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Bio-Coag-Flocculation of Refined Petroleum Wastewater using Plant Extract: A Turbidimeric Approach

Victor I. Ugonabo, Loveth N. Emembolu, Chinenye A. Igwegbe

Department of Chemical Engineering, Nnamdi Azikiwe University, Awka, Nigeria

ABSTRACT

The effectiveness of natural and locally available coagulant, Mucuna sloanei seed has been evaluated for reduction of turbidity in petroleum refined wastewater at room temperature. The effect of pH, coagulant dose and settling time on the coagulation process was studied using the conventional jar test method. Highest turbidity reduction efficiency of 92.41% was recorded at pH 2 and coagulant dose of 60mg/l at settling time of 40 minutes. Solution pH was found to have a great significant effect on the turbidity reduction efficiency. Kinetic results show that the coag-flocculation reaction order (α), coag-flocculation rate constant that influences the rate of aggregation (K) and coagulation period (τ 1/2) of 2, 2 x 10-3m3/kg/s and 250s were recorded at the optimal operational conditions respectively. Therefore, in practical situations, selection of pH medium should go with the coagulant dosage for efficient turbidity reduction. Utilization of extract from plant origin (Mucuna sloanei) was found to be efficient and effective in the remediation of refined petroleum wastewater.

Keywords: Bio-Coag-flocculation, Petroleum refined wastewater, Plant Extract, Turbidimetry.

INTRODUCTION

The increased level of industrialization and urbanization over the years have resulted in waste generation from domestic and industrial sources, which variably make the environment unsafe and dangerous to both man and aquatic animals. Petroleum refinery industries are one of the major contributors of hazardous and toxic waste [1].

Petroleum refinery effluents contain large quantities of toxic and aromatic compounds as benzene, toluene, ethyl benzene and xylene, not limited to them, which are recognised as the most hazardous compounds released into the environment [1, 2, 3]. Therefore, the need for the treatment of petroleum wastewater before discharge is very imperative [4].

There are many available processes for industrial wastewater treatment, physicochemical, chemical and biological methods, adsorption, electrolysis, etc [5]. Amongst these methods, physicochemical process has been effective for purification of petroleum refined wastewater [4]. Coag-flocculation is the process of destabilizing colloids, aggregating them and binding them together for ease of sedimentation [6].

The use of plant materials as natural coagulants to clarify turbidity of water is common practice since ancient times [7]. Many studies have highlighted the viability of coagulants made from polysaccharides, proteins and starches in reducing suspended solids in water by physical processes [8, 9]. The main advantages of using natural plant-based coagulants for water treatment are apparent; they are cost effective, unlikely to produce treated water with extreme pH and highly biodegradable [10]. Many problems are associated with the use of chemicals like alum in water treatment which include Alzheimer's disease and neurological diseases [11]. Sludge produced is voluminous and non – biodegradable after treatment and therefore poses disposal problems leading to increase in cost of treatment with the use of chemicals [11].

Mucuna sloanei, one of the most widespread plant species that grows quickly at low altitudes in the whole tropical belt. Many researchers have reported on the various uses of *Mucuna sloanei* as coagulant and coagulant aid [12, 13].

In Nigeria, much has not been done on *Mucuna sloanei* as a natural coagulant in water treatment technology. This study aims to investigate the potentials of *Mucuna sloanei* extract in treating petroleum refinery wastewater in Nigeria.

THEORETICAL PRINCIPLES AND COAG-FLOCCULATION KINETICS

The kinetics of coagulation of particles controlled by Brownian motion can be described by

$$\frac{dN_t}{dt} = \frac{1}{2}\sum_{i=j} K_{ij} N_i N_j - N_z \sum_{i=1} K_{iz} N_i \quad (1)$$

Where K_{ij} is a second order coagulation rate constant, t is the time, and N_z is the total particle concentration of z-fold aggregates.

The kinetics of Brownian coagulation of monodispersed particles at the early stage is described by Smoluchowski [14] and Menkiti et al. [15]. The authors showed that the kinetics of coagulation being controlled by Brownian motion have best performance at the early stage ($t > 30\ mins$).

For Brownian coag-flocculation

$$-\frac{dN_t}{dt} = K\, N_t^{\alpha} \quad (2)$$

Lineralizing equation 2 yields

$$In\left[-\frac{dN_t}{dt}\right] = In\, K + \alpha\, In\, N_t \quad (3)$$

where K is the coagulation rate constant, α is the order of coagulation reaction and N_t is the concentration of the particles (MSS) at time, t.

