

Evaluation of Perikinetics Compliance for the coag-flocculation of Brewery Effluent by *Brachystegia eurycoma* Seed Extract

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Abstract– This work subjects at room temperature the coag-flocculation behavior of *Brachystegia eurycoma* coag-flocculant (BEC) to perikinet system at varying dosage and Brewery effluent (BRE) pH. The study employed standard nephelometric jar test while BEC production was based on method reported by Ghebremichael. Perikinet data generated were fitted to specific models for the determination of parameters such as reaction order, rate constant, period etc. Results indicate that reaction order, rate constant, period, pH and dosage recorded optimum values at 2, 5×10^{-5} l/mg.min, 4.063 minutes, 10 and 100mg/l, respectively. Maximum efficiency recorded at 95.510% for 30minutes indicates that the system is perikinet controlled. The results have established at the conditions of the experiment the use of BEC for the removal of particles from BRE.

Keywords– *Brachystegia eurycoma*, Brewery Effluent, Coag-flocculation and Perikinetics

I. INTRODUCTION

The production of lager beer is accompanied by significant generation of waste water, commonly referred to as brewery effluent (BRE). Raw BRE typically contains suspended solids in the range 10-60mg/l, biochemical oxygen demand in the range 1000-1500mg/l, COD in the range 1800-3000mg/l and nitrogen in the range 30-100mg/l. Phosphorus can also be present at concentrations of the order of 10-30mg/l. Effluents from individual process steps vary [1].

The development of new technologies, practices and bio raw materials for the treatment of BRE or the optimization of existing ones is vital for efficient growth of the industry, while minimizing impacts to the environment. Coag-flocculation techniques can readily be applied to these ends.

The terms coagulation/flocculation (coag-flocculation) are used as synonyms, though they are distinct and sequential steps [2-4]. Both represent the whole process of agglomeration of particles. Specifically, coag-flocculation is a chemical process used to destabilize the colloidal particles. The addition of a chemical agent generates positively charged ions in water, which conventionally contains negatively charged colloids. As a result, there is a suppression of the repulsion between the particles [5-6]. Flocculation is the aggregation of particles in suspension into visible flocs that sediment under gravity [7-8]. This agglomeration is a function of the Van der Waals forces, temperature, pH etc [6]

The formation of flocs can occur spontaneously only through the successive collisions between the several particles, if the system has energy available to do so, due to the agitation of the system. However, very intense stirring can disaggregate the flocs, leading to restabilization of the fluid medium.

A number of aggregating agents are used in water treatment processes. They include inorganic coagulants (salts of Al and Fe), synthetic and natural organic polymers [9-11]. Aluminium sulfate is widely used globally as a coagulant, but recently its use has been questioned due to evidence that Alzheimer's disease may be associated with aluminium in the water intended for human consumption. Moreover, aluminium is biorecalcitant, poses disposal problems and requires treatment of the generated sludge.

For developing economies, importation of alum is additional cost to the nation. In this context, natural aggregants which are eco-friendly, locally abundant and cheap can be introduced as a viable alternative for the treatment of waste water. Among such natural aggregants is *Brachystegia eurycoma* seed. *B. eurycoma* is genus of tree of the sub-family *caesalpinioideae*. It is native to tropical climate of Eastern Nigeria and has 13.26% protein, 70.44% carbohydrate, 6.8% crude fibre and 22.4% moisture content [12]. The seed is edible, non-toxic and biodegradable substance. Its successful application in the treatment of coal washery effluent [13], gives impetus to its utilization in the treatment of BRE.

In this present study, therefore, the coag-flocculation kinetics of BEC treated BRE at varying temperature was investigated. The efficiency of the treatment process as a function of time, pH, and dosage was also studied. Data generated will add to existing pool of resource to enhance the development of water treatment technology in our local communities.

