Coag-flocculation kinetics of phosphorus containing effluent using *Corchorus Olitorious* seed

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**Abstract:** Corchorus olitorius, (CR) an environmentally friendly biomass was used as a coagulant in this work for the treatment of phosphorus containing effluent using Nephelometric method. The research evaluates the coag-flocculation efficiency of CR coagulant as well as kinetic parameter response of CR to varying pH and dosage of the waste water effluent. Coag-flocculation reaction order α, coag-flocculation rate constant K, and coagulation period were determined. The maximum coag-flocculation performance is recorded at rate constant, K of $5 \times 10^{-5}$ l/mg.mm, dosage of 500mg/l, pH of 6 and coagulation period of 5.4 mins. While the coag-flocculation efficiency obtained $E > 70\%$ at the condition of the experiment.

**Keywords:** Coagulation, *Corchorus Olitorious*, Kinetics, Phosphorus

1. Introduction

Coagulation is the destabilization of colloids by neutralizing the forces that keep them apart. Cationic coagulants provide positive electric charges to reduce the negative charge (Zeta potential) of the colloids. As a result, the particles collide to form larger particles (flocs). Rapid mixing is required to disperse the coagulant throughout the liquid. Care must be taken not to overdose the coagulants as this can cause a complete charge reversal and re-stabilize the colloid complex. Flocculation is the action of polymers to form bridge between the flocs, and bind the particles into large agglomerate or clumps [1]. Many coagulating agents are used in processes for treating water, such as inorganic coagulants (salts of aluminum and iron), synthetic and natural organic polymers [2]. Aluminum sulphate is widely used worldwide as a coagulant, but recently its use has been questioned due to evidence that Alzheimer’s disease may be as a result of excessive intake of alum [3, 4]. Moreover, aluminum is not biodegradable, and can cause disposal problems and require treatment of the generated sludge [5]. The search for an environmentally friendly and inexpensive coagulant as a viable alternative to conventional coagulants has therefore become an important challenge in the water treatment process. Some of these natural coagulants and flocculants that have been investigated by other researchers include: chitosan, aqueous extracts of the seed of *Moringa Oleifera* and extracts of Okra seed [6, 7, 8]. This study proposes the use of *Corchorus Olitorious* seed as a viable alternative for conventional coagulants in the treatment of industrial waste water.

*Corchorus Olitorious* called “ayoyo” in Hausa and “ewedu” in Yoruba is a popular green vegetable plant [9]. The vegetable is also known by several names in different countries including Jews mallow or Jute mallow in English, Egyptian spinach, and Bush okra in South Africa [10].

Aqueous extracts of the seeds of *Corchorus Olitorious* were reported to possess peripheral and central anti-nociceptive, anti-inflammatory and anti-pyretic activities [11]. The seeds are used as a purgative and have been found to contain cardenolide glycosides on preliminary analysis while the methanol extracts of the seeds have been reported to possess a broad spectrum of antibacterial activity [12].

Although much work has not been reported on coagulating application of CR to phosphorus removal, CR is available in large quantities in our local communities in Nigeria.

2. Materials and Methods
The turbid effluent was collected from the Federal Superphosphate fertilizer company, Kaduna, Nigeria. A 20-litre polyethylene bottle was thoroughly cleaned and rinsed with effluent sample before the final sample collection, after which the bottle was tightly closed and taken to the laboratory for experimental work. 

The sample of the CR seed was sourced from a local market in Ibadan, Oyo State. The shell or covering testa of the seeds was removed and winnowed in order to separate the shell from the cotyledon of the seeds. The cotyledons were then dried at 100°C for 2hrs in a hot air oven. The dried seeds were then ground and processed into a coagulant using standard method.

The coagulant and the effluent samples were characterized and the results of their characterization are presented in Table 3.2 and 3.1 respectively.

