Optimization of Dye Removal Using Waste Natural Material and Polymer Particles

Assist. Lect. Bashar J. Kadhim
Chemical Engineering Department
University of Technology
Email: basharjawad2@gmail.com

Assist. Lect. Afraa H. Kamel
Chemical Engineering Department
University of Technology
Email:a.k_eng@yahoo.com

Lecturer Bashir A
Chemical Engineering Department
University of Technology
Email: Basheer510@yahoo.com

ABSTRACT

In this paper waste natural material (date seed) and polymer particles(UF) were used for investigation of removal dye of the potassium permanganate. Also study effect some variables such as pH, dye concentration and adsorbent concentration on dye removal. 15 experimental runs were done using the itemized conditions designed established on the Box-Wilson design employed to optimize dye removal. The optimum conditions for the dye removal were found: (pH) 12, (dye con.) 2.38 ppm, (adsorbant con.) 0.0816 gm for date seed with 95.22% removal and for UF (pH) 12, (dye con.) 18 ppm, (adsorbant con.) 0.2235 gm with 91.43%. The value of R-square was 85.47% for Date seed and (88.77%) for UF.

Keywords: optimization; dye of the potassium permanganate, Date, polymer particles UF, Response surface Methodology.

الاستخدام الافضل لإزالة الصبغة بواسطة المخلفات الطبيعية ودقائق البوليمر

م.م بشار جواد
قسم الهندسة الكيمياوية
الجامعة التكنولوجية

م.م عفراء هلال
قسم الهندسة الكيمياوية
الجامعة التكنولوجية

م. بشير احمد
قسم الهندسة الكيمياوية
الجامعة التكنولوجية

الخلاصة

تم ازالة صبغة برمنغنات البوتاسيوم باستخدام مخلفات طبيعية (نوى التمر) ودقائق البوليمر (يوريا فورمالديهايد)، كذلك تم دراسة تأثير بعض المتغيرات مثل الاس الهيدروجيني وتركيز الصبغة و تركيز المادة الممتزة. تم استخدام طريقة الافضل للحصول على افضل قيم للمتغيرات بواسطة طريقة بوكس ولسن لتحديد عدد التجارب وتم تحديد 15 تجربة لكل مادة. كانت القيم الافضل للمتغيرات هي: الاس الهيدروجيني 12، تركيز الصبغة 2.38 جزء بالمليون و المادة الممتزة 0.0816 غرام مع نسبة الازالة 95.22% باستخدام المخلفات. بالنسبة لاستخدام البوليمر كانت القيم الافضل الاس الهيدروجيني 12، تركيز الصبغة 18 جزء بالمليون و المادة الممتزة 0.2235 غرام مع نسبة الازالة 91.43%.

الكلمات الرئيسية: صبغة برمنكنات البوتاسيوم، نوى التمر، اليوريافورمالديهايد، تحليل البيانات، استخدام الافضل

1. INTRODUCTION

The freeing of the coloured dyes into the environment is a source of pollution, of biological process, and of disturbances in the water. Some of color and their disintegration products such as aromatic amines are highly hazardous, **Mohamed, 2004**. The production of the potassium permanganate in industry is generally one of the sources for dye in wastewater. The dye of the potassium permanganate must by removal before freeing into the environment because the color can change in physical and chemical properties of the receiver environment. It puts to death bacteria by decreasing the rate of oxygen intake by biological and chemical processes. It is toxic to phytoplankton, excitation to the cuticles. It can and when in direct connection with organic matter cause highly detonative and vexation to the cuticles **Vijay, et al., 2003, and Claude et al.,1999**. To reduce or minimize the trouble that arises from this color pollution by chemical, physical and biological processes These include adsorption, membrane separation, chemical oxidation, filtration, nanofiltration, colloidal gas aphrons, ultrasonic decomposition, electro coagulation, coagulation and precipitation, electrochemical oxidation, photo-oxidation, predispersed solvent extraction ,ozonation, liquid-liquid extraction, and microbic degradation **Han, et al.,2007 and Subhrajyoti, 2010**. One of the most effective ways of treatment of color of wastewater is adsorption, it is a physical process. In adsoption the activated carbon is usually employed, the activated carbon is expensive that lead costs producing therefore need another material that is more cost effective **Gupta, et al., 2005**. In recent times, many workers studied the increase of effective adsorbents.

Kori S., 2008 studied potassium permanganate concentration [2, 6 and 10 mg/L] that be effected as sublethal with nitrogenous waste: total plasma bilirubin, creatinine, uric acid, and urea. He found these concentration effects on them.