II. MODEL DEVELOPMENT

A. Coag-flocculation kinetic

For a coag-flocculating phase, the rate of successful collision between particles of sizes i and j to form particle of size k is [14-17]:

$$\frac{dn_k}{dt} = \frac{1}{2} \sum_{i+j=k} \beta_{BR}(i, j)n_i n_j - \sum_{i=1}^{\alpha} \beta_{BR}(i, k)n_i n_k \quad \dots 1$$

Where $\beta_{BR(i,j)}$ is Brownian aggregation factor for flocculation transport mechanism, $n_i n_j$ is particle aggregation concentration for particles of size i and j , respectively. It has been established that [16-18]:

$$\beta_{BR} = \frac{8}{3} \varepsilon_p \frac{K_B T}{\eta} \quad \dots 2$$

$$\text{and } K_R = 8\pi a D' \quad \dots 3$$

Where K_R is the Von Smoluchowski rate constant for rapid coagulation. K_B, T and η are Boltzmann constant, temperature and viscosity, respectively. ε_p is collision efficiency factor, D' is the diffusion coefficient and a is particle radius.

Equations 2 and 3 can be transformed to

$$\frac{1}{2} \beta_{BR} = K_m \quad \dots 4$$

Where K_m is defined as Menkonu coag-flocculation rate constant accounting for Brownian coag-flocculation transport of destabilized particles at α^{th} order. It can also be shown that coag-flocculation is governed by [4][13][19-20]:

$$-\frac{dN_t}{dt} = \varepsilon_p K_R N_t^\alpha \quad \dots 5$$

$$\text{Where } \varepsilon_p K_R = 0.5 \beta_{BR} \quad \dots 6$$

$$\text{Thus } -\frac{dN_t}{dt} = K_m N_t^\alpha \quad \dots 7$$

N_t is the concentration of SDP at time, t .

Empirical evidence shows that in real practice, $1 < \alpha < 2$ [4] [9-11], [21]. Graphical representation of linear form of equation (7) at $\alpha=2$ provides for K_m from the slope of linear equation below:

$$\frac{1}{N} = K_m t + \frac{1}{N_0} \quad \dots 8$$

where N_0 is the initial N_t at time = 0; N is N_t at upper time limit > 0

Equation 8 can be solved to obtain coag-flocculation period, $\tau_{1/2}$:

$$\tau_{1/2} = (0.5 N_0 K_m)^{-1} \quad \dots 9$$

Equation 1, solved exactly, results in generic expression for microscopic aggregation:

$$\frac{N_{m(t)}}{N_0} = \frac{\left[\frac{1}{\tau_{1/2}} \right]^{m-1}}{\left[1 + \frac{t}{\tau_{1/2}} \right]^{m+1}} \quad \dots 10$$

$m=1$ (monomers), $m=2$ (dimers), $m=3$ (trimers)
Efficiency of coag-flocculation is expressed as:

$$E(\%) = \left[\frac{N_0 - N_t}{N_0} \right] 100 \quad \dots 11$$

III. MATERIALS AND METHODS

A. Materials collection, preparation and characterization

1). Brewery effluent (BRE)

The effluent was taken from a major brewery located in Enugu, Enugu State, Nigeria. The characterization of the effluent presented in table 1 was determined based on standard method [22].

2). *Brachystegia eurycoma* seed sample

Brachystegia eurycoma seed samples (precursor to BEC) were sourced from Nsugbe, Anambra State, Nigeria. BEC was prepared according to procedure reported by Ghebremichael [23]. The characteristics of the sample on the bases of AOAC [24] standard method are presented in table 2.

B. Coag-flocculation Experiments

Experiments were conducted using conventional jar test apparatus. Appropriate dosage of BEC in the range 100-500mg/l was added directly to 200ml of BRE. The suspension, tuned to pH range 2-10 by application of $H_2SO_4/NaOH$ was subjected to 2 minutes of rapid mixing(250rpm), 20 minutes of slow mixing(20rpm) and followed by 30 minutes of settling. During settling, samples were withdrawn from 2cm depth and changes in SDP (in mg/l) measured for kinetic analysis. The aggregation kinetics readings at room temperature were monitored and collected at 3,5,10,15,20,25 and 30 minutes. The data were subsequently fitted in appropriate kinetic models.

IV. RESULTS AND DISCUSSION

A. Nephelometric Kinetic Results

The kinetic tests were performed using standard nephelometric jar test, for a sample of BRE with an initial SDP of 10031.87mg/l, BEC dosage range 100-500mg/l and pH range 2-10. The kinetic parameters have significant influence on the design, fabrication and operational efficiency of any coag-flocculation unit. Such important functional parameters are presented in tables 3-7.

