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Scientific Research

Coag-Flocculation Kinetics of *Mucuna sloanei* Seed for Phosphorus Removal from Waste Water

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ABSTRACT

Mucuna sloanei (MS) an environmentally friendly biomass was used as a coagulant for treatment of phosphorus containing waste water. The study evaluates the coag-flocculation efficiency of MS and its functional kinetic parameter response to varying pH and dosage of the waste water effluent. Coag-flocculation reaction order α, coag-flocculation rate constant K, and coagulation period $\tau_{1/2}$ were determined. The maximum coag-flocculation performance (97.4%) is recorded at rate constant, K of 1.24×10^{-4} l/mg·min, dosage of 400 mg/l, pH of 8 and coagulation period $\tau_{1/2}$ of 0.100 min while the minimum (61%) is recorded at K of 3×10^{-5} l/gm·min, dosage 100 mg/l, pH of 2 and $\tau_{1/2}$ of 8.900 mins. The results confirm that MS coagulant is an effective coagulant obeying the theory of fast coagulation in the conditions of the experiments.

Keywords: Coag-Flocculation; *Mucuna slonaei*; Phosphorus

1. Introduction

Coagulation is an established process for transforming small particles into larger aggregates (flocs) and for adsorbing dissolved organic matter onto particulate aggregates so that these impurities can be removed in subsequent sedimentation and filtration stages [1].

Coag-flocculation of waste water may be accomplished with any of the common water coagulants including lime, iron and aluminum salts and synthetic polymers.

However, the search for a better alternative to conventional coagulants has become an important challenge in the water treatment process with the aim of minimizing the detrimental effects associated with the use of such coagulants. The use of coagulants of biological origin has become imperative. Some of the coagulants and flocculants of biological origin that have been used include Chitosan [2], tannins [3], aqueous extract of the seed of Moringa Oleifera [4], extract of Okra, nirmali seed [5] and *Mucuna sloanei* which is the subject of the study.

Mucuna sloanei are wild plants found in some parts of the semi and sub-Saharan and tropical zones of Africa. The seeds are edible and are used for the thickening of soups in some parts of Nigeria. They possess unique characteristic behavior in hot water displaying different degrees of the viscoelastic properties [6]. The seeds are toasted for easy removal of the hull or par-boiled and then ground to obtain a fine powder or paste, when wet milled. The powder may be used as recipes of some food items and in beverages [7]. Consumption of Mucuna as food has also been reported from Mozambique and Malawi [8].

Mucuna gum is a galactomannan consisting of D-galactose and D-mannose as the main sugars [9]. The endosperm was found to constitute 67.15% of the whole seed with about 32.6% as gum. It may also be a rich source of crude protein [10].

The chemical and nutritional evaluation of the raw seed of *M. sloanei* suggested that this could be a rich source of crude protein after cooking. The galactoxyloglucan isolated from the cotyledon consists of Glc:Xyl:Gal in a molar ratio of 1:8:1.7:1.0 and a molar mass of 1.6×10^6 g·mol^{-1} [11]. This work, however, attempts to

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explore and generate interest in the utilization of *Mucuna sloanei* (MS) seed as a coagulant. Coag-flocculation performance and kinetic of MS under various pH of the industrial waste effluent are also investigated.

2. Materials and Methods

The sample of *Mucuna sloanei* seed was sourced from a village market, in Ihiala, Anambra State. The seeds were dried, dehulled and ground into fine power after which it was sieved through 0.2 mm sieve. The fraction with particle size less than 0.2 mm was then processed into a coagulant using standard method [12].

The jar test was conducted based on standard Bench Schale Nehelometric method (single angle procedure) for the examination of water and waste water [13,14] using model WZS-185MC Turbidimeter, Gulenhamp magnetic stirrer and Delta 320 pH meter.

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

$$\text{Removal efficiency } E(\%) = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

where C_0 and C are the initial and residual concentration of the waste water effluent respectively.

Theoretical Principle

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.

$$\frac{\mathrm{d}c}{\mathrm{d}t} = -KC^{\alpha} \quad (2)$$

Integrating Equation (1) gives

$$\ln\left(-\frac{\mathrm{d}c}{\mathrm{d}t}\right) = \ln K + \alpha \ln C \quad (3)$$

From which K and α can be determined from a plot of $\ln\left(\frac{\mathrm{d}c}{\mathrm{d}t}\right)$ against $\ln C$.

