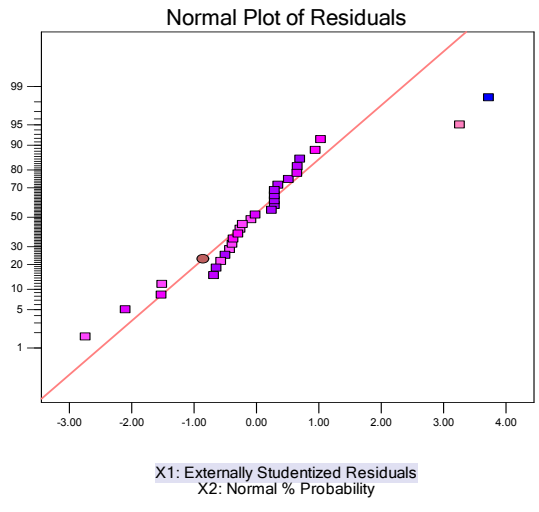
Supplementary Materials:

TSM1. Experimental matrix and results for RSM design.

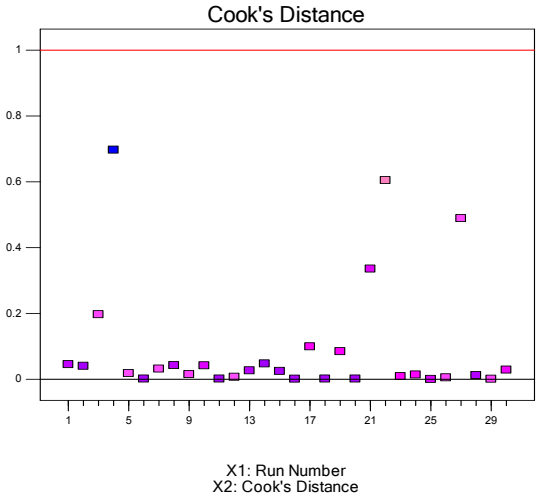
Std	Run	X_1: Step pot.	X_2: Ampl.e	X_3: pH	X_4: Modif. %
2	1	0.5	1.7	0.02	12.5
14	2	0.5	1.7	0.03	17.5
8	3	0.5	5	0.03	12.5
6	4	0.5	1.7	0.03	12.5
3	5	0.17	5	0.02	12.5
27	6	0.335	3.35	0.025	15
12	7	0.5	5	0.02	17.5
1	8	0.17	1.7	0.02	12.5
15	9	0.17	5	0.03	17.5
17	10	0.005	3.35	0.025	15
25	11	0.335	3.35	0.025	15
4	12	0.5	5	0.02	12.5
10	13	0.5	1.7	0.02	17.5
13	14	0.17	1.7	0.03	17.5
5	15	0.17	1.7	0.03	12.5
29	16	0.335	3.35	0.025	15
21	17	0.335	3.35	0.015	15
28	18	0.335	3.35	0.025	15
24	19	0.335	3.35	0.025	20
26	20	0.335	3.35	0.025	15
19	21	0.335	0.05	0.025	15
20	22	0.335	6.65	0.025	15
23	23	0.335	3.35	0.025	10
22	24	0.335	3.35	0.035	15
18	25	0.665	3.35	0.025	15
16	26	0.5	5	0.03	17.5
11	27	0.17	5	0.02	17.5
9	28	0.17	1.7	0.02	17.5
7	29	0.17	5	0.03	12.5
30	30	0.335	3.35	0.025	15

TSM2. Results of experimental runs compared with the predicted values by the model.

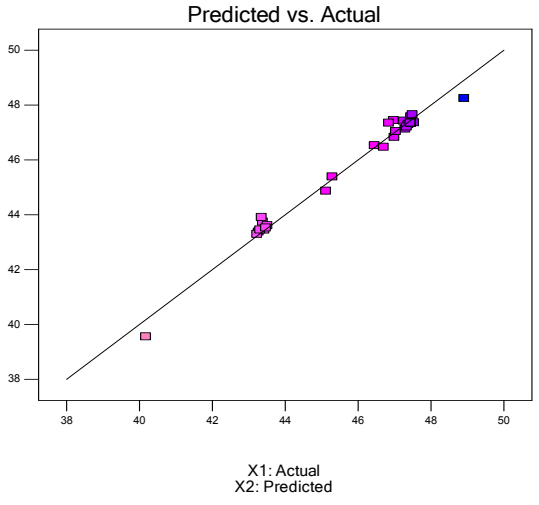
Variable	Step potential (V)	Amplitude (V)	pH	Modifier %
Optimized values	0.023	0.500	2	16.5
Suggested model	Quadratic			
Aver. predicted response	48.5056			
95% CI low and high	48.0814-48.9299			
Predicted Std Dev	0.378001			
Observed response (n=3)	48.63 (±0.57)			



