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Parametric Response Evaluation for *Xanthosoma* spp. Induced Coag-Flocculation of Brewery Effluent

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ABSTRACT

This paper presents the kinetic and functional parametric behavior of cocoyam coagulant (CYC) in respect of pH and time variation in brewery effluent at room temperature. The study employed standard nephelometric jar test while CYC production was based on method reported by Ndabigengesere. Coag-flocculation parameter such as order of reaction α, rate constant K, coagulation period, $\tau_{1/2}$ etc. were determined. Maximum parameter values are recorded at K of 6×10^{-1} L/mg·min; dosage of 200 mg/L, pH 8 and $\tau_{1/2}$ of 0.00146 min while the minimum values are recorded at 3×10^{-7} L/mg, dosage of 100 mg/L, pH 10 and $\tau_{1/2}$ of 20.4 min. The maximum coag-flocculation efficiency E (%) obtained was 92.28, thus establishing CYC as a potential effective coag-flocculaant.

KEYWORDS

1. Introduction

With increased industrial growth and urbanization, the volume of domestic and industrial effluent is in the increase. In developed nations, these wastes are disposed off in accordance with regulatory standard. However, in some developing nations, there is no strict compliance to the laws governing the disposal of these wastes.

Globally, lager beer production has been on the increase with accompanied large wastewater generation. The effluent from brewery contains suspended solid in the range of 1000 - 1500 mg/L, COD in the range of 1800 - 3000 mg/L and nitrogen in the range of 30 - 100 mg/L [1]. Brewery effluent is of great environmental concern due to its potential harm to public health and the environment.

The treatment methods of wastewater include: activated carbon adsorption, oxidation, chemical coagulation/flocculation, electro-chemical methods, using various electrodes and electrolytes, nano-flitration and dif-ferent combinations of these methods [2-4].

Coagulation/flocculation is a commonly used process in water and wastewater treatment in which compounds such as alum, ferric chloride and/or polymer are added to wastewater in order to destabilize the colloidal materials and hence cause the small particles to agglomerate into large settle able flocs. Several studies have reported the application of this process for the treatment of industrial wastewater produced from textile, dye and beverages industries using inorganic chemicals [5,6]. While the effectiveness of these chemical as coagulant is well-recognized, there are nonetheless disadvantages associated with usage of these coagulants. These include ineffectiveness in low-temperature water, relatively high procurement costs, detrimental effects on human health, production of large sludge volumes and the fact that they significantly affect the pH of treated water. It is therefore desirable to replace these chemical coagulants with plants and animal based coagulant to minimize the challenges [7,8].

A part of possible solution to these problems might be the development of new bio coagulants which are eco/

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health friendly. In recent years, there has been intense interest in the application of plant based coagulants [9,10].

In this work, therefore, the potentials of cocoyam (*Xanthosoma)* tuber as a coagulant for the removal of particles from brewery effluent had been studied. According to Enwere [11], the flour of cocoyam is used traditionally as soup thickener. From the composition of cocoyam, shown in **Table 1**, it is of view that this property could be extended to coagulation process.

The purpose of this work is, therefore, to study the coagulation/flocculation behavior of cocoyam in brewery effluent, for the removal of both total suspended and dissolved particles. Also, it studied the effects of variation of dosage, settling time, pH etc., during coagulation.

2. Theoretical Principles

The Kinetics of Brownian coagulation can be descried by [12-14]:

$$\frac{dN_n}{dt} = \frac{1}{2}\sum_{i+j=n} K_{ij}N_iN_j - N_n\sum_{i=1} K_{in}\ N_i \quad (1)$$

where K_{ij} is a second order coagulation rate constant, t is the time, and N_n is the total particle concentration of n-fold clusters.

However, for the kinetic of Brownian coagulation of mono-dispersed particles at the early stage is describe generally by [12,14,15]:

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

where K = coagulation rate constant; α = order of coagulation reaction; N_t = concentration of the particles (TDSP) at time t.

Linear form of Equation (2) gives

$$\text{In}\left(\frac{dN_t}{dt}\right) = \alpha\ln N_t + \ln K \quad (3)$$

From Equation (3), α and K could be determined.