In Equation (1), K is coagulation rate constant/collision frequency

α: is the order of coagulation reaction

C: is the concentration of the particles (TSS)

It has been shown by some researchers that for the conditions described above [15].

$$K = 8\pi R'D \quad (4)$$

where $R' = 2a$

From Einstein's equation [16]

$$D = K_B(T/B) \quad (5)$$

where B is the friction factor, T is the absolute temperature (^0K) and K_B is the Boltzman constant (Molar gas constant per particle).

For the simplest case of a smooth spherical particle of radius "a" immersed in a fluid of viscosity μ, B is given by Stoke's relation.

$$B = 6\pi\mu a \quad (6)$$

Putting Equation (6) into Equation (5) gives

$$D = \frac{K_B T}{6\pi a \mu} \quad (7)$$

But $R' = 2a$

$$\text{Therefore } D = \frac{2K_B T}{6\pi\mu R'} = \frac{K_B T}{3\pi\mu R'} \quad (8)$$

Putting Equation (8) into Equation (4) gives

$$K = 8\pi R'\left(\frac{K_B T}{3\pi R'\mu}\right) = \frac{8}{3}\left(\frac{K_B T}{\mu}\right) \quad (9)$$

Putting Equation (9) into Equation (2) when $\alpha = 2$ yields

$$\frac{\mathrm{d}c}{\mathrm{d}t} = -\frac{8}{3}C^2\left(\frac{K_B T}{\mu}\right) \quad (10)$$

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

At $t = 0$, $C = c_0$ at $t = t$, $C = C$, yields

$$-\frac{\mathrm{d}c}{\mathrm{d}c^2} = K\mathrm{d}t \quad (11)$$

Integrating Equation (11) above yields

$$\frac{1}{c} = \frac{1}{c_0} + Kt \quad (12)$$

Multiply both sides of Equation (12) by C_0 to give

$$\frac{C_0}{C} = 1 + C_0 Kt \quad (13)$$

Making "C" the subject of the formular, yields

$$C = \frac{C_0}{1 + C_0 Kt} = \frac{C_0}{\left[1 + \frac{t}{(1/C_0 K)}\right]} \quad (14)$$

$$\text{Let } (1/C_0 K) = \tau \quad (15)$$

Therefore Equation (14) becomes

$$C = \frac{C_0}{1 + \frac{t}{\tau}} = \tau \quad (16)$$

When $t = \tau$ then Equation (16) becomes

$$C = \frac{C_0}{1+1} = \frac{C_0}{2} \quad (17)$$

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. For Brownian coagulation of mono dispersed particles at early stage ($t \leq 30$ minutes), the time evolution of the cluster-size distribution for colloidal particle is usually described thus:

$$\frac{\mathrm{d}C_n}{\mathrm{d}t} = \frac{1}{2}\sum_{1+j=n}\beta(i,j)c_i c_j - \sum_{i=1}^{\infty}\beta(i,n)c_i c_n \quad (18)$$

where $\frac{\mathrm{d}C_n}{\mathrm{d}t}$ is the rate of change of concentration of particle of size n (concentration/time).

β is a function of the coag-flocculation transport mechanism. The appropriate value of β for Brownian transport is given by [15].

$$\beta_{BR} = \frac{8}{3}\varepsilon_P \frac{K_B T}{\mu} \quad (19)$$

where K_B is Boltzman's constant (J/K)

T is Absolute temperature (K)

For Brownian aggregation at early stages ($t \leq 30$ minutes) Equation (18) can be solved exactly, resulting in the expression [16].

$$\frac{C_{n(t)}}{C_0} = \frac{\left[\frac{t}{2}\left(\frac{1}{KC_0}\right)\right]^{n-1}}{\left[1+\frac{t}{2\left(\frac{1}{KC_0}\right)}\right]^{n+1}} \quad (20)$$

Recall from Equation (15) $\left(\frac{1}{C_0 K}\right) = \tau$, Putting Equation (15) in Equation (20)

We have $$\frac{C_{n(t)}}{C_0} = \frac{\left(\frac{t}{2\tau}\right)^{n-1}}{\left(1+\frac{t}{2\tau}\right)^{n+1}} \quad (21)$$