G. Z. Kyzas etal., 2012 studied dye removal from synthetic wastewater and real textile wastewaters by using Greek coffee in fix bed reactor after the optimization of conditions, the result were fitted to the Langmuir, Freundlich and Langmuir-Freundlich (L-F) model , he found the maximum adsorption capacities as 241 mg/g (pH=2) and 179 mg/g (pH=10).

Angham G., **2013** studied decoloriztion of methyl orange from aqueous solutions using synthesized natural bio polymer (Chitosan) from fish shells. Initial color concentration, Chitosan dosage , time and pH parameters effects were studied on color removal and he indicated that Chitosan could be employed as a biosorbent to remove the azo dyes from contaminated water.

Indira K., 2013 studied adsorption Of Methylene Blue Dye From Aqueous Solutions By using Neem Leaf And Orange Peel Powder, the optimum for same parameter such as contact time, dye concentration and amount of adsorbents was studied and the data were fitted on Langmuir adsorption equations. He found at 0.3 gm form adsorbent the maximum removal of 90-95%.

Hussain Majeed, et al., 2014 was studying sorption of reactive azo dye from aqueous solution, some parameter such as adsorbent dosage, initial dye concentration , temperature, and pH and found their effect on the removal of dye. The Box-Wilson design was used to optimize the results, the optimum conditions were found as initial dye concentration 70 mg/l, biomass concentration 17.5 g/l, pH 3, and temperature 35℃, with (R^2) value of 0.8919.

Iraq is one of the countries that export Date because the palms exist in huge quantity in Iraq. The Date seeds are considered waste of the date therefor we will use in this research as a natural material additional to polymer (UF) which has a low cost production. It is synthesized from reacting urea with formalin. Both Date seeds and polymer (UF) were used in removal dye potassium permanganate violet from wastewater. Same parameter was investigated such as absorbent dosage, pH, and concentration of dye. The box-Wilson method was applied to determine the optimum conditions for these parameters.

2. MATERIALS AND METHOD

2.1 Materials

The Potassium permanganate formula is $KMnO_4$, it was supplied from (BDH Chemicals Ltd, Poole, England), molar mass (158.034 g/mol), density (2.703 g/cm^3).

The (UF) polymer was prepared by condensation reactions between urea and formalin.

Urea amount was (25g) and formalin was (50ml). The pH was adjusted to (8-9) under total reflux for 50 min, after this pH changed to (5) by using Acetic acid and let it total reflux for 50 min, finally it was returned to pH (8-9) by NaOH and let it total reflux until the desired viscosity was reached **D.C. Montgomery, 1976.** The product is filtered to separate water, the polymer is dried in an oven at 70^0C and finally grinding it.

The second material is date seeds, it is collected, cleaned and grinded. The powder date seeds are washed with distilled water finally dried in oven at 105 ^{O}C.

2.2 Method

The aqueous solution was prepared from potassium permanganate violet, where 0.5 gm of dye is dissolved in 1000 ml in distilled water to create a stock solution of 500 mg/l. The experimental solution was braced by diluting definite volume of the stock solution to produce the coveted concentration. The used dye concentration was (2-18) ppm.

Spectrophotometer (JASCO) was used to specify the maximum wavelength λ for the concentration of the dye solution in the experimente. It was equal to (525 nm), after this standerd calibration curve was prepared between absorbance and concentration. The adsorbent materials (polymer and date seeds) were used in dosage range [0.02-0.28] gm. After testing the polymer, it was found that under 50 ^{o}C gave best adsorption for dye, therefore under this temperature all experiments for polymer were run. The PH parameter range is (2, 4.5, 7, 9.5, and 12).

The samples are analysed using UV spectrophotometer (JASCO, japan) rang 800-200 nm.

Instruments:-
Laboratory oven (England)
Magnetic stirrer (Germany)

Electronic balance
Digital pH meter
Centrifuge (Germany). Removal percent was calculated by this eq:
% dyes removal = $(C_o - C_t)/C_o * 100$ (1)

Where C_o is the initial concentration of the dye, C_t is the concentration dye at time (t).

The Box-Wilson experimental design is a general series if experiments have been developed for second order response surface. This method is most likely to be useful in practice in this type of design. The independent factors are specified at five levels. The specific value of these five levels for each factor depends on the number of factors in the model and the range over which they are studied.

