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Evaluation of Coag-flocculation Kinetics and Functional Parameters Response for the Treatment of Brewery Effluent using three Natural Coagulants

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Abstract: This study evaluated the coag-flocculation performance of three coagulants prepared from Okra pods (*Hibiscus esulentus* L), Detarium Microcarpum and Cocoyam (*Xanthosoma* spp.) in the treatment of brewery effluent. A conventional laboratory bench – scale Jar Test was used for the experiment. The coagulant dosages range from 100 – 500mg/L and effluent pH varied from 2.0 – 10.0. Coag-flocculation efficiency and functional kinetic parameter response at various pH and dosages studied were evaluated. The maximum coag-flocculation performance for Okra Pod Coagulant (OPC), was recorded at pH 2, 200mg/L dosage, rate constant, K, of 5 × 10^{-3} L/mg.min, and coagulation period, $\tau_{1/2}$ of 0.52mins; for Detarium Microcarpum Coagulant(DMC), pH 2, 200mg/L dosage, rate constant, K, 8 × 10^{-4} L/mg.min,and coagulation period, $\tau_{1/2}$ of 3.28min; and for Cocoyam Coagulant(CYC), pH 2, 400mg/L dosage, rate constant, K, 9 × 10^{-2} L/mg.min, and coagulation period of 0.03min respectively. The maximum coag-flocculation performance efficiency recorded at pH 2 after 30minutes of coag-flocculation for three coagulants studied range between 70-92%. Analysis of variance (ANOVA) was used to determine statistical difference of the coag-flocculation performance of the three coagulants at various pH and dosages. The test of significant indicates that increasing the coagulant dosage from 100 to 500mg/L has no significant difference on the coag-flocculation performance at the same pH.

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Introduction

The menace of indiscriminate discharge of industrial wastewater into the surrounding lands and rivers attract great attention to the populace. Thus, the need for treatment before the effluent is discharged to the environment. Coag-flocculation method is the most conventional ways for treating water and wastewater. Many conventional coagulants alum, ferric chloride etc has found wide application in treatment of water and wastewater.

Studies have shown an increasing attention to the application of natural polyelectrolytes as auxiliary coagulant for the treatment of water and wastewater (Shwetha and Usha, 2013; Ndabigengesere and Narasiah, 1998; Okuda et al, 2001).

Coag-flocculation processes are commonly used method of removing particulates and organic matter from water and wastewater, by addition of chemicals such as alum and ferric chloride. These chemicals cause destabilization of the colloidal materials and hence the small particles agglomerate into large settlable flocs. The coagulant bond to the suspended particles and hence makes them less stable in suspension. Flocculation is the binding or physical enmeshment of these destabilized particles, which result in flocs that are heavier and easier to settle (Okolo et al, 2014; Menkiti et al, 2010).

There is also strong evidence linking aluminumbased coagulant used in most conventional water treatment plants to the development of Alzheimer's disease in human being. It is important to replace this conventional inorganic coagulants with plant-based coagulant that are biodegradable and environmental friendly (Okolo et al, 2014); Sciban et al, 2009). For these reasons, it is desirable to make a progressive replacement of these chemical coagulants with a number of effective coagulants from plant origin: Okra, Nirmali, moringa oleifera (Gunaratna et al, 2007), Detarium Microcarpum (Okolo et al, 2014; Ani et al, 2012), cacutus latifera, and seed powder of prosopis julifora (Diaz et al, 1999), which have been used in treating waste water as coagulants.

Many researchers have identified the coagulant component from plant seed extract as a cationic protein. The seed kernel contains significant quantities of series of low molecular weight and soluble proteins, which impart positive charge to solution (Ndabigengesere and Narasiah, 1998). The protein is considered to act similar to a synthetic positively charge polymer coagulant.

When this protein is added to waste water, it binds with the predominantly negatively charged particulates which make the waste water turbid (Ndabigengesere and Narasiah 1998; Ndabigengesere and Narasiah, 1995; Gassenschmilt et al, 1995). Coag-flocculation performance depends on the coagulant used, the dosage, pH, and the nature of the organic compound present in the waste water (Ebelling et al, 2006).

