JEAS

JOURNAL OF ENGINEERING
AND
APPLIED SCIENCES

Journal of Engineering and Applied Sciences 12 (2018), 1-10

# Process Optimization for Turbidity Removal from Paint Wastewater Using Bio-Coagulant

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**Abstract**

Coag-flocculation process was used to treat paint wastewater with okra pod powder (OPP) as coagulant. The proximate analysis of the coagulant was carried out according to AOAC standard method. Percentage moisture, ash, fat, crude protein, crude fiber and carbohydrate content were determined for both coagulants. Jar test experiments were employed for the coag-flocculation process and response surface methodology (RSM) was used to optimize the process. A box-Behnken design (BBD) of Design Expert 9.0.6 was used to evaluate the effects and interactions of coagulant dosage, pH and stirring time on the treatment efficiency. The optimal conditions obtained were coagulant dosage of 100.53mg/L, pH of 2.001 and stirring time of 24.47mins with 90.44% turbidity removal (desirability value of 1.0). This shows that the response surface methodological approach was appropriate for optimizing the coag-flocculation process in turbidity removal in paint wastewater.

**Keywords:** Coag-flocculation, okra pod powder, pollutants, optimization, response surface methodology

## 1. Introduction

Water is abundant on the planet as a whole, but fresh potable water is not always available at the right time or right place for human or ecosystem use (Karikar & Ansa, 2004). Water pollution occurs as a result of large amount of harmful substances present in water body. The world is facing formidable challenges in meeting the rising demands for safe drinking water supply due to population growth, increasing pollution of water bodies from industrial and agricultural activities, drought and competing demands from a variety of users (Okoli, 2012). The pollution of water resources due to discharge of poor quality effluents poses a serious threat to human being and aquatic organisms since they rely on water for sustenance (Elhassadi, 2008).

The problem is more severe in developing countries where rapid population growth and industrialization has increased complexity of effluents. Latex paints generally consist of organic and inorganic pigments, due to varying degree of chemicals used; the wastewater contains appreciable concentration of carbon (biological oxygen demand (BOD) or chemical oxygen demand (COD)), suspended solid, toxic compounds and colour (Ajjabi & Chouba, 2009). The discharge of such wastewater into the environment impedes light penetration, damages the quality of the receiving stream and may be toxic to treatment process, to food chain organism and to aquatic life (Gomez, 2007). Hence, the need to treat to meet Nigerian environmental regulatory standard before discharge becomes imperative (NESRA, 2007). There are various methods of treatment of wastewaters such as advanced oxidation, membrane filtration, ion exchange, coag-flocculation and adsorption. Among these methods, coag-flocculation is selected due to its simplicity and efficient (Menkiti, et al., 2012). But the conventional coagulants used in treatment results in large sludge volume and its effects on human life, hence the need for an alternative cost effective and environmentally friendly substitute (Antov, et al., 2012).

In this study, the main objective is to use okra pod powder in removing turbidity from paint wastewater and optimizing the process using Response Surface Methodology (RSM). The RSM reveals the interaction effects of the variables, and can develop mathematical model for process prediction. For this purpose, the Box-Behnken method was applied. The design was conducted for three main variables (coagulant dosage, pH and settling time) at three level using design expert software versions 9.0.6.

## 2.0 Material and methods

### 2.1 Collection and Methods of Analyses of Paint Wastewater

The paint wastewater sample was collected from a paint industry located in Enugu, Nigeria. The characterization and analyses of the wastewater were determined using standard methods for examination of water and wastewater (APHA, 2005). The pH of the wastewater was determined using Mettler Toledo Delta 320 pH Meter, also the electrical conductivity was determined using, Digital Conductivity Meter (model number 161) and initial turbidity was measured using Digital Turbidimeter (model WZS- 185 Japan).

