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Treatment of Synthetic Dairy Waste Water Using Tamarind Tree Branch as Coagulant

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Abstract: *Studies have shown that Alzheimer's disease can be linked to residual aluminium in treated water as most of the water treatment plants make use of aluminium salt in flash mixing unit. Also, in developing countries, chemical coagulants are usually imported, and this importation contributes to high cost of acquisition. Use of natural coagulants has been identified as a potential solution to these problems because these substances are not only readily available at low or no cost, they are also presumably safe. In this work, coagulation/flocculation efficiency of tamarind branch coagulant (Tambrant) in the treatment of synthesized dairy wastewater has been investigated. In order to achieve the aim of the study, experiments were carried out at varying coagulant dosage and time without adjusting the pH of the synthetic wastewater under treatment. The effect of these factors on the removal of turbidity and chemical oxygen demand (COD) and the dynamic of pH during the treatment were studied. Kinetics and isotherm studies were also carried out. The results obtained showed that Tambrant was effective in treating turbidity and COD in the wastewater. However, the pollutant removal efficiency of the coagulant was affected by the variation of coagulant dosage and/or treatment time. On the other hand, pH variation during the treatment was found not to be significantly affected by these factors. COD removal was best explained by both first and second-order kinetic models (irreversible). Freundlich model was found to best fit turbidity data. More studies need to be done to improve the effectiveness of the coagulant for wastewater treatment.*

Keywords: *Tambrant, COD, turbidity, isotherm model, pH dynamics, coagulation/flocculation kinetics.*

1. INTRODUCTION

Treatment of industrial wastewater has always been a paramount issue as human needs increase continuously alongside with population which lead to manufacturing of new products or expansion in production capacity of the existing plants due to higher demands. Dairy products are essentials for human well-being. Thus, demands for the products are considered high. Production of these products require large quantities of water due to various operations involved [1] and the resulting wastewater may have adverse environmental effect if discharged without proper treatment [2]. As the whole world is targeting green technology, it is important to find eco-friendly and cost-effective means of recycling with aim of reducing fresh water industrial demand and make our environment safer.

Conventionally, water and wastewater treatment plants usually apply chemical coagulants such as aluminium and iron salt to water and wastewater. The use of aluminium salt has been linked to health issue while iron salt has also been associated with generation of large volume of sludge, which increases the treatment cost [3,4]. Besides, most chemical coagulants used in developing countries are imported at high foreign exchange rate which leads to increase in price of the commodity, thus, high treatment cost.

`In the recent decade, the works on natural coagulants application have increased significantly due to availability of their sources; low cost of acquisition and processing; environmental friendliness; and multifunction and biodegradable nature [5,6]. Besides, use of these coagulants results in generation of lesser sludge with high nutritional value. So, the sludge handling and treatment cost is minimal [7-9].

Though, many works concerning natural coagulation have been reported by many researchers, Menkiti *et al.* [9] noted there was need for more work to be done in the area adsorption of component of biocoagulation process since coagulation/flocculation can be adsorptive and non-adsorptive type. Therefore, in this work, coagulation/flocculation of tamarind branch coagulation to remove turbidity and COD from simulated wastewater was investigated, including adsorptive and non-adsorptive (chemical reaction controlled) component.

2. MATERIALS AND METHODS

2.1 Coagulant Preparation

The moist tamarind branch (Figure 1a) obtained from Abubakar Tafawa Balewa University premises located in Bauchi was debarked. The debarked branch was then cut into pieces and dried in an oven at a temperature of 70 ^{o}C for about 20 h. The dried branch was then milled into powder using mortar and pestle. The resulting powder was later sieved using a laboratory shaker with 0.3 mm pore size to obtain a finer powder which was used as coagulant (Figure 1b). the summary of the preparation procedure is given schematically in Figure 2.


(a) (b)

Figure 1: Raw tamarind branch (a); the prepared tamarind branch coagulant (b)

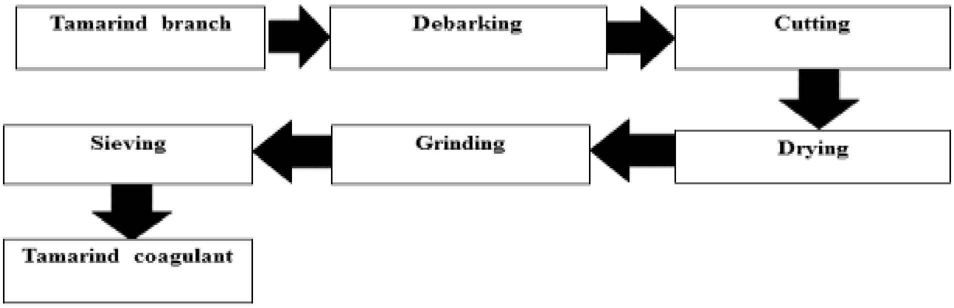

Figure 2: Coagulant preparation

2.2 Synthesis of Dairy Wastewater

The wastewater used in this research work was prepared by dissolving instant powdered milk in borehole water. The solution was thoroughly shaken and left at room temperature in a tightly covered container for about 48 h.