The main objective of this work is preliminary evaluation of three natural coagulants; OPC, DMC and CYC to demonstrate their potential for effective application in treatment of brewery effluent.

Laboratory bench-scale jar tests were conducted to determine the optimum dosage and pH. The proximate analysis of the plants presented in **Table 1**, revealed presence of reasonable percentage of protein, which suggest that they can be used as a precursor to coagulant. The abilities of these plant based coagulants in the removal of turbidity and the coag-flocculation kinetics were investigated. The efficiency of the coag-flocculation processes applying statistical tools, like analysis of variance (ANOVA) to obtain the interaction between the process variables and response were evaluated (Gupta et al, 2004).

Table 1. Proximate Composition of Okra,Detarium Microcarpum and Cocoyam.

Parameter	Okra	DM	CYC
Moisture content (%)	12.0	6.0	14.0
Ash content (%)	7.2	2.0	2.0
Fat content (%)	11.0	7.5	0.5
Crude protein (%)	23.0	28.0	8.9
Carbohydrate (%)	33.3	41.5	73.1
Crude fiber (%)	13.5	15.0	1.5

2. Materials and Methods

2.1. Coagulants Preparation

The materials used in this work were obtained from different plants in Enugu, Nigeria.

2.1.1. Okra Pods (*Hibiscus esculentus* L)

Okra is a perennial shrub plant, erect and a semi woody stem, which belong to the family of Malvaceae. It is found all round the world from Mediterranean to equatorial regions (Edilson et al, 2013). The okra pods were sun dried for one week and dried finally in hot air oven at 60°C for an hour. After drying, okra pods were ground in common food processor and sieved through a 600µm sieve to achieve liquid extraction of active ingredient in the seed. Tap water was added to the powder to make 2% suspension (2g of powder seed in 100ml water). The suspension was stirred for 30minutes using magnetic stirrer to promote water extraction of the coagulant proteins. The suspension was passed through filter paper (Whatman No42). The filtrate portion, called crude extract was used for coagulation. To avoid changes in pH, viscosity and coagulation activity, fresh solution are prepare daily.

2.1.2. Detarium Microcarpum

It is a moderate size tree found in West Africa and some Asian countries. It is used as soup thickener. It is non toxic biodegradable plant product which has the potential to act as coagulant. From the proximate analysis in **Table 1**, has shown that its percentage protein content is high and can be used as a precursor to coagulant. The preparation is the same as in 2.1.1.

2.1.3. Cocoyam (Xanthosoma spp.)

Cocoyam is a vegetative propagated mono-cot tuber of the family Araceae, (Opoku-Agyeman et al, 2004). The cormels of cocoyam are used traditional as soup thickener.The cocoyam were peeled, washed and sliced into chips. The chips were sun dry enough to break sharply between hands, and ground to a fine powder. 2g of the powder was used to prepare the coagulant extract as in 2.1.1. The proximate analyses of sample based on AOAC standard method (AOAC, 1993) are presented in **Table 1.**

2.3. Wastewater Sampling

The brewery effluents were collected from brewery plant located in Enugu, Nigeria. The effluent samples were characterized using standard methods (AWWA et al, 2012).

Table 2.	Characterization	of Brewery	Effluent.
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Parameter	Values
Temperature (°C)	27.0
pH	7.68
Turbidity (NTU)	316.63
Conductivity (µs/cm)	5290.0
Total hardness (mg/L)	41.0
Ca hardness (mg/L)	36.0
Mg hardness (mg/L)	5.0
Ca^{2+} (mg/L)	14.4
$Mg^{2+}(mg/L)$	1.5
Fe^{2+} (mg/L)	0.178
So_4^{2-} (mg/L)	46.224
No_3^{2-} (mg/L)	0.136
$Cl^{-}(mg/L)$	80.826
TDS (mg/L)	3438.5
TSS (mg/L)	30.40
E. Coil	Nil
$BOD_5(mg/L)$	640.0

2.3. Coag-flocculation Experiments (Jar Test)

The coag-flocculation has been practice since ancient time, by addition of coagulants/flocculants to water or wastewater, for the removal of suspended, colloidal and non- settlable matter from the waste water.

