International Journal of Applied Engineering Research ISSN 0973-4562 Volume 12, Number 23 (2017) pp. 13084-13091
© Research India Publications. http://www.ripublication.com

Treatment of Industrial Mineral Oil Wastewater - Optimisation of Coagulation Flotation process using Response Surface Methodology (RSM)

E K Tetteh[*], S Rathilal and M N Chollom

Department of Chemical Engineering, Durban University of Technology,
Steve Biko Campus (S4 Level 1) Box 1334 Durban 4000 South Africa.

[a,*]*Orcid : 0000-0003-1400-7847*

Abstract

With a wide range of applications of petrochemical products, most of the production consumes a larger amount of water than water produced. Oil in water is the major pollutant in the wastewater generated from these petrochemical and oil refinery industries. However, improper treatment when discharged will cause severe environmental issues. Therefore, it is important to recover most of the mineral oil (MO) and to purify the water for reuse. This is a good option to conserve and prolong the supply of the available water and oil. In this study response surface methodology (RSM) based on Box–Behnken design (BBD) matrix was used to optimise the coagulation flotation process and evaluate the behaviour of the manipulated variables. Three most influential factors viz pH, coagulant dosage and flotation time were adopted for this study to yield maximum removal of soap oil and grease (SOG), turbidity and total suspended solids (TSS) as the responses. The experimental results were consistent with the RSM predicted models of over 80% removal of the contaminants. This has proved to be effective to evaluate multiple factors simultaneously to identify the main factor to control for effective treatment and improve effluent quality. In this study, the coagulant dosage was deduced to be most influential factor to control.

Keywords*:* Coagulation flotation, response surface methodology, mineral oil wastewater

INTRODUCTION

The quality of fresh water sources is deteriorating due to indiscriminate discharge of various industrial wastewaters into rivers and other water bodies. Sources of industrial wastewater vary depending on the manufacturing processes involved. Industrial mineral wastewater is generated in high quantities from petrochemical industries and during crude oil refinery processes. It is characterized as a complex emulsion with high content of various petrochemical hydrocarbons, heavy metals, SOG, turbidity and TSS. If left untreated it can affect both physical and chemical receiving bodies, such as causing corrosion or clogging of treatment pipe lines, retarding plant growth due to inefficient nutrients and aquatic suffocation of fishes due to lack of oxygen [1, 2]. However, previous studies have shown that the coagulation process alone is not sufficient for the removal of these contaminants. It is therefore necessary to choose the appropriate treatment method for the elimination of these contaminants.

Coagulation flotation, which is a physicochemical process, has been seen as the most effective application over sedimentation in the wastewater treatment industries. Therefore, to obtain optimum efficiency of the coagulation process it is paramount to integrate another treatment method such as dissolved air flotation [3-5]. Coagulation flotation for treatment of industrial mineral oil wastewater involves the addition of chemical coagulants to destabilize the contaminants and the oil droplets and injection of dissolved air as a driving force for the rising up of the large oil droplet flocs formed [6]. Sulphates and chlorides of aluminium and iron are the most widely used inorganic coagulants in water and wastewater treatment. In order to overcome the negative effects of inorganic coagulants such as large amount of sludge produced, most studies are focusing on the use and optimisation of organic coagulants. The use of polymeric and synthetic organic coagulants such as poly ferric chloride Zetag8140, Zetag-7692; Z553D; FS/A50 and chitosan are also being used [7-9]. Factors such as flotation time, pH, coagulant type and coagulant dosage affect the efficiency of the coagulation flotation process and needs to be optimized [6]. The optimization of the treatment process is important due to the variation in the quality of effluent. Optimization can help to satisfy strict environmental regulations and reduce industrial mineral oil wastewater treatment costs for effective treatment efficiency.

The recent trend in global research and industrial development is advancing. This has raised concern for engineers and practicing scientists to seek effective ways of optimization. Response surface methodology (RSM) is a statistical tool for designing experiments, optimising processes and investigating the influence of various factors on the response. It describes the interaction between the set of data. It also generates models and predicts the demanded response. The RSM is superior over other traditional methods of optimization in terms of rates of experiments and multi-factor interaction over a demanded water quality [7, 8, 10]. The RSM analysis are predominantly done with the Doehlert design (DD), central composite design (CCD), the Box–Behnken design (BBD) and the three-level full factorial design. The BBD is said to be more advantageous due to fewer number of design points, thus making it less expensive to run the same number of factors [11, 12]. According to [13] the BBD coupled with RSM is a viable statistical method for optimizing the treatment of industrial wastewater. The BBD-RSM matrix also requires three operational parameters such that (+1, 0, -1) as the highest, middle and the lowest points. Evaluating the interactions of factors for the coagulation flotation process is therefore important, due to the physical and chemical nature of the conventional treatment of the industrial wastewater, which can be very complex. Therefore, RSM-BBD is the alternative option for optimisation of the treatment process to improve upon the water quality and reduced treatment cost for further downstream process.