Smoluchowski [14] and Menkiti et al. [15] showed that

$$K = 8\pi R_1 D_1 \quad (4)$$

$$\alpha = 1$$

$$R_1 = 2a \quad (5)$$

Where a is the particle radius, D_1 is the diffusivity.

According to Fridrikhsberg [16] and Danov et al. [17], Einstein equation for diffusivity is given by

$$D_1 = K_B \frac{T}{B} \quad (6)$$

Where K_B is the Boltzmann constant, B is the friction factor and T is the absolute temperature in Kelvin

From Stokes's equation

$$B = 6\,\pi\,\eta\,a \quad (7)$$

where η is the viscosity of the medium (wastewater)

Substituting equations 7, 6 and 5 in 4 gives

$$K = \frac{8}{3} K_B \frac{T}{\eta} \quad (8)$$

Substituting equation 8 into 2, gives

$$\frac{dN_t}{dt} = -\frac{8}{3}\frac{K_B\, T}{\eta} N_t^2 \quad (9)$$

Separating variables and integrating equation 2 at t = 0, $N_t = N_o$ and t = t, $N_t = N_t$ and putting α = 2

$$-\frac{dN_t}{N_i^2} = -Kdt$$

$$\int_{N_0}^{N_t} N_t^{-2}\, dN_t = K\int_0^t dt$$

$$[N_t^{-1}]_{N_0}^{N_t} = K[t]_0^t$$

$$\frac{1}{N_t} - \frac{1}{N_0} = Kt \quad (10)$$

Making $\frac{1}{N_t}$ the subject of equation 10 and multiply both sides by N_0

$$\frac{N_0}{N_t} = N_0Kt + 1 \tag{11}$$

Making N_t the subject of equation 11:

$$N_t = \frac{N_0}{1 + N_0Kt}$$

Similarly,

$$N_t = \frac{N_0}{1+ N_0t/(1/N_0t)} \tag{12}$$

Let $N_0 = \frac{1}{N_0K} = \tau$ (13)

Substituting equation 13 into 12 yields

$$N_t = \frac{N_0}{1+\frac{t}{\tau}} \tag{14}$$

But when t = τ, equation 14 becomes

$$N_t = \frac{N_0}{1+1} = \frac{N_0}{2} \tag{15}$$

According to Smoluchowski theory where the coagulation of spherical particles is controlled entirely by Brownian diffusion, the coagulation rate constant for doublet formation of an initially monodisperse suspension is given by

$$K_{ij} = 2K = \frac{8}{3}\frac{K_BT}{\eta} \tag{16}$$

Solving equation 1 analytically and assuming K_{ij} = K_{ii} yields [18, 15]:

$$\frac{N_{z(t)}}{N_0} = \frac{(K_{ii}N_0\frac{t}{2})^{n-1}}{(1+ K_{ii}N_0\frac{t}{2})^{n+1}} \tag{17}$$

Similarly

$$\frac{N_{z(t)}}{N_0} = \frac{2\left[\frac{1}{KN_0}\right]}{\left[\left(1+\frac{1}{2}\left[\frac{1}{KN_0}\right]\right)\right]} \tag{18}$$

Substituting 13 into 18 gives

$$\frac{N_{z(t)}}{N_0} = \frac{\left[\frac{t}{2\frac{1}{\tau}}\right]^{n-1}}{\left[1+\frac{t}{2\tau}\right]^{n+1}} \tag{19}$$

Assume 2 τ = τ^1 (20)

Substituting 20 into 19 yields

$$\frac{N_{z(t)}}{N_0} = \frac{\left[\frac{1}{\tau}\right]^{n-1}}{\left[1+\frac{t}{\tau^1}\right]^{n+1}} \tag{21}$$

Equation 21 represents the general expressions of particle of any i^{th} order.

