



## Coagulation Kinetics for bakery wastewater treatment using *Vigna Subterranea* husk as coagulant

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**Abstract:** This work studied the coagulation kinetics for bakery wastewater treatment using *Vigna Subterranea* husk as coagulant. The coagulation study was done using the jar test method based on standard bench scale Nephelometric method for the examination of water and wastewater. The kinetic data was fitted to first and second order models. It was observed that kinetic data fitted well to second order model at all p H and lower concentrations due to high correlation coefficient. p H of 6 recorded higher correlation coefficients for all the concentrations studied for the two models which show that pH of 6 is the best pH for the coagulation study. It can be concluded that the theory of perikinetics is the controlling mechanism of the coagulation owing to the high correlation coefficients (>0.9) recorded at different pH. There was complete removal of lead and nitrate after coagulation, while chemical oxygen demand and biological oxygen demand were reduced. There was 40.8% increase on the dissolved oxygen after coagulation.

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**Keywords:** Bakery wastewater, Bambara nut husk, Coagulation, First order model, Second order model

### 1. Introduction

Coagulation plays a prominent role in water and waste water treatment processes. Understanding of this process is necessary because of numerous factors inherent in the process that affect it.

Coagulation is the process of destabilizing colloids, aggregating them and binding them together for ease of sedimentation (AL-Sameraiy 2017). This is achieved by adding simple salts or by charge neutralization resulting in a tendency in the aggregates to be small and dense (Al-Sameraiy 2017). In the area of water and wastewater treatment, coagulation refers to destabilization by the dosing of appropriate additives and flocculation refers to the formation of aggregates usually by some form of fluid motion (Gregory 2006).

The phenomenon of coagulation of colloidal system is similar in many ways to chemical reaction, proceeding at a definite rate dependent on temperature and concentration (Brandy et al 1952). Frequently, however, it is a diffusion controlled process to which the standard kinetics methods based on equilibrium between reactant, activated complex and products cannot be applied. It is only when the probability of coalescence of the particles taking part in a collision is reduced that is when the particles are relatively stable, that an equilibrium state can be postulated.

During coagulation-flocculation, both floc particles size and structure undergo transitional phases. Initially, upon coagulation dosing, there is a

period of rapid floc growth in which the size and structure of the floc aggregates are dynamic in nature (Ramphal and Sibiya 2014). This is followed by a steady-state region or equilibrium between particle growth and fragmentation for specific period, during which the floc particle size does not change. The shape of the particle size distribution curve is critical as it influences coagulation-flocculation kinetics, the rate of floc growth, floc characteristics and solid removal processes (Selomulya et al 2001; Spicer et al 1996).

Many coagulants have been used in treating wastewater, but little attention has been given to plant wastes. This necessitated the study on bambara nut husk (*Vigna Subterranea*) as a coagulant. This work studied the coagulation kinetics of bakery waste water using bambara nut husk as coagulant.

### 2. Materials and methods

#### Collection of wastewater

The bakery wastewater was collected from Deking bakery at Abakpa Nike Enugu, Enugu State Nigeria.

#### Characterisation of Wastewater

The characterization of wastewater before and after coagulation was done according to standard method (APHA, 1998).

#### Jar test method

The jar test method was conducted based on standard bench scale Nephelometric method for the examination of water and wastewater using turbidimeter, magnetic stirrer and pH meter.

**Preparation of bambaranut husk as a coagulant**

The seed shell was collected from abakpa market in Enugu as a waste generated after grinding and sieving the seed. It was washed and dried to constant weight. The dried husk was ground to 600µm and then processed for further study.

**Coagulation kinetics**

The time evolution of the cluster size distribution for colloidal particles can be described by the equation 3.1 (Swift and Friedlander (1964); Jin 2005)

$$\frac{dn_k}{dt} = \sum_{i=2}^k \beta(i, j) n_i n_j - \sum_{i=k}^{\infty} \beta(i, k) n_i n_k \quad (3.1)$$

Where  $\frac{dn_k}{dt}$  is the rate of change of concentration of particle of size K (concentration / time),  $n_k(t)$  is the time independent number concentration of n-fold cluster, t is the time,  $n_{kij}$  are the elements of rate kernel which control the rate of the coagulation between an i-fold and j-fold cluster.

