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Optimal and Coag-flocculation kinetics Evaluation of Pharmaceutical Industry Effluent using Organic and Inorganic Coagulants

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ABSTRACT

This work investigates the treatment of pharmaceutical effluent system using organic and inorganic coagulants at optimal conditions. To minimize total dissolved and suspended solids, experiments were carried out using standard Jar test method to determine the effects and responses of the operating conditions (medium pH, coagulant dosage, settling time) on the treatment efficiency. The results indicates that the optimum conditions are 10,13, 0.1g/l and 40 minutes for coagulating medium pH, coagulant dosage and settling time for alum and Mucuna prurien seed coagulant respectively. At optimum, the TDSS were reduced from: 920.00 mg/l to 861.12 mg/l representing 93.26% alum and 2200.00mg/l to 2040.50mg/l representing 92.75% Mucuna prurien seed coagulant. In general terms, Mucuna prurien has proved to be better alternative to alum over wide range of coagulant dosages.

Keywords: Coag-flocculation, pharmaceutical industry effluent, organic, inorganic coagulants, optimal conditions.

INTRODUCTION

The increasing environmental awareness at both local and international levels invigorated the existing urge to shield the ecosystem against pollution threats arising from anthropogenic activities. With the growing anthropogenic activities especially in the areas of greater industrialization and its associated discharge of objectionable pollutant deleterious to the environment. This situation raises critical challenges confronting the environmental management faced by most developing countries where discharge of effluent such as pharmaceutical industry effluent is common with lack of stringent measure on the part of regulatory bodies.

Pharmaceutical industry effluent (PIE) is the resulting wastewater from the washery unit of pharmaceutical products plant. Pharmaceutical industry effluent is regarded as significant environmental pollutant of the considerable organic loads such as; Biological oxygen demand (BOD), colloids, chemical Oxygen demand (COD), total dissolved and suspended Solids (TDSS), bacteria, color etc which are target for removal during treatment process such as coag-flocculation [1-5].

Coag-flocculation is a treatment option in water and wastewater purification accompanied by addition of coagulant (aggregating agents) which in solution furnishes ionic charges opposite to those of the colloidal particles in the effluent. This will lead to neutralization of the repelling charges on the colloidal particles, forming a Jelly – like spongy mass called a floc. Similarly, flocculation causes considerable increase in the size and density of coagulated particles resulting in a faster rate of settling of particles in the effluent or solution [6 - 9].

Over the years, high efficient inorganic coag-flocculants such as aluminum and iron salts have been commonly applied for water and wastewater purifications. However, the production of large volume of non biodegradable sludge, and medical disorders associated with their post usage underscores their continuation. These impediments necessitated the search for more eco-friendly coagulant, an alternative coagulant that is safe, no health hazard associated with its post usage. One such substance is *Mucuna prurien* seed coagulant – an organic aggregating agent from plant origin.

Mucuna prurien is an annual twinning tropical plant with pods containing bean seed commonly found in the Eastern Nigeria. The seed kernels of *Mucuna prurien* contain significant quantities of positively charged water-soluble protein which is confirmed by the characterization result stated in table 2. This outstanding traits facilitates its easily aggregation with the colloids and total dissolved and suspended solid (TDSS) (inherently with negative charges) in the effluent sample to promote floc formation [10] ; [11] .

Mucuna Prurien seed are edible (used as a thickener in melon soup preparation), biodegradable substance. It has been widely used as an effective renewable organic aggregating agent with extensive application in large scale water treatment technology in different effluent media. Previous works with Mucuna in coal washery and pharmaceutical effluents reported by [12] and [13] confirmed its effectiveness in wastewater purification particularly in alkaline medium.

The import of this work is therefore directed towards the provision of kinetic data, the mathematical relationship that predicts the behavior of TDSS with the coag-flocculants, coag-flocculation variables. The results obtained will aid in ascertaining whether the performance of organic coagulant is better than the inorganic one. Thus, if so, ultimately, the post usage handling and health challenges associated with inorganic coagulant can be reduced.

2.0 Theory and Model Development.

For a uniformly interacting coag-flocculation system where Brownian stiochastic force dominates; the heating/stirring of the system produces temperature gradient which causes migration of the particles driven by thermally excited gradients of surface tension [14]; [15]; [3].

$$\nabla_S \sigma = - E_T \frac{\nabla_S T}{T} \qquad 2.1$$

Where $E_T = - \left(\frac{\partial \sigma}{\partial \ln T \; r_1} \right)$

∇_S is the surface gradient operator; σ is the surface tension and E_T is the coefficient of interfacial thermal elasticity. The effect is that particles moving randomly with different velocity can coag-flocculate to form larger flocs.

Assuming monodisperse, perfect elasticity and bi-particle collisions, the general mode for microkinetic coag-flocculation is given as [16]; [17].

$$\frac{dn_k}{dt} = \frac{1}{2} \sum_{i=1}^{k-i} a_{cf}^{i,k-i} \, n_i \; n_{k-i} \, q_k - n_k \sum_{i=1}^{\infty} a_{cf}^{k,i} \, n_{i+} \, q_k \qquad 2.2$$

(k = 1,2,3)

$\frac{dn_k}{dt}$ is the rate of change of concentration of particle of size, K

Where t is time, n_1 denotes number of mono particles per unit volume;

n_k is number of the flocs of K aggregates (k = 2,3,4…..) per unit volume; a_{cf} (i,j =- 1,2,3….) is a function of coag flocculation transport mechanism; q_k denotes flux of flocs of size k.

In case of **irreversible coagulation q_k** = 0. The total concentration of flocs, N and total concentration of the constituent particles (including those in flocculated form) N_t, are given by the expressions

$$N = \Sigma n_k,\ N_t = \Sigma_{K=1} K n_k \qquad 2.3$$

Also $a_{cf} = 4\pi D^{o}{}_{i,j}\,(R_i + R_j)\,E_{i,j}$ 2.4

Similarly, for Brownian transport is given as [17]

$$(a_{cf})_{BR} = \frac{8}{3}\,\varepsilon_p \frac{k_B T}{\eta} \qquad 2.5$$

Where $D^{(0)}_{i,j}$ is the relative diffusion coefficients for two flocs of radii R_i and R_j, and aggregation number i and j, respectively; $E_{i,j}$ is the collision efficiency [18]; $\varepsilon_p = E_{i,j}$ collision efficiency. The aggregation rate of intending potential particles during coag-flocculation can be obtained by the combination of equations 2.2 and 2.5 yields

$$-\frac{dN_t}{dt} = K N_t^{\alpha} \qquad 2.6$$

where N_t is the total concentration of constituent particles at time t as expressed in equation 2.3 above

K is the coag-flocculation constant

α is the order of coag-flocculation process.

Equally, $(a_{cf})_{BR} = \varepsilon_p K_f N_t^{\alpha}$ 2.7

Where K_f is rate constant of flocculation for rapid flocculation. However, for second order (n_o^2) reaction rate constant (K_f)

$$K_f = 8\pi R_o D^1 \qquad 2.8$$

Where R_o is particle radius
D^1 is diffusion coefficient for intending flocculating particles i and j

$$R_p = R_i + R_j \qquad 2.9$$

Where R_p is relative particle radius for R_i and R_j
Putting $R_i = R_o$ and $R_j = R_o$
Equation 2.9 transposes to $R_p = 2R_o$ 2.10

From Einstein's approach to the theory of diffusivity D^1.

$$D^1 = \frac{k_B T}{B} \qquad 2.11$$

And from stokes equation $B = \frac{F}{V}$ 2.12

Where K_B – is Boltzman's constant (J/K)
T – is absolute temperature (K)
B – is the friction factor
V – is the velocity acquired by potential aggregating particles under the influence of stochastic force (as result of heat and stirring of the system).

