Coagulation Kinetics and Performance Evaluation of *Corchorus Olitorus* Seed in Pharmaceutical Effluent

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***Abstract*– Under room temperature conditions, *corchorus olitorus* extract, a natural biodegradable resource was used as an eco-friendly coagulant in pharmaceutical effluent treatment at varying dosage and effluent pH. Conventional nephelometric jar test was employed while *Corchorus Olitorus coagulant* (COC) preparation was based on method reported by (Gunaratna, *et al.*, 2007). The kinetic functional parameters obtained were fitted into specific model equations for evaluation. Such parameters are τ_2^1, rate constant, reaction order etc. Results show that reaction order, τ_2^1, rate constant, pH and dosage recorded optimum values at 2, 20.70 seconds, 7E – 05 m^3/kg.s, 7 and 0.1 x 10^{-3} kg/m^3, respectively. At the conditions of the experiment, maximum efficiency of 83.19% at 30 minutes demonstrated satisfactory performance of COC for TDSP removal from pharmaceutical effluent.**

***Keywords*– *Corchorus Olitorus*, Pharmaceutical Effluent, Coag-flocculation and Nephelometric**

I. INTRODUCTION

Pharmaceutical processes are among the many industrial processes that generate waste/waste water that are not environmental friendly. This is because they produce coloured waste waters that are heavily polluted by suspended and colloidal materials and chemical ruminants from antibiotics, analgesics, antiseptics, lipid regulating drugs, personal care products etc (Heberer and Stan., 1997; Buser, et al., 1998a, b; Buser and Poiger., 1999).

Coagulation, flocculation, sedimentation, filtration and disinfection are the most common treatment processes used in the improving waste water quality. Coagulation/flocculation processes are of much importance in solid-liquid separation practice (Akbar, et al., 2010; Yukselem and Gregory, 2004).

Coagulation process involves the addition of chemical salts during relatively intense mixing to destabilize colloidal particles or to precipitate additional particles (Suidan, 1988). Flocculation is the formation of aggregates of the destabilized colloids and requires gentle mixing to allow effective collisions between particles to form big flocs which can be removed from water by settlement. The use of chemical salts is known to have some inherent problems associated with it. For instance, with aluminum salt, there is a concern about residuals in the treated water and Alzheimer disease. Whilst iron salts may be cheap, the cost of its importation can be a serious problem for developing countries like, Nigeria (Ghebremichael, 2004). It is against this back drop, that the need to develop cost effective, easier and environmental friendly coagulants arose.

The natural coagulants may be of plant (seed, leaves, roots), (Gunaratna, et al., 2007) and animal origin (Qin, et al., 2006). Among such natural coagulants is corchorus seed, a genius of herb of the family malvaceae. It is abundantly found in the western Nigeria. The seed is edible, non toxic and biodegradable substance. Successful application of other plants origin coagulants such as; Moringa Olifera (John, 1988), Okra, red bean, red maize (Gunaratna. et al., 2007), Cactus latifera and seed powder of prosopsi juliflora (Diaz, et al., 1999) led to its utilization in the treatment of pharmaceutical effluent.

This present study is therefore aimed at reducing the level of turbidity (caused by high TDSP) from waste water using COC. Also the efficiency of the treatment process as a function of time, pH and dosage at room temperature was studied. The results of the current study can be used as the valuable data for the development of local waste water treatment facilities.

II. THEORETICAL PRINCIPLES AND MODEL DEVELOPMENT

The general model for Brownian coagulation of mono dispersed particles at early stage (t≤30) is given by (Smoluchowski, 1917).

$$r_k = \frac{dn_k}{dt} = \frac{1}{2}\sum_{i+j=k} \propto \beta(Vi, Vj)n_i n_j - \sum_{i=1} \propto \beta(Vi, Vj)n_i n_k \quad (1)$$

Where $r_k = \frac{dN_k}{dt}$ is the rate of change of concentration of particle size *k* (conc./ time)

Where $\propto$ is the particle collision efficiency (fraction of collisions that result in particle attachment, β is the collision function (rate that particles are brought into contact by Brownian, shear, ad differential sedimentation), n is the particle number concentration in a size interval and i j are subscripts designating particle size class.

The first term of equation 1, represents the formation of particle size K by collision of particle size i and j. The second term represents the loss of particle size k by collision with all other particles. The value of β for Brownian transport mechanism is given by (Smoluchowski, 1917).

$$\beta_{Br} = \frac{8}{3}\varepsilon_P \frac{K_B T}{\eta} \quad (2)$$

Where K_B Boltzman's constant (j / k)
η - is the viscosity of the fluid (effluent medium)
ε_p - is collision efficiency
T - is the absolute temperature (k)

The general equation representing aggregation rate of particles is obtained by solving the combination of equations 1 and 2 analytically to yield.

$$\frac{dN_t}{dt} = K N_t^{\propto} \quad (3)$$

Where N_t is the total particle concentration at time t, $N_t = \sum \eta_k$ (mass/volume)

K is the $\propto^{th}$ order coagulation-flocculation constant
$\propto$ is the order of coagulation-flocculation.

