Coag-Flocculation Studies of Breadfruit-Testa Coagulant (BFTC) in A Natural Rubber Lump Effluent: Nephelometric Approach

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ABSTRACT

The coag-flocculation behaviour of (Treculiar Africana), breadfruit seed testa coagulant (BFTC) in respect of the process variable of temperature in the treatment of Bio-chemical Oxygen Demand(BOD) of the natural rubber lump effluent collected at three various maturation periods of T = 0, T = 4, and T = 8 days was investigated at room temperature. The effluents were characterized for BOD before and after treatment. BOD measurement was carried out using the single angle (90^o) nephelometric standard test, while BFTC processing was based on work reported by Adeyeye, et al,. Analysis for the pollution causative factor of BOD before and after treatment was done according to the standard method of ASTM (1982). MATLAB R2013a Version 8.1 software was employed in the fitness of the experimental results specifically for the determination of rate related results at optimal values of the process variable. The effects of the process variable on the effluents were also accessed. The result showed that BOD was 88.37% removed at temperature of 45^oC for effluent T = 8. The accuracy of fit of the studied model with the experimental data was greater than 0.95 for effluent T = 8 at varying temperature and constant coagulant dosage of 100mg/l, 1hour contact time, and pH of 8. In general, the parameters obtained lied within the range of previous works, while it can be concluded that the coagulant performance of breadfruit seed testa biomass is adequate.

Keywords: Breadfruit-testa, Kinetics, Coagulation, Coag-Flocculation, Natural rubber effluent

INTRODUCTION

African breadfruit (Treculiar Africana), belongs to the family of moraceae (Orwa et al, 2009). It enjoys wide distribution in West Africa. It is native to many tropical countries like West Indies, Ghana, Sierra

Leone, Nigeria, and Jamaica (Appiah et al, 2011). Its seeds are commonly called ‘afon’ and ‘ ukwa’ by the Yoruba and Igbo of Nigeria; it is popular as a traditional food item. The testa is the neglected/wasted outer covering of the seed. It is composed mainly of cellulose and other polysaccharides, lignin, cutin, proteins, phenolic compounds, pigments waxes, fats and resinous matter, providing the most protection against damage (Bewley et al, 1994). It is a non-toxic, non-edible and biodegradable substance.

The natural rubber has been identified as one of the major sources of environmental pollution. The export incentives of the Federal Government between 1994 and early part of 1999 led to the increase in the number of rubber processing industries in the country. The boom led to the astronomical increase in the activities of the rubber industries (Momodu, 1993). Apart from the foreign exchange earnings, employment of graduates and young school leavers, engagement of able youths (male and female) in the tapping of rubber latex with high financial benefit, hiring and leasing of rubber estates by native owners to rubber processing industries with attendant economic benefits have been linked with increased activities associated with rubber industry. The production and processing activities of these factories generate effluent which is discharged untreated into nearby streams, rivers, ponds, and even farmlands. The size and capacity of the factory determines the quantity of effluent discharged. It is estimated that an average of 450,000 litres of effluent is discharged form a single 20 - 30 metric tones of rubber per rubber factory daily (Nordin et al, 1989).

Coagulation and flocculation are the processes used to remove particles responsible for turbidity and colour. The colloidal particles present in waste waters generally carry a negative electrical charge. These particles are surrounded by an electrical double layer (due to attachment of positively charged ions from the ambient solution), and thus inhibit the close approach of each other. They remain finely divided and don’t agglomerate. Due to their low specific gravity, they don’t settle out. Coagulation is accomplished by the addition of ions having the opposite charge to that of the colloidal particles. In Coagulation, a coagulant (generally positively charged) is added which caused compression of the double layer and thus the neutralization of the electrostatic surface potential of the particles. The resulting destabilized particles stick sufficiently together when contact is made. Rapid mixing (a few seconds) is important at this stage to obtain uniform dispersion of the chemical and to increase the opportunity for particle-to-particle contact. Flocculation, which follows coagulation, consists of slow gentle stirring. During flocculation, the microscopic coagulated particles aggregate with each other to form large flocs. The flocs then are able to aggregate with suspended polluting matter. These flocs are large enough to settle rapidly under the influence of gravity, and may be removed from suspension by filtration (Rao, 2005).