The general form of a quadratic (second order model) polynomial is illustrated by the following equation

$$Y = B_0 + \sum_{i=1}^{k} B_i X_i + \sum_{i=1}^{k} B_{ii} X_i + \sum_{i}^{1} \sum_{1} B_{ii}^{K} X_i^{K} X_i + \epsilon \ldots\ldots i < j \quad (2)$$

Where ϵ is a random error component and Y is the objective function and ki is the number of variables in the quadratic polynomial model can be determined as follows

$$n = \frac{(K_j+1)(K_j+2)}{2} \qquad n{=}number\ of\ terms$$

For three variables, the quadratic polynomial equation can be represented as follows:

$$Y = B_0 + B_1 X_1 + B_2^2 X_2 + B_{11}^2 X_1^2 + B_{22} X_2 + B_{33} X_3 + B_{12} X_1 X_2 + B_{12} X_1 X_3 + B_{23} X_2 X_3 \quad (2)$$

The corresponding coefficients of the above polynomial are called “the regression coefficient”, the total number of experiments (N) needed according to the central composite rotatable design is estimated according to the following equation:

$N=2^k+2k+l$

Where

2^k= is the fractional point, 2k= is the axial point, l= is the center point according to **D.C. Montgomery, et al.,1976 and C.F.Jeffwn, 2000**.

The regression coefficients calculating by using The Minitab computer software.

3. RESULTS AND DISCUSSION

First of all, the optimum time for removal at standard conditions was found by experiments (81.56 dye removal at 30 min for polymer & 94.8656 dye removal at 50 min for Date), it is fixed for all runs. Box-

Wilson method was used for skillfulness dismissal of color and for deciding the relation between these parameters. Table 1 shows a roster of code variable levels and real variables that are presented in 15 experiments for three factors at five levels. The factors of the response functions in equation (2a for Uf &2b for date) found from the experiments are summarized in table (1) by the analysis response surface design in Minitab program., These coefficients of equation (2) are shown in Table 2.

$$y = 29.2 + 6.34\,x1 + 4.15\,x2 - 121\,x3 - 0.942\,x1*x1 - 0.320\,x2*x2 - 800\,x3*x3 + 0.087\,x1*x2 + 40.5\,x1*x3 + 22.4\,x2*x3 \tag{2a}$$

$$y = -107.9 + 36.4\,x1 + 3.01\,x2 + 763\,x3 - 1.438\,x1*x1 - 0.191\,x2*x2 - 1714\,x3*x3 - 0.243\,x1*x2 - 82.3\,x1*x3 + 18.5\,x2*x3 \tag{2b}$$

Computed Dye removal value were compared with those measured to determine the goodness of fit of the equation. From Table 3, R^2 for Dye removal was 85.47% for date and (88.77%) for UF. By using analysis of variance the importance and acceptability of the second-order equation was determined. Tables 4a &4b summarize the result of the analysis of variance.

3.1 Response Surface Curves

The optimum values of the variables were determined by using plots of the regression model at the ranges that were set. Each 3D plot and 2D contour was determined drawing by combinations of the two variables while the other variable maintained at zero level (center) according to **Gopinadh, et al., 2015 and KURUVALLI, et al., 2015**. The interactive effect of pH, dye concentration and adsorbent concentration on dye removal are shown in figures (1-3) for UF and date respectively. The effect of pH and dye concentration in combinations on dye removal presented in figures (1a&1b) at a constant absorbent concentration value, from this figures the optimum values can be easily found. Figures (2a&2b) show the interactive effect of pH and adsorbent concentration on removal at a constant level (center) for the dye concentration. Figures (3a&3b) presented effected combinations of dye concentration with adsorbent concentration on removal keeping the pH value at center level. In the contour plots the ellipse shows the utmost value for removal. Figures (4a&4b) present the optimal value for variables by employing the response optimizer. The maximum removal was 91% (UF) and 95% (Date). The optimal values of variables: (pH) 12, (dye con.) 2.38 ppm, (adsorbant con.) 0.0816 gm at Date and for UF (pH) 12, (dye con.) 18 ppm, (adsorbant con.) 0.2235 gm.

4. CONCLUSIONS

The removal of the potassium permanganate dye was optimized employing polymer UF and waste natural Date. The effect of pH, dye concentration and absorbent concentration on dye removal was investigated by using response surface methodology. The optimum values of combination variables that gave the maximum removal of dye was found. The maximum color removal was found as 91.43% and 95.22% for UF and Date respectively. The analysis response surface design showed a good agreement between the model and experimental data. The RSM is the best way to determine the maximum result in a momentary time and minimal experiment number.

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Table 1. Design experiments and experimental results.

