Biochar-capped iron oxide nanocomposites prepared by ultrasonic method as nanophotocatalysts for the degradation of organic dyes using response surface methodology

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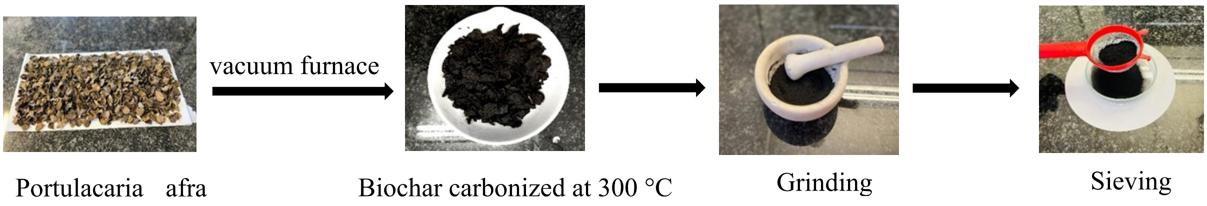


Scheme S1. Preparation of *Portulacaria afra* biochar.

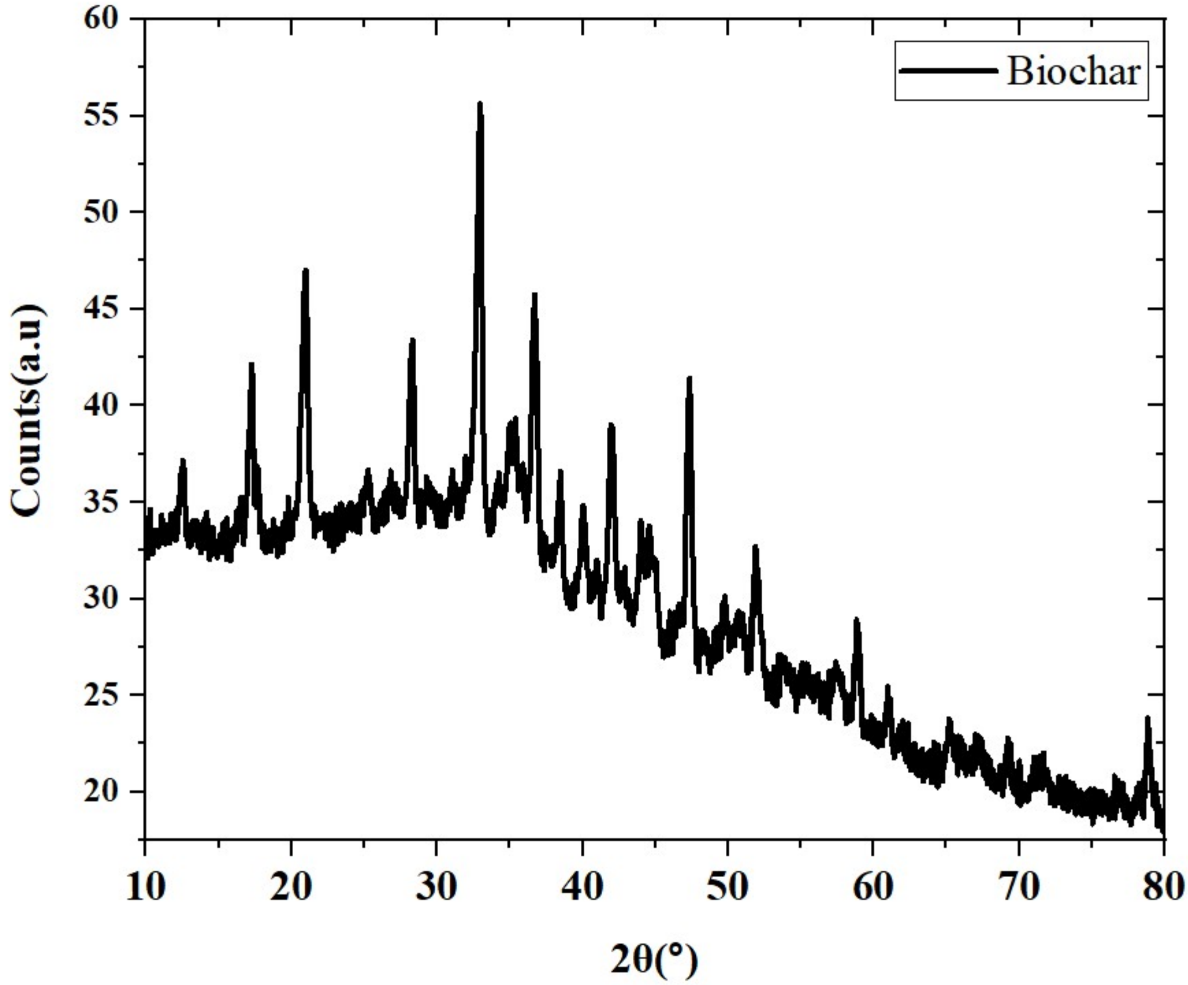


Figure S1. p-XRD pattern of biochar.

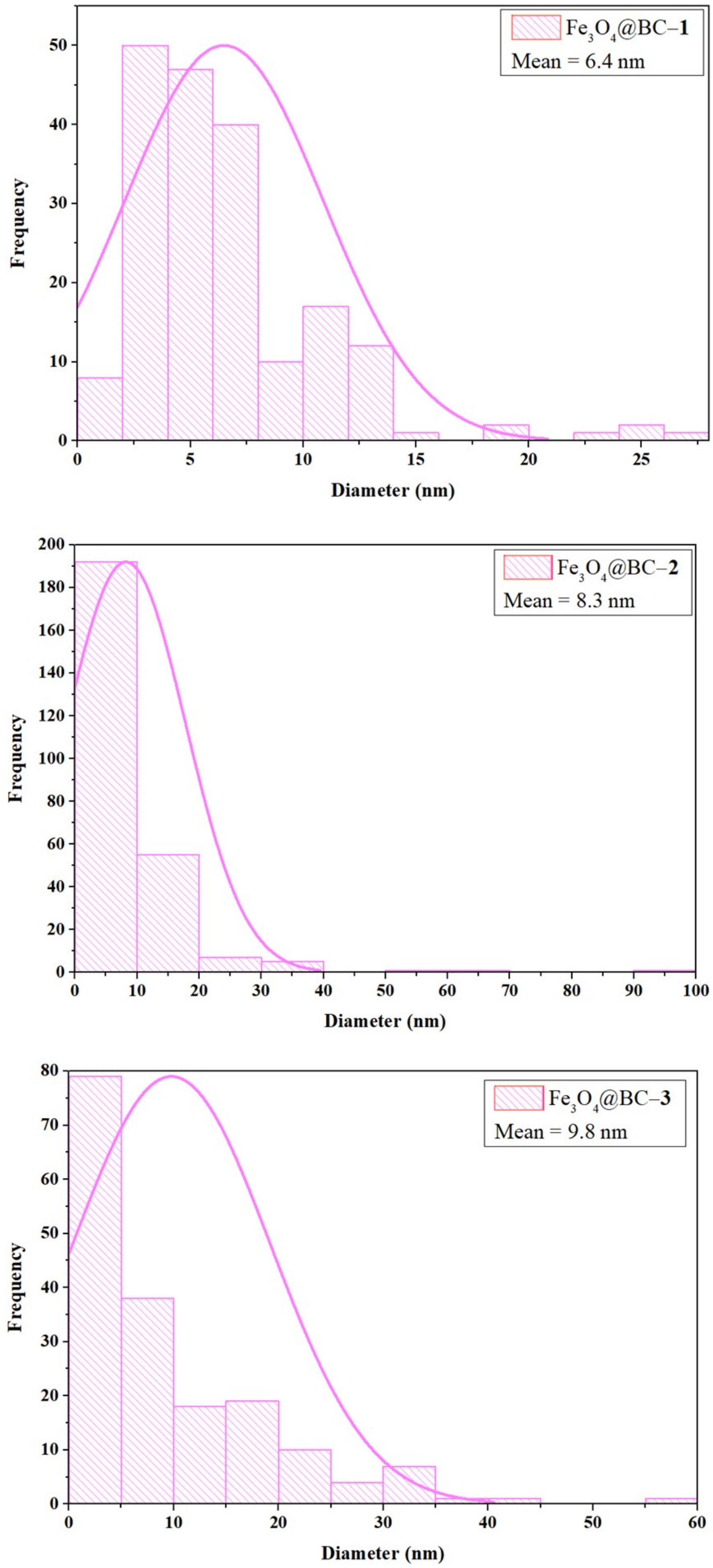


Figure S2. Size distributions of iron oxide nanocomposites prepared at different ultrasound irradiation times

