Tailoring the Exposed Facets of Anatase Titania and Probing their Correlation with Photocatalytic Activity- An Experimental and Statistical Study

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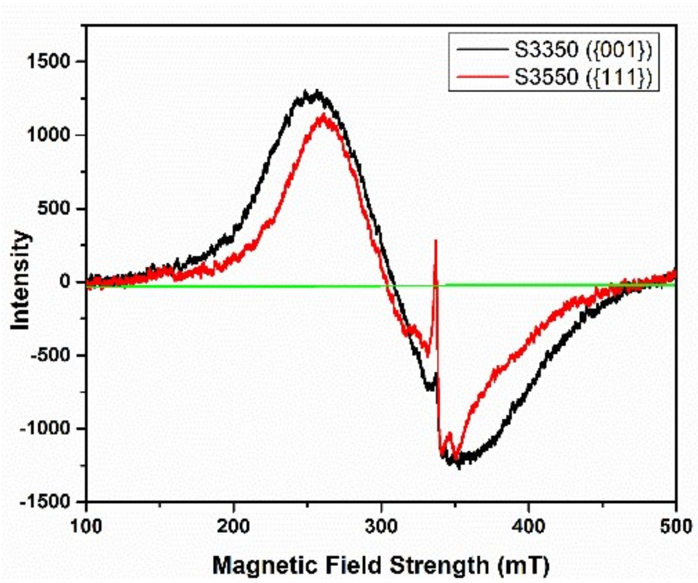


Figure S1 ESR spectra of {001} (S3350) and {111} (S3550) faceted titania [2]

The samples S3350 and S3550 are further characterized by ESR in order to confirm the presence of different facets in the samples. The value of g is calculated from the ESR spectra (Figure S1B) using following equation

$$g = \frac{h\nu}{\mu BH}$$

and was found to be 1.99, 2.2 for S3550 titania and 2.18 for S3350 titania confirming the presence of {111} facet in sample S3550. This implies that electrons/atoms in the studied samples have different environment and thus, indicating the presence of more oxygen vacancies in case of S3550 which could be attributed to the presence of high energy facets.

