Einstein's equation (Fridrikhsberg, 1984., Danov, et al, 2001).

$$D_1 = K_B\frac{T}{B} \qquad (6)$$

Where, K_B = Boltzman constant (Molar gas constants per particle)

B = The friction factor

T = Absolute temperature ($^{o}_{k}$).

From Stokes equation

$$B = 6\pi\eta a \qquad (7)$$

Substituting equations 7, 6 and 5 in 4, gives

$$K = 8\pi 2a \quad K_B\frac{T}{6\pi\eta a}$$

$$K = \frac{8}{3} K_B \frac{T}{\eta} \qquad (8)$$

Where, η = Viscosity of the medium (Coagulating and flocculating effluent).

Substituting equation 8 into 2, yields.

$$\frac{dN_t}{dt} = -\frac{8}{3}\frac{KBT}{\eta} N_t^2 \qquad (9)$$

Using separable variable method and integrating equation 2

At $t = o\ N_t = N_o$

$t = t\ N_t = N_t$

$$-\frac{dNt}{N_t^2} = -kdt \qquad (10)$$

$$\int_{N_0}^{N_t} N_t^{-2}\, dN_t = K \int_0^t dt \qquad (11)$$

$$\left(N_t^{-1}\right)_{N_o}^{N_t} = K\left(t\right)_o^t$$

$$\frac{1}{N_t} - \frac{1}{N_o} = kt \qquad (12)$$

Similarly, $\frac{1}{N_t} = kt + \frac{1}{N_o}$ (13)

Multiplying both sides of equation 13 by N_o, yields

$$\frac{N_o}{N_t} = N_o Kt + \frac{N_o}{N_o} \qquad (14)$$

$$\frac{N_o}{N_t} = N_o Kt + \frac{1}{1} \qquad (15)$$

Making N_t the subject matter

$$N_t = \frac{N_o}{1 + N_o Kt}$$

Similarly,

$$N_t = \frac{N_o}{1 + t/(1/N_{ok})} \qquad (16)$$

Let $N_o = \frac{1}{N_o K} = \tau$. (17)

Substituting equation 17 in 16, yield

$$N_t = \frac{N_0}{1 + \frac{t}{\tau}} \qquad (18)$$

When, $t = \tau$, equation 18 becomes

$$N_t = \frac{N_o}{1+1} = \frac{N_o}{2} \qquad (19)$$

According to the theory of smoluchowski where the coagulation of the spherical particles is controlled entirely by Brownian diffusion, the coagulation rate constant for doublet formation of an initially monodisperse suspension is given by:

$$Kij = 2k = \frac{8}{3}\frac{K_B T}{\eta} \qquad (20)$$

Solving equation 1, analytically and assuming kij = kii yields (Holthof, et al, 1996., Menkiti, et al, 2008).

$$\frac{N_{z(t)}}{N_o} = \frac{(K_{11}N_o\, {}^t/_2)^{n-1}}{(1 + K_{11}\, N_o\, {}^t/_2)^{n+1}} \quad (21)$$

Similarly $$\frac{N_z(t)}{N_o} = \frac{\left(\frac{t}{2\,[\frac{1}{KN_o}]}\right)^{n-1}}{\left(1 + {}^t/_2[\frac{1}{KN_o}]\right)^{n+1}} \quad (22)$$

Substitute equation 17 in 22.

$$\frac{N_z(t)}{N_o} = \frac{\left(\frac{t}{2\,\frac{1}{\tau}}\right)^{n-1}}{\left(1 + {}^t/_{2\tau}\right)^{n+1}} \quad (23)$$

Assume $2\tau = \tau^1$ (24)

Substitute equation 24 in 23, gives

$$\frac{N_z(t)}{N_o} = \frac{\left(\frac{1}{\tau^1}\right)^{n-1}}{\left(1+\frac{t}{\tau^1}\right)^{n+1}} \quad (25)$$

Equation 25, represents general expression for particle of any ith order. For mono particles (i = 1)

$$N_1 = N_o \left(\frac{1}{(1+\frac{t}{\tau^1})^2}\right) \quad (26)$$

For dimers (i = 2)

$$N_2 = N_o \left(\frac{(\frac{t}{\tau^1})}{(1+\frac{t}{\tau^1})^3}\right) \quad (27)$$

For trimers (i = 3)

$$N_3 = N_o \left(\frac{(\frac{t}{\tau^1})^2}{(1+\frac{t}{\tau^1})^4}\right) \quad (28)$$

Mathematically, the theoretical quantity τ can be evaluated with aid of equation 17.

i.e $\tau = {}^1/N_oK$.

