Available online at www.derpharmachemica.com

ISSN 0975-413X
CODEN (USA): PCHHAX

Der Pharma Chemica, 2016, 8(20):1-12
(http://derpharmachemica.com/archive.html)

Optimization of coagulation-flocculation process for particle removal from dye using natural polymers: Response surface methodological approach.

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ABSTRACT

Performance of natural polymer coagulants were studied for total dissolved solids removal from acid red dye. Response surface methodology (RSM) using face-centred central composite design (FCCD) optimized four variables of the coagulation-flocculation process including pH, coagulant dosage, dye concentration and time. Acidic solution pH increased the Total dissolved solid (TDS) removal efficiency. Accurate control of coagulant dosages gave optimum destabilization of charged particles and re-stabilization occurred at above 800mg/L dosages. Polymer performances were measured through time-dependent decrease in particle concentrations following aggregates growth. Charge neutralization, sweep flocculation and polymer adsorption were the active mechnisms in the coagulation-flocculation process. The verification experiments agreed with the predicted values with less than 4% standard error values. Overlay contour plot established an optimum condition for the multiple responses studied. The response surface methodological approach was appropriate for optimizing the coagulation-flocculation process while minimizing the number of experiments. Coagulants studied were highly effective in the TDS removal process.

Keywords: Coagulation-Flocculation**,** Crystal Ponceau 6R, Response Surface Design, Total Dissolved Solids, Natural Polymer Coagulants, multiple response optimization.

INTRODUCTION

Pollution and contamination of environment by wastewater discharges have caused several environmental, social, economic and public health problems [1]. Dye containing wastewaters are among the contaminants discharge on the environment bodies because of their toxic characteristics. The removal of these toxic contaminants from wastewater is of concern for the production of safe wastewater for environmental disposal or reuse [2]. Presently, estimation has showed that over 10,000 of different commercial dyes and pigments are available and over 7.11 X 10^7 kg/yr is produced worldwide [3]. Dye production industries such as textile, rubber, pulp, paper, plastic, cosmetics, food, pharmaceutical, leather tanning, printing, medicine, etc. and many industries that uses dyes and pigments generate wastewater characteristically high in colour, organic and inorganic contents. These dye wastewaters are toxic, carcinogenic, slow down self-purification of streams by reducing light penetration, retard photosynthetic activity and inhibit growth of biota [4-6].

The techniques used for contaminant removals from dye wastewater can be divided into three main categories; physical, chemical and biological. Physical treatments such as precipitation, ion exchange, membrane filtration, irradiation, ozonation and adsorption are widely used techniques. Physic-chemical treatment methods are coagulation-flocculation, precipitation, photo-catalysis, oxidation and chemical sludge oxidation. Lastly, biological treatment techniques used are aerobic degradation, anaerobic degradation, and living/dead microbial biomass [7]. Coagulation-flocculation is an already established method for contaminant removal from wastewater ranging from wastewater containing: BOD [8-16].

Coagulation-flocculation is considered best process because it is highly efficient, removes multiple contaminants and simple in operation [13]. It is a chemical treatment as it implies the addition of a coagulant. Typical coagulant agents are inorganic salt such as $Al(SO_4)_3$ or $FeCl_3$, as well as synthetic organic polymer [17-18]. Although these chemicals are rather effective in removing dyes and suspended matters from the aqueous solution, several disadvantages have recently arisen, such as their impact on human diseases like Alzheimer's caused by inorganic salts [19].

Natural polymer coagulants are of emerging trend by many researchers because of their abundant source, low price, environmental friendly, multifunction, and biodegradable in water. Plant-based coagulants are used more because animal-based precursors are more expensive and difficult to source [20]. Most plant-based coagulants contain soluble cationic protein. Some have been studied and they show natural coagulant ability [17, 21-25].

The mechanisms associated with different polymer coagulants include double layer compression, sweep flocculation, adsorption/charge neutralization and adsorption/inter-particle bridging [26-28]. High ionic concentration salts can cause compression of the double layer [27], which destabilizes the particulates. Sweep flocculation occurs when a coagulant encapsulates suspended particulates enhancing flocs formation. Charge neutralization refers to the sorption of two particulates with oppositely charged ions while inter-particle bridging occurs when a coagulant provides a polymeric chain which sorbs particulates [27].

Response surface methodology (RSM), a statistical design tool used for problem analysis in which a response of interest is influenced by several variables and the objective is to optimize this response. It is a combination of mathematical and statistical techniques useful for development, improving and optimizing processes and can be used for factor evaluation in complex interactions. In this context, RSM makes process modelling simple, efficient, less time of operation and resource utilization. RSM is also applicable in the optimization of the process variables in coagulation-flocculation process [29-30, 9].

In this study, RSM is used to develop a mathematical correlation between pH, coagulant dosage, initial dye concentration and settling time for the TDS removal from the dye containing wastewater. A face-centred central composite design (FCCD), a very efficient design tool for fitting the second-order models [31] was selected and design-expert (version 9. 0. 1.0) software achieved this purpose. Design-expert also demonstrated the analysis of variance (ANOVA), 3D surface plot, numerical optimization and multiple response optimization (MRO) using overlay contour plot.

We studied the potentials and effectiveness of using active coagulant proteins from plant seeds for effective TDS (Total dissolved solids) removal aqueous solutions of acid red 44. Newer approach of extracting active coagulant agent was adopted in the coagulation-flocculation process. In addition, choices of ionic nature of coagulants and dye were necessary for high efficiency performance. For this purpose, the response surface methodology (RSM) is used to develop a mathematical correlation between the pH, coagulant dosages, dye concentration, and time, for the TDS removal process. RSM was used to determine the optimum operational conditions and regions that satisfy the operating specifications.

MATERIALS AND METHODS

2.1 Preparation of Natural Coagulants Seed Powder

Sample 1: *Vigna unguiculata*
Sample 2: *Telfairia occidentalis*
Sample 3: *Brachystegia eurycoma*
Sample 4: *Vigna subterranean*
Sample 5: *Moringa oleifera*
Coagulant precursors were prepared as follows:

Dried seeds of *Vigna unguiculata* were purchased from local market of Enugu city. Matured seeds showing no signs of discolouration were used.

Matured pods containing *Telfairia occidentalis* seeds were purchased from local market of Enugu city. The seeds were removed from the pod, dried under sun for days, and the external shells were removed. Matured seeds showing no signs of discolouration, softening or extreme desiccation were selected.