This rate constant K is a product of collision efficiency ε_p, and the Smoluchowski rate constant for rapid coagulation K_{11}

$$K = \varepsilon_p K_{11} \quad (4)$$

where ε_p = collision efficiency

K_{11} = Von Smoluchowski rate constant for rapid coagulation [12].

But Smoluchowski rate constant for rapid coagulation is given by

$$K_{11} = 4\pi R D_1 \quad (5)$$

$$R = 2a \quad (6)$$

where a = particle radius; D_1 = particle diffusion coefficient

Table 1. Characteristics of cocoyam (CYC precursor).

Parameter	Value
Moisture Content (%)	14.0
Ash Content (%)	2.0
Fat Content (%)	0.5
Crude Protein (%)	8.9
Carbohydrate (%)	73.1
Crude Fiber (%)	1.5

From Einstein's Equation

$$D_1 = K_B T / B \quad (7)$$

From Stokes relation,

$$B = 6\pi\eta a \quad (8)$$

$$a = \frac{R}{2} \quad (9)$$

where K_B = Boltzman's constant (molar gas constant per particle); B = friction factor

$$\eta = \text{fluid visocsity}$$

T = absolute temperature (K)
Putting Equation (9) into (8) yields

$$B = \frac{6\pi\eta R}{2} = 3\pi\eta R \quad (10)$$

Also, putting Equation (10) into (7)

$$D_1 = \frac{K_B T}{3\pi\eta R} \quad (11)$$

Putting Equation (11) into (5), produces

$$K_{11} = \frac{4K_B T}{3\eta} \quad (12)$$

Also, putting (12) into (4), yields

$$K = \varepsilon_p\left[\frac{4K_B T}{3\eta}\right]N^{\alpha} \quad (13)$$

Hence substituting (13) into (2)

$$\frac{dN_t}{dt} = -\varepsilon_p\left[\frac{4K_B T}{3\eta}\right]N^{\alpha} \quad (14)$$

WST [16] and Menkiti [15] reported that in real practice, $1 \leq \alpha \leq 2$. Based on this, what is required to evaluate K is to determine the line of better fit between $\alpha = 1$ and 2, while the experimental data are fitted into linearized form of Equation (2).

For $\alpha = 2$, Equation (2) yields

$$\frac{dN}{dt} = -KN^2 \quad (15)$$

Hence:

$$\int_{N_0}^{N_t} \frac{dN_t}{N_t^2} = -K \int_o^t dt \qquad (16)$$

$$\frac{1}{N_t} - \frac{1}{N_o} = Kt \qquad (17)$$

Making N_t the subject.

$$N_t = \frac{N_o}{1 + N_o Kt} \qquad (18)$$

$$N_t = \frac{N_o}{1 + \dfrac{t}{1/N_o K}} \qquad (19)$$

Let

$$\tau = 1/N_o K \qquad (20)$$

Hence

$$N_t = \frac{N_o}{1 + 1/\tau} \qquad (21)$$

when $t = \tau$, Equation (21) becomes

$$N_t = \frac{N_o}{2} \qquad (22)$$

Therefore as $N_o \to 0.5 N_o$; $\tau \to \tau_{1/2}$
Hence

$$\tau_{1/2} = 1/0.5 N_o K \qquad (23)$$

For Brownian aggregation at early stages (≤ 30 minutes), Equation (1) can be solved exactly, resulting in the expression [17,18].

$$\frac{N_{m(t)}}{N_o} = \frac{\left[t/2 \left[\dfrac{1}{KN_o} \right] \right]^{m-1}}{\left[1 + \dfrac{t}{2\left[\dfrac{1}{KN_o}\right]} \right]^{m+1}} \qquad (24)$$

where $\tau = \dfrac{1}{N_o K}$

Therefore

$$\frac{N_{m(t)}}{N_o} = \frac{[t/2\tau]^{m-1}}{1 + [t/2\tau]^{m+1}} \qquad (25)$$

$$2\tau = \tau' \qquad (26)$$

Substitute Equation (26) in (25), gives

$$\frac{N_{m(t)}}{N_o} = \frac{[t/\tau']^{m-1}}{[1 + t/\tau']^{m+1}} \qquad (27)$$

Equation (27) gives a generic expression for particle of

m-order.
Hence,
For Singlets ($m = 1$)

$$N_1 = N_o \left[\frac{1}{[1 + t/\tau']^2} \right] \qquad (28)$$

For doublets ($m = 2$)

$$N_2 = N_0 \left[\frac{t/\tau'}{[1 + t/\tau']^3} \right] \qquad (29)$$

For triplets ($m = 3$)

$$N_3 = \left[\frac{[t/\tau']^2}{[1 + t/\tau']^4} \right] \qquad (30)$$

Turbidity (NTU) can be converted to TSS (mg/L) using Equation (31) [19].

$$TSS(mg/L) = (TSS_f). T \qquad (31)$$

where T = Turbidity (NTU); (TSS_f) = Conversion factor to TSS.