Recall from equation 8, $K = \frac{8}{3}\frac{K_BT}{\eta}$

Substitute equation 8 in 17

$$\tau = \frac{1}{N_o}\,\frac{8}{3}\,\frac{K_BT}{\eta} = \frac{3\eta}{8K_BTN_o} \qquad (29)$$

$$\text{As } N_o \longrightarrow N_{o/2},\ \tau \longrightarrow \tau_{1/2}$$

$$\therefore \quad \tau_{1/2} = \frac{3\eta}{8K_BT(0.5\,N_o)}$$

Similarly,

$$\tau_{1/2} = \frac{3\eta}{4K_BTN_o} \qquad (30)$$

III. MATERIALS AND METHODS

A) Material Sampling, Preparation and Characterization

The wastewater was taken from a pharmaceutical industry in Ogidi, Anambra State, Nigeria. The characterization of the wastewater presented in table 1 was determined based on standard method (WST, 2005.,AWWA, 2005).

1) Telfairia Occidentalis Seed Sample: Telfairia occidentalis sample (precursor to TOC) was sourced from Enugwu-Ukwu, Anambra State, Nigeria. In the preparation of TOC, the procedure described hence was followed, first, the Telfairia occidentalis pod was broken and the nuts were washed thoroughly with tap water. The nuts were then cracked using knife and the seeds were removed. The Seeds were dried under sun light at room temperature for one week after which they were crushed using – laboratory mortar and pestle. The pulverized particles were again sun-dried for 4 hrs to remove any residual moisture left in them. Thereafter, they were sieved using mesh size of 4μm and used for the entire coag-flocculation experimental work.

2) Characterization of Telfairia Occidentialis Coagulant (TOC): 100g of TOC was characterized in line with the procedure reported by Rezig, et al., (2012) and presented in Table 2.

B) Coagulation – Flocculation Experiment

Experiments were carried using conventional jar test apparatus. Appropriate dose of TOC in the range of (0.1 – 0.6)g/m^3 was added to 250ml of pharmaceutical effluent. The suspension, tuned to pH range 1 – 13 by addition of 10M HCL/NaOH was subjected to 2 minutes of rapid mixing (120 rpm), 20 minutes of slow mixing (10 rpm), followed by 30 minutes of settling. During settling, samples were withdrawn from 2cm depth and changes in TDSP measured for kinetic analysis (Lab-Tech. model 212R Turbidimeter) at various time intervals of 2, 4, 6, 10, 20 and 30 minutes. The whole experiment was carried out at room temperature. The data obtained were subsequently fitted in appropriate kinetic model for evaluation.

Table 1: Characteristics of wastewater sample before treatment

Parameter	Values
Temperature (^{o}C)	27
Electrical Conductivity μS/cm	4.9
pH	3.87
phenols (mg/l)	Nil
Odour	acidic
Total hardness (mg/l)	6000
Calcium (mg/l)	594
Magnesium (mg/l)	250
Chlorides (mg/l)	100
Dissolved oxygen (mg/l)	20
Biochemical Oxygen Demand (mg/l)	5
Chemical Oxygen Demand (mg/l)	1.00
Turbidity (NTU)	128
Iron mg/l	Nil
nitrate mg/l	Nil
Total acidity (mg/l)	250
Total viable count (cfu/ml)	9x10^1
Total coliform MPN/100ml	Nil
Total Coliform count cfu/ml	1x10^1
Faecal count MPN/ml	Nil
Clostridium perfrigens MPN/ml	Nil

Table 2: Characteristics of 100g of the seed kernel (TOC precursor)

Parameter	Value
Moisture Content %	0.01
Crude Protein Content %	27.0
Crude Fibre %	3.0
Ash Content %	2.0
Fat & oil Content %	53.0
Carbohydrates Content %	15.0

Table 3: Coagulation kinetics for varying TOC dosages at pH = 1

TOC Doses (g)	K (Lg min^{-1})	α	R^2	Rate Equation (-r)	τ(min)	τ^1(min)
0.1	1.0987E-02	1.2	0.996	-r = 1.0E-02$N_t^{1.2}$	0.0989	0.1978
0.2	1.1749E-02	1.2	0.994	-r = 1.1E-02$N_t^{1.2}$	0.0925	0.0185
0.3	6.8878E-03	1.2	0.995	-r = 6.8E-02$N_t^{1.2}$	0.157	0.3156
0.4	2.9897E-02	1.1	0.994	-r = 2.9E-02$N_t^{1.1}$	0.0364	0.0728
0.5	1.4567E-02	1.2	0.995	-r = 1.4E-02$N_t^{1.2}$	0.0746	0.1492
0.6	8.7824E-03	1.3	0.995	-r = 8.7E-03$N_t^{1.3}$	0.1238	0.2476