The purpose of this study is to characterize MOW, design an experiment, optimize and investigate the effects of treatment operating parameters viz pH, coagulation dosage and flotation time using RSM-BBD for the removal of contaminants to enhance the treatment efficiency of a local South African oil refinery effluent. In this work, a study on effects of adding a polymeric organic coagulant (Zetag8140) to improve the treatment efficiency was considered. The analysis of variance (ANOVA) was also used to evaluate the contribution of the input variables on the responses surface models (SOG, turbidity and TSS) from the data generated.

MATERIAL AND METHODS

The sample used in this study was industrial oil wastewater obtained from a local South Africa oil refinery in the Kwazulu Natal province .This was characterized in accordance with the standard methods for examination of water and wastewater [14] . It contains 1134 mg/L of SOG, 2478 NTU of turbidity, 1026 mg/L of TSS and at a pH of 7.The type of polymeric coagulant used was the Zetag8140 (Zetachem South Africa) with properties shown in **Table 1.**

Table 1. -Typical properties of polymeric coagulant (Zetag8140)

Description	Properties/Value
Physical form	White granular solid
Cationic charge	Medium
Molecular weight	High
Specific gravity	0.75 g/cm^3
Bulk density	46.8 lb/ft^3
pH 1% solution	4 - 6
Apparent viscosity @25^{0}C	
Concentration	0.25%
Viscosity (cPs)	450

Coagulation flotation setup

The DAF jar tester (Model DBT6, EC Engineering, and Edmonton, Alberta, Canada) equipped with six 1L rectangular jars and 8-L recycle air saturator was used for this study. According to the process condition required, the sample pH was adjusted with 1.0 M HCl or 1.0 M NaOH stock solution. The jar test procedure followed was according to the American Standard for Testing and Materials [15] .The sample and the coagulant dose was rapidly mixed for 2 minutes at constant high speed of 250 rpm, then reduced to a low speed of 30 rpm for 15 minutes. At a constant air saturator pressure of 350 kPa, the oil droplets flocs formed was allowed to float based on the required time. All the experiment was carried out as shown in figure 1 stepwise. The percentage removal for all responses was calculated using equation (1).

$$Y_n(\%) = \frac{y_0 - y_n}{y_0} \times 100 \qquad (1)$$

Where Y_n , y_0 and y_n represents the demanded response (water parameter), initial and final water parameters.

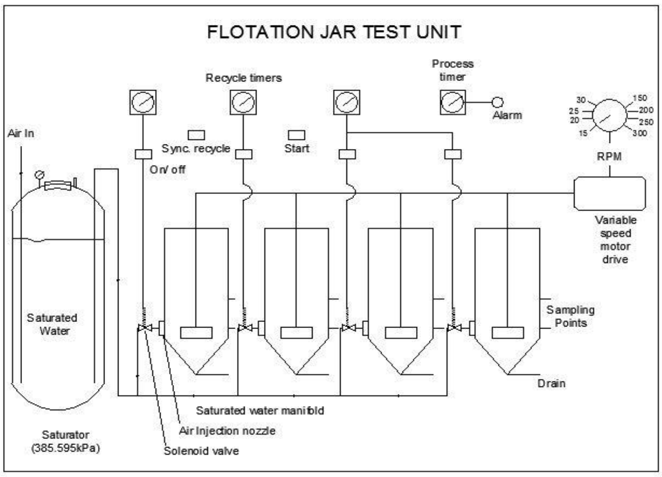

Figure 1: Schematic diagram of coagulation flotation process

Experimental design and data analysis

The software Design Expert 10.0.3 was use for the experimental design, statistical analysis of data, development of regression models and the optimization of the process conditions. Three different operating factors viz pH (X_1), coagulant dosage (X_2) and flotation time (X_3) were considered as the most vital factors. In this study, to determine the main interactions and the effects of the designated factors with respect to the targeted response whereas optimising the process to maximise treatment efficiency. The RSM-BBD matrix selected, the number of factors and responses was set to 3 and 4 respectively (**Table 2**).