Wet seeds of *Brachystegia eurycoma* were purchased from local market of Enugu city. Matured seeds showing no signs of discolouration were used. The seeds were de-hulled and sun dried.
Powder of *Vigna subterranean* was bought from local market of Enugu city.

Moringa oleifera seed pods were purchased from local market of Enugu city. Matured seeds showing no signs of discolouration, softening or extreme desiccation were used. The seeds were de-hulled and sun dried.

The dry seeds of the five samples were grounded to fine powder (63 - 600µm) using an ordinary food processor (Model BL 1012, Khind) to achieve solubilisation of active ingredients. The seed powders were then ready for extraction of the active components.

2.2 Extraction of Active Component

The active component from coagulants was extracted by adding 2g of powdered samples to 100mL distilled water. Magnetic stirrer (Model 78HW-1, U-Clear England) stirred the stock solution vigorously for 20min at room temperature to promote water extraction of the coagulant proteins. Filter paper (What. no. 42, 125mm diameter) filtered the suspension. The filtrate portions were used as coagulant at required dosages. Fresh solutions were prepared daily and kept refrigerated to prevent any ageing effects (such as change in pH, viscosity and coagulation activity). Before each experiment, solutions were shaken vigorously and used immediately for each sequence of experiment.

2.3 Characterization of the Coagulants

Yield, bulk density, moisture content, ash content, protein content, fat content and fibre content of the seed powders were determined by the standard official methods of analysis A.O.A.C [32], while carbohydrate content was calculated by difference. Surface structures and morphologies of the seed powders were studied using scanning electron microscope (SEM, Phenom Prox., world Eindhoven, Netherlands).

2.4 Buffered Solution

All assays were done in a pH-stable medium. Buffered solutions (pH 2, 4, 6, 7, 8 and 10) were prepared by the standards established according to the National bureau of standards (NBS, US) and were standardized using a digital HANNA pH meter. All reagents used were of analytical purity grade.

2.5 Dye Preparation

Acid Red 44 (water soluble dye) was provided by May & baker England with a molecular structures as shown in Fig. 1. The characteristics of acid red 44 (AR 44) are summarized in Table 1. Dye with commercial purity was used without further purification. Stock solution of 1000mg/l of dye was prepared by dissolving accurately weighed amounts of AR 44 in separate doses of 1L distilled water. The desirable experimental working concentrations of 200-1000mg/l were prepared by diluting the stock solution with distilled water when necessary.

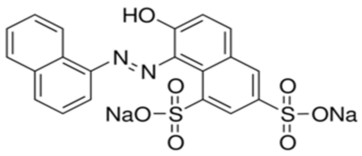


Figure 1 Structure of Crystal Ponceau 6R dye (Acid Red 44)

Table 1 Physical properties of Crystal Ponceau 6R dye

Property	Data
Chemical name	Crystal Ponceau
Chemical formula.	$C_{20}H_{12}N_2O_7S_2Na_2$.
Molecule Weight (g/mol)	502.43
CAS number	2766 -77 - 0
EC number	E 126
UV/Visible Absorbance	Max (water): 511 +6nm
C.I number	16250
Class	AZ0
C.I name	Acid Red 44.

2.6 Coagulation Studies

A conventional jar test apparatus (Phipps and Bird, VA, USA) equipped with six beakers of 1L capacity and six paddle stirrers was used to perform the coagulation-flocculation experiment. The jar test was conducted to evaluate the performances of the active agent extracted based on standard methods [33, 25]. The procedure involved 4min of rapid mixing at 100rpm. The mixing speed was reduced to 40 rpm for another 25min. The additional centrifuging (5000rpm for 5min) was performed to obtain clear liquid for all samples before analysis. All the suspensions were left for settling (60 - 420min). After settling, supernatant sample was withdrawn for TDS determination. A multipurpose electronic Jenway 4520 conductivity/TDS meter was used to measure TDS after coagulation-

flocculation experiment. The instrument was calibrated by using standard solution with known concentration of TDS. After the calibration, the TDS probe was dipped in the solution and the TDS of each run noted. Removal efficiency of was obtained according to the formula given below:

$$\text{TDS removal (\%)} = \left(\frac{TDS_0 - TDS}{TDS_0}\right) \text{X } 100 \quad (1)$$

where TDS_0 and TDS are the initial and final TDS concentration (mg/l) in dye solutions before and after coagulation-flocculation treatment, respectively.

2.7 Experimental Design and Data Analysis

Central composite design (CCD), a very efficient design tool for fitting the second-order models [34], is used as an RSM in the experimental design. The CCD was first introduced by Box Wilson in 1951, and is well suited for fitting quadratic surface, which usually works well for the process optimization [29]. In this research, the face-centred experimental plan was implemented as a CCD. A CCD is made face-centred by the choice of $\alpha = 1$ [34]. Face-centre is having the position of the star points at the face of the cube portion on the design [31]. The choice of face-centred CCD was made considering that it is an option in the CCD design and due to the cumbersome nature of the design. Also face-centred option ensures that the axial runs will not be any more extreme than the factorial portion. The independent variables selected for this study were pH (A), coagulant dosage (B), dye concentration (C), and time (D). A 2^4 two-level factorial for four independent variables consisting of 16 factorial points coded to the usual ± notation, 8 axial points and 6 replicate at centre point where conducted for each sample. A total of 30 experiments were conducted for each response. Mathematically, Eq. (2) was used to determine the total number of runs performed. The total number of experiments, N with k factors is:

$$N = 2^k + 2k + n \quad (2)$$

where k is the number of factors and n is centre points.

The experimental design table is presented in Table 2. For statistical calculations, the variables Z_i (the real value of an independent variable) were coded as X_i (dimensionless value of an independent variable) according to Eq. (3):

$$X_i = \frac{Z_i - Z_i^*}{\Delta Z_i} \quad (3)$$

where Z_i stands for the uncoded value of ith independent variables, Z_i^* stands for the uncoded value of ith independent variables at centre point and ΔZ_i is a step change value.

