

Supplementary Information

Table-S1: Expressions of different reaction mechanisms ($f(\alpha)$, $g(\alpha)$) of solid-state reactions

Mechanism		$f(\alpha)$	$g(\alpha)$
Power law (PL)	n= 1/2 (PL1)	$2\alpha^{1/3}$	$\alpha^{1/2}$
	n= 1/3 (PL2)	$3\alpha^{2/3}$	$\alpha^{1/3}$
	n= 1/4 (PL3)	$4\alpha^{3/4}$	$\alpha^{1/4}$
Chemical reaction (CR)	First order reaction (FOR)	$1 - \alpha$	$-\ln(1 - \alpha)$
	Second order reaction (SOR)	$(1 - \alpha)^2$	$(1 - \alpha)^{-1} - 1$
Diffusion reaction (D)	One dimensional (OD)	0.5α	α^2
	Two dimensional (TD)	$[-\ln(1 - \alpha)]^{-1}$	$(1 - \alpha)\ln(1 - \alpha) + \alpha$
	Three dimensional-Jander (TDJ)	$1.5(1 - \alpha)^{2/3} [1 - (1 - \alpha)^{1/3}]^{-1}$	$[1 - (1 - \alpha)^{1/3}]^2$
	Three dimensional-Ginstling-Brounshtein (TDGB)	$1.5[(1 - \alpha)^{1/3} - 1]^{-1}$	$(1 - 2\alpha/3) - (1 - \alpha)^{2/3}$
Phase interfacial	One dimension (ODPIR)	1	α

reaction	Two dimension (TDPIR)	$2(1 - \alpha)^{1/2}$	$1 - (1 - \alpha)^{1/2}$
	Three dimension (TrDPIR)	$3(1 - \alpha)^{2/3}$	$1 - (1 - \alpha)^{1/3}$
Nucleation and growth nuclei reaction	Two dimension (TDNGR)	$2(1 - \alpha)[- \ln(1 - \alpha)]^{1/2}$	$[- \ln(1 - \alpha)]^{1/2}$
	Three dimension (TrDNGR)	$3(1 - \alpha)[- \ln(1 - \alpha)]^{2/3}$	$[- \ln(1 - \alpha)]^{1/3}$

Table S2: Predicted and experimental values of three oxyanions and three cations removal efficiencies for each test run along with their respective percent errors (optimization-1)

Runs	Experimental values (% removal)						Predicted values (% removal)						Errors (%)					
	Cr ⁶⁺	Co ²⁺	Ni ²⁺	As ³⁺	Cd ²⁺	V ⁵⁺	Cr ⁶⁺	Co ²⁺	Ni ²⁺	As ³⁺	Cd ²⁺	V ⁵⁺	Cr ⁶⁺	Co ²⁺	Ni ²⁺	As ³⁺	Cd ²⁺	V ⁵⁺
1	78.72	52.47	61.77	59.04	95.94	73.63	78.30	50.44	60.98	58.15	95.65	67.57	0.53	3.86	1.27	1.51	0.30	8.23
2	77.25	51.24	56.54	71.90	95.98	72.58	77.82	52.27	60.14	66.05	95.28	64.13	0.74	2.01	6.38	8.14	0.73	11.64
3	80.86	56.02	69.66	54.10	94.67	44.13	79.87	52.97	65.26	59.06	95.07	46.52	1.23	5.46	6.31	9.17	0.43	5.41
4	80.03	53.38	59.03	56.51	95.37	65.33	78.76	51.58	57.49	58.83	95.28	59.36	1.58	3.39	2.59	4.10	0.09	9.14
5	81.01	52.73	64.03	54.63	96.49	73.66	81.01	52.73	64.03	54.63	96.49	73.66	0.00	0.00	0.00	0.00	0.00	0.00
6	82.50	50.21	63.57	55.37	96.68	70.44	82.23	51.46	66.44	52.73	96.19	62.07	0.33	2.48	4.51	4.77	0.51	11.87
7	77.54	52.94	63.44	62.41	95.90	68.20	77.81	51.70	60.58	65.05	96.39	76.56	0.35	2.35	4.51	4.24	0.52	12.26
8	81.01	52.73	64.03	54.63	96.49	73.66	81.01	52.73	64.03	54.63	96.49	73.66	0.00	0.00	0.00	0.00	0.00	0.00
9	80.51	51.50	63.79	55.40	95.35	57.09	79.93	50.47	60.18	61.25	96.04	65.54	0.71	2.00	5.66	10.56	0.73	14.80
10	77.26	49.27	58.64	55.06	94.94	52.38	77.68	51.29	59.43	55.95	95.23	58.44	0.54	4.11	1.34	1.62	0.31	11.57
11	81.01	52.73	64.03	54.63	96.49	73.66	81.01	52.73	64.03	54.63	96.49	73.66	0.00	0.00	0.00	0.00	0.00	0.00
12	81.61	50.84	67.30	54.72	94.68	56.73	80.76	51.05	66.56	57.95	94.88	56.81	1.04	0.42	1.10	5.86	0.21	0.15
13	76.57	48.35	55.04	71.54	96.45	64.81	77.57	51.41	59.44	66.58	96.04	62.42	1.29	6.32	7.99	6.93	0.42	3.69
14	81.40	50.31	64.29	54.16	95.43	49.18	82.25	50.09	65.04	50.95	95.23	49.09	1.04	0.42	1.16	5.92	0.21	0.17
15	80.42	50.48	63.35	55.82	94.64	46.61	81.69	52.29	64.88	53.51	94.73	52.59	1.57	3.59	2.42	4.15	0.09	12.82