Exp. No.	Coded variables			Real variables			Dye Removal Efficiency.	
	X1	X2	X3	PH	Dye concentration	Adsorbent con.	Polymer	Date
1	-1	-1	-1	4.5	6	0.085	73.69	67.65
2	1	-1	-1	9.5	6	0.085	47.38	94.56
3	-1	1	-1	4.5	14	0.085	60.67	54.45
4	1	1	-1	9.5	14	0.085	51.48	95.22
5	-1	-1	1	4.5	6	0.215	63.99	46.70
6	1	-1	1	9.5	6	0.215	77.64	40.00
7	-1	1	1	4.5	14	0.215	87.95	76.33
8	1	1	1	9.5	14	0.215	91.43	43.7
9	-2	0	0	2	10	0.15	53.2	47.40
10	2	0	0	12	10	0.15	64.23	63.26
11	0	2	0	7	2	0.15	41.34	78.29
12	0	2	0	7	18	0.15	82.25	79.80
13	0	0	-2	7	10	0.02	52.65	73.04
14	0	0	2	7	10	0.28	84.82	51.59
15	0	0	0	7	10	0.15	81.56	94.86

Table 2. Coefficient of equation 2.

Polymer		Date	
coeffecient	value	coeffecient	value
b0	29.2	b0	-107.9
b1	6.34	b1	36.4
b2	4.15	b2	3.01
b3	-121	b3	763
b11	-0.942	b11	-1.438
b22	-0.320	b22	-0.191
b33	-800	b33	-1714
b12	0.087	b12	-0.243
b13	40.5	b13	-82.3
b23	22.4	b23	18.5

Table 3a. Estimated Regression Coefficients for dye removal with UF**.**

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	9	3272.56	363.62	4.39	0.059