A

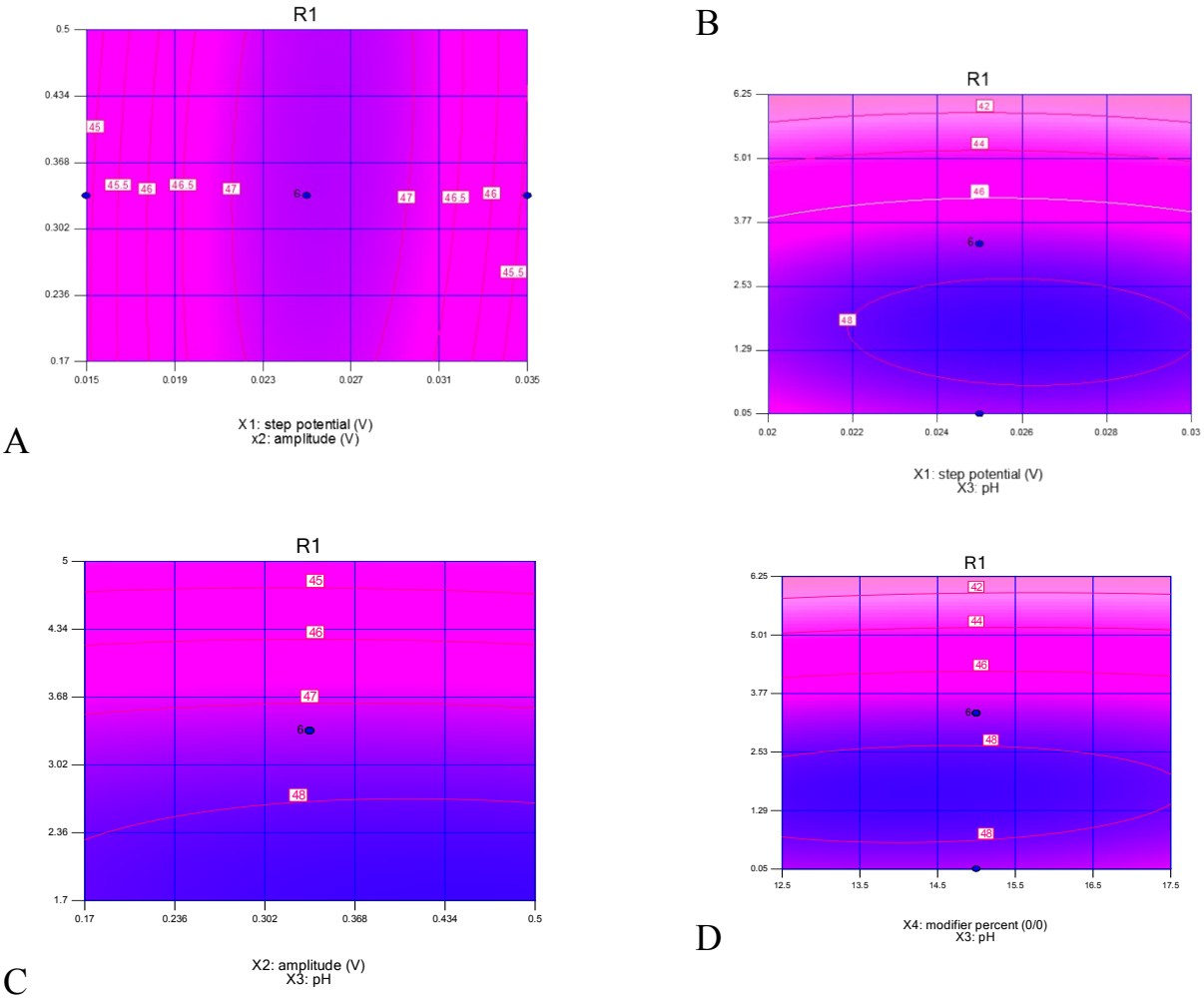


B



C

FSM1. A) Normal probability of internally residuals; **B)** Cook's distance results for diagnostic of distribution of data; **C)** Predicted versus actual values.



FSM2. Some selected 2D counters plots for showing visualize interaction effects of step potential (X_1), amplitude (X_2), pH (X_3), modifier% (X_4), and their interaction on CV response of Fe(II) in the presence of permanganate.