Table 4: Coagulation Kinetics for Varying TOC dosages at pH = 3

TOC Doses (g)	K (Lg min^{-1})	α	R^2	Rate Equation (-r)	τ(min)	τ^1(min)
0.1	3.7553E-02	1.2	0.989	-r = 3.7E-02$N_t^{1.2}$	0.0121	0.0242
0.2	4.9095E-02	1.2	0.991	-r = 4.9E-02$N_t^{1.2}$	0.0092	0.0184
0.3	1.1282E-01	1.1	0.987	-r = 1.1E-01$N_t^{1.1}$	0.004	0.008
0.4	4.6236E-02	1.2	0.988	-r = 4.6E-02$N_t^{1.1}$	0.0098	0.0196
0.5	5.0590E-02	1.2	0.990	-r = 5.0E-02$N_t^{1.2}$	0.0312	0.0624
0.6	9.4894E-02	1.1	0.972	-r = 9.4E-02$N_t^{1.1}$	0.0047	0.0094

Table 5: Coagulation Kinetics for Varying TOC Dosages at pH = 5

TOC Doses (g)	K (Lg min^{-1})	α	R^2	Rate Equation (-r)	τ(min)	τ^1(min)
0.1	5.3184E-02	1.1	0.994	-r = 5.3E-02$N_t^{1.1}$	0.0078	0.0156
0.2	5.3611E-02	1.1	0.992	-r = 5.3E-02$N_t^{1.1}$	0.0077	0.0154
0.3	3.6334E-03	1.2	0.995	-r = 3.6E-02$N_t^{1.2}$	0.0115	0.0230
0.4	5.1099E-02	1.2	0.997	-r = 5.1E-02$N_t^{1.2}$	0.0081	0.0162
0.5	4.1878E-02	1.2	0.992	-r = 4.1E-02$N_t^{1.2}$	0.0099	0.0198
0.6	8.7423E-03	1.1	0.995	-r = 8.7E-03$N_t^{1.1}$	0.0047	0.0094

Table 6: Coagulation Kinetics for Varying TOC Dosages at pH = 7

TOC Doses(g)	K (Lg min^{-1})	α	R^2	Rate Equation (-r)	τ(min)	τ^1(min)
0.1	6.5454E-03	1.3	0.996	-r = 6.5E-03$N_t^{1.3}$	0.1107	0.2214
0.2	1.6391E-02	1.2	0.994	-r = 1.6E-02$N_t^{1.2}$	0.0442	0.0884
0.3	4.1402E-03	1.5	0.995	-r = 4.1E-03$N_t^{1.5}$	0.1750	0.3500
0.4	9.1500E-03	1.4	0.994	-r = 9.1E-03$N_t^{1.4}$	0.0792	0.1584
0.5	5.6983E-02	1.2	0.995	-r = 5.6E-02$N_t^{1.2}$	0.0127	0.0254
0.6	4.4582E-03	1.5	0.995	-r = 4.4E-03$N_t^{1.5}$	0.1625	0.3250

Table 7: Coagulation Kinetics for Varying TOC Dosages at pH = 10

TOC Doses (g)	K (Lg min^{-1})	α	R^2	Rate Equation (-r)	τ(min)	τ^1(min)
0.1	1.0163E-02	1.3	0.994	-r = 1.0E-02$N_t^{1.3}$	0.0713	0.1426
0.2	1.3884E-02	1.3	0.983	-r = 1.3E-02$N_t^{1.3}$	0.0522	0.1044
0.3	5.8460E-03	1.4	0.994	-r = 5.8E-03$N_t^{1.4}$	0.00012	0.00024
0.4	2.0020E-02	1.3	0.994	-r = 2.0E-02$N_t^{1.3}$	0.0362	0.0724
0.5	7.3064E-03	1.4	0.977	-r = 7.3E-03$N_t^{1.4}$	0.0992	0.1984
0.6	2.6729E-02	1.3	0.990	-r = 2.6E-02$N_t^{1.3}$	0.0271	0.0542

Table 8: Coagulation Kinetics for Varying TOC Dosages at pH = 13

TOC Doses (g)	K (Lg min^{-1})	α	R^2	Rate Equation (-r)	τ(min)	τ^1(min)
0.1	1.5932E-03	1.6	0.951	$-r = 1.5E\text{-}03N_t^{1.6}$	0.3032	0.6064
0.2	5.9106E-03	1.5	0.977	$-r = 5.9E\text{-}03N_t^{1.5}$	0.0817	0.1634
0.3	5.8018E-02	1.2	0.994	$-r = 5.8E\text{-}02N_t^{1.2}$	0.0083	0.0166
0.4	4.1254E-02	1.3	0.995	$-r = 4.1E\text{-}02N_t^{1.3}$	0.0117	0.0234
0.5	1.1498E-01	1.1	0.994	$-r = 1.1E\text{-}01N_t^{1.1}$	0.0042	0.0084
0.6	9.1905E-02	1.2	0.987	$-r = 9.1E\text{-}02N_t^{1.2}$	0.0052	0.0104