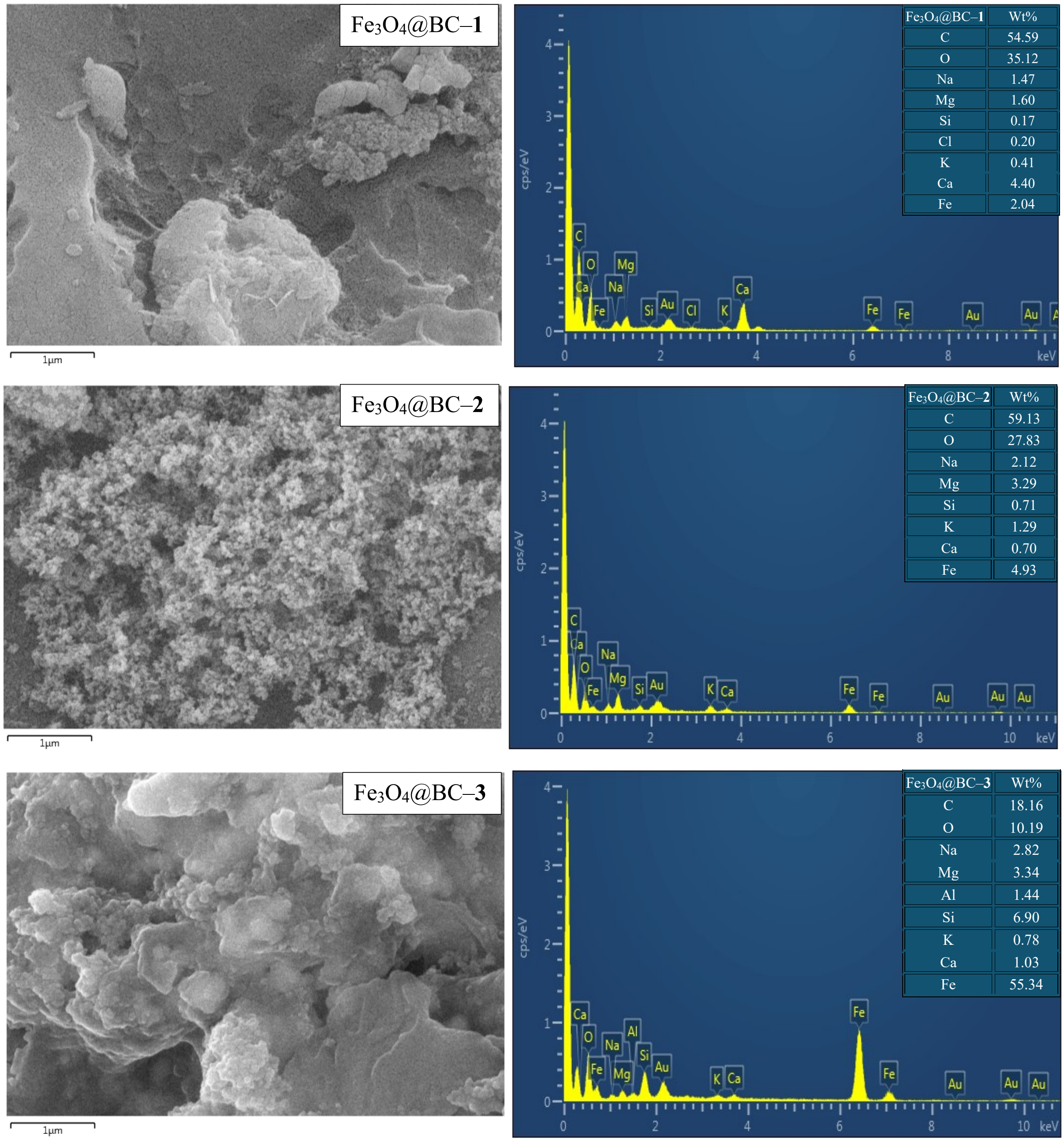


Figure S3. SEM images and EDX spectra of Fe_3O_4@BC nanocomposites.

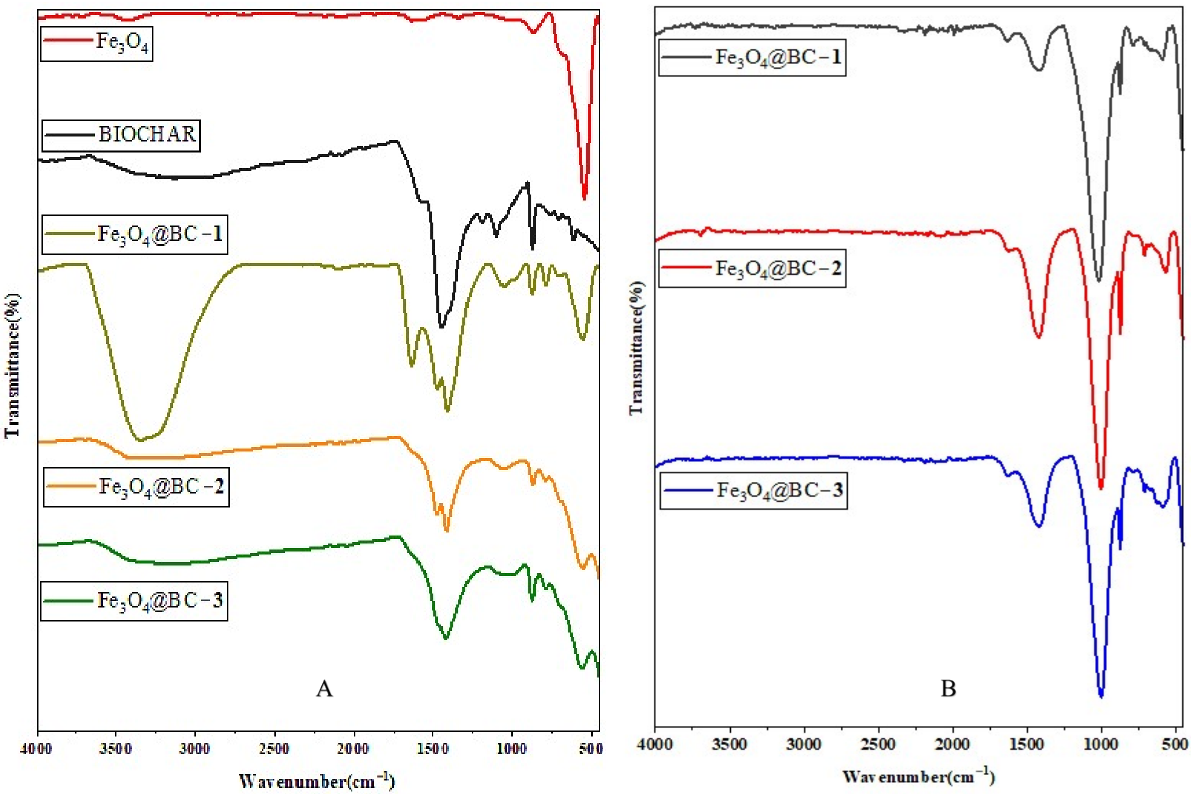
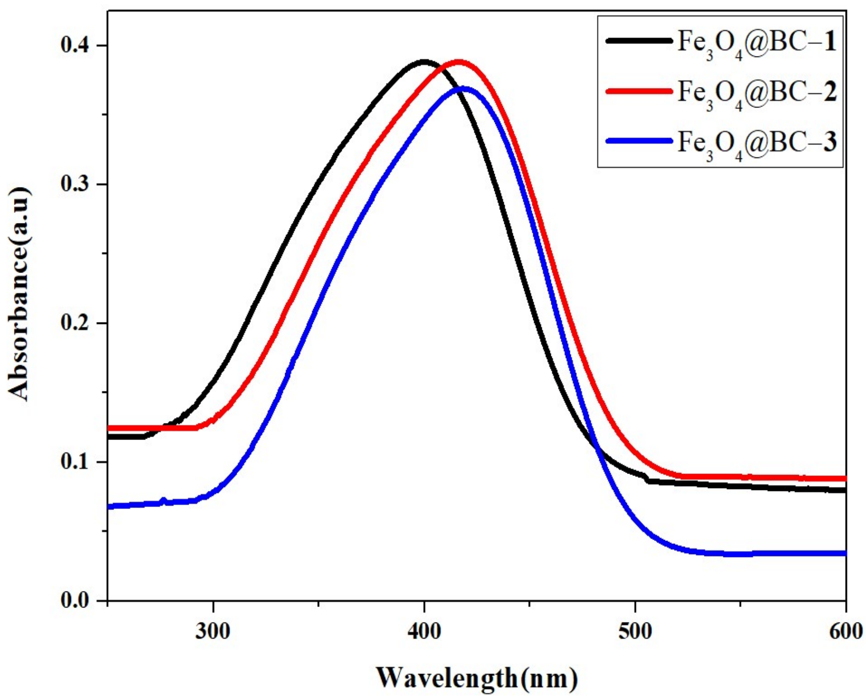


Figure S4. FTIR spectra of magnetite nanoparticles, biochar and Fe_3O_4@BC nanocomposites before (A) and after (B) photocatalysis.