Table S3: Performance of the developed models for their predicted outcomes based on PIs

Errors	Optimization-1						Optimization-2					
	Cr ⁶⁺	Co ²⁺	Ni ²⁺	As ³⁺	Cd ²⁺	V ⁵⁺	Cr ⁶⁺	Co ²⁺	Ni ²⁺	As ³⁺	Cd ²⁺	V ⁵⁺
MAE	0.583	1.251	1.857	2.649	0.290	4.176	0.476	0.662	0.521	0.455	0.239	0.423
RMSE	0.719	1.607	2.423	3.311	0.370	5.409	0.736	0.948	0.733	0.673	0.347	0.542

Runs	Experimental responses (% removal)						Predicted responses (% removal)						Errors (%)					
	Cr ⁶⁺	Co ²⁺	Ni ²⁺	As ³⁺	Cd ²⁺	V ⁵⁺	Cr ⁶⁺	Co ²⁺	Ni ²⁺	As ³⁺	Cd ²⁺	V ⁵⁺	Cr ⁶⁺	Co ²⁺	Ni ²⁺	As ³⁺	Cd ²⁺	V ⁵⁺
1	56.31	81.06	78.22	58.86	96.55	79.56	56.31	81.06	78.22	58.86	96.56	79.56	0.00	0.00	0.00	0.00	0.00	0.00
2	55.97	77.22	83.17	49.63	93.10	76.54	54.38	76.49	82.60	50.95	93.33	75.94	2.84	0.95	0.69	2.65	0.15	0.77
3	53.10	79.71	83.16	51.86	95.31	76.72	54.21	79.20	82.75	51.20	94.76	77.36	2.06	0.65	0.49	1.27	0.58	0.83
4	56.31	81.06	78.22	58.86	96.55	79.56	56.31	81.06	78.22	58.86	96.56	79.56	0.00	0.00	0.00	0.00	0.00	0.00
5	54.41	76.95	80.48	56.40	94.61	77.34	55.89	78.70	81.65	55.03	94.93	77.95	2.69	2.26	1.44	2.44	0.32	0.78
6	54.85	75.10	72.37	71.86	95.79	81.28	54.82	76.21	72.57	71.93	96.21	82.01	0.05	1.47	0.26	0.08	0.43	0.91
7	56.31	81.06	78.22	58.86	96.55	79.56	56.31	81.06	78.22	58.86	96.56	79.56	0.00	0.00	0.00	0.00	0.00	0.00
8	56.93	81.19	77.99	63.32	97.31	81.82	56.14	79.30	76.99	64.13	96.77	81.15	1.39	2.33	1.29	1.27	0.55	0.81
9	53.90	76.31	73.66	71.45	95.39	81.88	54.43	76.46	74.46	70.74	95.39	81.10	0.97	0.19	1.08	0.99	0.00	0.95
10	55.75	82.79	81.69	61.50	96.84	79.82	55.35	81.65	80.31	62.28	96.39	80.59	0.71	1.38	1.69	1.25	0.46	0.96
11	56.31	81.06	78.22	58.86	96.55	79.56	56.31	81.06	78.22	58.86	96.56	79.56	0.00	0.00	0.00	0.00	0.00	0.00
12	56.31	81.06	78.22	58.86	96.55	79.56	56.31	81.06	78.22	58.86	96.56	79.56	0.00	0.00	0.00	0.00	0.00	0.00
13	55.59	82.19	82.00	54.81	96.09	80.43	55.33	83.50	83.23	54.61	96.78	79.72	0.48	1.58	1.49	0.37	0.71	0.88