Evaluation of coagulation-flocculation efficiency is given as

$$E(\%) = \left[\frac{N_o - N_t}{N_o} \right] \times 100 \qquad (32)$$

3. Materials and Methods

3.1. Wastewater Sampling

The brewery effluent collected from brewery plant located in Enugu, were characterized and the analyses are given in **Table 2**. The samples were stored in black plastic container to avoid photo reaction

3.2. Preparation of Stock Solution of Natural Coagulant

The cocoyam (*Xanthosoma* spp.) used in this work was purchased from Ogbette Market, Enugu State Nigeria and stored at room temperature. The cocoyam was peeled, washed and sliced into chips. The chips were sun dried enough to break sharply between hands. The chips were ground to powder of approximately 600 µm using a kitchen blender to ensure solubilization of active ingredients in the tuber. The characteristics of the sample on the bases of AOAC [20] standard method are presented in **Table 1**.

2% suspension (2 g of powdered cocoyam in 100 mL tap water) of the powder was prepared and vigorously shaken for 30 min using magnetic stirrer (APP No 688644A Gulenhamp) to promote water extraction of the coagulating agent. The suspension was filtered using Whatman No 1 filter paper. The filtered solution (stock solution) was termed CYC. Fresh solution was prepared daily and kept refrigerated to prevent any ageing effects

Table 2. Characteristics of brewery effluent.

Parameter	Value
Temperature	27
pH	7.68
Turbidity (NTU)	316.63
Electrical Conductivity μ/cm	5290.0
Total hardness (mg/L)	41.0
Ca hardness (mg/L)	36.0
Mg hardness (mg/L)	14.0
Ca^{2+} (mg/L)	15.6
Mg^{2+} (mg/L)	0.6
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)	30.406
E. coli	Nil
BoD_5 (mg/L)	640.0

(such as change in pH, viscosity and coagulation activity). CYC was shaken vigorously before use.

A conventional jar test apparatus was used in this experiment. 100 - 500 mg/L range of CYC dosage was prepared in a standard 1000 mL beaker containing 300 mL of the effluent. The suspension, tuned to pH range 2 - 10 by addition of 0.1 M H_2SO_4/0.1 M NaOH was subjected to 2 min of rapid mixing (200 rpm), 20 min of slow mixing (30 rpm) using a magnetic stirrer. After agitation, the suspension was transferred into a 250 mL cylinder of height, 34 cm, diameter, 4 cm and the suspension height, 29 cm. During settling, 10 mL of the supernatant was withdrawn from 2 cm depth and changes in TDSP (mg/L) measured for kinetic analysis (using WZS-185 MC Turbidimeter) at various intervals of 3, 5, 10, 15, 20, 25 and 30 min. The procedure was carried out at room temperature. The data obtained were subsequently fitted to appropriate kinetic models.

4. Results and Discussion

4.1. Kinetic Analyses

The Kinetic analyses were performed for a sample of Brewery effluent (BRE) with an initial TDSP of 728.249 mg/L. The CYC dosage used was in the range of 100 - 500 mg/l and pH was 2 - 10. From **Table 2**, the pH of the Brewery effluent was 7.68 indicating that the effluent was slightly alkaline. The high value for turbidity, TDS and TSS shows that the effluent has high pollution potentials and as a result, treatment is required before discharged to the environment. **Table 1** also indicates that quantity of polysaccharides or proteins available in the powder shows the potential of the CYC to be applied to water treatment. Similar result has been obtained [11].

The results obtained from the analyses were evaluated as the coag-flocculation functional parameters which are presented in **Tables 3-7**.

Solving Equation (15), by integration method (taking α = 2), yields 17, from which K could be determined from slope of (1/N) Vs t plot. Representative plots of (1/N) vs t is depicted in **Figure 1**.