But for a solid sphere of radius R_o, the stokes equation gives

$$B = 6\,\pi\eta R_o \qquad 2.13$$

where, η - is the viscosity of the coag-flocculating fluid.

Substituting equation 2.11, 2.13 into 2.8 yields

$$K_f = \frac{4}{3}\,\frac{k_B T}{\eta} \qquad 2.14$$

Combining equations 2.7 to 2.14 gives:

$$K = \frac{1}{2}\,(a_{cf})_{BR} \qquad 2.15$$

Substituting equations 2.5 and 2.15 into 2.6 yields

$$-\frac{dN_t}{dt} = \frac{4}{3}\,\varepsilon_p\,\frac{k_B T}{\eta}\,N_t^{\alpha} \qquad 2.16$$

For microkinetic aggregation, α theoretically equals 2 as given, [19].

From Ficks first law; number of particles entering sphere with radius R_P per unit time J_t.

$$J_t = 4\pi R_p^2\,D^1\,\frac{dN_t}{dR_p} \qquad 2.17$$

where J_t is flux (number of particles per unit surface and unit, time at position R_P integrating equation 2.16 at initial conditions $N_t = 0$, $R_p = 2R_o$.

$$\frac{J_t}{4\pi}\,\frac{dR_p}{R_p^2}\int_o^{R_p} dR_p = \int_{N_o}^{N_t} d\,N_t \qquad 2.18$$

Thus $J_t = 8\pi D^1 R_o N_o$ 2.19

Generally, for particle of same size under the influence of Brownian motion. The initial rate of coag-flocculation is

$$-\frac{dN_t}{dt} = J_t\,\varepsilon_p\,N_o \qquad 2.20$$

Substituting equations 2.12, 2.13 and 2.19 into 2.20 yields

$$-\frac{dN_t}{dt} = \frac{4}{3}\,\varepsilon_p\,\frac{k_B T}{\eta}\,N_o^2 \qquad 2.21$$

Similarly

$$-\frac{dN_t}{dt} = \frac{4}{3}\,\varepsilon_p\,\frac{k_B T}{\eta}\,N_t^2 \quad \text{at } t > o$$

Hence, from 2.20 putting, α = 2; equation 2.6 transposed to

$$-\frac{dN_t}{dt} = -KN_t{}^{\alpha} \qquad 2.22$$

Integrating

$$\int_{N_o}^{N_t}\frac{dN_t}{N_t} = -K\int_0^t dt \qquad 2.23$$

$$\text{Thus } \frac{1}{N_t} = Kt + \frac{1}{N_o} \qquad 2.24$$

Plot of $\frac{1}{N}$ vs t gives a slope of K and intercept of $\frac{1}{N_o}$

On evaluation of equation 2.24, $\tau_{1/2}$ (Coagulation period) can be determined.

$$N_t = \frac{N_o}{\left(1 + \left(\frac{t}{\frac{1}{N_{ok}}}\right)\right)} \qquad 2.25$$

Where $\tau = \left(\frac{1}{N_{ok}}\right)$ 2.26

Substituting equation 2.26 into 2.25 yields

$$N_t = \frac{N_o}{\left[\,1 + \frac{t}{\tau}\,\right]} \qquad 2.27$$

As t = τ equation 2.26 transpose to;

$$N_t = \frac{N_o}{2} \qquad 2.28$$

Similarly

N_t= 0.5N_o

As $N_o \rightarrow 0.5\ N_o$; $\tau \rightarrow \frac{\tau}{2}$,

Hence equation 2.25 becomes

$\frac{\tau}{2} = (0.5\ N_{oK})^{-1}$ 2.29

For a coagulation period, where total number of concentration N_t is halves, solving equation 2.2 results in the general expression for particle of mth order.

$$\frac{N_m(\mathrm{t})}{N_o} = \frac{\left[\frac{KN_o t}{2}\right]^{\mathrm{m}-1}}{\left[1 + \frac{KN_o t}{2}\right]^{\mathrm{m}+1}} \qquad 2.30$$

Recall; $\frac{\tau}{2} = \frac{N_{oK}}{2}$ or $(0.5N_{oK})^{-1}$

For single particle (m = 1)

$$\frac{N_1 t}{N_o} = \frac{1}{\left(1 + \left(\frac{KN_o t}{2}\right)^{2}\right)} \qquad 2.31$$

$$\therefore \quad N_1 \mathrm{t} = N_o \frac{1}{\left(1 + \left(\frac{KN_o t}{2}\right)\right)^{2}} \qquad 2.32$$

For double particles (m = 2)

$$\frac{N_2 t}{N_o} = \frac{\left(\frac{KN_o t}{2}\right)^2}{\left(1 + \left(\frac{KN_o t}{2}\right)\right)^3} \qquad 2.33$$

$$\therefore N_2 t = N_o \frac{\left[\frac{KN_o t}{2}\right]^2}{\left(1 + \left(\frac{KN_o t}{2}\right)\right)^3} \qquad 2.34$$

For triple particles (m = 3)

$$\frac{N_3 t}{N_o} = \frac{\left[\frac{KN_o t}{2}\right]^3}{\left(1 + \left(\frac{KN_o t}{2}\right)\right)^4} \qquad 2.35$$

$$\therefore N_3 t = N_o \frac{\left[\frac{KN_o t}{2}\right]^3}{\left(1 + \left(\frac{KN_o t}{2}\right)\right)^4} \qquad 2.36$$

Finally, the evaluation of coag-flocculation efficiency or coag-flocculant performance of the process was obtained by applying the relation below.

$$E_{i,j}\,(\%) = \left(\frac{N_o - N_t}{N_o}\right) \times 100 \qquad 2.37$$

EXPERIMENTAL SECTION

3.1 Materials Collection, Preparation and Characterization.

3.1.1. Pharmaceutical Industry Effluent Sample.

The effluent was taken from pharmaceutical industry located in Anambra State, Nigeria. The preservation and characterization were done in accordance with the standard method for the examination of water and waste water analysis [15] and presented in table 1.

3.1.2 Mucuna Prurien Seed Sample

The seed sample was sourced from Eke Ovoko market, Ovoko in Nsukka, Enugu State, Nigeria and processed to biocoagulant, based on the work reported by [11] and posted in Table 2. While the sample of aluminum sulphate (analytical grade) which has been homogenized to fine powder was sourced from bridge head market located in Onitsha, Anambra State, Nigeria.

3.2 Coag-flocculation Experiments

Experiments were conducted using 500ml Jar beaker apparatus. Appropriate dose of mucuna prurien seed coagulant in the range of (0.1 – 0.7) g/l was added to 250ml of pharmaceutical industry effluent. The suspension tuned to varying pH of 1,3,5,7,10 and 13 by addition of 10M HCL/Na0H was subjected to 2mins rapid mixing (120rpm), 20mins of slow mixing (20rpm) and followed by 40mins settling time. During settling, sample were withdrawn from 2cm depth and change in total dissolved and suspended solids (in mg/l) measured for aggregation kinetics using lab-tech. model 212R turbidimeter at 2, 4, 6, 10, 20, 30 and 40 minutes under room temperature. The same procedure was repeated using aluminum sulphate coagulant for comparative purposes. The data obtained were subsequently analysed by fitting into appropriate mathematical relations (kinetic models) for performance evaluations.