Biochemical Oxygen Demand (BOD) is the amount of oxygen required to stabilize the decomposable matter (organic) present in the effluent (i.e convert them into non polluting forms) by anaerobic biochemical action. Oxygen demand is exerted by carbonaceous material, oxidizable nitrogen and certain reducing chemical compounds. The effluent contains solids whose major proportion is in the form of dissolved solids and which form excellent substrate for the proliferation of micro-organisms (RRIM, 1974) generating a higher BOD and COD. The effect is that the DO content of the river is utilized by these bacteria in the conversion process. With diminishing O_2 supply, survival of the higher forms of lives becomes difficult. Even after the DO is exhausted; the anaerobic bacteria still survives by deriving the energy from the organic matter. This process leads to putrefaction and hence the stream has an unpleasant appearance with a foul odour leading to loss of ground water and recreational facilities. Natural coagulants are the local aggregating agents that are locally abundant, cheap and eco-friendly. They are introduced as a viable alternative to the conventional inorganic coagulant (salts of Al and Fe) and synthetic organic polymers. Although these synthetic chemicals are very effective and widely used, there are obvious inherent draw backs. They impact on the pH value of water, increase the soluble residues volume and metal content of sludge. With Alum, there is risk of Alzheimer's disease and similar health related problems (www.scirp.org/acesss). Obviously the issues of cost and availability of the chemicals are major drawbacks since they have to be imported in hard currency. In other to alleviate the prevailing challenges, approaches that focus on sustainable water treatments that are low cost, eco-friendly, robust and require minimal maintenance and operator skills become imperative. Steep water, cactus, moringa, breadfruit-testa, etc possess these qualities and provide the remedy for the identifiable deficiencies associated with non-natural coagulants (Menkiti, 2010).

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

METHODS

EQUIPMENTS USED

These include: Jar-test apparatus equipped with a five unit multiple stirrer system, Jen way Model 330 thermometer, No. 688644A Gulenhamp Magnetic stirrer and Digital Oxygen Kit (9500 Model).

Materials collection, Preparation and Characterization

- Natural rubber lump effluent

The effluent was taken from a major rubber processing factory located in Emeabiam, Owerri West local government area of Imo State in Nigeria. The effluent was matured for T = 0, T = 4, and T = 8 days before treatment. The characterization of the effluent before and after treatment for BOD presented in table 1 was determined based on standard method of ASTM (1982).

- Treculiar Africana seed Testa sample

Treculiar Africana seed testa sample (Precursor to BFTC) were procured from Ozuomee Urualla, Ideato North L.G.A, Imo State, Nigeria. BFTC was prepared according to procedures reported by Adeyeye et al, 2012. The characterization of the sample on the basis of AOAC (1990) standard method are presented in table 2.

Coag-Flocculation Experiments

Experiments were conducted using conventional jar test apparatus equipped with a five unit multiple stirrer system. Five sets of T = 0 effluent samples (200ml each) had their temperature varied as 25, 30, 35, 40, and 45^{o}C by heating while the coagulant dosage, pH, and contact time were kept constant at 100mg/l, 8, and 1hour respectively. The suspensions were then subjected to 2minutes of rapid mixing (250 rpm), 20minutes of slow mixing (40 rpm), followed by 30minutes of settling. The mixture was left for 1 hour to enhance the process of decantation and particle flotation. During settling, samples were withdrawn from 2cm dept and changes in the pollution causative factor of BOD was measured for kinetic analysis. The kinetics of coag-flocculation and extent of aggregation were monitored at optimal conditions at 3, 5, 10, 15, 20, 25, and 30minutes.The data were subsequently fitted in the appropriate kinetic model. All the determinations were done in triplicates. The procedure was then repeated for T = 4, and T = 8 effluents.

MODEL DEVELOPMENT

For a coag-flocculation phase, the rate of successful collision between particles of size i and j to form particles of size k according to Thomas et al, (1999) is given by:

$$\frac{dnk}{dt} = \frac{1}{2}\frac{\varepsilon}{i+j=k}\beta_{BR}(i,j)n_i n_j - \sum_{i=1}^{\infty}\beta_{BR}(i,k)n_i n_k \cdot \quad \ldots\ldots\ldots\ldots 1$$

Where — is the rate change in the count of particles of size k.

