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Coag-flocculation approach to removal of colloidal particles from brewery waste water using okra seed extract.

Abstract

This work explores the potential for an effective use of Okra seed extract as an efficient bio coagulant for treatment of brewery effluent. The study was carried out using nephelometricjar test. The perikinetic data generated were fitted to specific models for the determination of reaction order, rate constant, period etc. The maximum coag-flocculation performance is recorded at rate constant, K_m of 3.6×10^{-3}L/mg.min, dosage of 100mg/L; pH of 6 and coagulation periodof 0.38min while the minimum is recorded at K_m of 2.95×10^{-5} L/mg.min, dosage of 500mg/L , pH of 10 and period of 93min. The optimum efficiency recorded at 88.31% for 30minutes shows that the system is perikinetic controlled. The results indicates that okra extract can serve as a potential t coagulant for thetreatment of brewery effluent.

Keywords: Okra seed, Brewery Effluent, Coag-flocculation,coilloidal particles, Perikinetics

1 INTRODUCTION

There has been an increasing demand of water usage in brewery industry, as a result, a large volume of wastewater is been generated. In brewery industry, the main section that consumes much water is the brew house, cellars and packaging [1].

The large quantity of wastewater produced contains significant amount of pollutants that usually pose serious risk to human beings, environment, and aquatic life if not properly treated prior to disposal. There are so many ways to treat this wastewater, but this work will focus on coagulation and flocculation processes. Over the years, it hasremained the widely used method for water and wastewater treatment. In coagulation/flocculation processes, three important steps are considered: coagulant formation, colloid particles destabilization and inter particle collision and aggregation[2,3,4,5].

The coagulation/flocculation process involves the addition of inorganic/organic coagulants such as Aluminum sulphate, polyamine and *Xanthosomaspp etc.*When added in wastewater, theyneutralizes the negative charges in the dispersed non-settle able solids, resulting in the formation of micro flocs [6,7].

Since Alzheimer disease of is associated with Aluminum sulphate ,coupled with significant generation recalcitrant of sludge,there is need to create an alternative room for natural coagulant which are eco-friendly and locally abundant.[8].

This work is therefore, to study the coagulation/flocculationbehavior of okra in brewery effluent with respect to pH and dosage variation. Also the kinetic of the process would be investigated.

2.0 COAGULATION THEORY AND MODEL DEVELOPMENT

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2.1 The theory of rapid coagulation

For an aqueous coagulating suspension, where Brownian particle collision is in force, the number of collision occurring per unit time per unit volume, K_{ij}, for two species of particles of volumes $v_i$and v_j is expressed as,

$$K_{ij} = \beta_{BR}(V_iV_j)nin_j \qquad 1$$

Where $\beta_{BR}(V_iV_j)$ is collision frequency

$n_in_j$is no of concentration of particles

The formation rate r_f of particles of volume V_k, resulting from collisions of volumes V_i and V_j is given by[9].

$$r_f = {}^1/_2 \sum_{i+j=k} K_{ij}2$$

The summation of *i* +*j* implies an overall collision for which

$$V_k = V_i + V_j \qquad 3$$

Conversely, the rate of particle loss by collision is

$$r_l = \sum_{i=1}^{\infty} K_{ik} \qquad 4$$

Hence the rateof change due to Brownian motion in the fluid medium is :

$$\frac{dn_k}{dt} = {}^1/_2 \sum_{i+j=k} K_{ij} - \sum_{i=1}^{\infty} K_{ik} \qquad 5$$

Putting equation 1 into equation 5, yields

$$\frac{dn_k}{dt} = {}^1/_2 \sum_{i+j} \beta_{BR}\,(V_iV_j)n_in_j - n_k \sum_{i=1}^{\infty} \beta_{BR}\,(V_iV_k)n_i \qquad 6$$

For kernel like particles,

$$K_{ij} = 4\pi(D_i + D_j)(a_i + a_j) \qquad 7$$

Also, $K_{ij} = {}^2/_3 \left(\frac{K_BT}{\eta}\right)$ 8

Combining equations 7 and 8 yields

$$(D_i + D_j) = \frac{K_BT}{6\pi\eta}\left(\frac{1}{a_i} + \frac{1}{a_j}\right) \qquad 9$$

Putting ($D_i + D_j$) of equation 9 into equation 7 yields

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$$K_{ij} = \frac{2}{3}\frac{K_B T}{\eta}\frac{(a_i+a_j)^2}{a_i a_j} \quad 10$$

For particles of difference radii with dimmer formation of an initially monodispersed suspension:

$$\frac{(a_i+a_j)^2}{a_i a_j} = \begin{pmatrix} 4\ for\ ai=a_j \\ >4\ for\ a_i \neq a_j \end{pmatrix} \quad 11$$

Hence, for the case of $a_i = a_j$, equation 10 becomes :

$$K_{11} = \frac{8}{3}\frac{K_B T}{\eta} \quad 12$$

Where K_{11} is the Smoluchowski coagulation rate constant.

