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Deturbidization of Pharmaceutical Industry Wastewater Using Natural Coagulant: Response Surface Methodology Applied

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Abstract – ***Mucuna prurien*** **seed, a feedstock for an eco-friendly coagulant used to deturbidize pharmaceutical Industry wastewater was investigated via response surface methodology (RSM) . This was carried out at different operating conditions such as coagulation pH (X1: 1 - 13), coagulant dosage (X2: 0.1 – 0.7g/l) and setting time (X3: 2 – 40mins). The experimental data were fitted to appropriate kinetic model, and the following results were obtained, coagulation rate constant K = 2.18E-04 (l/g.min) coagulation period τ ½ = 0.33min at coagulant dosage of 0.1g/l. Subsequently, the experimental data were also fitted to a second order polynomial equation using regression analysis and ANOVA to examine the adequacy of the developed mathematical model.**
Analysis of variance (ANOVA) demonstrated that the contribution of the quadratic model was significant for the response.
The optimization result gave 98.97% as turbidity removal efficiency at the optimal conditions of pH 13, dosage of 0.1g/l and the settling time of 40 mins. The experimental and predicted values were in close agreement. Based on the foregoing, it was suggested that ***mucuna prurien*** **seed could be a potential natural coagulant for turbidity removal in pharmaceutical industry wastewater.**

Keywords – Deturbidization, natural coagulant, pharmaceutical industry wastewater, Response Surface Methodology.

I. Introduction

Increased urbanization and industrialization in developing countries is associated with environmental pollution [1]. Majority of these pollutants emanates from industries. Wastewater from industries such as pharmaceuticals are characterized by various levels of pollutants like chemical oxygen demand (COD), biological oxygen demand (BOD), pH, temperature, turbidity, total suspended solids (TSS), Electrical conductivity and total hardness, etc [2] ; [3] . For obvious reasons, it becomes imperative that the wastewater should be treated to acceptable standard before discharge to the environment [4]. The present difficulty in wastewater treatment emanates primarily from the increasing pollution of streams, rivers and ground water by organic matter that are sparingly decomposed biologically, owing to resistance posed by these substances for self-purification qualities of the rivers as well as decomposition in conventional wastewater treatment plant [5]; [6].

Many methods are available for the treatment of wastewater, such as coag-flocculation, ion exchange, chemical precipitation, bioremediation and membrane separation processes [7];[8]; [9] among others have been used to treat various industrial wastewater.

However, many of these methods / technologies are either too expensive or not efficient in the treatment of wastewater and water. Among these methods, coag-flocculation seems to have the most potential usage in industrial wastewater treatment due to its proven efficiency, cost effective, simple to operate and environmental friendliness [10];[9].

Coagulation involves the addition of organic or inorganic substances having the opposite charge to that of the colloidal particles in the wastewater. The coagulation process occurs in successive phases intended to overcome the forces stabilizing the suspended particles in wastewater, allowing collision of particles and growth of floc. The first coagulation stage, destabilizes the particles charges, implying that the coagulants with opposite charges to the suspended solids are added to the water to neutralize the negative charges on dispersed non-settleable solids such as clay and colour-producing organic substances in the wastewater. Subsequently, the neutralized smaller particles are capable of sticking together, while the larger particles formed through the process called micro-flocs [12]; [13].

Coagulation is one of the commonly used unit operation for the treatment of water and wastewater and the mode of operation is batchwise [9]. Aluminum Sulphate is the most used coagulant. Due to its health related problem called Alzheimer disease high cost, production of large quantity of sludge post treatment hence its usage is not comparable with the environment [9]. Against this back drop, there is a shift towards the use of non-conventioanl low cost, eco-friendly and locally available coagulants [14].

Some of the non-conventional coagulants which I refer to here as natural coagulants are of both plant and animal origins. They are *Moringa Oleifera* seed, *Telfairia occidentalis* seed, *Corchorus Olitorus* seed, *Pleurotus tuberrgnum* tuber, snail shell, fish bone, chitosan among others, have been investigated [12]; [18];[14];[15] ; [13] ; [16].;[19]. Though, mucuna prurien seed has been investigated on the areas of kinetics of coag-flocculation. In line with the quest to discover the influence of coag-flocculation parameters on the treatment efficiency by employing optimization studies and response surface methodology including the optimal kinetic parameters.

