Supplementary Information

Modelling and Optimisation of Methylene Blue Adsorption using Fucus Serratus, Coconut Shell and Oak Hydrochars

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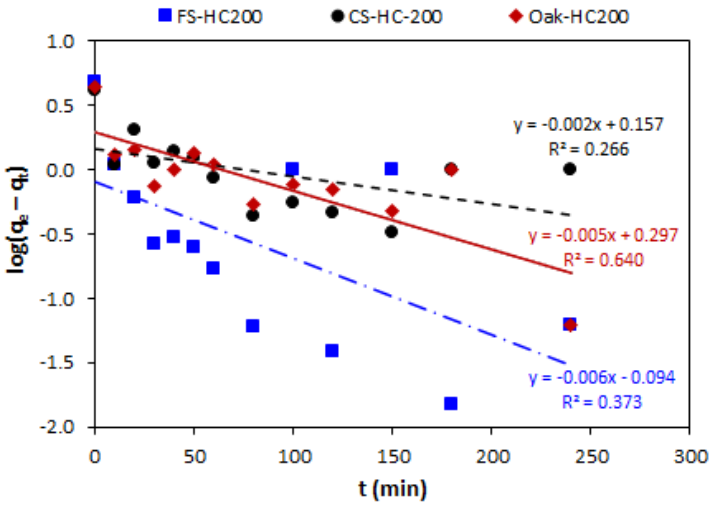
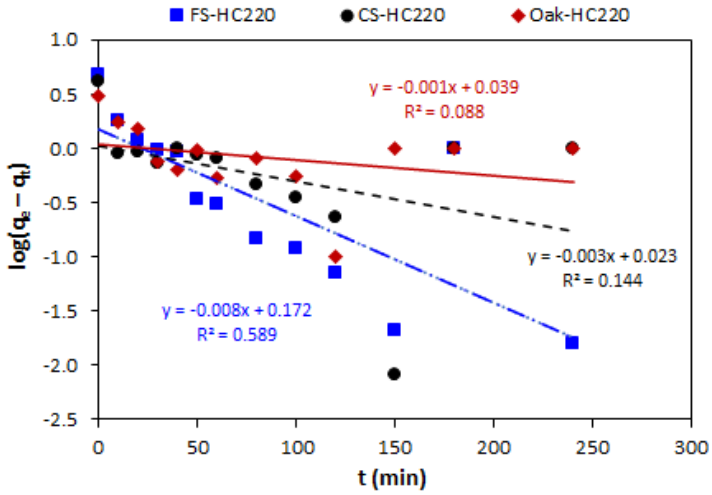


(a)



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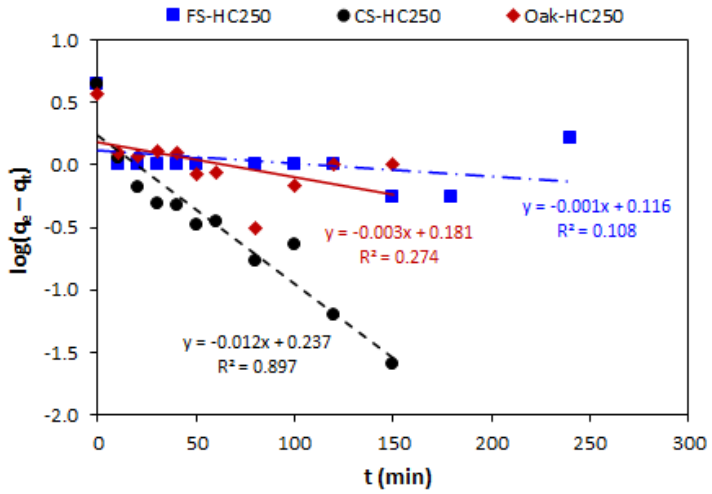

(c)

Figure S1. Pseudo first-order adsorption kinetics plots for hydrochars produced at: (a) 200 °C; (b) 220 °C; and (c) 250 °C.

Table S1. Pseudo first-order kinetic parameters for adsorption of MB dye onto FS, CS, and Oak hydrochars.