Application of integral method on equation 7(at $\alpha=2$), results in equation 8, from which K_m can be determined from slope of $(1/N)$ vs t plot. Linear regression coefficient (R^2) was employed in evaluation of the level of accuracy of fit of the experimental data on the main model expressed as equation 8. Results in tables 3-7 indicate that majority of R^2 in the tables are greater than 0.9. Hence, it can be concluded that the reaction is second order with various speed constant, K_m posted in tables 3-7. This means that the speed of reaction is proportional to (N_t) and K_m as described by equation 7. Representative results for the various dosages and pH as displayed in tables 3-7 is graphically depicted in figure 1. It

should be noted that the graphical trends (not shown) for the various dosages and pH are identical.

$K_m = (0.5\beta_{BR})$ expressed as equation 4 is displayed in tables 3-7. The highest value of K_m of 5.0×10^{-5} l/mg.min is recorded at pH 10 and 100mg/l BEC. The least K_m (9×10^{-6} l/mg.min) is recorded at pH 2,8 and 500mg/l BEC. Apparently, the best performances at the conditions of these experiments were achieved at basic medium with the exception of 400mg/l BEC where optimum result holds at pH 4. It is known that coag-flocculation is favoured in alkaline medium following easy delamination of the coag-flocculation phase [25], [26].

ϵ_p and K_R are functional parameters with considerable influence on coag-flocculation process. K_R is a linking factor between temperature and viscosity of the fluid medium. The direct impact of temperature and viscosity underscores the weight of K_R during coag-flocculation. Due to invariant temperature and viscosity ranges employed in this study, insignificant variation in the values of K_R was recorded as shown in tables 3-7. At approximately non – varying K_R , ϵ_p relates directly to $2K_m = B_{BR}$ as expressed in equation 4. Hence, high ϵ_p results in high kinetic energy necessary to overcome prevalent electrostatic repulsion preventing the agglomeration of interacting particles. Low repulsive forces translate to low zeta potential, a feature that is desirable in coag-flocculation phase. The advantage of low zeta potential lies in the low use of the coag-flocculant and probably low consumption of energy during water treatment. The implication in this study is that relatively low repulsion exists in alkaline medium, indicated by highest K_m at pH 10. It has been reported that $\tau_{1/2}$, ϵ_p and K_R are considered to be effectiveness factor, postulated to be accounting for the coag-flocculation efficiency before flocculation commences [2], [13].

The coag-flocculation period, $\tau_{1/2}$ indicates the time taken for the initial concentration of SDP to reduce by half. It is evaluated from equation 9. It is generally an index of the speed of the treatment process. Low period indicates fast rate of aggregation. The major drive in process design is to keep the period as low as possible. From equation 9, it can be inferred that period is a function of rate constant and initial SDP concentration, mathematically expressed as $\tau_{1/2} = f(n/N_0, K_m)$. The implication from equation 9, is that, the higher the N_0 , the lesser the period. This explains the prevalent high rate of settling in high turbidity water. Specifically, in this study, it is observed that lowest period is recorded at high K_m . Thus high K_m corresponds to low period. There are some inherent deviations in the results. The discrepancies observed in table 6 are due to unattainable assumption that mixing of BRE particles and BEC throughout the dispersion is 100% efficient before aggregation sets in [3] [27], [28], [29]. Second account is the interplay between Vander Wall's and hydrodynamic forces which typically alters the theoretically predicted values by a factor of ± 2 .

B. Microscopic Particle Aggregation As a Function Of Time

By substituting $\tau_{1/2}$ from equation 9 into 10, the microscopic particles aggregation can be graphically illustrated by the interaction of singlet ($m=1$), doublets ($m=2$)

and triplets ($m=3$). Representative results are shown in figures 2 and 3. The response of equation 10 to two different $\tau_{1/2}$ of 4.062 and 25.391 minutes are demonstrated as cases I and II, respectively.