2.3 Jar Test Procedure

Coagulation-flocculation studies were performed in a conventional jar-test apparatus using 400 ml of the simulated wastewater. Each of 0.2, 0.4, 0.6, 0.8 and 1 g of the prepared tamarind branch coagulant (Tambrant) was added to the specified volume of the simulated wastewater contained in five different beakers mounted on the jar test equipment. The mixtures were each agitated rapidly for 3 min and slowly for 7 min at 140 and 40 rpm respectively, at ambient temperature. Samples were withdrawn at 2 min interval for pH, turbidity and COD measurement. After the coagulation process, the mixture was allowed to settle for about 40 minutes and filtered to obtain the supernatant which was later used for turbidity, COD and pH measurement. The turbidity of the synthesized dairy wastewater was measured before and after the treatment (experiment) using Hach Colorimeter (DR/890). A pH meter was also used to measure the pH of the synthesized wastewater.

2.4 Statistical Analysis

In order to evaluate the effects of variation of coagulant dosage and treatment time on the pollutant removal efficiency of Tambrant, experimental data were analysed using Response Surface Methodology in Design Expert Environment with the minimum, maximum values of Tambrant dosage and time of 0.2 g and 1 g; and 2 min and 10 min respectively. Based on the suggestion given in the Fit Summary, residual turbidity and residual COD data were modelled using cubic polynomial equation, which was later modified to improve the significance of more model terms. On the other, pH data was modelled using linear equation. Significance of the statistical models developed were evaluated using analysis of variance results.

2.5 Kinetics and Isotherm Studies

In an attempt to study the kinetics of COD removal with the use of Tambrant, the batch experimental data were modelled using irreversible first and second order equation in linearized form given in Equations 1 and 2 respectively. The isotherm studies were carried out using Langmuir, Freundlich and Temkin models given in Equations 3, 4 and 5. Also, given in these equations are the variables plotted to fit the data. These isotherms models were used because they were found easy to use.

$$\ln\frac{C_o}{C_t} = k_1 t, \qquad \ln\frac{C_o}{C_t} \ vs \ t \tag{1}$$

$$\frac{1}{C_t} = \frac{1}{C_o} + k_2 t, \qquad \frac{1}{C_t} \ vs \ t \tag{2}$$

$$\frac{C_e}{q_e} = \frac{1}{KQ_a^o} + \frac{C_e}{Q_a^o}, \qquad \frac{C_e}{q_e} \ vs \ C_e \tag{3}$$

$$\log q_e = \log K_f + \frac{1}{n}\log C_e, \quad \log q_e \ vs \ \log C_e \tag{4}$$

$$q_e = \frac{RT}{b_T}\ln A_T + \frac{RT}{b_T}\ln C_e, \quad q_e \ vs \ \ln C_e \tag{5}$$

In these equations, C is the pollutant concentration, and subscripts o, t and e are initial, time t, and equilibrium respectively. K_F & n, K, A_T & b_T; k_1 and k_2 are isotherm constants for Freundlich, Langmuir, Temkin, first and second order reaction rate constants. The adsorption capacity at time t, q_t and that at equilibrium, q_e were calculated using the expressions given Equations 6 and 7,

$$q_t = \frac{(C_o - C_t)V}{m} \tag{6}$$

$$q_e = \frac{(C_o - C_e)V}{m} \tag{7}$$

where V is the volume of simulated wastewater (L) and m is the amount in gram of the adsorbent used for each experiment. Adsorption capacity is expressed in mg/g for COD and NTU.L/g for turbidity.

3. RESULTS AND DISCUSSION

3.1 Effect of Tambrant Dosage and Time Variation

Figures 3 and 4 respectively represent the results obtained when the dosage of Tambrant was varied between 0.2 g and 1 g during the coagulation/flocculation the simulated dairy wastewater. As obviously seen in these figures, the two independent variables considered here affected both the pH and pollutant removal efficiency of the coagulant. The pH variations observed at various treatment time and coagulant dosage are shown in Figure 3. For all dosage values except 0.8 g (2 g/L), the residual pH increased with increasing treatment time for up to 2 min after which stability was attained. However, for 0.8 g of Tambrant the pH increased from the initial value of 5.8 to a maximum of 6.4 after 2 min and later started decreasing until a stable pH of 6.2 was reached. All in all, the pH variation during treatment was not significant as all the values was still in slightly acidic region. This is in line with observation reported by Kaushal and Goyal [10]. In their work, the researchers found that treatment of municipal and dairy wastewater with coagulants prepared from Moringa oleifera and okra seeds led to little or insignificant variation in pH of the wastewaters before and after treatment. The slight increase in pH could be as a result of presence of more hydroxyl ion in the water.

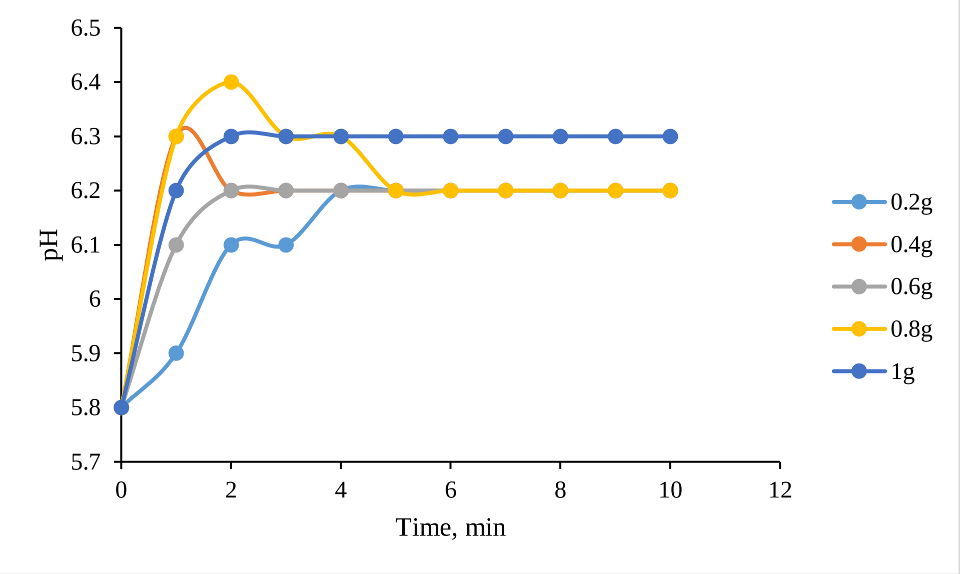

Figure 3: Effect of treatment time and Tambrant variation on final pH of the simulated wastewater