The percentage of turbidity removal was calculated using equation (1)

\[
\text{Removal efficiency: } \quad E(\%) = \left( \frac{C_0 - C_1}{C_0} \right) \times 100
\]  

where \( C_0 \) and \( C_1 \) are the initial and residual concentration of the waste water effluent respectively, mg/l.

2.1. Theoretical Principles

The rate of flocculation is a function of the particles (count) concentration \( C \), and the intensity of Brownian motion characterized by the diffusivity \( D \). Consideration of the particle diffusion flux in a mono dispersed system toward a particle of radius ‘a’ (chosen as the central one) on the basis of Fick’s equation yields an expression for the rate of decrease in the particle number.

\[
\frac{dC}{dt} = -KC^\alpha
\]  

Integrating Eq (1) gives

\[
\ln\left(-\frac{dC}{dt}\right) = \ln K + \alpha \ln C
\]  

From which \( K \) and \( \alpha \) can be determined from a plot of \( \ln(-\frac{dC}{dt}) \) against \( \ln C \).

In eq. (2), \( K \) is coagulation rate constant/collision frequency \( \alpha \) is the order of coagulation reaction \( C \) is the concentration of the particles (TSS), mg/l

It has been shown by some researchers that for the conditions described above [16]

\[
K = 8\pi R'D
\]  

Where \( R' = 2a \)

From Einstein’s equation [15, 17]

\[
D = K_B \left( \frac{T}{\mu} \right)
\]  

Where \( B \) is the friction factor, \( T \) is the absolute temperature (°K) and \( K_B \) is the Boltzmann constant (Molar gas constant per particle).

For the simplest case of a smooth spherical particle of radius ‘a’ immersed in a fluid of viscosity \( \mu \), \( B \) is given by Stoke’s relation [15]

\[
B = 6\pi\mu a
\]  

Putting Eq(6) into Eq(5) gives

\[
D = K_B T / 6\pi\mu
\]  

But \( R' = 2a \)

Therefore

\[
D = 2K_B T / 6\pi\mu R' = \frac{K_B T}{3\pi\mu R'}
\]  

Putting Eq(8) into Eq(4) gives

\[
K = 8\pi R' \left( \frac{K_B T}{3\pi\mu R'} \right) = \frac{8}{3} \left( \frac{K_B T}{\mu} \right)
\]  

Putting Eq(9) into Eq(2) when \( \alpha = 2 \) yields

\[
\frac{dC}{dt} = -\frac{8}{3} C^2 \left( \frac{K_B T}{\mu} \right)
\]  

Applying the method of separable variable and integrating Eq (2) within the following limits:

At \( t = 0, C = C_0 \) at \( t = t, C = C \), yields

\[
\frac{-dC}{dc^2} = K dt
\]  

Integrating Eq (11) above yields

\[
C = \frac{1}{C_0} + K t
\]  

Multiply both sides of Eq (12) by \( C_0 \) to give

\[
\frac{C_0}{C} = 1 + C_0Kt
\]  

Making ‘C’ the subject of the formular, yields

\[
C = \frac{C_0}{1 + C_0Kt} = \frac{C_0}{1 + \left( \frac{t}{C_0K} \right)}
\]  

Let

\[
\left( \frac{C_0K}{C} \right) = \tau
\]  

Therefore Eq(14) becomes
\[ C = \frac{C_0}{1 + \frac{1}{\tau}} = \tau \]  
(16)

When \( t = \tau \) then Eq(16) becomes

\[ C = \frac{C_0}{1 + \frac{C_0}{2}} \]  
(17)

Thus at \( t = \tau, C = \frac{C_0}{2} \). This quantity is called the coagulation period, which is the time during which the initial concentration of particles is halved