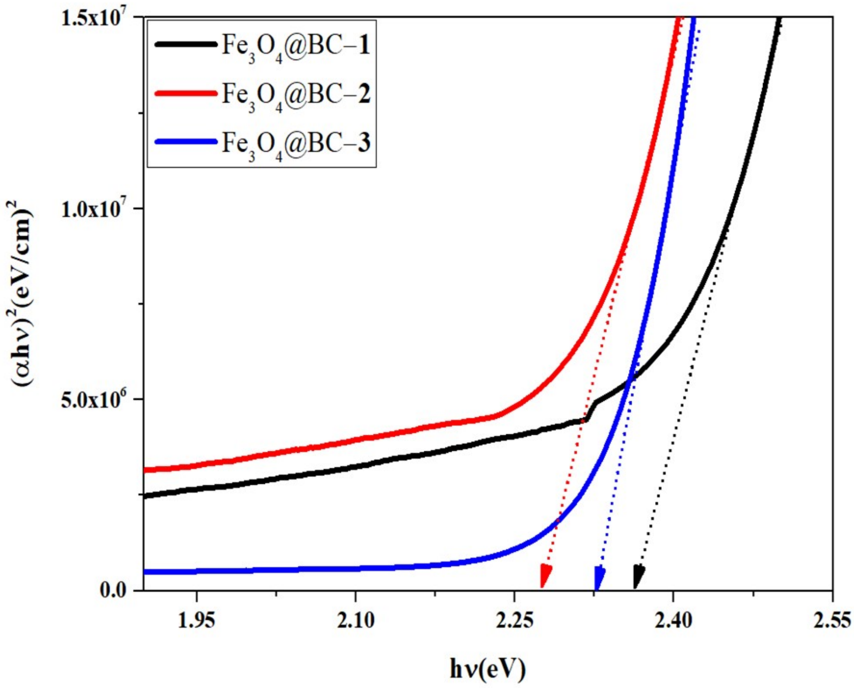


Figure S5. UV-Vis spectra and Tauc plots of iron oxide nanocomposites.

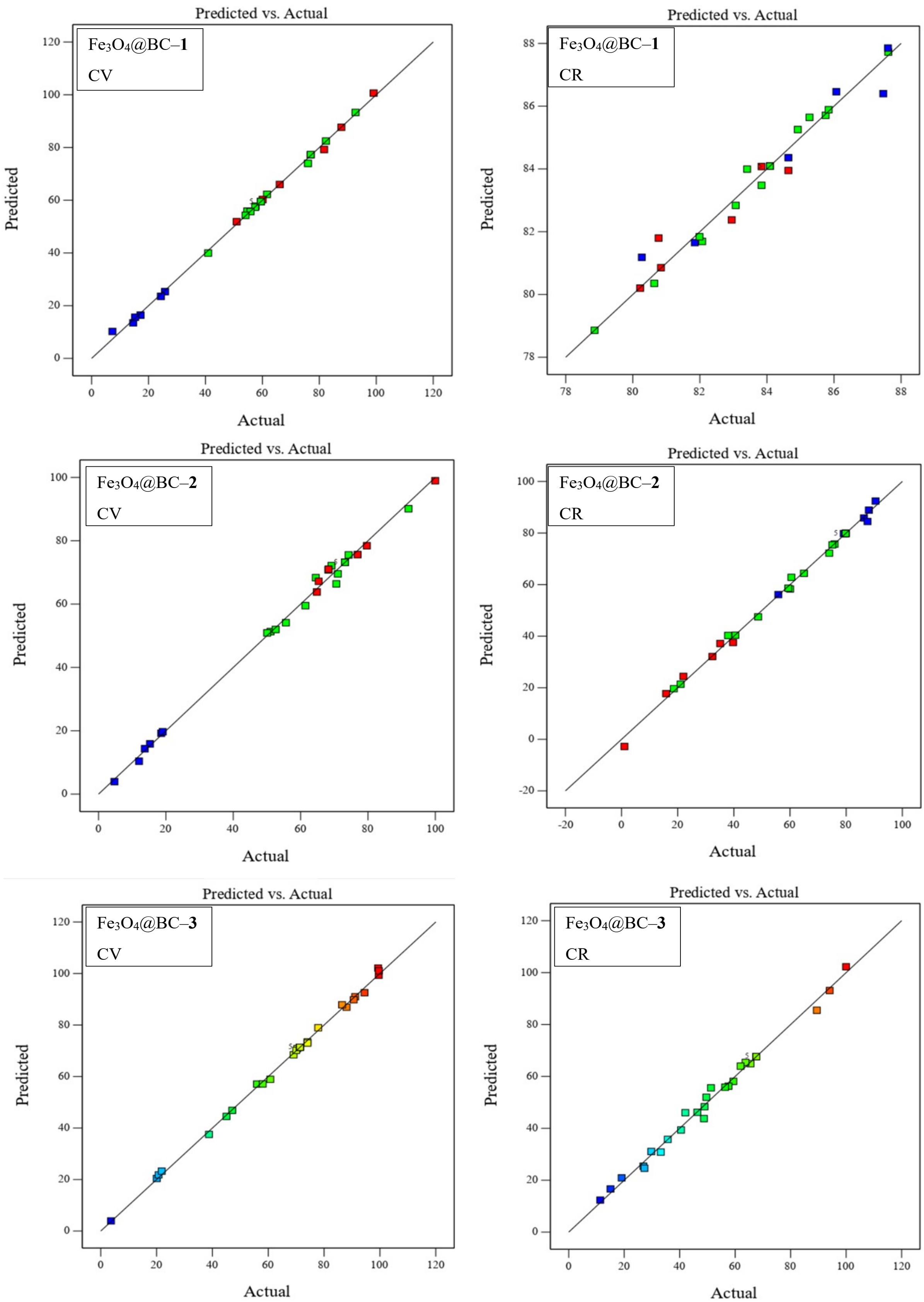


Figure S6. Predicted versus actual degradation of CV and CR.

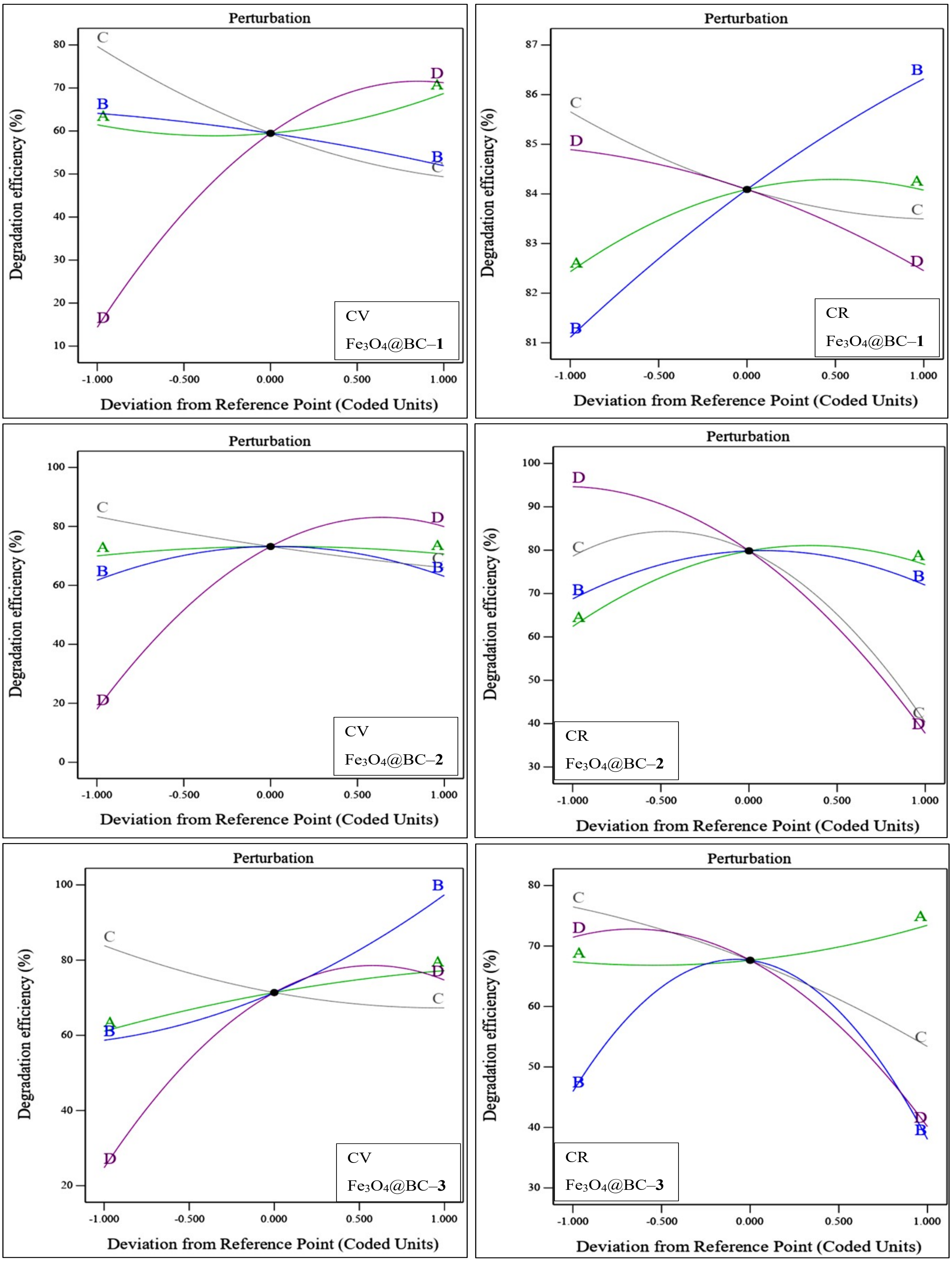


Figure S7. Perturbation plots showing the effect of the independent variables on CV dye and CR degradation.