Adsorbent	**Pseudo first-order**		
	k_1 (min^{-1})	q_e (mg/g)	R^2
FS-HC200	0.006	0.81	0.37
CS-HC200	0.002	1.44	0.27
Oak-HC200	0.005	1.98	0.64
FS-HC220	0.008	1.49	0.59
CS-HC220	-0.003	1.05	0.14
Oak-HC220	0.001	1.09	0.09
FS-HC250	0.001	1.31	0.11
CS-HC250	0.012	1.73	0.90
Oak-HC250	0.003	1.52	0.27

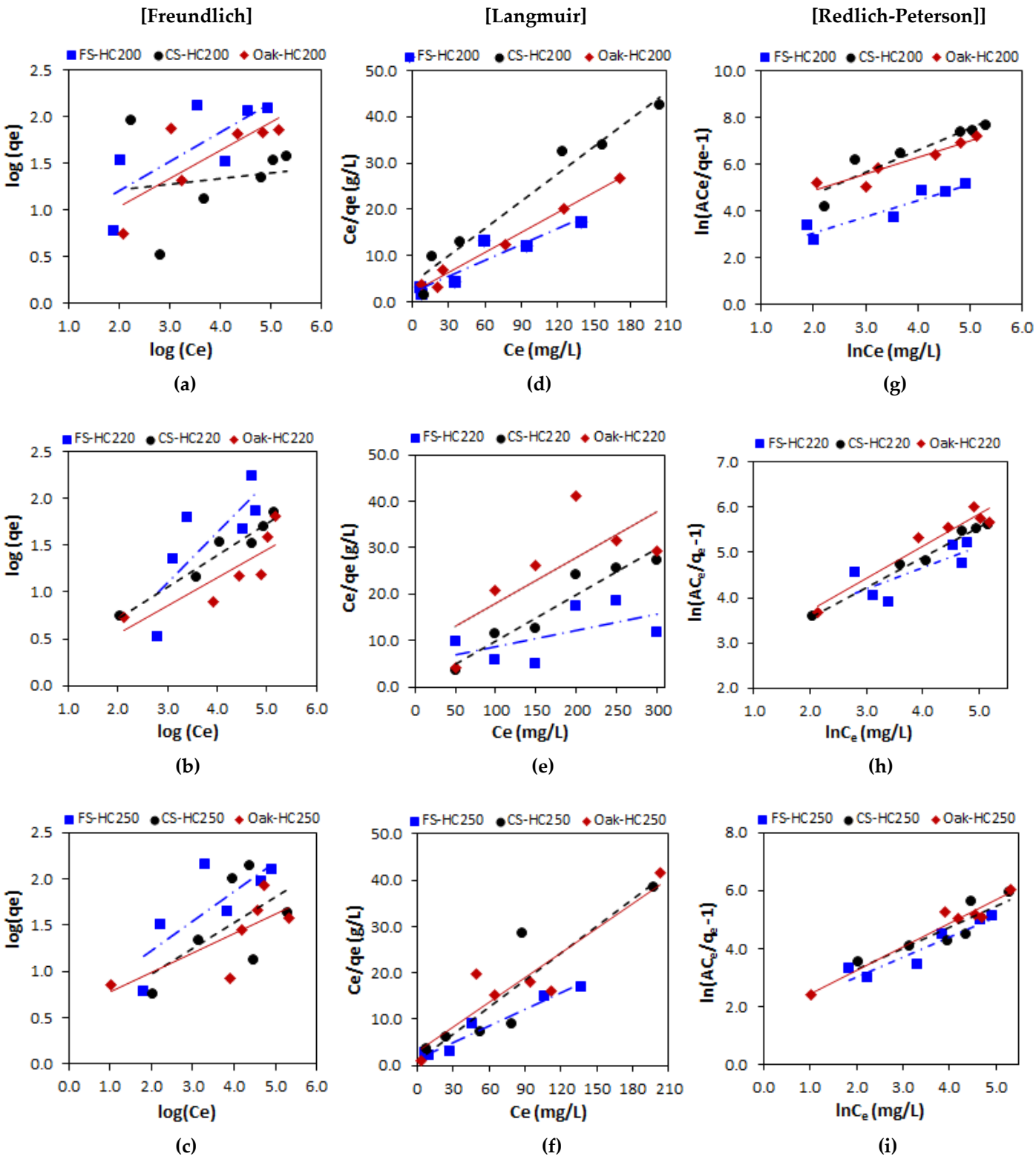

Figure S2. Freundlich (a–c), Langmuir (d–f), and Redlich-Peterson (g–i) adsorption isotherm models of MB on FS-HCs, CS-HCs and Oak-HCs produced at (a, d, g) 200 °C; (b, e, h) 220 °C; and (c, f, i) 250 °C.

Table S2. Analysis of variance (ANOVA) for initial concentration models.

Source	Sum of squares	DF	Mean square	F value	P value	
Adsorption capacity - FS						
Model: Linear	234.70	2	117.35	47.23	< 0.0001	significant
HTC Temperature (T)	0.2701	1	0.2701	0.1087	0.7430	not significant
Initial concentration (C_0)	234.70	1	234.70	94.47	< 0.0001	significant
Residual	124.22	50	2.48			
Lack of fit	47.75	15	3.18	1.46	0.1759	not significant
Pure Error	76.47	35	2.18			
Corrected total	358.52	52				
R^2	0.654					
Percentage removal - FS						
Model: Linear	4987.66	2	2493.83	10.73	0.0001	significant
Temperature (T)	46.75	1	46.75	0.2011	0.6558	not significant
Initial concentration (C_0)	4898.42	1	4898.42	21.07	< 0.0001	significant