And $K = \frac{1}{2}\beta_{BR}$ (4)

Where β_{BR} is collision factor Brownian transport

Also, $\beta_{BR} = \varepsilon_p k_R$ (5)

Combining equations 3, 4 and 5 yields

$$\frac{dN_t}{dt} = \frac{1}{2}\varepsilon_p k_R N_t^{\propto} \quad (6)$$

Where K_R is the Von smoluchowski rate constant for rapid coagulation (Fridrkhsberg, 1984; Van-Zanten and Elimelech., 1992) given as:

$$K_R = 8\pi R D^1 \quad (7)$$

$$R_p = 2a \quad (8)$$

Where D^1 is particle diffusion coefficient, a is particle radius

From Einstein's equation, particle Diffusion coefficient is given as ((Fridrkhsberg, 1984; Danov, et al., 2001)

$$D^1 = \frac{K_B T}{B} \quad (9)$$

Where B is the friction factor from strokes equation:

$$B = 6\pi\eta a \quad (10)$$

Where η is viscosity of the fluid (coagulating and flocculating effluent medium) combining 6 to 10 gives

$$-\frac{dN_t}{dt} = \frac{4}{3}\varepsilon_P \frac{K_B T}{\eta} N_t^{\propto} \quad (11)$$

Comparing equations 3 and 11 show that $k = \frac{4}{3}\varepsilon_P \frac{K_B T}{\eta}$ (12)

For perikinetic aggregation $\propto$ theoretically equals 2 i.e. $\propto = 2$ (Fridrkhsberg, 1984; Hunter, 1993; Menkiti, et al., 2010).

From fick's law

$$J_f = D4\pi R_p^2 \frac{dN_t}{dR} \quad (13)$$

Where J_f is flux – number of particles per unit surface entering sphere with radius r

Re-arranging and integrating equation 13 at initial condition $N_t = O$, $R_p = 2a$

$$\frac{J_f}{4\pi D^1} \int_o^{R_p} \frac{dR_p}{R_p} = \int_{No}^{N_t} dN_t \quad (14)$$

$$J_f = 8\pi D^1 a N_o \quad (15)$$

For central particle of same size undergoing Brownian motion, the initial rate of rapid coagulation - flocculation is:

$$- \frac{dN_t}{dt} = J_f \varepsilon_p N_o \quad (16)$$

On substitution of equation 15 into 16 yields

$$\frac{- dN_t}{dt} = 8\pi a D^1 N_o \varepsilon_p \quad (17)$$

On substitution of equations 9 and 10 into 17 gives

$$\frac{- dN_t}{dt} = \frac{8\pi a K_B T N_o \varepsilon_p}{6\pi\eta a} \quad (18)$$

Thus

$$\frac{- dN_t}{dt} = \frac{4}{3} \varepsilon_p \frac{K_B T}{\eta} N_0^2 \quad (19)$$

Similarly at $t > 0$

$$- \frac{dN_t}{dt} = \frac{4}{3} \varepsilon_p \frac{K_B T}{\eta} N_t^2 \quad (20)$$

Hence equation 20 has confirmed the theoretical value $\propto = 2$

For $\propto = 2$, equation 3 yields

$$\frac{dN_t}{dt} = -KN_t^2 \quad (21)$$

Re – arranging and integrating equation 21, yields

$$\int_{N_o}^{N_t} \frac{dN_t}{N_t^2} = - K \int_0^t dt \quad (22)$$

$$\frac{1}{N_t} = Kt + \frac{1}{N_o} \quad (23)$$

Plot of $\lin\left(\frac{1}{N_t}\right)$ VS.t gives a slops of K and intercept of $\frac{1}{N_o}$

From equation 23, making N_t the subject matter yields a relation for the evaluation of coagulation period, τ½

$$\text{Thus } N_t = \frac{No}{1 + No\ Kt} \quad (24)$$

$$\text{Similarly, } N_t = \frac{No}{1 + \left(\frac{t}{N_o K}\right)} \quad (25)$$

$$\text{Let } \tau = \left(\frac{1}{N_o K}\right) \quad (26)$$

Putting equation 26 into equation 25 produces

$$N_t = \frac{No}{1 + \left(\frac{t}{\tau}\right)} \quad (27)$$

When $t = \tau$, equation 27, yields $N_t = \frac{N_o}{2}$ (28)

Therefore as $N_o \longrightarrow 0.5N_o$; $\tau \longrightarrow \tau½$

$$\text{Hence } \tau½ = \frac{1}{0.5N_oK} \quad (29)$$

For particle concentration or aggregation of singlets, doublets and triplets (Being controlled by Brownian mechanism) as a function of time ($t \leq 30$ mins) at early stages, can be obtained by solving equation 1 exactly, resulting in general expression of m^{th} order (Holthoff, et al.,1996).

$$\frac{Nm(t)}{N_o} = \frac{\left(\frac{t}{2}\left(\frac{1}{KN_o}\right)\right)^{m-1}}{\left(1 + \frac{t}{2\left(\frac{1}{KN_O}\right)}\right)^{m+1}} \quad (30)$$

$$\text{Similarly } \frac{Nm(t)}{N_o} = \frac{\left(t/\tau^1\right)^{m-1}}{\left(1 + t/\tau^1\right)^{m+1}} \quad (31)$$

Equation 31 gives a general expression for particle of m^{th} order Hence for singlets (m = 1)

For doublets (m = 1)

$$N_1 = N_o \left(\frac{1}{(1 + {}^t/\tau^1)^2}\right) \quad (32)$$

For doublets (m = 2)

$$N_2 = N_o \left(\frac{(t/\tau^1)}{(1 + t/\tau^1)^3}\right) \quad (33)$$

For triplets (m = 3)

$$N_3 = N_o \left[\frac{(t/\tau^1)^3}{(1 + t/\tau^1)^4} \right] \quad (34)$$

Evaluation of coagulation – flocculation efficiency is given as:

$$E(\%) = \left[\frac{N_o - N_t}{N_o} \right] x\ 100 \quad (35)$$

III. MATERIALS AND METHODS

A. Materials Sampling, Preparation and Characterization

1) Pharmaceutical Waste Water (PHWW)

The effluent was taken from a pharmaceutical industry located in Awka, Anambra State, Nigeria. The characterization of the waste water presented in table 1 was determined based on standard method (APHA, AWWA, WST. 2005).