Design-expert software 9.0 (State Ease, Minneapolis, USA) was used for regression and graphical analysis, fitting to a second-order polynomial model to optimize the variables in the coagulation-flocculation process. Each response was used to develop an empirical model which correlated the response to the dye coagulation-flocculation variables using a second degree polynomial equation as given by Eq. (4):

$$Y = b_0 + \sum_{i=1}^{n} b_i X_i + \sum_{i=1}^{n} b_{ii} X_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij} X_i X_j + \varepsilon \quad (4)$$

where Y is the predicted response, b_0 the constant coefficient, b_i the linear coefficients, b_{ii} the quadratic coefficients, b_{ij} the interaction coefficient, X_i X_j are the coded values of the variables, n is the number of independent test variables and ε is the random error. Adequacy of the proposed model is then revealed using the diagnostic checking tests provided by analysis of variance (ANOVA). The quality of the polynomial fit model was expressed by the coefficient of determination (R^2). The R^2 values provide a measure of how much variability in the observed response values can be explained by the experimental factors and their interactions. These analyses are done by means of Fisher's 'F' test and P-value (probability). Model terms were evaluated by the P-value with 95% confidence level. Finally, the optimal values of the critical parameters were obtained by analyzing the surface and counter plots and by solving the regression equation. The range and levels of the experimental design table is presented in Tables 2.

Table 2 Levels and range of the variables tested in the CCD design

Variables	Factors	Unit	Range and levels				
			Lowest -α	Low -1	Center 0	High +1	Highest +α
pH	A	-	2	2	6	10	10
Coagulants dosage	B	mg /l	2000	2000	6000	10000	10000
Dye concentration	C	mg/l	200	200	600	1000	1000
Time	D	min.	60	60	240	420	420

RESULTS AND DISCUSSION

3.1 Characterization Result

The proximate analyses of coagulant precursors were summarized in Table 3. The moisture content values show water absorption ability of the coagulants. High crude protein contents recorded in all the precursors especially in *Telfairia occidentalis* indicates the presence of protein, which is in agreement with the literatures that the protein contents of the precursors are cationic poly-peptides [13]. Fibre contents present established that the precursors were organic polymer with repeating small molecules that could extend as tails and loops when dispersed in water [28]. The proximate results justify the use of these seed powders as potential source of coagulant in this work.

Table 3 Proximate compositions determination of the coagulant precursor

S/No.	Parameters	Values				
		Vigna unguiculata (Cowpea)	*Telfaria occidentalis (fluted pumpkin seed)*	*Brachystegia eurycoma (Black timber)*	*Vigna subterranean (Bambara nut)*	*Moringa oleifera seed*
1.	Yield	11.5	38.40	28.31	14.6	32.68
2	Bulk density (g/mL)	0.299	0.354	0.235	0.241	0.425
3.	Moisture Content (%)	9.0	12.58	7.25	10.0	5.02
4.	Ash content (%)	3.48	1.52	3.48	2.97	2.12
5.	Protein content (%)	25.14	55.09	19.77	18.15	39.34
6.	Fat content (%)	0.53	17.17	10.53	6.30	19.47
7.	Fibre content (%)	6.78	0.87	2.20	1.64	1.16
8.	Carbohydrate (%)	55.07	12.77	56.76	60.94	32.89

Table 4 CCD in coded unit and results obtained for TDS removal from AR 44

	Factors				Responses									
Run	A	B	C	D	Yvuc		Ytoc		Ybec		Yvsc		Ymoc	
	-	mg/ L	mg/ L	min	Yexp	Ypre	Yexp	Ypre	Yexp	Ypre	Yexp	Ypre	Yexp	Ypre
1	1	-1	1	-1	34.7	32.79	38.2	37.59	13.8	13.72	49.8	48.14	34.2	31.99
2	0	0	1	0	67.2	66.91	74.9	73.82	35.3	35.32	57.4	57.83	67.3	66.49
3	-1	1	-1	-1	74.3	73.93	73.4	72.71	60.4	60.24	75.3	71.85	78.4	75.22
4	0	0	0	0	71.1	71.61	77.3	77.43	40.7	40.56	62.9	62.80	71.9	72.62
5	-1	1	1	1	96.4	96.17	97.5	96.85	85.7	84.51	94	94.39	97	96.03
6	-1	-1	-1	1	92.8	92.23	91	90.85	82.9	82.99	93.7	92.82	93.6	89.03
7	0	1	0	0	76.5	76.32	81.5	82.74	44.5	44.54	58.6	62.89	77.7	76.58
8	1	-1	1	1	64.2	64.64	70.4	70.26	43.9	43.59	79.9	82.56	63.9	65.15
9	1	-1	-1	-1	42.3	42.59	48.7	48.52	24.5	25.21	58.7	57.52	42.7	41.74
10	0	0	0	0	71.1	71.61	77.3	77.43	40.7	40.56	62.9	62.80	71.9	72.62
11	0	0	0	0	71.1	71.61	77.3	77.43	40.7	40.56	62.9	62.80	71.9	72.62
12	-1	0	0	0	79.7	76.13	77.6	74.84	62.5	62.52	75.8	73.91	79.5	77.06
13	-1	-1	1	-1	53.3	54.50	53.9	54.67	43.9	43.45	45.1	46.89	52.9	52.19
14	0	0	0	-1	61.9	61.58	65.4	66.35	30.7	31.21	50.8	50.99	61.8	60.34
15	-1	-1	1	1	84.5	85.08	84.7	85.91	74.1	74.89	84.9	83.98	83.7	85.58
16	0	-1	0	0	66.5	65.66	73.9	72.40	35.3	35.53	65.2	61.12	68.1	67.77
17	0	0	0	0	71.1	71.61	77.3	77.43	40.7	40.56	62.9	62.80	71.9	72.62
18	0	0	0	1	91.8	91.09	97.5	96.29	62.5	62.27	83	83.02	91.3	91.32
19	1	1	-1	-1	53.2	52.81	58.6	58.28	34	33.61	49	50.65	48.5	48.91
20	1	1	1	-1	44.6	45.23	49.9	49.22	22.8	22.24	42.9	42.99	32	34.63
21	0	0	0	0	71.1	71.61	77.3	77.43	40.7	40.56	62.9	62.80	71.9	72.62
22	1	1	1	1	75.9	75.36	79.5	80.16	52.9	53.78	73.6	71.29	64.4	62.27
23	1	-1	-1	1	72.7	72.77	78.5	78.87	54.7	54.21	89.4	90.62	74.6	75.83
24	0	0	-1	0	75	74.27	80	80.82	44.8	45.05	66.3	66.08	76	75.36
25	1	1	-1	1	82.4	81.26	88.5	86.90	64.3	64.28	80.2	77.62	78.7	77.48
26	0	0	0	0	71.1	71.61	77.3	77.43	40.7	40.56	62.9	62.80	71.9	72.62
27	-1	1	-1	1	99	101.10	98.4	99.91	92	92.48	99.1	101.0	99.5	104.01
28	-1	1	1	-1	67.2	67.32	66.8	67.33	50.5	51.40	63.9	63.42	67.1	68.16
29	-1	-1	-1	-1	62.6	63.33	61.7	61.93	52.9	52.42	54	57.05	50.3	54.72
30	1	0	0	0	52.8	55.35	57.3	59.80	33.3	33.55	60.5	62.60	52.7	53.69

3.3 Development of Regression Model

To study the combined effect of the factors, experiments were performed for different combinations of the parameters. Table 4 presents the experimental design matrix together with the experimental (exp) and predicted (pre) decolourization efficiencies for VUC, TOC, BEC, VSC and MOC. The experiments compute the coagulation-flocculation model for the responses studied. The responses were correlated with the four independent variables (pH, coagulant dosage, dye concentration and time), using the second-order polynomial (Eq.4).