Residual	11624.49	50	232.49			
Lack of fit	5372.27	15	358.15	2.00	0.0449	significant
Pure Error	6252.22	35	178.63			
Corrected total	16612.15	52				
R^2	0.300					
Adsorption capacity - CS						
Model: Quadratic	97.00	5	19.40	8.79	< 0.0001	significant
Temperature (T)	2.43	1	2.43	1.10	0.2991	not significant
Initial concentration (C_0)	77.24	1	77.24	35.01	< 0.0001	significant
TC_0	1.91	1	1.91	0.8665	0.3566	not significant
T^2	0.0006	1	0.0006	0.0003	0.9872	not significant
C_0^2	16.85	1	16.85	7.64	0.0081	significant
Residual	105.90	48	2.21			
Lack of fit	52.48	12	4.37	2.95	0.0060	significant
Pure Error	53.42	36	1.48			
Corrected total	202.90	53				
R^2	0.478					
Removal efficiency - CS						
Model: Linear	10537.97	2	5268.99	17.30	< 0.0001	significant
Temperature (T)	661.34	1	661.34	2.17	0.1467	not significant
Initial concentration (C_0)	9876.64	1	9876.64	32.43	< 0.0001	significant
Residual	15531.82	51	304.55			
Lack of fit	8922.67	15	594.84	3.24	0.0019	significant
Pure Error	6609.15	36	183.59			
Corrected total	26069.80	53				
R^2	0.404					

Non-significant lack of fit is required. FS = Fucus Serratus hydrochar; CS = Coconut shell hydrochar; Oak = Oak hydrochar.

Table S2. Analysis of variance (ANOVA) for initial concentration models – Continues.