Various dosages of the coagulants in the range 100-500mg/L were placed in six 500ml beakers and made up to 300ml with the effluent. The six 500ml beakers were placed in the slots of a jar tester. The pH of the solution was varied from 2-10 using sulphuric acid (H_2So_4) or sodium hydroxide (NaOH). Then, solutions were subjected to 2minutes rapid mixing at 250rpm and 20minutes of slow mixing at 20rpm, followed by 30minutes of settling.

During the settling period, 20ml of the supernatant were withdrawn from 2cm depth at intervals of 3, 5, 10, 15, 20, 25, and 30mins; and the turbidity were measured and recorded.

2.4. Statistical Procedures

Analysis of variance is a technique for analyzing the way in which the mean of a variable is affected by different types and combinations of factors (Gupta et al, 2004). It also gives a single overall test of whether there are differences between groups or treatment.

In this work, the amount of variation due to each of the independent factors (coagulation dosage and pH) separately and then comparing these estimates due to assignable factor (coagulant performance) using ANOVA were evaluated.

The tests of significant based on F-distribution was carried out to compare the performance of the coagulants. Hence, the computed value of F for d.f. at specified level of significance, α =0.05% were computed as shown below (Gupta et al, 2004).

$$F = \frac{MSST}{MSSE} = \frac{14.71}{34.98} = 0.42$$
(1)

3. Theoretical Principles and Coag-flocculation Kinetics

The coagulation of two clusters of the kind i and j are given by the following relation (Smoluchowski et al, 1917).

$$i mer + j mer \xrightarrow{K_{ij}} (i + j) mer = n mer$$
 (2)

Where K_{ij} is the concentration-independent coagulation constant or kernel. Smoluchowski shows that all the coagulation rates between all kinds of i mers and j mers are identical.

For a coag-flocculation phase, the rate of successful collision between particles of size i and j to form particles of size K, (Zanten and Elimelechi, 1992; Hunter, 1993; Swift and Friedlander, 1964) is

$$\frac{dC_n}{dt} = \frac{1}{2} \sum_{i+1=1}^{\infty} K_{ij} C_i C_j - C_n \sum_{i=1}^{\infty} K_{ni} C_i (3)$$

Where $\frac{dc_n}{dt}$ is the rate of depletion of concentration of particles size, $C_n(t)$ is the time- dependent number concentration of n-fold clusters, t is the time, K_{ij} elements of the rate kernel of coagulation between an i-fold and j-fold cluster, C_iC_j is the particle aggregation concentration for particle of size i and j respectively.

Coagulation rate constant for doublet formation of an initially mono-disperse suspension is given by

$$K_{ij} = K_{11} = \frac{8}{3} \frac{K_B T}{\eta}$$
(4)

Where, K_B the Boltzmann constant, T is is the temperature, and η is the viscosity of the medium (effluent), Holthof et al, 1996; Zanten and Elimelechi, 1992).

The generic aggregation rate of particles (during coag-flocculation) can be derived by combination of Equations (3) and (4) to yield

$$-\frac{dc_t}{dt} = KC^{\alpha} \tag{5}$$

Linearizing Equation (5) yields

$$\ln\left[-\frac{dc}{dt}\right] = \ln K + \alpha \ln C \tag{6}$$

Plotting $\ln \left[-\frac{dc}{dt} \right] vs \ln C$, K and α can be determined. Where K is the coagulation rate constant/collision frequency, α is the order of coagulation reaction and C_t is concentration of the suspended particles (SP) at time t.

For mono-dispersed aggregation model, the rate of coagulation can be found using Equations (3) and (4). This shows that for Brownian controlled coagulation, Equations (3) and (4) are equal (Okolo et al, 2014; Smoluchowski et al, 1917; Nnaji et al 2014).