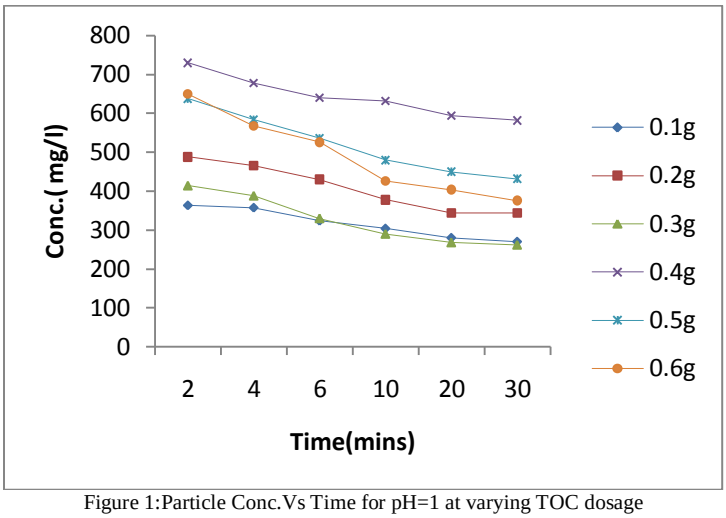

Figure 1:Particle Conc.Vs Time for pH=1 at varying TOC dosage

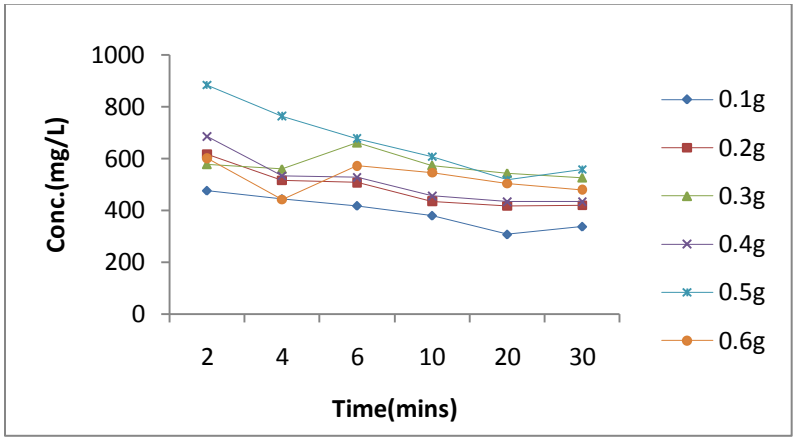

Figure 2:Particle Conc.Vs Time for pH=3 at varying TOC dosage

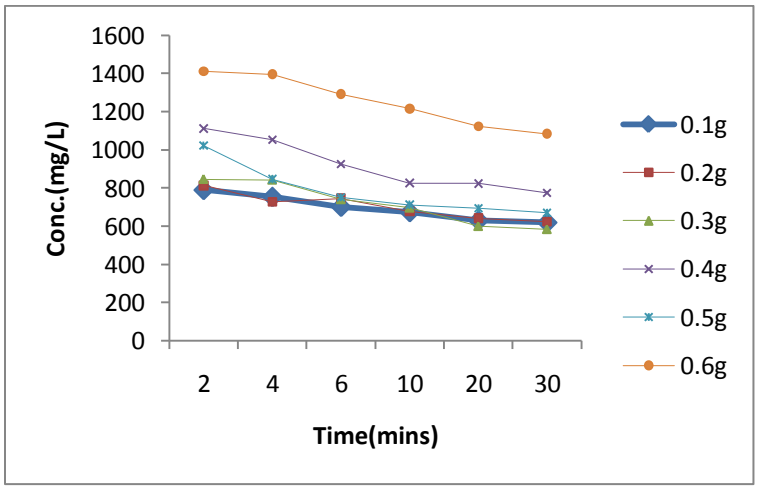

Figure 3:Particle Conc.Vs Time for pH=5 at varying TOC dosage

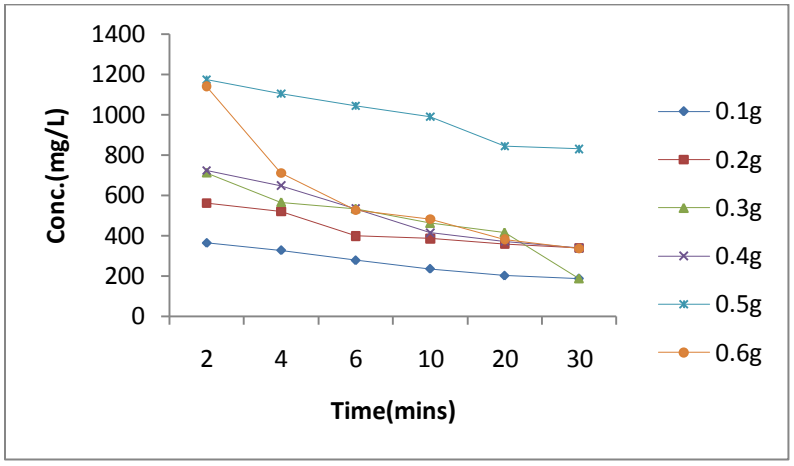