Table S4: Predicted and experimental values of three oxyanions and three cations removal efficiencies for each test run along with their respective percent errors (optimization-2)

Table S5: The expressions of the regression models for E values evaluation using model free methods for OPT2-ads and the parent PF samples

Conversion (α)	Obtained model equations	E (kJ/mol)	R ²	Obtained model equations	E (kJ/mol)	R ²
OPT2-ads-KAS method				OPT2-ads-Friedman method		
0.1	-9026.76X+17.12	75.05	0.6261	-16112.3X+42.55	133.96	0.8639
0.2	-16511.0X+20.54	137.27	0.9376	-16017.8X+26.26	133.17	0.9484
0.3	-18305.3X+22.12	152.19	0.9983	-17454.8X+27.94	145.12	0.9975
0.4	-17358.0X+19.41	144.31	0.9988	-14508.2X+22.15	120.62	0.9998
0.5	-16097.9X+16.50	133.84	0.9990	-18119.7X+27.75	150.65	0.9944
0.6	-17810.3X+18.64	148.07	0.9979	-20290.1X+30.60	168.69	0.9979
0.7	-20148.9X+21.61	167.52	0.9993	-24622.6X+36.36	204.71	0.9956
0.8	-31711.9X+37.95	263.65	0.9909	-39478.4X+56.95	328.23	0.9813
0.9	-48142.8X+57.76	400.26	0.6888	-55976.6X+75.43	465.39	0.6598
Average		180.24			205.61	
Conversion (α)	Obtained model equations	E (kJ/mol)	R ²	Obtained model equations	E (kJ/mol)	R ²
Parent PF-KAS method				Parent PF-Friedman method		
0.1	-3180.3X-1.88	26.44	0.7422	-2901.8X+0.1597	24.12	0.7688
0.2	-16245.4X+19.81	135.06	0.9975	-16237.6X+26.56	135.00	0.9989
0.3	-15446.7X+16.91	128.42	0.9949	-14697.8X+22.91	122.20	0.9921
0.4	-15364.4X+15.81	127.74	0.9905	-17264.7X+26.76	143.54	0.9786
0.5	-16421.2X+16.93	136.52	0.9942	-18769.8X+28.79	156.05	0.9985
0.6	-18493.8X+19.64	153.76	0.9954	-21884.3X+33.02	181.95	0.9998
0.7	-21647.1X+23.79	179.97	0.9992	-23916.3X+34.95	198.84	0.9722
0.8	-24079.2X+25.95	200.19	0.8797	-26273.5X+36.31	218.44	0.8162
0.9	-25524.3X+25.12	212.21	0.7665	-25188.1X+31.06	209.42	0.7023
Average		144.48			154.39	

Table S6: Comparison of E values of the parent PF and OPT2-ads samples with some other biomasses