For $K_{ij \to K_{11}} = \beta_{BR}(V_i V_j) n_i n_j$, equation 6 solves exactly to yield

$$\frac{N_t}{N_o} = \frac{\left(K_{11} N_o {}^{t}/_{2}\right)^{n-1}}{\left(1+K_{11} N_o {}^{t}/_{2}\right)^{n+1}} \quad 13$$

It has been established that for aggregating system at n=1; extending into flocculation regime, such that $K_{11} \approx K_m$[10]equation 13, transforms to equation 14 :

$$\frac{1}{\sqrt{N_L}} = \left(\frac{K_m N_o}{\sqrt[2]{N_o}}\right) t + \frac{1}{\sqrt{N_o}} \quad 14$$

Where $K_m = {}^{1}/_{2}\,\beta_{BR}$

$$= \frac{2}{3}\varepsilon_p \frac{K_B T}{\eta}$$

$K_m$is defined as Menkonu coag-flocculation rate constant accounting for Brownian coag-flocculation transport of destabilized particle at αth order

$\varepsilon_p$is collision efficiency

From equation 13,coag-flocculation period is obtained as

$$\tau_{1/2} = \frac{1}{(0.5 K_M N_o)} \quad 15$$

Turbidity values obtained could be converted to TSS(mg/L)[11].

by TSS(mg/L) =Tss_f x (NTU) 16

where TSS is total suspended solid and $Tss_f$is factor that converts turbidity to TSS

The concentration of singlets, doublets and triplets during coagulation can be evaluated by solving equation 13.

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Hence ,forsinglets(m=1)

$$N_1 = N_o \left[\frac{1}{1+{}^{t}/_{\tau'}}\right] \quad 17$$

For doublets(m=2)

$$N_2 = N_o \left[\frac{{}^{t}/_{\tau'}}{\left(1+{}^{t}/_{\tau'}\right)^3}\right] \quad 18$$

For triplets(m=3)

$$N_3 = N_o \left[\frac{\left({}^{t}/_{\tau'}\right)^2}{\left(1+{}^{t}/_{\tau'}\right)^4}\right] \quad 19$$

Where τ' = 2τ

Evaluation of coagulation –flocculation efficiency is given as

$$E(\%) = \left[\frac{N_o - N_t}{N_o}\right] x100 \quad 20$$

3.0 Materials and Method

3.1 Material Sampling, Preparation andCharacterization

3.1.1 Brewery Effluent

The effluent was collected from brewery plant located in Enugu, Enugu State Nigeria. The characterization of the effluent and the analysis was based on standard method (WST, 2005; AWWA 2005).

3.1.2 Okra Seed Sample

The Okra(*Hibiscus esculentus*) was bought from Ogbete market, Enugu State Nigeria. The Okra seed pods was prepared according procedure reported by Agarwal et al[12]. The characteristics of the sample was on the bases of AOAC[13] standard method.

3.2 Coagulation- flocculation Experiment

Experiment was conducted using conventional jar test apparatus. Desired dosages of Okra coagulant between 100-500mg/L were directly dosed into 300mL of BRE contained in standard 1000mL beaker(G.C17). The suspension, tuned to pH 2-10 using H_2SO_4/NaoH, was subsequently subjected to 2 minutes of rapid mixing(200rpm), 20 minutes of slow mixing (30rpm) using a magnetic stirrer . After

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agitation, the coagulated fluid was transferred into a cylinder (JayTec.Uk) of height 33.5cm. During settling, 10mL of the supernatant was withdrawn from 2cm depth and changes in TDSP (mg/L) measuredat 3,5,10,15,20,25 and 30 minutes. The data were subsequently fitted in appropriate kinetic model.

4.0 Results and discussion

4.1 Plot of Efficiency E % Vs Time, pH and dosage

The removal efficiency E(%) with time, pH and dosage is obtained based on the evaluation of equation20. This is presented in figures 1-7. This was obtained at 100,200,300,400 and 500mg/L dosage for pH 2,4,6,8 and10. From figs 1-7, it can be shown that efficiency increases with time, but its magnitude varies for difference pH and dosage. Also at 30 minutes , the efficiency was between 67.58 and 73.39 % at pH 2. Then at 30minutes of coag-flocculation, the best performance was 88.31 at pH 2 and 200mg/L dosage. Figure 6 shows that the performance of Okra seed coagulant(OSC) in removing TDSP from brewery effluent is not significantly affected by the dosage. The performance of the coagulant reached the optimum value at pH 2and4. Meanwhile figure 7 shows that variation in pH has significant effect on efficiency(E%), recording better performance in an acidic medium. The poor performance at high doses(especially 500 mg/L) could be attributed to the phenomenon of excess coagulant being adsorbed on the colloidal surface and producing restabilized colloids.