Table 2: Experimental design inputs and factors

Input variables	Coded levels (X)		
	-1	0	1
X_1:pH	4	5	6
X_2:Coagulant dosage (mg/L)	30	40	50
X_3 :Flotation time (min)	10	15	20

The input variables were coded according to equation (2).

$$X_n = \frac{x_n - x_0}{\Delta x_n} \qquad (2)$$

Where X_n, x_n, x_0, and Δx_n represents the coded level, the real value, the center point value and the variable step change respectively.

RESULTS AND DISCUSSION

The Zetag8140 was used as a chemical pre-treatment of the industrial mineral oil wastewater. The efficiency of the treatment process was determined using the percentage removal of the contaminants as an indicator. The outcome from the experimental design is shown in **Table 3.** The adjustment of the pH increased the adhesion of the oil droplets to the coagulants by decreasing the repulsion between the air bubble and the oil droplets. In addition the pH destabilised the oil droplet and dissociated the metallic salt in the wastewater to enhance separation [4]. The addition of the Zetag8140 also reduced the surface tension and the air bubble charge, thereby increasing the agglomerative force of the oil droplets to form larger floc size for easy separation [16]. Increasing the Zetag8140 dosage increased the charge intensity of the ions structure via the mechanism of disperse and vigorous mixing which then increased the growth of the oil droplet floc size. All the factors were set on three different levels to generate 17-sets of experimental trials and the result as illustrated in table 3. The analysis of variances (ANOVA) was used to test the fitness of the response models as well as the effects of their interactions. To determine the most critical factors and their region of influence the coagulant dosage was deduced to be most influential factor to control. Thus in removing most contaminants during the treatment process.

Table 3: RSM-BBD matrix and experimental data

Random run	Standard run	pH	Coagulant dosage (mg/L)	Flotation time (min)	SOG (mg/L)	Turbidity (NTU)	TSS (mg/L)
14	1	0	0	0	93	81	75
15	2	0	0	0	92	84	74
11	3	0	-1	1	82	74	67
3	4	-1	1	0	89	80	72
6	5	1	0	-1	87	79	70
13	6	0	0	0	88	82	73
12	7	0	1	1	90	85	73
4	8	1	1	0	90	84	71
7	9	-1	0	1	85	84	72
17	10	0	0	0	92	86	72
8	11	1	0	1	86	85	71
1	12	-1	-1	0	85	72	65
5	13	-1	0	-1	86	81	70
2	14	1	-1	0	74	73	69
10	15	0	1	-1	91	85	73
9	16	0	-1	-1	73	75	64
16	17	0	0	0	90	83	71

Table 4: ANOVA response model lack of fits

Responses	Model Source	Standard Deviation	Actual R^2	Actual R^3	Pred. R^2	P-value	P>F value
SOG	Linear	4.43	0.5208	0.4102	0.1977	4.71	0.0195
	2FI	4.4	0.6355	0.4168	0.0382	1.05	0.4131
	Quadratic	2.7	0.9041	0.7808	0.0999	6.54	0.0194
	Cubic	2	0.9699	0.8797		2.92	0.1639
TSS	Linear	3.15	0.6194	0.5315	0.3297	3.43	0.1237
	2FI	3.53	0.6334	0.4134	0.3581	4.93	0.0722
	Quadratic	2.15	0.9047	0.7823	0.106	1.58	0.3271
	Cubic	1.92	0.9563	0.8254		2.92	1.639
Turbidity	Linear	2.3	0.5291	0.4204	0.2549	2.6	0.1854
	2FI	2.44	0.5892	0.3428	0.1101	3.32	0.1328
	Quadratic	1.54	0.8866	0.7408	0.178	0.87	0.528
	Cubic	1.58	0.9313	0.7251		2.92	1.639

Model and ANOVA analysis

The study on the interactions of the factors and selections of a model depends on the analysis of variance (ANOVA) due to the variance in normality. The models correlated with the experimental data was selected depending on the highest coefficient of determination viz actual R^2, adjusted R^2 and the predicted R^2 values. Although there were, several models derived from the responses, thus linear, 2 factors interactive (2FI), quadratic and cubic models. The suggested model to represent the correlation between all the responses and the experimental data was also based on the lowest standard deviation and p-value. The ANOVA was used to evaluate the numerical models generated from the quantitative data as shown in **Table 4.**

In other to evaluate the significance of these models types and selected the most appropriate model, thus the quadratic model with the lowest standard deviation and the p- value making the models significant. However, the cubic model was not selected due to insufficient points to analysis the results. It was found that the closer the determination (R^2) value to 1, the better the model satisfies all the ANOVA terms of model significance. In addition, at 95% confidence level, there exist a tendency of correlation between the predicted models and the observed values of the responses. Therefore, all the empirical models must be tested by doing confirmation runs, thus using the actual input variables in their corresponding units (Equation 3-5).