Source	Sum of squares	DF	Mean square	F value	P value	
Adsorption capacity - Oak						
Model: Quadratic	123.16	5	24.63	14.34	< 0.0001	significant
Temperature (T)	9.45	1	9.45	5.50	0.0232	significant
Initial concentration (C_0)	89.58	1	89.58	52.15	< 0.0001	significant
TC_0	0.0348	1	0.0348	0.0202	0.8874	not significant
T^2	20.30	1	20.30	11.82	0.0012	significant
C_0^2	6.32	1	6.32	3.68	0.0611	not significant
Residual	82.44	48	1.72			
Lack of fit	27.51	12	2.29	1.50	0.1686	not significant
Pure Error	54.94	36	1.53			
Corrected total	205.60	53				
R^2	0.599					
Percentage removal -Oak						
Model: Quadratic	14310.34	5	2862.07	13.20	< 0.0001	significant
Temperature (T)	836.80	1	836.80	3.86	0.0553	not significant
Initial concentration (C_0)	10450.94	1	10450.94	48.20	< 0.0001	significant
TC_0	0.0069	1	0.0069	0.0000	0.9955	not significant
T^2	2588.33	1	2588.33	11.94	0.0012	significant
C_0^2	660.59	1	660.59	3.05	0.0873	not significant
Residual	10406.95	48	216.81			
Lack of fit	4796.91	12	399.74	2.57	0.0144	significant
Pure Error	5610.04	36	155.83			
Corrected total	24717.29	53				
R^2	0.579					

Non-significant lack of fit is good. FS = Fucus Serratus hydrochar; CS = Coconut shell hydrochar; Oak = Oak hydrochar.

Table S3. Analysis of variance (ANOVA) for initial pH models.

Source	Sum of squares	DF	Mean square	F value	P value	
Percentage removal - FS						
Model: Quadratic	1764.87	5	352.97	6.62	< 0.0001	significant
HTC Temperature (T)	808.93	1	808.93	15.17	0.0003	significant
Initial pH (pH)	185.52	1	185.52	3.48	0.0682	not significant
T.pH	348.37	1	348.37	6.53	0.0138	significant
T^2	15.15	1	15.15	0.2842	0.5964	not significant
pH^2	459.51	1	459.51	8.62	0.0051	significant
Residual	2559.10	48	53.31			
Lack of fit	1570.07	12	130.84	4.76	0.0001	significant
Pure Error	989.03	36	27.47			
Corrected total	4323.97	53				
R^2	0.408					
Percentage removal - CS						
Model: 2FI	7232.86	3	2410.95	9.26	< 0.0001	significant
Temperature (T)	86.17	1	86.17	0.3309	0.5677	not significant
Initial pH (pH)	6316.58	1	6316.58	24.26	< 0.0001	significant
T.pH	1235.01	1	1235.01	4.74	0.0342	significant
Residual	13018.43	50	260.37			
Lack of fit	9656.74	14	689.77	7.39	< 0.0001	significant
Pure Error	3361.69	36	93.38			
Corrected total	20251.29	53				
R^2	0.357					
Removal efficiency - Oak						
Model: Linear	9456.24	2	4728.12	46.25	< 0.0001	significant
Temperature (T)	411.40	1	411.40	4.02	0.0502	
Initial pH (pH)	9044.84	1	9044.84	88.48	< 0.0001	significant
Residual	5213.27	51	102.22			
Lack of fit	2107.56	15	140.50	1.63	0.1144	not significant
Pure Error	3105.71	36	86.27			
Corrected total	14669.51	53				
R^2	0.645					

Non-significant lack of fit is required. FS = Fucus Serratus hydrochar; CS = Coconut shell hydrochar; Oak = Oak hydrochar.

Table S4. Analysis of variance (ANOVA) for contact time models.