Using separable method and integrate Equation (6) within the following limits.

For
$$\alpha = 2$$
, at, t= 0, C = C_o
at, t = t, C = C

yields
$$-\frac{dc}{dc_t^2} = Kdt$$
 (7)

$$\int_{C_o}^{C_t} C^{-2} dC_t = K \int_o^t dt$$
(8)
$$\frac{1}{C_t} = \frac{1}{C_o} + Kt$$
(9)

Plot of $(1/C_t)$ vs t produce a slope of K and intercept of $1/C_o$. Multiply both sides of Equation (9) by C_o .

by
$$C_o$$
.
 $\frac{c_o}{c_t} = 1 + C_o K t$ (10)

$$C_t = \frac{C_o}{1 + C_o K t} \tag{11}$$

$$C_t = \frac{\frac{C_0}{C_0}}{\frac{1}{1+\frac{t}{1+$$

Let
$$\left[\frac{1}{C_o K}\right] = \tau_{1/2}$$
 (13)

 \therefore Equation (12), becomes,

$$C_t = \frac{c_o}{1 + t/\tau}$$
(14)
When $t = \tau$ then Equation (14) becomes

$$C_t = \frac{C_o}{2}$$
(15)

)

Therefore, as
$$C_o \rightarrow 0.5C_o, \tau \rightarrow \tau_{1/2}$$

Hence $\tau_{1/2} = \frac{1}{0.5C_o K}$ (16)

The particle concentration of singlet and doublet as a function of time can be obtained by solving Equation (3) analytically.

Assuming $K_{ij} = K_{11}$ yields (Smoluchowski et al, 1917; Zanten and Elimelechi, 1992; Hunter, 1993; Swift and Friedlander, 1964; Holthof et al, 1964).

$$\frac{c_n(t)}{c_o} = \frac{\left(K_{11}c_ot/2\right)^{n-1}}{\left(1+K_{11}c_ot/2\right)^{n+1}}$$
(17)

Similarly

$$\frac{c_{n(t)}}{c_{o}} = \frac{\left[\frac{t}{2}\left(\frac{1}{K_{11}c_{o}}\right)\right]^{n-1}}{\left[\frac{1+t}{2}\left(\frac{1}{K_{11}c_{o}}\right)\right]^{n+1}}$$
(18)

Substitute Equation (13) into (18)

$$\frac{C_n(t)}{c_o} = \frac{\left[\frac{t}{2\tau}\right]^{n-1}}{\left[1 + \frac{t}{2\tau}\right]^{n+1}}$$
(19)

Let
$$\tau' = 2\tau$$
 (20)
Substitute Equation (20) into (19) gives

$$\frac{c_n(t)}{c_o} = \frac{\left[\frac{1}{\tau'}\right]^{n-1}}{\left[1 + \frac{t}{\tau'}\right]^{n+1}}$$
(21)

Equation (21) gives a generic expression for particle(s) of n-order.

Hence for singlet (n=1)

$$C_{1} = C_{o} \left[\frac{1}{\left[1 + t/\tau_{t} \right]^{2}} \right]$$
For doublets (n=2)

$$C_2 = C_o \left[\frac{t/\tau}{\left[1 + t/\tau \right]^3} \right]$$
For triplets (n=3)

$$C_{3} = C_{o} \left[\frac{(t/_{\tau l})^{2}}{\left[1 + t/_{\tau l} \right]^{4}} \right]$$
(24)

Equations (22), (23) and (24) represent time evolution of particle size cluster distribution. The efficiency of coag-flocculation was determined using the following expression.

$$E(\%) = \frac{c_o - c_t}{c_o} \times 100$$
(25)

Following the work of Metcalf and Eddy (Burton, 2003), the relationship between turbidity and total suspended solid is as follows:

TSS $(mg/L) = (Tss_f) .T$ (26) Where T is turbidity (NTU), Tss_f is conversion factor=2.3.