ANOVA and SOG model analysis

The SOG quadratic model can be used to make predictions about the response for the given levels of each factor. By default, the high levels of the factors in the model are useful for identifying the relative impact of the factors. It was found that the lack of fit (LOF) value of 2.92 is not significant relative to the pure error. Also there is a 16.39% chance that the F-value this large could occur due to noise. It was also found that the adjusted R^2 of 0.7808 is not close to the actual R^2 of 0.9041 thus the differences being more than 0.2 hence a confirmation test run might be needed when using an empirical model. The measured adequate precision value was 8.453 with a coefficient of variance percentage of 3.12%.

$$Y_1 = -48.25 + 9.5A + 3.225B + 5.45C + 0.3AB + (1.6174 \times 10^{-15})AC - 0.05BC - 2.25A^2 - 0.0425B^2 - 0.11C^2 \quad (3)$$

ANOVA and TSS model analysis

For the TSS model, the chance for the lack of fit value for a large noise to occur was found to be 32.7%, which makes it not significant to be a pure error. The supposed difference of 0.2 between the adjusted R^2 of 0.7823 is not close to the actual R^2 of 0.9047 was found to not be as close as proposed thus reduction and transformation of the models will require a confirmation test. The measured adequate precision value was 8.498 and a coefficient of variance percentage of 2.66%.

$$Y_2 = -16.8 + 12.5A + 3.43B - 1.68C + 0.075AB + 0.15AC + (5 \times 10^{-3})BC - 1.7255A^2 - 0.04225B^2 + 0.031C^2 \quad (4)$$

ANOVA and turbidity model analysis

The turbidity is the collided oil droplets presence in the wastewater. The turbidity quadratic model was found to be significant with the F-value of 6.08 and 1.33%indicating a chance for its large value to occur due to noise. The lack of fit (LOF) value was also found to be 0.87 with 52.80% that is not relevant to a pure error. The difference between adjusted R^2 of 0.7823 is not close to the actual R^2 of 0.9047 values was found to be greater than 0.2. Therefore, a reduction and transformation of the models will require a confirmation test. The measured adequate precision value was 8.498 with a coefficient of variance percentage of 2.66.

$$Y_3 = -60.5 + 17.25A + 3.25B + 2.35C - 0.125\text{AB} - 0.05AC - 0.015BC - 1.125A^2 - 0.02625B^2 - 0.045C^2 \qquad (5)$$

Effects of input factors on SOG, TSS and turbidity percentage removal

The Paretto chart represents the coded input variables, indicating their principal effect and their interactions on the response. The positive terms in each model suggest that by varying that particular factor the response increases, while the negative terms represents the verse versa i.e. the response decreases.

Fig. 2 shows that the SOG percentage removal is affected positively by coagulant dosage (B=5.75) and the interactions between pH and coagulant dosage (AB=3). Therefore increasing coagulant dosage (B) with a decrease in pH (A) will increase the SOG removal. However, **Fig. 3**, the removal of TSS shows that although (B=5) affects its removal, the control on the interactions between (AB=0.75; AC=0.75) will have the same effects. In addition, almost the same significance was noticed in **Fig. 4,** the removal of turbidity (B=3; AB=1.25). Therefore increasing coagulant dosage (B) at a lower pH (A) will increase the percentage removal of the turbidity.