2) Corchorus Olitorus Seed Sample

Corchorus Olitorus seed samples (precursor to COC), was sourced from Ado Ekiti, Ekiti State, Nigeria. COC was prepared based on the procedure reported by (Gunaratna, *et al*, 2007).

B. Nephelometric Experiments

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

Table 1: Characteristics of wastewater sample before treatment

Parameter	Values
Temperature (^oC)	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: Nephelometric Kinetic Parameters of COC in Pharmaceutical Effluent at Varying pH and 0.1 x 10^{-3} kg/m^3 dosage

Parameter	pH = 1	pH = 3	pH = 5	pH = 7	pH = 10	pH = 13
α	2	2	2	2	2	2
R^2	0.85	0.92	0.71	0.80	0.75	0.47
K_m (m^3/kg.S)	7E - 06	9E - 06	5E - 06	5E - 05	6E - 05	4E - 05
βBr(m^3/kg.S)	1.4E – 05	1.8E-05	1E - 05	1E - 04	1.2E-04	8E - 05
K_R(m^3/S)	$1.54x10^{-19}$	$1.54x10^{-19}$	$1.58x10^{-19}$	$1.54x10^{-19}$	$1.56x10^{-19}$	$1.56x10^{-19}$
ε_p(kg^{-1})	$9.09x10^{13}$	$1.17x10^{14}$	$6.33x10^{13}$	$6.49x10^{14}$	$7.69x10^{14}$	$5.13x10^{14}$
τ_2^1(S)	207.04	120.77	289.86	28.99	24.16	27.17
No(mg/l)	625.00	1000.00	625.00	333.33	555.56 7	14.29
(-r)	$7E\text{-}06N_t^2$	$9E\text{-}06\ N_t^2$	$5E\text{-}06\ N_t^2$	$5E.05\ N_t^2$	$6E\text{-}05\ N_t^2$	$4E\text{-}05\ N_t^2$

Table 3: Nephelometric Kinetic Parameters of COC in Pharmaceutical Effluent at Varying pH and 0.2 x 10^{-3} kg/m^3

Parameter	pH = 1	pH = 3	pH = 5	pH = 7	pH = 10	pH = 13
α	2	2	2	2	2	2
R^2	0.95	0.83	0.83	0.89	0.89	0.36
K_m (m^3/kg.s)	9E - 06	1E - 05	7E - 06	6E – 05	6E - 05	1E - 05
βBr(m^3/kg.s)	1.8E-05	2E-05	1.4E-05	1.2E-04	1.2E-04	2E-05
K_R(m^3/s)	$1.54x10^{-19}$	$1.54x10^{-19}$	$1.58x10^{-19}$	$1.54x10^{-19}$	$1.56x10^{-19}$	$1.56x10^{-19}$
ε_p(kg^{-1})	$1.17x10^{14}$	$1.33x10^{14}$	$8.86x10^{13}$	$7.79x10^{14}$	$7.69x10^{14}$	$1.28x10^{14}$
τ_2^1(s)	161.03	108.70	207.04	24.16	24.16	108.70
No(mg/l)	1000.00	1111.00	1000.00	526.32	666.67	714.29
(-r)	$7E\text{-}06N_t^2$	$1E\text{-}05\ N_t^2$	$7E\text{-}06\ N_t^2$	$6E.05\ N_t^2$	$6E\text{-}05\ N_t^2$	$1E\text{-}05\ N_t^2$

Table 4: Nephelometric Kinetic Parameters of COC in Pharmaceutical Effluent at Varying pH and 0.3 x 10^{-3}kg/m^3

Parameter	pH = 1	pH = 3	pH = 5	pH = 7	pH = 10	pH = 13
α	2	2	2	2	2	2
R^2	0.89	0.97	0.71	0.80	0.85	0.60
K_m (m^3/kg.s)	1E - 05	3E - 05	1E – 05	7E- 05	2E – 05	1E - 05
βBr(m^3/kg.s)	2E - 05	6E - 05	2E – 05	1.4E-05	4E - 05	2E - 05
K_R(m^3/s)	$1.54x10^{-19}$	$1.54x10^{-19}$	$1.58x10^{-19}$	$1.54x10^{-19}$	$1.56x10^{-19}$	$1.56x10^{-19}$
ε_p(kg^{-1})	$1.30x10^{14}$	$3.90x10^{14}$	$1.27x10^{14}$	$9.09x10^{13}$	$2.56x10^{14}$	$1.28x10^{14}$
τ_2^1(s)	144.93	36.23	144.93	20.70	72.46	108.70
No(mg/l)	833.33	1250.00	1000.00	500.00	1000.00	1000.00
(-r)	$1E\text{-}05N_t^2$	$3E\text{-}05\ N_t^2$	$1E\text{-}05\ N_t^2$	$7E.05\ N_t^2$	$2E\text{-}05\ N_t^2$	$1E\text{-}05\ N_t^2$

Table 5: Nephelometric Kinetic Parameters of COC in Pharmaceutical Effluent at Varying pH and 0.4 X 10-3 Kg/m^3

Parameter	pH = 1	pH = 3	pH = 5	pH = 7	pH = 10	pH = 13
α	2	2	2	2	2	2
R^2	0.92	0.84	0.92	0.87	0.88	0.58
K_m (m^3/kg.s)	1E - 05	1E - 05	1E – 05	4E- 05	2E - 05	1E - 05
βBr(m^3/kg.s)	2E - 05	2E - 05	2E - 05	8E-05	4E - 05	2E - 05
K_R(m^3/s)	1.54x10^{-19}	1.54x10^{-19}	1.58x10^{-19}	1.54x10^{-19}	1.56x10^{-19}	1.56x10^{-19}
ε_p(kg^{-1})	1.30x10^{14}	1.30x10^{14}	1.27x10^{14}	5.19x10^{14}	2.56x10^{14}	1.28x10^{14}
τ_2^1(s)	144.93	108.70	144.93	36.23	72.46	108.70
No(mg/l)	1000.00	1250.00	1000.00	625.00	1250.00	1250.00
(-r)	1E-05N$_t^2$	1E-05 N$_t^2$	1E-05 N$_t^2$	4E.05 N$_t^2$	2E-05 N$_t^2$	1E-05 N$_t^2$