Mucuna prurien is a tropical legume known as velvet beans, native to Africa and Asia. The plant is notorious for extreme itching, it produces on contact, particularly with the young foliage and seed pods. The proximate analysis showed that mucuna prurien have 20% moisture, 12% ash, 7.5% lipid, 40.75% crude protein, 5.25% carbohydrate and 8.50% crude fibre [17]. This study will also attempts to investigate the potential of mucuna prurien seed which is considered as waste in Nigeria as a coagulant for removal of turbidity and detoxification of pharmaceutical wastewater.

II. Experimentation

2.1. Wastewater Sample

The wastewater used for the study was collected from a local pharmaceutical plant situated at Anambra state, Nigeria. The characteristics result of the wastewater indicate that the initial turbidity is 11731.330g/l, implying that there is presence of high amounts of organic and inorganic matters inherent in the wastewater [17]. All the chemicals used are of the analytical grade and they were purchased at bridge head, Onitsha.

2.2. Mucuna prurien seed preparation.

The mucuna seed precursor to derivative of *mucuna prurien*-seed coagulant (MPC) were collected from the bushes around Enugwu-ukwu town in Anambra State, Nigeria. The seed husks were removed, the seed kernel, air dried at room temperature and pulverized using clean blender into fine powdered MPC, stored in a air-tight container ready for the experiment.

2.3. Coag-flocculation Operation

Experiment were carried out at room temperature in a conventional jar-test apparatus equipped with a six-unit multiple stirrer system. Appropriate dosage of MPC in the range of (0.1 – 0.7) g/l was added to 250ml of pharmaceutical wastewater. The suspension tuned to pH range of (1 – 13) by addition of 10M HCL/NaOH, and subjected to 2mins of rapid mixing (120rpm), 20mins of slow mixing (10rpm) followed by 40mins of settling. During settling, samples were withdrawn using pipette from 2cm depth and analyzed and changes in Turbidity measured in order to determine the optimal conditions with respect to pH, dosage and settling time through 2^3 - CCD and kinetic rate parameters. Manipulated variables range and levels for the process optimization are presented in Table 1, while Table 2, depicts the full 2^3 - CCD factorial design matrix with response. The experimental results of the 2^3 - CCD were studied and interpreted by software, MATLAB 7.0 to estimate the response of the dependent variable. The kinetics of coag-flocculation operation and extent of aggregation were monitored at settling time of 2,4, 8, 10, 20, 30 and 40mins. The data were subsequently fitted in developed polynomial and kinetic model equations for appropriate evaluation.

III. Theoritical Principless

3.1. Coag-flocculation kinetics

For a homogenous aggregating particles (í, j) in equilibrium state with negligible influence of gravitational buoyancy, drag, vander waals and repulsive forces [13];[20];[21]

$$\mu_i = u_i \left(\frac{\delta(nu)}{\delta\eta_i} \right) n_i S_i n V_i n_j \qquad (1)$$

Also

$$\mu_i = u_i \left(\frac{\delta(nu)}{\delta \eta_i}\right) P, T, n_j = \text{a constant} \quad (2)$$

Thus $\mu_i = \mu_i = O$

For a homogeneous phase solutions

$\mu í = \mu í + RT$ in Ci (3)

where

μ_i is chemical potential of component i

U_i is internal energy of component í

μ_i is Gibb's free energy of component í

n_i is the number of moles of component í

n_j is the number of moles of component j indicating that all moles are held constant except the í[th]

η is the number of particles

T is absolute temperature

C_i is concentration of particle component í

R is molar gas constant.

Similarly, a general model for micro-kinetic coag-flocculation of mono dispensed particle under the influence of Brownian motion is given[13].

$$C_K = \frac{dC_K}{dt} = \frac{1}{2} \sum_{i+j=k} \alpha\beta(v_i, v_j) C_i C_j - \sum_{i=1} \alpha\beta(V_i, V_j) C_i C_j \quad (4)$$

Where $C_K = dC_K/d_t$ is the rate of change of concentration of particle size K (Conc/time).