Linear regression coefficient (R^2) was employed in evaluation of the accuracy of fit of the experimental data on the main model expressed as Equation (17). For all cases of dosages and pH, the value of α is 2. With the exception of few, the corresponding value of R^2 is generally >0.9. The high values of R^2 indicate a high measure of agreement that the reaction follows a second order kinetic model. This means that the rate of reaction is proportional to (N^2) and K as described by Equation (15). The highest value of K of 6×10^{-1} L/mg·min is recorded at pH 8, and 200mg/L CYC. The least K of 3×10^{-7} L/mg·min is recorded at pH 10, and 100 mg/L. Observation from the results shows that coagulation/flocculation with low dosage is more favored in alkaline medium.

$\tau_{1/2}$ indicates the time taken for the initial concentration of TDSP to reduce by half, and is evaluated from Equation (23). In this study, it is observed that lowest $\tau_{1/2}$ (0.00416min) is recorded at K 6×10^{-1} L/mg·min. From Equation 23, $\tau_{1/2}$ is a function of initial TDSP (N_o) concentration and rate constant K. From Equation (23), the higher the N_o, the lesser the $\tau_{1/2}$. This explains the prevalent high rate of settling in high turbidity water. ε_p, which is particle collision efficiency relates proportionally to the kinetic energy acquired by the colliding particles. It has been reported that by Hunter [14] that low period is necessary for efficient system.

4.2. Variation of Coag-Flocculation Efficiency as a Function of Time, pH and Dosage

The variation of coag-flocculation efficiency of CYC with time, pH and dosage is obtained based on the evaluation of Equation (32). The plots of the results presented in **Figures 2-6**, are obtained at 100, 200, 300, 400 and 500 mg/L CYC for pH 2, 4, 6, 8, 10. The general observable coag-flocculation behavior shows that efficiency increases with time, but the magnitude varies for different pH and dosage. The efficiency at 3 min was generally between 36% and 61.5% at pH 2 and 4, respectively. At end of 30 min of coag-flocculation, the efficiency removal reached 70% to 92.28% for pH 2 and 4, respectively. But the best performance was achieved at pH4 of 100 mg/L and at pH 2 of 500 mg/L dosage at 88.64% and 92.28%, respectively. The high level performance for these biomaterials are in line with previous results [7,13,18].

4.3. Microscopic Particle Distribution Behavior

The particle distribution plots are obtained based on the

Table 3. Coag-flocculation kinetic parameter of CYC in BRE at varying pH and 100 mg/L dosage.

Parameter	pH = 2	pH = 4	pH = 6	pH = 8	pH = 10
A	2	2	2	2	2
R^2	0.822	0.994	0.9765	0.9808	0.9907
K (L/mg·min)	2.07×10^{-2}	1.37×10^{-3}	4.50×10^{-6}	3.011×10^{-6}	3.155×10^{-7}
ε_p (mg^{-1})	1.668×10^{13}	1.106×10^{12}	3.629×10^{9}	2.427×10^{9}	2.543×10^{8}
$\tau_{1/2}$(min)	0.133	2.0	8.5	1.8	20.4
T' (min)	0.266	4.0	17	3.6	40.8

Table 4. Coag-flocculation kinetic parameter of CYC in BRE at varying pH and 200 mg/L.

Parameter	pH = 2	pH = 4	pH = 6	pH = 8	pH = 10
A	2	2	2	2	2
R^2	0.9748	0.9542	0.8589	0.9753	0.9326
K (L/mg·min)	1.553×10^{-3}	1.407×10^{-3}	4.925×10^{-4}	6.59×10^{-1}	8.9×10^{-2}
ε_p (mg^{-1})	1.2519×10^{12}	1.1342×10^{12}	3.9703×10^{11}	5.312×10^{14}	7.17×10^{13}
$\tau_{1/2}$(min)	1.76	1.95	0.179	0.00416	0.03
T' (min)	3.52	3.9	0.358	0.00832	0.06

Table 5. Coag-flocculation kinetic parameter of CYC in BRE at varying pH and 300 mg/L.