The first term on the right hand side is the Brownian aggregation factor for flocculation transport mechanism showing increase in particle of size of k by flocculation of particles of sizes i and j. The second term on the right hand side is the Brownian aggregation factor showing the loss of particles of size K by virtue of their aggregation with other particles sizes.

In collision frequency, β for Brownian transport is given by

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Equation 2 is based on the following assumptions:

- is unity for all collisions
- The particles are monodispersed (i.e. all of the same size)
- Collision involves only two particles
- All particles and floccs are spherical
- Fluid motion undergoes laminar shear
- No breakage of flocs occurs

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Where K_R is the Von smoluchowski rate constant for rapid coagulation. K_B, T and η are Boztmann 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

$^1/_2\beta_{BR} = K_m$ ………………………………………………………………………….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 (Menkiti, 2010) that coag-flocculation is governed by

……………………………………………………………..5

Where $\varepsilon_p K_R = 0.5$

Thus ………………………………………………………………….7

N_t is the concentration of pollutant at time, t

Empirical evident shows that in real practice, 1< α <2 (Menkiti, 2010). Graphical representation of linear form of equation 7 at $\alpha = 2$ provides for k_m from the slope of linear equation 8 below:

Where N_o is the initial N_t at time = 0, N is N_t at upper time limit >o

Equation 8 can be solved to obtain coag-flocculation period, t½:

$t_{½} = (0.5\ N_o\ k_m)^{-1}$ ……………………………………………………………..9

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

m=1 (mononers), m=2 (dimmers), m=3 (trimmers)

Efficiency of coag-flocculation is expressed as:

] x 100……………………………………………………………11

RESULTS

The results of the characterization of the effluents in respect of BOD before and after coag-flocculation treatment are presented in table 1. Three different effluents were involved; T=0 effluent representing effluent collected immediately after natural rubber latex was coagulated with acetic acid, T=4 was effluent collected after allowing it to mature for 4 days and T=8 effluent was collected on the 87th day of maturation. The values of the biochemical oxygen demand (BOD) before the treatment were all high for the 3 effluents. This means that the waste waters have high organic contents and therefore high pollution potentials. They should therefore be treated before discharge into the environment. Comparison of the BOD values before and after treatment shows that it is 80.73%, 86.16% and 88.37% reduced after treatment for T=0, T=4, and T=8 effluents respectively. Table 2 presents the results of the proximate composition of the bread fruit flour (BTF) used as natural coagulant in the coag-flocculation treatment process. The protein content suggested that it could be a potential natural coagulant for water treatment hence it was used in the coag-flocculation treatment of the natural rubber effluents. It implies that BTF contains significant quantity of positively charged (+) water soluble proteins which bind with the negatively charged (-) particles in water to promote floc formation (Adeyeye et al., 2012).

DISCUSSION

The results of the coag-flocculation treatment of pollution factor of BOD for all the 3 effluents are presented in table 3. The result is obtained when the temperature is varied while keeping the contact time, coagulant dosage and pH constant at 1hr, 100mg/l and 8 respectively. BOD pollution potentials decreased progressively with temperature increase for all the effluents.

Table 4 shows the summary of maximum removal efficiency of BOD and the optimum process variable of temperature. The result implies that for all the effluents, maximum reduction of BOD values occurred at process condition of 45^{o}C. The efficiency is 80.73% for T=0 effluent, 86.16 for T=4 and 88.73% for T=8 effluent.

The results of coag-flocculation kinetic parameters of BFTC in NRE in respect of the BOD at varying temperature and coagulant dosages of 100mgl, contact time of 1hr and pH 8 is represented in table 5 for all the effluents. The kinetic parameters generated have significant influence on the design, fabrication and operational efficiency of coag-flocculation unit.

To ensure highest collision, ϵ_p which is the collision efficiency factor is assumed to be unity and used in equation 2.

