processes

Supplementary Materials

Response Surface Methodology for Modeling and Optimization of Chromium Adsorption onto Magnetic Carbon Nanocomposites

Jasmina Nikić [1], Marko Šolić [1], Aleksandra Kulić Mandić [1], Jovana Pešić Bajić [1], Minja Bogunović Koljaja [1], Malcolm Watson[1]*, Jasmina Agbaba [1]

[1]University of Novi Sad, Faculty of Sciences, Department of Chemistry, Biochemistry and Environmental Protection, Trg Dositeja Obradovića 3, 21000 Novi Sad, Republic of Serbia
*Correspondence: malcolm.watson@dh.uns.ac.rs

List of tables

Table S1. Experimental conditions and corresponding experimental and RSM-fitted chromium removal efficiencies for MAC and MBC.

Table S2. Experimental and RSM-fitted chromium uptake qt values for MAC and MBC.

Table S3. Sensitivity analysis of ln(qt) using the full quadratic RSM models.

Table S4. LOOCV performance of RSM and machine-learning models for the MBC dataset

Table S5. Block-aware sensitivity and bootstrap uncertainty analysis for the MBC dataset.

Table S1. Experimental conditions and corresponding experimental and RSM-fitted chromium removal efficiencies for MAC and MBC.

Run	MAC		MBC	
	Experimental removal efficiency (%)	Predicted removal efficiency (%)	Experimental removal efficiency (%)	Predicted removal efficiency (%)
1	96.16	90.13	13.92	17.88
2	51.81	47.30	20.89	14.23
3	4.72	9.12	14.81	18.26
4	45.81	55.67	15.99	16.95
5	14.31	23.14	5.57	2.39
6	15.83	8.75	8.96	8.79
7	0.39	7.72	7.33	10.43
8	30.66	29.05	13.11	10.45
9	48.11	43.56	26.59	24.27
10	53.94	47.30	10.68	14.23
11	10.16	5.31	4.30	0.92
12	53.14	51.14	14.36	13.23
13	97.38	100.33	9.71	13.38
14	27.33	24.15	26.47	25.68
15	54.60	66.10	19.92	18.89
16	42.69	51.14	10.02	13.23
17	50.14	37.03	9.55	10.07
18	24.67	26.23	18.24	18.52
19	20.05	15.49	2.73	1.46
20	20.05	23.30	12.54	15.41
21	19.68	23.09	6.69	10.42
22	9.83	5.24	15.07	11.07
23	46.56	59.4	18.98	16.04
24	32.4	41.0	17.23	19.29
25	35.6	21.5	6.69	9.37
26	99.9	90.0	22.62	20.30
27	53.2	57.8	16.75	17.79
28	15.8	23.1	9.41	14.40
29	96.5	88.0	42.30	37.05

Note: Predicted chromium-removal values exceeding 100% are mathematical outputs of the unconstrained quadratic RSM model and do not represent physically achievable removal efficiencies. Such values were therefore retained as model outputs but were not interpreted physically. The numerical optimization should additionally be interpreted with caution because, although constrained within the nominal factor ranges, the predicted optimum extends beyond the region directly sampled by the Box–Behnken design.

Table S2. Experimental and RSM-fitted chromium uptake qt values for MAC and MBC.

Run	MAC Experimental qt (mg g^{-1})	MAC RSM-fitted qt (mg g^{-1})	MBC Experimental qt (mg g^{-1})	MBC RSM-fitted qt (mg g^{-1})
1	0.087	0.085	0.013	0.016
2	23.574	18.326	9.506	6.638
3	11.817	25.184	37.071	42.687
4	0.042	0.053	0.015	0.014
5	13.011	20.499	5.067	4.148
6	14.389	17.560	8.150	9.129
7	0.968	4.321	18.350	21.648
8	7.672	5.539	3.281	2.981
9	12.040	4.149	6.654	5.900
10	24.545	18.326	4.858	6.638
11	4.625	4.367	1.955	1.883
12	24.178	31.452	6.536	5.654
13	0.049	0.094	0.005	0.005
14	12.433	16.595	12.046	11.131
15	0.273	0.242	0.100	0.092
16	19.424	31.452	4.558	5.654
17	25.070	31.523	4.777	5.263
18	11.225	9.374	8.298	9.120
19	100.261	57.928	13.658	14.239
20	9.124	10.770	5.707	6.020
21	4.924	7.472	1.673	2.341
22	24.613	19.190	37.711	27.476
23	11.652	25.811	4.751	4.254
24	29.540	43.345	15.667	16.414
25	89.102	47.589	16.735	19.050
26	0.091	0.073	0.021	0.020
27	24.190	35.685	7.620	7.953
28	14.373	14.230	8.555	8.396
29	0.088	0.105	0.038	0.040

Note: Experimental qt values were calculated from the measured removal efficiency, initial Cr(VI) concentration, and adsorbent dose. RSM-fitted qt values are in-sample fitted values obtained from quadratic models fitted to $\ln(q_t)$ and back-transformed to the original scale using a smearing correction.