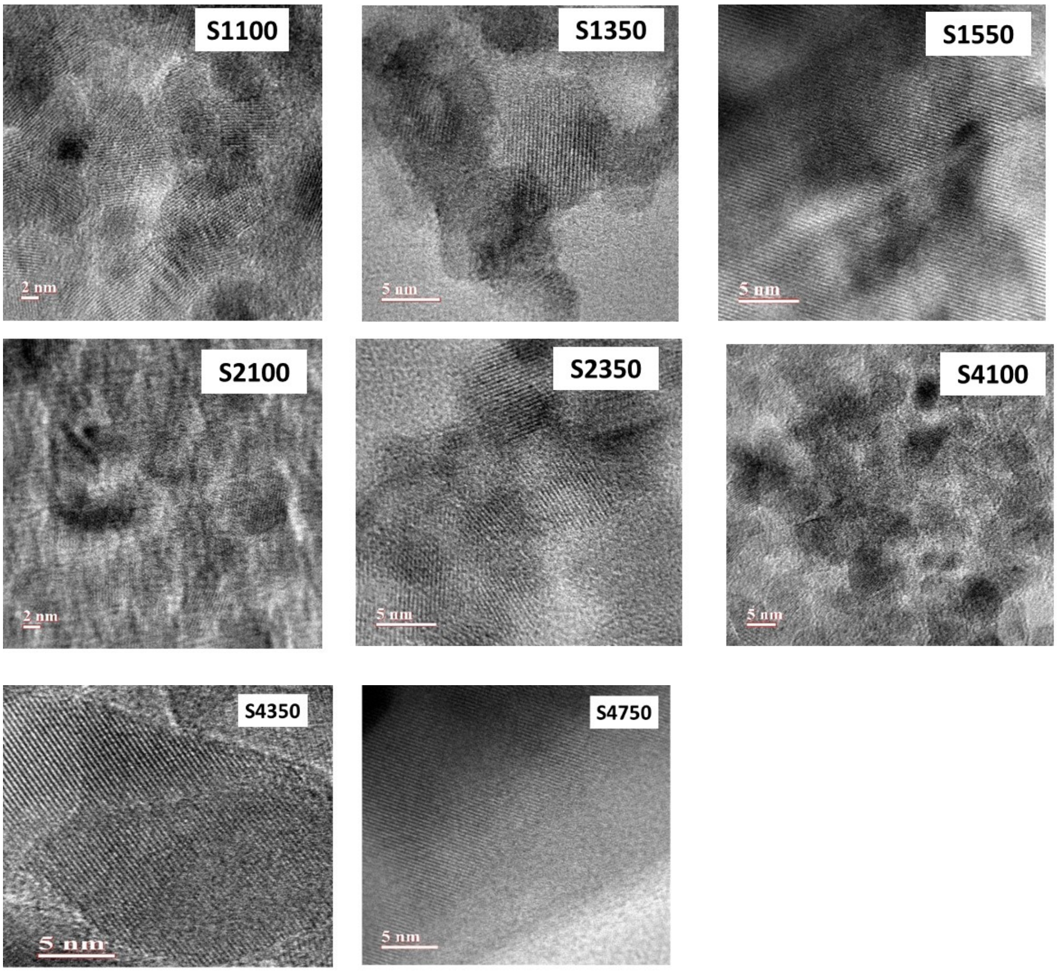


Figure S2 HR-TEM of few as synthesized titania samples

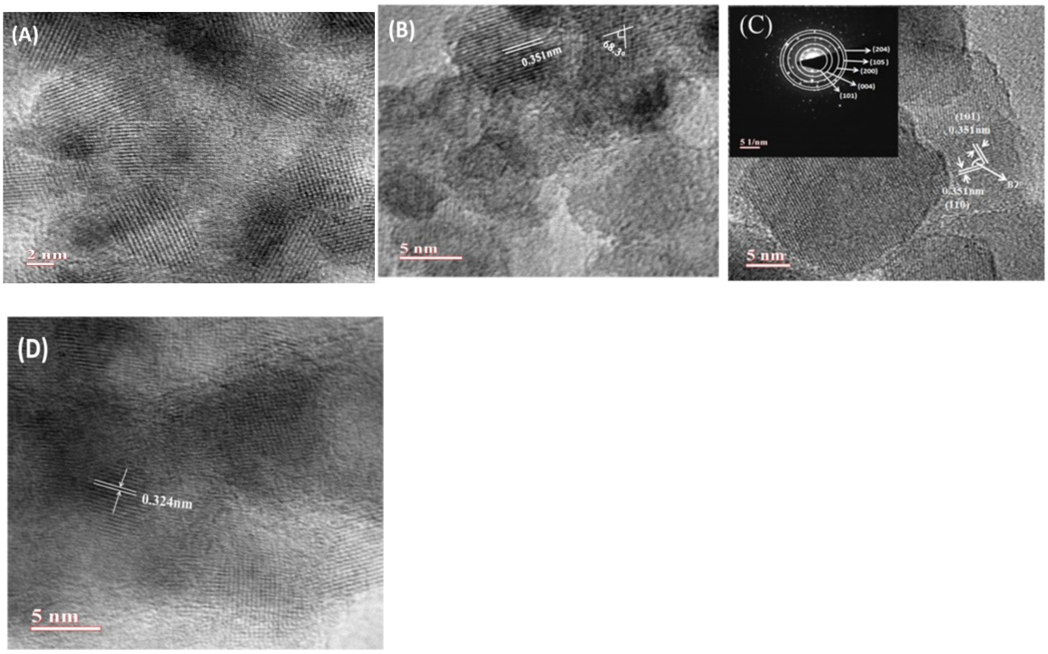


Figure S3 HR-TEM of S-3 series titania samples as reported in literature [1]

Theoretical evaluation of percentage of {001} facets

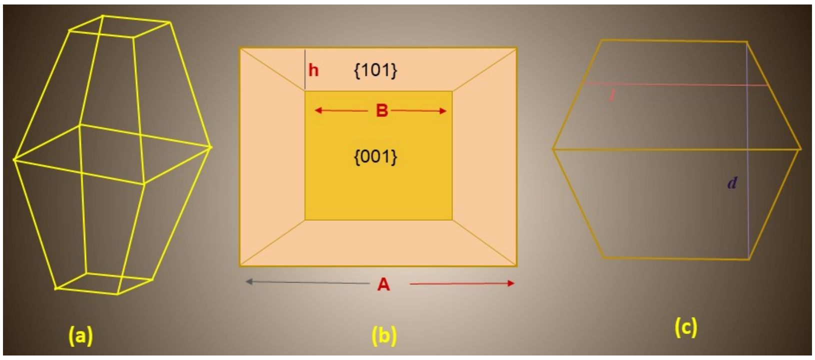


Figure S4 (a) Equilibrium shape of anatase TiO_2 with exposed {001} facets (b) Top view of TiO_2 crystal with exposed {001} facets. (c) Cross section of [001] direction

TiO_2 with exposed {001} facets have an octahedral structure, its equilibrium shape can be seen as in (**Figure S4a**), top view (**Figure S4b**) and its cross section along [001] direction can be illustrated as in **Figure S4c**. According to Scherrer formula, the average length (l) related to (200) peak and thickness (d) related to (004) peak can be calculated from the following equation:

$$D = \frac{K\lambda}{\beta cos\theta}$$

The average length (l) can be obtained according to the values of FWHM and α of (200) peak, and thickness (d) to (004) peak.

The calculation of the percentage of high reactive {001} facet is as follows:

$$B = l - \frac{d}{2} / \tan\theta$$

$$A = l + \frac{d}{2} / \tan\theta$$

$$h = \frac{d}{2} / \sin\theta$$

$$S_{(001)} = 2 \times B \times B = 2(l - \frac{d}{2} / \tan\theta)^2$$

(S_{001} is the area of all {001} in a TiO_2 single crystal)