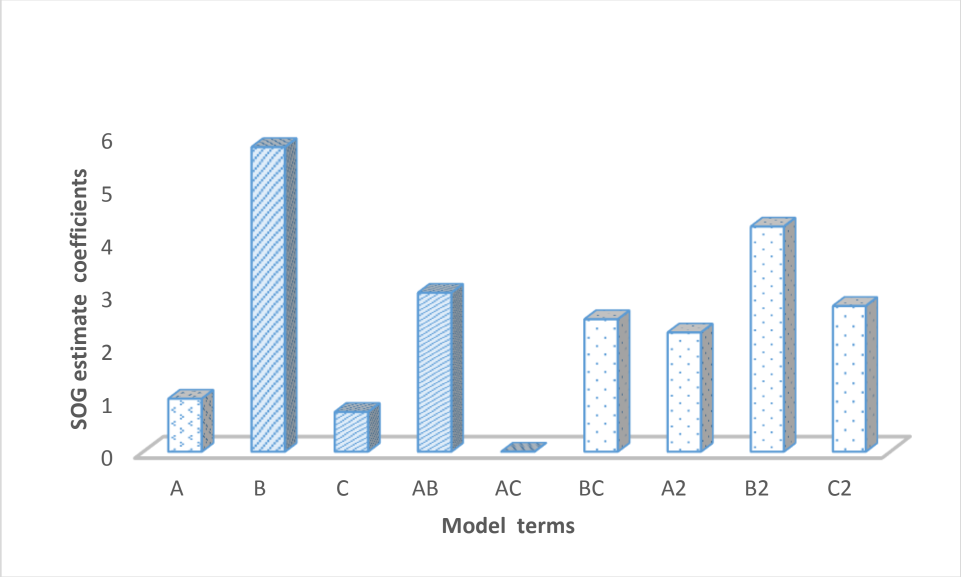

Figure 2: Parreto chart; contributions of (A,B,C) on the removal of SOG
$(Y_1 = 91 - A + 5.75B + 0.75\text{C} + 3\text{AB} - 2.5BC - 2.25A^2 - 4.25B^2 - 2.75C^2)$

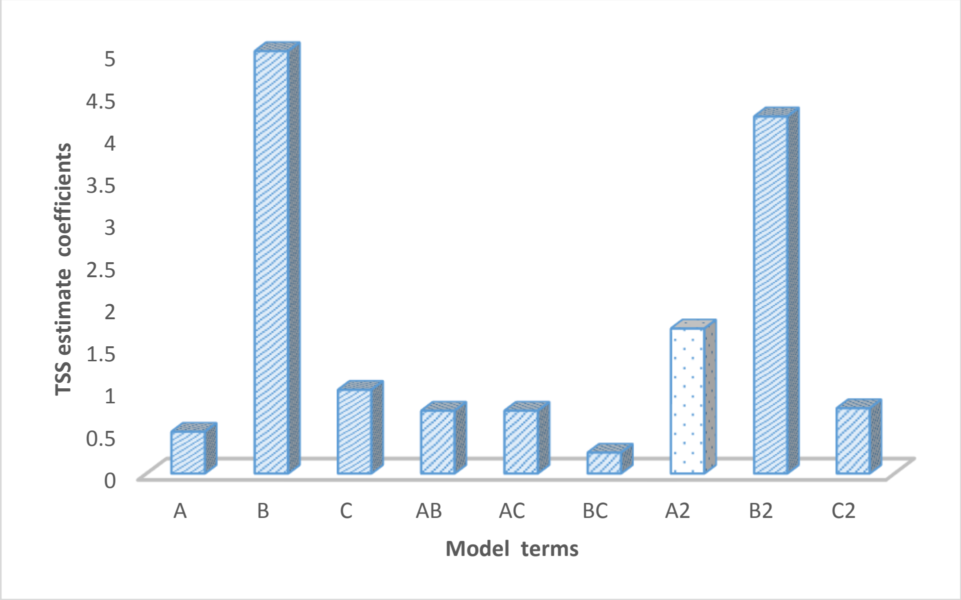

Figure 3: Parreto chart; contributions of (A, B, C) on the removal of TSS
$(Y_2 = 83.2 + 0.5A + 5B + \text{C} + 0.75\text{AB} + 0.75AC + 0.25BC - 1.73A^2 - 4.23B^2 + 0.78C^2)$