As shown in Figure 4, It could be noticed that increasing coagulant dosage and treatment time led to improved COD removal. At a dosage of 0.2 g, residual turbidity decreased from the initial value of 8342.4 mg/L to 5128 .8 mg/L after 10 min of treatment. This can compare well with 4297.6, 3665.6, 3665.6 and 2654.4 mg/L obtained for 0.4, 0.6, 0.8 and 1 g Tambrant dosage at 10 min coagulation/flocculation. Thus, the maximum COD removal achieved was 68.18 % in the acidic region with final pH of 6.2 as shown in Figure 3 earlier.

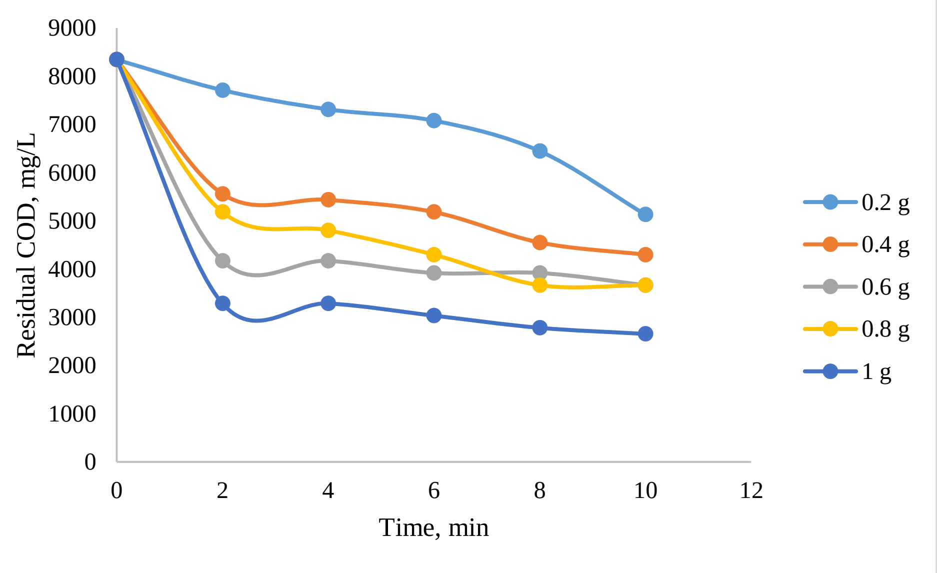

Figure 4: Effect of treatment time and Tambrant variation on residual COD of the simulated wastewater (Initial COD: 8342.4 mg/L NTU, initial pH: 5.8)

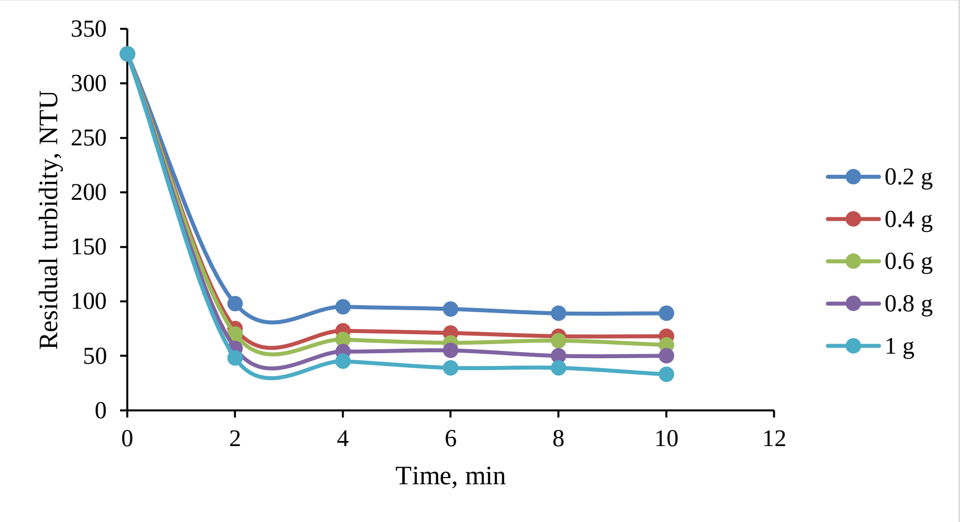

Figure 5: Effect of treatment time and Tambrant variation on residual turbidity of the simulated wastewater (Initial turbidity: 327 NTU, initial pH: 5.8),

Similarly, as shown in Figure 5, turbidity removal was also affected by variation of treatment time and the coagulant dosage. For all Tambrant dosages except 0.6 g, residual turbidity reduced with time until equilibrium was achieved. But looking at the figure further, it could be noticed that increasing the coagulant dosage led to increasing turbidity removal. For instance, at the end of 2 min coagulation/flocculation experiment, the residual turbidity values obtained for 0.2, 0.4, 0.6, 0.8 and 1 g Tambrant dosages were 98, 75, 70, 57 and 48 NTU respectively. Similarly, at 10 min treatment time, residual turbidity reduced from 89 NTU to 33 NTU when the dosage was increased from 0.2 g to 1 g.