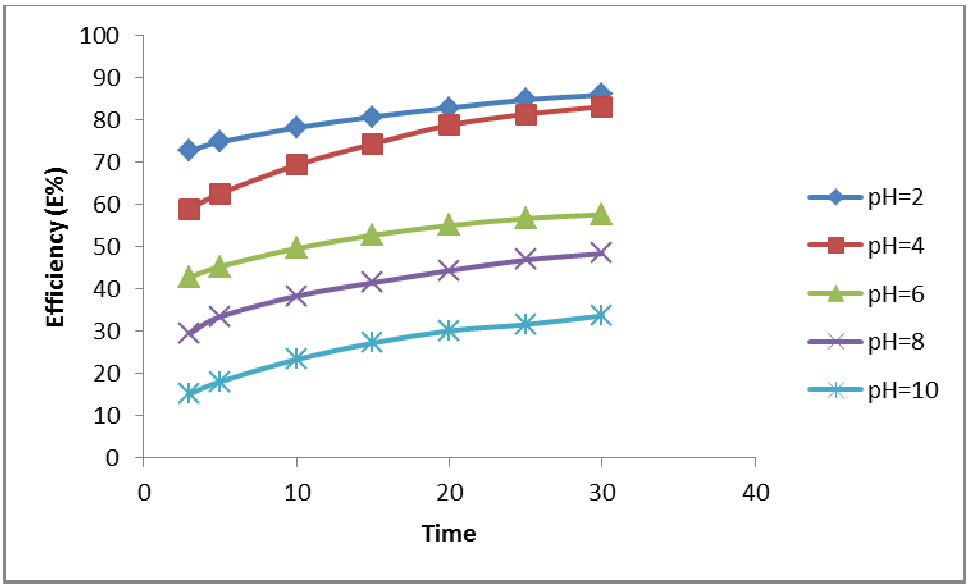

Figure 1: Plot of Efficiency (E%) Vscoag-flocculation time for 100mg/L Okra at varying pH

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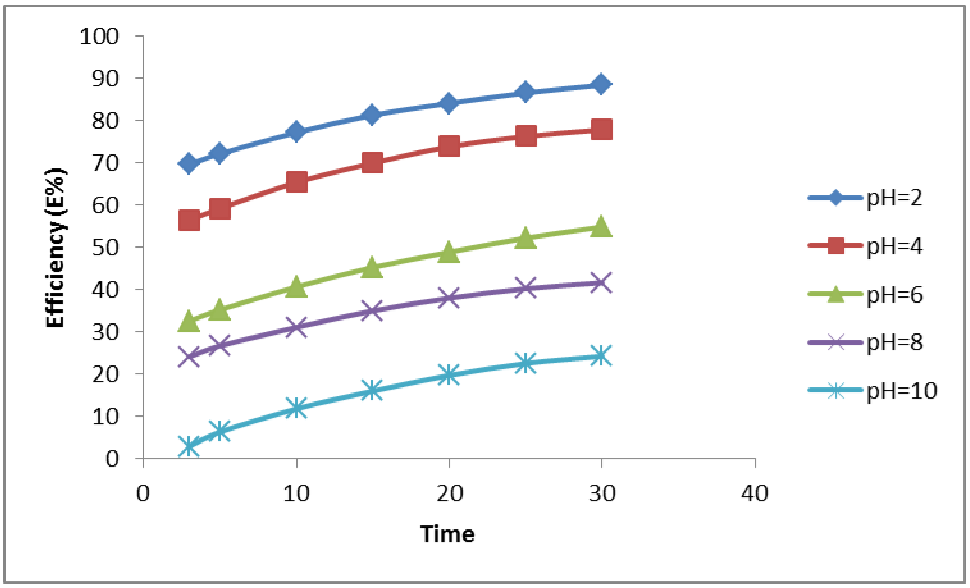

Figure 2: Plot of Efficiency (E%) Vscoag-flocculation time for 200mg/L Okra at varying pH