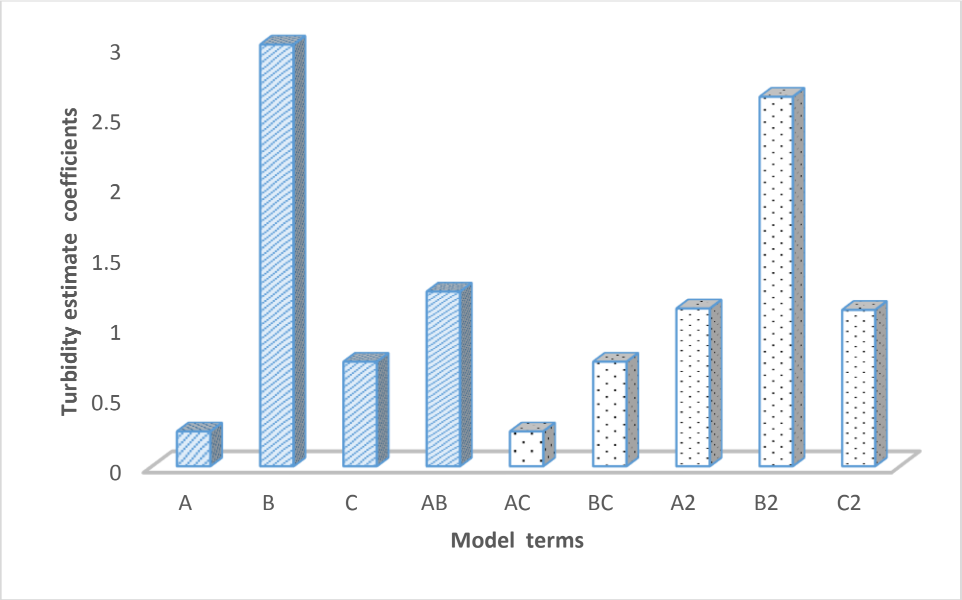

Figure 4: Parreto chart; contributions of (A, B, C) on the removal of turbidity
$(Y_3 = 73 + 0.25A + 3B + 0.75C - 1.25\text{AB} - 0.25AC - 0.75BC - 1.13A^2 - 2.63B^2 - 1.12C^2)$

Optimization of SOG, TSS and turbidity percentage removal

The addition of the Zetag8140 was important in the removal of the contaminants, thus the coagulant dosage increases the efficiency of the coagulation flotation process. Moreover, this phenomenon is due to the mechanism of the complexity of the coagulant that forms a precipitate of H^+ and OH^- ions with an increase in its solubility [1]. The optimization of the operating factors shows that there exist a good correlation between the predicted values and the experimental data as shown in **Fig. 5.**

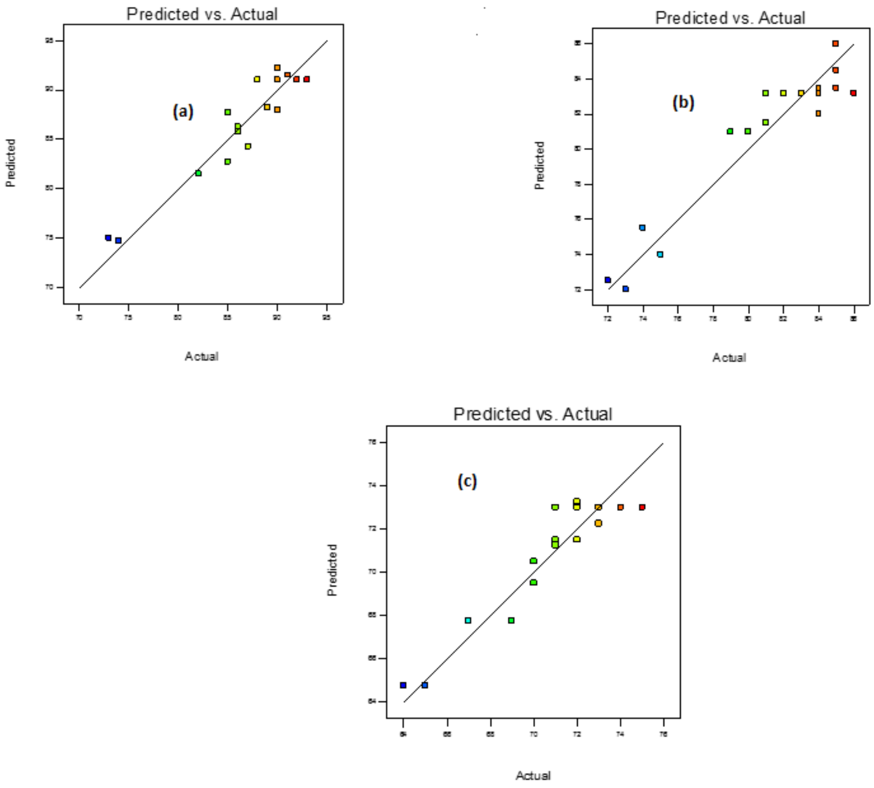

Figure 5: Comparrsison between actual and predicted values for (a) SOG (b) TSS and (c) turbidity percentage removal