Material	Models	Heating rate (°C/min)	E (kJ/mol)	reference
PFs	KAS, Friedman	5, 10, 20, 30	180.24, 205.61 (OPT2-ads), 144.48, 154.39 (Parent PF)	Present study
Coffee silver skin	Starink, OFW	5,7,10,15	285.91, 268.03	Pinzi et al. (2020)
Typha Lalifolia	FWO, KAS	10, 30, 50	182.67, 184.58	Ahmad et al. (2017)
Banana leaves	KAS, FWO, Friedman, Kissinger, Starink	10,20,30	84.02, 7.36, 73.89, 70.75, 92.12	Singh et al. (2020)
Horse manure	Friedman, KAS, FWO	1,2,5,10	194.6, 200.2, 199.3	Chong et al. (2019)
Maize	KAS, FWO, Friedman	5, 20, 50	236.08 – 242.46	Zsinka et al. (2024)
Sunflower husk			202.70 – 218.96	
Industrial wood chips			263.93 – 269.90	
Wheat			200.70 – 206.54	
Piney biomass	KAS, FWO	5,10,20	87.10 – 92.44	Patidar et al. (2022)
Mustard stalk			130.62, 132.47	
Pine tree saw dust	Friedman, KAS, DAEM, OFW	5-25	168.58, 171.66, 206.62, 179.29	Mishra et al. (2018)
Cotton stalk	FWO, KAS	5-30	115.75, 107.6	Gupta et al. (2020)
Camphor wood	FWO, KAS	5, 20, 40	192.66, 192.63	Xu et al. (2020)
Prosopisjuliflora	Friedman, KAS, Kissinger, OFW	2,5,10,15,15,20,25	219.3, 204, 164.6, 203.2	Chandrasekaran et al. (2017)
Sugarcane leaves	FWO, KAS	5-40	226.97, 226.75	Kumar et al. (2019)

Table S7: Thermodynamic parametric values at different heating rates (5, 10, 20, and 30 °C/min) using Coats-Redfern method for OPT2-ads sample for all reaction mechanisms

Mechanism	Heating rate (°C/min)	E (kJ/mol)	k ₀ (min ⁻¹)	ΔG [‡] (kJ/mol)	ΔH [‡] (kJ/mol)	ΔS [‡] (kJ/mol/K)	R ²
OD	5	27.57	8.75E+05	127.76	22.69	-0.179	0.8944
	10	26.99	1.47E+06	129.20	21.89	-0.175	0.8907
	20	29.35	4.58E+06	126.75	24.21	-0.165	0.8915
	30	30.76	9.04E+06	126.06	25.54	-0.160	0.8914
TD	5	30.72	1.33E+06	128.87	25.84	-0.175	0.9027