Case I:

This is distribution profile associated with moderately rapid destabilization of charge particles. This is graphically demonstrated in figure 2. In this case, the monomers and particles can be seen to decrease more. This case depicts moderately hyper slope with time. The physically sensible response of the process is moderately low period that runs into units of minutes instead of subminutes. Elsewhere, period of less than 1.5 seconds had been reported in literature [17]. The period evaluated for Fig. 2 is an indicative of middle level zeta potential that leads to moderately sweeping away of SDP under gravity from the bulk fluid.

Case II:

Fig. 2 predicts the distribution of particles with time in favour of even distabalization regime, low entrapment profile and moderate bridging mechanism. Arguably, the shear resistance among the particles is relatively high, but not strong enough to operate outside perikinetics controlled process. The curve clearly demonstrates the exclusion of sweeping phenomenon being in action. This is supported by period of up to 25.391 minutes, a rather high value for most treatment operations. The high discrete nature of formation of doublets and triplets supports the existence of perceived energy barrier in view of the gentle trends of the graphs.

C. Variation Of Removal Efficiency, E(%) As a Function Of Time, pH and Dosage

The variation of removal efficiency(%) with time, pH and dosage is obtained based on the evaluation of equation 11. The graphical results, represented in figures 4-8 are obtained for Ph 2,4,6,8,10 at 100,200,300,400,500mg/l BEC dosages. Generally, the efficiency increases with increase in time, though the magnitude differs for particular pH and dosage. The efficiency at 3 minutes was generally between 81 and 95.51% at pH 2 and 10, respectively. From figures 4-8, it can be observed that at 30 minutes of coag-flocculation, the least efficiency achieved is more than 90%. The physical implication is that at least 80% and 90% of initial SDP load of 10031.87 mg/l were removed at 3 and 30 minutes, respectively. Best performance was achieved at pH 10 of 100mg/l dosage. It has earlier been adduced that the good performance at alkaline conditions is due to delmination of the BRE by NaOH. Mechanisim of coag-flocculation has been postulated to have effects on the influence of dosage on the aggregation. Effective treatment could be achieved with relatively lower doses of BEC especially when complete charge neutralization is not required and process controlled by combine impacts of electrostatic patch and bridging mechanism [25]. Following the performance of 100mg/l BEC, it is considered for comparison with conventional alum in Fig. 9.

D. Comparative Removal Efficiency(%) of BEC and Alum

The comparison of removal efficiency between alum and BEC at same experimental conditions is presented in figure 9 at 100mg/l and pH 2, 4, 6, 8,10. If recalled, the best performance was recorded at Ph 10. The least performance shown in the figure is achieved at Ph2. In general, the least E(%) is 92.791%, a value that is good by most performance standard. Similar results (not shown) were obtained for 200, 300, 400, 500mg/l BEC dosages. For practical and efficient purposes, BEC at all pH of 100mg/l compared favorably with alum. The major advantage of BEC being that it is environment friendly, cheap, abundant with simple preparation protocol.

V. CONCLUSION

At the conditions of the experiment, the effectiveness and efficiency of BEC for the coag-flocculation treatment of BRE was successfully conducted. This presents novelty in this work. The value of percentage of SDP removed from BRE at 30 minutes indicates clearly of perikineti controlled system. The system operates best at 100mg/l and pH 10, with maximum efficiency of 95.50% achieved.

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Table 1: Characteristics of Brewery Effluent

Parameters	Values
pH	6.940
Turbidity (NTU)	4269.700
Total hardness(mg/l)	68.000
Ca hardness (mg/l)	51.000
Mg hardness (mg/l)	18.000
Ca ²⁺ (mg/l)	20.400
Mg ²⁺ (mg/l)	5.400
Fe ²⁺ (mg/l)	0.180
SO ₄ ²⁻ (mg/l)	48.140
NO ₃ ²⁻ (mg/l)	0.150
Cl ⁻ (mg/l)	18.994
E.cond(μm/m ²)	480.000
TDS (mg/l)	268.810
TSS (mg/l)	27.301
T.Coliform	13.001
Plate Count	72.000
E-Coli	Nil
BOD ₃	672.003

Table 2 :Characteristics of BEC precursor

Parameter	Value
Moisture content (%)	2.240
Ash content (%)	3.300
Lipid content (%)	6.200
Crude protein (%)	15.024
Carbohydrate (%)	68.420
Crude fiber (%)	4.816