Linear	3	2211.87	737.29	8.91	0.019
x1	1	0.85	0.85	0.01	0.923
x2	1	764.91	764.91	9.24	0.029
x3	1	1446.11	1446.11	17.47	0.009
Square	3	436.44	145.48	1.76	0.271
x1*x1	1	383.85	383.85	4.64	0.084
x2*x2	1	289.97	289.97	3.50	0.120
x3*x3	1	126.65	126.65	1.53	0.271
2-Way Interaction	3	624.25	208.08	2.51	0.173
x1*x2	1	6.04	6.04	0.07	0.798
x1*x3	1	346.06	346.06	4.18	0.096
x2*x3	1	272.15	272.15	3.29	0.130
Error	5	413.91	82.78		
Total	14	3686.47			

Table 3b. Estimated Regression Coefficients for dye removal (Date)

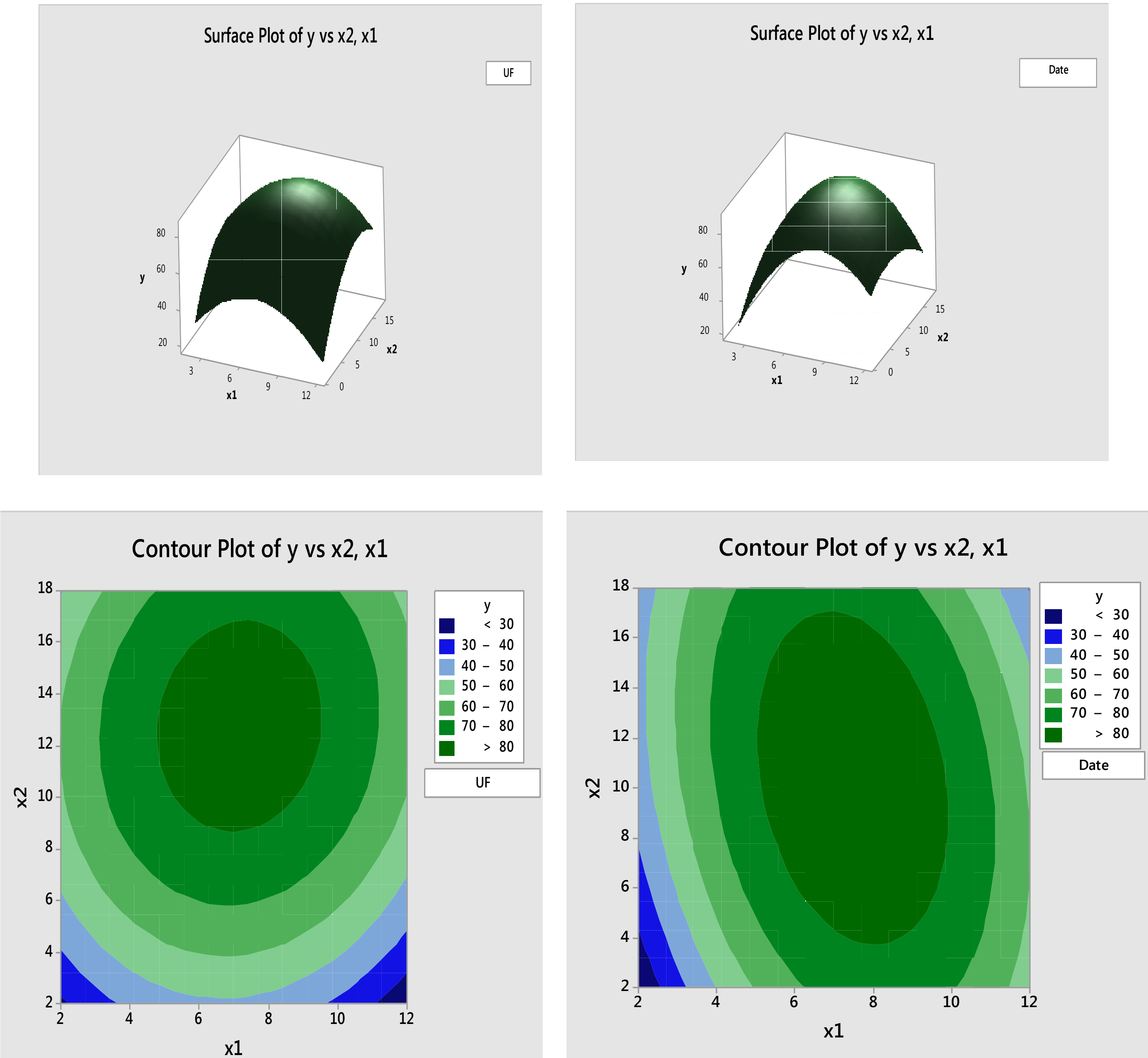
Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	9	4465.55	496.17	3.27	0.103
Linear	3	1612.68	537.56	3.54	0.104
x1	1	225.53	225.53	1.49	0.277
x2	1	16.81	16.81	0.11	0.753
x3	1	1370.34	1370.34	9.03	0.030
Square	3	1189.23	396.41	2.61	0.164
x1*x1	1	894.70	894.70	5.89	0.060
x2*x2	1	103.61	103.61	0.68	0.446
x3*x3	1	580.76	580.76	3.83	0.108
2-Way Interaction	3	1663.63	554.54	3.65	0.099
x1*x2	1	47.35	47.35	0.31	0.601
x1*x3	1	1431.26	1431.26	9.43	0.028
x2*x3	1	185.03	185.03	1.22	0.320
Error	5	759.05	151.81		
Total	14	5224.60			