Table S3. Sensitivity analysis of $\ln(q_t)$ using the full quadratic RSM models

Model term	MAC F-value	MAC p-value	MBC F-value	MBC p-value
Block	2.0811	0.1675	4.2925	0.0392
pH	0.1416	0.7133	10.9349	0.0063
Initial concentration	164.3737	0.0000	1713.1575	0.0000
Adsorbent dose	3.1161	0.1029	184.9273	0.0000
Contact time	2.7989	0.1202	21.8473	0.0005
pH^2	1.8958	0.1937	4.8085	0.0488
$Concentration^2$	62.5920	0.0000	836.8930	0.0000
$Dose^2$	0.2224	0.6457	8.1736	0.0144
$Contact\ time^2$	7.2886	0.0193	6.2050	0.0284
pH × concentration	0.1765	0.6819	1.4828	0.2467
pH × dose	1.9817	0.1846	0.2094	0.6554
pH × contact time	0.6146	0.4483	18.8783	0.0010
Concentration × dose	0.0491	0.8284	15.2593	0.0021
Concentration × contact time	0.2442	0.6301	0.0017	0.9675
Dose × contact time	1.8079	0.2036	0.0001	0.9941
Original-scale fit after smearing correction	R^2		RMSE (mg g^{-1})	MAE (mg g^{-1})
MAC	0.6888		12.7662	7.3822
MBC	0.9328		2.4350	1.2639

Note: This supplementary analysis is intended as a response-metric sensitivity check. Because q_t is calculated directly from initial concentration, removal efficiency, and adsorbent dose, strong effects of these variables on q_t should not be interpreted as independent mechanistic evidence.

Table S4. LOOCV performance of RSM and machine-learning models for the MBC dataset

Model	Validation Method	R^2	RMSE	MAE
RSM	LOOCV	-0.044	8.243	7.145
Random Forest	LOOCV	0.168	7.359	5.747
Support Vector Regression	LOOCV	0.166	7.367	5.707

Table S5. Block-aware sensitivity and bootstrap uncertainty analysis for the MBC dataset

A) Sensitivity of RF and SVR performance to inclusion of experimental block

Model	Block included	R^2	RMSE	MAE
Random Forest	No	0.168	7.359	5.747
Random Forest	Yes	0.087	7.711	6.317
Support Vector Regression	No	0.166	7.367	5.707

B) Bootstrap 95% confidence intervals for LOOCV performance

Model	R^2	95% CI for R^2	RMSE	95% CI for RMSE	MAE	95% CI for MAE
RSM	−0.044	−1.575 to 0.355	8.243	6.848 to 9.563	7.145	5.670 to 8.659
Random Forest	0.168	−0.373 to 0.333	7.359	5.200 to 9.615	5.747	4.189 to 7.557
Support Vector Regression	0.166	−0.511 to 0.426	7.367	5.012 to 9.983	5.707	4.182 to 7.529

(C) Paired bootstrap differences between models

Comparison	ΔR^2	95% CI	ΔRMSE	95% CI	ΔMAE	95% CI
Random Forest − RSM	0.334	−0.201 to 1.396	−0.931	−3.046 to 1.075	−1.385	−3.309 to 0.472
Random Forest − SVR	−0.004	−0.349 to 0.318	0.022	−1.022 to 1.296	0.044	−1.073 to 1.234
RSM − SVR	−0.329	−1.329 to 0.215	0.919	−1.231 to 3.013	1.412	−0.127 to 2.946

Note: Bootstrap confidence intervals were obtained from 10,000 paired resamples of the observed responses and corresponding LOOCV predictions. For ΔR^2, positive values favor the first-listed model; for ΔRMSE and ΔMAE, negative values indicate lower prediction error for the first-listed model. All 95% confidence intervals for pairwise model differences included zero.