Table 6: Nephelometric Kinetic Parameters of COC in Pharmaceutical Effluent at Varying pH and 0.5 x 10^{-3} kg/m^3

Parameter	pH = 1	pH = 3	pH = 5	pH = 7	pH = 10	pH = 13
α	2	2	2	2	2	2
R^2	0.97	0.85	0.89	0.85	0.97	0.62
K_m (m^3/kg.s)	3E - 05	1E - 05	2E - 05	4E- 05	2E – 05	2E - 06
βBr(m^3/kg.s)	6E - 05	2E - 05	4E - 05	8E-05	4E – 05	4E - 06
K_R(m^3/s)	1.54x10^{-19}	1.54x10^{-19}	1.58x10^{-19}	1.54x10^{-19}	1.57x10^{-19}	1.57x10^{-19}
ε_p(kg^{-1})	3.90x10^{14}	1.30x10^{14}	2.53x10^{14}	5.19x10^{14}	2.55x10^{14}	2.55x10^{13}
τ_2^1(s)	48.31	108.70	72.46	36.23	72.46	543.48
No(mg/l)	1190.48	1428.57	1000.00	833.33	1000.00	1250.00
(-r)	3E-05N$_t^2$	31-05 N$_t^2$	2E-05 N$_t^2$	4E.05 N$_t^2$	2E-05 N$_t^2$	2E-06 N$_t^2$

Table 7: Nephelometric Kinetic Parameters of COC in Pharmaceutical Effluent at Varying pH and 0.6 x 10^{-3} kg/m^3

Parameter	pH = 1	pH = 3	pH = 5	pH = 7	pH = 10	pH = 13
α	2	2	2	2	2	2
R^2	0.94	0.92	0.82	0.91	0.83	0.90
K_m (m^3/kg.s)	2E - 05	1E - 05	1E - 05	3E- 05	2E - 05	6E - 06
βBr(m^3/kg.s)	4E - 05	2E - 05	2E – 05	6E-05	4E - 05	1.2E - 05
K_R(m^3/s)	1.54x10^{-19}	1.54x10^{-19}	1.58x10^{-19}	1.54x10^{-19}	1.56x10^{-19}	1.57x10^{-19}
ε_p(kg^{-1})	2.60x10^{14}	1.30x10^{14}	1.27x10^{14}	3.90x10^{14}	2.56x10^{14}	7.64x10^{13}
τ_2^1(S)	72.46	108.70	144.93	48.31	72.46	181.16
No(mg/l)	1000.00	1428.57	111.11	833.33	1250.00	1333.33
(-r)	2E-05N$_t^2$	1E-05 N$_t^2$	1E-05 N$_t^2$	3E.05 N$_t^2$	2E-05 N$_t^2$	6E-06 N$_t^2$

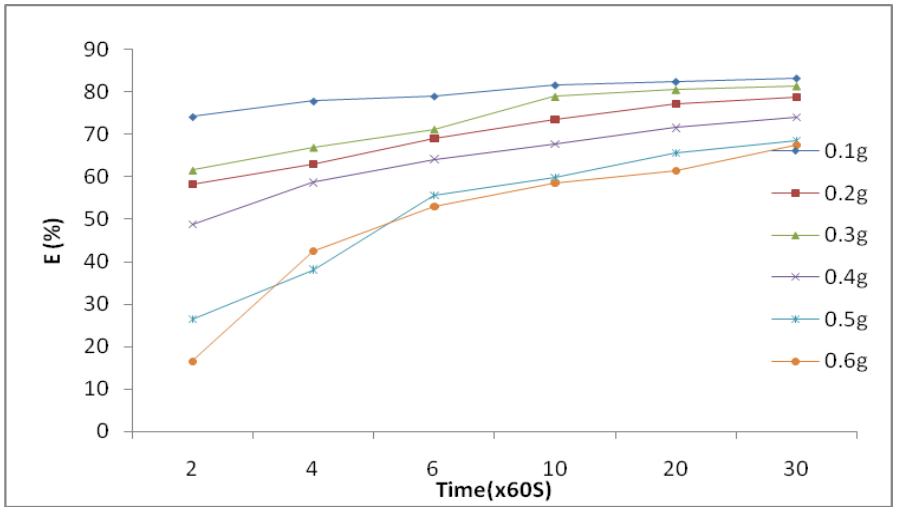

Fig. 1: Representative efficiency Plot for varying COC dosage at pH = 7 effluent medium