4. Results and Discussion

4.1 Effect of Coagulant Dosage

In coag-flocculation process, dosage is one of the most important factors that have been considered to

determine the optimum condition for the performance of coagulants.



Figure.1: Turbidity removal with different coagulants dosages at pH 2.

It is evident that insufficient dosage or over dosing results in poor performance. So, it is significant to determine the optimum dosage in order to minimize sludge formation and obtain optimum performance in treatment (Ndabigengesere and Narasiah 1995).

The coagulation efficiency primarily depends on the self-aggregation that occurs after the neutralization of the negative charges of colloidal particles in the brewery wastewater by the positive charges of the coagulant (Diaz et al, 1999).

A comparative study of turbidity reduction efficiency of different coagulants are presented in **Table 3** and graphically represented in **Figure 1**. The coagulants dosages range from 100-500mg/L were used. The efficiency of turbidity removal increased rapidly to 87-92.43% for the three coagulants at 200mg/L dosage, with DMC having the maximum turbidity removal efficiency at 92.28%. The second highest among the coagulants used for the study was okra with 89.3%. The studies also show that higher dosage did not significantly increase removal and thus, not economical.

Table 5.

Percentage Turbidity Removal varying dosages								
(%)								
OPC	CYC	DM						
85.82	78.10	92.43						
88.31	86.46	89.76						
85.68	85.94	86.64						
84.73	83.34	85.35						
85.59	83.56	84.22						
	Removal v %) OPC 85.82 88.31 85.68 84.73 85.59	OPC CYC 85.82 78.10 88.31 86.46 85.68 85.94 84.73 83.34 85.59 83.56						

At this point it is important to note that optimum dosage of the three coagulants was 200mg/L. Previous work by (Diaz et al, 1999) showed that the plant coagulant can give turbidity removal up to 99.3%.

4.2. Effect of pH on Coag-flocculation

The effect of pH on coag-flocculation was studied and the optimum dosage of 200mg/L was selected to examine the effect of different pH on the removal of turbidity in wastewater. These effects are recorded in **Table 4** and graphically represented in Figure 2. It was observed that optimum pH value of 2 enhanced substantial removal of turbidity. At pH 2, maximum removal was observed with Detarium Microcarpum at 92.42%, followed by Okra at 85.82% and cocoyam at 78.10%.

Table 4	. Percentage	Turbidity	Removal	varying
pH (%)				

pН	OPC	CYC	DMC
2	85.82	78.10	92.43
4	83.04	88.64	90.07
6	57.55	73.06	63.26
8	48.31	71.43	59.07
10	33.61	27.71	33.08



Figure 2: Turbidity removal with varying pH at optimum coagulants dosages.

The pH will not only affects the surface of coagulant, but also affects the stabilization of the suspension. According to Huang and Pan (2002), at lower pH and coagulant dosage, the mechanism for destabilization of particles is charge neutralization. Also, good coag-flocculation at lower pH could be attributed to higher degree of protonation of amine group of the coagulant (Ebelling et al, 2006).

4.3. Analysis of Variance (ANOVA)

The effect of dosages of the three coagulants on coag-flocculation as shown in **Figure 1** shows that the performances with time have little significant difference for the different coagulants dosages as ANOVA results presented in **Table 5** reveal.

Also coag-flocculation carried out with different pH, between pH 2 and 10, with coagulant dosage of 200mg/L, presented in **Figure 2** was tested for significant difference. From the figure, there is no significant difference in pH for the three coagulants. The best turbidity removal at pH 2 recorded 96.43%, 88.82% and 78.10% and the worst turbidity removal at pH 10, recorded 33.8%, 33.61% and 27.71% for DMC, OPC, and CYC respectively.

It can be concluded from the analysis of variance (ANOVA) results presented in **Tables 5 and 6**, that $\alpha = 0.05$, since the computed value of test statistic; $F_{cal.} < F_{crit.}$ Where $F_{cal.} = 0.42$ (coagulation dosage) and also $F_{cal.} = 0.02$ (pH variation), is less than the critical value 3.89. Hence we fail to reject H_o and conclude that the null hypotheses of equality of means may be taken as true.