α – is the fraction of collisions that result in particle attachment. C_i and C_j are the concentrations of i and j components.

β is a function of coag-flocculation transport for Brownian, shear and differential sedimentation mechanisms V_i and V_j are the potential velocities of i and j components.

The value of β for transport mechanism is given as [22].

$$\beta_{BR} = \frac{8}{3} \frac{\varepsilon_\rho K_B T}{\eta} \quad (5)$$

$$\text{and } K_R = 8\pi RD' \quad (6)$$

Where ε_ρ is collision efficiency

η is the viscosity of effluent medium.

K_B is Boltzman's constant (J/K)

T is a absolute temperature (K)

K_R is the Von smoluchowski rate constant for rapid coagulation.

D^1 is the diffusion coefficient

From the works of [22]:[13], combination of equations 5 and 6 could be transformed to give

$$\tfrac{1}{2} \beta_{BR} = \varepsilon_\rho K_R \quad (7)$$

$$\text{or } \varepsilon_\rho K_R = 0.5\beta_{BR} \quad (8)$$

$$\text{Similarly } \tfrac{1}{2} \beta_{BR} = K_R \quad (9)$$

Also it can be shown that coag-flocculation operation is controlled by [13];[22]:[21];[23];[24].

$$\frac{-dC_t}{dt} = K C_t^\alpha \quad (10)$$

$$\text{Thus } \frac{-dC_t}{dt} = K C_t^\alpha \quad (11)$$

C_t is the concentration of TDSS at time, t. it has been shown that for practical purposes $1 < \alpha < 2$ [22];[13].

Re-arranging and integrating equation

$$\text{i.e } \int_{C_o}^{C_t} \frac{dC_t}{C_t} = K \int_o^t dt$$

Yields

$$\frac{1}{C_t} = K t + \frac{1}{C_o} \quad (12)$$

Where C_o is the initial C_t at time t = 0; C_t at upper time limit > 0

Graphical representation of equation (12) provides for k from the slope (K) and intercept as $1/C_o$.

Making C_t the subject matter, equation 11 can be solved to obtain coag-flocculation period $\tau_{½}$

$$\tau_{½} = (0.5\, C_o K)^{-1} \quad (13)$$

For microkinetics aggregation of singlets , doublets and triplets under the influence of Brownian transport mechanism as a function of time ($t \leq 40$mins) at early stages can be obtain by solving equation 4 to give the general expression of m[th] order

$$\frac{C_m t}{C_o} = \frac{\left(\frac{1}{\tau_{½}}\right)^{m-1}}{\left(1 + \frac{t}{\tau_{½}}\right)^{m+1}} \quad (14)$$

M = 1 (singlets), m = 2 (doublets), m = 3 (triplets). Evaluation of coag-flocculation efficiency is given as

$$E\% = \left(\frac{C_o - C_t}{C_o}\right) x\ 100 \quad (15)$$

3.2. Experimental Design

Response surface optimization is an improvement on the traditional used one-factor-at-a-time (OFAT) design.

The RSM uses a set of mathematical and statistical procedures to describe the interaction between the variables. This interaction is described by a polynomial model equation in relation to the experimental data, in order to continually optimize the responses [25];[15].

Thus in this study, response surface experimental design with three parameters at three levels was used to generate the experimental matrix and the model equations for the optimization. The coag-flocculation parameters are pH (X_1), MPC dosage (X_2) and settling time (X_3). The outcome of the coag-flocculation response in terms of the turbidity removal of the wastewater is highly dependent on the these parameters/manipulated variables [11].

The manipulated variables range and levels for the process optimization are presented in Table 1, whereas the 2^3 Central composite design (CCD) factorial design matrix with response are shown in Table 2. The experimental data of the 2^3 – CCD were examined and interpreted by MATLAB 7.0 software to evaluate the response of the dependent variable (response). Subsequently, the dependence of the response on these manipulated variables was determined using first and second-order polynomials as shown below

$$Y = \beta_o + \sum_{i=1}^{n} \beta_i X_i + \Sigma \qquad (16)$$

Where β_o, is the model constant, β_i – are the coefficient of the linear parameters respectively, X_i – are the manipulated variables in coded values, ε is the random error.