Let $2\tau = \tau'$ and put in Equation (21)

$$\frac{C_{n(t)}}{C_0} = \frac{(t/\tau')^{n-1}}{(1+t/\tau')^{n+1}} \quad (22)$$

Equation (22) gives general expression for particle of n-th order. Hence for primary particles ($n = 1$)

$$C_1 = C_0\left[\frac{1}{(1+t/\tau')^2}\right] \quad (23)$$

For twins ($n = 2$)

$$C_2 = C_0\left[\frac{(t/\tau')}{(1+t/\tau')^3}\right] \quad (24)$$

For triplets ($n = 3$)

$$C_3 = C_0\left[\frac{(t/\tau')^2}{(1+t/\tau')^4}\right] \quad (25)$$

The process of aggregation is a complicated phenomenon. Analysis shows that Equation (16) holds for the overall concentration of all particles, which monotonically decreases in time like the number of primary particles:

$$\sum C_i = \frac{C_0}{1+t/\tau'} \quad (26)$$

Linearising Equation (26) gives

$$\frac{1}{\sum C_i} = \frac{1}{C_0} + \frac{1}{\tau' C_0}t \quad (27)$$

where a plot of $\frac{1}{\sum C_i}$ versus t gives

Slope = $\frac{1}{\tau' C_0}$, Intercept = $\frac{1}{C_0}$

Now that τ' can be obtained from slope of Equation (27) while the theoretical quantities τ' is found with the aid of Equation (15) [16].

$$\tau = \frac{1}{C_0 K} = \frac{3\mu}{8K_B T C_0} \quad (28)$$

As $C_0 \to \frac{C_0}{2}, \tau \to t_{1/2}$

Therefore, $$t_{1/2} = \frac{3\mu}{8K_B T(0.5C_0)} = \frac{3\mu}{4K_B T C_0} \quad (29)$$

where $t_{1/2}$ is coagulation period/half life.

In the work of [16] it was shown that the coagulation rate constant could be determined by monitoring the changes in the turbidity of the coagulation liquid with time.

The particle concentration during early stages of coagulation can be determined directly, by visual particle counting or indirectly from turbidity measurement [17].

3. Results and Discussion

Figures 1-5 show the effect of coagulant dosage on the turbidity removal at various pH. It can be seen from the figure that turbidity removal increases with increase in coagulant dosage. **Figures 1-4** show the removal efficiency as function of time for various MS coagulant dosages at pH of 2, 4, 6 and 8 respectively. It can be seen from the figure that the removal efficiency increases very fast within the first ten minutes for a particular dosage after which a decrease in efficiency began to set in. The figures also show that the removal efficiency of MS co-

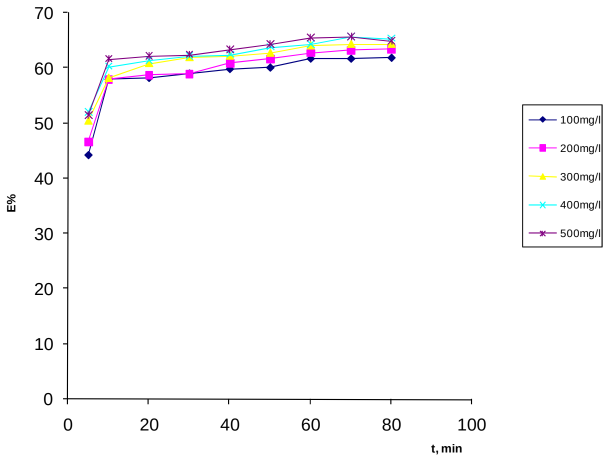

Figure 1. Coagulation efficiency profile for varying MS dosage at pH = 2.

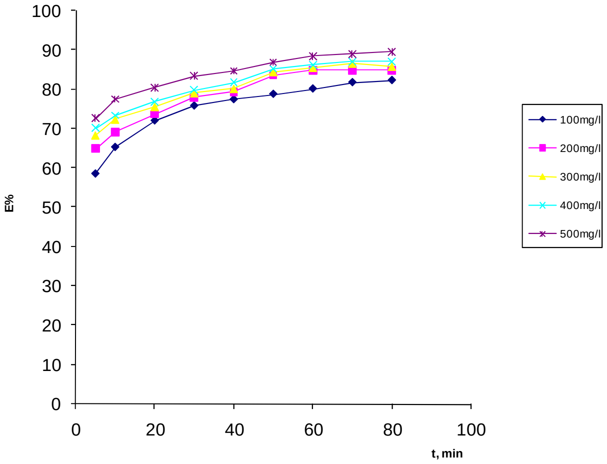

Figure 2. Coagulation efficiency profile for varying MS dosage at pH = 4.