### 3. Results and Discussion

Table 3.2 shows the characterization results of the CR coagulant. In all the analyzed parameters (moisture content, ash content, lipid content, crude protein, carbohydrate and crude fibre) protein happens to be the active agent responsible for the coagulation in these substrates [18]. The percentage protein content of CR is 31.25%. Wastewater effluent before and after treatment was characterized and the results obtained are presented in Table 3.1. The result of the wastewater sample indicates that some heavy metals such as iron, lead and copper which are 2.75 mg/l, 0.9 mg/l and 12.00 mg/l before treatment respectively were totally removed during the coagulation process. Between 85% and 91% of magnesium, sulphates, chlorides and phosphates were also removed during the process. Figs. 1 to 5 show the effect of coagulant dosage on turbidity removal at various pH. It can be observed from the figures that the removal of turbidity increases with increase in coagulant dosage. Fig 1-3 show the removal efficiency as a function of time for various CR coagulant dosages at pH of 2.4 and 6 respectively. It is observed from the figures that the rate of removal increases very fast within the first ten minutes for a particular dosage particularly as from pH of 4, after which the rate of increase begins to reduce. The sharp increase in removal efficiency at the early stages of coagulation is a product of either floc mechanism or combination of entrapment bridging mechanism[18]. The decrease, thereafter in the rate of removal efficiency was due to the fact that as the reaction proceeds the amount of the suspended particles available for coagulation decreases.

The figures also show that the removal efficiency of CR coagulant increases with dosage. However, in fig. 4-5, it was observed that as pH was increased further from 6 to 10, the rate of removal began to decrease. It could be deduced from the observation that the optimum turbidity removal of CR coagulant occurred at the optimum pH of 6 and 400 mg/l.

The values of coag-flocculation kinetic parameters at various dosages and pH are presented in tables 1-5. The \( R^2 \) and coagulation rate constant K contained in the various tables were determined from the linear kinetic plots \( 1/C_t \) versus time as shown in figures 6-10. The values of \( R^2 \), being greater than 0.9000 with the exception of few are satisfactory and this confirms the theory of perikinetics as the controlling mechanism of coag-flocculation under study[18] It is observed that high value of K corresponds to low value of a relationship that establishes a link among collision efficiency \( \varepsilon \), coagulation period \( \tau \) and coagulation rate constant K. This is supported by the highest value of K = 5x10^{-5}/mg.min, and the lowest value of \( \varepsilon \), \( \tau \) and K indicate repulsion in the system.

### Table 3.1. Characterization result of wastewater effluent before and after treatment.

| Parameter                        | S.I. Unit | Before coagulation | After coagulation |
|----------------------------------|-----------|--------------------|-------------------|
| Colour                           | Hazen     | 250                | 18.50             |
| pH                               |           | 8.0                | 10                |
| Conductivity                     | µ/ cm²    | 1.88 x 10^4        | 2.1 x 10^4        |
| Turbidity                        | NTU       | Not clear          | Mild clear        |
| Total solid                      | mg/l      | 6530               | 471.8             |
| Alkalinity                       | mg/l      | 485                | 505               |
| Manganese                        | mg/l      | 410.7              | 3.35              |
| Potassium                        | mg/l      | 420                | 1.28              |
| Chloride                         | mg/l      | 996.43             | 150               |
| Nitrogen                         | %         | 27.65              | 1.93              |
| Chemical oxygen demand           | mg/l      | 289.77             | 71.77             |
| Dissolved Oxygen                 | mg/l      | 28.52              | 76.50             |
| Biochemical oxygen demand        | mg/l      | 318.29             | 48.27             |
| Sulphate                         | mg/l      | 185                | 18.6              |
| Nitrate                          | mg/l      | 0.1                | N.D               |
| Copper                           | mg/l      | 12                 | N.D               |
| Phosphorus                       | mg/l      | 378.34             | 35.67             |
| Total Hardness                   | mg/l      | 80                 | 50                |
| Lead                             | mg/l      | 0.9                | N.D               |
| Magnesium                        | mg/l      | 19.46              | 12.16             |
| Iron                             | mg/l      | 2.75               | N.D               |