Parameter	pH = 2	pH = 4	pH = 6	pH = 8	pH = 10
A	2	2	2	2	2
R^2	0.9905	0.9821	0.8508	0.8814	0.9105
K (L/mg·min)	2.28×10^{-4}	5.78×10^{-3}	7.86×10^{-5}	1.02×10^{-1}	1.68×10^{-5}
ε_p (mg^{-1})	1.84×10^{11}	4.66×10^{12}	6.34×10^{10}	8.2×10^{13}	1.35×10^{10}
$\tau_{1/2}$(min)	12.04	0.475	14.6	0.027	18.8
T' (min)	24.08	0.95	29.2	0.054	37.6

Table 6. Coag-flocculation kinetic parameter of CYC in BRE at varying pH and 400 mg/L.

Parameter	pH = 2	pH = 4	pH = 6	pH = 8	pH = 10
A	2	2	2	2	2
R^2	0.962	0.8744	0.9809	0.991	0.9735
K (L/mg·min)	9.05×10^{-2}	3.14×10^{-2}	1.71×10^{-4}	7.7×10^{-5}	3.94×10^{-6}
ε_p (mg^{-1})	7.3×10^{13}	2.53×10^{13}	1.38×10^{11}	6.2×10^{10}	3.17×10^{9}
$\tau_{1/2}$(min)	0.03	0.087	16.08	12.68	10.6
T' (min)	0.06	0.174	32.16	25.36	21.2

Table 7. Coag-flocculation kinetic parameter of CYC in BRE at varying pH and 500 mg/L.

Parameter	pH = 2	pH = 4	pH = 6	pH = 8	pH = 10
A	2	2	2	2	2
R^2	0.9774	0.9955	0.9307	0.9178	0.7682
K (L/mg·min)	1.25×10^{-3}	2.96×10^{-3}	3.05×10^{-3}	6.02×10^{-5}	2.3×10^{-5}
ε_p (mg^{-1})	1.01×10^{12}	2.39×10^{12}	2.46×10^{12}	4.86×10^{10}	1.86×10^{10}
$\tau_{1/2}$(min)	2.18	0.927	0.9	13.5	17.8
T' (min)	4.36	1.854	1.8	27	35.6

evaluation of Equations (28) - (30). The microscopic particles aggregation behavior were evaluated and presented in **Figures 7** and **8**. From the graphical illustration, it shows that the number of total particles m, singlets, doublets and triplets decreased as a function of time.

Minimum $\tau_{1/2}$ value was recorded at 0.00416 min, corresponding to the period of rapid coagulation, which indicated that there are greater forces of attraction than
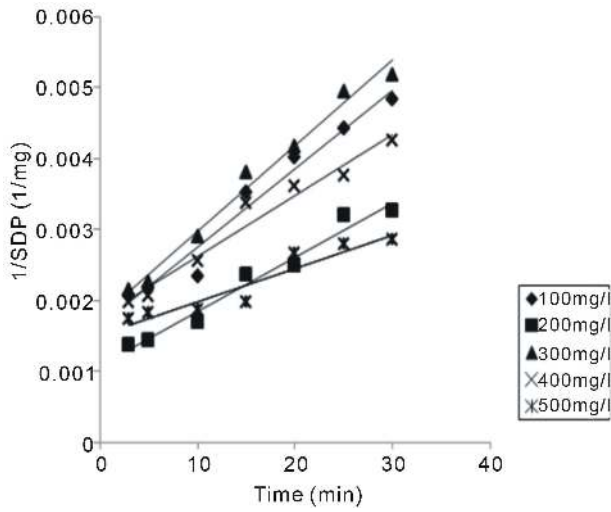
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Figure 1. Representative plot of 1/SDP as a function of time for 100 mg/L CYC.
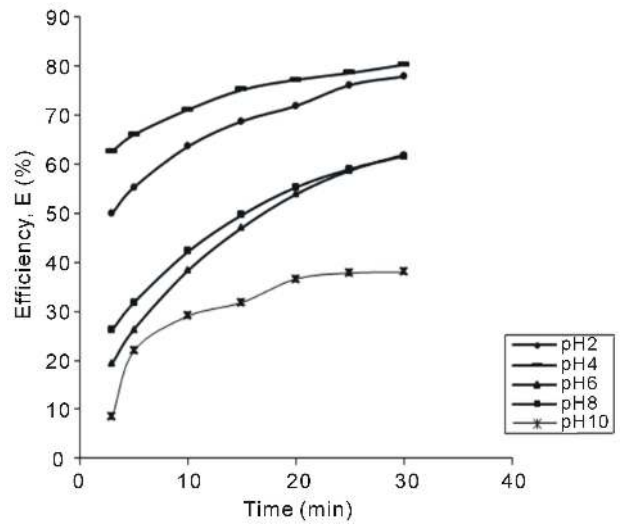