 Table 5. ANOVA result for coagulants dosages

 effect on coagulation performance of DMC, CYC

 and OPC

Source of variance	SS	df	MS	$F_{cal.}$	$F_{crit.}$
Between samples	29.48	2	14.71	0.42	3.98
Within samples	419.77	12	34.98		
Total	449.25	5 14			

Table 6.

ANOVA result for pH variation effect on coagulation performance of DMC,CYC and OPC

Source of variance	SS	df	MS	F _{cal}	F _{crit.}
Between samples	138.6	50 2	69.3	0.02	3.89
Within samples	6746.	87 12	2 562.2	24	
Total	6885	5.47 1	4		

4.4. Kinetics of Coagulation

The values of coag-flocculation reaction parameters for varying dosages and constant pH 2 of different coagulants are presented in **Tables 7-9**.

The values of coefficient of regression R^2 for pH and dosages are within $0.82 \le R^2 \ge 0.99$ which are high. This confirms that the study is consistent with Brownian coagulation (Smoluchowski et al, 1917).

Integration of Equation 5 (at $\alpha = 2$), yields Equation 6, from which K can be determined from slope of

 $\ln\left(-\frac{dc}{dt}\right) vs \ln C$ plot. The regression coefficient R^2 was used in evaluating the level of accuracy of fit of the experimental data.

From the results in **Tables 7-9** indicate that majority of \mathbb{R}^2 are greater than 0.9, hence it concludes that reaction is second order (Menkiti et al, 2010). A higher K corresponds to low $\tau_{1/2}$; a relationship that establish strong correlation among K, $\tau_{1/2}$ and rate of reaction. The highest value of K, $8 \times 10^{-2} L_{/mg.min}$, was recorded at pH 2, dosage 200mg/L and coagulation period, $\tau_{1/2}$ of 3.28 min for DMC, $5 \times 10^{-3} L_{/mg.min}$, dosage 200mg/L at pH 2 and coagulation period of 0.52min for OPC and $9 \times 10^{-4} L_{/mg.min}$, dosage 400mg/L at pH 2 and coagulation period of 0.03min for CYC.

 Table 7. Coag-flocculation Kinetics Parameters for DMC at varying Dosages and pH 2

Parameters	100mg/L	200mg/L	300mg/L	400mg/L	500mg/L
α	2	2	2	2	2
R^2	0.9781	0.9755	0.9682	0.9815	0.991
$K(Lmg^{-1}min^{-1})$	3×10^{-4}	8×10^{-4}	3×10^{-4}	2×10^{-4}	1×10^{-4}
$\tau_{1/2}$ min	8.79	3.28	8.7	10.86	26.48
τ' min	17.58	6.56	17.4	21.72	52.96
$(-r) \operatorname{mg} min^{-1}$	$3 \times 10^{-4} C_t^2$	$8 \times 10^{-4} C_t^2$	$3 \times 10^{-4} C_t^2$	$2 \times 10^{-4} C_t^2$	$1 \times 10^{-4} C_t^2$

Table 8

Coag -floccullation Kinetics Parameters for OPC at varying Dosage and pH 2

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Parameters	100mg/L	200mg/L	300mg/L	400mg/L	500mg/L	
α	2	2	2	2	2	
R^2	0.9977	0.9977	0.9873	0.9977	0.9981	
$K(Lmg^{-1}min^{-1})$	5×10^{-3}	4×10^{-3}	5×10^{-3}	4×10^{-3}	4×10^{-3}	
$\tau_{1/2}min$	0.59	0.52	0.53	0.57	0.6	
τ' min	1.18	1.04	1.06	1.14	1.2	
(-r) mg min ⁻¹	$5 \times 10^{-3} C_t^2$	$4 \times 10^{-3} C_t^2$	$5 \times 10^{-3} C_t^2$	$4 \times 10^{-3} C_t^2$	$4 \times 10^{-3} C_t^2$	