3.2 Analysis of Variance

Statistically, the effects of these factors on the pH, turbidity and COD removal were also investigated. Analysis of Variance (ANOVA) results showed that the effects of coagulant dosage and treatment time variation on turbidity and COD removal efficiency are best represented by modified cubic model. The developed residual turbidity model (Equation 1) was found to be significant with probability value of less than 0.0001. Also, based on the probability value on 95% confidence level, the significant terms of the model were observed to be A, B, A^2 and A^3. This implies that variation of Tambrant dosage and time at linear, quadratic and cubic level caused shift in the value of the response as evident in their p-values being less than 0.05 (see Table 1). Also, from the signs of coefficients of the model (Equation 1), it can be said that residual turbidity (RT) reduced with increasing Tambrant dosage and time. R-squared value of the model (Equation 1) being close to unity is an indication that the model adequately represents the relationship between the residual turbidity variation with respect to change in the coagulant dosage and time. Also, the adjusted and predicated R-squared values were reasonably close.

$$RT = +143.881 - 260.7625A - 3.0184B + 355.4965A^2 + 0.1432B^2 - 187.5A^3 \text{….} \quad (1)$$

$$RCOD = +12440.29 - 31846.75A - 3.65B + 277.35AB + 43381.26A^2 - 27.05B^2 - 21318..06A^3 \quad (2)$$

$$pH = +6.1177 + 0.15A + 0.001667B \quad (3)$$

Table 1: ANOVA for residual turbidity model

Source	Sum of Squares	Df	Mean Square	F-value	p-value Prob > F	
Model	4991.57	5	998.31	213.28	< 0.0001	significant
A-Tambrant dosage	178.71	1	178.71	38.18	< 0.0001	
B-Time	202.8	1	202.8	43.33	< 0.0001	
A^2	23.03	1	23.03	4.92	0.0485	
B^2	14.58	1	14.58	3.11	0.1053	
A^3	97.2	1	97.2	20.77	0.0008	
Residual	51.49	11	4.68			
Cor Total	5043.06	16				

R-squared: 0.9898, Adj R-squared: 0.9857, Pred R-squared: 0.9755

Table 2: ANOVA of residual COD model

Source	Sum of Squares	Df	Mean Square	F Value	p-value Prob > F	
Model	2.68E+07	6	4.47E+06	33.2	< 0.0001	Significant
A-Tambrant dosage	1.75E+05	1	1.75E+05	1.3	0.2801	
B-Time	3.15E+06	1	3.15E+06	23.38	0.0007	
AB	8.37E+05	1	8.37E+05	6.22	0.0318	
A^2	1.78E+06	1	1.78E+06	13.26	0.0045	
B^2	5.20E+05	1	5.20E+05	3.87	0.0775	
A^3	1.26E+06	1	1.26E+06	9.34	0.0121	
Residual	1.35E+06	10	1.35E+05			
Cor Total	2.81E+07	16				

R-squared: 0.9522, Adj R-squared: 0.9235, Pred R-squared: 0.8223

Similarly, the developed modified cubic model (Equation 2) for residual COD (RCOD) of the simulated dairy wastewater was found to be significant with p-value of less than 0.0001. Also, using the same criterion, the significant terms of the model were B, AB, A^2 and A^3. Although, unlike RT model, A was not singly significant for this model but its interaction with time was found to affect the model (Equation 2) significantly. As shown in Figure 6, increasing both the time and Tambrant dosage simultaneously led to reduction in residual COD value. As it can be noticed from the figure all the simulated points fell within the design points in the range of 7710 and 2654.4 mg/L residual turbidity. In addition, the R-squared value of the residual COD model was 0.9522 and there was marginal difference between the adjusted and predicted R-squared. All these indicate the adequacy of the model in representing the residual COD and Tambrant dosage-Time relationship.