Linearization of equation 7 at α = 2 resulted in equation 8, from which is determined as slope of – settling time plot. The implication is that the order of the reaction is 2. The accuracy of the fit of the studied model (equation 8) with the experimental data is based on square linear regression coefficient (R^2). The results shows that the accuracy of the fit of the studied model with the experimental result is mostly >0.95. This implies that the experimental data obtained for the effluents at specified process conditions are significantly described by the linearized form of equation 8. The high value of R^2 indicated a high measure of agreement to the model equation common to coagulation process. Hence, it can be concluded that the reactions are second order with various speed constant, posted as shown by the table. This means that the speed of the reaction is proportional to (N_t) and as described by equation 7.

Maximum rate of coagulation is driven by optimum rate constant, . is proportional to the rate of coag-flocculation, = (0.5) expressed as equation 6 and displayed in the table. The highest value of of 6.2793 x 10^{-4}lit/mg.min is recorded for T = 8 effluent at 1hr contact time, coagulant dosage of 100mg/L, pH of 8 and varying temperature. The least of 2.0407 x 10^{-4} lit/mg.min is recorded for T = 0 effluent at those conditions. The implication of the result is that the maximum rate of coagulation driven by optimum rate constant during BOD removal is achieved at 100mg/l dosage, pH 8 ,1hr contact time and varying temperature using T=8 effluent.

The coag-flocculation period, indicates the time taken for initial concentration of pollutants to reduce by half. It is evaluated from equation 9. It is generally an index of speed of the treatment process. Low period indicate 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 the period is a function of rate constant and initial pollution concentration, mathematically expressed as _ (/) . The implication from equation 9, is that the higher the , the lesser the period. This explains the prevalent high rate of settling in high turbidity water. Specifically in this study, it is observed that the lowest period of 4.5861mins is recorded at high of 6.2793×10^{-4} l/mg.min for T = 8 effluent, while the highest period of 11.8886 mins occurred at low of 2.0407×10^{-4} l/mg.min for T = 0 effluent. Thus high corresponds to low period.

The efficiency of treatment process, E and the rate of coag-flocculation reaction rate –r could be ascertained using the concentration of BOD at time, t as depicted in table 5.

Figure 1 shows the graphical results as depicted in table 3 while figures2, 3 and 4 are for values of the kinetic parameter shown in table 5

CONCLUSIONS

The application of BFTC as an effective coag-flocculant in the treatment of high BOD effluent such as NRLE has been established. The removal of 88.37% of initial value of BOD within the first four minutes of the treatment justifies that the process was rapid with high rate constant and low coagulation period. The system operated optimally at pH of 8, 100mg/l coagulant dosage, and 25minutes settling time with varying temperature.