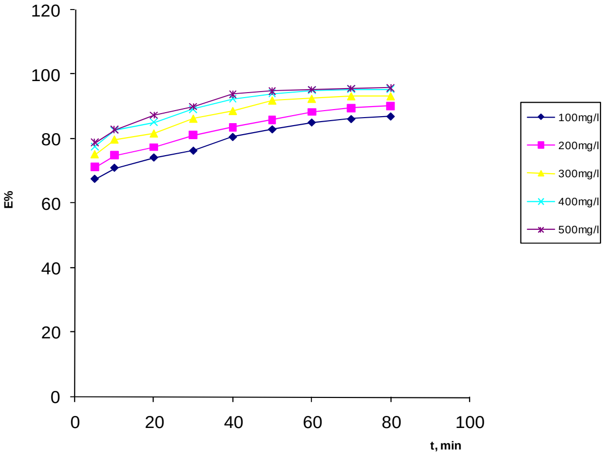

Figure 3. Coagulation efficiency profile for varying MS dosage at pH = 6.

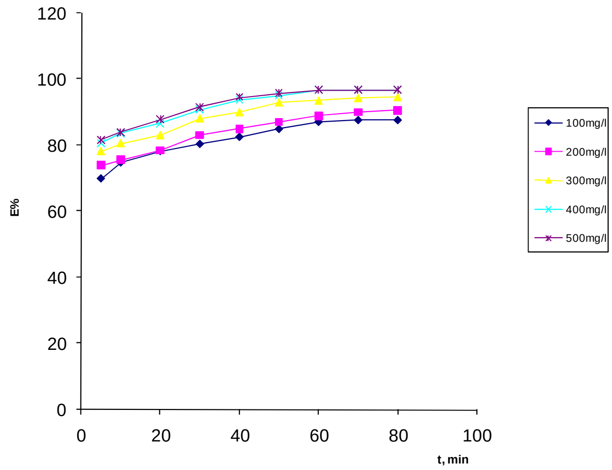

Figure 4. Coagulation efficiency profile for varying MS dosage at pH = 8.

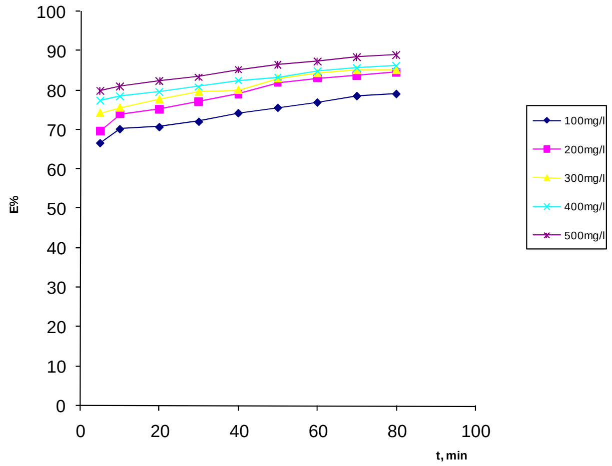

Figure 5. Coagulation efficiency profile for varying varying MS dosage at pH = 10.

agulant increases with dosage. However, in **Figure 5**, it was observed that as pH was increased further to 10, the rate of removal began to decrease. It could be deduced from the above observation that the optimum turbidity removal of MS coagulant occurred at the optimum pH of 8 and 400 mg/l dosage.

The values of coag-flocculation parameters at various dosages and pH are presented in **Tables 1** to **5** above. The R^2 and coag-flocculation rate constant K contained in the various tables were determined from plots $1/c_t$ versus time as shown in **Figures 6** to **10**.