	10	30.10	2.21E+06	130.26	25.01	-0.171	0.8970
	20	32.41	6.64E+06	127.90	27.26	-0.162	0.8994
	30	33.76	1.28E+07	127.24	28.55	-0.157	0.8999
TDJ	5	35.7	1.60E+06	132.93	30.82	-0.174	0.9113
	10	35.03	2.61E+06	134.34	29.93	-0.170	0.9020
	20	37.19	7.38E+06	132.14	32.05	-0.161	0.9050
	30	38.44	1.37E+07	131.56	33.23	-0.156	0.9055
TDGB	5	32.28	5.04E+05	135.16	27.40	-0.183	0.9065
	10	31.65	8.36E+05	136.77	26.55	-0.179	0.8996
	20	33.92	2.46E+06	134.51	28.77	-0.170	0.9023
	30	35.24	4.69E+06	133.95	30.02	-0.165	0.9028
FOR	5	20.94	8.39E+05	121.33	16.06	-0.179	0.9093
	10	20.54	1.48E+06	122.79	15.44	-0.175	0.8969
	20	21.52	3.43E+06	120.40	16.38	-0.168	0.9001
	30	22.08	5.69E+06	119.79	16.86	-0.164	0.9003
SOR	5	35.00	9.54E+07	112.31	30.12	-0.140	0.8257
	10	34.19	1.45E+08	113.05	29.09	-0.137	0.8191
	20	34.59	2.77E+08	110.88	29.44	-0.131	0.8238
	30	34.79	4.11E+08	110.18	29.57	-0.128	0.8222
ODPIR	5	13.79	6.02E+04	127.02	8.911	-0.201	0.8944
	10	13.49	1.09E+05	128.96	8.399	-0.196	0.8907
	20	14.67	2.70E+05	126.62	9.534	-0.189	0.8915
	30	15.38	5.01E+05	125.76	10.16	-0.184	0.8914
TDPIR	5	16.61	8.82E+04	127.99	11.73	-0.198	0.9085
	10	16.28	1.58E+05	129.87	11.19	-0.193	0.9009
	20	17.41	3.95E+05	127.40	12.26	-0.186	0.9036
	30	18.06	6.79E+05	126.85	12.84	-0.181	0.9041
TrDPIR	5	17.85	9.27E+04	128.98	12.97	-0.197	0.9113
	10	17.51	1.65E+05	130.87	12.41	-0.193	0.9020
	20	18.59	4.06E+05	128.45	13.45	-0.185	0.9050
	30	19.22	6.90E+05	127.93	14.01	-0.181	0.9055
TDNGR	5	10.47	5.14E+04	124.48	5.594	-0.202	0.9093
	10	10.27	9.52E+04	126.46	5.176	-0.197	0.8969
	20	10.76	2.11E+05	123.99	5.620	-0.191	0.9001
	30	11.04	3.36E+05	123.49	5.825	-0.187	0.9003
TrDNGR	5	6.98	1.70E+04	126.38	2.103	-0.211	0.9093
	10	7.02	3.29E+04	128.61	1.927	-0.206	0.8969
	20	7.14	6.98E+04	126.08	2.032	-0.201	0.9001
	30	7.36	1.10E+05	125.64	2.145	-0.196	0.9003