Table 1: Characteristic of pharmaceutical industry effluent sample before treatment

Parameter	Values
Temperature (^oC)	28
Electrical conductivity (µs/cm)	4.9×10^2
pH	3.87
Phenol (mg/l)	Nil
Odor	acidic
Total hardness (mg/l)	6,000
Calcium (mg/l)	594
Magnesium (mg/l)	250
Chlorides (mg/l)	100
Dissolved oxygen (mg/l)	20
Biochemical oxygen demand (mg/l)	50
Turbidity (mg/l)	1256
Iron (mg/l)	Nil
Nitrate (mg/l)	Nil
Total acidity (mg/l)	250
Total dissolved solids (mg/l)	225
Total suspended solids (mg/l)	57.25
Total viable court (cfu/mil)	9×10^1
Total coliform MPN/ 100ml	Nil
Total coliform count, cfu/nil	1×10^1
Faecal count MPN/mL	Nil
Clostridium perfrigens MPN/ml	Nil

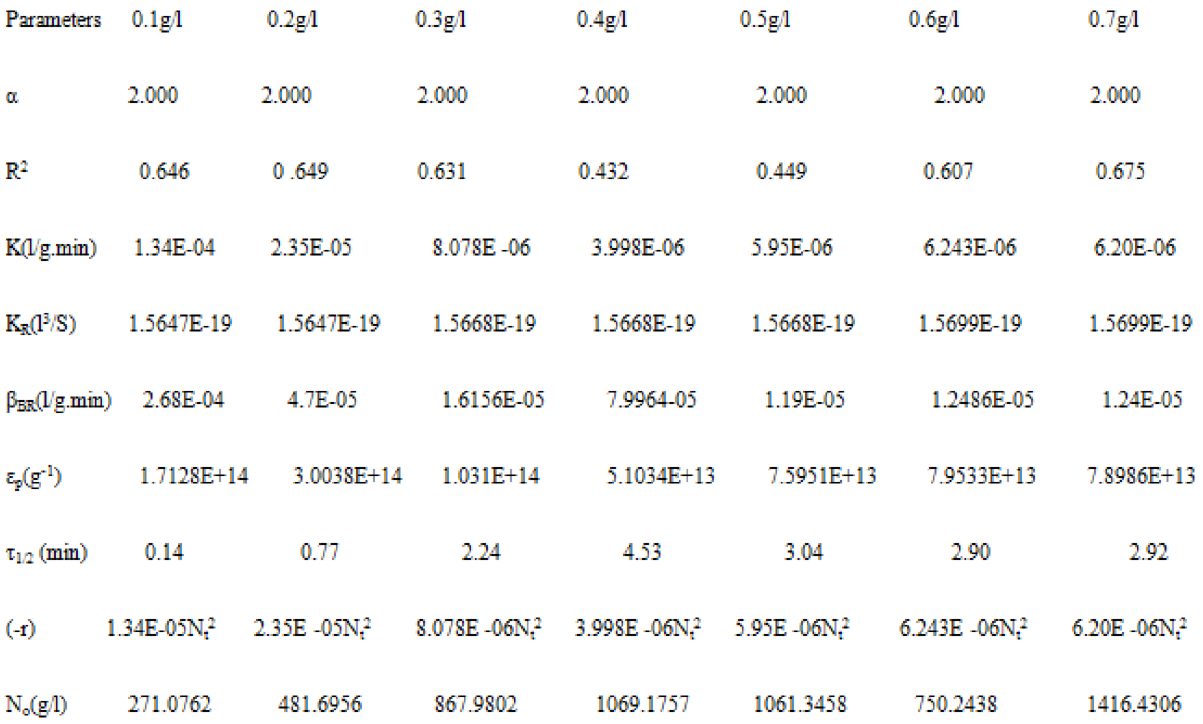
Table 2: Characteristics of organic-caogulant precursor (*Mucuna prurien* seed)

Parameter	Value
Moisture content %	20.00
Ash content %	15.00
Fat content %	8.50
Crude fibre %	9.50
Crude protein %	40.75
Carbohydrate %	6.25

Table 3: Optimum kinetic parameters and linear regression coefficient of MPSC in PIE at varying dosage and pH of 13.

Parameters	0.1g/l	0.2g/l	0.3g/l	0.4g/l	0.5g/l	0.6g/l	0.7g/l
α	2.000	2.000	2.000	2.000	2.000	2.000	2.000
R^2	0.925	0 .665	0.902	0.897	0.952	0.788	0.743
K(l/g.min)	2.18E-05	1. 51E-04	1.3540E -04	9. 215E-05	1.20E-05	6.846E-05	8.92E-05
K_R(l/min)	1.5724E-19	1.5724E-19	1.5724E-19	1.5734E-19	1.5734E-19	1.5734E-19	1.5734E-19
β_{BR}(l/g/.min)	4.36E-04	3.02E-04	2.708E-04	1.843E-04	2.4E-04	1.3692E-04	1.784E-04
$\varepsilon_P(g^{-1})$	2.7728E+15	1.9206E+15	1.7222E+15	1.1713E+15	1.5254E+15	8.7022E+14	1.1339E+14
$\tau_{1/2}$ (min)	0.33	0.48	0.54	0.79	0.60	1.06	0.81
(-r)	2.18E-05N_t^2	1.51E-04N_t^2	1.3540E-04N_t^2	9.215E-05N_t^2	1.20E-05N_t^2	6.846E-05N_t^2	8.92E-05N_t^2
N_o(g/l)	459.5588	441.1116	385.1338	452.0183	932.3140	435. 8058	257.9314

Table 4: Optimum kinetic parameters and linear regression coefficient of ALUM in PIE at varying dosage and pH of 10



Parameters	0.1g/l	0.2g/l	0.3g/l	0.4g/l	0.5g/l	0.6g/l	0.7g/l
α	2.000	2.000	2.000	2.000	2.000	2.000	2.000
R^2	0.646	0 .649	0.631	0.432	0.449	0.607	0.675
K(l/g.min)	1.34E-04	2.35E-05	8.078E -06	3.998E-06	5.95E-06	6.243E-06	6.20E-06
K_R(l^3/S)	1.5647E-19	1.5647E-19	1.5668E-19	1.5668E-19	1.5668E-19	1.5699E-19	1.5699E-19
β_{BR}(l/g.min)	2.68E-04	4.7E-05	1.6156E-05	7.9964-05	1.19E-05	1.2486E-05	1.24E-05
ε_p(g^{-1})	1.7128E+14	3.0038E+14	1.031E+14	5.1034E+13	7.5951E+13	7.9533E+13	7.8986E+13
$\tau_{1/2}$ (min)	0.14	0.77	2.24	4.53	3.04	2.90	2.92
(-r)	1.34E-05N_t^2	2.35E -05N_t^2	8.078E -06N_t^2	3.998E -06N_t^2	5.95E -06N_t^2	6.243E -06N_t^2	6.20E -06N_t^2
N_o(g/l)	271.0762	481.6956	867.9802	1069.1757	1061.3458	750.2438	1416.4306