Table 4a. Analysis of Variance for dye removal (UF)

Term	Effect	Coef	SE Coef	T-Value	P-Value	VIF
Constant		82.96	8.02	10.34	0.000	
x1	0.92	0.46	4.55	0.10	0.923	1.00
x2	27.66	13.83	4.55	3.04	0.029	1.00
x3	38.03	19.01	4.55	4.18	0.009	1.00
x1*x1	-47.1	-23.5	10.9	-2.15	0.084	2.07
x2*x2	-40.9	-20.5	10.9	-1.87	0.120	2.07
x3*x3	-27.1	-13.5	10.9	-1.24	0.271	2.07
x1*x2	7.0	3.5	12.9	0.27	0.798	1.00
x1*x3	52.6	26.3	12.9	2.04	0.096	1.00
x2*x3	46.7	23.3	12.9	1.81	0.130	1.00

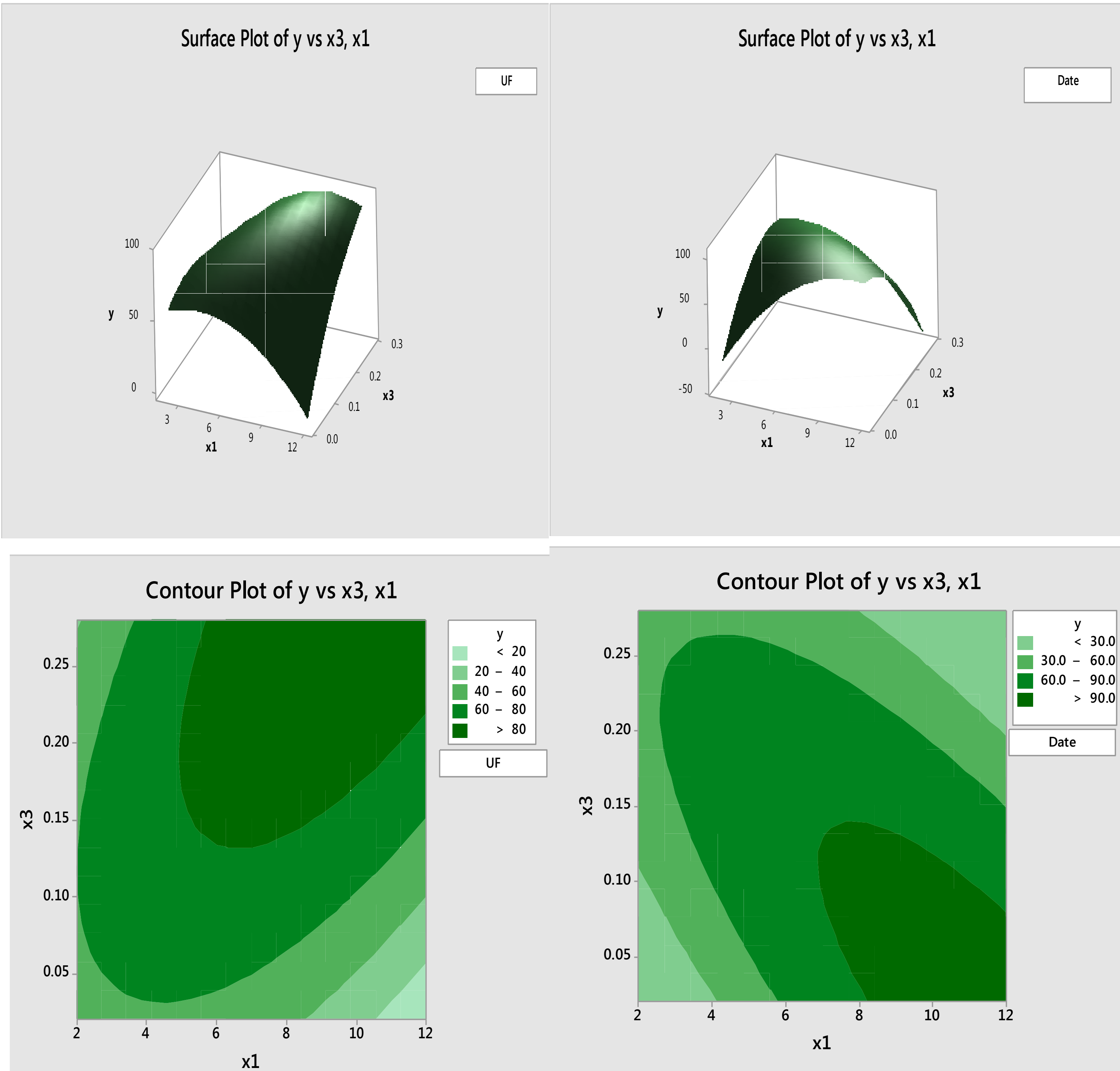
Table 4a. Analysis of Variance for for dye removal (Date)

Term	Effect	Coef	SE Coef	T-Value	P-Value	VIF
Constant		87.7	10.9	8.07	0.000	
x1	15.02	7.51	6.16	1.22	0.277	1.00
x2	4.10	2.05	6.16	0.33	0.753	1.00
x3	-37.02	-18.51	6.16	-3.00	0.030	1.00
x1*x1	-71.9	-35.9	14.8	-2.43	0.060	2.07
x2*x2	-24.5	-12.2	14.8	-0.83	0.446	2.07
x3*x3	-57.9	-29.0	14.8	-1.96	0.108	2.07
x1*x2	-19.5	-9.7	17.4	-0.56	0.601	1.00
x1*x3	-107.0	-53.5	17.4	-3.07	0.028	1.00
x2*x3	38.5	19.2	17.4	1.10	0.320	1.00