Source	Sum of squares	DF	Mean square	F value	P value	
Percentage removal - FS						
Model: Quadratic	35124.46	5	7024.89	19.30	< 0.0001	significant
HTC Temperature (T)	1562.68	1	1562.68	4.29	0.0406	significant
Contact time (t)	6211.25	1	6211.25	17.07	< 0.0001	significant
Tt	1748.71	1	1748.71	4.81	0.0305	significant
T^2	530.58	1	530.58	1.46	0.2298	not significant
t^2	19079.58	1	19079.58	52.43	< 0.0001	significant
Residual	40393.07	111	363.90			
Lack of fit	38466.70	33	1165.66	47.20	< 0.0001	significant
Pure Error	1926.37	78	24.70			
Corrected total	75517.53	116				
R^2	0.465					
Percentage removal - CS						
Model: Quadratic	34858.10	5	6971.62	28.97	< 0.0001	significant
HTC Temperature (T)	2233.14	1	2233.14	9.28	0.0029	significant
Contact time (t)	15143.77	1	15143.77	62.93	< 0.0001	significant
Tt	180.87	1	180.87	0.7516	0.3879	not significant
T^2	0.9238	1	0.9238	0.0038	0.9507	not significant
t^2	8825.64	1	8825.64	36.67	< 0.0001	significant
Residual	26712.85	111	240.66			
Lack of fit	23609.20	33	715.43	17.98	< 0.0001	significant
Pure Error	3103.65	78	39.79			
Corrected total	61570.95	116				
R^2	0.566					
Removal efficiency - Oak						
Model: Quadratic	37580.10	5	7516.02	35.50	< 0.0001	significant
HTC Temperature (T)	2373.70	1	2373.70	11.21	0.0011	significant
Contact time (t)	17635.89	1	17635.89	83.29	< 0.0001	significant
Tt	34.96	1	34.96	0.1651	0.6853	not significant
T^2	7070.94	1	7070.94	33.39	< 0.0001	significant
t^2	5169.98	1	5169.98	24.42	< 0.0001	significant
Residual	23502.98	111	211.74			
Lack of fit	17723.88	33	537.09	7.25	< 0.0001	significant
Pure Error	5779.10	78	74.09			
Corrected total	61083.08	116				
R^2	0.615					

Non-significant lack of fit is required. FS = Fucus Serratus hydrochar; CS = Coconut shell hydrochar; Oak = Oak hydrochar.

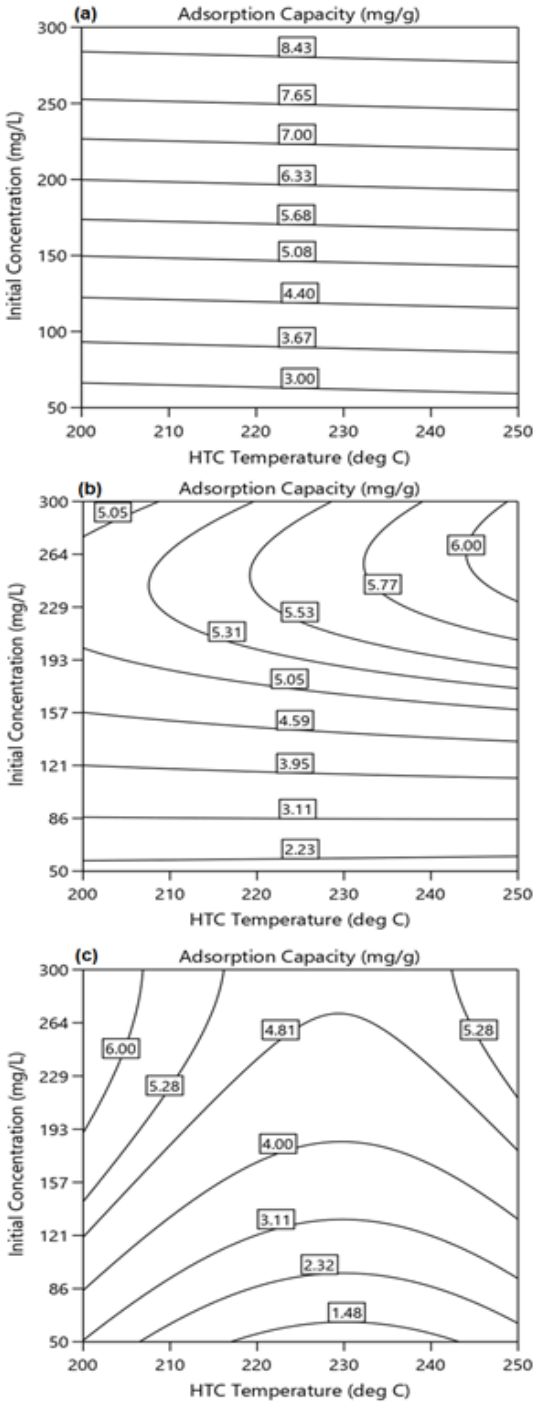

Figure S3. Contour plots showing the effect of initial MB dye concentration and HTC temperature on adsorption capacity: (a) FS-HCs; (b) CS-HCs; and (c) Oak-HCs.