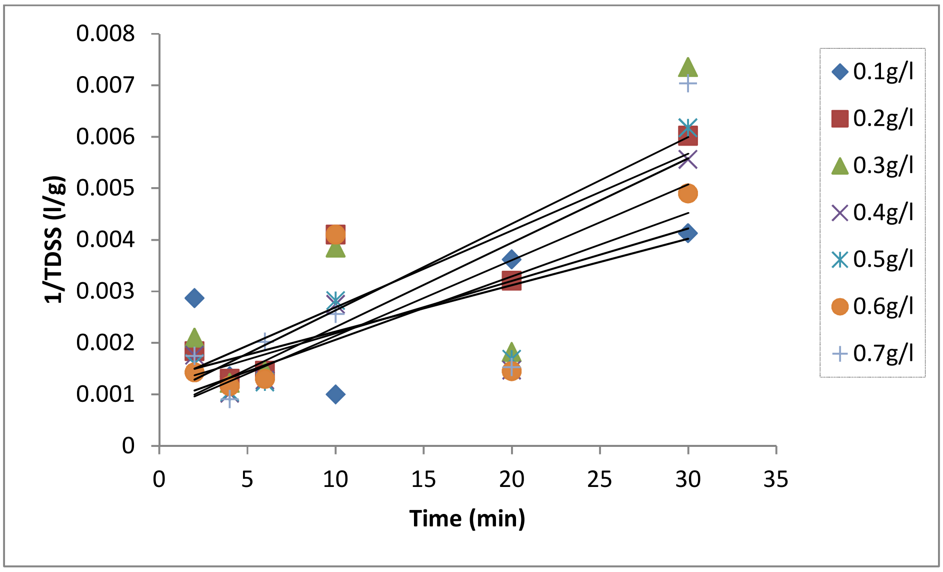


Fig.1: Rate plot at optimum pH and settling time for MPSC

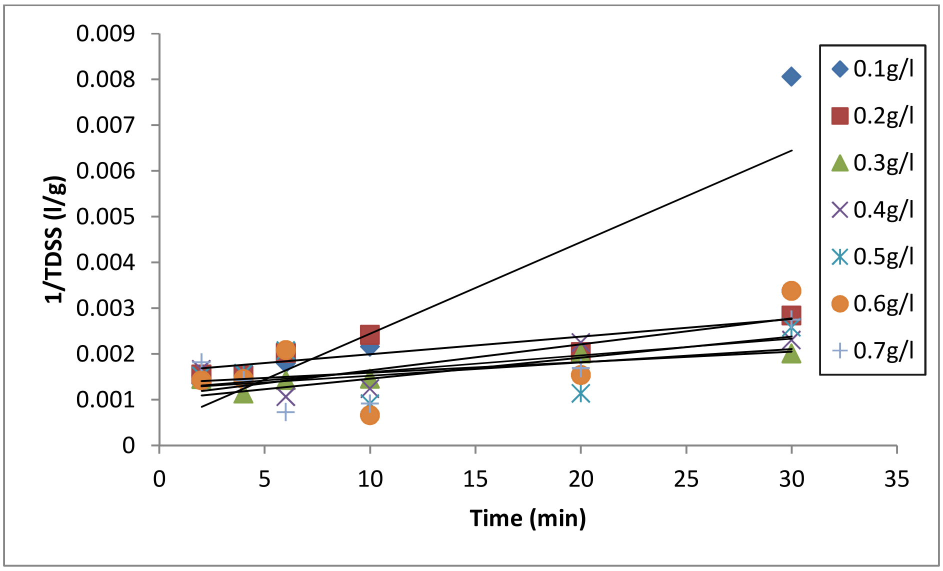


Fig.2: Rate plot at optimum pH and settling time For ALUM

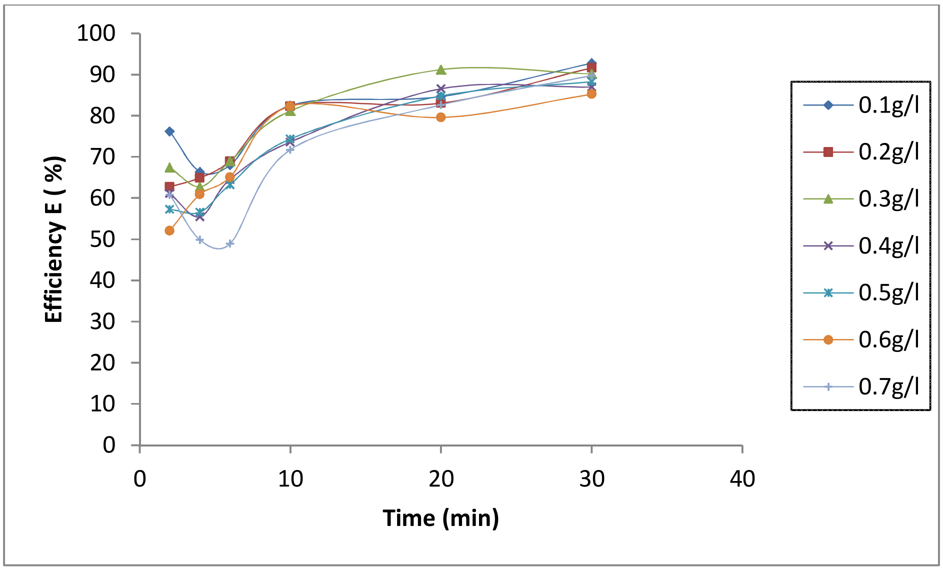


Fig.3: Coag-flocculation efficiency at optimum pH and settling time for MPSC

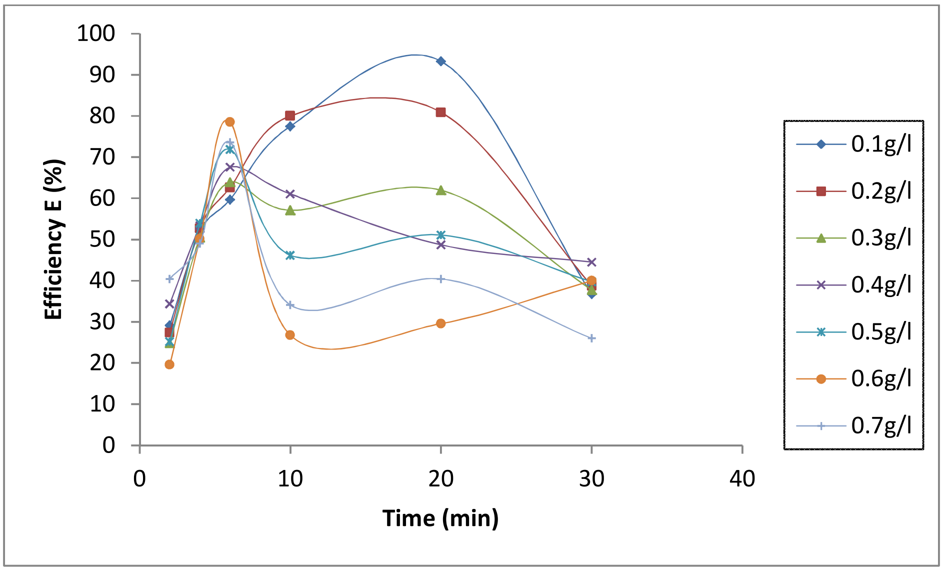


Fig.4: Coag-flocculation efficiency at optimum pH and settling time for ALUM

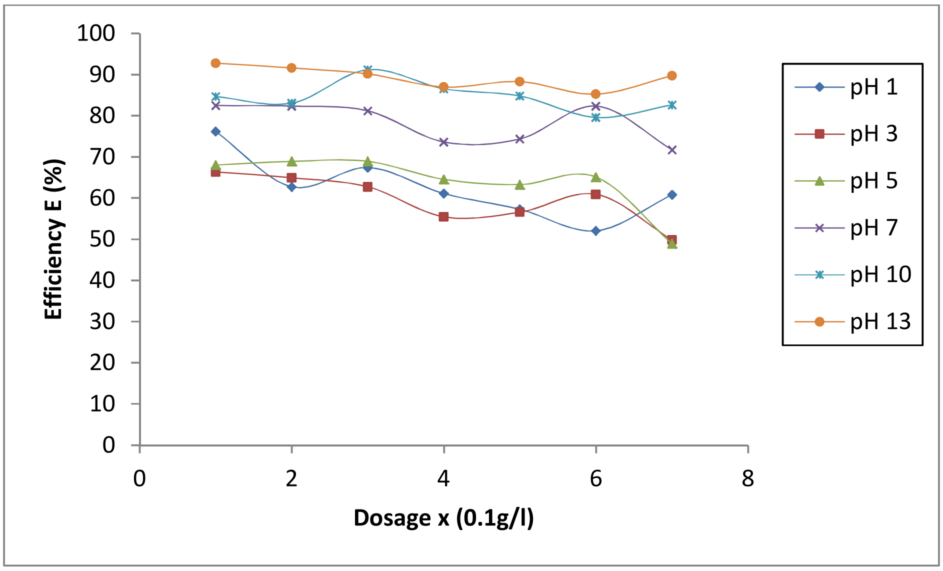