The critical points in the RSM plot are obtained from the quadratic polynomial equation.

$$Y = \beta_o + \sum_{i=1}^{n} \beta_i X_i + \sum_{i=1}^{n} \beta_{ii} X_{ii}^2 + \sum_{i<j}^{n} \beta_{ij} X_i X_j + \Sigma \qquad (17)$$

Where X_j and X_i represent the factors.
β_{ii} represents the coefficient of the quadratic parameters and β_{ij} represents the coefficient for the interaction parameters [18];[26].

Table 1: Optimization range and levels of manipulated process variable.

Manipulated Variable	Lower Limit(-1)	Base Level (0)	Upper Limit (+1)
pH(X_1)	1	7	13
Dosage X_2 (g/l)	0.1	0.4	0.7
Settling Time (mins)	2	21	40

Table 2: Full design matrix and response results for the experimental variables

S/No	X_1	X_2	X_3	X_1X_2	X_1X_3	X_2X_3	X_1^2	X_2^2	X_3^2	Y_1	Y_2	$\bar{Y}_{ave}$
1	0	0	0	0	0	0	0	0	0	239	241	240
2.	-1	-1	-1	1	1	1	1	1	1	604	602	603
3.	1	-1	-1	-1	-1	-1	1	1	1	918	920	919
4.	-1	1	-1	-1	1	-1	1	1	1	1288	1284	1286
5.	1	1	-1	1	-1	-1	1	1	1	380	383	381.5
6.	0	0	0	0	0	0	0	0	0	239	237	238
7.	-1	-1	1	1	-1	-1	1	1	1	348	350	349
8.	1	-1	1	-1	1	-1	1	1	1	100	103	101.5
9.	-1	1	1	-1	-1	1	1	1	1	572	575	573.5
10	1	1	1	1	1	1	1	1	1	142	144	143
11.	0	0	0	0	0	0	0	0	0	239	240	239.5
12.	-1	0	0	0	0	0	1	0	0	616	614	615
13.	1	0	0	0	0	0	1	0	0	214	218	216
14.	0	-1	0	0	0	0	0	1	0	276	281	278.5
15.	0	1	0	0	0	0	0	1	0	398	405	401.5
16.	0	0	-1	0	0	0	0	0	1	1076	1082	1079
17.	0	0	1	0	0	0	0	0	1	364	367	365.5

The experimental data was analyzed by multiple regression analysis in order to evaluate the significance of various mathematical models such as linear, interactive and quadratic terms. Analysis of variance (ANOVA) was used to examine the statistical significance of mathematical model using F-test and the significance of F-values at probability levels ($P \leq 0.05$).

Consequently, the data generated from the mathematical models were used for the construction of three dimensional response surface plots to investigate the relationship between the manipulated and dependent variables [18].

IV. Results and Discussion

4.1. Coag-flocculation Efficiency at optimal pH and settling time.

The operational efficiency graphically presented in figure is obtained upon evaluation of equation 15.

Where E% is efficiency, C_o, C_t are TDSS concentrations at time zero and t, respectively. The figure depicts that at optimum pH and settling time, the variation of efficiency. E% depends on the coagulant dosage (0.1, 0.2,0.3, 0.4, 0.5, 0.6, 0.7)g/l. The general features of figure 1, indicates that the coag-flocculation process was fast at early minutes with about 70% efficiency recorded at 4mins for all the dosages considered, confirming that there were minimal influence of repulsive forces among the particle kernels and why the observed trend in figure 1, appear to almost floc together. The implication shows that there is near particle bridging and sweep floc at early minutes of the process. Best rest was obtained at the least coagulant dosage of 0.1g/l with increased turbidity removal efficiency of 92.75% for pH of 13 and 40mins settling time. This phenomenon is linked to particles charge neutralization and adsorption mechanism in action. This is an indication that the cationic polymer (MPC) has high charged density because low dosages of polymers have been found to achieve a fast and efficient removal of turbidity as reported by [13];[19];[27].

However, at a longer settling time/sedimentation for all the dosages considered satisfactory efficiency >85% were obtained at the same pH of 13 though 0.1g/l dosage produced the highest.

The implication is that the coag-flocculation process of MPC in pharmaceutical wastewater was more effective in high alkaline medium.