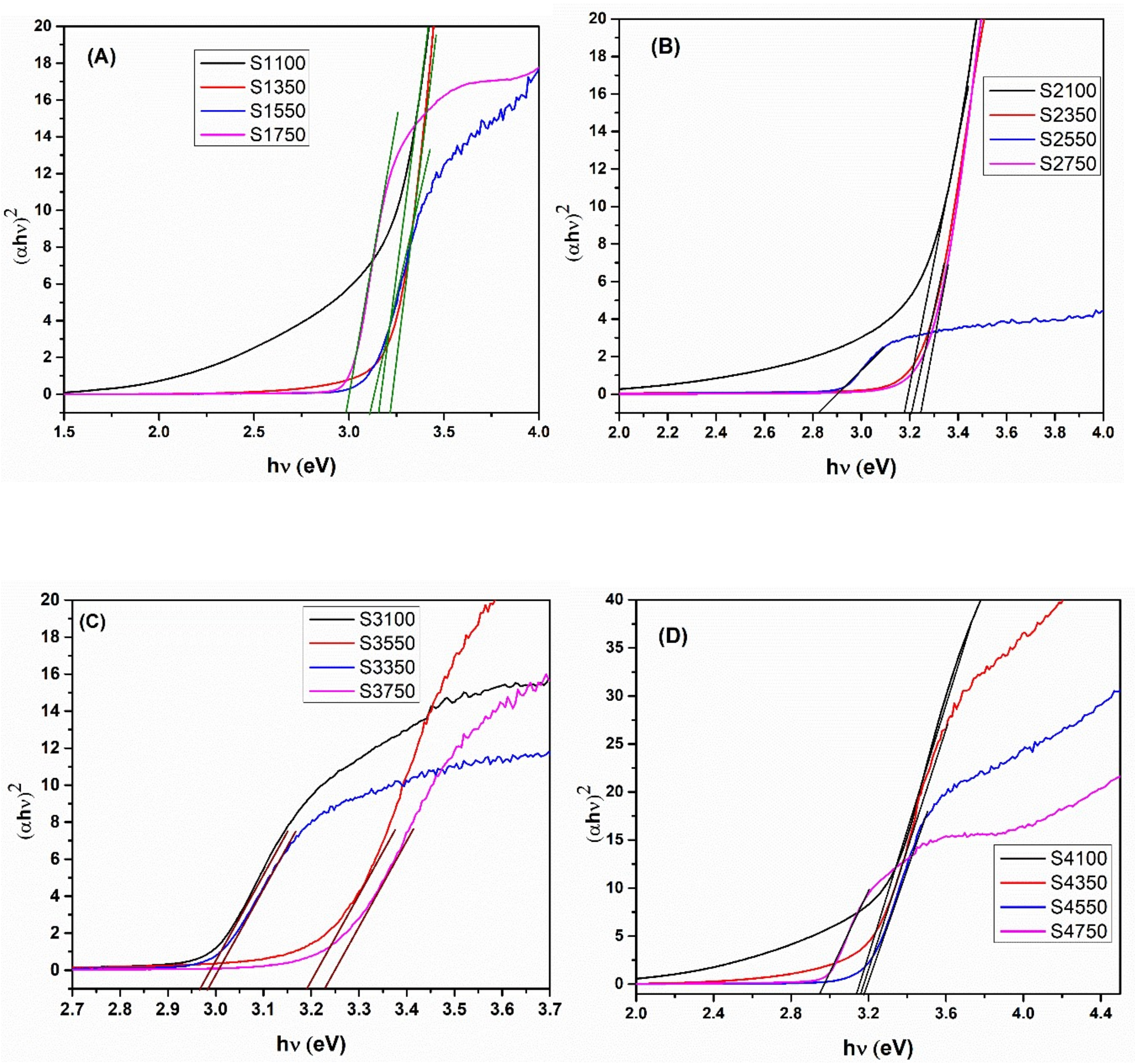
$$S_{(101)} = 8 \times h \frac{A+B}{2} = 8hl = 4dl / \sin\theta \ (S_{101} \text{ is the area of } \{101\} \text{ facets})$$

$$P_{(001)} = \frac{S_{(001)}}{S_{(001)} + S_{(101)}}$$

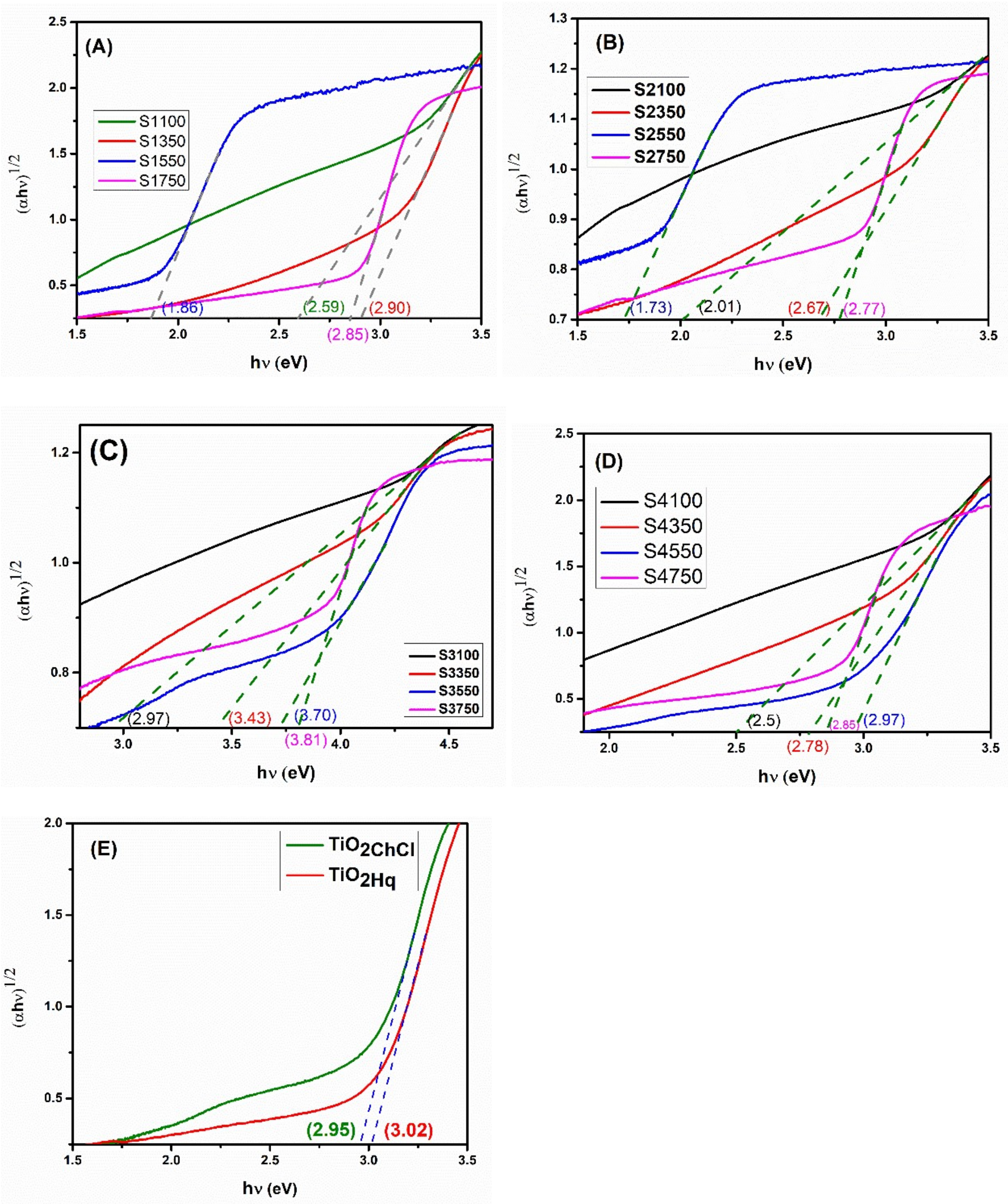
Where Θ = 68.3° is the theoretical value for the angle between [001] and [101] axes of anatase TiO_2.