Fig. 5 : Coag-flocculation efficiency at optimum settling time and dosage for MPSC

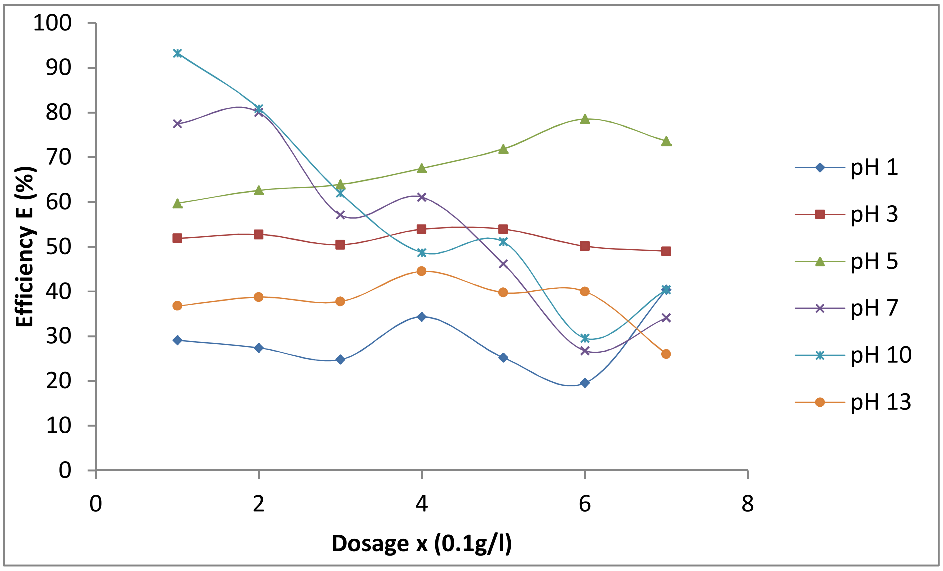


Fig. 6 : Coag-flocculation efficiency at optimum settling time and dosage for ALUM

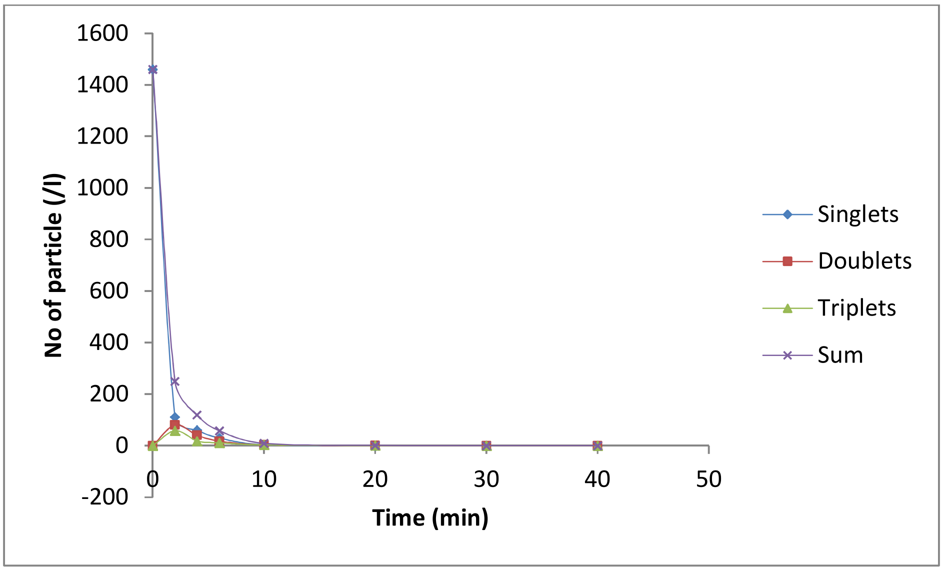


Fig. 7 : Microscopic particles aggregation profile for half life of 0.33min for MPSC

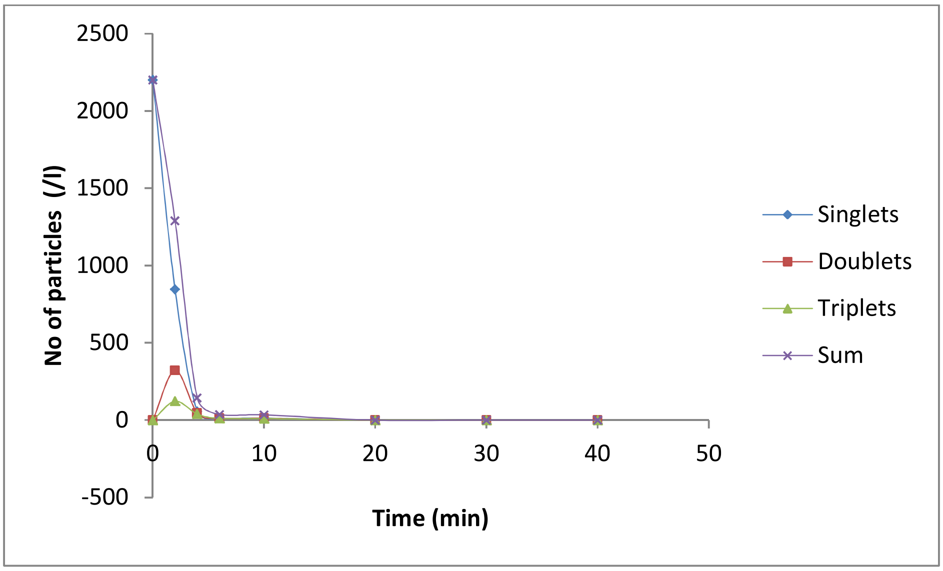


Fig. 8 : Microscopic particles aggregation profile for half life of 1.06min (MPSC)