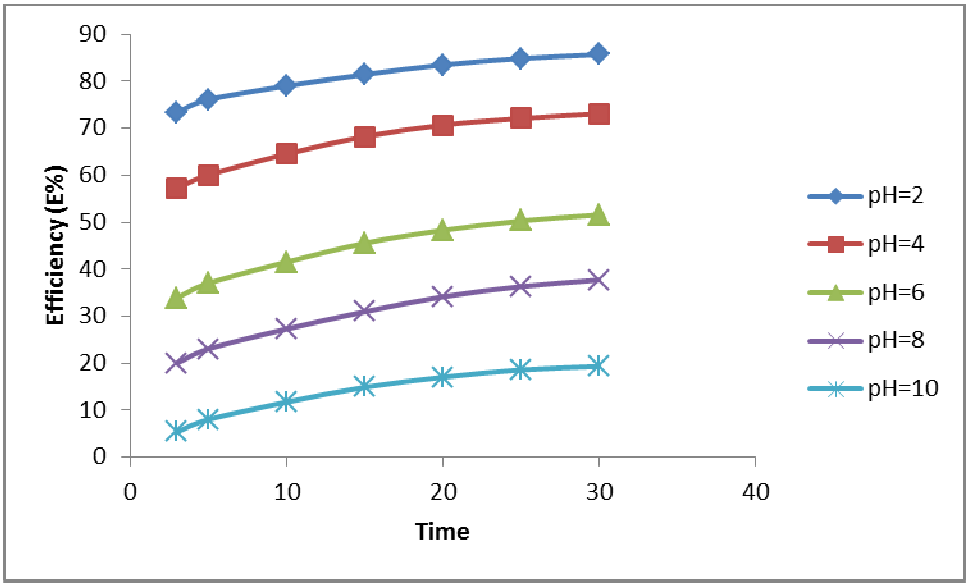

Figure 3 : plot of Efficiency (E%) Vscoag-flocculation time for 300mg/L Okra at varying pH

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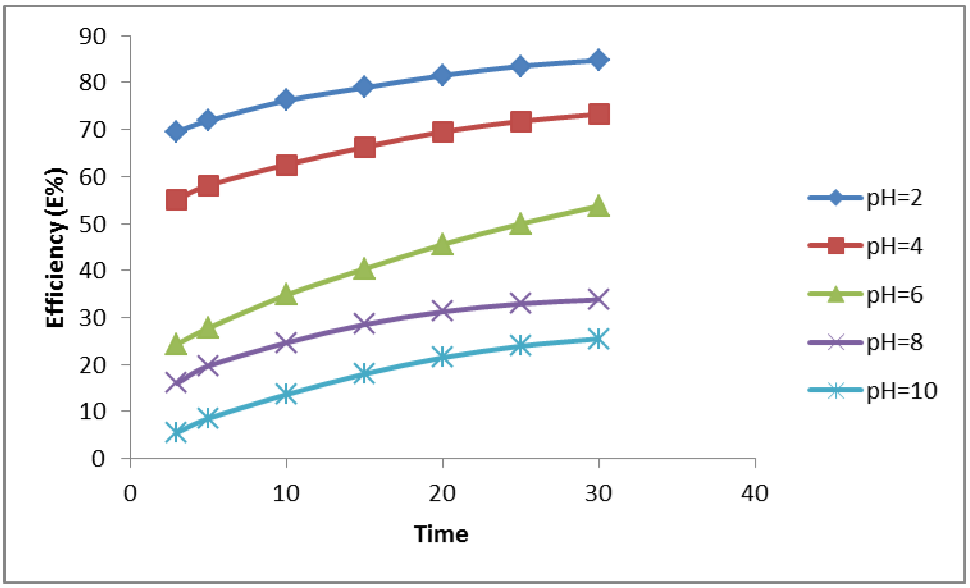

Figure 4: Plot of Efficiency (E%) Vscoag-flocculation time for 400mg/L Okra at varying pH

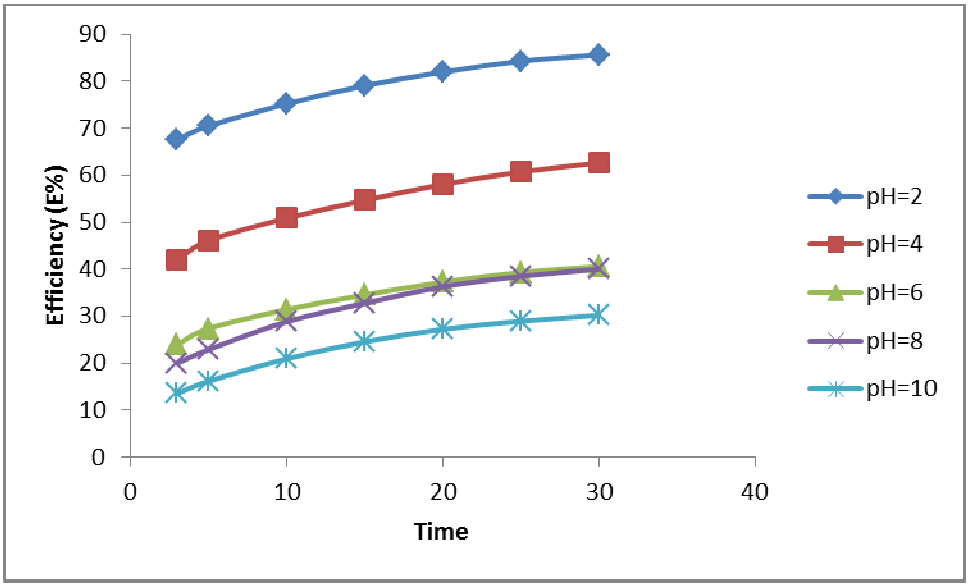

Figure 5 : Plot of Efficiency (E%) Vscoag-flocculation time for 500mg/L Okra at varying pH