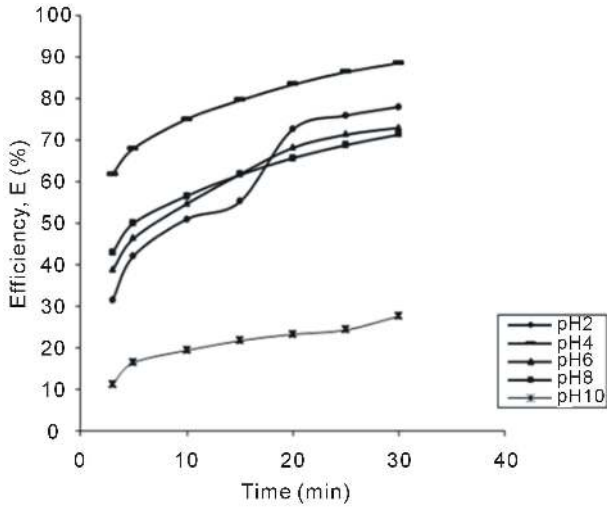**Figure 4. Selected plot of E (%) vs time for 300 mg/L.**

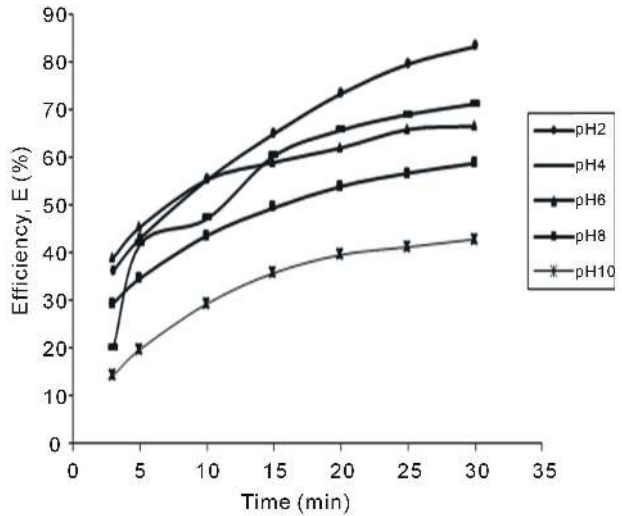**Figure 2. Selected plot of E (%) vs time for 100 mg/L.**

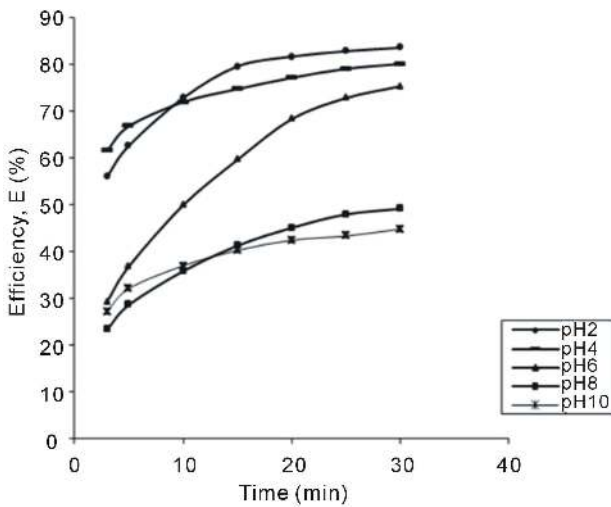**Figure 5. Selected plot of E (%) vs time for 400 mg/L.**