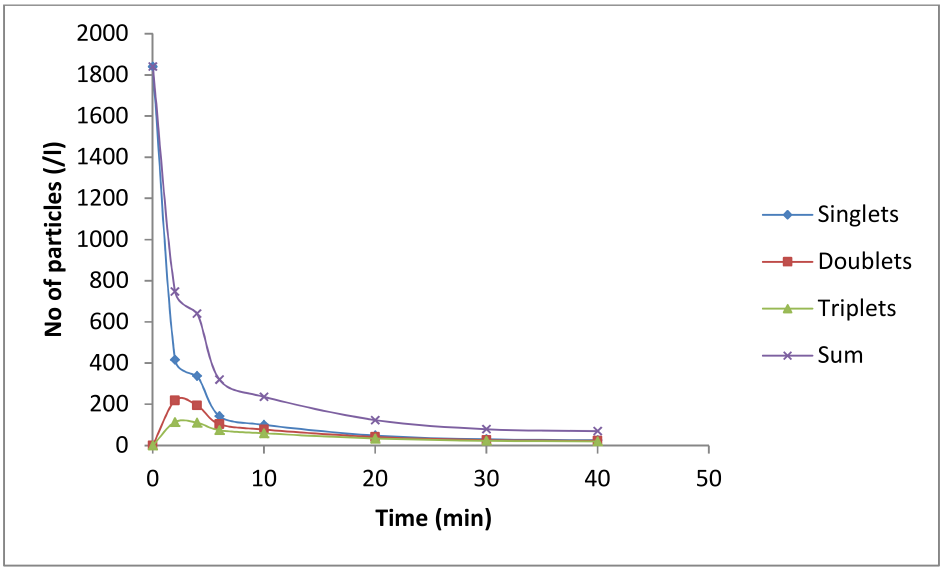


Fig. 9 : Microscopic particles aggregation profile for half life of 0.140min (ALUM)

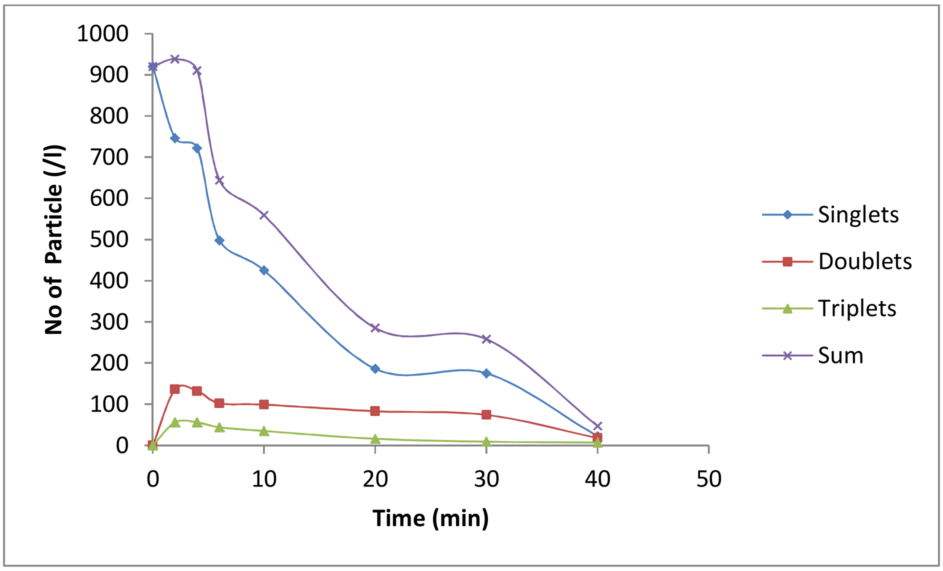
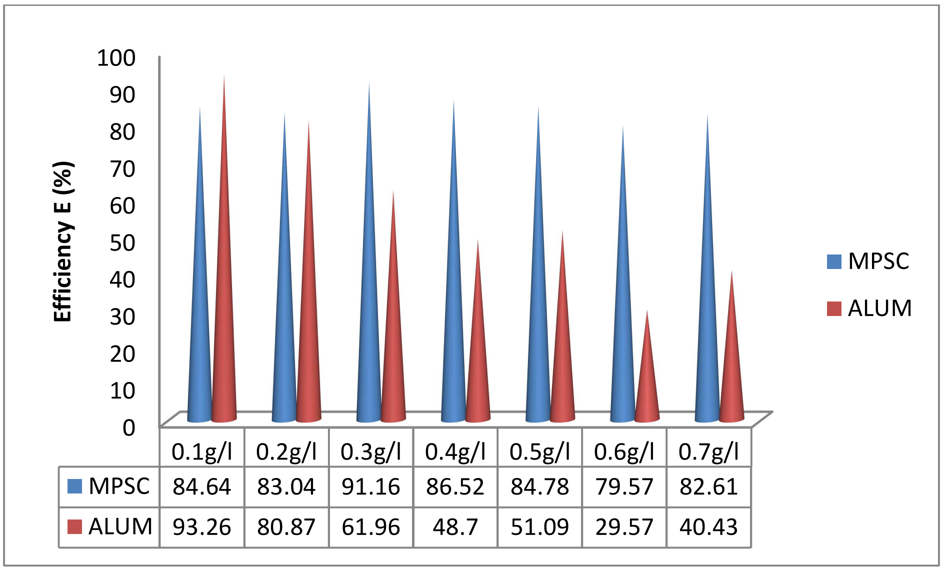


Fig. 10 : Microscopic particles aggregation profile for half life of 4.53min (ALUM)



	0.1g/l	0.2g/l	0.3g/l	0.4g/l	0.5g/l	0.6g/l	0.7g/l
MPSC	84.64	83.04	91.16	86.52	84.78	79.57	82.61
ALUM	93.26	80.87	61.96	48.7	51.09	29.57	40.43