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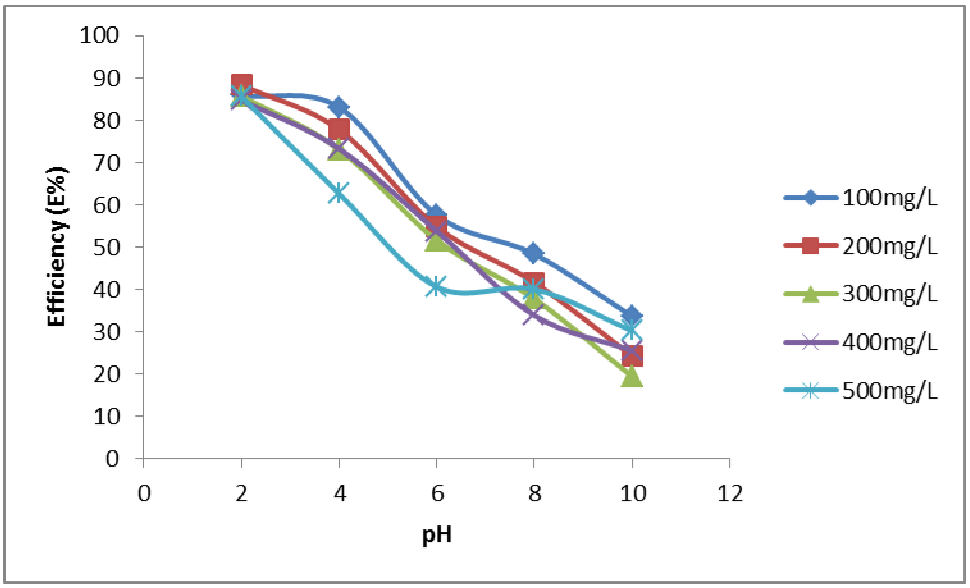

Figure 6 : Plot of Efficiency (E%) Vs pH at varying Okra dosage

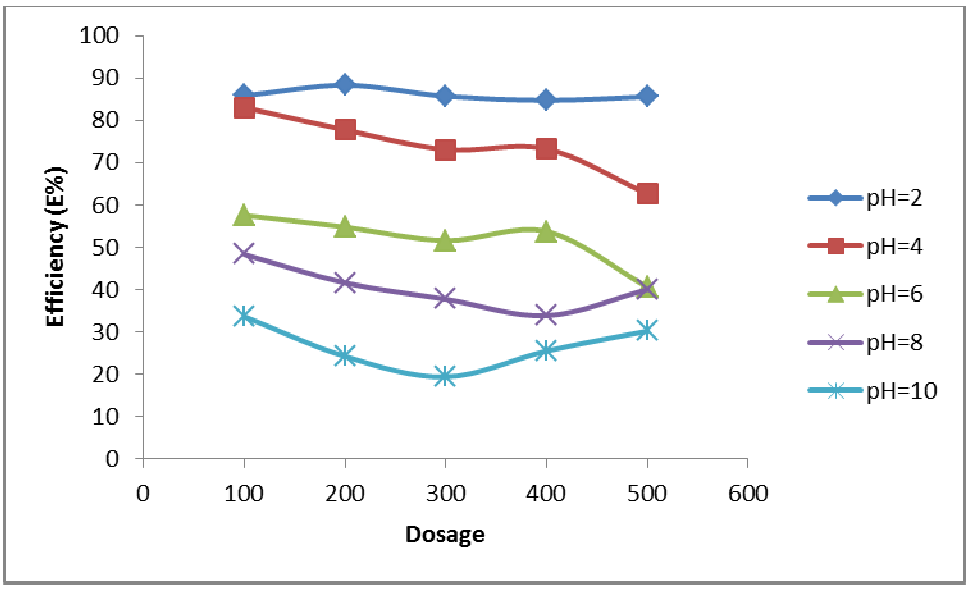

Figure 7 : Plot of Efficiency (E%) Vs dosage at varying pH

4.2 Nephelometric Kinetic Result

This test was performed for a sample of BRE with an initial SDP of 728.249mg/L at 100-500mg/L and pH 2-10 OSC dosage and pH range, respectively .

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Assuming perikinetic aggregation condition, where α=2 ,solving equation 13, gives equation 14,which is presented in the selected linear plots in figure 8. The plots of $\frac{1}{\sqrt{N_t}}$ Vs t yields, $K_m$and $\frac{1}{\sqrt{N_o}}$, as the slope and intercept, respectively. The results presented in tables 1-5, show that majority of R^2values are high, which shows that the reaction is a second order with various constant.