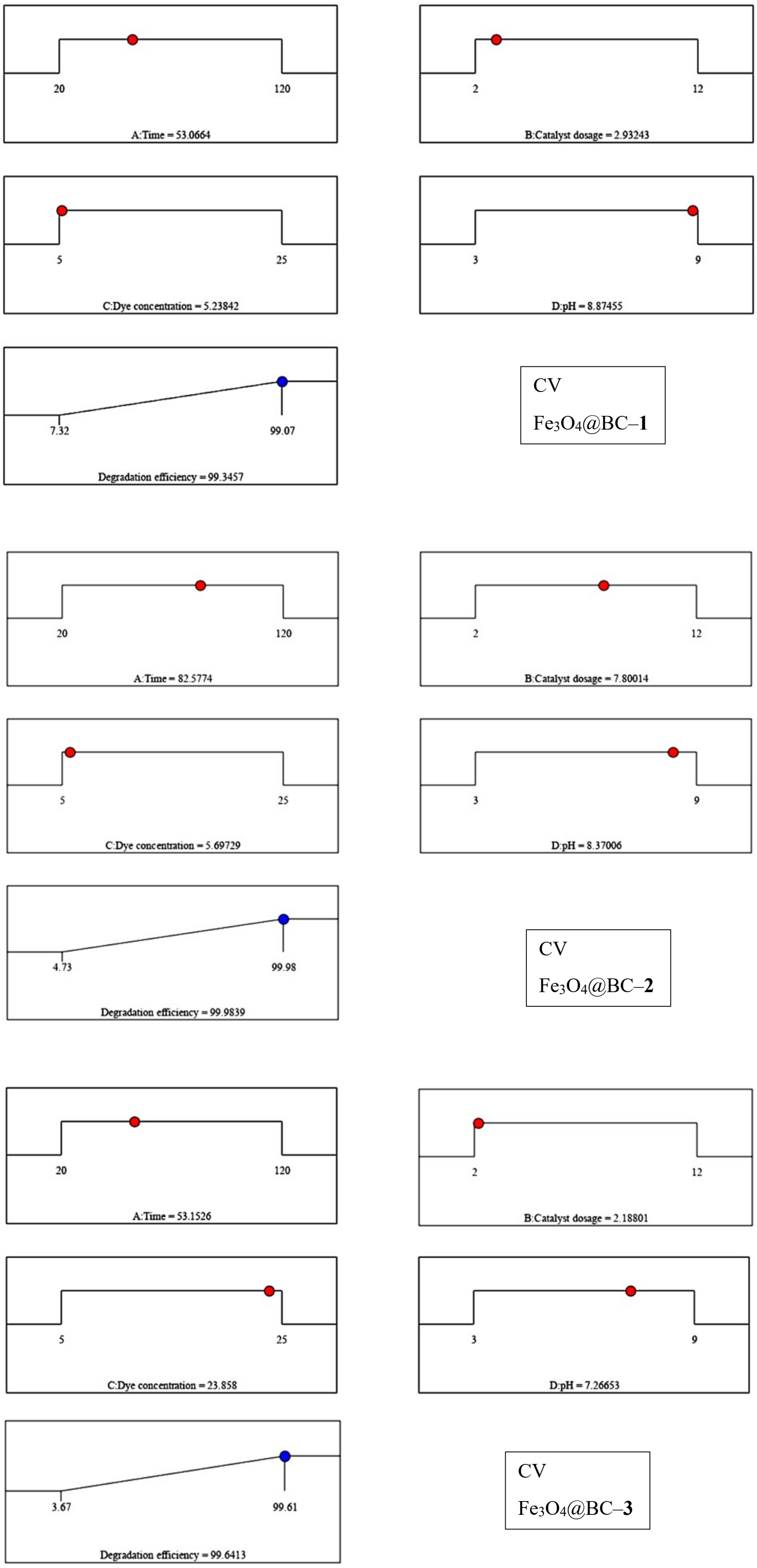


Figure S8. Ramp plot showing numerical optimization for CV degradation.

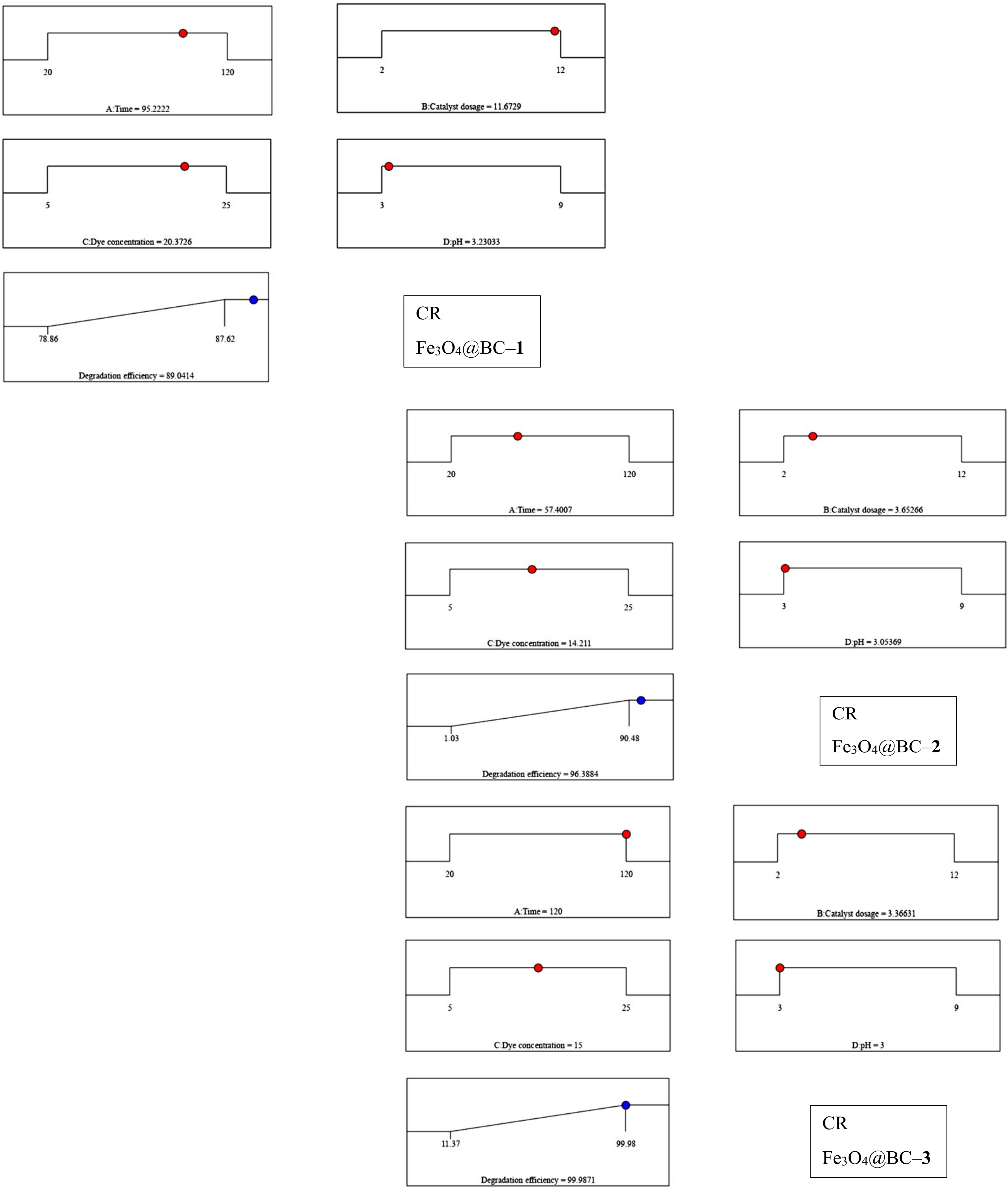


Figure S9. Ramp plot showing numerical optimization for CR degradation.