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FIGURES

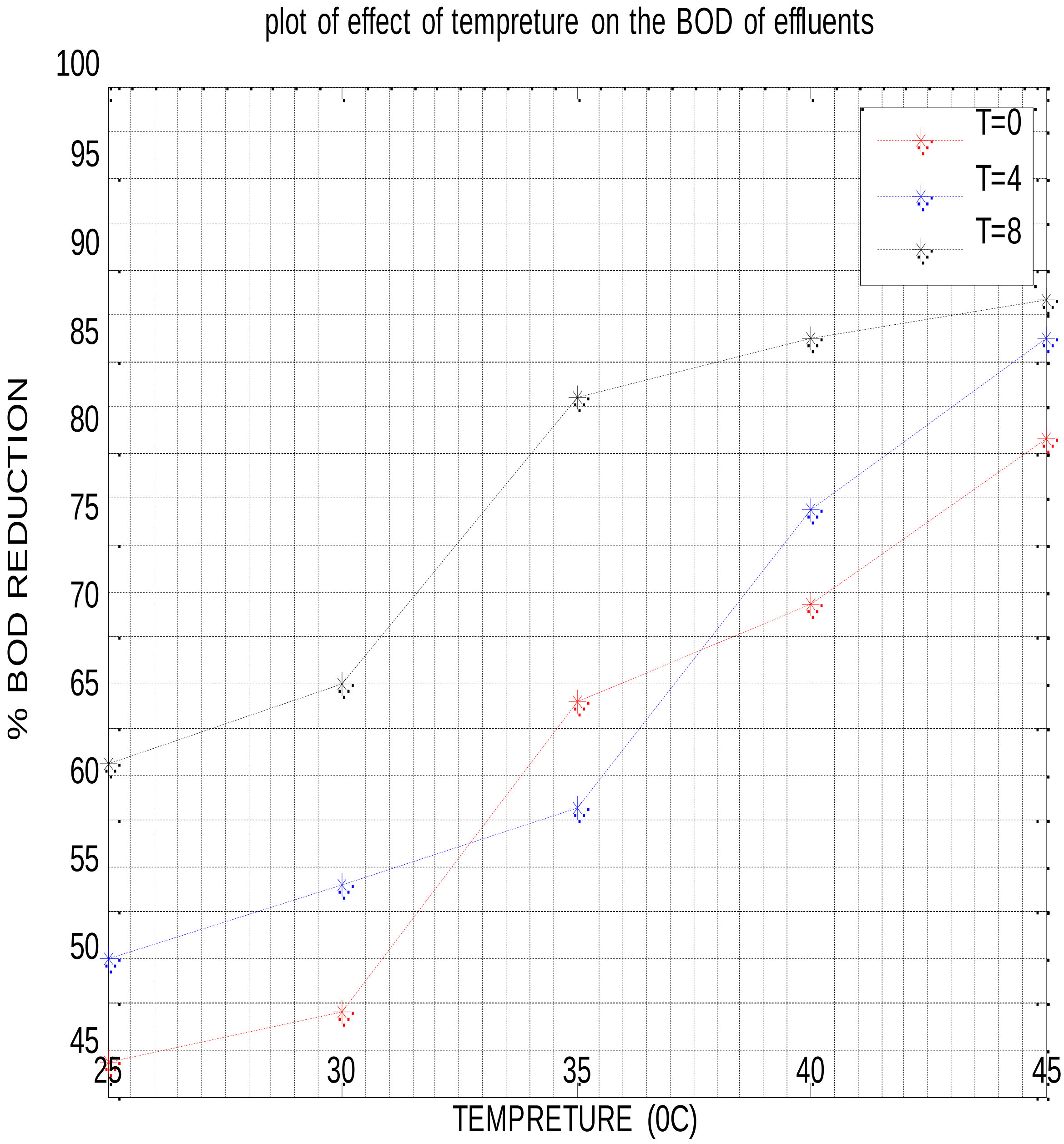

Figure 1: Plot of effect of temperature on BOD of the effluents