For mono particles ($i = 1$)

$$N_1 = N_0\left[\frac{1}{\left[1+\frac{t}{\tau^1}\right]^2}\right] \tag{22}$$

For dimmers ($i = 2$)

$$N_2 = N_0\left[\frac{(\frac{t}{\tau^1})}{\left[1+\frac{t}{\tau^1}\right]^3}\right] \tag{23}$$

For trimmers ($i = 1$)

$$N_3 = N_0 \left[\frac{(\frac{t}{\tau 1})^2}{\left[1+\frac{t}{\tau 1}\right]^4} \right] \quad (24)$$

The theoretical quantity τ can be evaluated mathematically using equation 13, that is,

$$\tau = \frac{1}{N_0} K$$

Substituting equation 8 into 13

$$\tau = \frac{1}{N_0} \frac{8}{3} K_B \frac{T}{\eta} = \frac{3\eta}{8K_B T N_0} \quad (25)$$

As $N_0 \rightarrow N_0/2, \tau \rightarrow \tau_{1/2}$

Therefore,

$\tau_{1/2} = \frac{3\eta}{8K_B T(0.5N_0)}$ which can be written as

$$\tau_{1/2} = \frac{3\eta}{4K_B T N_0} \quad (26)$$

MATERIALS AND METHODS

Material Preparation and Characterization

Petroleum Refinery Wastewater Characteristics

The petroleum refinery wastewater was collected from a refinery and petrochemical company in Delta state, Nigeria. The wastewater was characterized based on standard method [19]. The unstable pH and temperature were analyzed on site using portable pH meter and thermometer respectively.

Mucuna Sloanei Seed

Mucuna sloanei seed (MSS) was sourced from Eke-Awka Market, Awka, Nigeria. The washed and dried sample was dehulled, ground, sieved through a screen of 20mesh sizes to get finer particle and stored in an airtight container. Subsequently, the sample was characterized based on method reported by AOAC [20].

Preparation of Coagulant

Extraction method for coagulant preparation is aimed at improving the material's coagulation performance and therefore reduces the rate of coagulant consumption to make water turbidity removal more cost effective [21]. *Mucuna sloanei* seed extract was prepared by adding different weights of MSS powder in 100ml distilled water. Then the desired concentrations were used for the experiment. Dried seed powder and then stirred for 15min using a magnetic stirrer in order to extract active coagulants. Then the solution was allowed to stand without disturbance for 15min and then filtered. Obtained filtrates were stored in a refrigerator to avoid ageing effect. The filtrate (extract) was used for coagulation studies.

Coag-Flocculation Experiments

The experiments were carried out using conventional jar test apparatus (Chemix floc-test model CL6), turbidity meter (HI 93703 portable microprocessor turbidity meter) (HANNA instruments, 2008) and Delta 320 pH meter. Varying coagulant doses of 20, 40, 60, 80 and 100 mg/l was added in 250ml of petroleum water sample. The pH of the suspension was adjusted to different pHs of 2, 4, 6, 8 and 10 by the addition of 10M HCl/NaCl and stirred for 2mins rapid mixing of 150rpm and 20mins of slow mixing (20rpm) followed by 3, 5, 10, 15, 20, 25, 30, 40 min setting time. At different settling time, 2cm depth of the sample was withdrawn and the total dissolved and suspended solid particle (in mg/l) measured for coagulation kinetics under room temperature.

The turbidity removal (coagulation) efficiency was evaluated using equation 27 as follows [21]:

$$E(\%) = \frac{T_0 - T}{T_0} X\, 100 \quad (27)$$

RESULTS AND DISCUSSION

Petroleum Refined Wastewater Characteristics

Table 1 shows the properties of the wastewater. It indicates that the presence of total dissolved solids (TDS) and total suspended solids (TSS) which caused the water to be turbid which shows the need for the turbiometric treatment of the wastewater.

Table1. *Petroleum refinery wastewater sample characteristics before treatment*

Parameter	Value
Temperature	27.30˚C
pH	8.25
Total solids (TS)	4225mg/l
Total dissolved solids (TDS)	1645mg/l
Total suspended solids (TSS)	2580mg/l
Turbidity	39.9NTU
Dissolved Oxygen (DO)	28.6mg/l
Biological Oxygen Demand (BOD)	286mg/l
Chemical Oxygen Demand (COD)	264mg/l
Phenol	28.9mg/l
Conductivity	2570µS/cm

Mucuna Sloanei Seeds Characteristics

The proximate analyses of MSS are presented in table 2. The protein content was 26.32% and it was suggested that proteins are active components in plant extracts, responsible for coagulation processes [22, 23]. This shows that MSS is a good coagulant.