### 2.2 Preparation of Coagulant Stock Solution

Okra pod was procured from Ogbette main market in Enugu, Nigeria, washed, dried and ground to a fine powder using a kitchen blender to make an approximate size of 600 μ to achieve solubilization of active ingredients in the seed. The characterization of the sample was carried out based on standard method (AOAC, 2005). Two percent suspension (2 g of sample in 100 mL water) of okra pod powder was prepared and vigorously shaken for 30 min using magnetic stirrer to promote water extraction of the coagulating agent (Agarwal, et al., 2003). The suspension was filtered using Whatman No 1 filter paper. The stock solution was named okra pod coagulant (OPC). Fresh solution was prepared daily and kept refrigerated to prevent any ageing effects.

### 2.3 Coagulation-Flocculation Experiment

The conventional jar test procedure (AWWA) was employed with 300ml of paint wastewater in a beaker after adjusting the initial pH using 0.1M HCL and 0.1M NaOH. Then varying dosage of biocoagulant was added and stirred rapidly for 1 min at 250 rpm to disperse the coagulant in the wastewater. Then this is followed by a slow stirring at 40 rpm for 10min for floc formation. Then stop the stirring and allow the suspension to settle for 30min. At 5 min interval the supernatant was analyzed using Turbidimeter to determine the turbidity removal. The turbidity (NTU) can be converted to total suspended solid (TSS) using Equation (1), while the turbidity removal efficiency, E (%), was evaluated using Equation (2).

$$TSS\ (mg/L) = (TSS_f).\ T \quad \text{(MetCalf \& Eddy, 2003).} \qquad (1)$$

where T = Turbidity in NTU; $(TSS_f)$ = Conversion factor to TSS = 2.35

$$E\ (\%) = \frac{N_o - N_t}{N_o} \qquad (2)$$

$N_o$ = Initial particle concentration and $N_n$ = particle concentration at time, t. The range of the variables to be optimized was concentration of 100 to 500 mg/L, effluent pH of 2 to 10 and stirring time of 5 – 30 min.

### 2.4 Response Surface Methodology

The three levels Box-Behnken experimental design with three factors was employed to optimize the coag-flocculation process for turbidity removal. The design was composed of three levels (low, medium and high) and a total of 17 runs were carried out to optimize the chosen variables, such as coagulant dosage, pH and settling time. For the purpose of statistical analysis, the three independent variables were denoted as $X_1$, $X_2$ and $X_3$, respectively. According to the preliminary experiments, the range and levels used in the experiments are selected and presented in Table 3. The main effects and interactions between factors were determined. The experimental design matrix by the Box-Behnken design is presented in Table 4. For RSM, the most commonly used second- order polynomial equation develop to fit the experimental data and determine the relevant model terms using equation (3)

$$Y = b_o + \sum_{i=1}^{k} b_i X_i + \sum_{i=1}^{k} b_{ii} X_i^2 + \sum_{i}^{k} \sum_{j} b_{ij} X_i X_j \quad (3)$$

Where Y is the response variable to be modeled; $X_{i,}$ and $X_j$ are the independent variables which influence Y, $b_{o,}$ $b_{i,}$ $b_{ii}$ and $b_{ij}$ are the offset terms, the ith linear coefficient, the quadratic coefficient and the ijth interaction coefficient, respectively.

**Table 3**: **Experimental range and levels of BBD**

| Range/ Level | | | |
|---|---|---|---|
| Variables | -1 | 0 | 1 |
| $X_1$, Coagulant dose (mg/L) | 100 | 300 | 500 |
| $X_2$, pH | 2 | 6 | 10 |
| $X_3$, Stirring time (min) | 5 | 15 | 30 |

### 3.0 Results and Discussions
### 3.1 Characterization Results

#### 3.1.1 Characteristic of paint wastewater

The characteristic of paint wastewater are shown in Table 1. The values in Table 1 indicated the presence of total suspended solid, total dissolved solid, which contributed to observed turbidity and cloudiness of PW. This justified the treatment of the wastewater.