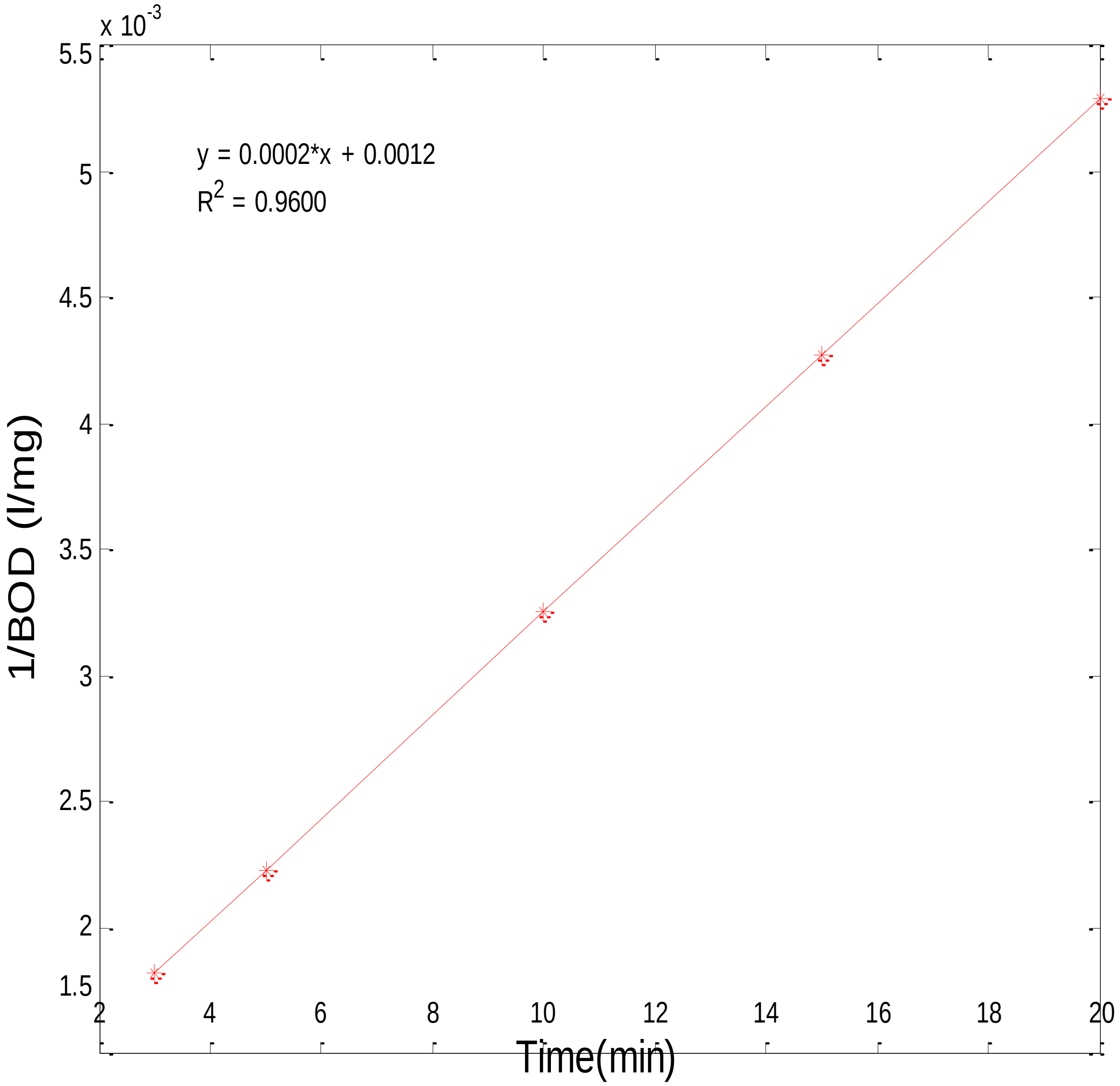

Figure 2: Plot of BOD Pollutant vs settling Time for Effluent T = 0 at varying Temperature