$\beta$  is a function of the coag-flocculation transport mechanism. In the Smoluchowski analysis, the coagulation process is approximated to be controlled by Brownian motion and monodispersed suspension (Babayemi et al. 2013). So the analysis attempts to interpret the kinetics of rapid coagulation on the basis of diffusion (Brownian) motion which is best studied during the early parts of the coagulation process (t ≤ 30mins) (Holthof et al. 1996; WST, 2005).

The appropriate value of  $\beta$  for Brownish transport is given by (Smoluchowski 1917):

$$\beta_{BR} = \frac{8}{3} = \epsilon_p \frac{K_B T}{D} \quad (3.2)$$

Where  $K_B$  is Boltzmann's constant (J/K)  
T is absolute temperature (K)

The rate of depletion of particle count (Turbidity removal) can generally be expressed as:

$$\frac{-dN_t}{dt} = KN_t^\alpha \quad (3.3)$$

Where  $N_t$  is total particle concentration at time t,  
 $N_t = \sum nk$  (mass volume)

K is the  $\alpha$ th order coag-flocculation constant.  
 $\alpha$  is the order of coag-flocculation process and

$$K = \frac{1}{2} \beta_{BR} \quad (3.4)$$

Where  $\beta_{BR}$  is collision factor for Brownian transport.

Also  $\beta_{BR} = \epsilon_p K_R \quad (3.5)$

Combining equation 3.3, 3.4 and 3.5  
Produces

$$\frac{-dN_t}{dt} = \frac{1}{2} \beta_{BR} N_t^\alpha \quad (3.6)$$

$$= \frac{1}{2} \epsilon_p K_R N_t^\alpha \quad (3.7)$$

Where  $K_R$  is the Smoluchowski rate constant for rapid coagulation.

However,  $K_R = 8\pi R D \quad (3.8)$   
 $= 2a \quad (3.9)$

Where D is particle diffusion coefficient  
a is particle radius

From Einstein's equation,

$$D = K_B T / B \quad (3.10)$$

From Stokes equation,

$$\beta = 6\pi\eta a \quad (3.11)$$

Where  $\beta$  is the friction factor.  
 $\eta$  is the viscosity of the fluid.

Combining equation 3.7 to 3.11 gives

$$= \frac{4}{3} \epsilon_p \frac{K_B T}{D} N_t^\alpha \quad (3.12)$$

Comparing equation 3.3 and 3.12 shows that

$$K = \frac{4}{3} \epsilon_p \frac{K_B T}{D} \quad (3.13)$$

For perikinetic aggregation,  $\alpha$  theoretically equals 2 as would be shown below (Fridkhsberg 1984).

From Fick's Law,

$$J_f = D^4 4\pi R p^2 \frac{dN_t}{dR} \quad (3.14)$$

Integrating equation 3.14 at initial conditions,

$$N_t = 0, R = 2a$$

$$\frac{J_f}{2\pi 4\pi} \int_0^{Rp} \frac{dRp}{Rp^2} = \int_{N_0}^{N_t} dN_t \quad (3.15)$$

Therefore,  $J_f = 8\pi D^4 \alpha N_0 = \frac{1}{2} K_R \cdot N_0 \quad (3.16)$

For central particle of same size undergoing Brownian motion, the initial rate of rapid coagulation is

$$\frac{-dN_t}{dt} = J_f \cdot \epsilon_p \cdot N_t^2 \quad (3.17)$$

$$= \frac{1}{2} K_R \cdot \epsilon_p \cdot N_t^2 \quad (3.18)$$

$$= \frac{4}{3} \epsilon_p \frac{K_B T}{D} \cdot N_0^2 \quad (3.19)$$

$$= \frac{4}{3} \epsilon_p \frac{K_B T}{D} N_t^2 \text{ at } t > 0 \quad (3.20)$$

Hence, from equation 3.20,  $\alpha = 2$

However, in real practice, empirical evidence shows that in general,

$1 \leq \alpha \leq 2$  (WST, 2005). Based on this, what is required to evaluate K is to determine the line of better fit between  $\alpha = 1$  and  $\alpha = 2$  while the experimental data are fitted into a linearised form of equation 3.3.