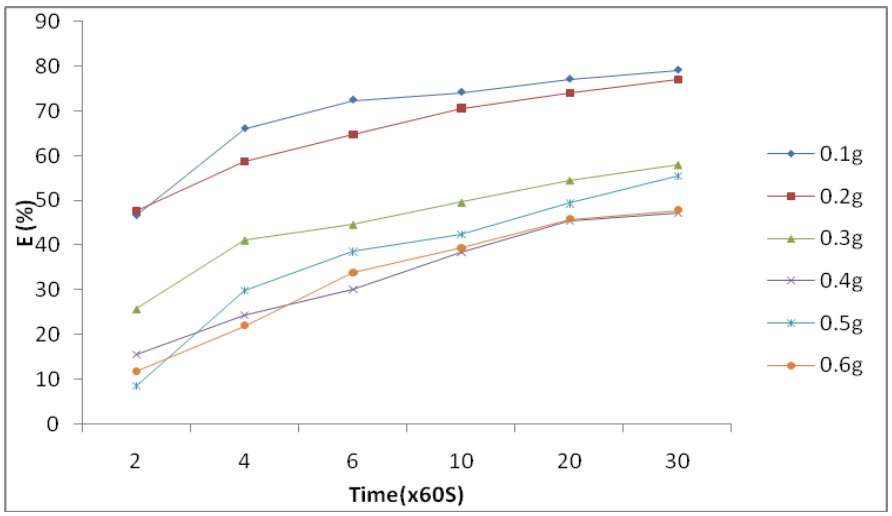

Fig. 2: Reprentative efficiency Plot for varying COC dosage at pH = 10 effluent medium

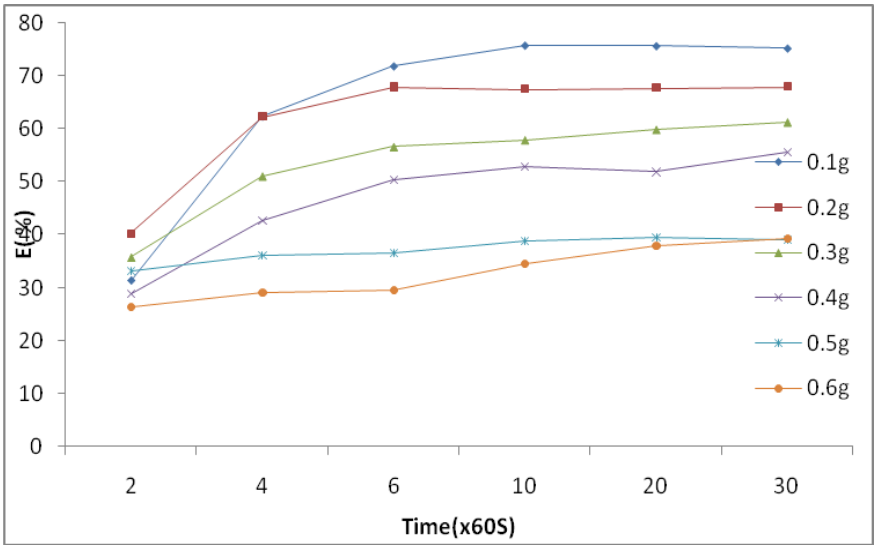

Fig. 3: Representative efficiency Plot for varying COC dosage at pH = 13 effluent medium

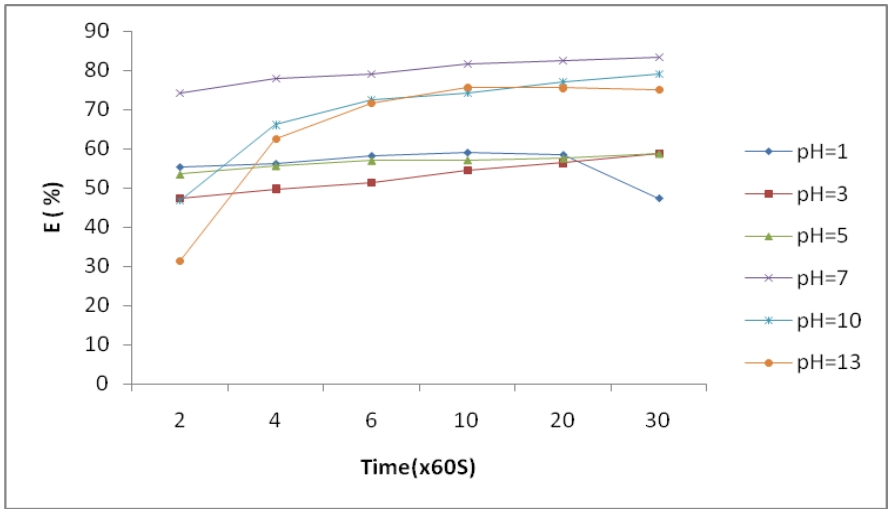

Fig. 4: Representative aggregation efficiency Plot for varying pH effluent medium at 0.1 x 10-3 kg/m3 COC dosage

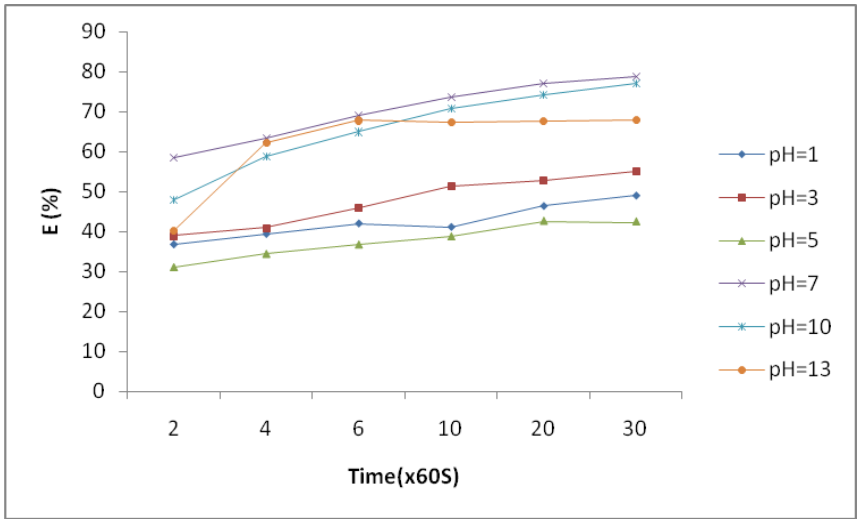

Fig. 5: Representative aggregation efficiency Plot for varying pH effluent medium at 0.2 x 10-3 kg/m3 COC dosage