**Table 1: Characterization of Paint wastewater (PW)**

| pH | T(NTU) | E.C | TDS | Fe | $SO_4^{2-}$ | $NO_3^-$ | $Cl^-$ | TSS | BOD | Temp |
|---|---|---|---|---|---|---|---|---|---|---|
| 6.68 | 339.63 | 654.43 | 186.0 | 10.68 | 38.17 | 0.136 | 20.80 | 248.86 | 876.50 | 27 |

T: turbidity; TH: total hardness (mg/LCaCo$_3$); EC: electrical conductivity; BOD: biological oxygen demand, * Temp in ºC, other parameters in mg/L

#### 3.1.2 Okra pod powder (OPP)

The proximate analyses of OPP are presented in Table 2. The protein content was 23.0%, this proves that OPC is a good precursor for coagulant.

**Table 2: Characterization of Okra pod Powder (OPP)**

| | Moisture (%) | Ash content (%) | Fat Content (%) | Crude Protein (%) | Crude fiber (%) | Carbohydrate (%) |
|---|---|---|---|---|---|---|
| OPP | 12.0 | 7.2 | 11.0 | 23.0 | 13.5 | 33.3 |

### 3.2 Box-Behnken Statistical Analysis

The BBD matrix for experimental design and observed response for percent removal of turbidity are presented in Table 4. From the table, it shows that almost all the runs give an acceptable quality of coagulated water excerpt for runs 1, 5, 7, 8, 13 and 17. Also from the results, it is run 14 that gave the optimum coagulation condition with high percentage of turbidity removal. Although run 12 provide high percentage removal, but they utilized higher coagulant dosage. The conditions for run 14 were dosage 100mg/L, pH of 2 and settling time of 24.5.

**Table 4: Box-Behken design matrix for experimental design turbidity removal using OPC**

| Run | FACTORS | | | % Turbidity Removal (OPC) |
|---|---|---|---|---|
| | $X_1$ | $X_2$ | $X_3$ | |
| 1 | -1 | 1 | 0 | 29.66 |
| 2 | 1 | -1 | -1 | 55.68 |
| 3 | 1 | -1 | 1 | 71.25 |
| 4 | 1 | -1 | 0 | 66.33 |
| 5 | 1 | 1 | 1 | 34.02 |
| 6 | -1 | 0 | 0 | 50.50 |
| 7 | 0 | 1 | 0 | 34.71 |
| 8 | -1 | 0 | -1 | 39.16 |
| 9 | -1 | 0 | 1 | 63.26 |
| 10 | -1 | -1 | 0 | 84.09 |
| 11 | 1 | 0 | 1 | 46.52 |
| 12 | 0 | -1 | 0 | 92.72 |
| 13 | -1 | 1 | 1 | 33.80 |
| 14 | -1 | -1 | 1 | 90.42 |
| 15 | 0 | 0 | 1 | 61.24 |
| 16 | 0 | -1 | 1 | 86.63 |
| 17 | 0 | 1 | 1 | 41.44 |

The experimental data were statistically analyzed by multiple regression analysis using the Design Expert software version 9.0.6. The response variable and test variables were related by the following second order polynomial equation.

$$Y_{OPC} = 105.16701 - 0.063956X_1 - 14.15601X_2 + 1.27380X_3 + 5.3623X_1X_2 + 1.05424X_1X_3 - 3.21568EX_2X_3 + 1.66837EX_1^2 + 0.58279X_2^2 - 0.026795X_3^2 \quad (4)$$

Where $X_1$ =Coagulant dosage, $X_2$ = pH, $X_3$ = stirring time respectively. The coefficient in front of $X_1, X_2\ and X_3$ represent the linear coefficient while coefficient in front of $X_1*X_2$, $X_1*X_3$, $X_2*X_3$ represent the interaction between factors and ${X_1}^2$, ${X_2}^2$ and ${X_3}^2$ represent the quadratic effect respectively.