Table2. *Characteristics of plant coagulant precursor (Mucuna sloanei seeds, MSS)*

Parameter	Value
Protein content	26.32%
Bulk density	0.42g/ml
Ash content	4.04%
Oil content	5.13%
Moisture content	11.95%
Carbohydrate	52.38%

Effect of Coagulant Dose on Coagulation/Turbidity Removal Efficiency

Figure 1 shows the coagulation efficiency at different coagulant dose (20, 40, 60, 80 and 100mg/l) at pH of 8.25. The highest turbidity efficiency was obtained at dosage of 60mg/l which was used for further studies. The coagulation efficiency increased from 20mg/l to 60mg/l, the positively charged coagulant adsorbed on the surface negatively charged colloid particles by charge neutralization. The decrease after 60mg/l was due to the adsorbed aggregation completely covered the particle surface and prevented the particles from flocculating [22].

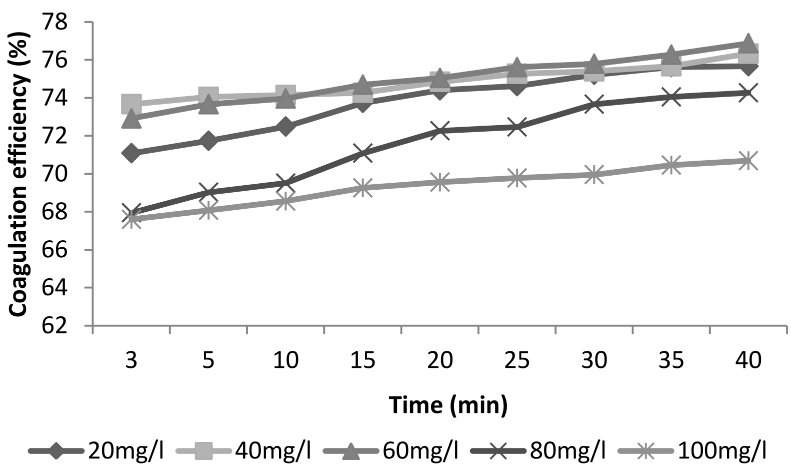

Fig1. *Coagulation efficiency versus time for MSS extract at pH of 8.25*

Effect of Solution pH on Coagulation Efficiency

Figure 2 shows the coagulation/performance efficiency at different pH (2, 4, 6, 8 and 10) at dosage of 60mg/l. pH of 2 gave the highest performance efficiency of 92.41% which was adopted as the optimum pH. At this pH, precipitation of flocs was more and better than the other pH. This shows the process was highly dependent on the pH of the sample. The coagulation activity was poorer at pH > 6.

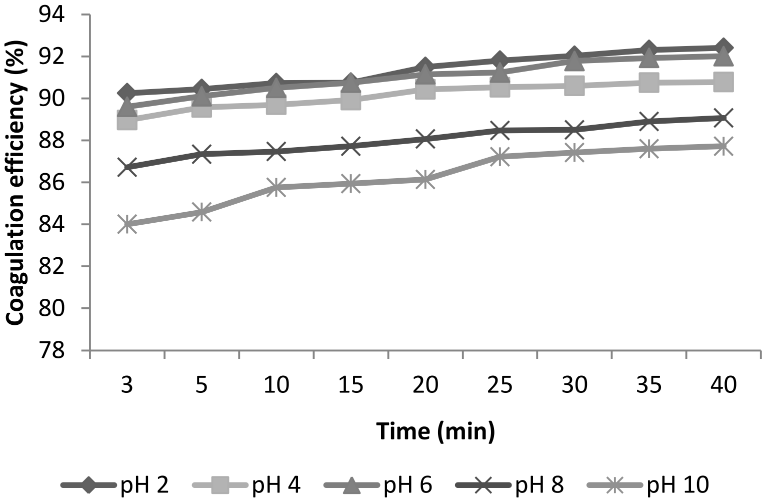

Fig2. *Coagulation efficiency versus time for MSS extract at optimum dosage of 60mg/l*

Coag-Flocculation Kinetics

The coagulation kinetic parameters are presented in table 3 at different pH (2, 4, 6, 8 and 10) and constant coagulant dose of 60mg/l. K obtained from equation 10 using the slope of linear plot of $\frac{1}{N_t}$ versus time, t (not shown). K is a constant that influences the rate of aggregation [4]. Coagulation order, α value of 2 was obtained is in agreement with the theory of Smoluchowski which is associated with coagulation process being predominantly controlled by Brownian motion [24, 15]. Coefficient of regression, R^2 was employed to ascertain the level of accuracy of fit of the experimental data on the model expressed as equation 10. The R^2 values are within $0.979 \leq R^2 \leq 0.891$ which are moderate and high and reveal the effectiveness of equation 10 in describing the coag-flocculation processes. Coag-flocculation at pH of 2 has the minimum $\tau_{1/2}$ value (table 3) suggesting very fast coagulation rate of 250s at pH of 2.