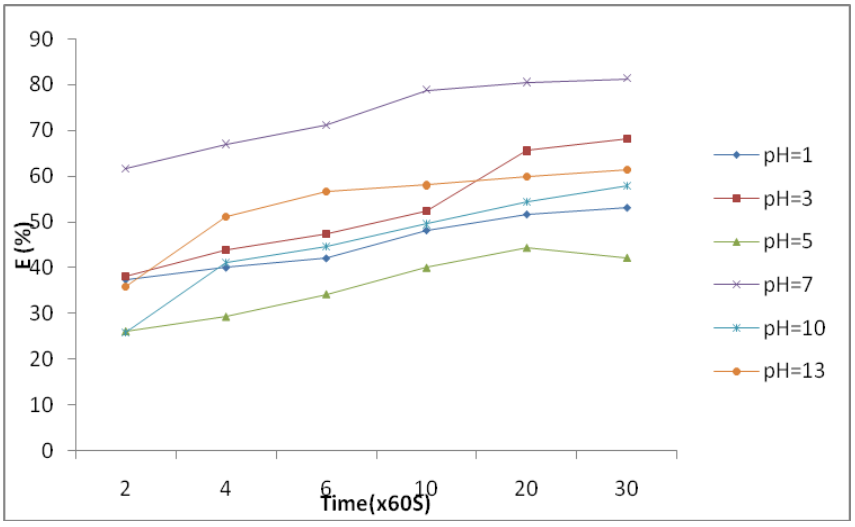

Fig. 6: Representative aggregation efficiency Plot for varying pH effluent medium at 0.3 x 10-3 kg/m3 COC dosage

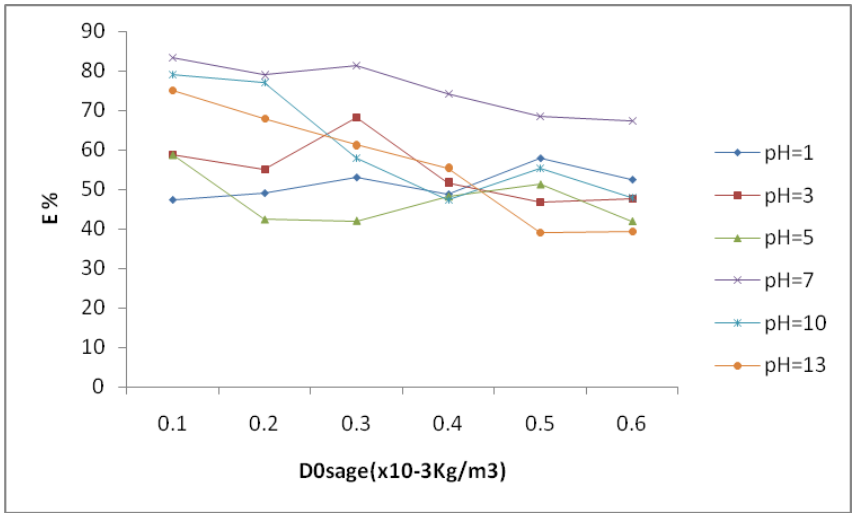

Fig. 7: Plot of E% Vs COC dosage at 30mins for varying pH effluent

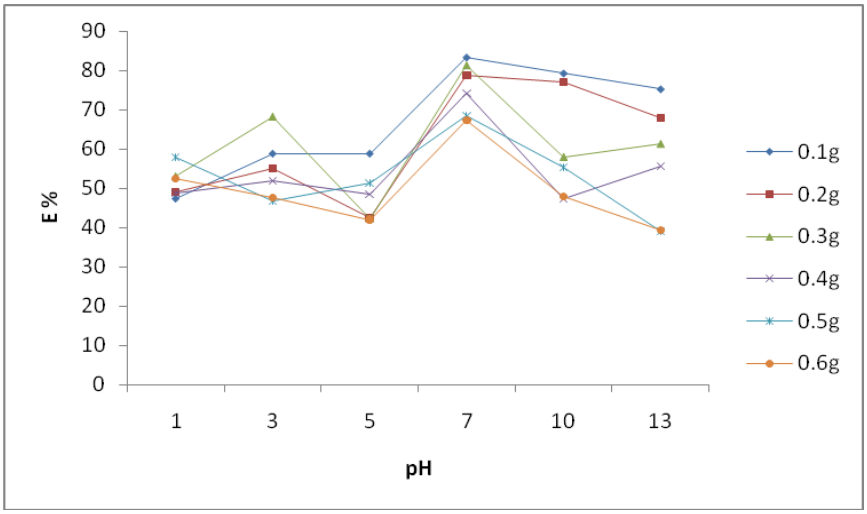

Fig. 8: Plot of E% Vs pH at 30mins for varying COC dosage

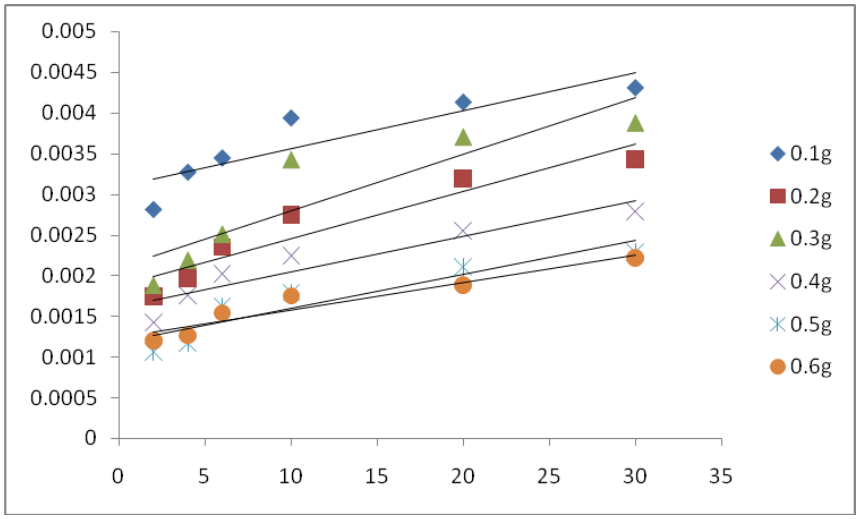

Fig. 9: Representative Linear Plot of 1/TDSP as a function of time for varying COC dosage at pH=7