3.4 Analysis of Variance (ANOVA) for Response Surface Quadratic Model.

The adequacy of the model was justified through ANOVA as shown in Table 5. The quadratic regression analysis shows the models were significant at 95% confidence level by the Fisher's test. These were confirmed obtaining F-values of 201.28, 210.18, 1704.77, 67.34 and 76.31 for VUC, TOC, BEC, VSC and MOC, respectively. The P-values result of less than 0.05 (P-values of regression ≤0.05) shows statistically significant models. The models did not exhibit lack-of-fit indicating insignificant lack-of-fit. Significant and insignificant lack-of-fit results do not guarantee a good model. A noisy experimental environment and ignoring important variables in the experiment could make the residual large [35].

Coefficient of determination (R^2) measures the model's overall performance. Greater than 0.2 differences between predicted R^2 and adjusted R^2 indicate that non-significant term may be included in the model [34]. A high R^2 value, close to 1, is desirable and ensures a satisfactory adjustment of the quadratic model to the experimental data. The R^2 values of 99.47%, 99.49%, 99.94%, 98.43% and 98.62% for VUC, TOC, BEC, VSC and MOC indicate that the models could not explain 0.53%, 0.51%, 0.06%, 1.57% and 1.38% of the total variations, respectively. The values of predicted R^2 and adjusted R^2 were less than 0.2 as shown in Table 5, indicating model accuracy. The coefficients terms such as pH (A), coagulant dosage (B), dye concentration (C) and settling time (D), whose $P < 0.05$ were significant whereas some of the interaction terms (AB, AC, AD, BC, BD and CD) and the square terms (A^2, B^2, C^2 and D^2) were also significant to the response. Nevertheless, the interactive and square terms with P-value > 0.05 could be considered to have no effect on the colour removal.

Positive signs in front of Eq. (5-9) indicate an interactive effect among the factors. In conclusion, the overall quadratic models for the responses measured are significant and adequate.

Table 5 ANOVA results for the five responses: Y_{vuc}, Y_{toc}, Y_{bec}, Y_{vsc} and Y_{moc}.

Y_{vuc}	Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F		R- Squared
	Model	6787.44	14	484.82	201.28	< 0.0001	significant	
	A-pH	1942.72	1	1942.72	806.54	< 0.0001		
	B-Dosage	510.93	1	510.93	212.12	< 0.0001		
	C-Dye concentration	244.20	1	244.20	101.38	< 0.0001		
	D-Time	3919.08	1	3919.08	1627.04	< 0.0001		
	AB	0.14	1	0.14	0.058	0.8123		
	AC	0.95	1	0.95	0.39	0.5393		
	AD	1.63	1	1.63	0.67	0.4242		
	BC	4.95	1	4.95	2.06	0.1722		
	BD	2.98	1	2.98	1.24	0.2839		
	CD	2.81	1	2.81	1.16	0.2975		
	A^2	89.36	1	89.36	37.10	< 0.0001		
	B^2	1.00	1	1.00	0.42	0.5281		
	C^2	2.71	1	2.71	1.13	0.3056		
	D^2	57.90	1	57.90	24.04	0.0002		
	Lack of Fit	36.13	10	3.61				
	R - Squared							0.9947
	Adjusted R - Squared							0.9898
	Pred R - Squared							0.9712

Y_{toc}	Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F		R- Squared
	Model	6214.45	14	443.89	210.18	< 0.0001	significant	
	A-pH	1018.51	1	1018.51	482.25	< 0.0001		
	B-Dosage	481.53	1	481.53	228.00	< 0.0001		
	C-Dye concentration	220.50	1	220.50	104.40	< 0.0001		
	D-Time	4032.02	1	4032.02	1909.11	< 0.0001		
	AB	1.05	1	1.05	0.50	0.4914		
	AC	13.51	1	13.51	6.39	0.0232		
	AD	2.03	1	2.03	0.96	0.3424		
	BC	3.52	1	3.52	1.66	0.2165		
	BD	2.98	1	2.98	1.41	0.2537		
	CD	5.41	1	5.41	2.56	0.1305		
	A^2	264.71	1	264.71	125.34	< 0.0001		
	B^2	0.052	1	0.052	0.025	0.8770		
	C^2	0.030	1	0.030	0.014	0.9065		
	D^2	39.25	1	39.25	18.58	0.0006		
	Lack of Fit	31.68	10	3.17				
	R - Squared							0.9949
	Adjusted R - Squared							0.9902
	Pred R - Squared							0.9734

Y_{bec}	Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F		R- Squared
	Model	9954.74	14	711.05	1704.77	< 0.0001	significant	
	A-pH	3775.81	1	3775.81	9052.58	< 0.0001		
	B-Dosage	365.40	1	365.40	876.06	< 0.0001		
	C-Dye concentration	426.32	1	426.32	1022.11	< 0.0001		
	D-Time	4340.01	1	4340.01	10405.29	< 0.0001		
	AB	0.33	1	0.33	0.79	0.3873		
	AC	6.38	1	6.38	15.29	0.0014		
	AD	2.48	1	2.48	5.95	0.0276		
	BC	0.016	1	0.016	0.037	0.8491		
	BD	2.81	1	2.81	6.73	0.0204		
	CD	0.77	1	0.77	1.84	0.1955		
	A^2	144.79	1	144.79	347.13	< 0.0001		
	B^2	0.71	1	0.71	1.71	0.2108		
	C^2	0.36	1	0.36	0.87	0.3653		
	D^2	98.81	1	98.81	236.89	< 0.0001		
	Lack of Fit	6.26	10	0.63				
	R - Squared							0.9994
	Adjusted R - Squared							0.9988
	Pred R - Squared							0.9949