Hence for  $\alpha = 1$ , equivalent of equation 3.3 yields

$$\frac{dN}{dt} = -KN \quad (3.21)$$

Integrating within the limits produce,

$$\int_{N_0}^N \frac{dN}{N} = - \int_0^t K dt \quad (3.22)$$

Hence, in  $\left(\frac{1}{N}\right) = Kt - \ln N_0 \quad (3.23)$

Plot of  $\ln(1/N)$  vs.t gives a slope of K and intercept of  $(-\ln N_0)$

For  $\alpha = 2$ , equivalent equation 3.3 gives;

$$\frac{dN}{dt} = -KN^2 \quad (3.24)$$

Hence  $\int_{N_0}^N \frac{dN}{N^2} = -K \int_0^t dt \quad (3.25)$

$$\frac{1}{N} = Kt + \frac{1}{N_0} \quad (3.26)$$

A plot of  $\left(\frac{1}{N}\right)$  Vs t produce a slope of K and intercept of  $\left(\frac{1}{N_0}\right)$

For the equation of coagulation period ( $\tau$ ), from equation 3.26,

$$N = \frac{N_0}{1 + N_0 K \tau} \quad (3.27)$$

$$= \frac{N_0}{\left[1 + \frac{t}{\tau}\right]} \quad (3.28)$$

Where  $\tau = \left[\frac{1}{N_0 K}\right]$

$$N = \frac{N_0}{1 + t/\tau} \quad (3.29)$$

Hence,

$t = \tau$ , equation 3.29 becomes

$$N = N_0/2 \quad (3.30)$$

When

This quantity is called the coagulation period which is the time during which the initial concentration of particle is halved.

Therefore, as  $N_0 \rightarrow 0.5 N_0, \tau = \rightarrow \tau_{1/2}$

Hence,

$$\tau_{1/2} = \frac{1}{0.5 N_0 K} \quad \text{for } 2^{\text{nd}} \text{ order} \quad (3.31)$$

$$\tau_{1/2} = \frac{\ln 2}{K} \quad \text{for } 1^{\text{st}} \text{ order} \quad (3.32)$$

The result obtained for turbidity of sample in NTU were multiplied by a factor of 2.20 for conversion to TSS concentration (mg/l) (Ozacar and Sengli 2000)

### 3. Results and Discussions

Characterisation of the bakery wastewater are shown on table 1 and have been discussed extensively on our previous work (Ejikeme 2018).

Table 1. Characterisation of bakery wastewater before and after treatment

Parameters	Unit	Untreated Bakery wastewater	Treated bakery wastewater
Alkalinity	mg/l	Nil	150
Acidity	mg/l	1500	150
Hardness	mg/l	200	24
Chloride	mg/l	1420	184
COD	mg/l	266	196
BOD	mg/l	44.43	15.1
DO	mg/l	22.5	55.1
Total suspended solid	mg/l	9500	1100
Total dissolved solid	mg/l	2350	700
Total solid	mg/l	11850	1800
Conductivity	mg/l	1010	280
Temperature	°C	28.0	29.0
Lead	mg/l	0.0107	Nil
Copper	mg/l	18.481	0.9238
Iron	mg/l	0.3789	0.01047
pH	mg/l	5.6	7.0
Phosphorus	mg/l	0.3484	0.01047
Magnesium/calcium	mg/l	100.928	20.1856
Sulphate	mg/l	418.46	92.6
Turbidity	mg/l	563.3	5.6
Nitrate	mg/l	6.2	Nil

The kinetic results of total suspended solid removal from bakery effluent at various pH and coagulant concentration is presented on table 2. The parameters contained on the tables were determined from the plot of first order and second order equation. The value of  $R^2$  being greater than 0.900 for almost all the conditions confirmed the theory of perikinetic as the controlling mechanism of coagulation under study (Menkiti, 2000). First and second order equations were tested and it was observed that the data fitted well to second order for all the pH values studied at lower coagulant concentration of 400mg/l, though higher  $R^2$  was recorded at 600mg/l but for pH of 6 only. The significance of this is that the optimum pH is 6 and it is fitted well to second order. For the cases where the kinetics followed first order, it can be attributed to a shift from theoretical expectation but in line with empirical evidence (WST, 2005).