Performing the analysis of ANOVA for the quadratic model was required to test the significance and adequacy of the model. From Table 5, it shows that the model, linear ($X_1$, $X_2$ and $X_3$), the interactive terms ($X_1X_2$) and the quadratic terms ($X_1^2$, $X_2^2$) were significant, with small p-value less than 0.05. The coefficient of determination $R^2$ is close to 1, which indicates a better correlation between the experimental data and predicted (Shama et al., 2009). Also the adjusted $R^2$ and predicted $R^2$ are in reasonable agreement which shows the model is significant (Abu Amr et al., 2014). The Adequate Precision (AP) ratio should be higher than 4 for the predicted model to be used to navigate the space. For this study, AP for the model is 23.4595, which is an adequate signal for the model. It also suggested that the data obtained through predicted quadratic model is reliable, and can be used to navigate the design space (Kousha et al., 2012). The coefficient of variation (CV) and standard deviation (SD) indicates the degree of precision. Low values of CV and SD show the adequacy with which the experiment was conducted. In this study, a CV value was 7.8567while an SD value was 4.3754 for OPC. Based on F-ratio and p-value the insignificant factors are discarded resulting in the final equation 5.

**Table 5: ANOVA Table for removal of turbidity**

| Source | OPP | |
|---|---|---|
| | F-value | Prob. Value |
| Model | 45.80562 | 1.92E-7 |
| $X_1$ | 5.6438 | 0.034197 |
| $X_2$ | 224.6438 | 1.15E-8 |
| $X_3$ | 29.30448 | 0.000212 |
| $X_1X_2$ | 22.4343 | 0.000613 |
| $X_1X_3$ | 1.1473 | 0.30705 |
| $X_2X_3$ | 2.1944 | 0.000576 |
| $X_1^2$ | 11.0471 | 0.006786 |
| $X_2^2$ | 8.008 | 0.01637 |
| $X_3^2$ | 2.024 | 0.182559 |

| Response | | $R^2$ | $R^2_{adj}$ | AP | SD | CV | PRESS |
|---|---|---|---|---|---|---|---|
| Turbidity removal | OPP | 0.9740 | 0.9528 | 23.4595 | 4.3754 | 7.8567 | 800.80 |

AP: adequate precision; SD: standard deviation; CV: coefficient of variation; PRESS: prediction error sum of square

$$Y_{OPC} = 105.16701 - 0.063956X_1 - 14.15601X_2 + 1.27380X_3 + 5.36233X_1X_2 - 3.21568X_2X_3 + 1.66837X_1^2 + 0.58279X_2^2$$

### 3.2.1 Test for significance of regression model

A good estimated regression model explains the variation of the dependent variable in the sample. If the points of the residual plot approximate a straight line, then the normality assumption is satisfied. Normality indicates whether or not a set of data is normally distributed by plotting the data against the theoretical normal distribution in order to form an approximate straight line (Montgomery, 2005).

Normalization plots indicated in Figure 1 help in judging if the model is satisfactory. The first plot, normal probability is shown in Figure 1. The data were plotted against a theoretical normal distribution in such a way that the points should form an approximate straight line and a departure from this line would indicate a departure from a normal distribution. From the result, the data points are slightly deviating from the normal distribution given, but not very critical (Antony, 2003). Also the second plot of residuals versus the fitted value (Figure 1) shows that the data points are scattered randomly and does not form a trend. However, all the data points in the plot are within the boundaries marked by the red lines. Therefore, there are no outlier data. Lastly, the predicted versus the actual (Figure 1), the data point are distributed randomly on the 45 degree line, indicating that the model provides an acceptable fit for the experimental data. The data also indicate an adequate agreement between experimental data and the output from the model (Zainal-Abideen, et al., 2012).