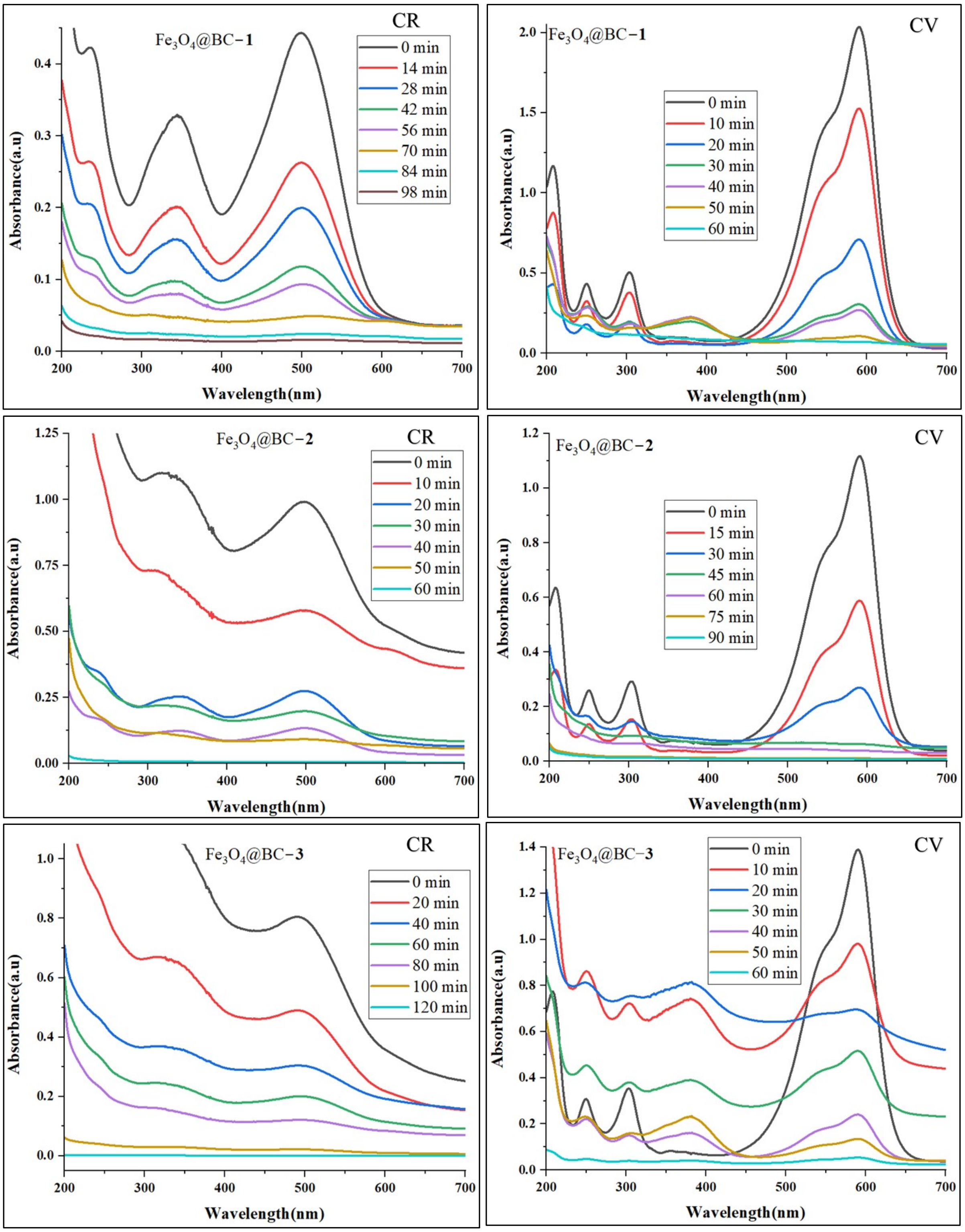


Figure S10. Absorption spectra of Congo red (CR) and crystal violet (CV) dyes degradation by iron oxide nanocomposites.

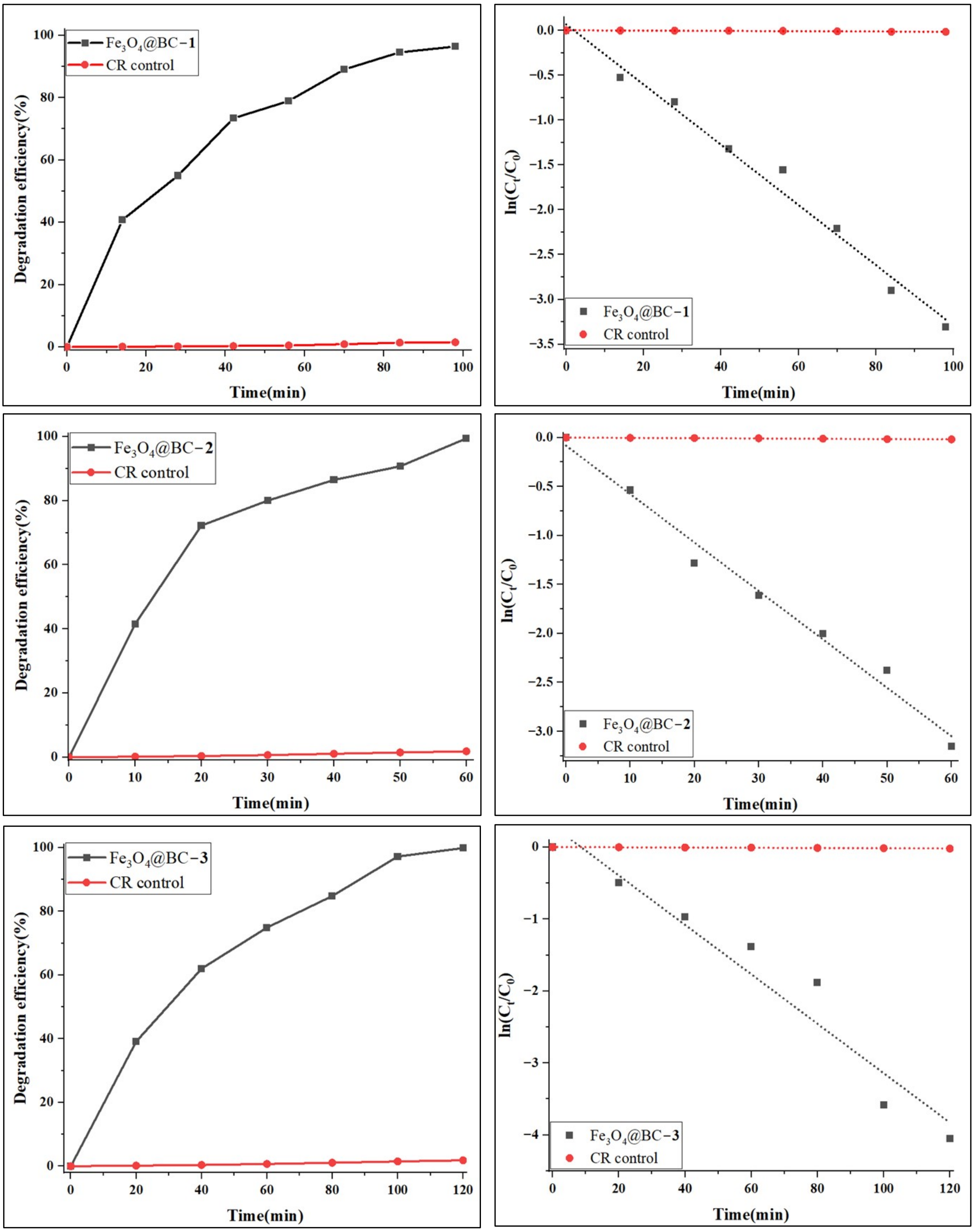


Figure S11. Congo red photocatalytic degradation efficiency curve and kinetic plots.