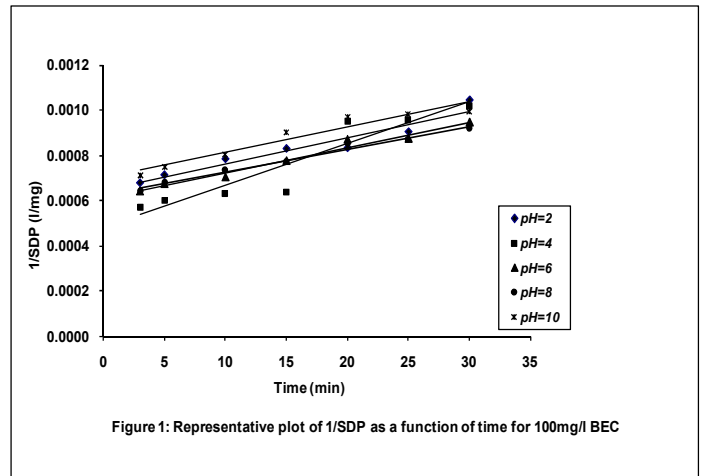


Figure 1: Representative plot of 1/SDP as a function of time for 100mg/l BEC

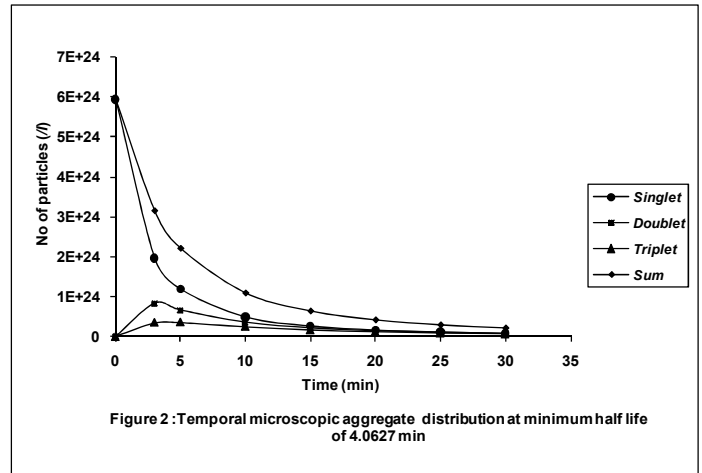


Figure 2: Temporal microscopic aggregate distribution at minimum half life of 4.0627 min

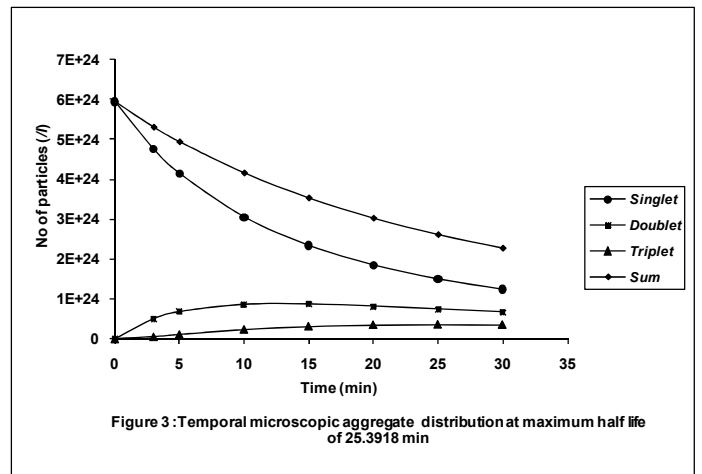


Figure 3: Temporal microscopic aggregate distribution at maximum half life of 25.3918 min