Fig. 11 : Particles aggregation profile at optimum settling time and pH 10

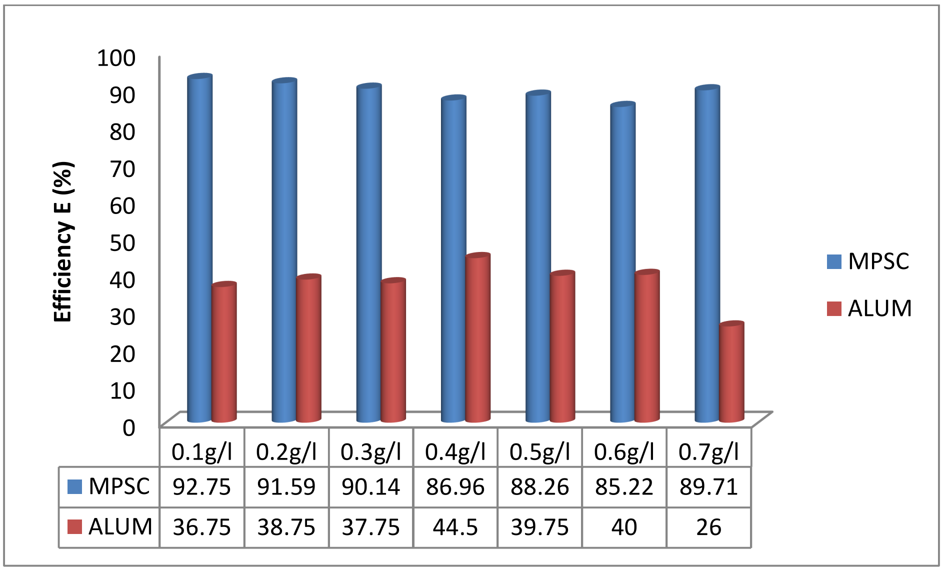


Fig. 12 : Particles aggregation profile at optimum settling time and pH 13

RESULTS AND DISCUSSION

4.1 Characterization results

Tables 1 and 2 presents the results of industry effluent (PIE) and *Mucuna prurien* seed coagulant (MPSC). From table 1, the main factors determining the level of turbidity, are biochemical oxygen demand, total dissolved solids, and total suspended solids. The relatively high values of these parameters, automatically translates to the high level of turbidity in the PIE, necessitated this study. The pH value (3.87) show that PIE is acidic. This phenomenon is supported by high level of electrical conductivity (490µs/cm), suggesting that PIE sample is enriched with charged ions, which favors coag-flocculation treatment option. The low pH value obtained in PIE sample before treatment with MPSC, might be due to high levels of free CO_2, inherent which may subsequently affect the level of biological organism in the wastewater [20]. Though the values of TDS (225mg/l) and TSS (57.25mg/l) are relatively high but quite settleable, in form of sludge which can be used for erosion control practice such as land filling/reclamation. With Zero metal, and high levels of calcium and magnesium in table 1, suggest that the PIE sample can be recycled for agricultural purposes probably as a soil conditioner. In Table 2, the substantial percentage of protein, has been shown to be a principal active ingredient responsible for the coag-flocculation properties of MPSC and other natural coagulants of this type [1]. The reasonable traits of protein in MPSC is an indication that it is endowed with higher percentage of amino groups. During treatment this amino substance could be converted to nitrite and nitrate by some bacteria present in the effluent consequent on this could lead to increase in the nitrites and nitrates levels of the post treated effluent, invariably improving on the nutrients levels of the sludge for use as soil conditioner as aforementioned [21]. Conclusively, from post characteristic results, though not shown MPSC has antimicrobial effects. This is predictable because experience and evidence from literature has shown that turbidity removal is a precondition for removal of bacterial and virus [20].

4.2 Coag-flocculation efficiency at optimum pH and settling time.

This actually depicts the time course removal efficiency in assessing the effectiveness of given dose of MPSC and Alum respectively at optimal pH and settling time in removing TDSS from PIE. The results of this assessment are shown in figs.3 and 4. Generally, the process was relatively fast at the onset with about 62.61% recorded at 6mins for all the coagulants and dosages considered with the exception of 0.1g/l and 0.7g/l dosages for Alum and MPSC respectively. Best results were obtained at low dosage of 0.1g/l for both coagulants and optimum pH of 10 and 13 for Alum and MPSC respectively. In fig.3 increase in settling time affected TDSS removal efficiency positively whereas it is the reverse in fig.4. The consequences of this account could be linked to the high degree of solubility of Alum in PIE. Similarly, high coagulant dosages decreases the removal efficiency as shown in fig. 4. This phenomenon is justified because high dosages could lead to overdosing resulting in the saturation of the polymer bridge sites. Hence, there will be restabilization of the destabilized particles due to insufficient number of particles to form more inter-particle bridges. Whereas in fig. 3, increase in coagulant dosages has negligible influence, on the removal efficiency. The coagulation activity in fig. 3 is linked to adsorption and neutralization of charges or adsorption and bridging of destabilized particles mechanisms. Whereas in fig 4, is linked to partial bridging and charge neutralization mechanism.

4.3 Coag-flocculation efficiency at optimum settling time and dosage.

This is presented in figs. 5 and 6. The figures displays at optimum settling time and dosage the variation of efficiency, E(%) as a function of pH of the effluent medium. The general trend in the figures show that coagulants performed better at higher pH. The optimum removal efficiency of the coagulants is found to occur at different pH. Figs 5 and 6 for example showing the best result at optimal pH and dosage of 13, 10 at 0.1g/l each. The addition of coagulants exceeding their optimum dosages is found to give no additional positive effect as shown in figs. 5 and 6 which reduces the separation process. This might be due to counter ionic re-stabilization causing the dispersion of the flocs and subsequently affecting the settling of the particles [22]. In concrete terms, in fig. 5, in PIE some of MPSC chains of amino groups might react with hydroxide ions, leading to a smaller number of active amino groups to react with TDSS. Ideally, it is expected that increase in the MPSC dosage will enhance its performance, because high dosages of MPSC will result in a higher number of amino groups. However, it was observed that increase in MPSC dosages resulted in the decline in efficiency. This occurrence may be as a result of entanglement between polymer chains themselves caused by interaction among amino groups on MPSC chains, thereby reducing the number of active amino groups for coagulation with TDSS in PIE.

However, it is worthy to mention that in fig. 5, the best efficiency of the MPSC was recorded at pH of 13 for all the dosages considered. Whereas in fig.6, increasing the dosage of Alum brought about decrease in the efficiency. This reduction may be due to higher concentration of hydroxyl group in high dosage of alum that will compete with TDSS in PIE for adsorption sites. In addition, settling of metal hydroxides is favored at high pH [9]. Fig. 6, also show that beyond pH of 10, the efficiency drastically reduced. This may be that at higher pH, the cationic charge of alum becomes less positive and as a result, less adhesion to anionic TDSS in PIE. Generally, the implication of results presented in Figs. 5 and 6 are that the maximum rate of coagulation led by optimum rate constant, K are achieved at 0.1g/l dosage each and pH of 13, 10 respectively.

4.4 Optimal coag-flocculation and regression coefficient parameters.

The linear correlation coefficient (R^2) were evaluated from the plot of $1/N_t$ or 1/TDSS against time expressed as equation (2.26) and presented in figs. 1 and 2. The rate related result obtained at optimal pH and settling time were posted in tables 3 and 4. Linear correlation coefficient (R^2) was employed in evaluation of the level of accuracy of fit of experimental data on equation (2.26). Table 3 and 4 indicates that data ($R^2 > 0.60$) were adequately described by equation (2.26) at the optimal pH and dosages considered except 0.4 and 0.5g/l as shown in table 4. This is an indication that generally, the process of attraction of TDSS on the chains of amino groups in MPSC and metal hydroxides in Alum during hydrolysis is controlled by monolayer sorption mechanism [9]. Hence, confirming the theory of micro kinetics that show $\alpha = 2$. Meanwhile, equation (2.24) show that α relates with K inversely. Thus, for a higher α to be obtained, a lower K is a necessary condition. K, which is coag-flocculation rate constant is evaluated by fitting the experimental data on equation (2.26) (linear plot of $1/N_t$ against time) as slope of the linear plot. For $K = 0.5\ (a_{cf})_{BR}$ expressed as equation (2.15) and posted in tables 3 and 4 shows the least and maximum values K (0.00006846 l/g min) obtained at 0.6g/l and K (0.000218 l/g. min); K (0.000003998 l/g.min) obtained at 0.4g/l and K (0.00134 l/g. min) obtained at 0.1g/d for MPSC and Alum respectively. Low rate obtained at higher dosages at the conditions of this study can be attributed to returbidization of the medium causing the dispersion of the flocs and subsequently affecting the settling of the particles. In addition, K is a rate at which two or more intending particles approaches each other [23]. By implication K is linked to energy barrier between these potential coag-flocculating particles caused by the presence of shear forces or potential hump between them. The value of $\tau_{1/2}$ obtained from equation 2.31 and solved: for 0.1 g/l and 0.6g/l dose (0.33min and 1.06mins)-- table 3; 0.1g/l and 0.4 g/l dose (0.14mins and 4.53 mins) – table 4. This justifies the optimal values of K recorded at 0.1g/l for both coagulants.