N.D: Not detected

### Table 3.2. Characterization results of coagulants.

| Parameter                | CR   |
|--------------------------|------|
| Moisture content (%)     | 10.00|
| Ash content (%)          | 14.50|
| Lipid content (%)        | 19.63|
| Crude protein (%)        | 31.25|
| Carbohydrate (%)         | 35.05|
| Crude fibre (%)          | 20.00|
### Table 1. Coagulation Kinetic Parameters of CR at varying pH and 100mg/l dosage.

| Parameters | pH = 2 | pH = 4 | pH = 6 | pH = 8 | pH = 10 |
|------------|--------|--------|--------|--------|--------|
| α          | 2.0000 | 2.0000 | 2.0000 | 2.0000 | 2.0000 |
| R²         | 0.9650 | 0.8330 | 0.9610 | 0.9860 | 0.9550 |
| K (l/mg.min) | 1x10⁻⁵ | 3x10⁻⁵ | 4x10⁻⁵ | 3x10⁻⁵ | 3x10⁻⁵ |
| βₛᵤ(l/mg.min) | 2.0 x10⁻⁵ | 6.0 x10⁻⁵ | 8.0 x10⁻⁵ | 6.0 x10⁻⁵ | 6.0 x10⁻⁵ |
| εₛ (l/mg) | 1.8x10⁻² | 5.4x10⁻¹² | 7.3 x10⁻¹² | 7.3 x10⁻¹² | 5.4 x10⁻¹² |
| τ(min)     | 26.8000 | 9.0000 | 6.7000 | 9.0000 | 9.0000 |

### Table 2. Coagulation Kinetic Parameters of CR at varying pH and 200mg/l dosage.

| Parameters | pH = 2 | pH = 4 | pH = 6 | pH = 8 | pH = 10 |
|------------|--------|--------|--------|--------|--------|
| α          | 2.0000 | 2.0000 | 2.0000 | 2.0000 | 2.0000 |
| R²         | 0.9140 | 0.7940 | 0.9610 | 0.9770 | 0.9530 |
| K (l/mg.min) | 1x10⁻⁵ | 3x10⁻⁵ | 4x10⁻⁵ | 4x10⁻⁵ | 3x10⁻⁵ |
| βₛᵤ(l/mg.min) | 2.0 x10⁻⁵ | 6.0 x10⁻⁵ | 8.0 x10⁻⁵ | 8.0 x10⁻⁵ | 6.0 x10⁻⁵ |
| εₛ (l/mg) | 1.8x10⁻¹² | 5.4x10⁻¹² | 7.3 x10⁻¹² | 7.3 x10⁻¹² | 5.4 x10⁻¹² |
| τ(min)     | 26.8000 | 9.0000 | 6.7000 | 6.7000 | 9.0000 |

### Table 3. Coagulation Kinetic Parameters of CR at varying pH and 300mg/l dosage.

| Parameters | pH = 2 | pH = 4 | pH = 6 | pH = 8 | pH = 10 |
|------------|--------|--------|--------|--------|--------|
| α          | 2.0000 | 2.0000 | 2.0000 | 2.0000 | 2.0000 |
| R²         | 0.9230 | 0.9730 | 0.9870 | 0.9870 | 0.9700 |
| K (l/mg.min) | 1x10⁻¹⁵ | 4x10⁻⁵ | 4x10⁻⁵ | 4x10⁻⁵ | 4x10⁻⁵ |
| βₛᵤ(l/mg.min) | 2.0 x10⁻⁵ | 8.0 x10⁻⁵ | 8.0 x10⁻⁵ | 8.0 x10⁻⁵ | 8.0 x10⁻⁵ |
| εₛ (l/mg) | 1.8x10⁻¹² | 7.3 x10⁻¹² | 7.3 x10⁻² | 7.3 x10⁻² | 7.3 x10⁻² |
| τ(min)     | 26.8000 | 6.7000 | 6.7000 | 6.7000 | 6.7000 |