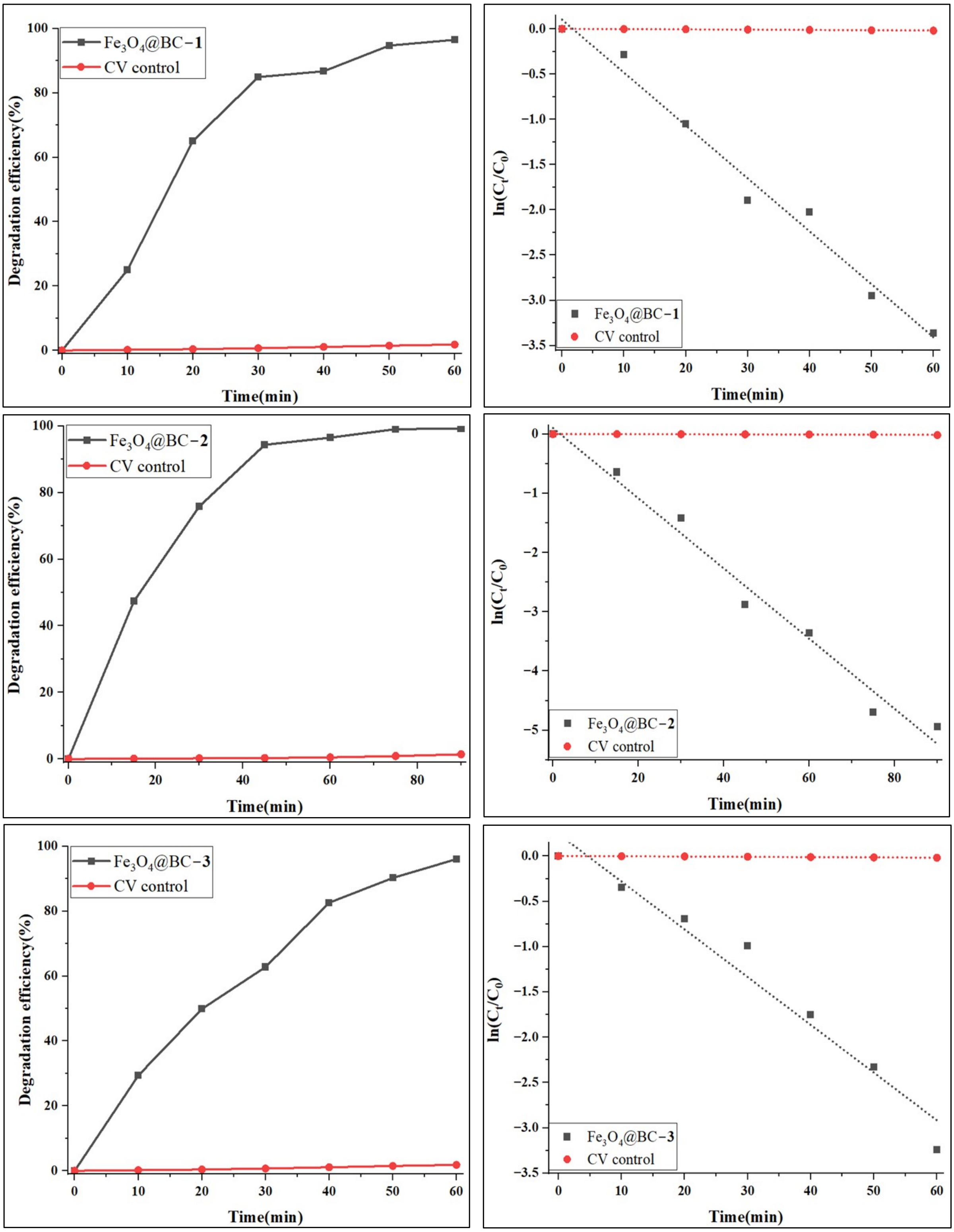


Figure S12. Crystal violet photocatalytic degradation efficiency curve and kinetic plots.

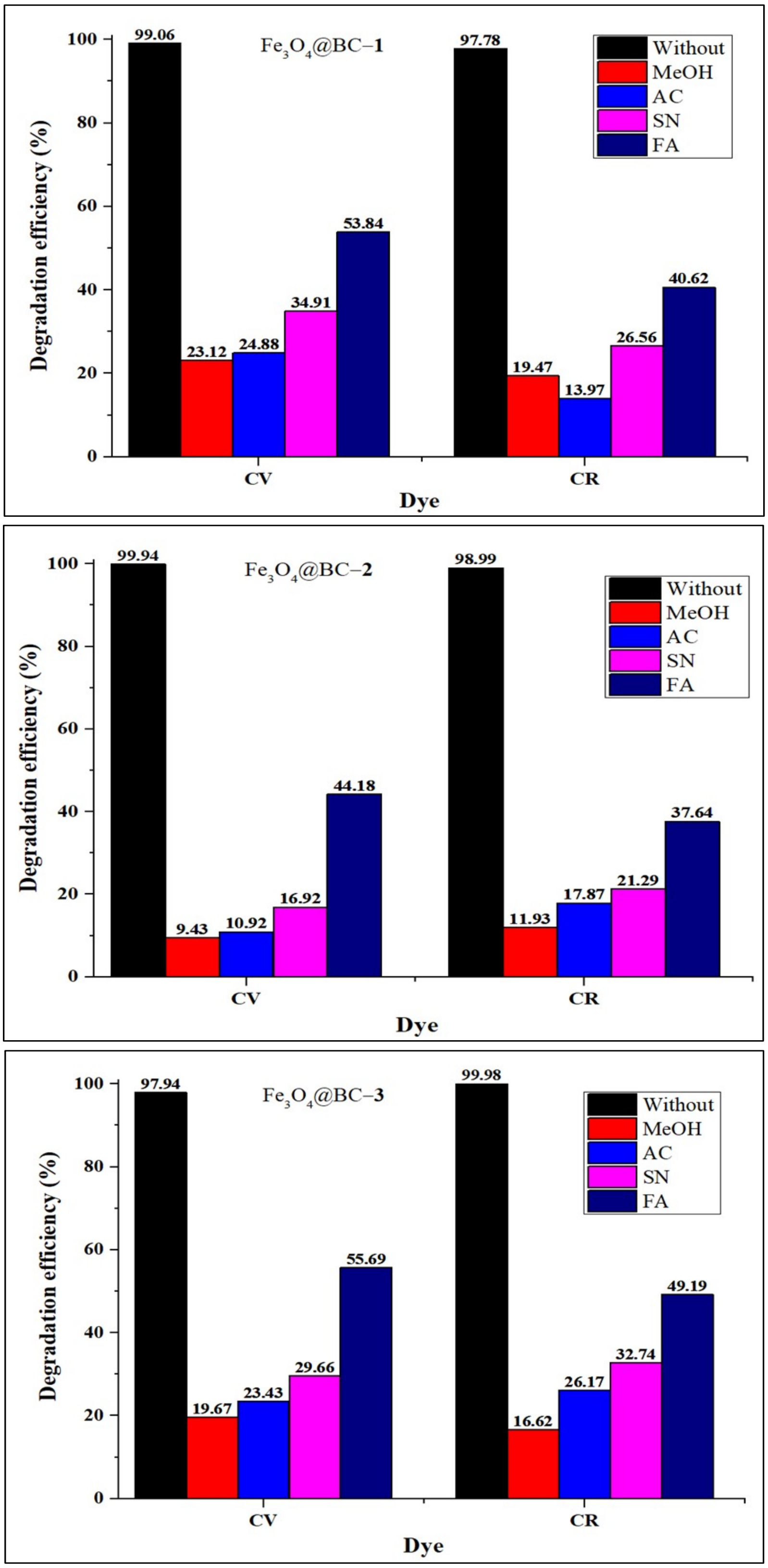


Figure S13. Effect of scavengers on the degradation of Congo red and crystal violet dye by iron oxide nanocomposites.