The values of, R^2, being greater than 0.9000 with the exception of the results at pH of 2, are satisfactory and this confirms the theory of perikinetic as the controlling mechanism of coag-flocculation under study [18]. The-highest value of K is recorded for 400 mg/l at pH of 8 while the least value is recorded for K at pH of 2 as presented in **Table 4**. The corresponding value of $\tau_{1/2}$ is 0.100 min at pH of 8 and 400 mg/l dosage. For pH of 2, and 400 mg/l dosage, $\tau_{1/2}$ is 8.900 mins. This indicates that the best coagulation performance could be achieved

Table 1. Coagulation kinetic parameters of MS at varying pH and 100 mg/l dosage.

Parameters	pH = 2	pH = 4	pH = 6	pH = 8	pH = 10
γ	1.0×10^{-3}	1.0×10^{-3}	1.0×10^{-3}	1.0×10^{-3}	1.0×10^{-3}
α	2.0000	2.0000	2.0000	2.0000	2.0000
R^2	0.5870	0.9540	0.9794	0.9840	0.9713
K (l/mg·min)	3×10^{-5}	1.2×10^{-4}	1.8×10^{-4}	2.0×10^{-4}	6×10^{-5}
β_{BR} (l/mg·min)	6×10^{-5}	2.4×10^{-4}	3.6×10^{-4}	4.0×10^{-4}	1.2×10^{-6}
ε_p (l/mg)	5.40×10^{12}	2.18×10^{13}	3.30×10^{13}	3.60×10^{13}	1.10×10^{13}
$\tau_{1/2}$ (min)	8.900	2.200	1.400	1.300	4.400
C_0 (mg/l)	373	373	373	373	373
$(N_p)_0$	8.60×10^{25}	4.45×10^{25}	3.31×10^{25}	2.89×10^{25}	5.18×10^{25}

Table 2. Coagulation kinetic parameters of MS at varying pH and 200 mg/l dosage.

Parameters	pH = 2	pH = 4	pH = 6	pH = 8	pH = 10
γ	1.0×10^{-3}	1.0×10^{-3}	1.0×10^{-3}	1.0×10^{-3}	1.0×10^{-3}
α	2.0000	2.0000	2.0000	2.0000	2.0000
R^2	0.7070	0.9836	0.9749	0.9854	0.9742
K (l/mg·min)	3×10^{-5}	1.8×10^{-4}	2.4×10^{-4}	2.6×10^{-4}	1.2×10^{-4}
β_{BR} (l/mg·min)	6×10^{-5}	3.6×10^{-4}	4.8×10^{-4}	5.2×10^{-4}	2.4×10^{-4}
ε_p (l/mg)	5.4×10^{12}	3.30×10^{13}	4.40×10^{13}	4.70×10^{13}	2.20×10^{13}
$\tau_{1/2}$ (min)	8.900	1.400	1.100	1.000	2.200
C_0 (mg/l)	373	373	373	373	373
$(N_p)_0$	8.37×10^{25}	3.37×10^{25}	2.59×10^{25}	2.47×10^{25}	3.79×10^{25}

Table 3. Coagulation kinetic parameters of MS at varying pH and 300 mg/l dosage.

Parameters	pH = 2	pH = 4	pH = 6	pH = 8	pH = 10
γ	1.0×10^{-3}	1.0×10^{-3}	1.0×10^{-3}	1.0×10^{-3}	1.0×10^{-3}
α	2.0000	2.0000	2.0000	2.0000	2.0000
R^2	0.7420	0.9738	0.9616	0.9610	0.9696
K (l/mg·min)	3×10^{-5}	1.8×10^{-4}	4.7×10^{-4}	5.6×10^{-4}	1.2×10^{-4}
β_{BR} (l/mg·min)	6×10^{-5}	3.6×10^{-4}	9.4×10^{-4}	1.1×10^{-5}	2.4×10^{-4}
ε_p (l/mg)	5.4×10^{12}	3.30×10^{13}	8.54×10^{13}	1.01×10^{14}	2.18×10^{13}
$\tau_{1/2}$ (min)	8.900	1.400	0.500	0.400	2.200
C_0 (mg/l)	373	373	373	373	373
$(N_p)_0$	8.06×10^{25}	3.25×10^{25}	1.68×10^{25}	1.44×10^{25}	3.49×10^{25}

Table 4. Coagulation kinetic parameters of MS at varying pH and 400 mg/l dosage.