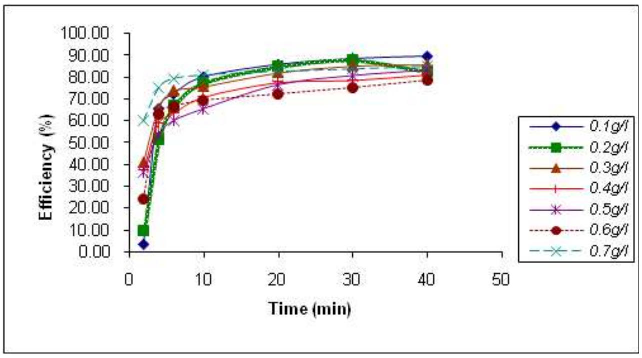

Fig.1; Efficiency as a function of time for varying dosage at constant pH

4.2. Coag-flocculation Kinetics

This subsection attempts to highlights the activities of the particle kernels as they tend to adsorp on the coagulant (MPC) surfaces in a homogenous system. Equations 1 and 2 in subsection 3.1, gave credence to the fact that i and j particle components needs reasonable amounts of chemical potentials (μ) and Gibb's free energy (G) for them to be propelled onto adsorption on the surfaces of the coagulant, if the conditions are appropriate (i.e minimal effects of gravitational, buoyancy, drag, vander waals and repulsive forces). Equation 4, accounts for the rate of depletion of i and j particle components in wastewater sample. Upon evaluation of equation 4, coag-flocculation kinetic parameters presented in Table 3 were generated.

Table 3: Coag-flocculation kinetic parameters and linear regression coefficient of MPC at varying dosage and pH of 13.

Parameter	0.1g/l	0.2g/l	0.3g/l	0.4g/l	0.5g/l	0.6g/l	0.7g/l
Y	2.18E-04 X+2.176E-03	1.51E-04 X+2.267E-03	1.3540E-04 X+2.5965E-03	9.215E-05 X+2.2123E-03	1.20E-05 X+1.0726E-03	6.846E-05 X+2.2946E-03	8.92E-05 X+3.877E-03
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	0.783	0.743
K (l/g. min)	2.18E-04	1.51E-04	1.3540E-04	9.215E-05	1.20E-05	6.846E-05	8.92E-05
K_R(l/min)	1.5417E-19	1.5468E-19	1.5750E-19	1.5341E-19	1.5699E-19	1.5699E-19	1.5772E-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
ε_p (g^{-1})	2.7728E+15	1.9206E+15	1.7222E+15	1.1713E+15	1.5254E+15	8.7022E+14	1.1339E+14
τ ½ (min)	0.33	0.48	0.54	0.79	0.60	1.06	0.81
(-r)	2.18E-04C_t^2	1.51E-04C_t^2	1.3540E-04C_t^2	9.215E-05C_t^2	1.20E-05C_t^2	6.846E-05C_t^2	8.92E-05C_t^2
C_o (g/l)	459.5588	441.1116	385.1338	452.0183	932.3140	435.8058	257.9314

The overview on the MPC results posted in Table 3, show that all the coagulation period $\tau_{½}$ values recorded with the corresponding relatively high coagulation rate constant K for different dosages considered at the same pH medium, are capable of achieving maximum coag-flocculation. This is expected because all the $\tau_{½}$ values obtained except that of 0.6g/l dosage are within sub-minutes and k having a link with the rate of particle aggregation and $\tau_{½}$. Consequent on this low $\tau_{½}$ value is a necessary condition for high K value for effective and efficient coag-flocculation operation which invariably translates to high response value (turbidity removal efficiency). However, optimum performance was achieved at 0.1g/l dosage, giving credence to the high potency value of the chosen coagulant (MPC) in high alkaline medium. Graphical representation of equation 12 as a linear plot is shown in figure 2, there from, the slope and intercept were evaluated as K and 1/Co respectively.

Observations from Table 3, show that, majority of the R^2 are greater than 0.667, indicates that 66.7% of the variability of the experimental data is explained by the kinetic model, showing relatively good fit of the model. However, the optimum coefficient of regression R^2 is 0.925 i.e 92.5% variability.