(a) (b) (c)

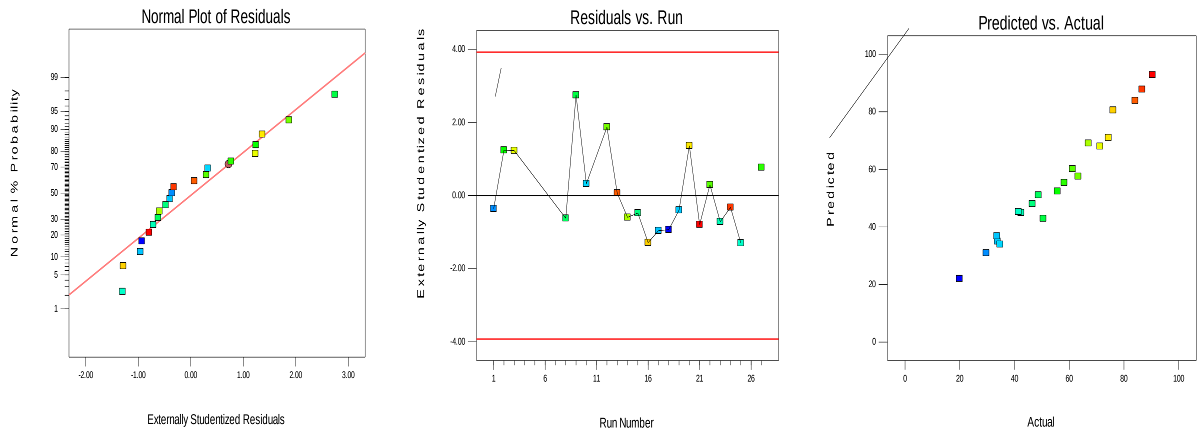
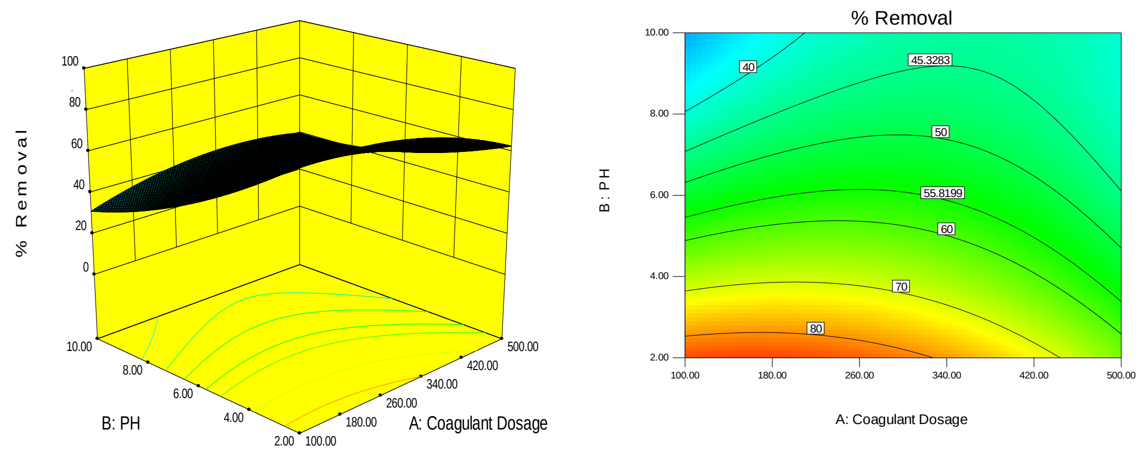