High values of the collision factor for Brownian Transport ( $B_{BR}$ ) which directly relates to collision efficiency results in higher kinetic energy to overcome the zeta potential. The implication is that the double

layer is either reduced or the colloids destabilized to actualize low  $\tau_{1/2}$  in favour of coagulation rate (Menkiti et al, 2010). The result shows that high value of  $\tau_{1/2}$  corresponds to low  $K$  and  $B_{BR}$ , an indication of repulsion in the system.

The discrepancies recorded in the order of the reactions,  $K$ ,  $N_0$ , and  $-r$  can be explained by the unattainable assumption that mixing of particles and coagulants throughout the dispersion is 100% efficient before aggregation occurs. The effects of these limitations will be local increase in particle ratios during the mixing phase given uneven dispersion of particles/coagulants complexes. These complexes make it impossible for all to be second order (Yates, et al, 2001).

The values of  $K$  obtained from the linearized equations were used to formulate the rate equation for the total suspended solid removal from the bakery wastewater. The highest value of  $K$  was obtained at pH 6.

Table 2. Kinetic data for 1<sup>st</sup> order

Parameter	pH <sub>2</sub>	pH <sub>4</sub>	pH <sub>6</sub>
<b>400mg/l</b>			
$R^2$	0.917	0.8931	0.8575
$K$	0.0146	0.0203	0.0259
$\beta_{BR}$	0.0292	0.0406	0.0518
$\tau_{1/2(sec)}$	47.5	34.1	26.8
$N_0$	165.5	154.18	98.2
$-r$	0.0146C	0.0203C	0.0259C
<b>600mg/l</b>			
$R^2$	0.9211	0.9533	0.9575
$K$	0.0785	0.0229	0.0489
$\beta_{BR}$	0.037	0.0458	0.0978
$\tau_{1/2(sec)}$	37.5	30.2	14.2
$N_0$	155.6	137.2	84.5
$-r$	0.0785C	0.0229C	0.0489C
<b>800mg/l</b>			
$R^2$	0.9437	0.9734	0.9805
$K$	0.0244	0.0252	0.0401
$\beta_{BR}$	0.0488	0.0504	0.0802
$\tau_{1/2(sec)}$	28.4	27.5	17.3
$N_0$	157.5	127.8	82.9
$-r$	0.0244C	0.0252C	0.0401C

4.3. Kinetic data for 2<sup>nd</sup> order

Parameter	pH <sub>2</sub>	pH <sub>4</sub>	pH <sub>6</sub>
<b>400mg/l</b>			
R <sup>2</sup>	0.9343	0.9135	0.9843
K	0.0002	0.0002	0.0005
β <sub>BR</sub>	0.0004	0.0004	0.0010
τ <sub>1/2(sec)</sub>	50	58.0	29.2
No	200	172.4	137.0
-r	0.0002C <sup>2</sup>	0.0002C <sup>2</sup>	0.0005C <sup>2</sup>
<b>600mg/l</b>			
R <sup>2</sup>	0.8494	0.9825	0.9944
K	0.0002	0.0003	0.0019
β <sub>BR</sub>	0.0006	0.0006	0.0038
τ <sub>1/2(sec)</sub>	49	43.3	0.4
No	204.1	153.8	238.1
-r	0.0002C <sup>2</sup>	0.0003C <sup>2</sup>	0.00019C <sup>2</sup>
<b>800mg/l</b>			
R <sup>2</sup>	0.8939	0.9041	0.9682
K	0.0004	0.0005	0.0017
β <sub>BR</sub>	0.0008	0.0010	0.0034
τ <sub>1/2(sec)</sub>	17.5	16.4	5.06
No	285.7	243.9	232.6
-r	0.0004C <sup>2</sup>	0.0005C <sup>2</sup>	0.00017C <sup>2</sup>

**Conclusion**

Kinetic data fitted well to second order model due to higher correlation coefficient recorded when compared to first order. The discrepancies recorded in the order of the reaction can be explained by the unattainable assumption that mixing of particles and coagulants throughout the dispersion is 100% efficient before aggregation occurs. It can be concluded that the theory of perikinetis is the controlling mechanism of the coagulation owing to the high correlation coefficients (>0.9) recorded at different pH.

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