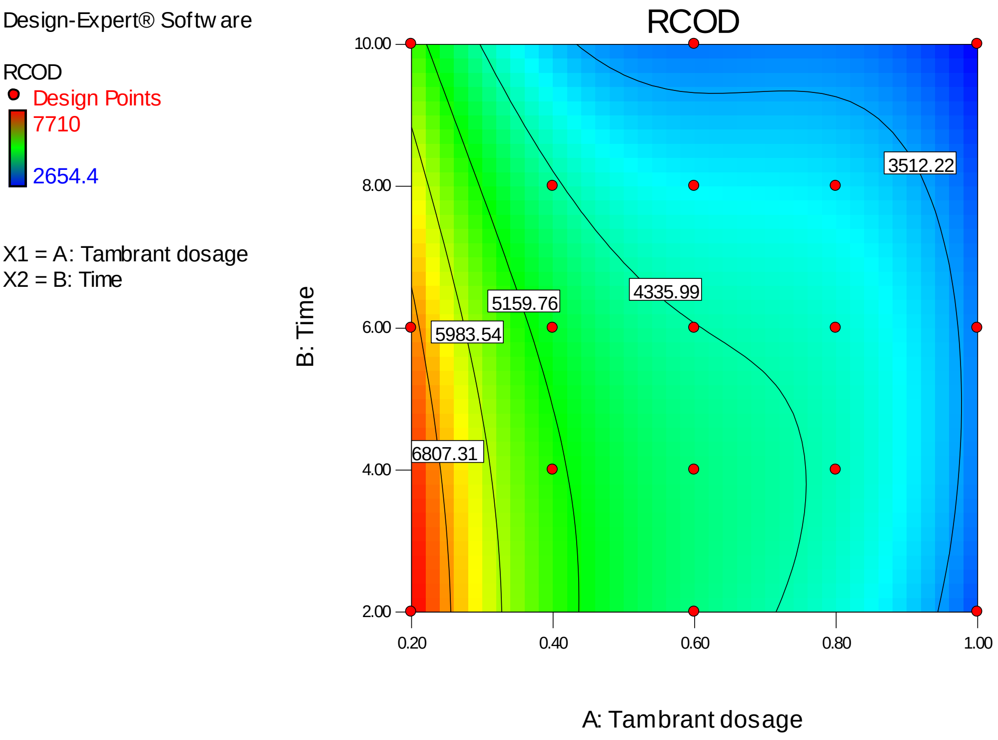

Figure 6: The effect of coagulant dosage and time variation on COD removal

Table 3: ANOVA of final pH model

Source	Sum of Squares	df	Mean Square	F-value	p-value Prob > F	
Model	0.027	2	0.014	11.01	0.0013	Significant
A-Tambrant dosage	0.027	1	0.027	21.76	0.0004	
B-Time	3.33E-04	1	3.33E-04	0.27	0.6124	
Residual	0.017	14	1.24E-03			
Cor Total	0.045	16				

R-squared: 0.6114, Adj R-squared: 0.5559, Pred R-squared: 0.3857

The model developed for final pH and the results of analysis of variance are given in Equation 3 and Table 3 respectively. As it can be understood from the model, the pH increased with increase in Tambrant dosage while the significance of this term is indicated by its p-value of 0.0004. Though, increase in time per unit min also led to increase in pH. But the effect on the response is statistically insignificant as evident from p-value of B being greater than 0.05. The results obtained here corroborates the observation made in section 3.1 as regards the final pH.

3.3 Kinetic Modelling

The kinetics of the batch coagulation/flocculation of the simulated wastewater was studied at various coagulant dosage and the results obtained were as follows. Given in Figure 7 and Table 4 are the results obtained when experimental data were fitted to first order reversible model. Though for all the coagulant dosages straight lines were obtained with coefficient of determination (R-squared) ranging from 0.78 to 0.94, none of the graphs gave a zero intercept as expected. The intercepts were observed to increase with increasing coagulant dosage; when the Tambrant dosages were 0.2, 0.4, 0.6, 0.8 and 1 g respectively the obtained intercepts were 1.1828, 1.448, 1.5322, 1.7156 and 1.8219. This deviation from first order kinetic model may be as result of another mechanistic step contributing to the disappearance of suspended particles quantified as turbidity. Also, the rate constant values were observed to increase as the coagulant dosage increased (Table 4).

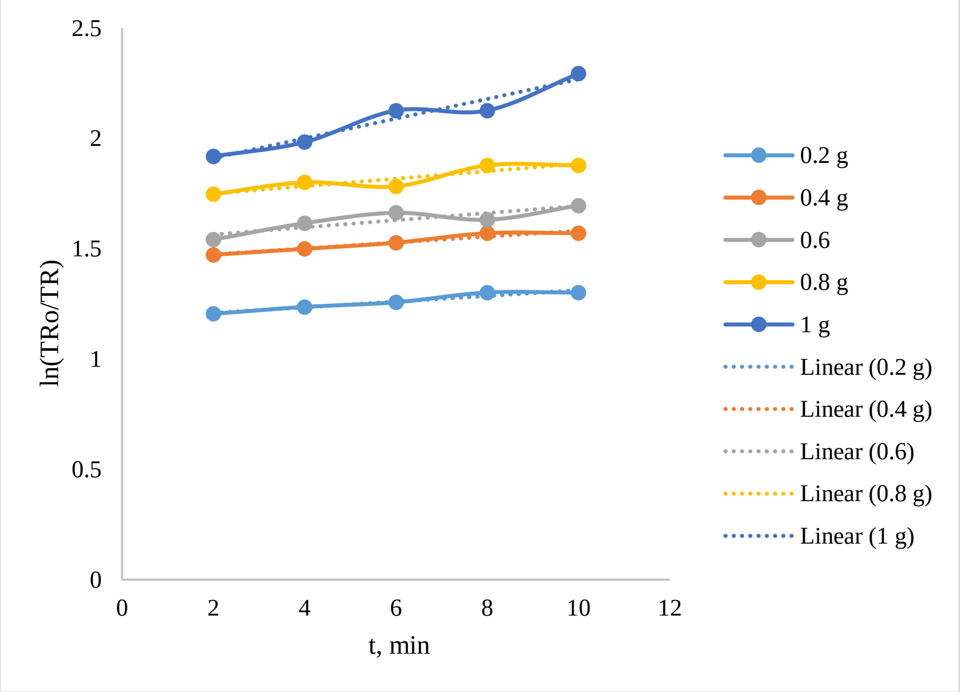

Figure 7: Irreversible first-order kinetic plots for turbidity removal

Table 4: Irreversible first-order kinetic parameters for turbidity removal

Dosage (g/0.4 L)	Rate Constant (min^{-1})	Intercept	R-squared
0.2	0.0129	1.1828	0.9475
0.4	0.0133	1.448	0.9498
0.6	0.0162	1.5332	0.7808
0.8	0.017	1.7156	0.8342
1	0.0446	1.8219	0.9399