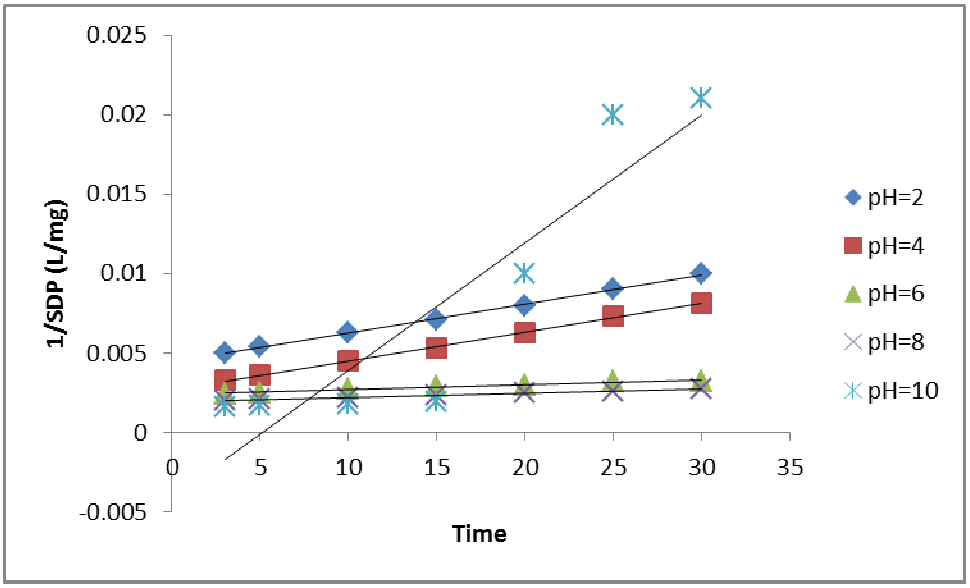

Figure 8 : Representative kinetic plot of 1/SDP as a function of time for 100mg/L Okra dosage

Meanwhile, the value ofK_m =0.5β_{BR} can be obtained from equation 15. However, the highest value of K_m of $3.6 \times 10^{-3}\, {}^{l}/_{mg.min}$ for the process is recorded at pH of 6 and 100mg/L OSC. The least of K_m of 2.95×10^{-5}L/mg.min is recorded at pH of 10 and 500mg/L.. In this study, the lowest $\tau_{1/2}$(0.38 unit) is recorded at high $K_m 3.6 \times 10^{-3}$ L/mg.min, which favors fast coag-flocculation process[9]. Generally, $K_m$values wereobtained from f equation 14 and the representative kinetic plot presented in figure 8. In the tables 1-5, the variation of K_R is minimal, following insignificant changes in values of temperature and viscosity of the effluent medium

Table 1:Coag-flocculation kinetic parameter of Okra in BRE at varying pH and 100mg/L dosages

Parameters	pH=2	pH=4	pH=6	pH=8	pH=10
α	2	2	2	2	2
R^2	0.9977	0.9938	0.969	0.9864	0.9601
K(L/mg.min)	5.09×10^{-3}	4.04×10^{-3}	3.6×10^{-3}	3.23×10^{-3}	2.89×10^{-3}
β_{BR}(L/mg.min)	1.0×10^{-2}	8.16×10^{-3}	7.2×10^{-3}	6.46×10^{-3}	5.78×10^{-3}
K_r(L/min)	7.3×10^{-19}	7.65×10^{-19}	7.45×10^{-19}	7.45×10^{-19}	7.45×10^{-19}
$\varepsilon_p(mg^{-1})$	1.37×10^{16}	1.08×10^{16}	9.67×10^{15}	8.67×10^{15}	7.76×10^{15}
$\tau_{1/2}$(min)	0.54	0.68	0.38	0.85	0.95
τ'(min)	1.08	1.36	0.76	1.7	1.9
(-r)mg/min	$5.09 \times 10^{-3}N_t^2$	$4.04 \times 10^{-3}N_t^2$	$3.6 \times 10^{-3}N_t^2$	$3.23 \times 10^{-3}N_t^2$	$2.89 \times 10^{-3}N_t^2$

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Table 2: Coag- flocculation kinetic parameter of Okra in BRE at varying pH and 200mg/L dosage

Parameters	pH=2	pH=4	pH=6	pH=8	pH=10
α	2	2	2	2	2
R^2	0.997	0.9911	0.9896	0.9498	0.9671
K(L/mg.min)	4.61×10^{-3}	$4.o5 \times 10^{-3}$	3.27×10^{-3}	3.15×10^{-3}	2.78×10^{-3}
β_{BR}(L/mg.min)	9.22×10^{-3}	8.1×10^{-3}	6.54×10^{-3}	6.3×10^{-3}	5.56×10^{-3}
K_r(L/min)	7.44×10^{-19}	7.43×10^{-19}	7.45×10^{-19}	7.45×10^{-19}	7.5×10^{-19}
ε_p (mg^{-1})	1.24×10^{16}	1.09×10^{16}	8.78×10^{15}	8.46×10^{15}	7.4×10^{15}
$\tau_{1/2}$ (min)	0.59	0.68	0.84	0.87	0.98
τ'(min)	1.18	1.36	1.68	1.74	1.98
(-r)mg/min	$4.61 \times 10^{-3} N_t^2$	$4.05 \times 10^{-3} N_t^2$	$3.27 \times 10^{-3} N_t^2$	$3.15 \times 10^{-3} N_t^2$	$2.78 \times^{-3} N_t^2$