Figure 4:Particle Conc.Vs Time for pH=7 at varying TOC dosage

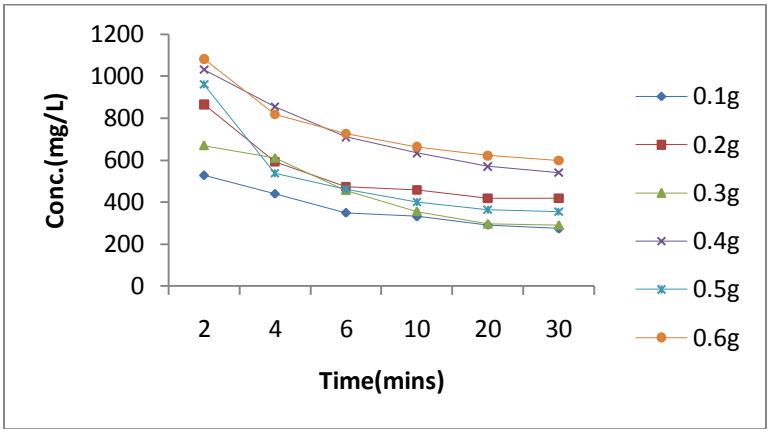

Figure 5:Particle Conc.Vs Time for pH=10 at varying TOC dosage

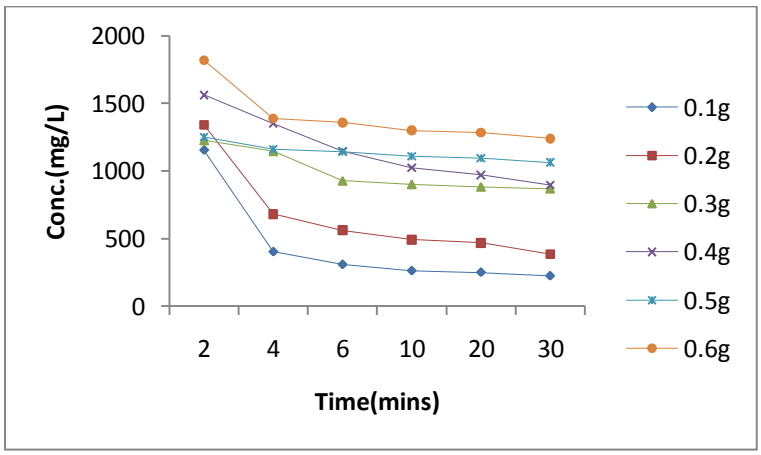

Figure 6: Particle Conc.Vs Time for pH=13 at varying TOC dosage

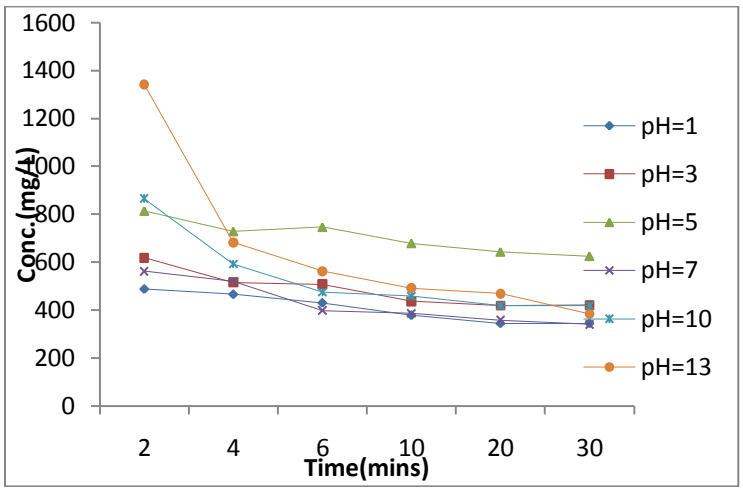

Figure 7: Selected plot of Particle Conc.Vs Time for 0.2g TOC dosage at varying pH