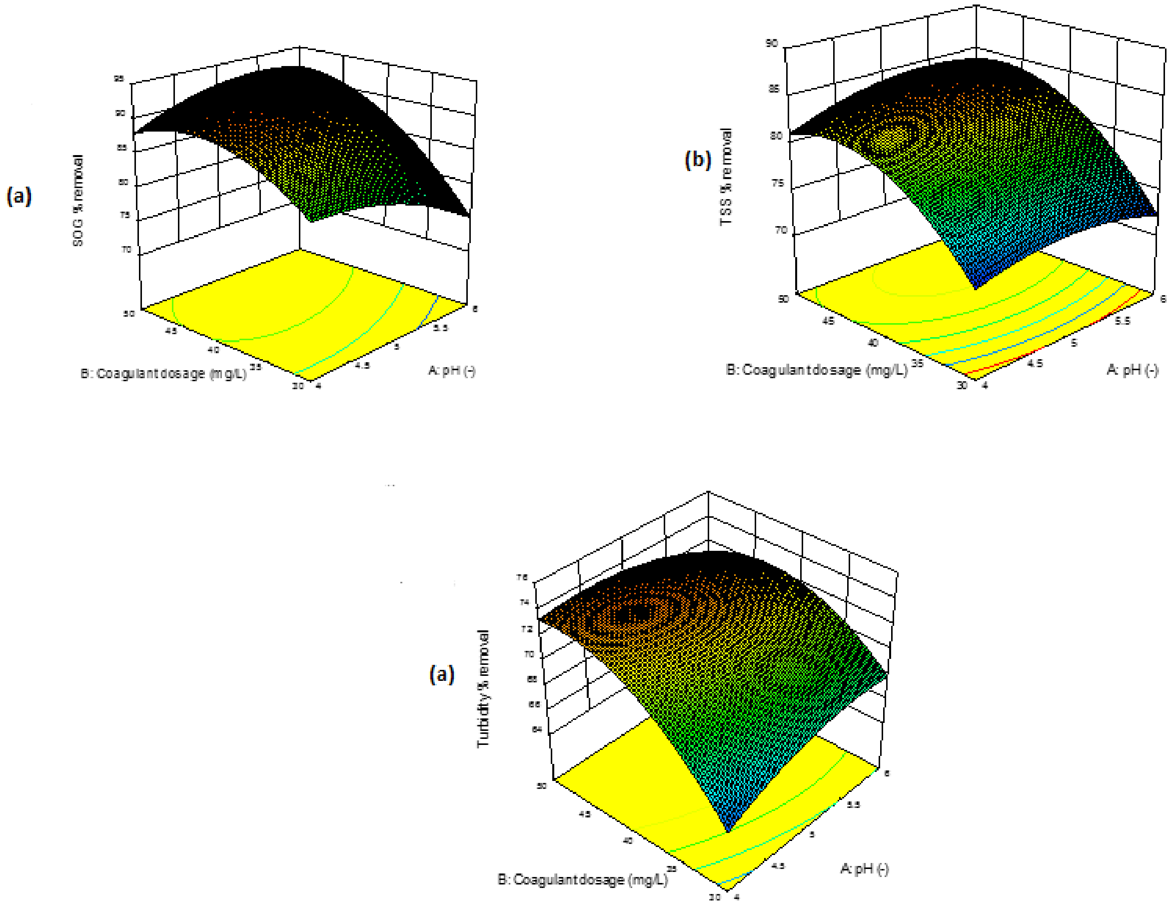

Figure 6: 3D of (a) SOG (b) TSS and (c) Turbidity percentage removal for pH vs Coagulant dosage (mg/L) at flotation time (16 min).

The desirability of the model was observed at optimum conditions of the pH at 5, coagulant dosage at 45 mg/L and the flotation time at 16 minutes to generate the 3D-graphical surface plots as shown in **Fig. 6**. It was found that a high coagulant dosage at 50 mg/L does not contribute to a noticeable increase in the removal of the contaminants by the model predictions. In addition, the 3D plots of the SOG, TSS and turbidity models shows the optimum efficiency removal as 92%, 85% and 75% respectively. In the RSM-BBD, the desirable function for the maximum removal of the models must be within the range of pH (4.5 to 5.5), coagulant dosage of mg/L and the flotation time at 15 minutes. Moreover, this optimal condition for the removal of the contaminants were determine by the response models obtained from the experimental data.