Y_{vsc}	Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F		R- Squared
	Model	6466.48	14	461.89	67.34	< 0.0001	significant	
	A-pH	575.74	1	575.74	83.94	< 0.0001		
	B-Dosage	14.05	1	14.05	2.05	0.1729		
	C-Dye concentration	305.87	1	305.87	44.60	< 0.0001		
	D-Time	4617.60	1	4617.60	673.24	< 0.0001		
	AB	469.81	1	469.81	68.50	< 0.0001		
	AC	0.60	1	0.60	0.088	0.7713		
	AD	7.16	1	7.16	1.04	0.3233		
	BC	2.98	1	2.98	0.43	0.5201		
	BD	37.52	1	37.52	5.47	0.0336		
	CD	1.76	1	1.76	0.26	0.6203		
	A^2	77.20	1	77.20	11.26	0.0043		
	B^2	1.62	1	1.62	0.24	0.6338		
	C^2	1.83	1	1.83	0.27	0.6127		
	D^2	45.89	1	45.89	6.69	0.0206		
	Lack of Fit	102.88	10	10.29				
	R - Squared							0.9843
	Adjusted R - Squared							0.9697
	Pred R - Squared							0.8907

Y_{moc}	Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F		R- Squared
	Model	8091.05	14	577.93	76.31	< 0.0001	significant	
	A-pH	2457.01	1	2457.01	324.43	< 0.0001		
	B-Dosage	349.36	1	349.36	46.13	< 0.0001		
	C-Dye concentration	353.78	1	353.78	46.71	< 0.0001		
	D-Time	4318.30	1	4318.30	570.19	< 0.0001		
	AB	177.56	1	177.56	23.44	0.0002		
	AC	52.20	1	52.20	6.89	0.0191		
	AD	0.051	1	0.051	6.685E-003	0.9359		
	BC	20.48	1	20.48	2.70	0.1209		
	BD	30.53	1	30.53	4.03	0.0630		
	CD	0.86	1	0.86	0.11	0.7414		
	A^2	136.09	1	136.09	17.97	0.0007		
	B^2	0.52	1	0.52	0.068	0.7971		
	C^2	7.46	1	7.46	0.99	0.3366		
	D^2	26.57	1	26.57	3.51	0.0807		
	Lack of Fit	113.60	10	11.36				
	R - Squared							0.9862
	Adjusted R - Squared							0.9732
	Pred R - Squared							0.8907

Quadratic empirical models (Eq. 5-9) obtained in terms of actual significant factors as:

Y_{vuc} = +57.64613 +1.82770*pH +1.76936E-003*Dosage -4.10499E-003*Dye concentration +9.39074E-003*Time -0.36705*pH^2 -3.89254E-008* Dosage^2 (5)

Y_{toc} = +49.92534 +6.02224*pH +1.25054E-003*Dosage -8.19079E-003*Dye concentration +0.021269*Time -5.74219E-004*pH*Dye concentration + - 0.63174*pH^2 +1.20127E-004*Time^2 (6)

Y_{bec} = +67.36145 -8.91335*pH +1.31460E-003*Dosage -7.83662E-003*Dye concentration -7.25380E-003*Time -3.94531E-004*pH*Dye concentration -5.46875E-004*pH*Time +5.81597E-007*Dosage*Time +0.46721*pH^2 +1.90600E-004*Time^2 (7)

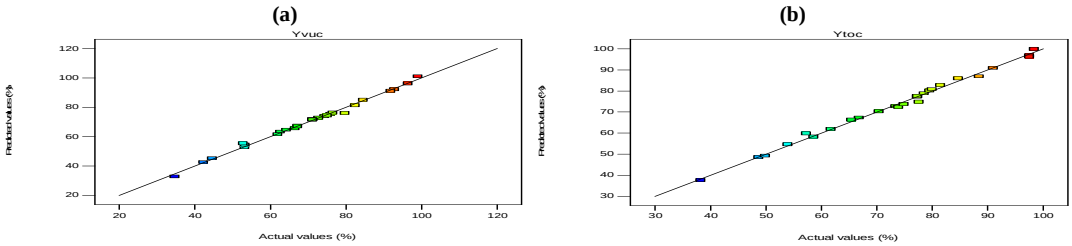
Y_{vsc} = +56.34976 -3.32568*pH -7.44426E-003*Dye concentration +0.042202*Time -3.38672E-004*pH*Dosage -2.12674E-006*Dosage*Time +0.34117*pH ^2 +1.29900E-004*Time^2 (8)

Y_{moc} = +36.65764 +4.46001*pH +3.57077E-003*Dosage +0.013433*Dye concentration +0.052509*Time -2.08203E-004*pH*Dosage -1.12891E-003* pH*Dye concentration -1.91840E-006*Dosage*Time -3.21181E-006*Dye concentration*Time -0.45296*pH^2 +9.88467E-005*Time^2 (9)

3.5 Model Adequacy Checking

3.5.1 Actual and predicted results of the percentage TDS removal.

A reliable model should have good prediction with experimental data. There is a good agreement between the experimental removal efficiencies (%) and predicted removal efficiencies (%) as shown in Fig. 4. The observed points on these plots reveal that the actual values are distributed relatively near to the straight line in most cases, indicating that the regression model is able to predict these removal efficiencies. A close relationship between predicted and experimental data indicates a good fit.



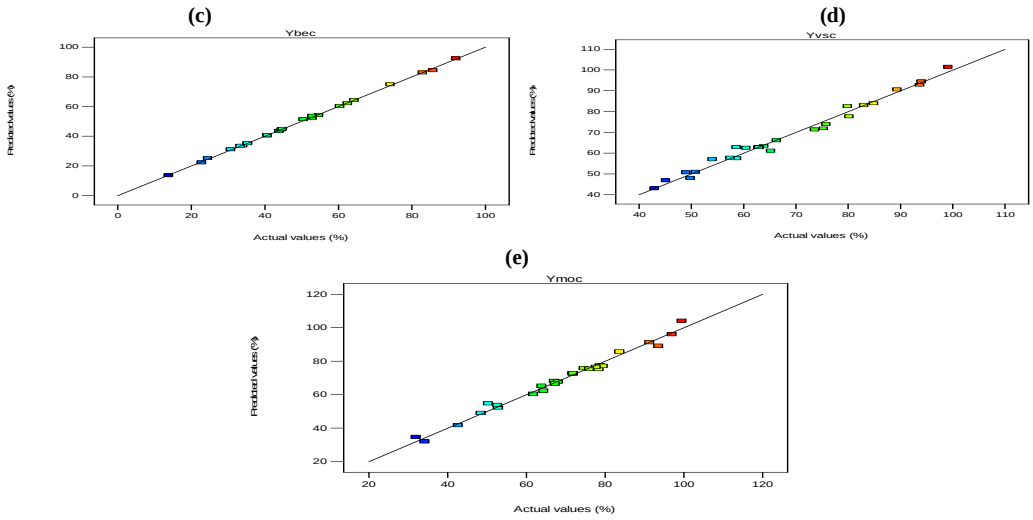


Figure 4 Parity plot for the actual values and predicted values of AR 44 TDS removal: (a) Y_{vuc}; (b) Y_{toc}; (c) Y_{bec}; (d) Y_{vsc}; (e) Y_{moc}