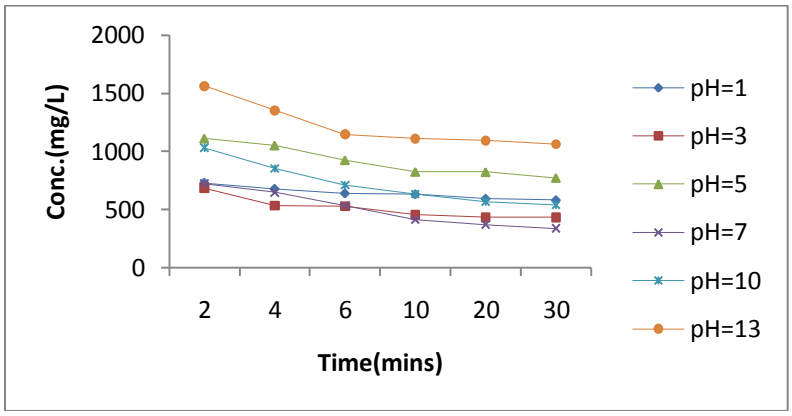

Figure 8: Selected plot of Particle Conc.Vs Time for 0.4g TOC dosage at varying pH

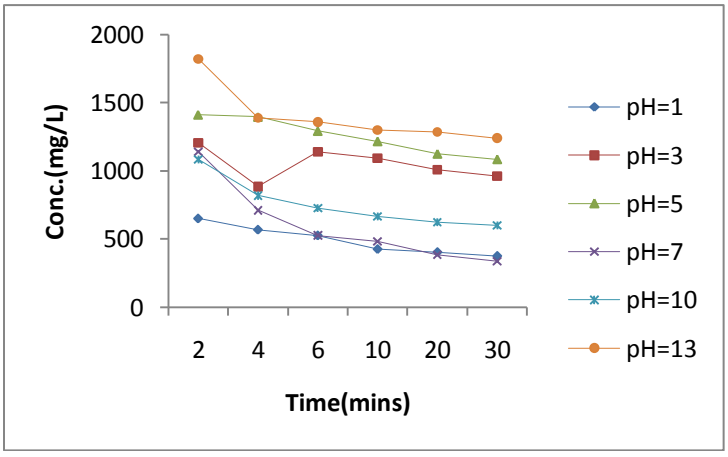

Figure 9: Selected plot of Particle Conc.Vs Time for 0.6g TOC dosage at varying pH