### Table 4. Coagulation Kinetic Parameters of CR at varying pH and 400mg/l dosage.

| Parameters | pH = 2 | pH = 4 | pH = 6 | pH = 8 | pH = 10 |
|------------|--------|--------|--------|--------|--------|
| α          | 2.0000 | 2.0000 | 2.0000 | 2.0000 | 2.0000 |
| R²         | 0.9120 | 0.9170 | 0.9760 | 0.9760 | 0.9390 |
| K (l/mg.min) | 1x10⁻¹⁵ | 4x10⁻⁵ | 4x10⁻⁵ | 4x10⁻⁵ | 4x10⁻⁵ |
| βₛᵤ(l/mg.min) | 2.0 x10⁻⁵ | 8.0 x10⁻⁵ | 8.0 x10⁻⁵ | 8.0 x10⁻⁵ | 8.0 x10⁻⁵ |
| εₛ (l/mg) | 1.8x10⁻¹² | 7.3 x10⁻¹² | 7.3 x10⁻² | 7.3 x10⁻² | 7.3 x10⁻² |
| τ(min)     | 26.8000 | 6.7000 | 6.7000 | 6.7000 | 6.7000 |

### Table 5. Coagulation Kinetic Parameters of CR at varying pH and 500mg/l dosage.

| Parameters | pH = 2 | pH = 4 | pH = 6 | pH = 8 | pH = 10 |
|------------|--------|--------|--------|--------|--------|
| α          | 2.0000 | 2.0000 | 2.0000 | 2.0000 | 2.0000 |
| R²         | 0.9750 | 0.9740 | 0.9940 | 0.9970 | 0.9530 |
| K (l/mg.min) | 1x10⁻¹⁵ | 3x10⁻⁵ | 5x10⁻⁵ | 4x10⁻⁵ | 4x10⁻⁵ |
| βₛᵤ(l/mg.min) | 2.0 x10⁻⁵ | 1.00 x10⁻⁴ | 8.0 x10⁻⁴ | 8.0 x10⁻⁴ | 8.0 x10⁻⁴ |
| εₛ (l/mg) | 1.8x10⁻¹² | 9.1 x10⁻¹² | 7.3 x10⁻¹⁵ | 7.3 x10⁻¹⁵ | 7.3 x10⁻¹⁵ |
| τ(min)     | 26.8000 | 7.4000 | 5.4000 | 6.7000 | 6.7000 |

Fig. 1. Coagulation efficiency profile for varying CR dosage at pH=2.

Fig. 2. Coagulation efficiency profile for varying CR dosage at pH=4.
Fig. 3. Coagulation efficiency profile for varying CR dosage at pH=6.

Fig. 4. Coagulation efficiency profile for varying CR dosage at pH=8.

Fig. 5. Coagulation efficiency profile for varying CR dosage at pH=10.

Fig. 6. Kinetic plot of $1/c$ versus time for varying CR dosage at pH=2.

Fig. 7. Kinetic plot of $1/c$ versus time for varying CR dosage at pH=4.

Fig. 8. Kinetic plot of $1/c$ versus time for varying CR dosage at pH=6.
4. Conclusion

The obtained kinetic results of low coagulation period, high collision efficiency and high coagulation rate constant are satisfactory. The high values of R² confirm the theory of perikinetics as the controlling mechanism of coag-flocculation under study. The removal efficiency E(%) > 70 recorded at the optimum pH of 6 and dosage of 500mg/l, its biodegradable and non-toxic nature present the potential of CR as a source of organic derived coagulant applicable in large scale water treatment.

Nomenclature

- $\beta_{BR}$: Collision factor for Brownian transport
- $\epsilon_p$: Collision efficiency
- $\tau$: Coagulation period /Half life
- $R^2$: Coefficient of Determination
- $\alpha$: Coag-flocculation reaction order
- CR: Corchorus olitorius
- $K$: Coagulation rate constant
- C: Concentration of particles

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