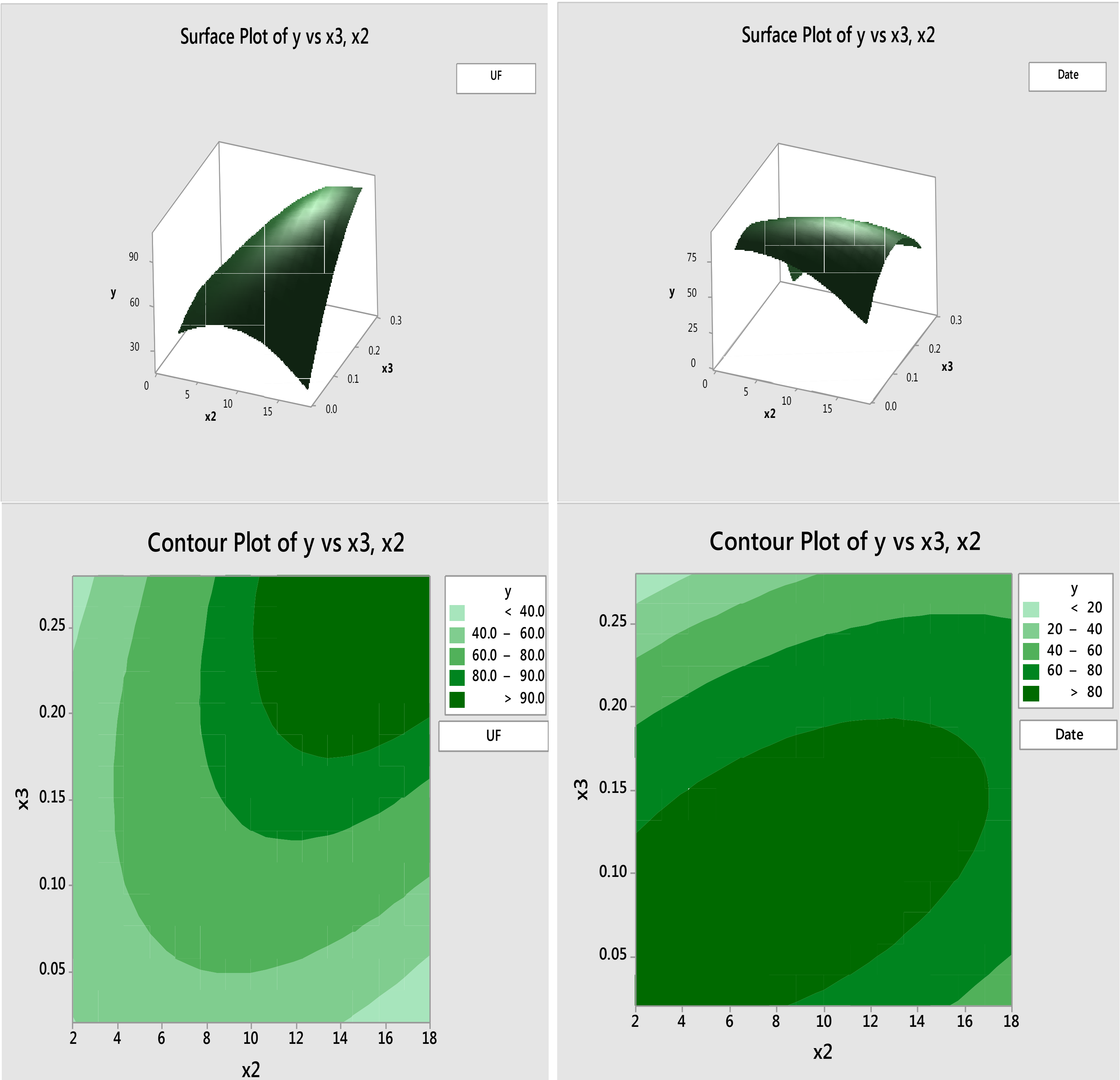
1.a **1.b**

Figure 1. The effect of pH (x1) and dye concentration (x2) on dye removal



2.a **2.b**

Figure 2. The effect of pH(x1) and adsorbent concentration(x3) on dye removal



3.a **3.b**

Figure 3. The effect of dye concentration (x2) and adsorbent Concentration (x3) on dye removal.