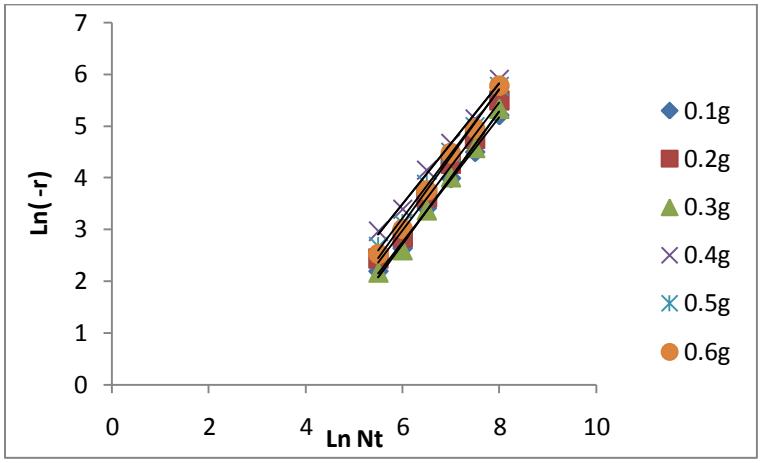

Figure 10: Selected linear Plot of Ln(-r) Vs LnN_t for pH=1

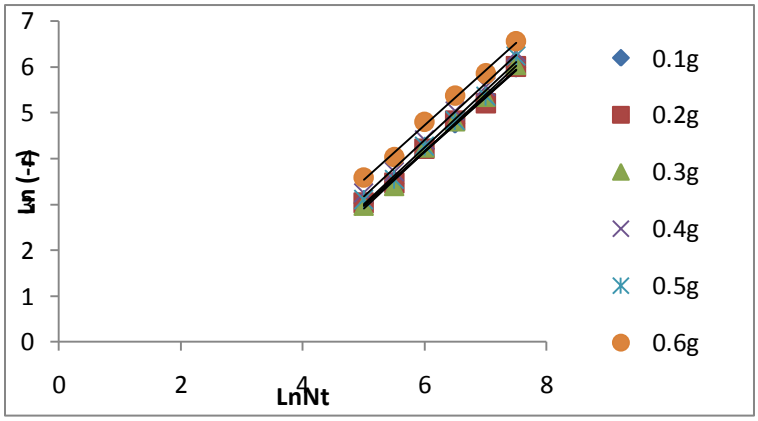

Figure 11: Selected linear Plot of ln(-r) Vs LnNt for pH=5

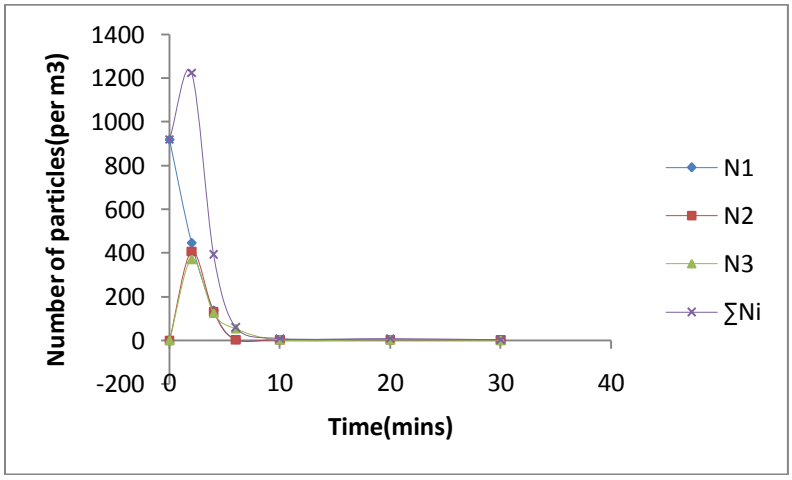

Figure 12: Selected Particle distribution plot as a function of time for pH=1

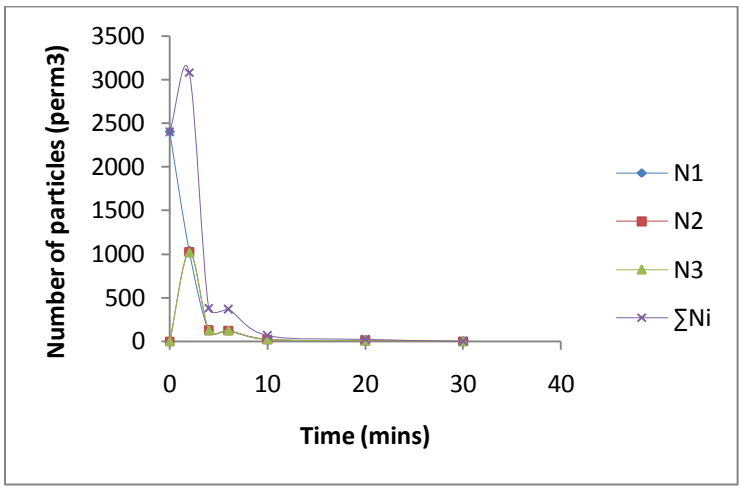

Figure 13: Selected Particle distribution plot as a function of time for pH=5

IV. RESULTS AND DISCUSSION

A) The effect of coagulant dosage variation on turbidity removal

The jar test results obtained in the unit of Turbidity (NTU) were converted to concentrations (mg/l) by multiplying by a factor of 2.0 (Ozacar and Sengil, 2003). These results are represented in figures 1-9. The general observable trend in figures 1-9 show that the TDSP (turbidity) removal is time dependent. The TDSP concentration is seen to decline linearly with time from initial value of 2070 mg/l. The decrease of turbidity with time is supportive of the fact that as the reaction proceeds the amount of TDSP available for the coagulation decreases. Hence resulting in the poor performance of TOC for binding and bridging phenomenon. The linear decline in turbidity from 0 – 5 minutes is a product of either floc mechanism or combination of entrapment – bridging mechanism. Figures 1 – 6, show that increase in coagulant dosage result in the increase in the rate of TDSP removal. The ability of TOC to remove TDSP from the pharmaceutical effluent reached the optimum value of 0.6g coagulant dosage. The least TDSP removal was recorded at the coagulant dosage of 0.1g. This is an indication that the least turbidity at 5 minutes time occurred for 0.6g coagulant dosage. This is due to the ability of TOC to initiate particle sweep.