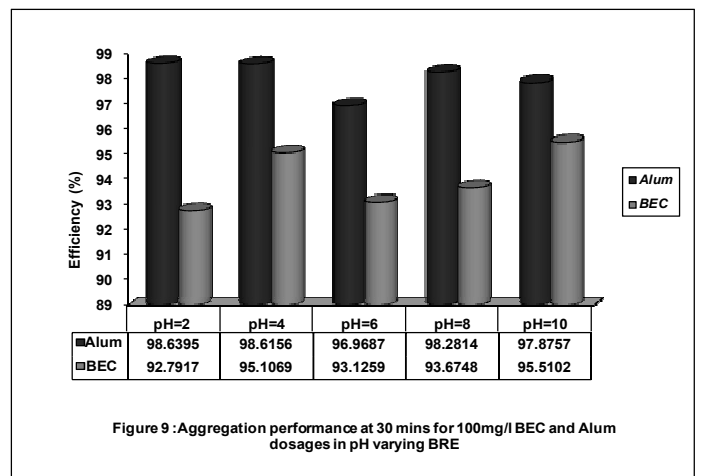
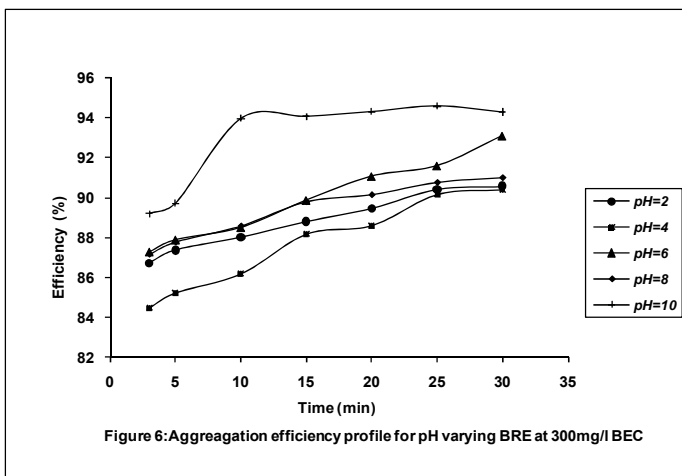
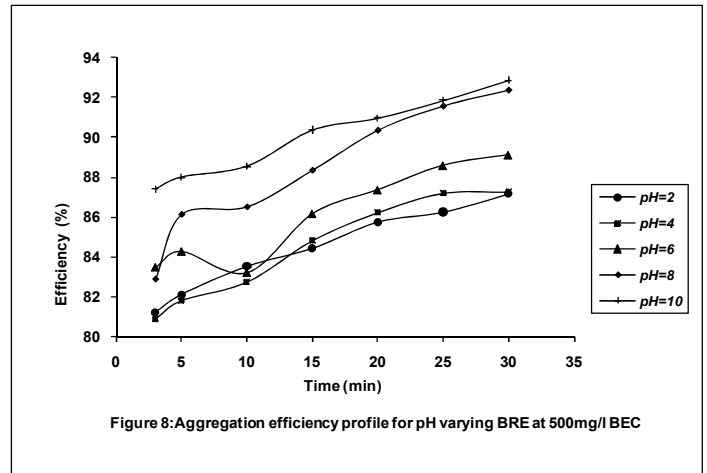
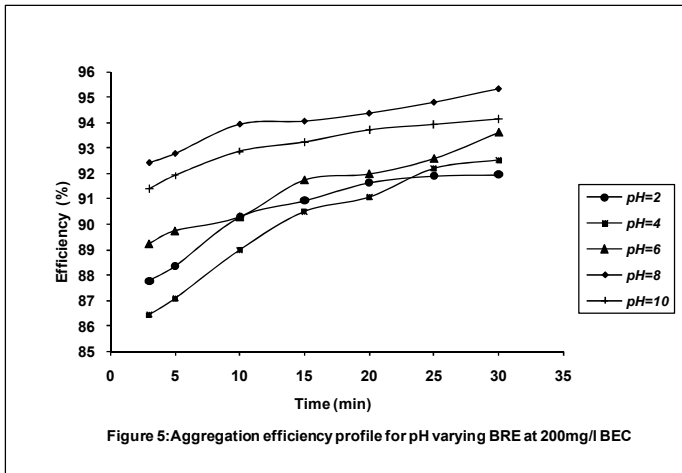
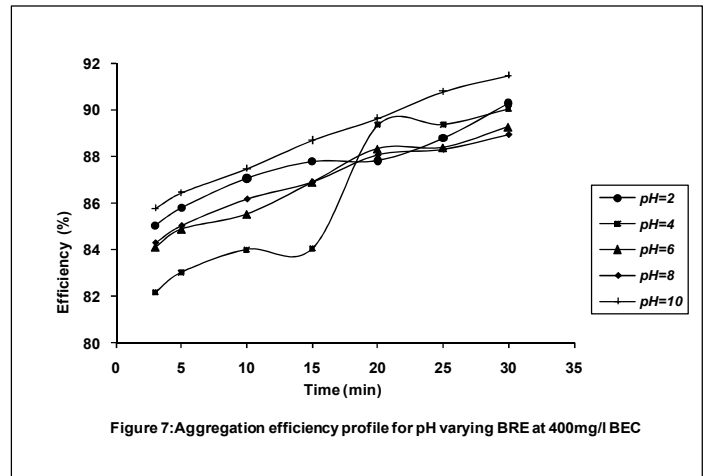
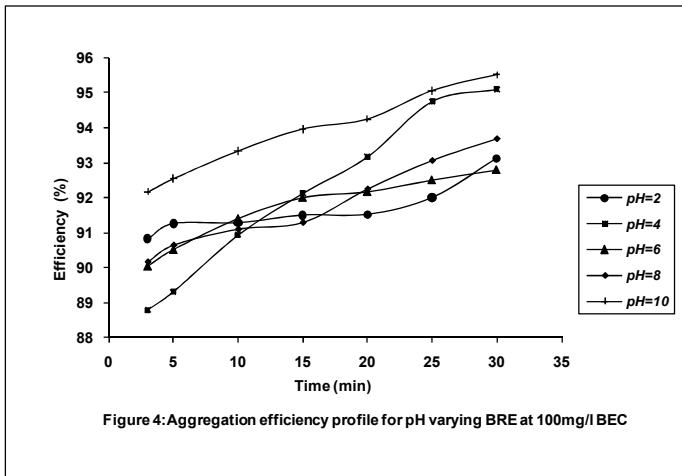