Particle Distribution Plots

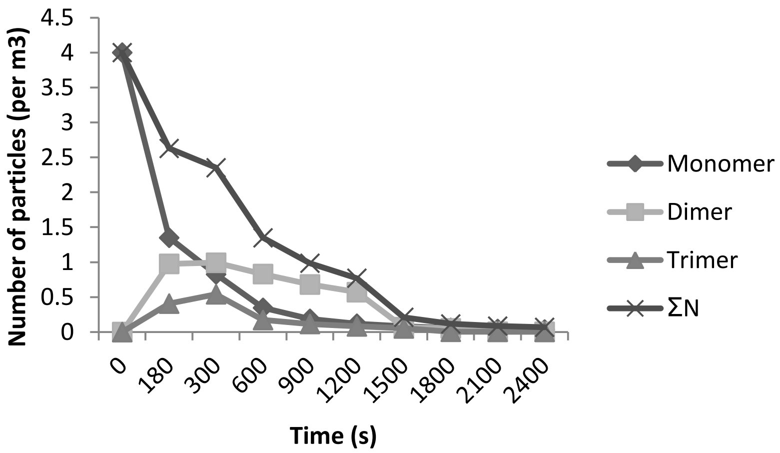

Fig3. *Particle distribution plot as a function of time at pH = 2 and dosage = 60mg/l*

Equation 21 was used to predict the time evolution of aggregating particles – monomers, dimmers and trimmers (for n = 1, 2 and 3 respectively). The trends of the aggregating particles as a function of time are shown in figure 3. The number of primary particles (monomers) decreased more rapidly than the total number of particles (ΣN). This is because dimmers and trimmers are formed because of the quick destabilization of monomers which facilitated coagulation process. These bring to limelight the suitability of equation 21 in particle size distribution.

Table3. *Coag-flocculation function parameters for varying pH and constant coagulant dose of 60mg/l MSS extract*

Parameter	pH				
	2	4	6	8	10
A	2	2	2	2	2
K (m^3/kg/s)	0.002	0.001	0.001	0.001	0.001
B (m^3/kg/s)	0.004	0.001	0.001	0.001	0.001
$\tau_{1/2}$ (s)	250	454.2	476.2	384.6	303
K_R (/kg^2/s)	2.6 x 10^{-19}	1.58 x 10^{-19}	1.58 x 10^{-19}	1.58 x 10^{-19}	1.58 x 10^{-19}
α_p^{Nn}	7.66 x 10^{17}	1.27 x 10^{18}	1.27 x 10^{18}	1.27 x 10^{18}	1.27 x 10^{18}
D (kg^2/m/s)	4.183 x 10^{-16}	2.324 x 10^{-16}	2.324 x 10^{-16}	2.324 x 10^{-16}	2.324 x 10^{-16}
R^2	0.979	0.911	0.965	0.973	0.891

CONCLUSION

The performance of a local material (*Mucuna sloanei* seed) has been evaluated in the treatment of petroleum refinery wastewater. MSS *was* found to be a good coagulant suitable for treatment of petroleum refinery wastewater at room temperature. The treatment of the wastewater was found to be highly dependent on coagulant doses, solution pH and settling time. Varying of coagulant doses had a significant difference on the coag-flocculation performance of *Mucuna sloanei* extract (MSE) at the same effluent pH condition. Optimum pH of 2 and dosage of 60mg/l were obtained at 40min. MSE stock solutions are pre-neutralized and are less acidic then alum. Thus, because of these advantages, process industries should employ the use of this coagulant to treat their waste/produced water contaminated with toxic compounds and suspended particles before discharging them into the environment. Also, Federal Government should encourage the use of local coagulants in effluent treatments.

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