Table 3: Coag-flocculation kinetic parameter of Okra in BRE at varying pH and 300mg/L dosage

Parameters	pH=2	pH=4	pH=6	pH=8	pH=10
α	2	2	2	2	2
R^2	0.9873	0.9639	0.9574	0.9407	0.881
K(L/mg.min)	5.22×10^{-3}	4.2×10^{-3}	3.37×10^{-3}	3.03×10^{-3}	2.82×10^{-3}
β_{BR} (L/mg.min)	1.04×10^{-2}	8.4×10^{-3}	6.74×10^{-3}	6.06×10^{-3}	5.64×10^{-3}
K_r (L/mg.min)	7.43×10^{-19}	7.43×10^{-19}	7.6×10^{-19}	7.45×10^{-19}	7.4×10^{-19}
ε_p (mg^{-1})	1.4×10^{16}	1.13×10^{16}	8.86×10^{15}	8.14×10^{15}	7.57×10^{15}
$\tau_{1/2}$ (min)	0.53	0.65	0.83	0.91	0.97
τ'(min)	1.06	1.3	1.66	1.82	1.95
(-r)mg/min	$5.22 \times 10^{-2} N_t^2$	$4.2 \times 10^{-3} N_t^2$	$3.37 \times 10^{-3} N_t^2$	$3.03 \times 10^{-3} N_t^2$	$2.82 \times 10^{-3} N_t^2$

Table4: Coag-flocculation kinetic parameter of Okra in BRE at varying pH and 400mg/L dosage

Parameters	pH=2	pH=4	pH=6	pH=8	pH=10
α	2	2	2	2	2
R^2	0.9977	0.9941	0.9998	0.9167	0.9514
K(L/mg.min)	4.78×10^{-3}	3.97×10^{-3}	3.1×10^{-3}	2.98×10^{-3}	2.82×10^{-3}
β_{BR} (L/mg.min)	9.4×10^{-3}	7.94×10^{-3}	6.2×10^{-3}	5.96×10^{-3}	5.64×10^{-3}
K_r (L/mg.min)	7.34×10^{-19}	7.45×10^{-19}	7.45×10^{-19}	7.45×10^{-19}	7.46×10^{-19}
ε_p (mg^{-1})	1.28×10^{16}	1.06×10^{16}	8.32×10^{15}	8.0×10^{15}	7.56×10^{15}
$\tau_{1/2}$ (min)	0.57	0.69	0.88	0.92	0.97
τ'(min)	1.14	138	1.76	1.84	1.95
(-r)mg/min	$4.78 \times 10^{-3} N_t^2$	$3.97 \times 10^{-3} N_t^2$	$3.1 \times 10^{-3} N_t^2$	$2.98 \times 10^{-3} N_t^2$	$2.82 \times 10^{-3} N_t^2$

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Table 5: Coag-flocculation kinetic parameter of Okra in BRE at varying pH and 500mg/L dosage

Parameters	pH=2	pH=4	pH=6	pH=8	pH=10
α	2	2	2	2	2
R^2	0.9981	0.9836	0.9719	0.9719	0.8947
K(L/mg.min)	4.58×10^{-3}	3.58×10^{-3}	3.03×10^{-3}	3.03×10^{-3}	2.95×10^{-5}
β_{BR} (L/mg.min)	9.0×10^{-3}	7.16×10^{-3}	6.06×10^{-3}	6.06×10^{-3}	5.9×10^{-5}
K_r(L/mg.min)	7.32×10^{-19}	7.45×10^{-19}	7.45×10^{-19}	7.45×10^{-19}	7.45×10^{-19}
ε_p (mg^{-1})	1.23×10^{16}	9.61×10^{15}	8.14×10^{15}	8.14×10^{15}	7.92×10^{13}
$\tau_{1/2}$ (min)	0.6	0.76	0.91	0.91	9.3
τ'(min)	1.2	1.52	1.82	1.82	186
(-r)mg/min	$4.58 \times 10^{-3} N_t^2$	$3.58 \times 10^{-3} N_t^2$	$3.03 \times 10^{-3} N_t^2$	$3.03 \times 10^{-3} N_t^2$	$2.95 \times 10^{-5} N_t^2$

4.3 Particles Distribution Plots

The particle distribution plots are presented in figures 9 and 10 for $\tau_{1/2}$=0.38min and $\tau_{1/2}$=9.3min ,respectively. In figure 9, the number of singlet particle decreases more rapidly than the sum particles. This indicate that early stage of this coag-flocculation is affected by colloidal destabilization and rapid sweep.

In figure 10, the plot exhibits opposing profile to that of figure 9. Here there is decreasein rapidity of flocculation resulting from destabilization inertia. The curve clearly demonstrates that there is slow colloidal destabilization, resulting to low particle entrapment and low bridging mechanism.