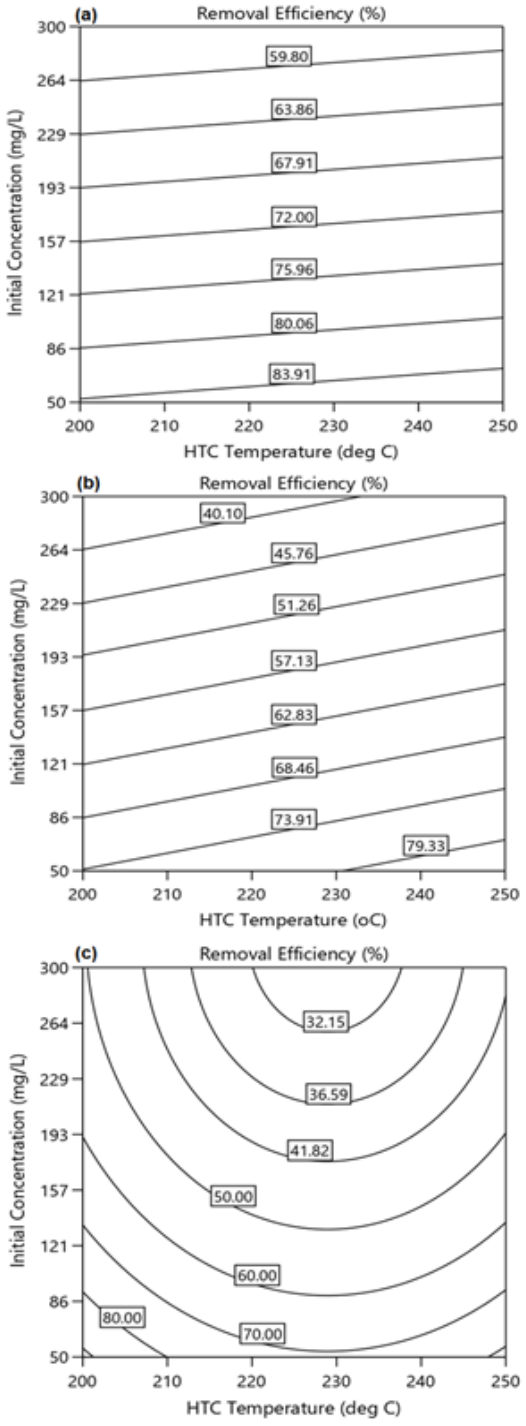

Figure S4. Contour plots showing the effect of initial MB concentration and HTC temperature on adsorption removal efficiency: (a) FS-HCs; (b) CS-HCs; and (c) Oak-HCs.