In general, there is insignificant variation in the values of K_R, ε_ρ and β_{BR}, indicating minimal variation in the operating temperature, because the experiment was conducted under room temperature. Equation 14 is employed to ascertain how each class of particle behaves in a coag-flocculation operation.

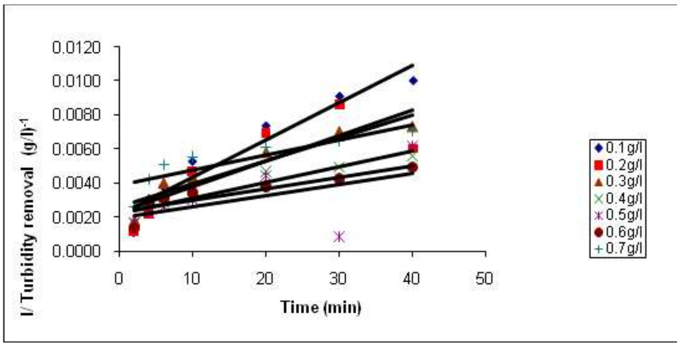

Fig.2: Rate of turbidity removal for dosage varying medium at pH of 13.

4.3. Statistical Analysis

An empirical relationship between the response and independent variables as expressed by second-order polynomial equation with interaction terms are analyzed using response surface methodology (RSM). The empirical model was developed in order to understand the interactive correlation between the response and the process variables. The results of analysis of variance for the response shown Table 4, depicts the effects of manipulated variables on the turbidity removal (response) and also Table 5, presents sequential model sum of squares and error results for the response.

Table 4: Result of ANOVA for Turbidity removal model.

Variables	Coefficient	Se	tstat	Pval	Fstat
Regression	341.6690	76.656	4.4572	0.0029461	Sse = 2.2465 x 10^5
X_1	-166.5500	56.65	-2.94	0.021715	dfe = 7
X_2	53.4500	56.65	0.9435	0.37684	dfr = 9
X_3	-273.6000	56.65	-4.8296	0.0019003	Ssr= 1.6049 x 10^6
X_1X_2	-175.4375	63.337	-2.7699	0.027698	F = 5.5564
X_1X_3	-11.1875	63.337	-0.17663	0.8648	Pval = 0.017052
X_2X_3	15.0625	63.337	0.23781	0.81884	
X_1^2	-3.0458	109.45	-0.027829	0.97858	
X_2^2	-78.5458	109.45	-0.71767	0.49621	
X_3^2	303.7042	109.45	2.7749	0.027498	
	R^2 = 0.8772	Adj R^2 = 0.7193			

Table 5. Sequential model sum of squares and error results for the response

Variables	Coefficient	Se	tstat	Pval	Fstat
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X_3	-273.6000	56.65	-4.8296	0.0019003	Ssr= 1.6049 x 10^6
X_1X_2	-175.4375	63.337	-2.7699	0.027698	F = 5.5564
X_1X_3	-11.1875	63.337	-0.17663	0.8648	Pval = 0.017052
X_2X_3	15.0625	63.337	0.23781	0.81884	
X_1^2	-3.0458	109.45	-0.027829	0.97858	
X_2^2	-78.5458	109.45	-0.71767	0.49621	
X_3^2	303.7042	109.45	2.7749	0.027498	
	R^2 = 0.8772	Adj R^2 = 0.7193			

The quadratic regression has a large F-value and the P>F value is less than 0.05 (95% confidence level), implying that the model is significant.

The linear term, X_3 has the highest F-value and the lowest P > F values, implying that the setting time has the greatest effect on the turbidity removal, followed by pH (X_1) and the coagulant dosage (X_2) as can be observed from Tables 4 and 5.

Also Table 5, the mean square of X_3 (settling time) has the highest value with the corresponding high F and low P – values respectively, hence reiterating the fact that settling time (X_3) has the highest effect on the system for turbidity removal. The error value accounts for the inadequacy of the model to represent the data in the experimental domain at points which were not included in the regression.

Consequently, the second-order model tested at the 95% (0.05) confidence level obtained for removal of turbidity from pharmaceutical industry wastewater – MPC system is as follows.

$$Y = 341.6690 - 166.5500X_1 - 273.6000X_3 - 175.4375X_1X_2 + 303.7042X_3^2 \quad (18a)$$

Equation 18a is the general model equation with the significant coefficient for the process.