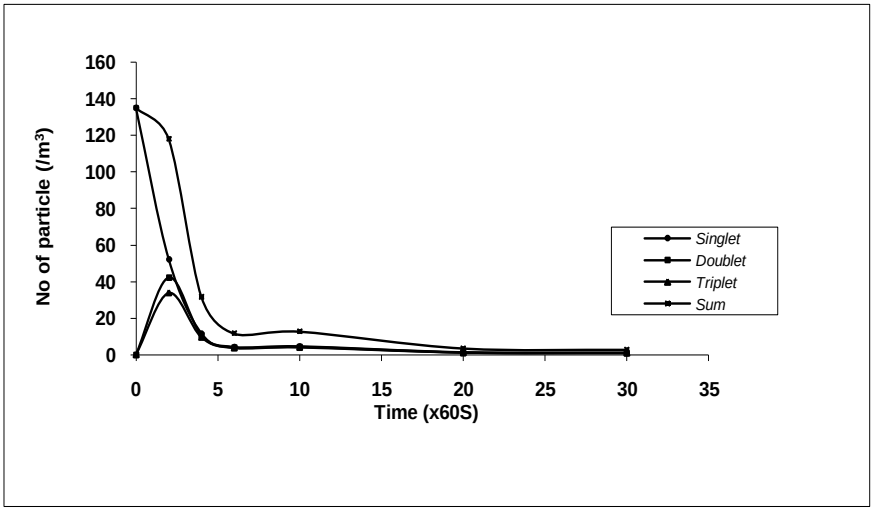

Fig 10: Microscopic particle aggregate distribution at minimum half at 20.70S

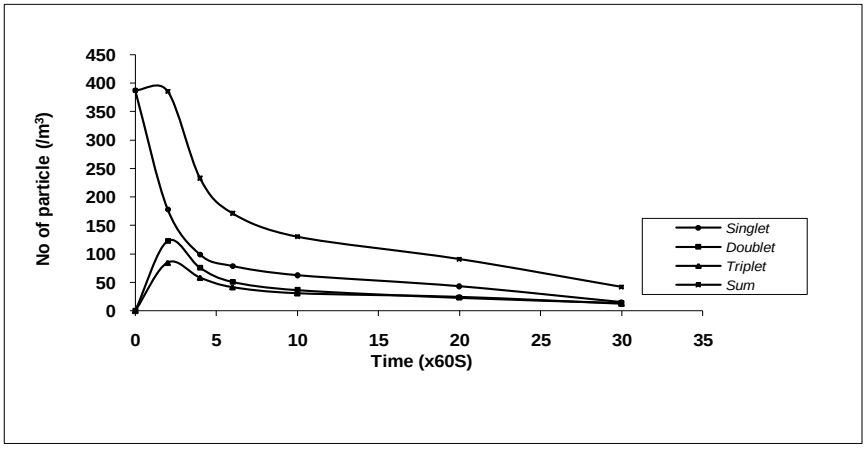

Fig. 11: Microscopic particle aggregate distribution at minimum half at 543.48S

IV. RESULTS AND DISCUSSION

A. Nephelometric Kinetic Parameters

The kinetic parameters were obtained from the standard nephelometric jar test analysis, for a sample of pharmaceutical effluent with COC dosage range (0.1 – 0.6) x 10^{-3} kg/m^3 and pH range 1 – 13. The values of kinetic parameters are presented in tables 2 to 7.

The integral solution of equation 22 (at $\alpha = 2$) results in equation 23, which is the generalized model equation. The linearized form of equation 22, plot of $^1/_{Nt}$ Vs t is presented graphically in a representative plot, figure 9; from which k and $^1/N_o$ was obtained as the slope and intercepts, respectively. The regression coefficient (R^2) was employed to measure the level of accuracy of fit of the experimental data on the generalized equation 23. The result presented in tables 2 – 7, show that majority of R^2 are greater than 0.85, which is a measure of the agreement of perikinetic aggregation associated with coag-flocculation process. This is an indication that the reaction is a second order with different rate constant. Also, the rate of reaction is proportional to the final concentration of TDSP represented as N_t and k as illustrated by equation 22. The various dosages and pH as presented in tables 2 – 7 are graphically represented in figure 9, where the figures exhibit a similar trend, though not shown . On evaluation of equation 4, $k = 0.5\beta Br$ with known values of k_m, various βBr for different dosages and pH were calculated and displayed on tables 2 – 7. The maximum value of k (7E – 05m^3/kg.s) is recorded at pH 7 and 0.3 x 10^{-3}kg/m^3. Generally, the best performances at the conditions of these experiments were achieved at neutral pH with the exception of 0.1 x 10^{-3} kg/m^3 COC where maximum value is recorded at pH 10.

Moreover, the experimental N_o values (equation 30) agrees with the theoretical N_o values (evaluated from equation 23 as the intercept), in that N_o values relates proportionally to τ_2^1, that is high $\tau_2^1$is a condition for high No and vice versa as presented in Table 2 – Table 7.