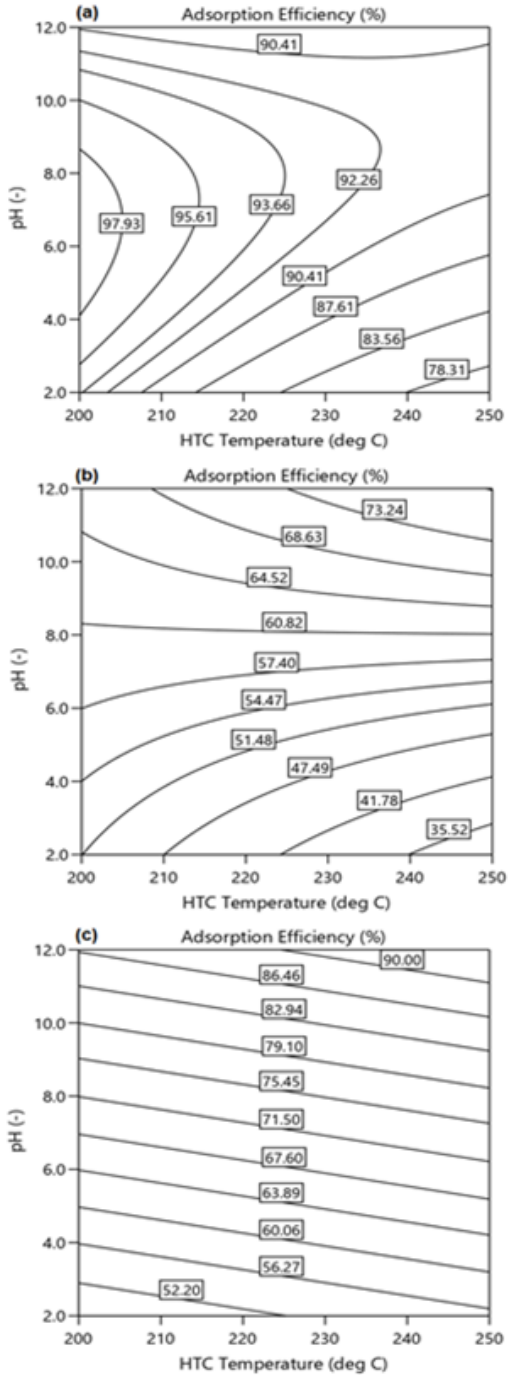

Figure S5. Contour plots showing the effect of solution pH and HTC temperature on adsorption removal efficiency: (a) FS-HCs; (b) CS-HCs; and (c) Oak-HCs.

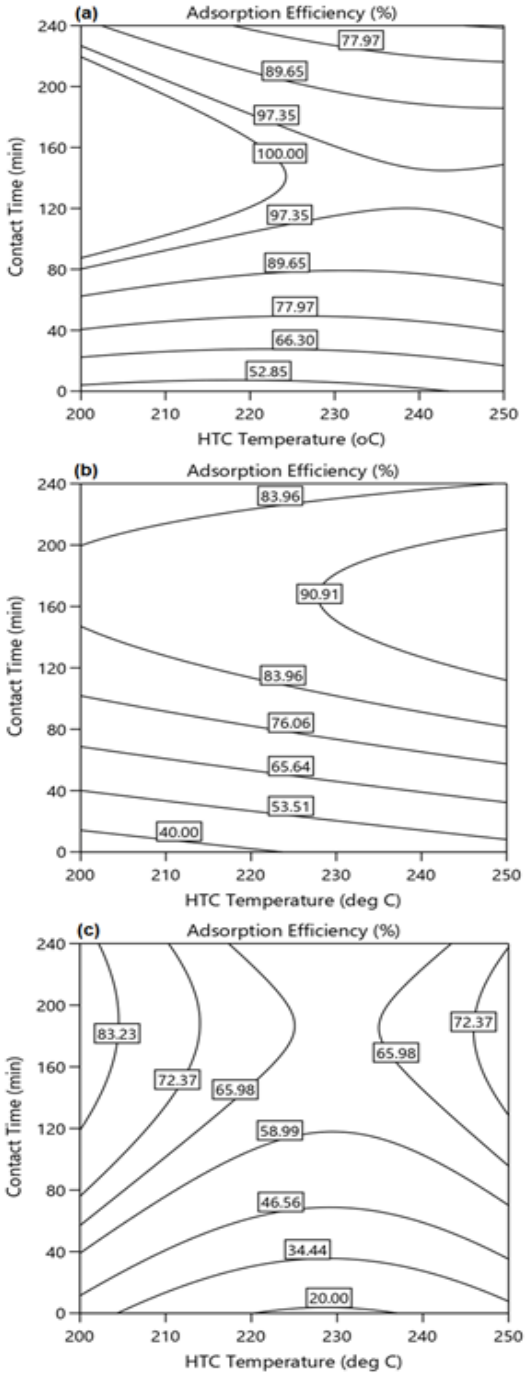

Figure S6. Contour plots showing the effect of adsorption time and HTC temperature on adsorption removal efficiency: (a) FS-HCs; (b) CS-HCs; and (c) Oak-HCs.