Rewriting equation 18a in terms of the actual factors/variables, the model equation is as follows.

%Y response for turbidity removal = 341.6690 – 166.5500*pH – 273.6000* settling time – 175.4375* pH* dosage + 303.7042* settling time^2 (18b)

The main graphical representation in RSM is the 3D-Surface plots shown in figures 3-5. These were generated by plotting equation 18a and allows to evaluate from qualitative point of how the activity of the whole system operates. Generally, in Table 4, the values of 'P' for the coefficients estimated indicate that among the tested variables used X_1, X_3, X_1X_2, and X_3^2 are significant model terms. A mere observation of equation 18a indicate that quadratic term of X_3 (X_3^2) has a positive sign, implying that the turbidity removal increases when the sample medium was left to settle for longer time. This gave credence to the result displayed in the subsection of coag-flocculation efficiency at optimal pH and settling time of this work. Hence having a positive and synergistic effect on the percentage turbidity removal. Whereas, the other variables X_1, X_3, and X_1X_2, with negative signs shows that they have negative and antagonistic effects on the percentage turbidity removal if increased, but favors turbidity removal as it decreases. This is in line with the works reported by [25];[18].

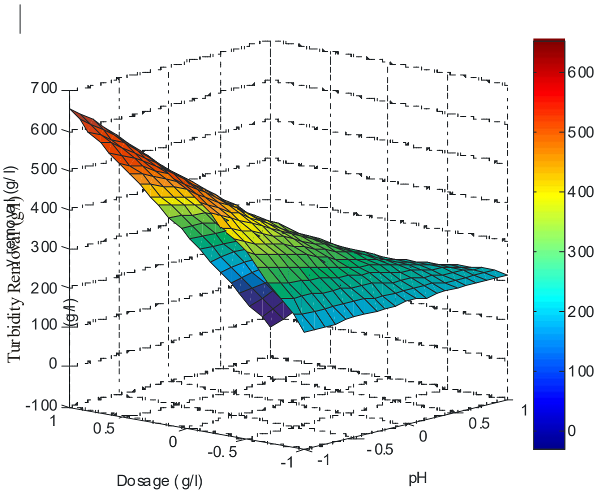

Fig. 3: Surface plot showing interaction of pH and dosage.

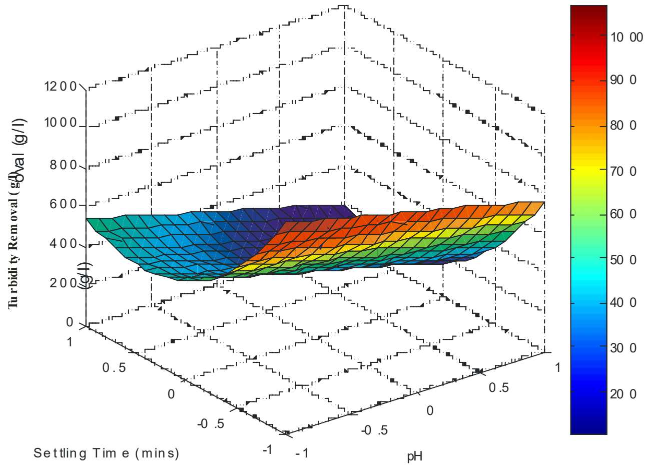

Fig. 4: Surface plot showing interaction of pH and settling time.

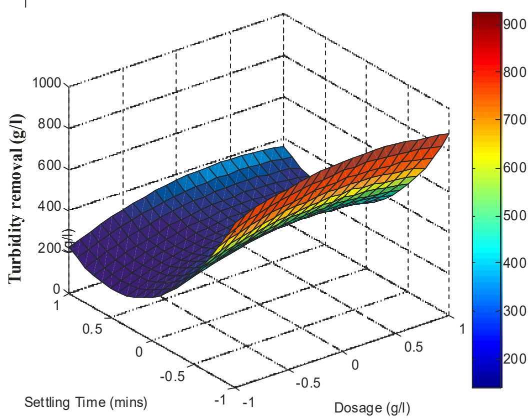

Fig. 5: Surface plot showing interaction of dosage and settling time.