Table 3 : Coag-flocculation kinetic parameters of BEC in BRE at varying pH and 100 mg/l dosage

Parameters	pH=2	pH=4	pH=6	pH=8	pH=10
α	2.0000	2.0000	2.0000	2.0000	2.0000
R^2	0.7566	0.9388	0.9597	0.9485	0.9533
$K_m (l/mg.min)$	1E -05	2E -05	1E -05	2E -05	5E -05
$\beta_{BR} (l/mg.min)$	2E -05	4E -05	2E -05	4E -05	1.0E -04
$K_R (l/min)$	8.5753×10^{-13}	8.6638×10^{-13}	9.3152×10^{-13}	9.4462×10^{-13}	9.4144×10^{-13}
$\varepsilon_p (l/mg)$	2.3322×10^7	4.6168×10^7	2.1470×10^7	4.2344×10^7	1.0621×10^8
$\tau_{1/2} (min)$	20.3135	10.1567	20.3135	10.1567	4.0627
$N_0 (mg/l)$	909.0900	769.2300	1000.0000	1111.1100	1428.5700
$(Np)_0$	5.4745×10^{23}	4.6323×10^{23}	6.0220×10^{23}	6.6911×10^{23}	8.6028×10^{23}

Table 4 : Coag-flocculation kinetic parameters of BEC in BRE at varying pH and 200 mg/l dosage

Parameters	pH=2	pH=4	pH=6	pH=8	pH=10
α	2.0000	2.0000	2.0000	2.0000	2.0000
R^2	0.9190	0.9902	0.9661	0.9647	0.9758
$K_m (l/mg.min)$	2E -05	2E -05	2E -05	3E -05	10E -06
$\beta_{BR} (l/mg.min)$	4E -05	4E -05	4E -05	6E -05	2E -05
$K_R (l/min)$	9.4569×10^{-13}	1.1017×10^{-12}	7.8159×10^{-13}	9.6469×10^{-13}	8.7746×10^{-13}
$\varepsilon_p (l/mg)$	4.2297×10^7	3.6307×10^7	5.1175×10^7	6.2195×10^7	1.8234×10^7
$\tau_{1/2} (min)$	10.1567	10.1567	10.1567	6.7711	25.3918
$N_0 (mg/l)$	1250.0000	1428.5700	1111.1100	769.2300	1111.1100
$(Np)_0$	7.5275×10^{23}	8.6028×10^{23}	6.6911×10^{23}	4.6323×10^{23}	6.6911×10^{23}