B) The effect of pH variation on turbidity removal

The pH parameter affects the surface charge of TOC and stabilization of the TDSP in the wastewater as well. In addition, the solubility of TOC in pharmaceutical wastewater sample is influenced by pH value, because high pH of the medium is seen to favour high degree of TOC solubility . In figures 7-9 it was observed that the trends were almost identical but with different percentage removal for particular pH. Figure 9, demonstrates that 88% turbidity removal can be achieved at pH of 13 at initial TDSP of 2070 mg/l. Therefore the optimum pH condition of the treatment system was pH of 13. The good performance at alkaline medium as observed may be due to adsorption of TDSP in the wastewater onto hydroxide flocs or that the positive charges on the TOC surface will significantly decrease as medium pH increases. The contribution by the charge neutralization of the TOC to destabilize the particles become less important as the pH increases. This result is in line with previous works (Sanghi and Bhattacharya, 2005., Menkiti, et al, 2010). Moreover, based on observation, the floc produced by TOC appears rapid at pH of 13 and subsequent aggregation into large floc, for easy settling and removal.

C) Coagulation – flocculation kinetic parameters

The values of coagulation – flocculation kinetic parameters obtained for varying TOC dosages at constant pH are presented in tables 3 to 7. The values of coagulation rate constant K, and the order of coagulation reaction α, are evaluated from the graphical illustration of equation 3, known as linearized selected plots presented in figures10-11 . The slope gives the value of α, while K is obtained as the exponential value of the intercept. The general trend in the tables indicate that K relates to α, inversely i.e. low value of α, is a condition for high value of K. This phenomenon is expected because K which is basically the rate per particle concentration i.e. the rate at which two particles approaches one another (Fridkhsberg, 1984). This analogy suggest that K is associated with energy barrier (KT) between two potential coagulating particles (Diterlizzi, 1994). In addition tables 3 – 7, indicate that the optimum value of K is recorded at pH of 3 for 0.3g dosage with the corresponding low α. Also the values of α, presented in the tables suggest that the system is not controlled by perikinetic mechanism. However, the values of α, obtained are in agreement with the theory of smoluchowski wihich is associated with coagulation process being predominantly controlled by Brownian motion (Metcalf and Eddy, 2003; Sterling, et al, 2003; Fridrikhsberg, 1984., Menkiti, et al, 2008). Linear regression coefficient (R^2) was employed to ascertain the level of accuracy of fit of the experimental data on the model expressed as equation 3. Results in tables 3 – 7, show that the values of R^2 obtained are

greater than 0.97. Ordinarily, this result suggests that the reaction is a second order but it contradicts the values of α, obtained from the experiment. This phenomenon could be attributed to the retarding effect of hydrodynamic interaction (Holthoff. et al 1996) which is not accounted for in Brownian Coagulation. The rate equation (-r) which accounts for the rate of depletion of particle concentration (in TDSP) is evaluated from equation 2 and presented in tables3 –7.

Finally, the values of τ and τ^1 are presented in tables 3-7.The values τ^1 is an important parameter that is associated with aggregation of ions or particles in a coagulation process. The highest and the least values of τ^1 are recorded at pH of 7 and 1 for 0.3g and 0.2g TOC dosage respectively.

D) Particle distribution plots

The particle distribution plots are obtained based on the evaluation of equations 26-28 for monomer, dimer and trimer particles respectively. The particle distribution pattern is presented in figures 12-13. These plots basically depicts the pattern and distribution of aggregation of ions /particles as they floc into visible blobs. Figures12-13 show that the particles and distribution plots exhibits similar trend, which is an indication of system being controlled by similar mechanism. Critical observation on the figures indicate that the total number of particles ($\sum N_i$) passes through the maximum because they are absent at t = o, N = o and at the end of coagulation-flocculation process all ($\sum N_i$, N_1, N_2, and N_3) tend towards t = infinity, $\sum N_i$, N_1, N_2, N_3 = o. Also the total number of particles ($\sum N_i$) decreases more rapidly than classes of particles. This phenomenon is peculiar to coagulation – flocculation process where there is presence of colloidal entrapment and high attractive forces prevailing. This indicate that the process is controlled by charge neutralization and high bridging mechanism which led to floc sweep in figure 12 from 8mins and10mins in figure 13 to t = infinity, respectively. Hence the formation of monomer, dimer and trimer appears to be affected by minimal energy barrier.

V. CONCLUSION

Within, the experimental condition, 88% turbidity reduction is achieved within 0 – 3 minutes of coagulation – flocculation process. This phenomenon presents TOC as a potential bio-coagulant that can be employed in large scale treatment of pharmaceutical wastewater. The coagulation process was found to be predominantly controlled by Brownian mechanism. The experimental results obtained are in agreement with previous works (Menkiti, et al, 2008.,Van-Zanten and Elimelech, 1992).

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