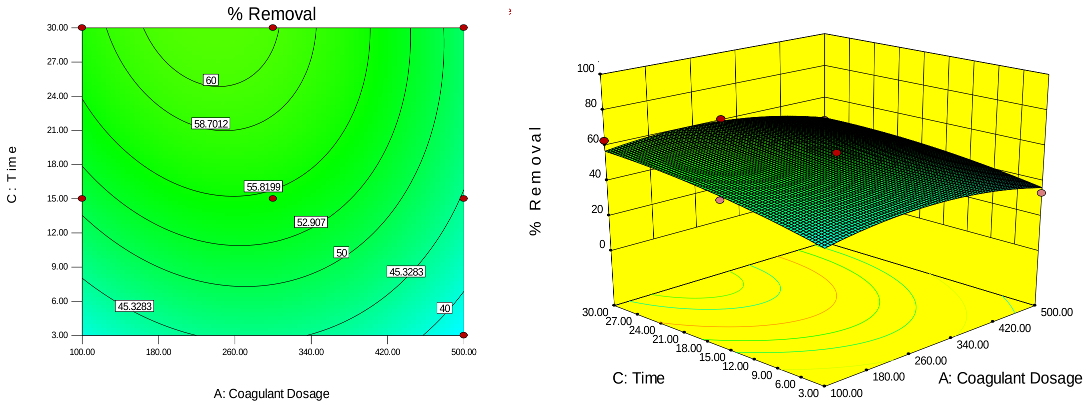

**Figure 1: Normalization plots: (a) Normal plot of residual, (b) residual vs runs and (c) predicted vs actual for OPC.**

Figure 2 shows the 3-D surface and 2-D contour plots, respectively. The 3D response surface plots are the graphical representation of the regression equation used to visualize the relationship between the response and experimental levels of each factor. It also provide routine avenue to observe the surface area of the plot within which the process performs at optimal level based on the effects of the interaction of the variables under consideration. The interactions of two factors are reflected in the contour of the plots, so that rounded contour line indicates a weak interaction of two factors and a distorted contour indicates a significant interaction of two factors (Holetz, et al., 2003). In figure 2a, the contour is distorted which indicates a significant interaction of coagulant dosage vs pH. In figure 2b, the contour plot was almost circular, indicating that the dosage vs settling time is not significant. In figure 2c, the contour is distorted showing that the interaction between pH vs settling time is significant. The highest percentage turbidity removal of 92.72% was recorded after 30 min settling time.

(a)




(b)




(c)

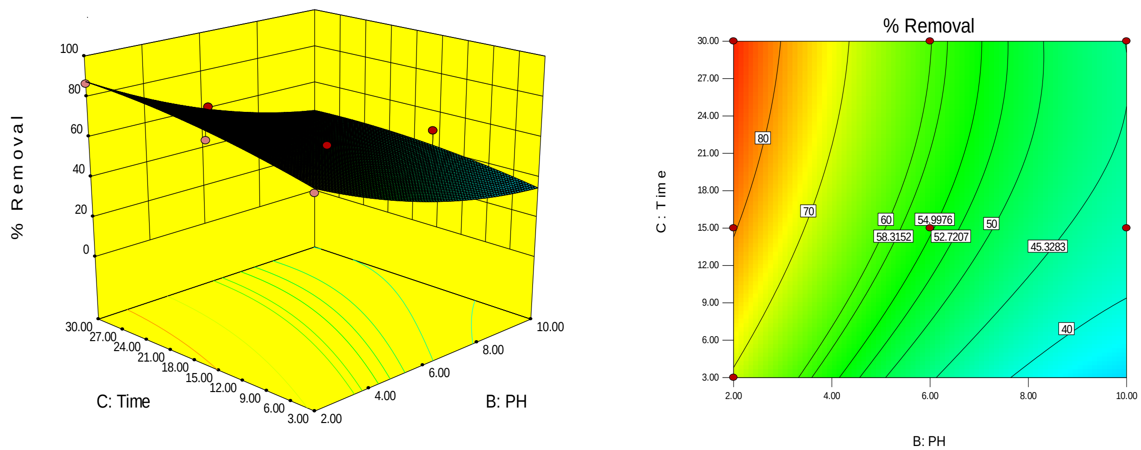



**Figure 2: Response surface and contour plots for the effect of (a) dosage vs pH, (b) dosage vs settling time (c) pH vs settling time for turbidity removal in PW using OPC**

This means that the removal of turbidity increases with coagulant loading depending on a particular pH range and stirring time. 90.0% maximum removal was achieved at 100mg/L and stirring time of 25min at pH 2. This result is similar with the report obtained by Yang & Qui, (2010).

### 3.2.2 Optimization using the desirability functions

Optimization using the desirability function was carried out using Design Expert software version 9.0.6. The aim is to optimize the desired maximum goal set for each factor and response. The results are shown in figure 5 and 6. Using these conditions, the maximum achieved turbidity removal was 90.44% at pH of 2.001, dosage of 100.53mg and settling time of 24.47min with desirability of 1.0.