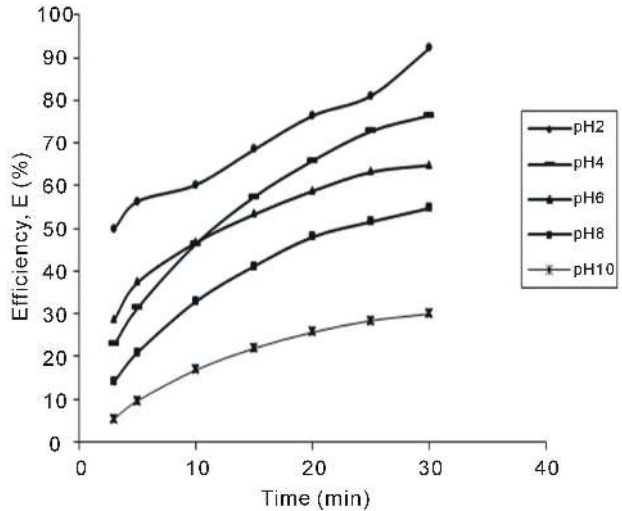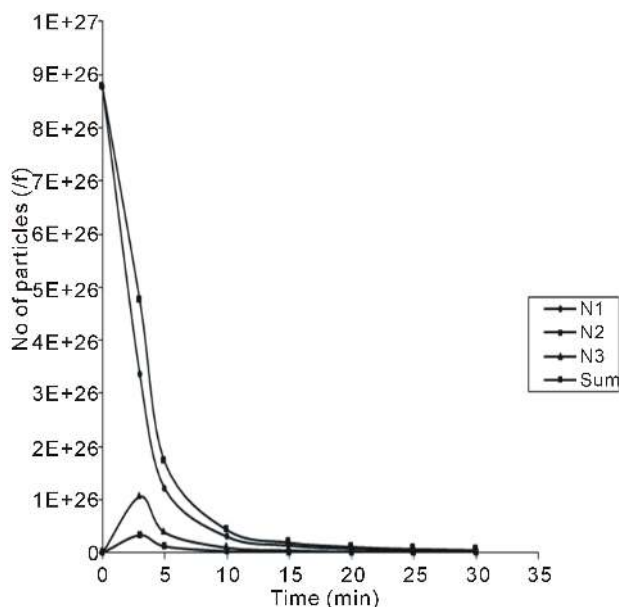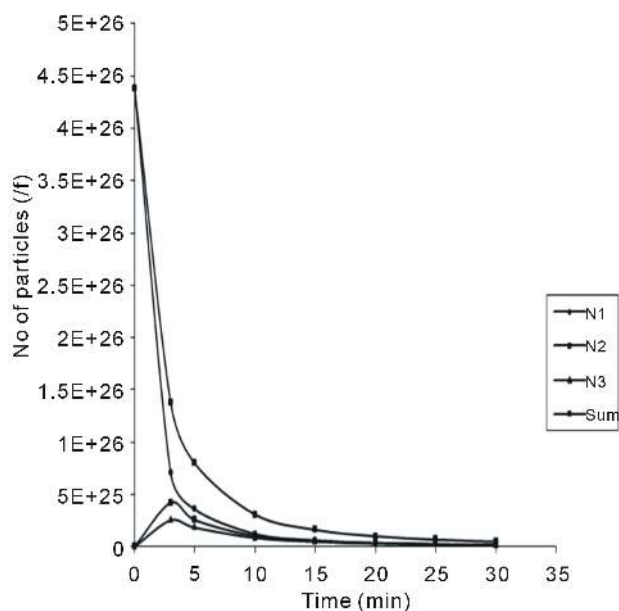**Figure 3. Selected plot of E (%) vs time for 200 mg/L.**

Figure 6. Selected plot of E (%) vs time for 500 mg/L.

Figure 7. Temporal microscopic aggregate distribution at minimum half-life of 0.00416.

Figure 8. Temporal microscopic aggregate distribution at maximum half-life of 20.4 min.

repulsion.

Also in **Figure 8**, the value of $\tau_{1/2}$ (20.4 min) was high, corresponding to low collision, suggesting inability of particles to acquire energy need for effective coagulation.

This is an indication that there is no particle sweep, only a fraction of the particles flocculated. Similar results have been reported elsewhere [1,15].

5. Conclusion

From experimental results, CYC is an effective coag-

flocculant for treatment of brewery effluent, at the conditions of the experiment. However, varying the pH and dosage has significant difference on the coag-flocculation performance. The clarification performed best at 100 mg/L and 200 mg/L at pH2 and 4, respectively. Maximum efficiency of 92.28% was achieved at 200 mg/L. It could be concluded that second order model described the process adequately.

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