Table 9. Coag-flocculation Kinetics Parameters for CYC at varying Dosage and pH 2

100mg/L	200mg/L	300mg/L	400mg/L	500mg/L
2	2	2	2	2
0.822	0.9748	0.9905	0.962	0.9774
2×10^{-2}	1.5×10^{-3}	2×10^{-4}	9×10^{-2}	1.3×10^{-3}
0.133	1.76	12.04	0.03	2.18
0.266	3.52	24.08	0.06	4.36
$2 \times 10^{-2} C_t^2$	$1.5 \times 10^{-3} C_t^2$	$2 \times 10^{-4} C_t^2$	$9 \times 10^{-2} C_t^2$	$1.3 \times 10^{-3} C_t^2$
	$ \begin{array}{r} 100 \text{mg/L} \\ 2 \\ 0.822 \\ 2 \times 10^{-2} \\ 0.133 \\ 0.266 \\ 2 \times 10^{-2} C_t^2 \end{array} $	$\begin{array}{c cccc} 100 \text{mg/L} & 200 \text{mg/L} \\ 2 & 2 \\ 0.822 & 0.9748 \\ 2 \times 10^{-2} & 1.5 \times 10^{-3} \\ 0.133 & 1.76 \\ 0.266 & 3.52 \\ 2 \times 10^{-2} C_t^2 & 1.5 \times 10^{-3} C_t^2 \end{array}$	$\begin{array}{c cccccc} 100 \text{mg/L} & 200 \text{mg/L} & 300 \text{mg/L} \\ \hline 2 & 2 & 2 \\ 0.822 & 0.9748 & 0.9905 \\ 2 \times 10^{-2} & 1.5 \times 10^{-3} & 2 \times 10^{-4} \\ 0.133 & 1.76 & 12.04 \\ 0.266 & 3.52 & 24.08 \\ 2 \times 10^{-2} C_t^2 & 1.5 \times 10^{-3} C_t^2 & 2 \times 10^{-4} C_t^2 \end{array}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

Using Equations 22-24, the microscopic particle aggregation can be graphically illustrated by the interaction of singlets (n = 1), doublets (n=2) and triplets (n=3). The trends of aggregating particles, as a function of time for various coagulants dosages and

at constant pH of 2.0 are shown in **Figures 3-5.** The particle distribution curves have features of a system being controlled by rapid coag-flocculation processes occasioned by colloidal destabilization mechanism.

The singlets, doublets and triplets are seen decreasing linearly with time until it gets to a point,

where coag-flocculation rate attains the maximum value. This agrees with previous work (Nowicki and Nowicka, 1991).

The minimal $\tau_{1/2}$ values in **Tables 7-9**, suggest very fast coag-flocculation rate.

In Figures 3-5, there are forces of repulsion and attraction between the approaching particles. These are electrostatic repulsion between singlets and the sum of the particles which leads to van der waals attraction of dispersed components. Mainly, the dominant mechanisms in the three graphs are charge neutralization combined with low bridging giving moderate speed of coagulation. The discrete nature of the formation of C_1, C_2 and C_3 is associated with moderate energy barrier (Smoluchowski et al, 1917).



Figure 3: Particle distribution behavior for DMC dosages of 100mg/L to 500mg/L at minimum half-life of 3.28 min.



Figure 4: Particle distribution behavior for CYC dosages of 100mg/L to 500mg/L at minimum halflife of 0.03 min



Figure 5: Particle distribution behavior for varying OPC dosages of 100mg/L to 500mg/L at minimum half-life of 0.59 min.

5. Conclusions

The coag-flocculation process for the treatment of brewery effluent with natural based coagulants showed a great potential towards turbidity removal. The optimum dosage of treatment for the three coagulants was found to be 200mg/L at pH 2 and 4. Assessing the coagulants, DMC is most effective natural coagulant with turbidity removal efficiency of 92.43%, followed by OKC 88.31% and CYC 78.10%.

For the future development of the use of plant materials for wastewater treatment other native plants and plant materials should also be investigated.

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