3.6 Response Surface Plotting for Evaluation of Operational Parameters

Figures 5 (a-e) shows the 3D response surface plots of quadratic models for TDS removal efficiency using VUC, TOC, BEC, VSC and MOC respectively. The maximum TDS removal efficiency using VUC is in the range of pH 2-4, coagulant dosage from 8000-10000mg/l at 600mg/l dye concentration and time 240min. Also for Fig. 5b, the maximum TDS removal efficiency using TOC is in the range of pH 4-6, coagulant dosage from 8000-10000mg/l at 600mg/l dye concentration and time 240min. In addition, Fig. 5c depicts that the maximum TDS removal efficiency using BEC is in the region of pH 2-3, time from 330-420min at coagulant dosage of 6000mg/l and dye concentration of 600mg/l. Furthermore, Fig. 5d indicates that the maximum TDS removal efficiency using VSC is in the pH ranged of 2-4, coagulant dosage of 6000mg/l, at time 330-420min and dye concentration of 600mg/l. Lastly, Fig. 5e shows that the maximum TDS removal efficiency using MOC is in the region where the pH ranged from 2-4, time ranged from 330-420min at coagulant dosage of 6000mg/l and dye concentration of 600mg/l. In general, the response surface plots indicate that the maximum TDS removal efficiencies are located inside the design boundary.

The pH must be controlled in order to establish optimum conditions in the process. The effectiveness of the polymers in TDS removal from AR 44 dye are highly dependent on pH as shown in Fig. 5. The polymers showed higher TDS removals at low pH values. In other words, TDS removal efficiency decreased with increasing pH. The highest removal efficiency was observed in MOC followed by VUC giving efficiencies of 95.0% and 94.9%, respectively. Charge on the hydrolysis products and precipitation of polymeric hydroxides are both controlled by pH variations [36-37]. This means that the functional groups of the dye is anionic, hydrolyses products of the organic biopolymers can neutralize the negative charges on dye molecules followed by flocculation mainly by polymer adsorption and charge neutralization. Conclusively, high removal efficiency at low pH values are predominant in organic contaminants removal from acid dyes. Similar results were reported [29, 30].

The result illustrated in Fig. 5 indicates that the removal efficiencies increased more at higher coagulant dosages. Maximum TDS removal efficiency was achieved at coagulant dosages of 8000 mg/l with MOC efficiency of 92.7% followed by VUC with efficiency of 92.3%. The high removal efficiencies of >75% was observed in all the coagulants for the 8000mg/l dosage. With the increase of coagulant dosages, the removal efficiency steadily increased and no “re-stabilization zones” with negative dye removals were found. The higher removal could be due to the sweep flocculation and adsorption mechanisms, which are inclined to occur at high dosages. The coagulant apparently served as condensation nuclei and the dye particles were enmeshed as the precipitate was settled. The high dosages of the organic polymer could also give rise to chain bridging and adsorption mechanism [12].

At dosages higher than 8000mg/L, removal efficiency decreased as observed in Fig. 5.This implies overdosing effect in the reaction solution. Overdosing deteriorates supernatant quality, referring to the “re-stabilization” of the particles, retarding coagulation and flocculation of charged particles. With excess polymer adsorption, the particle charge may be reversed.

Floc formation involves both interactions of coagulant hydroxide precipitate following hydrolyses reaction and contact with particles. Coagulation-flocculation performance is usually evaluated through time-dependent decrease in particle concentration and consequently growth of aggregates [15]. The longer coagulation-flocculation time (60-420min) in this process also confirms the presence of sorption mechanism (Fig. 5). The reduction in concentration

did not vary significantly after 420min showing equilibrium was achieved after 420min. Destabilization of the aggregate flocs could set in after this time due to saturation of the active sites.