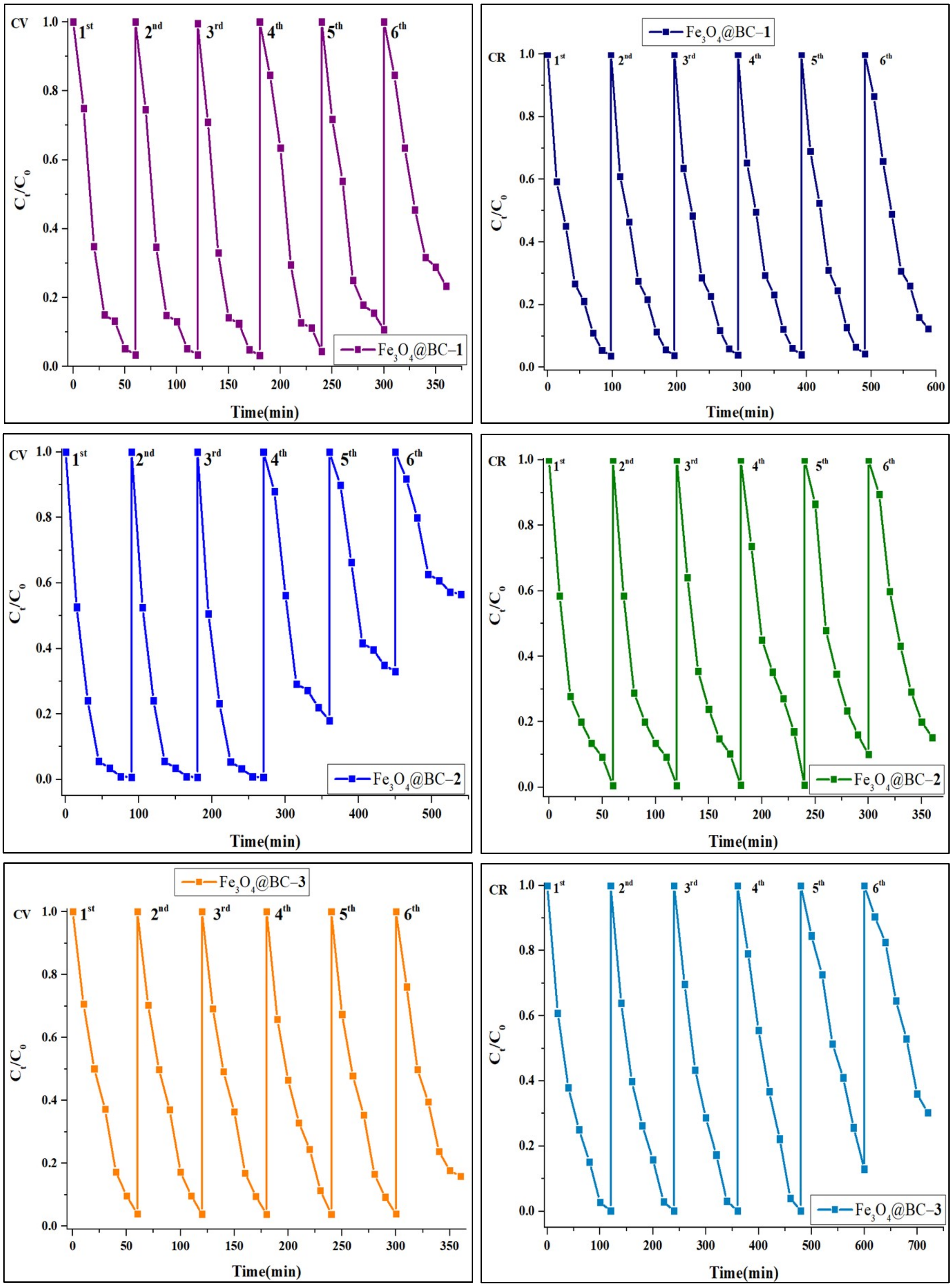


Figure S14. Recyclability of Fe_3O_4@BC nanocomposites over CV and CR dyes.

Table S1: Degradation efficiencies from triplicate trials under optimized conditions

Congo red (CR)						
	Predicted efficiency (%)	Experimental Efficiency **(1)** (%)	Experimental efficiency **(2)** (%)	Experimental efficiency **(3)** (%)	Mean degradation efficiency (%)	Standard deviation (%)
Fe_3O_4@BC–**1**	89.04	96.33	95.97	96.28	96.19	0.19
Fe_3O_4@BC–**2**	96.38	99.42	99.38	99.43	99.41	0.03
Fe_3O_4@BC–**3**	99.98	99.86	99.83	99.88	99.86	0.03
Crystal violet (CV)						
Fe_3O_4@BC–**1**	99.35	96.53	99.56	99.49	98.53	1.16
Fe_3O_4@BC–**2**	99.98	99.28	99.39	99.24	99.30	0.08
Fe_3O_4@BC–**3**	99.64	99.10	99.14	99.11	99.12	0.02

Table S2: Experimental design matrix and response results for Congo red (CR) and crystal violet (CV) by Fe_3O_4@BC–**1**.

Run	Time (min)	Catalyst dosage (mg)	Dye concentration (ppm)	pH	Congo red (CR)		Crystal violet	
					Predicted (%)	Experimental (%)	Predicted (%)	Experimental (%)
1	20	7	15	3	84.09	84.09	23.54	24.34
2	20	7	25	6	80.20	80.22	55.70	55.81
3	70	12	25	6	84.00	83.41	39.95	40.94
4	70	12	5	6	80.35	80.64	73.97	76.02
5	70	7	5	9	80.85	80.84	100.63	99.07
6	70	2	5	6	81.65	81.85	82.45	82.34
7	120	7	25	6	81.80	80.77	54.25	54.09
8	70	7	5	3	85.64	85.27	25.32	25.80
9	70	7	15	6	86.40	87.47	59.48	59.48
10	20	12	15	6	84.09	84.09	57.76	57.61
11	120	2	15	6	83.95	84.64	77.23	76.95
12	120	7	15	9	85.89	85.84	87.66	87.74
13	20	7	15	9	85.26	84.92	65.98	66.09
14	70	12	15	9	84.09	84.09	60.25	60.09
15	120	7	15	3	84.08	83.84	16.42	17.19
16	20	7	5	6	84.36	84.64	77.27	76.98
17	70	7	15	6	83.48	83.84	59.48	59.48
18	70	7	15	6	87.85	87.61	59.48	59.48
19	70	2	25	6	82.84	83.07	55.85	54.68
20	120	7	5	6	86.46	86.07	93.29	92.72
21	70	7	25	9	84.09	84.09	51.86	50.96
22	70	7	25	3	78.86	78.86	13.48	14.61
23	70	7	15	6	81.18	80.27	59.48	59.48
24	70	2	15	9	84.09	84.09	79.24	81.68
25	20	2	15	6	81.84	81.99	62.22	61.63
26	70	12	15	3	85.71	85.75	10.21	7.32

27	70	7	15	6	87.72	87.62	59.48	59.48
28	70	2	15	3	81.69	82.07	15.60	15.31
29	120	12	15	6	82.38	82.95	57.32	57.48

Table S3: Experimental design matrix and response results for Congo red (CR) and crystal violet (CV) by Fe_3O_4@BC–**2**.

Run	Time (min)	Catalyst dosage (mg)	Dye concentration (ppm)	pH	Congo red (CR)		Crystal violet	
					Predicted (%)	Experimental (%)	Predicted (%)	Experimental (%)
1	20	7	15	3	24.41	22.03	73.18	73.18
2	20	7	25	6	88.89	88.09	73.18	73.18
3	70	12	25	6	47.50	48.64	51.99	52.60
4	70	12	5	6	56.14	55.84	70.81	68.24
5	70	7	5	9	79.84	79.84	15.86	15.29
6	70	2	5	6	-2.78	1.03	59.51	61.43
7	120	7	25	6	37.16	35.13	10.39	12.04
8	70	7	5	3	64.38	64.97	19.22	18.61
9	70	7	15	6	40.37	40.54	63.83	64.83
10	20	12	15	6	21.36	21.03	3.95	4.73
11	120	2	15	6	75.73	75.87	14.34	13.73
12	120	7	15	9	17.72	15.87	98.96	99.98
13	20	7	15	9	37.52	39.71	66.39	70.61
14	70	12	15	9	62.81	60.49	75.51	74.26
15	120	7	15	3	75.39	75.08	78.43	79.67
16	20	7	5	6	79.84	79.84	71.01	68.31
17	70	7	15	6	85.83	86.34	75.64	76.92
18	70	7	15	6	92.40	90.48	73.18	73.18
19	70	2	25	6	32.10	32.35	51.31	51.09
20	120	7	5	6	40.28	37.94	50.91	50.08
21	70	7	25	9	58.61	59.36	68.35	64.51
22	70	7	25	3	58.28	60.04	90.12	92.04
23	70	7	15	6	79.84	79.84	69.55	71.05
24	70	2	15	9	79.84	79.84	73.18	73.18
25	20	2	15	6	84.48	87.61	72.15	69.18
26	70	12	15	3	79.78	79.16	54.12	55.64

27	70	7	15	6	19.64	18.62	67.20	65.37
28	70	2	15	3	72.20	73.97	73.18	73.18
29	120	12	15	6	79.84	79.84	19.70	19.07

Table S4: Experimental design matrix and response results for Congo red (CR) and crystal violet (CV) by Fe_3O_4@BC–**3**.