Table 5: Coag-flocculation kinetic parameters of BEC in BRE at varying pH and 300 mg/l dosage

Parameters	pH=2	pH=4	pH=6	pH=8	pH=10
α	2.0000	2.0000	2.0000	2.0000	2.0000
R^2	0.9854	0.9785	0.9518	0.9788	0.6955
$K_m (l/mg.min)$	1E -05	2E -05	2E -05	1E -05	3E -05
$\beta_{BR} (l/mg.min)$	2E -05	4E -05	4E -05	2E -05	6E -05
$K_R (l/min)$	9.0573×10^{-13}	1.0523×10^{-12}	8.0398×10^{-13}	1.0125×10^{-12}	8.6930×10^{-13}
$\varepsilon_p (l/mg)$	2.2081×10^7	3.8008×10^7	4.9752×10^7	1.9753×10^7	6.9020×10^7
$\tau_{1/2} (min)$	20.3135	10.1567	10.1567	20.3135	6.7711
$N_0 (mg/l)$	1428.5700	1666.6700	1428.57	1250.0000	1000.0000
$(Np)_0$	8.6028×10^{23}	1.0036×10^{24}	8.6028×10^{23}	7.5275×10^{23}	6.0221×10^{23}

Table 6 : Coag-flocculation kinetic parameters of BEC in BRE at varying pH and 400 mg/l dosage

Parameters	pH=2	pH=4	pH=6	pH=8	pH=10
α	2.0000	2.0000	2.0000	2.0000	2.0000
R^2	0.9309	0.8798	0.9754	0.9857	0.9381
$K_m \left(\frac{l}{mg \cdot min} \right)$	1E -05	2E -05	1E -05	1E -05	1E -05
$\beta_{BR} \left(\frac{l}{mg \cdot min} \right)$	2E - 05	4E - 05	2E - 05	2E - 05	2E - 05
$K_R (l/min)$	7.6431×10^{-13}	9.2826×10^{-13}	7.7682×10^{-13}	9.3457×10^{-13}	7.6928×10^{-13}
$\varepsilon_p (1/mg)$	2.6167×10^7	4.3091×10^7	2.5745×10^7	2.1400×10^7	2.5998×10^7
$\tau_{1/2} (min)$	20.3135	10.1567	20.3135	20.3135	20.3135
$N_0 (mg/l)$	1666.6700	2000.0000	1666.6700	1666.6700	1428.57
$(Np)_0$	1.0036×10^{24}	1.2044×10^{24}	1.0036×10^{24}	1.0036×10^{24}	8.6028×10^{23}

Table 7 : Coag-flocculation kinetic parameters of BEC in BRE at varying pH and 500 mg/l dosage

Parameters	pH=2	pH=4	pH=6	pH=8	pH=10
α	2.0000	2.0000	2.0000	2.0000	2.0000
R^2	0.9944	0.9707	0.9895	0.7537	0.9857
$K_m \left(\frac{l}{mg \cdot min} \right)$	9E -06	1E -05	1E -05	9E -06	2E -05
$\beta_{BR} \left(\frac{l}{mg \cdot min} \right)$	1.8E - 05	2E - 05	2E - 05	1.8E - 05	4E - 05
$K_R (l/min)$	7.6437×10^{-13}	9.4453×10^{-13}	7.3161×10^{-13}	8.6922×10^{-13}	7.6858×10^{-13}
$\varepsilon_p (1/mg)$	2.3548×10^7	2.1174×10^7	2.7337×10^7	2.0708×10^7	5.2044×10^7
$\tau_{1/2} (min)$	22.5705	20.3135	20.3135	22.5705	10.1567
$N_0 (mg/l)$	2000.0000	2000.0000	1666.6700	1666.6700	1428.57
$(Np)_0$	1.2044×10^{24}	1.2044×10^{24}	1.0036×10^{24}	1.0036×10^{24}	8.6028×10^{23}