Moreover, the quadratic term indicates presence of curvature on the 3D surface plots and the positive sign attached to coefficient of quadratic term X_3^2 in equation 18a, reveals that the quadratic curves for X_3^2 are convex. This means that removal of turbidity increases with increase in settling time and pH at the minimal coagulant dosage [11]. Table 4, shows that the value of the correlation coefficient of R^2 of 0.8772, indicate that only 12.28% of the total variation could not be explained by the empirical model. Also R^2 is reasonably in agreement with the R^2_{adj} of 0.7193 for the quadratic model.

4.4. Process Optimization and Analysis.

The optimization results was obtained by solving equation 18a as interpreted by MATLAB 7.0 are presented in Table 6.

This was applied to determine the optimal conditions for minimizing turbidity, the optimal pH, dosage and settling time were recorded at 13, 0.1g/l and 40mins, respectively.
Under these conditions, the turbidity was reduced from initial 117310.330g/l to 1206.6g/l, translating to 98.97% turbidity removal from the system. The high performance recorded at pH 13 is expected because at high alkaline medium, ensures high solubility of the coagulant (MPC), hence exposing a larger surface area for adsorption of total dissolved and suspended solid particles. This accounts for its high potency at that pH. At these conditions, the experimental removal efficiency of turbidity was 92.75%, which is in close agreement with the values predicted by the developed mathematical models. The 3D-surface plots illustrating turbidity removal as the response, and optimal conditions for the two interacting variables located inside the design boundary are presented in figures, 3-5. Observations from the figures indicates that there were significant interactive effects on turbidity removal between pH and dosage, (X_1X_2) significant effects of linear terms of X_1X_3, and quadratic term of X_3^2. It is remarkable to note that the values of responses are tied to the intensity of the colour of the plots. For the surface responses in figures 3-5, the residual turbidity results are 100g/l, 200g/l and 200g/l, respectively.

Table 6: Process optimization results for Turbidity removal

Sample	X_1 (pH)		X_2 (Dosage)		X_3 (Settling) time		$Y_{Turb.}$ removal g/l
	CV*	RV**g/l	CV*	RV** (g/l)	CV*	RV** (min)	
PIW	-1.0000	13	1.0000	0.1000	-1.0000	40.0000	1206.6

PIW - Pharmaceutical Industry wastewater
CV* - Coded Value
RV** - Real value

The interaction of pH and settling time in figure 3, recorded the best result at pH 7 – 13 and minimal coagulant dosage. Whereas in figures 4, and 5, representing the interactions between: pH and settling time; dosage and settling time respectively. For figure 4 pH and settling time recorded the best result at pH 7 – 13 and maximum settling time of 40mins; then figures 5, record best result at minimal dosage of 0.1g/l and entire settling time range.
In general, the 3D plots allows the researcher to analyze all variables and responses at the time and also identification of interacting variables. Hence obtaining the surface areas of the plot within which the process performs optimally. This is the advantage of employing RSM in the experiment as against the traditional "one factor at a time" (OFAT) method of study.

V. CONCLUSIONS

This study demonstrated the applicability of *mucuna prurien* seed (a feedstock for *mucuna prurien* coagulant (MPC) for the deturbidization of pharmaceutical industry wastewater, following, the optimization of the process parameters. The increasing in settling time and pH (2 – 40mins) (1 – 13) were found to have great impact on the response (percentage turbidity removal), whereas coagulant dosage beyond 0.1g/l led to returbidization of wastewater sample, hence a decrease in the percentage turbidity removal. The turbidity removal 98.97% obtained using RSM principles was better than the result obtained in the treatment of the pharmaceutical industry wastewater using "one factor at time" method (turbidity removal 92.75%). Quadratic model was developed from the experimental data and significance analyzed by ANOVA. ANOVA showed that there was significant effects on the turbidity removal percentage with increase in pH and settling time. Verification on the turbidity removal percentage values for predicted and experimental, showed that there was no significant difference between them. Therefore, MPC has shown its effectiveness in the treatment of pharmaceutical industry wastewater via RSM.

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