UV-vis DRS of all samples (Figure S5):

Direct transition:



Indirect Transition:



Statistical analysis

Central composite design (CCD) strategy was used to study the effect of three independent process variables i.e., initial concentration, catalyst loading and pH and their interactive effects imposed on the dye decolorizing efficiency (response). A quadratic polynomial model was developed so obtain the mathematical relationship between the response and the independent operational process. The experimental results for color removal efficiency of RBBR dye in various conditions are presented in Table 3 and the empirical relationship between the % degradation (response) and independent operational variables are depicted by Eq 9:

$$\%\text{degradation for cycle 1} = 161.61601 - 1.24410\ A - 4.25480\ B - 17.42596\ C + 0.00751136\ A^2 - 12.72727\ B^2 + 0.49495\ C^2 + 0.75417 AB - 0.030833\ AC + 5.63889\ BC$$

%degradation for cycle 2 = 195.49654 – 1.98306 A – 10.74975 B – 26.70967 C + 0.770833 AB + 0.019583 AC + 4.19444 BC + 0.012670A2 -3.13131B2 + 1.11313 C2

%degradation for cycle 3 = 176.21394 – 2.80083 A – 4.80177 B – 22.40758 C + 0.729167 AB + 0.059167 AC + 1.63889 BC + 0.023307 A2 + 5.80808 B2 + 0.913636 C2

Model validation

ANOVA was used to assess the goodness of fit of the second order polynomial model and the results are recorded in Table 4. From the results it is clear that R^2 value was found to be near 1 (0.9973) which depicted that the experimental and predicted data of the response complement each other which can also be clearly seen in Fig. S3 (a). R^2 value of 99.73% indicated that only 0.27% of the discrepancies between the experimental and predicted data were not explained by the quadratic model. In addition to this, the adequacy of the regression model is hardly explained by R^2 value thus, the value of adjusted R^2 and predicted $R^2$is found to be more reliable for the system having the variation in independent variables.

In this case, the value of adjusted R^2 (Adj-R^2) was found to be 0.9948 which was more very close to the value of R^2 indicating that the model is a good fit. As shown in table 4, the higher F-value of linear term pH (C) (F-value 2334.66) and quadratic term of initial concentration (A^2) (F-value 15.99) and pH (C^2)(F-value 35.14) implies that these factors have a higher significance in the decolorisation of the dye. The model suitability as revealed by its F-value of 410.56 was further scrutinised from the analysis of residuals i.e., the deviation between experimental and predicted response results.

As seen from the graph S2(b), it is quite clear that the data points follow a straight-line path indicating that the residuals follow a normal distribution. The fluctuation around the centre line in a random pattern in the residual v/s predicted plot (Fig S2(a)) align with the assumption of constant variance. The plot of normal probability of the residual for RBBR is depicted in Fig.S2(c). Similar type of results were obtained when the catalyst was recovered from first cycle of experiment and reused for another two cycles.

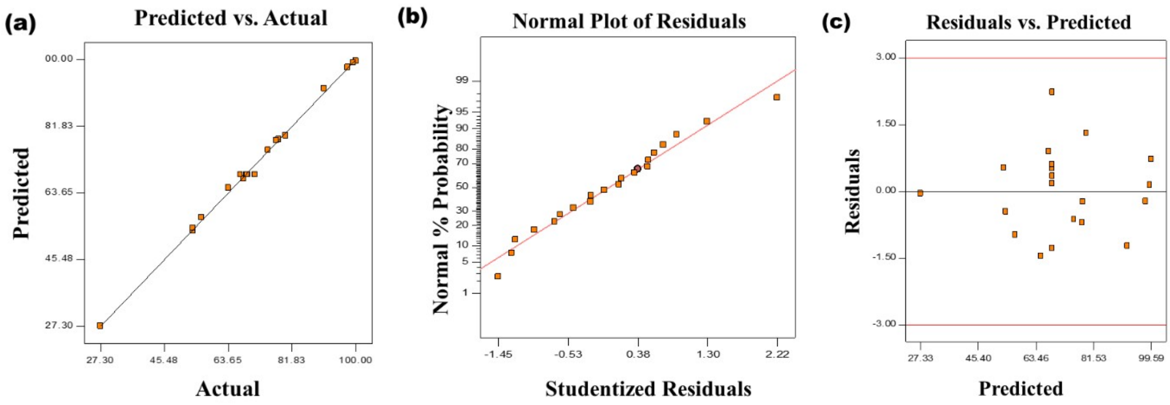


Figure S6 Plot of the relationship between (a) Normal % Probability and Residual (b) Residual and Predicted and (c) Predicted and Actual values of RBBR removal (%)

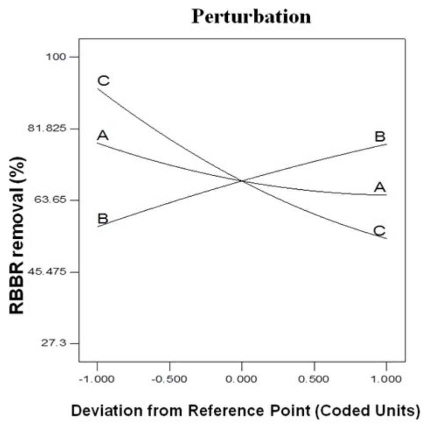


Figure S7 Perturbation plots for the dye removal efficiency of RBBR dye. (A) Initial concentration; (B) Catalyst Loading, and (C) pH