Also, given in Table 5 and Figure 8 are the results obtained when COD experimental data at various coagulant dosage were fitted to first order irreversible model. As it can be seen from the figure, the COD data fitted fairly to first order kinetic model tested, however, just in a similar way as the case of residual turbidity, the intercepts obtained for the linearized kinetic graphs were all non-zero. The values of the intercepts for models are smaller compared to those of the former. Also, as shown in Table 5, the R-squared values obtained for the kinetic plots were in the range of 0.86 and 0.95, slightly higher than those of first order kinetic models obtained for turbidity removal at various dosages. Indication, that COD removal by Tambrant partially followed first order kinetics which means that rate of disappearance of COD varied linearly with COD concentration. This is also applicable to turbidity removal rate.

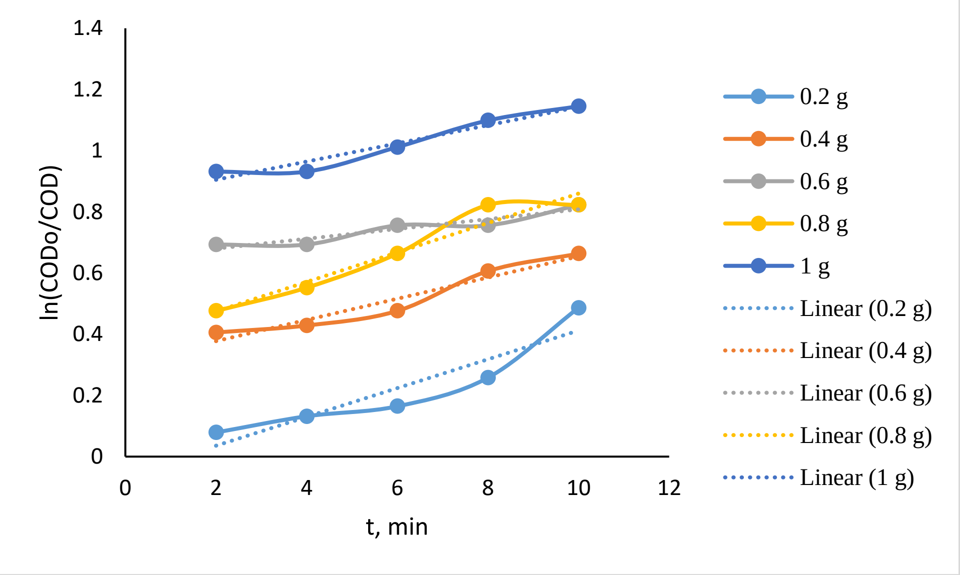

Figure 8: Irreversible first-order kinetic plots for COD removal

Table 5: Irreversible first-order kinetic parameters for COD removal

Dosage (g/0.4 L)	Rate Constant (min^{-1})	Intercept	R-squared
0.2	0.0471	-0.0585	0.8588
0.4	0.0346	0.3081	0.9368
0.6	0.016	0.6477	0.8892
0.8	0.0481	0.3784	0.9465
1.0	0.0297	0.8454	0.9419

However, the presence of non-zero intercepts, may be an indication that the biocoagulation is not pure chemical reaction but adsorption process. Since adsorption kinetic modelling usually involves use of adsorption capacity which is the quantity of adsorbate adsorbed per unit weight of adsorbent. The plots of adsorption capacity against time for turbidity and COD removal were made. These are given in Figures 9 and 10 respectively. At all coagulant dosages, COD adsorption capacity of Tambrant was observed to increase with increasing treatment time with no evidence of true equilibrium. But it can be noticed that the adsorption capacity reduced with increasing coagulant dosage (Figure 9). Also, turbidity adsorption capacity was found to change in a similar manner with that of COD but equilibrium being achieved after 6 min. Consequently, only turbidity data was investigated for adsorption isotherm study. On the other hand, COD data were later fitted to second order irreversible reaction model as it was perceived that within the treatment time considered COD disappearance should be chemical reaction controlled. The obtained graph and kinetic parameters are given in Figure 11 and Table 6 respectively.