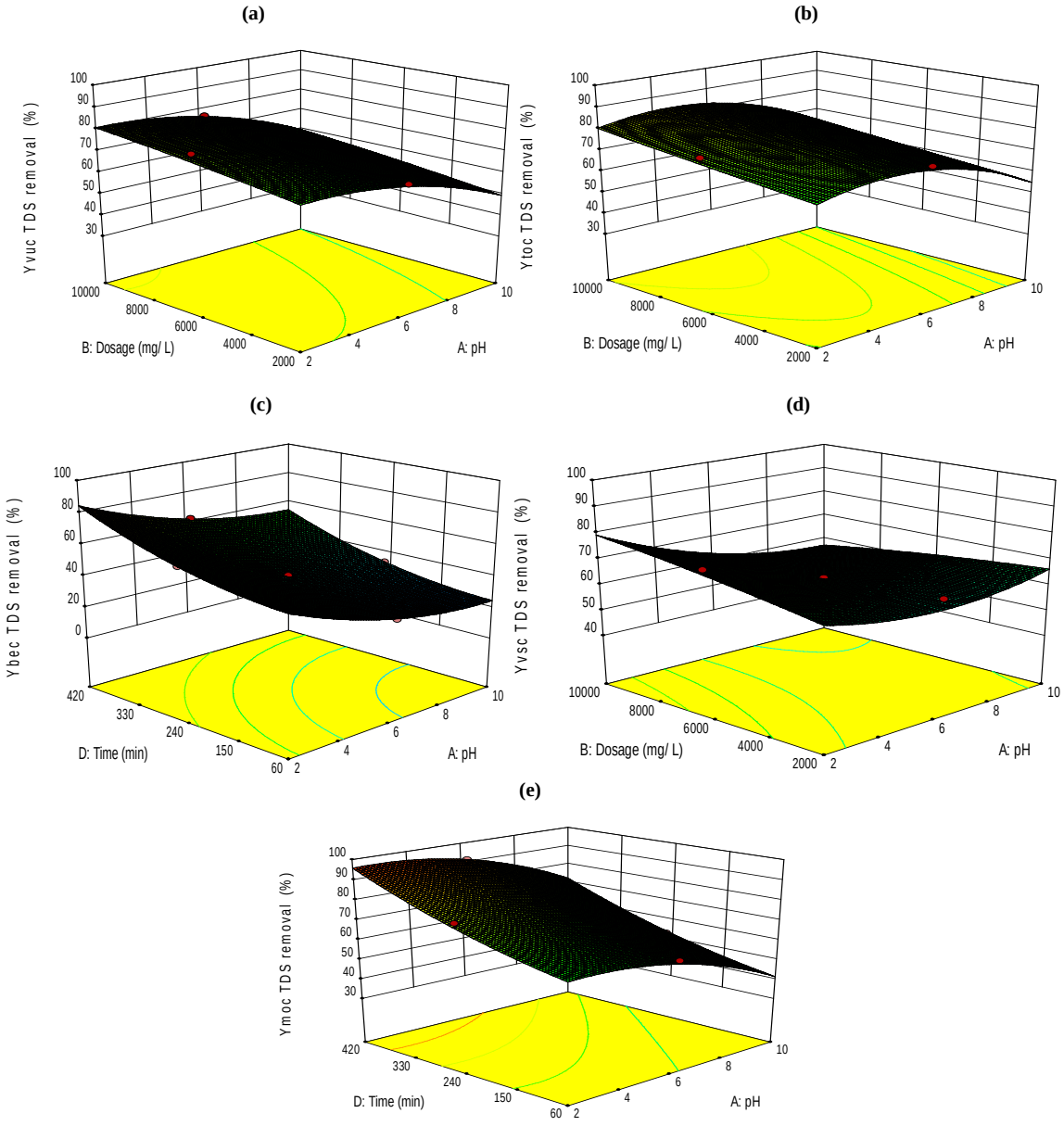


Figure 5 3D Surface plots for AR 44 TDS removal as a function of: (a) pH and dosage at dye concentration 600 mg/l, time 240 min for Y_{vuc}; (b) pH and dosage at dye concentration 600 mg/l, time 240 min for Y_{toc}; (c) pH and time at dye concentration 600 mg/l, dosage 6000mg/L for Y_{bec}; (d)) pH and dosage at dye concentration 600 mg/l, time 240 min for Y_{vsc}; (e) pH and time at dye concentration 600 mg/l, dosage 6000mg/L for Y_{moc}

3.7 Optimization Analysis

Design expert 9.0 was used to optimize the TDS removal efficiencies. Process optimization searches for a combination of factor levels that simultaneously satisfy the criteria placed on each responses and factors. Numerical optimization was employed and the desired maximum goal was set for each factor and responses. These goals are combined into an overall desirability function, for effective maximization of the function. Optimal conditions and the optimization results are shown in Table 5.

3.7.1 Model validation and confirmation experiments.

The optimum predicted values were further validated by carrying out the experiment at the optimal predicted conditions and the results of the experimental values were also shown in Table 5. The experimental data confirms good agreements with RSM results. The verification experiments demonstrated a good agreement between the experimental and predicted, indicating RSM approach adopted was appropriate for optimizing the coagulation-flocculation process. The maximum error (%) between the predicted and the experimental values were less than 4%

indicating good prediction by the model. The adequacy of the model was once again verified effectively by the experimental data validation.

Table 5 Confirmation analyses of the model predicted using optimum values for TDS removal.

TDS	pH	Dosage (mg/L)	Dye Concentration mg/L)	Time (min)	Predicted value (%)	Experimental value (%)	STD error (%)
AR 44 Y_{vuc}	2.20	9550	245	400	98.20	97.80	0.41
Y_{toc}	2	8028	338	420	97.01	94.88	2.20
Y_{bec}	2	7796	200.20	419	90.10	89.32	0.87
Y_{vsc}	2.01	7832.40	200.04	418.56	89.63	90.02	0.44
Y_{moc}	2.03	7394	200	420	99.05	97.25	1.82

3.7.2 Multiple response optimization (MRO)

Removal efficiencies of the colour using VUC, TOC, BEC, VSC and MOC yielded five individual responses, and these were achieved under different optimal conditions. A compromise among the optimum conditions for the five responses is desirable. The desirability function approach together with graphical optimization was used to achieve this goal [31]. With multiple responses, the optimum conditions where all parameters simultaneously meet the desirable treatment level can be visualized graphically by superimposing the contours of the response in an overlay plot. By defining the desired limits, the optimum condition can be visualized graphically by superimposing the contours of the five responses in an overlain plot, as shown in Fig. 6. The yellow shade called the "sweet spot" is the region that satisfies the goal for every response. Regions that do not fit the optimization criteria were shaded grey. As a result, the each TDS removal efficiency was optimized and the best conditions for the responses were determined. The overlain plot obtained confirms the relevance and flexibility of MRO in optimization analysis [35]. MRO is an efficient tool for optimizing and mostly applicable when there is an emergency because it reduces preparation time and cost of experiment.

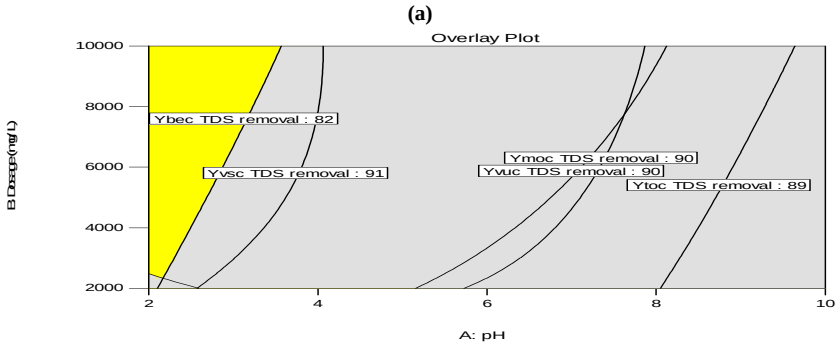


Figure 6 Overlay plots of the optimal regions for the AR 44 TDS removal at optimum dye concentration of 20mg/l and time of 420min

CONCLUSION

This research optimized the coagulation-flocculation process using VUC, TOC, BEC, VSC and MOC. The response surface methodology using FCCD investigates the effects of pH, coagulant dosages, dye concentration and time on the TDS removal efficiency. Combinations of operating parameters determined the maximum TDS removal. The TDS removal efficiency was highly influenced by pH, coagulant dosage and time. Apart from the sweep-flocculation and adsorption which were the primary mechanisms in the process, charge neutralization and inter-particle bridging played important roles in enhancing TDS removal process. Optimal conditions of pH 2, coagulant dosage 10000mg/l, dye concentration 215.97mg/l and time 419.29min were obtained from the compromise of the five desirable responses. The confirmation experiments demonstrated a good agreement to the predicted values, indicating RSM approach can be successfully applied for modelling and optimizing the coagulation-flocculation process. Therefore, RSM approach minimizes the number of experiment showing an economical way of obtaining the maximum amount of information in a short period of time.