Run	Time (min)	Catalyst dosage (mg)	Dye concentration (ppm)	pH	Congo red (CR)		Crystal violet	
					Predicted (%)	Experimental (%)	Predicted (%)	Experimental (%)
1	20	7	15	3	56.23	57.60	71.37	71.37
2	20	7	25	6	16.63	15.08	71.37	71.37
3	70	12	25	6	30.84	33.19	87.86	86.45
4	70	12	5	6	65.38	63.74	70.87	70.41
5	70	7	5	9	35.74	35.69	3.93	3.67
6	70	2	5	6	67.64	67.64	101.05	99.61
7	120	7	25	6	85.48	89.45	44.51	45.04
8	70	7	5	3	67.64	67.64	90.99	91.13
9	70	7	15	6	39.35	40.48	73.44	74.05
10	20	12	15	6	67.64	67.64	57.06	55.97
11	120	2	15	6	102.26	99.98	46.85	47.11
12	120	7	15	9	46.03	42.04	68.42	69.08
13	20	7	15	9	55.85	56.38	57.13	58.02
14	70	12	15	9	25.39	26.92	71.37	71.37
15	120	7	15	3	20.91	19.09	89.82	90.61
16	20	7	5	6	31.07	29.76	71.37	71.37
17	70	7	15	6	58.09	59.37	92.54	94.49
18	70	7	15	6	55.61	51.28	58.91	60.73
19	70	2	25	6	12.34	11.37	86.90	88.04
20	120	7	5	6	63.95	61.96	71.37	71.37
21	70	7	25	9	51.97	49.62	37.51	38.77
22	70	7	25	3	46.18	46.36	78.94	77.89
23	70	7	15	6	93.09	94.07	20.40	20.07
24	70	2	15	9	67.64	67.64	102.11	99.36
25	20	2	15	6	64.90	65.54	72.99	74.07
26	70	12	15	3	67.64	67.64	99.31	99.58

27	70	7	15	6	24.61	27.30	23.24	21.84
28	70	2	15	3	48.34	48.97	70.16	70.02
29	120	12	15	6	43.75	48.76	21.81	20.73

Table S5: Analysis of variance (ANOVA) for CR degradation using Fe_3O_4@BC–**1** composite.

Source	**Sum of**	**df**	**Mean Square**	**F-value**	**p-value**

	Squares				
Model	143.79	14	10.27	27.29	< 0.0001
A-Time	8.10	1	8.10	21.52	0.0004
B-Catalyst dosage	81.38	1	81.38	216.19	< 0.0001
C-Dye concentration	14.00	1	14.00	37.18	< 0.0001
D-pH	17.89	1	17.89	47.51	< 0.0001
AB	1.42	1	1.42	3.76	0.0729
AC	0.0000	1	0.0000	0.0001	0.9936
AD	10.02	1	10.02	26.61	0.0001
BC	0.1056	1	0.1056	0.2806	0.6046
BD	2.13	1	2.13	5.66	0.0321
CD	0.0144	1	0.0144	0.0383	0.8477
A^2	4.54	1	4.54	12.05	0.0037
B^2	0.9122	1	0.9122	2.42	0.1419
C^2	1.53	1	1.53	4.07	0.0631
D^2	1.13	1	1.13	3.00	0.1050
Residual	5.27	14	0.3764		
Lack of Fit	5.27	10	0.5270		
Pure Error	0.0000	4	0.0000		
Cor Total	149.06	28			

Table S6: Analysis of variance (ANOVA) for CR degradation using Fe_3O_4@BC–**2** composite.

Source	**Sum of**	**df**	**Mean Square**	**F-value**	**p-value**

	Squares				
Model	18873.23	14	1348.09	277.30	< 0.0001
A-Time	611.47	1	611.47	125.78	< 0.0001
B-Catalyst dosage	30.15	1	30.15	6.20	0.0260
C-Dye concentration	4396.84	1	4396.84	904.43	< 0.0001
D-pH	9712.83	1	9712.83	1997.92	< 0.0001
AB	194.74	1	194.74	40.06	< 0.0001
AC	41.73	1	41.73	8.58	0.0110
AD	26.68	1	26.68	5.49	0.0344
BC	248.06	1	248.06	51.03	< 0.0001
BD	20.48	1	20.48	4.21	0.0593
CD	4.08	1	4.08	0.8393	0.3751
A^2	689.77	1	689.77	141.88	< 0.0001
B^2	585.05	1	585.05	120.34	< 0.0001
C^2	2694.68	1	2694.68	554.29	< 0.0001
D^2	1206.73	1	1206.73	248.22	< 0.0001
Residual	68.06	14	4.86		
Lack of Fit	68.06	10	6.81		
Pure Error	0.0000	4	0.0000		
Cor Total	18941.29	28			

Table S7: Analysis of variance (ANOVA) for CR degradation using Fe_3O_4@BC–**3** composite.

Source	Sum of	df	Mean Square	F-value	p-value

	Squares				
Model	13838.96	14	988.50	112.28	< 0.0001
A-Time	109.81	1	109.81	12.47	0.0033
B-Catalyst dosage	187.55	1	187.55	21.30	0.0004
C-Dye concentration	1599.44	1	1599.44	181.68	< 0.0001
D-pH	2941.57	1	2941.57	334.13	< 0.0001
AB	614.30	1	614.30	69.78	< 0.0001
AC	469.16	1	469.16	53.29	< 0.0001
AD	2503.50	1	2503.50	284.37	< 0.0001
BC	2.81	1	2.81	0.3187	0.5813
BD	148.84	1	148.84	16.91	0.0011
CD	108.47	1	108.47	12.32	0.0035
A^2	49.89	1	49.89	5.67	0.0320
B^2	4267.33	1	4267.33	484.73	< 0.0001
C^2	47.96	1	47.96	5.45	0.0350
D^2	911.10	1	911.10	103.49	< 0.0001
Residual	123.25	14	8.80		
Lack of Fit	123.25	10	12.33		
Pure Error	0.0000	4	0.0000		
Cor Total	13962.21	28			

Table S8: Analysis of variance (ANOVA) for CV degradation using Fe_3O_4@BC–**1** composite.

Source	Sum of	df	Mean Square	F-value	p-value

	Squares				
Model	16444.33	14	1174.60	589.36	< 0.0001
A-Time	159.21	1	159.21	79.89	< 0.0001
B-Catalyst dosage	445.67	1	445.67	223.62	< 0.0001
C-Dye concentration	2755.48	1	2755.48	1382.58	< 0.0001
D-pH	9693.49	1	9693.49	4863.76	< 0.0001
AB	59.68	1	59.68	29.94	< 0.0001
AC	76.21	1	76.21	38.24	< 0.0001
AD	207.36	1	207.36	104.04	< 0.0001
BC	13.76	1	13.76	6.91	0.0199
BD	46.24	1	46.24	23.20	0.0003
CD	340.77	1	340.77	170.98	< 0.0001
A^2	204.26	1	204.26	102.49	< 0.0001
B^2	13.84	1	13.84	6.95	0.0196
C^2	164.47	1	164.47	82.52	< 0.0001
D^2	1807.30	1	1807.30	906.82	< 0.0001
Residual	27.90	14	1.99		
Lack of Fit	27.90	10	2.79		
Pure Error	0.0000	4	0.0000		
Cor Total	16472.23	28			

Table S9: Analysis of variance (ANOVA) for CV degradation using Fe_3O_4@BC–**2** composite.

Source	**Sum of**	**df**	**Mean Square**	**F-value**	**p-value**

	Squares				
Model	17848.45	14	1274.89	214.43	< 0.0001
A-Time	1.23	1	1.23	0.2067	0.6564
B-Catalyst dosage	5.23	1	5.23	0.8792	0.3643
C-Dye concentration	900.47	1	900.47	151.45	< 0.0001
D-pH	11507.83	1	11507.83	1935.55	< 0.0001
AB	246.96	1	246.96	41.54	< 0.0001
AC	348.57	1	348.57	58.63	< 0.0001
AD	4.64	1	4.64	0.7811	0.3917
BC	53.00	1	53.00	8.91	0.0098
BD	26.27	1	26.27	4.42	0.0541
CD	317.02	1	317.02	53.32	< 0.0001
A^2	53.43	1	53.43	8.99	0.0096
B^2	756.58	1	756.58	127.25	< 0.0001
C^2	14.42	1	14.42	2.43	0.1416
D^2	3811.71	1	3811.71	641.11	< 0.0001
Residual	83.24	14	5.95		
Lack of Fit	83.24	10	8.32		
Pure Error	0.0000	4	0.0000		
Cor Total	17931.68	28			

Table S10: Analysis of variance (ANOVA) for CV degradation using Fe_3O_4@BC–**3** composite.

Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**

Model	18476.04	14	1319.72	591.38	< 0.0001
A-Time	779.08	1	779.08	349.12	< 0.0001
B-Catalyst dosage	4488.81	1	4488.81	2011.50	< 0.0001
C-Dye concentration	823.86	1	823.86	369.18	< 0.0001
D-pH	7478.52	1	7478.52	3351.23	< 0.0001
AB	60.76	1	60.76	27.23	0.0001
AC	0.0650	1	0.0650	0.0291	0.8669
AD	215.65	1	215.65	96.64	< 0.0001
BC	240.72	1	240.72	107.87	< 0.0001
BD	265.53	1	265.53	118.99	< 0.0001
CD	0.2862	1	0.2862	0.1283	0.7256
A^2	32.20	1	32.20	14.43	0.0020
B^2	288.11	1	288.11	129.11	< 0.0001
C^2	114.54	1	114.54	51.32	< 0.0001
D^2	3040.48	1	3040.48	1362.48	< 0.0001
Residual	31.24	14	2.23		
Lack of Fit	31.24	10	3.12		
Pure Error	0.0000	4	0.0000		
Cor Total	18507.28	28			