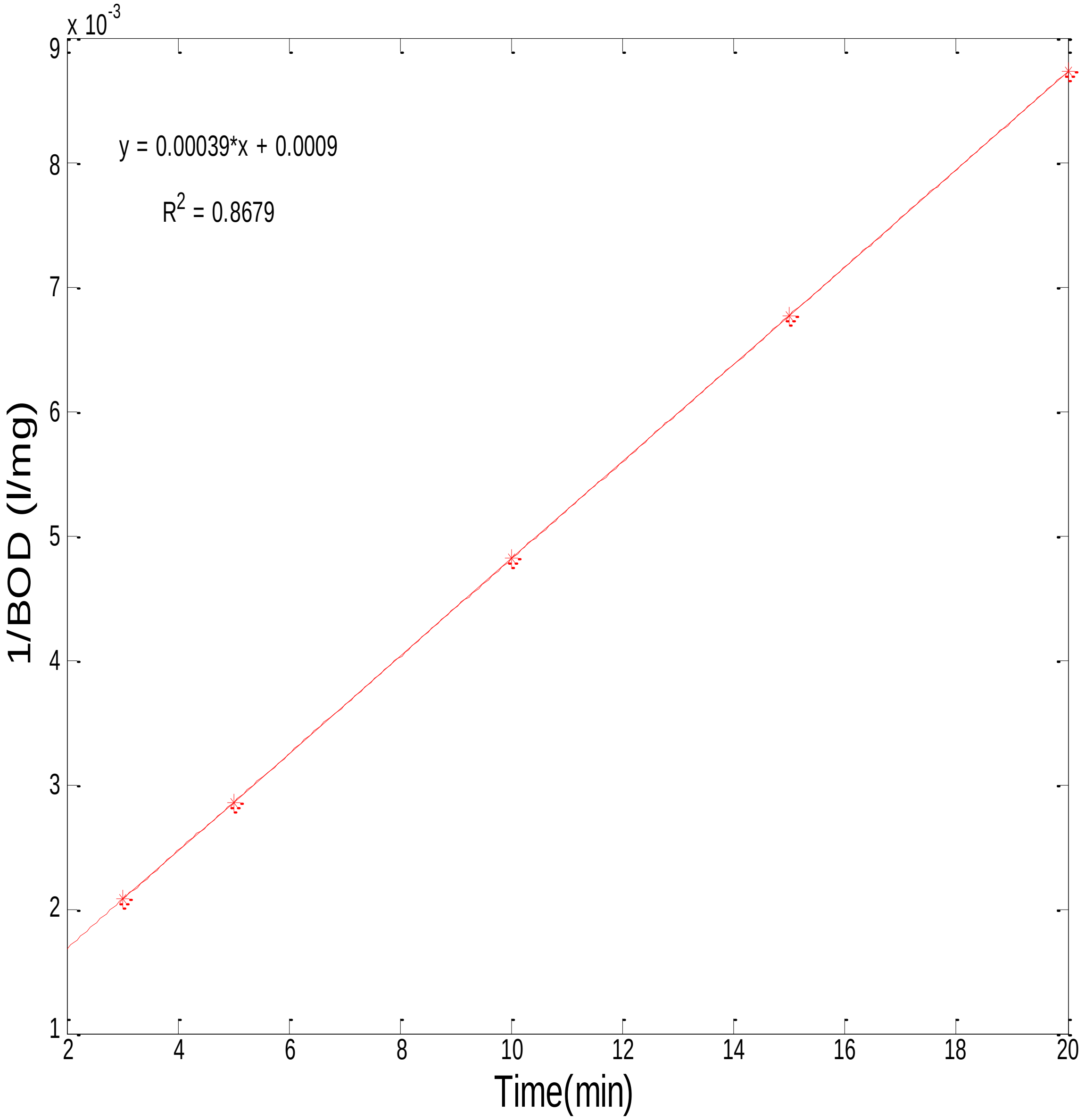

Figure 3: Plot of BOD Pollutant vs settling Time for Effluent T = 4 at varying Temperature