Interaction effects on response for cycle 1

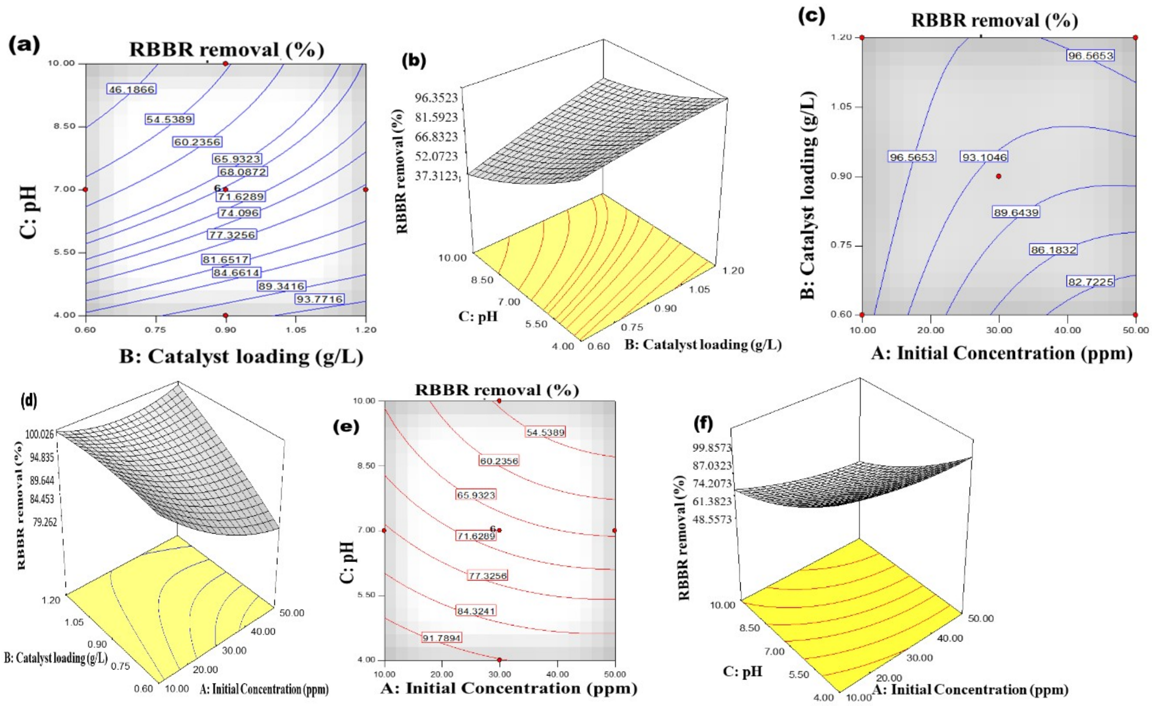


Figure S8 (a) 3D response surface plot and (b) contour plot showing interactionbetween Catalyst loading and pHand (c) 3D response surface plot (d) contour plot showing interaction between Initial Conc. And Catalyst loading and (e) 3D response surface plot and (f) contour plot showing interaction between pH and Initial conc.

Table S1: The 3-factor face-centered composite design matrix and the value of the response function after cycle 1, cycle 2 and cycle 3

Std	Run	Initial Conc.	Catalyst loading	pH	Predicted degradation (Cycle 1)	Actual degradation (Cycle 1)	Actual % degradation (Cycle 2)	Actual % degradation (Cycle 3)
19	1	30	0.9	7	69	68.60	52.2	43.8
14	2	30	0.9	10	53.60	53.30	45.3	36
1	3	10	0.6	4	97.70	97.83	95	83.8
10	4	50	0.9	7	63.70	64.99	53	47
6	5	50	0.6	10	27.30	27.33	22.4	19.3
3	6	10	1.2	4	100	99.59	100	99.6
13	7	30	0.9	4	91	92.09	87	70
18	8	30	0.9	7	67.10	68.60	55.1	40
20	9	30	0.9	7	71.20	68.60	51.8	41.7
5	10	10	0.6	10	53.60	53.30	44.2	35.2
11	11	30	0.6	7	56.10	56.97	46.5	40.4
12	12	30	1.2	7	77.30	77.93	65.2	50.2
9	13	10	0.9	7	78	78.21	69.4	61.2

7	14	10	1.2	10	75	75.36	65.5	55
2	15	50	0.6	4	80	79.26	67.3	55.6
4	16	50	1.2	4	99.20	99.12	92	87
8	17	50	1.2	10	68	67.49	61	59
16	18	30	0.9	7	69.20	68.60	55.1	45.9
15	19	30	0.9	7	68.80	68.60	50.1	42.2
17	20	30	0.9	7	69.30	68.60	53.2	46.3

Table S2. ANOVA for quadratic models for response function for S3550

Source	**Sum of squares**	**Degree of freedom**	**Mean square**	**F-value**	**p-value**
Model	5737.62	9	637.51	410.56	<0.0001
A-Initial Conc	436.92	1	436.92	281.38	<0.0001
B-Catalyst loading	1098.30	1	1098.30	707.31	<0.0001
C-pH	3625.22	1	3625.22	2334.66	<0.0001
AB	163.80	1	163.80	105.49	<0.0001
AC	27.38	1	27.38	17.63	0.0018
BC	206.04	1	206.04	132.69	<0.0001
A^2	24.83	1	24.83	15.99	0.0025
B^2	3.61	1	3.61	2.32	0.1584
C^2	54.57	1	54.57	35.14	0.0001
Residual	15.53	10	1.58		
Total	5753.15	19			

Table S3. ANOVA for quadratic models for response function for S3550 recovered after cycle 2

Source	Sum of squares	Degree of freedom	Mean square	F-value	p-value
Model	7098.54	9	790.04	128.25	<0.0001
A-Initial Conc	614.66	1	614.66	99.94	<0.0001
B-Catalyst loading	1172.89	1	1172.89	190.71	<0.0001
C-pH	4116.84	1	4116.84	669.39	<0.0001
AB	171.13	1	171.13	27.82	0.0004
AC	11.05	1	11.05	1.80	0.2099
BC	114.01	1	114.01	18.54	0.0015
A^2	69.63	1	70.64	11.32	0.0072
B^2	0.28	1	0.2184	0.045	0.8358
C^2	276.00	1	276.00	44.55	<0.0001
Residual	61.50	10	6.15		
Total	7160.05	19			