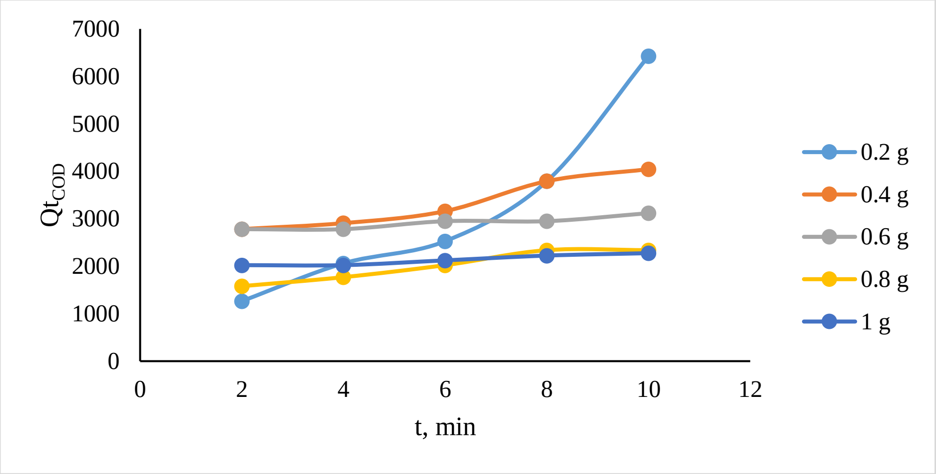

Figure 9: COD adsorption capacity against time

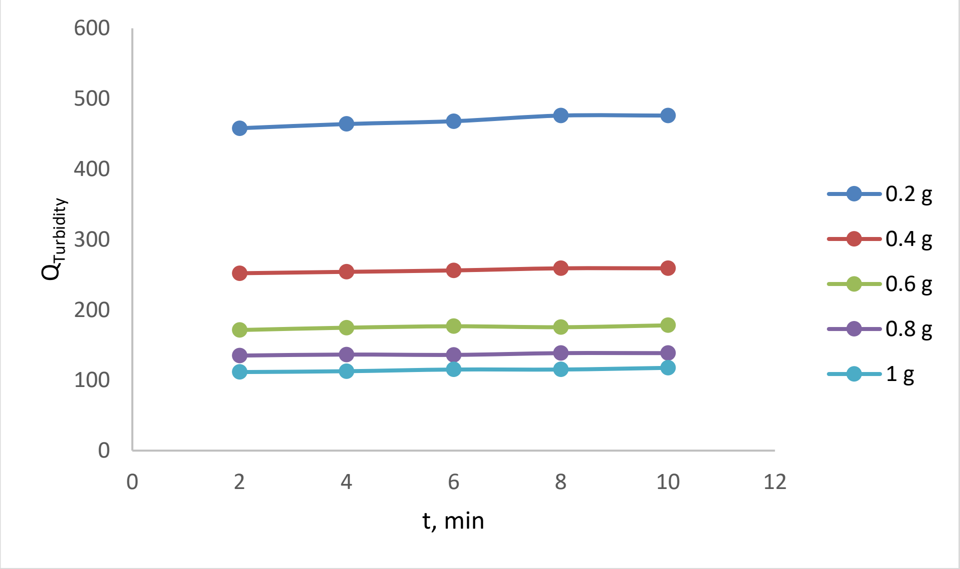

Figure 10: Turbidity adsorption capacity against time

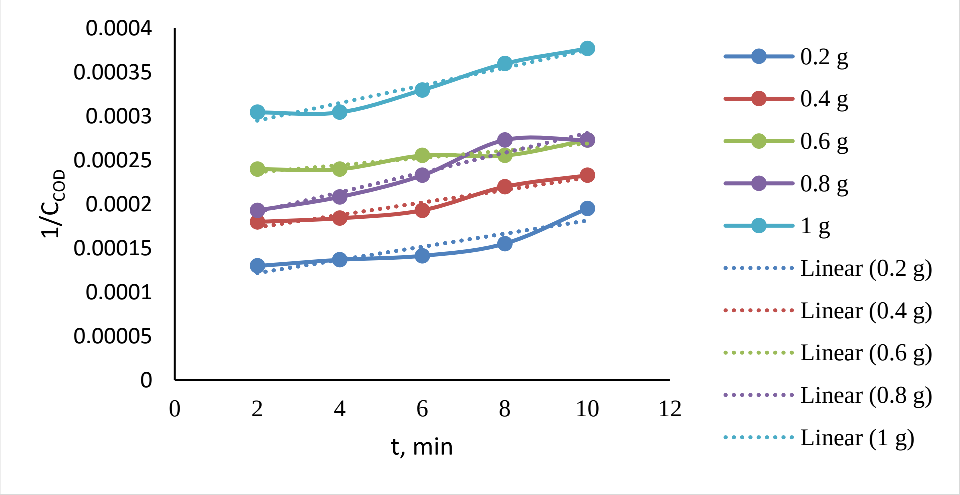

Figure 11: Irreversible second-order kinetic model for COD removal

Table 6: Irreversible second-order kinetic parameters for COD removal

Dosage (g/0.4 L)	Rate Constant (L/mg.min)	Intercept	R-squared
0.2	7.00E-06	0.0001	0.8212
0.4	7.00E-06	0.0002	0.9289
0.6	4.00E-06	0.0002	0.8847
0.8	1.00E-05	0.0002	0.9411
1	1.00E-05	0.0003	0.9404

Given in Figure 11 are linearized second order kinetic plots obtained for COD removal at various coagulant dosages. The pollutant disappearance was observed to fit to the model with intercepts in the range of 0.0001 and 0.0003 (which as opposed to 0.00013 (1/8342.4) expected theoretically (Table 6). Comparing, the results with the ones obtained when the COD data, it could be noted that both first and second order model represent COD disappearance, an indication that Tambrant removal rate of COD is shifting order type.

3.4 Adsorption Isotherms

In investigating turbidity adsorption mechanism of Tambrant, three models were considered. The results for each of the isotherms are given in Figures 12-14. As shown in Figure 12, turbidity equilibrium data fitted to Langmuir model with determination coefficient (R-squared) of 0.90 and negative slope meaning a negative adsorption parameter (Q_a^o). According to Kul and Caliskan [10] who also reported negative Langmuir parameters for adsorption of Zn ion on acid –activated kaolinite, electrostatic nature of the adsorption may be the reason for the negative value of the parameters.