Also equation 29, τ_2^1 relates inversely to K, low τ_2^1 value corresponds to high K as seen in tables 2 – 7. This accounts for high rate of settling in high turbidity water which is in agreement with previous work (Menkiti, et al., 2011).

It is known that coag-flocculation process is favored in alkaline medium following easy delamination of the coag-flocculation phase (Menkiti, et al., 2011; Chatterjee and Woo., 2009). However, the results obtained in this work indicate that the best performing medium is highly influenced by the nature of the coagulant. ε_p and K_R are the functional kinetic parameters instrumental to coag-flocculation process. K_R is related to temperature and viscosity of the effluent medium as can be seen in equation 11. Because the experiment was conducted under room temperature there were minimal variations in temperature and the effluent viscosity is constant. This may be attributed to the minimal variations experienced in the values of K_R obtained in the experiment as posted in tables 2 – 7. In a situation of such minimal variation in K_R, ε_p has a direct relationship with $2k = \beta Br$, which is in line with (Menkiti, et al., 2011) . Consequently, high ε_p requires enough kinetic energy necessary to overcome the repulsive forces of particles by complete colloid destabilization.

τ_2^1, which is understood to be one of the coagulation effectiveness factors, accounting for coagulation efficiency are evaluated based on equation 29, from thence it is intuitively obvious that τ_2^1 is an inverse function of k. As recorded in Table 2 – Table 7, τ_2^1 values are inversely proportionally to k. That is why the best coag-flocculation was recorded at pH of 7 supporting lowest and highest values of τ_2^1 and k.

Though, the least τ_2^1 recorded is 20.70S, at pH of 7, but considered to be high in view that milliseconds have been recorded. This is attributed to the fact that the aggregation process in pharmaceutical effluent is controlled by stabilizing repulsive interaction mechanism.

Finally, the rate equations are evaluated based on equation 3 and posted in Table 2 – Table 7. The rate equation is found to be a dependent function of k.

B. Variation of Removal Efficiency E(%) as a Function of Time, Dosage and pH

The removal efficiency E(%) variation with time, dosage and pH is obtained based on the evaluation of equation 32-34. The results represented by selected sample plots of figures 1 – 8 are obtained for pH 1, 3, 5, 7, 10, 13 at (0.1 – 0.6) x 10^{-3} kg/m^3 COC dosage. Generally, it was observed that figures 1 – 6 follow the same trend i.e. removal efficiency increases with increase in time, though the magnitude differ for a particular dosage and pH. As can be seen from the figures the optimum settling time for COC is 30 minutes. The figures show an increase in removal efficiency with flocculation time. This could be due to the redispersion and restabilization of flocs at higher flocculation time. The results obtained are in agreement with previous works Ozacar and Sengil. 2002; Nozaki, et al., 1993). This is an indication that better results are obtained at 30 minutes settling time. In addition, the trends that had been represented in figures 1–6, show poor performance of COC for binding and bridging, which is in line with previous work (Molid Ariffin and Liew., 2007). This is expected because at lower settling time (2minutes), the collisions between the flocculants and suspended particles were low and led to lower flocculation rate. Figure 7 shows that the optimum COC dosages are recorded for the pH of 7 at 0.1 x 10^{-3} kg/m^3 for 30 minutes, though the performances recorded for pH of 10, 13 at 0.1 x 10^{-3} kg/m^3 respectively are satisfactory. The minimum performance was recorded for pH of 13 at 0.5x10^{-3} kg/m^3. Critical observation of figure 13 shows that there is decrease in the removal efficiency of TDSP when the COC dosage concentration increases from (0.1 to 0.6) x 10^{-3} kg/m^3. This poor performance was due to the phenomenon of excess polymer is adsorbed on the colloidal surfaces and producing restabilized colloids. Thus there were no sites available on the particle surface for the formation of interparticle bridges. Consequently the restabilized colloidal particles can become positively charged, causing electrostatic repulsion among the TDSP.

Figure 8, shows that maximum efficiency of COC are recorded at pH of 7 followed by pH of 10 .Low doses of 0.1 x 10^{-3} kg/m^3, 0.3 x 10^{-3} kg/m^3 and 0.1 x 10^{-3} kg/m^3, 0.2 x 10^{-3} kg/m^3 exhibited high E% at pH of 7 and 10, respectively while high dose of 0.5 x 10^{-3} kg/m^3 performed minimally at pH of 13. This phenomenon is an indication that at pH of 7, COC has a high degree of solubility which decreases as the pH varies towards the acidic or basic condition. Below pH of 7, COC becomes insoluble in pharmaceutical effluent and exists as solid particles. This statement supported the obtained results in this work in which the performance of COC was poorer in acidic than basic medium.

C. Microscopic particle Flocculation as a function Time

The graphical illustration presented in figures 10 and 11 were evaluated based on equation 32-34. These figures specifically show the interaction of singlet (m = 1), doublets (m = 2) and triplets (m = 3). Particle aggregation at discrete regime are obtained for τ_2^1 = 20.70s and τ_2^1 = 543.48s. The two figures displayed similar trend, which is an indication of flocculation process being controlled by a similar mechanism. Figure 10 presents a curve where the values of singlet, doublets and triplets cluster together such that their aggregation with time is homogeneous. This is a case where little energy barrier is expected, hence the process of aggregation is purely diffusion limited.

V. CONCLUSION

The effectiveness and efficiency of COC as an alternative organic natural resource in pharmaceutical effluent treatment was successfully demonstrated.

The optimum dosage, pH and τ_2^1 recorded are 0.1 x 10^{-3} kg/m^3, 7 and 20.76s, respectively. In general, the results obtained are in accordance with previous work reported

elsewhere (Menkiti, et al.,2010;Holthoff, et al.,1996; Ma, et al.,1994a).

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