Parameters	pH = 2	pH = 4	pH = 6	pH = 8	pH = 10
γ	1.0×10^{-3}	1.0×10^{-3}	1.0×10^{-3}	1.0×10^{-3}	1.0×10^{-3}
α	2.0000	2.0000	2.0000	2.0000	2.0000
R^2	0.6830	0.9844	0.9703	0.9576	0.9850
K (l/mg·min)	3×10^{-5}	1.9×10^{-4}	7.9×10^{-4}	1.24×10^{-4}	1×10^{-4}
β_{BR} (l/mg·min)	6×10^{-5}	3.8×10^{-4}	1.58×10^{-5}	2.48×10^{-5}	2.0×10^{-4}
ε_p (l/mg)	5.4×10^{12}	3.45×10^{13}	1.44×10^{14}	2.25×10^{14}	1.81×10^{13}
$\tau_{1/2}$ (min)	8.900	1.400	0.300	0.100	2.600
C_0 (mg/l)	373	373	373	373	373
$(N_p)_0$	8.00×10^{25}	3.07×10^{25}	1.08×10^{25}	7.22×10^{24}	3.37×10^{25}

Table 5. Coagulation kinetic parameters of MS at varying pH and 500 mg/l dosage.

Parameters	pH = 2	pH = 4	pH = 6	pH = 8	pH = 10
γ	1.0×10^{-3}	1.0×10^{-3}	1.0×10^{-3}	1.0×10^{-3}	1.0×10^{-3}
α	2.0000	2.0000	2.0000	2.0000	2.0000
R^2	0.6830	0.9840	0.9749	0.2764	0.9882
K (l/mg·min)	3×10^{-5}	2.3×10^{-4}	8.9×10^{-4}	4.1×10^{-4}	1.5×10^{-4}
β_{BR} (l/mg·min)	6×10^{-5}	4.6×10^{-4}	17.8×10^{-4}	8.2×10^{-4}	3.0×10^{-4}
ε_p (l/mg)	5.4×10^{12}	4.18×10^{13}	1.61×10^{14}	7.45×10^{13}	2.72×10^{13}
$\tau_{1/2}$ (min)	8.900	1.100	0.300	0.600	1.700
C_0 (mg/l)	373	373	373	373	373
$(N_p)_0$	7.76×10^{25}	2.59×10^{25}	1.02×10^{25}	7.22×10^{24}	2.83×10^{25}

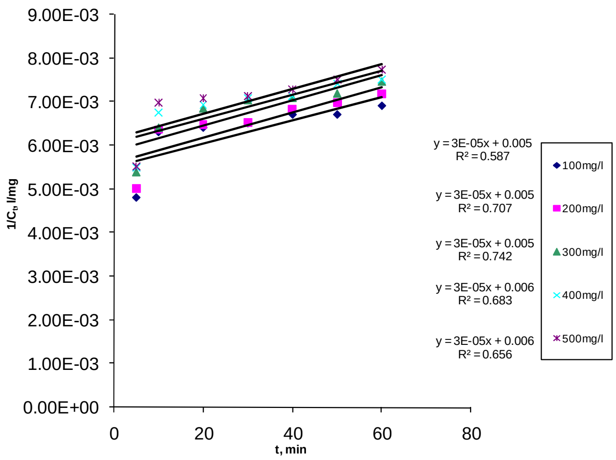

Figure 6. Kinetic plot of 1/C_t versus time for MS dosage at pH = 2.

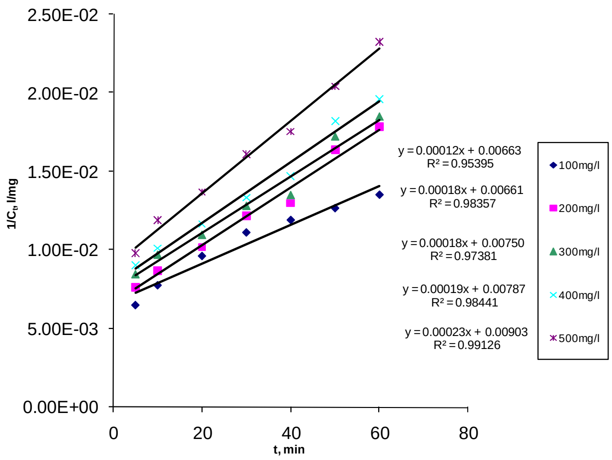

Figure 7. Kinetic plot of 1/C_t versus time for varying MS dosage at pH = 4.