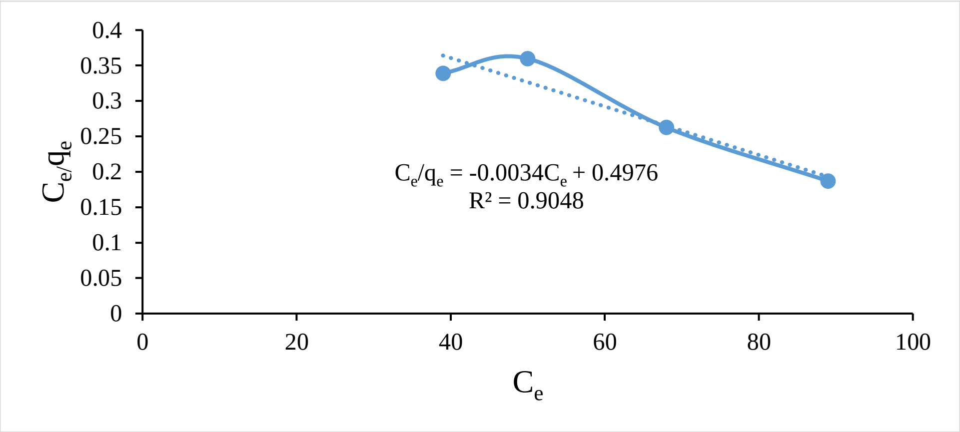

Figure 12: Langmuir plot for turbidity removal

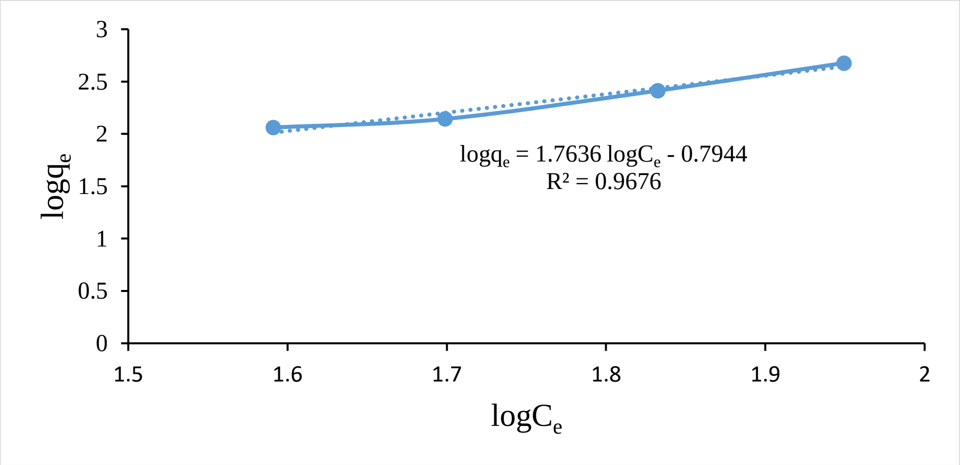

Figure 13: Freundlich plot for turbidity removal

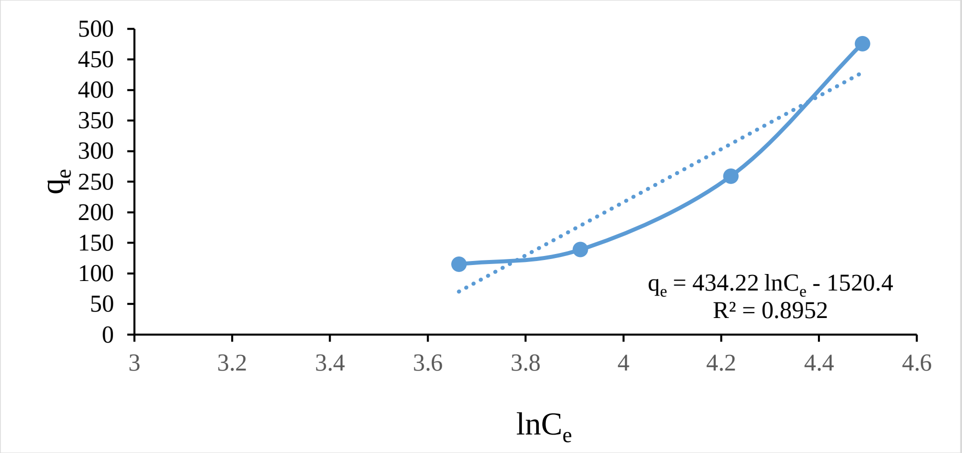

Figure 14: Temkin plot for turbidity removal

Looking at Figure 13, it can be noticed that Freundlich model fit turbidity adsorption with R-squared value of 0.97 while that with Temkin model was found to be approximately 0.9 (Figure 14). From all indications, adsorption of turbidity onto Tambrant is best described by Freundlich model. The parameter of the isotherm n was found to be 0.567, which shows that the process was not favorable as the value of the range (1-10) [9]. Also, K_f was not determinable as the intercept value was negative. The fraction value of n shows that marginal energy decreases with concentration of the pollutant on the adsorbent [11-13].

4.0 CONCLUSION

In this work, the use of tamarind branch-based coagulant for treatment of simulated dairy wastewater has been investigated. Tambrant pollutant removal efficiency was found to be affected by variation of its dosage and coagulation/flocculation time. The effects were confirmed to be statistically significant with residual turbidity and COD models having coagulant dosage and time or the factors interaction as significant model term based on probability value being less 5%. The COD disappearance rate was found to be irreversible shifting order type. Turbidity removal mechanism of Tambrant could be governed by physical adsorption. The maximum turbidity and COD removals achieved were 89.9 and 68.2%, at 10 min and 1g treatment time and Tambrant dosage respectively.

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