Table S4. ANOVA for quadratic models for response function for S3550 recovered after cycle 3

Source	Sum of squares	Degree of freedom	Mean square	F-value	p-value
Model	8316.19	9	924.02	186.23	<0.0001
A-Initial Conc	329.48	1	329.48	66.41	<0.0001
B-Catalyst loading	1136.36	1	1136.36	229.03	<0.0001
C-pH	4981.82	1	4981.82	1004.07	<0.0001
AB	158.42	1	158.42	31.93	0.0002
AC	64.98	1	64.98	13.10	0.0047
BC	89.78	1	89.78	18.09	0.0017
A^2	206.63	1	206.63	41.65	<0.0001
B^2	2.07	1	2.07	0.42	0.5326
C^2	295.62	1	295.62	59.58	<0.0001
Residual	49.62	10	4.96		
Total	8365.81	19			

Table S5. Coefficient of regression for each cycle

	Cycle 1	Cycle 2	Cycle 3
R^2	0.9973	0.9914	0.9941
Adjusted R^2	0.9949	0.9837	0.9887
Predicted R^2	0.9900	0.9667	0.9683

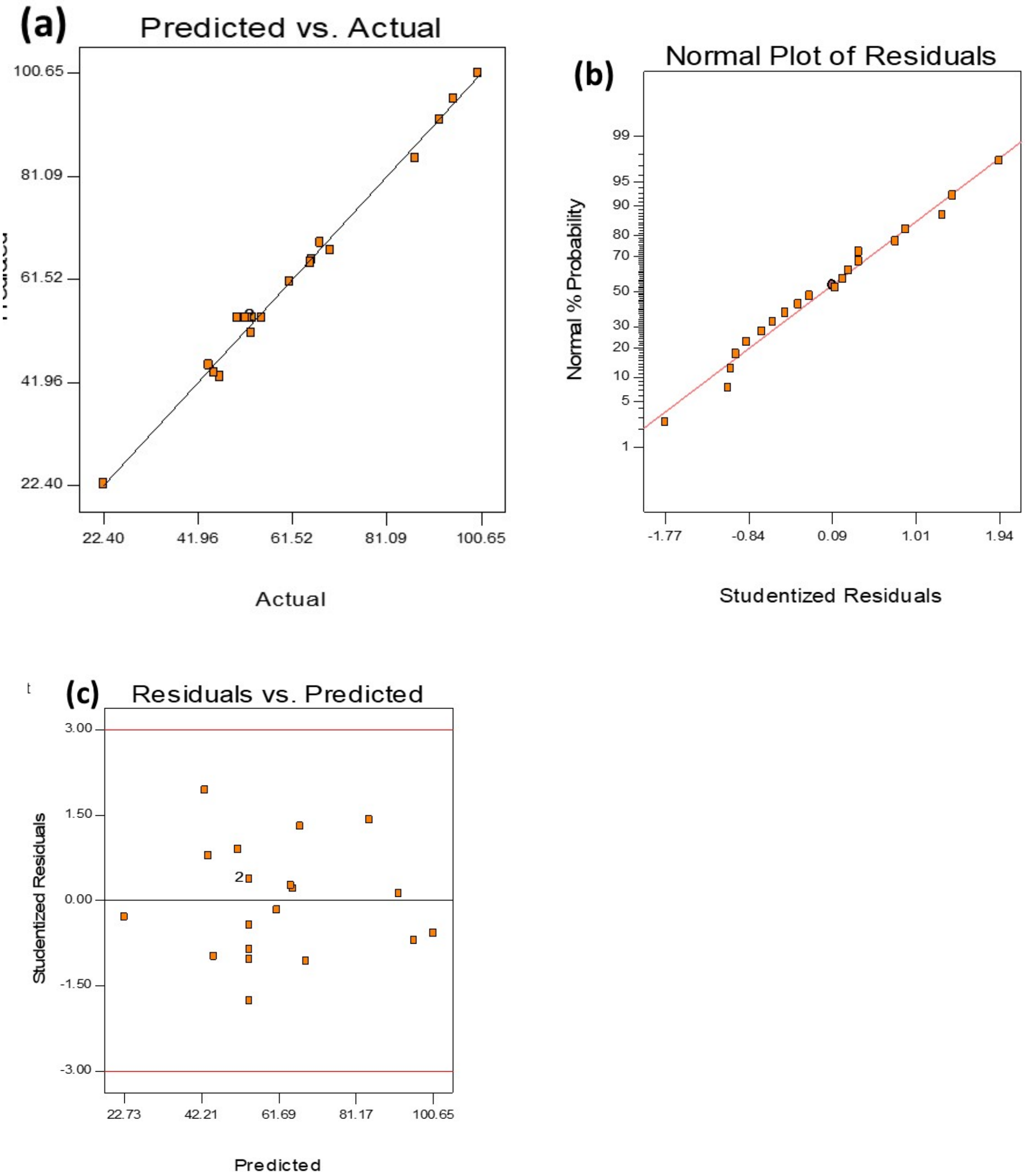


Figure S9 Plot of the relationship between (a) Normal % Probability and Residual (b) Residual and Predicted and (c) Predicted and Actual values of RBBR removal (%) for cycle 2