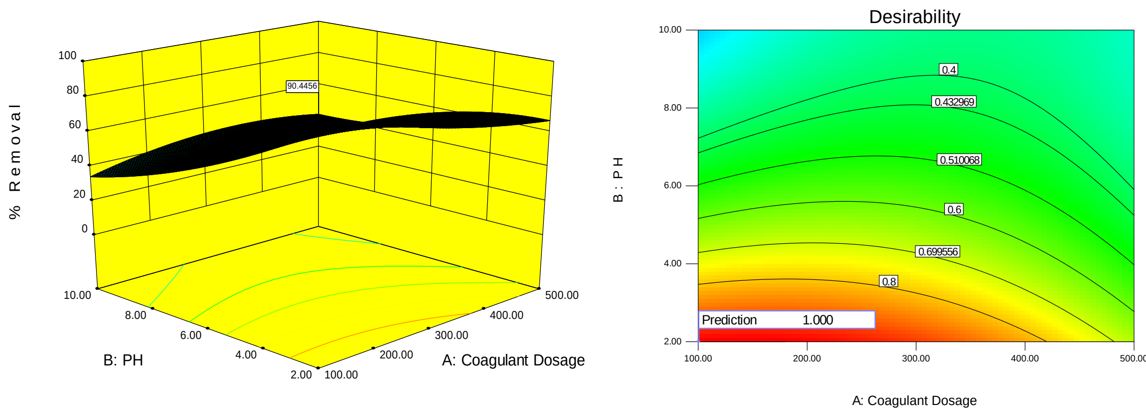



**Figure 4: Desirability function for optimization of pH and coagulant dosage for turbidity removal in PW using OPC.**

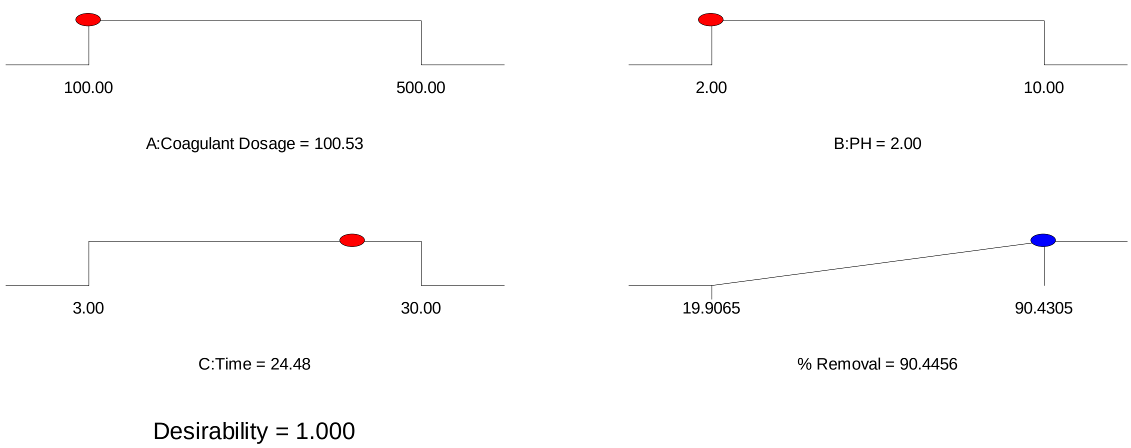



**Figure 5: Desirability ramp of optimized turbidity removal for OPC in PW**

## 4.0. Conclusion

The characterization of OPP revealed the presence of reasonable percentage of protein and carbohydrate (28% and 41.5%) which are polymeric compounds in nature as a good precursor for coagulation and flocculation process. This work has demonstrated the application of RSM in obtaining optimal conditions for coag-flocculation process with respect to turbidity removal. This demonstrates that RSM can be successfully applied for modeling and optimizing the coag-flocculation process and it is the economical way of obtaining the maximum dosage information in a short period of time and with the least number of experiments.