The period of 0.33min and 0.14 min are the lowest recorded for MPSC and Alum an indication of best performance at the corresponding dosages. The results posted in tables 3 and 4, show that high K corresponds to low $\tau_{1/2}$ and vice versa, a relationship that suggest strong link among K, $\tau_{1/2}$ and rate of aggregation. Comparatively, the value of K in table 4 is higher than that in table 3, this is an indication that higher particle aggregation (TDSS) on the alum interface is expected, translating to more TDSS removal.
ε_p and K_f were obtained from equations (2.5 and 2.14) respectively. On substitution of equation (2.14) into equation (2.5) gave rise to ε_p. K_f, rate constant for rapid flocculation is a function of temperature and viscosity of the effluent medium i.e K_f = fn (T, ŋ). The variation of K_f values obtained in this study are minimal, following negligible changes in the values of temperature and viscosity of the effluent medium. At k_f approximate to unit, ε_p relates proportionally to K i.e $2K = (a_{cf})_{BR}$ (equation 2.16). Thus a high ε_p results in high kinetic energy to overcome the electrostatic barrier or potential hump. Apparently, from theoretical background $\tau_{1/2}$ values requires low N_o and K values and vice versa. However, the results in tables 3 and 4, indicate that only K values satisfies the aforestated. This justifies high rate of settling obtainable in turbid waters.

Rate of reaction (-r) or (dN_t/dt) as seen in equation (2.23) relates directly with K and N^{α}_t. the implication is that high coag-flocculation rate constant K results in high rate of reaction. This accounts for the rate of sorption of TDSS on the coagulants interface at different dosages and pH. Thus more TDSS is expected to be removed at optimal conditions (K, dosage, setting time and pH). Apparently, high TDSS removal rate is a necessary condition for high K value and corresponding low $\tau_{1/2}$.

Generally, the deviations observed in the results of the functional parameters are due to unattainable assumptions that mixing of TDSS in PIE throughout the dispersion is completely homogenous prior to aggregation [24] ; [9]. The second account is the effect of interchange of action and reaction between and among the repulsive forces and hydrodynamic interactions.

4.5 Time evolution of particle size distribution

On substitution of K obtained from equation (2.26) into equation (2.32), then time evolution of aggregates (singlets, doublets, triplets for m = 1,2,3 respectively) were predicted. The curves in figs. 7 – 10 physically demonstrates the responses of periods 0.33min, 1.06min, 0.14min, and 4.53 min to particle cluster size distribution. Critical observation on the curves showing the behavior of particle sizes at the minimal period for MPSC and Alum presented in figs 7 and 9, indicate that the singlets and sum of particles are seen to fuse into one kernel from N = 1380 – 200 and N = 1840 – 720 with a steep slope. The implication is that there is negligible zeta potential between them at that point. In fig. 7, the singlets can be seen to fuse into doublets and triplet at t = 2mins – infinity, meanwhile there is space between the rest of the particles and sum at the time under consideration which was later overcome by electrostatic attraction at t = 20min. This occurrence is caused by the existence of minimal colloidal entrapment and low shear resistance prior to 20mins.

Whereas in fig. 9, all the particle sizes with exception of the sum of particles were seen fused together at about t = 18min - infinity. Then there is existence of potential hump between the rest of particles and the sum, from t = 2min - infinity. Generally, the behavior pattern of the particles in figs. 7 and 9, indicates the existence of minimal energy barrier, obtainable in a system with high coag-flocculation rate constant. The curves in figs. 8 and 10 show traits of system with relatively high zeta potential in existence which is more pronounced in fig. 10. This is evidence that there is difference in concentration of TDSS between the particles sizes and the sum. In figs. 8 and 10, the singlet and sum of the particle are seen decreasing linearly with time though the occurrence is more in fig. 10 which is expected because of its high $\tau_{1/2}$ with the corresponding low K. This situation does not guarantee effective coag-flocculation process. Fig. 8, show that the high shear resistance existing between the pairs of singlet – sum and doublet – triplet were overcome at 8min resulting in the agglomeration of singlet, doublet and triplet into a unique floc, with relatively low repulsive forces between them and sum of particles. This phenomenon was neutralized at t = 30min resulting in aggregation of various class of particles into large floc ready to be sweep away under gravitational influence at the optimum coag-flocculation settling time. Whereas in fig. 10, the high shear forces persisted until 40min, witnessed the formation of micro-floc resulting from the aggregation of singlet, doublet and triplet. The implication is that existence of this high shear forces resulted in resistance to particle collision.

4.7 Particles aggregation profile at optimum settling time and pH.

The coag-flocculation activity of MPSC and alum was compared at optimum settling time and pH and presented in figs. 11 and 12. The overview of fig. 12 show that MPSC and alum can effectively remove TDSS from PIE at the least dosage (ie. The pH domain of alum). Whereas, in fig. 11, MPSC has shown its effectiveness in removing TDSS at all dosages considered over alum. The general results indicate that MPSC performed better than alum at the pH and dosages studied except pH of 10 at 0.1g/l dosage where alum recorded a slightly higher efficiency. The remarkable advantage of MPSC over alum are the production of low volume biodegradable sludge, environmentally friendly, medically safe, capable of achieving efficient operation over a wide range of dosages in pH of 10 and 13.

CONCLUSION

This work has demonstrated the effectiveness of organic coagulant (MPSC) to remove TDSS from PIE over inorganic coagulant (alum), over wide range of dosages at optimum settling time and pH. Results reveals that the optimal conditions for process operation are: for pH 10, 93.26% TDSS removal efficiency - (alum); 84.64% TDSS removal efficiency – (MPSC) all were achieved at 0.1 g/l dosage and 40 minutes settling time, for pH 13, 44.50% TDSS removal efficiency, 0.4 g/l dosage- (alum); 92.75% TDSS removal efficiency, 0.1 g/l dosage – (MPSC). The results is in agreement with previous similar works [16] ; [17] [18] better than alum

NOMENCLATURE

K:	αth order coag-flocculation constant
$(acf)_{BR}$:	Collision factor for Brownian Transport
Σp:	Collision Efficiency
$\tau_{1/2}$:	Coagulation period/half life
Eij:	Coag-flocculation Efficiency for I and j particles.
R^2:	Coefficient of Determination
α:	Coag-flocculation reaction order
-r:	Coag-flocculation mass transfer rate
Organic coagulant:	*Mucuna prurien* seed coagulant (MPSC)
TDSS:	Total dissolved and suspended solids.

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