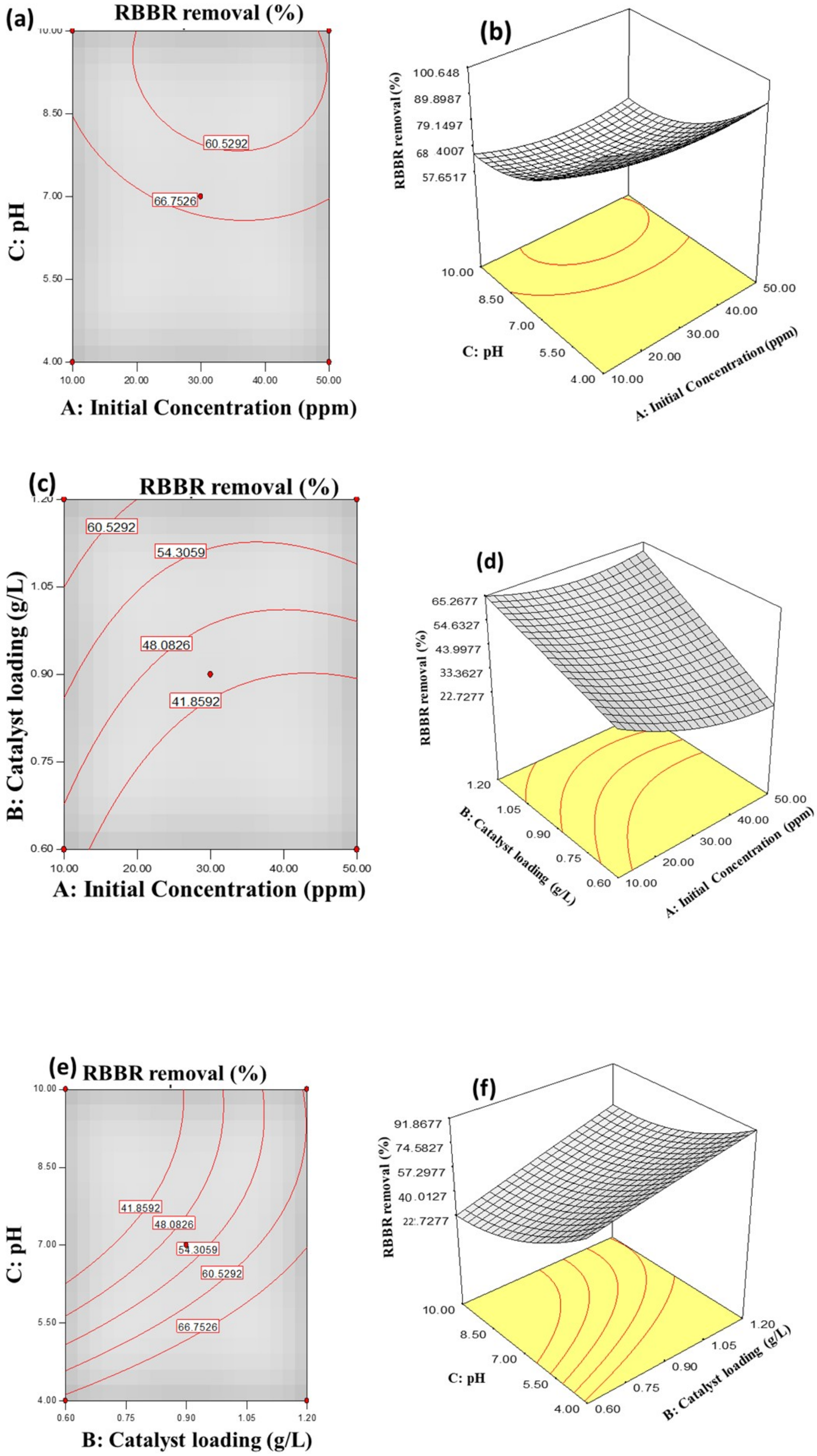


Figure S10 (a) 3D response surface plot and (b) contour plot showing interaction between Initial Conc. And pH (c) 3D response surface plot and (d) contour plot showing interaction between Initial concentration and Catalyst loading and (e) 3D response surface plot and (f) contour plot showing interaction between pH and Catalyst loading.