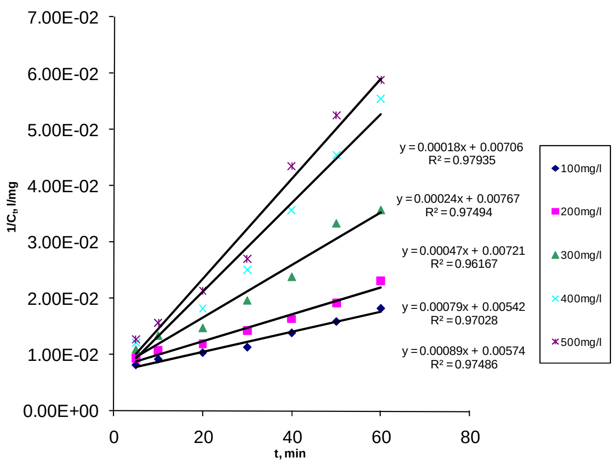

Figure 8. Kinetic plot of 1/C_t versus time for varying MS dosage at pH = 6.

of MS coagulant at $K = 1.24 \times 10^{-3}$ (mg·min)$^{-1}$ and $\tau_{1/2}$ = 0.100 mins.

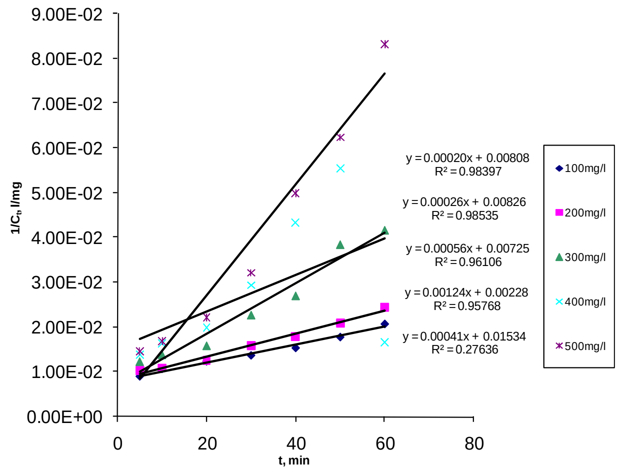

Figure 9. Kinetic plot of 1 C_t versus time for varying MS dosage at pH = 8.

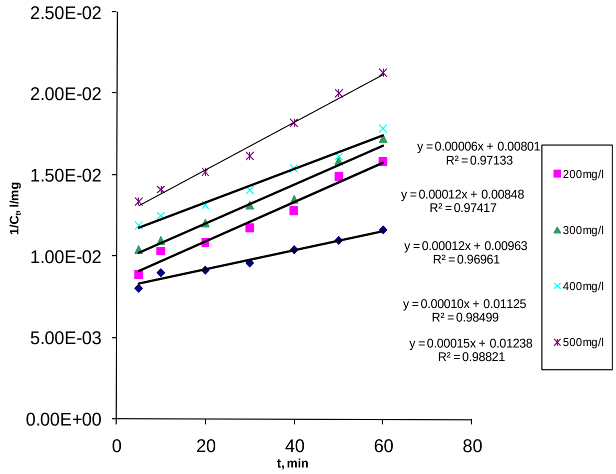

Figure 10. Kinetic plot of 1/C_t versus time for varying MS dosage at pH = 10.

At nearly invariant values of K, ε_p relates directly to $2K = \beta_{BR}$. The consequence is that high ε_p results in high 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 high rate of coagulation [18].

The results show that high values of $\tau_{1/2}$ correspond to low ε_p and K, an indication of repulsion in the system. Similar results were obtained by previous researches [19].

4. Conclusion

The removal efficiency $E > 80\%$ recorded at the optimum pH of 8 and dosage of 400 mg/l supported by the value of $\tau_{1/2}$ = 0.100 minute presents the potential of *Mucuna sloanei* as a source of organic derived coagulant applicable in large scale water treatment. The obtained results are in agreement with previous works [19].

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Nomenclatures

β_{BR}: Collision factor for Brownian transport
ε_p: Collision efficiency
$\tau_{1/2}$: Coagulation period/Half life
R^2: Coefficient of Determination
α: Coag-flocculation reaction order
MS: *Mucuna sloanei*
K: Coagulation rate constant
C: Concentration of particles