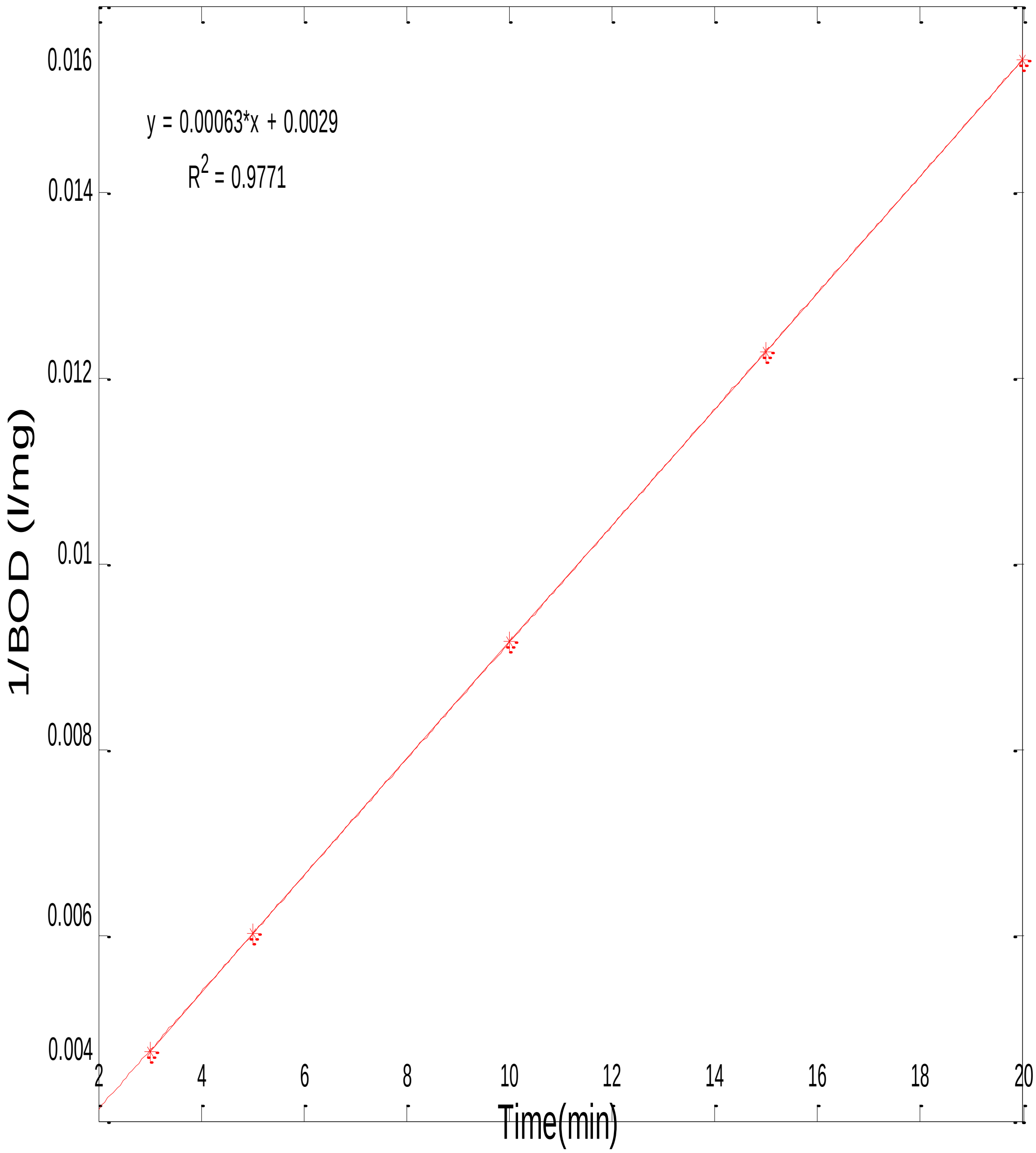

Figure 4: Plot of BOD Pollutant vs settling Time for Effluent T = 8 at varying Temperature

TABLES

Table 1: Result of Characterization of BOD (mg/l) for effluents before and after treatment

Effluents	Before Treatment (mg/l)	After Treatment (mg/l)
T = 0	923.78	178.00
T = 4	732.66	101.39
T = 8	576.38	67.18

Table 2: Result of proximate composition of the coagulant (BFT)

Parameter	**Value (%)**
Moisture content	4.63
Ash	4.71
Crude Fibre	9.54
Crude protein	2.45
Crude fat	1.56
Carbohydrate	77.10

Table 3: Result of Coag-flocculation treatment of BOD (mg/l) for T = 0, T = 4, and T = 8 effluents at constant contact time of 1hr, Coagulant dosage of 100mg/l and pH of 8 with varying temperature

Effluents	Temperature (^{o}C)				
	25	30	35	40	45
T = 0	490.00	465.00	310.00	260.00	178.00
T = 4	348.10	319.32	288.25	169.94	101.39
T = 8	313.18	188.10	98.72	79.42	67.18

Table 4: Summary of maximum Removal efficiency and optimal temperature for BOD of the effluents

Maximum removal efficiency(%)	Optimal value of temperature (^{o}C)	Effluent best at optimum value
80.73	45	T = 0
86.16	45	T = 4
88.37	45	T = 8

Table 5: Coag-Flocculation Kinetic Parameters of BFTC in NRE for the BOD at varying temperature, constant coagulant dosage of 100mg/l, contact time of 1hr, and pH of 8.

Kinetic Parameters	T = 0	T = 4	T = 8
ε_P (mg^{-1})	1	1	1
A	2	2	2
K_R (l/ min)	2.0407×10^{-4}	3.9123×10^{-4}	6.2793×10^{-4}
K_m (l/mg min)	2.0407×10^{-4}	3.9123×10^{-4}	6.2793×10^{-4}
β_{BR} (l/mg min)	4.0815×10^{-4}	7.8247×10^{-4}	1.3×10^{-3}
$T_{1/2}$ (min)	11.8886	9.1273	4.5861
E (%)	$100 - 0.1213N_t$	$100 - 0.0897N_t$	$100 - 0.2866N_t$
R^2	0.9600	0.8679	0.9771
N_O (mg/l)	824.3511	1.115×10^3	348.9627
-r	$2.0407 \times 10^{-4}N_t^2$	$3.9123 \times 10^{-4}N_t^2$	$6.2793 \times 10^{-4}N_t^2$