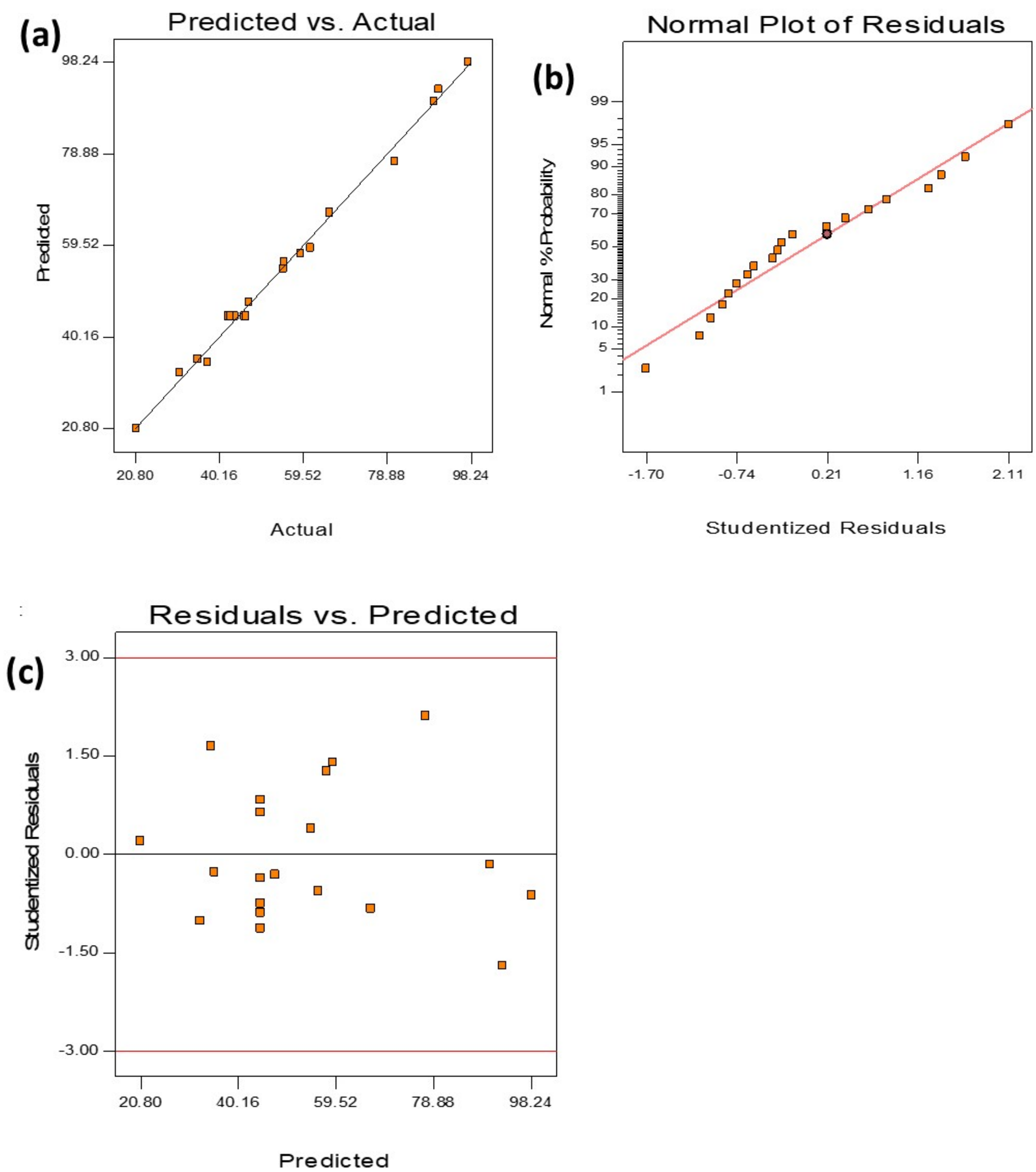


Figure S11 Plot of the relationship between (a) Normal % Probability and Residual (b) Residual and Predicted and (c) Predicted and Actual values of RBBR removal (%) for cycle 3

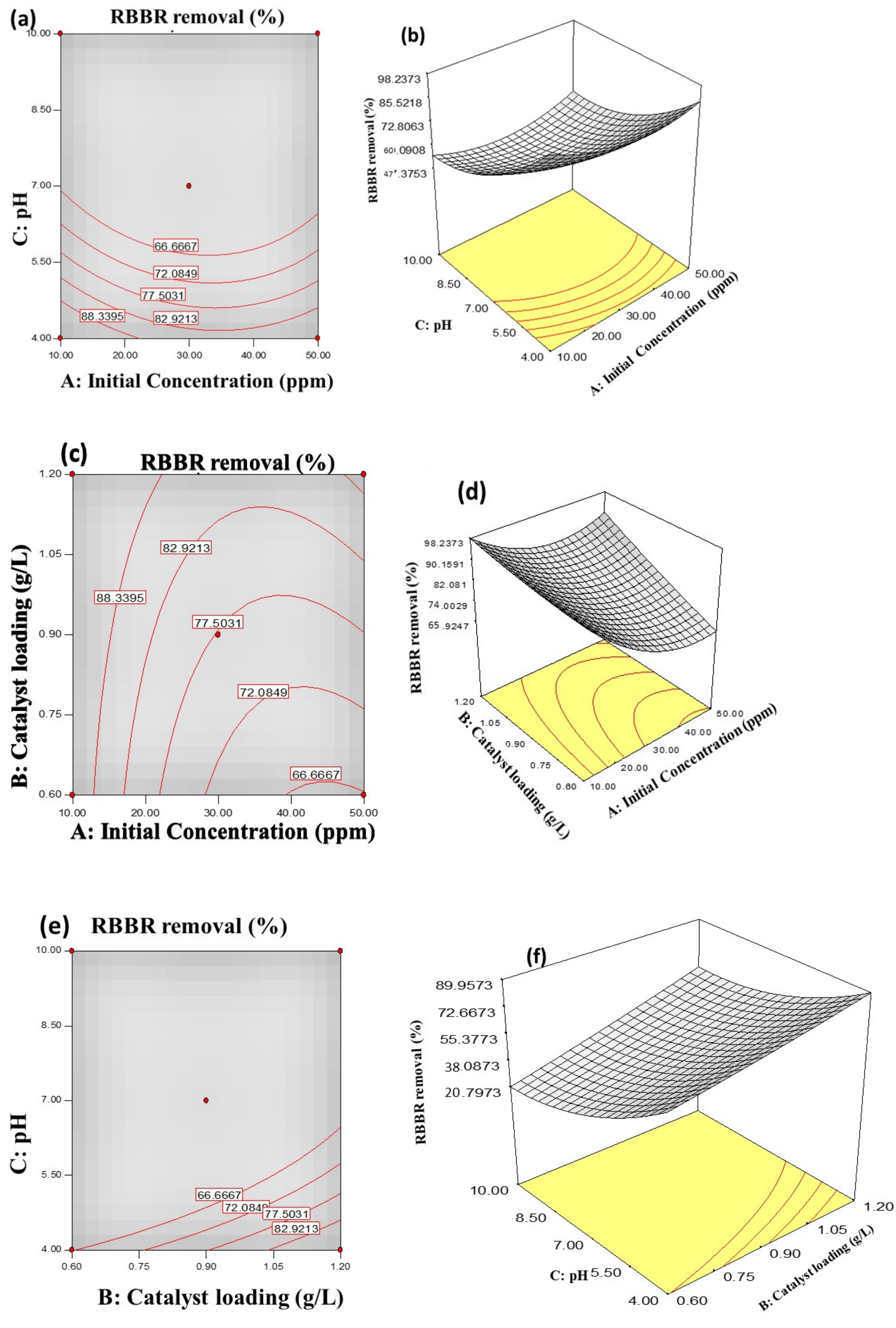


Figure S12 (a) 3D response surface plot and (b) contour plot showing interaction between Initial Conc. And pH (c) 3D response surface plot and (d) contour plot showing interaction between Initial concentration and Catalyst loading and (e) 3D response surface plot and (f) contour plot showing interaction between pH and Catalyst loading.

Reference:

1. S. Sandhu, S. K. Shahi and V. Singh,*New J. Chem.*, 2018, **42**, 12762-12765.

2. Sandhu S.; Kaur N.; Kaur M.; Singh V. Performance of {111}-TiO2/betanin/[Emim][NTf2]/Ag dye sensitized solar cell – combined experimental and DFT studies,*Mater. Lett.*,**2022**,131717.