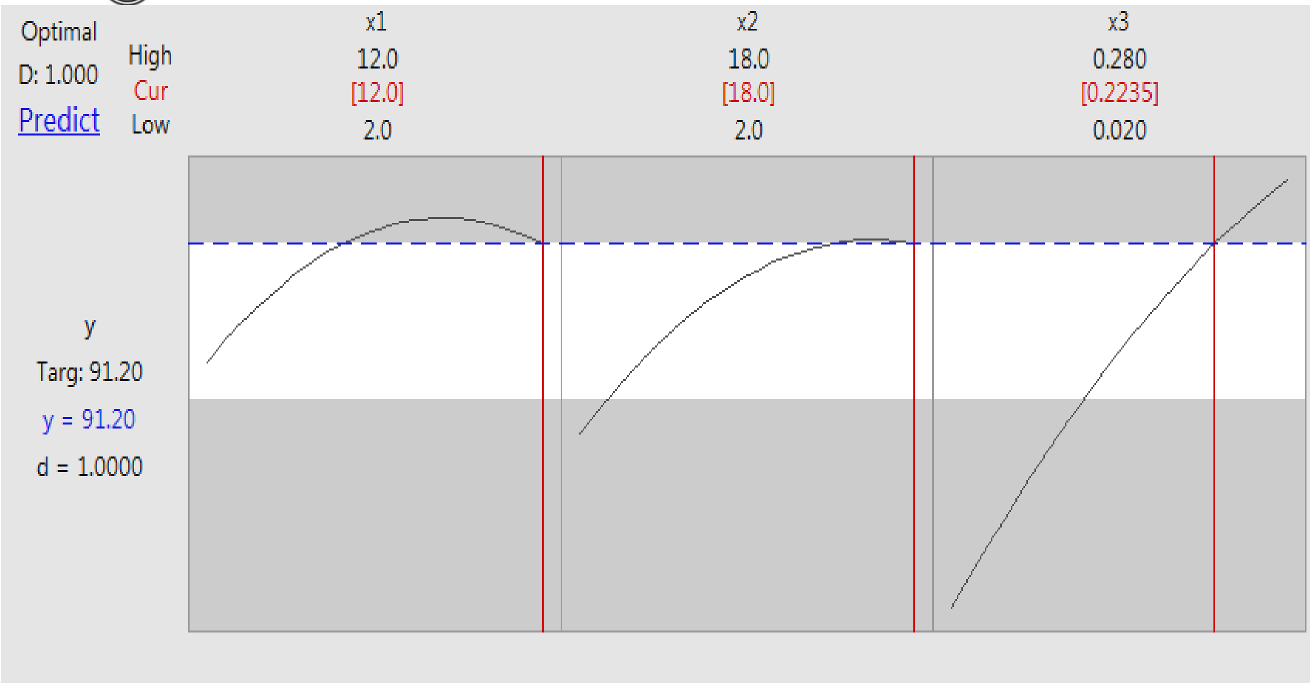


Figure 4a. Response optimizer for dye removal by UF

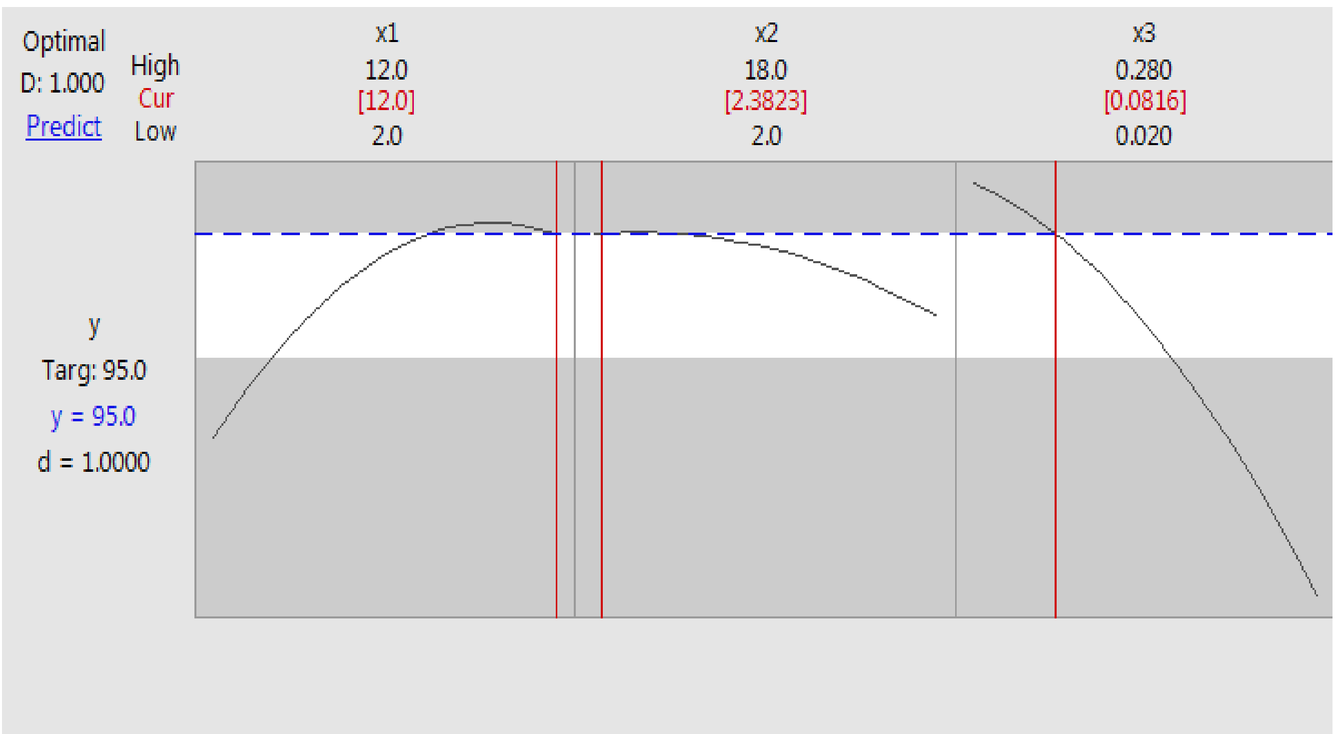


Figure 4b. Response optimizer for dye removal by Date

NOMENCLATURE

UF= Urea formaldehyde

RMS= Response surface methodology

B_0+B_1 +B_2+B_{11}+B_{22} +B_{33}+B_{12}+B_{13} +B_{23}= Constant

k= the number of variables

Cur= Optimum value