## References

Abu, Amr, S.S., Aziz, H.A., & Bashir, M.J.K. (2014). Application of surface response methodology (RSM) for optimization of semi-aerobic landfill leachate treatment using ozone.Appl. Water Sci. doi:10.1007/s13201-014.0156-z

Agarwal, M., Srinivasan, R. & Mishira, A. (2001) Study on flocculation efficiency of okra gum in sewage wastewater. Macromol Water and Eng.;286:560-563.

Ajjabi, L.C. & Chouba, L. (2009). Biosorption of $Cu^{2+}$and $Zn^{2+}$ from aqueous solution by dried marine green macroalga, *Chaetomorpha Linum, J. Environ. Manage*, 90, 3485-3489

Antony, J. (2003). Design of Experiments for Engineer and Scientists, Butter worth Heinemann,

Antov, M.G., Sciban, M.B. & Prodanovic, J.M (2012). Evaluation of the efficiency of natural coagulants obtained by ultrafiltration of common beans seed extract in water turbidity removal, Ecol. Eng. 49: 48-52

AOAC, (2005). Official Method of Analysis 14th Edition, Association of Official Analytical Chemist, Gaitherburg,
APHA, (2005)."Standard Methods for the Examination of Water and Wastewater", American Public Health Association, New York, NY, USA, 21st edition,
AWWA, (2012). Standard Methods for the Examination of Water and Wastewater Effluent, American Water Works Association, New York,.
El-haddad, E., 2012. Sorption and Desorption Processes of Organic Contaminants on Carbonaceous Materials (Ph.D. thesis). Fac. Of Sci. Technissche University. pp. 80.
Gómez, V., Larrechi, M. S. and Callao, M. P.(2007). Kinetic and adsorption study of acid dye removal using activated carbon. *Chemosphere*, 69,1151.
Holetz, F .B., Ueda-Nakamura, T., Filho, B.P.D., Cortez, D.A.G., Morgado-Diaz, J.A. & Nakamura, C.V.( 2003). Effect of essential oil of Ocimum gratissimum on the trypanosomatid Herpetomonas samuelpessoai. Acta Protozoologica. 42(4): 269–276. doi: 10.13140/RG.2.1.1605.5208
Karikari, A. Y. & Ansa-Asare, O. D. (2004). Physico-chemical and Microbial water Quality Assessment of Densu River of Ghana, C& IR-*Water Research Institute Accra*, Ghana.
Kousha, M., Daneshvar, E., Dopeikar, H., Taghavi, D. & Bhatnagar, A., (2012). Box-Behnken design optimization of Acid Black I dye bio-sorption by different brown macroalgae, Chem. Eng. J.179, 158-168
Menkiti, M.C., Onukwuli, O.D. (2012). Coag-flocculation of mucuna seed, coag-flocculation (MSC) in coal washery effluent (CME) using light scattering effect. *AICHE J.* 156(4), 303-313
Montgomery, D.C. (2005). Design and analysis of experiments. 6th ed. Hoboken NJ: JohnWiley& Sons. Inc.,
National Environmental (Standard for Discharge of Effluent into water or Land) Regulations (NESRA) Act.. No 5/2007
Okoli, C (2012). Development of Protein-Functionalized Magnetic Iron Oxide Nanoparticles: Potential Application in water Treatment. Doctoral Thesis
Sharma, P., Singh, L. & Dilbaghi, N. (2009). Optimization of process variables for decolorization of Disperse Yellow 211 by Bacillus subtitles using Box-Behnken design. J. Hazard. Mater. 164,1024-1029.
Yang, T., and Qiu, K. (2010). Preparation of activated carbons from walnut shells via vacuum chemical activation and their application for methylene blue removal. Chem. Eng. J. 165(1), 209-217
Zainal-Abideen, M.,Aris, A., Yusof, F., Abdul-Majid, Z. & Selamat, A. (2012.). Optimizing the coagulation process in a drinking water treatment plant – comparison between traditional and statistical experimental design jar tests, Water science and Technology 65.3.