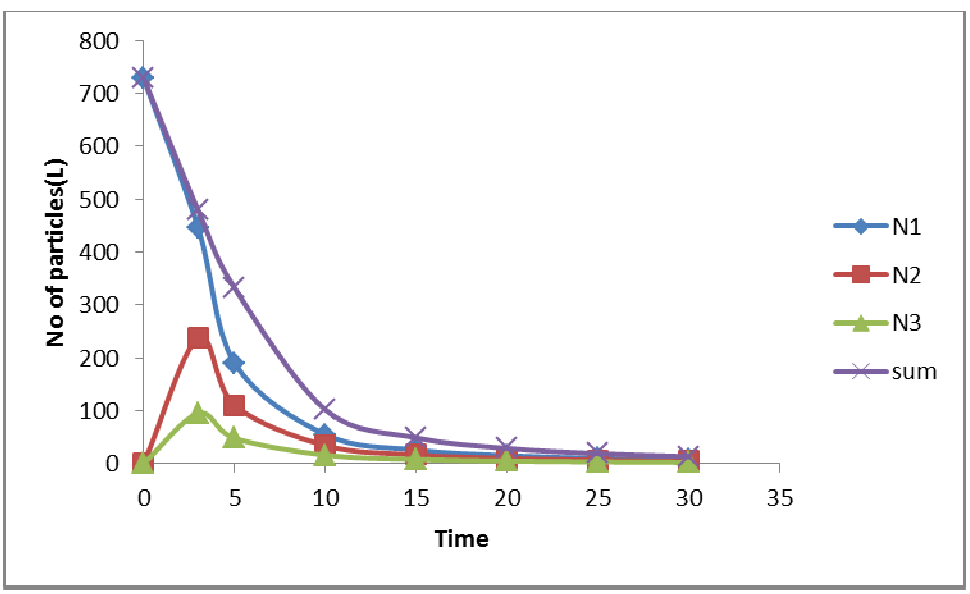

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Figure 9 : Particles distribution behavior for half life of 0.38min

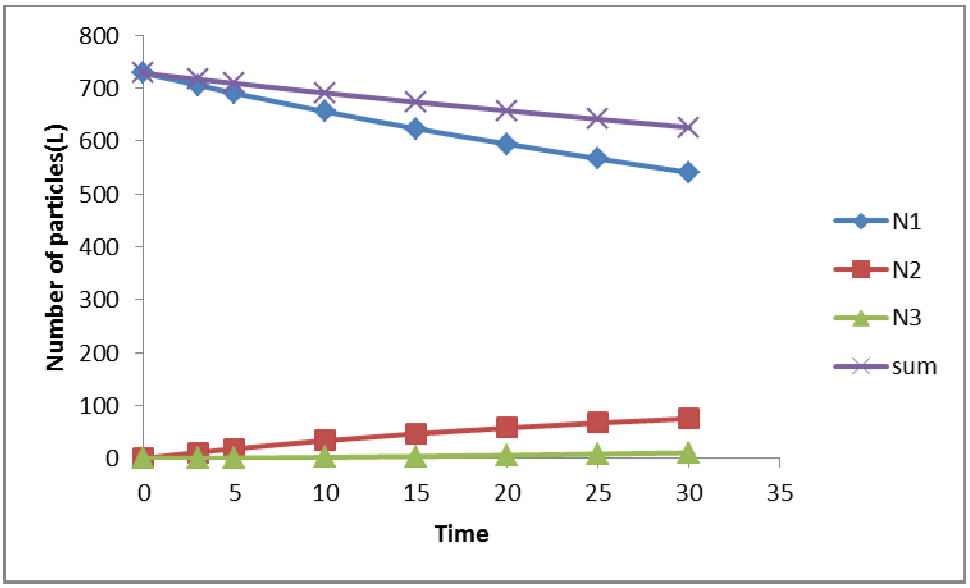

Figure 10 : Particles distribution behavior for half-life of 9.3min

5.0 Conclusion

The potential application of Okra seed as an effective plant coag-flocculation has been established. The process effectively removed 88.5% turbidity from the effluent. However, the jar test conducted wassensitive to pH and dosage. 200mg/L doseof Okra seed coagulant and pH 2 were found to be optimal conditions for the effluent treatment. It could be inferred at the experimental conditions that coag-flocculation process using okra seed was feasible for the treatment of brewery effluent.

Nomenclature

K_m: Menkonu coag-flocculation rate constant

β_{BR}: Collision factor for Brownian Transport

ε_p: Collision Efficiency

$\tau_{1/2}$: Coagulation Period/Half life

E: Coag-flocculation Efficiency

R^2: Coefficient of Determination

K_R: Smoluchowski coag-flocculation constant

α :Coag-flocculation reaction order

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-r :Coag-flocculation reaction rate

OSC : Okra Seed Coagulant

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