REFERENCES

[1] C. Vinicius, B.F. Flavio, Q.D. Karina, *Acta Scientiarum Technology*, **2013**, 35, 53 – 58.
[2] M. Grassi, G. Kaykioglu, V. Belgiornor, G. Lofrano, Removal of emerging contaminants from water and waste water by adsorption process, Department of civil Engineering, University of Saterno, 84084 Fisciano (SA) Italy, **2012**, 18 - 19.
[3] M.H. Zonoozi, R.M. Moghaddam, A.G. Arami, *Environ. Eng. and Manage. J.*, **2008**, 7, 695 – 699.

[4] G. Roop, G. Meenakshi, Activated carbon Adsorption; Adsorptive removal of organics from water, *Taylor and Francis Group*, **2005**, 373.
[5] Z. Eren, F.N. Acar, *Desalination*, **2006**, 194, 1 – 10.
[6] Y. Liu, J. Wang, Y. Zheng, A. Wang, *Chem. Eng. J*., **2012**, 184, 248 – 255.
[7] V.D. Gosavi, S. Sharma, *J. of Environ. Sci. and Technol*., 3, **2014**, 29-39.
[8] M.I. Aguilar, J. Saez, M. Liorens, A. Soler, J.F. Ortuno, *Chemosphere*, **2005**, 58, 47 – 56.
[9] I. Khouni, B. Marrot, P. Moulin, R.B. Amar, *Desalination*, **2011**, 268, 27 – 37.
[10] P. Jarvis, E. Sharp, M. Pidou, R. Molinder, S.A. Parsons, B. Jefferson, *Water research*, **2012**, 46, 4179 - 4187.
[11] N.D. Tzoupanos, A.I. Zouboulis, Y.C. Zhao, *Chemosphere*, **2008**, 73, 729 – 736.
[12] Zhu, G., Zheng, H., Chen, W., Fan, W., Zhang, P., Tshukudu, T., **2012**. *Desalination*, 285, 315 – 323.
[13] Gao, B.Y., Yue, Q.Y., Wang, Y., **2007**. *Separation and Purification Technology*, 56, 225 – 230.
[14] B.Y. Shi, G.H. Li, D.S. Wang, C.H. Feng, H.X. Tang, *J. Hazard Mater*., **2007**, 143, 567 - 574.
[15] R. Cheng, S. Liang, H. Wang, M. Beuhler, *J. Hazad. Mater*., **1994**, 168, 155 - 162.
[16] J. Beltrán-Heredia, J. Sánchez-Martín, *Fresenius Environmental Bulletin*, **2008**, 17 (12a), 2134 – 2140.
[17] I.A. Obiora-Okafo, M.C. Menkiti, O.D. Onukwuli, *Inter. J. of Appl. Sci. and Maths*., 2014, 1(1), 15 – 21.
[18] S. Papic, N. Koprivanac, A.L. Bozic, A. Metes, *Dyes pigments*, **2004**, 62 (2), 291- 298.
[19] P. Flaten, *Brain Res Bull*, **2001**, 55 (2), 187 - 196.
[20] M.G. Antov, B. Marina, N.J. Petrovic, *Bioresource Technology*, **2010**, 101, 2167–2172.
[21] S.S.D. Mariângela, O.C. André, M.G. Valdirene, *Biol. plant*, **2003**, 44, 417 – 421.
[22] A. Kuku, U.J. Etti, I.S. Ibironke, *Plant Physiol. Biochem*., **2014**, 39, 137 – 146.
[23] O.J. Ikegwu, N.U. Oledinmma, V.N. Nwobasi, I.C. Alaka, *Journal of food Technology*, **2009**, 7(2), 34 - 37.
[24] F.J. Massawe, S.S. Mwale, S.N. Azan-Ali, J.A. Roberts, *African J. of Biotechnology*, **2005**, 4(6), 463 – 471.
[25] A. Ndabigengesere, K.S. Narasiah, B.G. Talbot, *Water Res*., **1995**, 29, 703 – 710.
[26] S.M. Miller, E.J. Fugate, V.O. Craver, J.A. Smith, J.B. Zimmerman, *Environ Sci. Technol*., **2008**, 42, 4274 – 9.
[27] C.Y. Yin, *Process Biochemistry*, **2010**, 45, 1437–1444.
[28] B. Bolto, J. Gregory, *Water Res*., **2007**, 41, 2301 –2324.
[29] S.S. Moghaddam, M.R. Alavi Moghaddam, M. Arami, *Journal of Hazardous Materials*, **2010**, 175, 651 – 657.
[30] J. Beltran-Heredia, J. Sanchez-Martin, M.A. Davila-Acedo, *Journal of Hazardous materials*, **2011**, 186, 1704 – 1712.
[31] D.C. Montgomery, R.H. Myers, Response surface methodology: process and product optimization using designed experiments. 2nd ed. John Wiley and Sons, New York, **2002**.
[32] A.O.A.C, Official Methods of Analysis 15th Edition. Association of Official Analytical Chemists. Washington D. C, U.S.A, **1990**.
[33] T. Okuda, A.U. Baes, W. Nishijima, M. Okada, *Water Res*., **1999**, 33(15), 3373 – 3378.
[34] D.C. Montgomery, Design and Analysis of Experiments, 5th ed., John Wiley and Sons, New York, 2001.
[35] K.T. Thuy, S.K. Lim, *chemical engineering research and design*, **2011**, 89, 1126–1135.
[36] G. Li, J. Gregory, *Water Res*., **1991**, 25, 1137 – 1143.
[37] I.A. Obiora-Okafo, O.D. Onukwuli, *International Journal of Scientific & Engineering Research*, **2015**, 6 (12), 693 - 704.