CONCLUSION

The conventional technique of coagulation flotation mechanism was employed to evaluate the effects of three factors (pH, coagulant dosage and flotation time) on the removal of contaminants (SOG, TSS and NTU) from mineral oil wastewater. The treatment efficiency of Zetag8140 enhances destabilization, neutralization and agglomeration of the oil droplet flocs for separation. The interactions and combinations of pH-coagulant dosage (AB) have a high influence on the removal of SOG, TSS and turbidity. The RSM-BBD response model shows over 80% removal of the contaminants. However, replication of the models requires a confirmation test. The designing of the experiment, statistical analysis, modelling and evaluating of the responses using RSM was found to be outstanding. In addition, the use of RSM-BBD assisted the experimenter to optimize the chemical usage and the factors for effective treatment efficiency, thereby reducing treatment cost and improving the water quality in a large scale.

ACKNOWLEDGEMENTS

The authors wish to thank FFS Refiners Research and Development Department, and Umgeni Water Process Evaluation Facility (PEF), South Africa, for their joint support in this project.

We also acknowledge Durban University of Technology for their sponsorhip

REFERENCES

[1] Z. Daud, H. Awang, A. A. A. Latif, N. Nasir, M. B. Ridzuan, and Z. Ahmad, "Suspended Solid, Color, COD and Oil and Grease Removal from Biodiesel Wastewater by Coagulation and Flocculation Processes," *Procedia - Social and Behavioral Sciences,* vol. 195, pp. 2407-2411, 2015.

[2] G. Xu, X. Xu, W. Tang, W. Liu, J. Shi, M. Liu*, et al.*, "Fighting against water crisis in China—A glimpse of water regime shift at county level," *Environmental Science & Policy,* vol. 61, pp. 33-41, 2016.

[3] J. Edzwald and J. Haarhoff, *Dissolved air flotation for water clarification*: McGraw Hill Professional, 2011.

[4] C. Rattanapan, A. Sawain, T. Suksaroj, and C. Suksaroj, "Enhanced efficiency of dissolved air flotation for biodiesel wastewater treatment by acidification and coagulation processes," *Desalination,* vol. 280, pp. 370-377, 2011.

[5] N. M. Daud, S. R. Sheikh Abdullah, H. Abu Hasan, and Z. Yaakob, "Production of biodiesel and its wastewater treatment technologies: A review," *Process Safety and Environmental Protection,* vol. 94, pp. 487-508, 2015.

[6] K. M. Mousa and H. J. Hadi, "Coagulation/Flocculation Process for Produced Water Treatment," 2016.

[7] N. Li, Y. Hu, Y. Z. Lu, R. J. Zeng, and G. P. Sheng, "Multiple response optimization of the coagulation process for upgrading the quality of effluent from municipal wastewater treatment plant," *Sci Rep,* vol. 6, p. 26115, 2016.

[8] R. Pambi and P. Musonge, "Application of response surface methodology (RSM) in the treatment of final effluent from the sugar industry using Chitosan," *WIT Transactions on Ecology and the Environment,* vol. 209, pp. 209-219, 2016.

[9] S. E. Bailey, S. Hwang, M. C. Brooks, and P. R. Schroeder, "Evaluation of Chemical Clarification Polymers and Methods for Removal of Dissolved Metals from CDF Effluent," DTIC Document2006.

[10] L. Khannous, D. Abid, N. Gharsallah, N. Kechaou, and N. B. Mihoub, "Optimization of coagulation-flocculation process for pastas industry effluent using response surface methodology," *African Journal of Biotechnology,* vol. 10, pp. 13823-13834, 2011.

[11] J.-P. Wang, Y.-Z. Chen, X.-W. Ge, and H.-Q. Yu, "Optimization of coagulation–flocculation process for a paper-recycling wastewater treatment using response surface methodology," *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* vol. 302, pp. 204-210, 2007.

[12] A. Esmaeili, E. Hejazi, and Y. Vasseghian, "Comparison study of biosorption and coagulation/air flotation methods for chromium removal from wastewater: experiments and neural network modeling," *RSC Advances,* vol. 5, pp. 91776-91784, 2015.

[13] S. Zodi, O. Potier, F. Lapicque, and J.-P. Leclerc, "Treatment of the industrial wastewaters by electrocoagulation: Optimization of coupled electrochemical and sedimentation processes," *Desalination*, vol. 261, pp. 186-190, 10/15/ 2010.

[14] APHA, "AWWA WEF.(2012)," *Standard methods for the examination of water and wastewater*, vol. 22, 2012.

[15] C. ASTM, "494," *Standard specification for chemical admixtures for concrete*, vol. 4, 1999.

[16] R. Gregory and T. F. Zabel, "Sedimentation and flotation," *MCGRAW-HILL, INC.,(USA). 1194,* p. 1990, 1990.