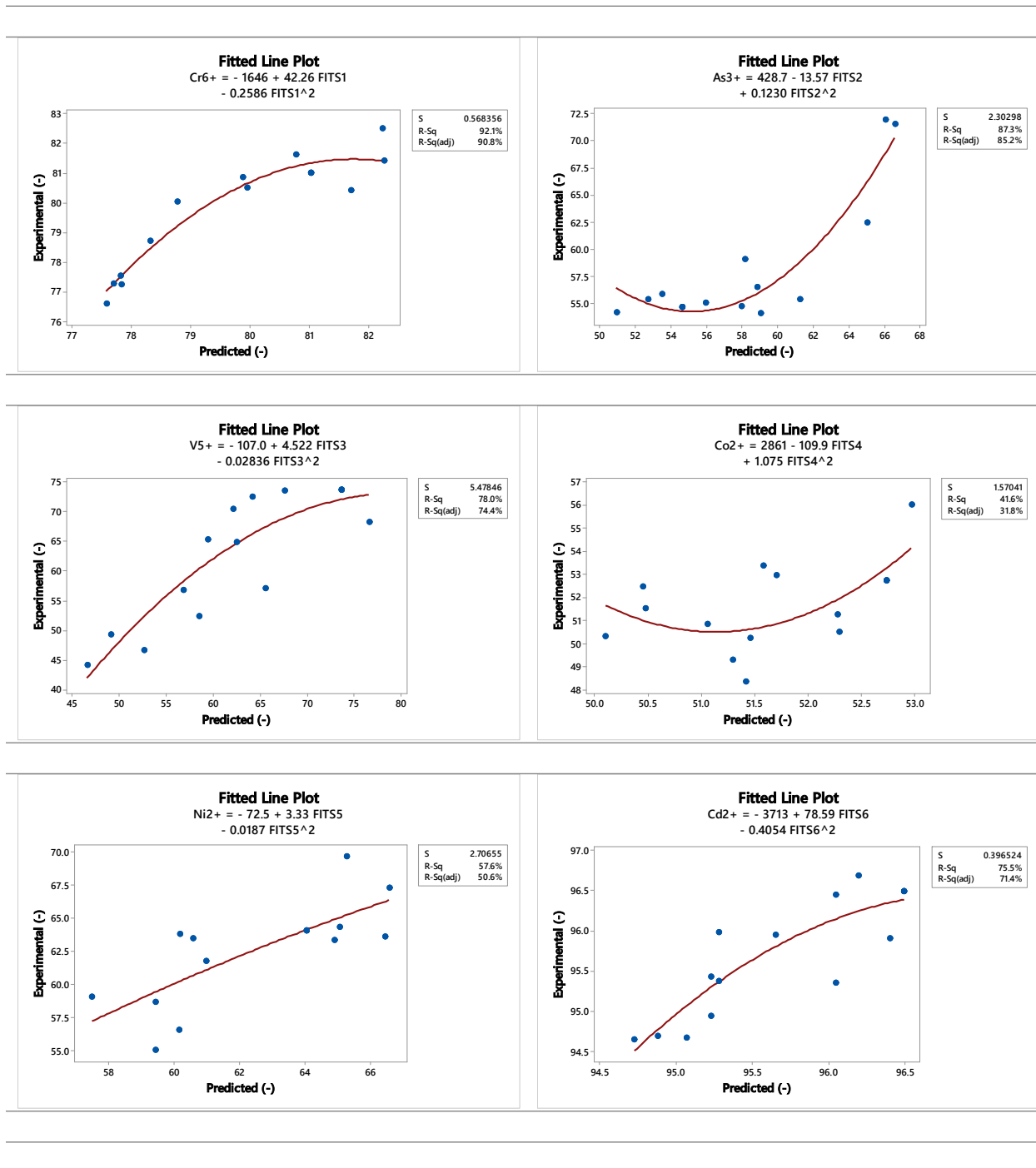
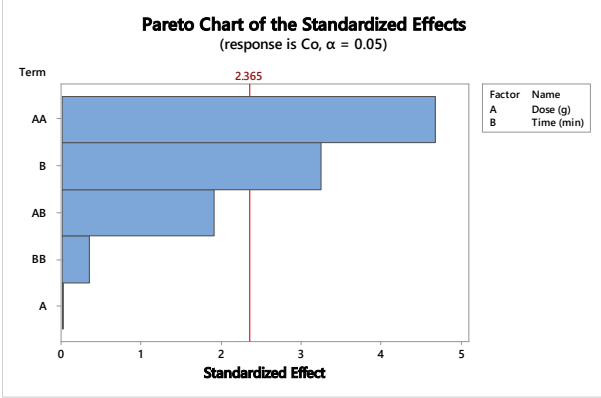
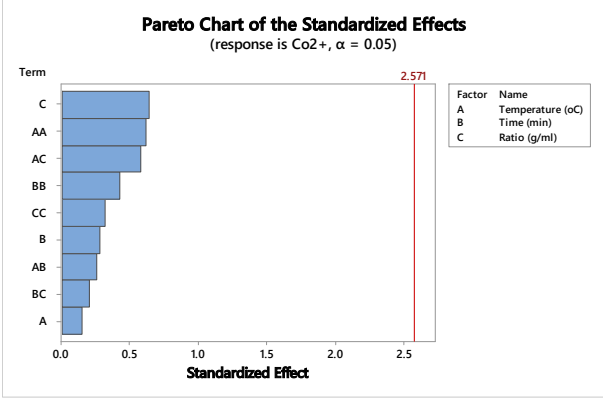
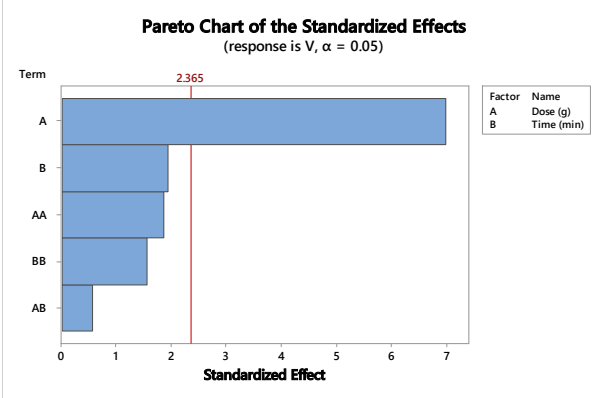
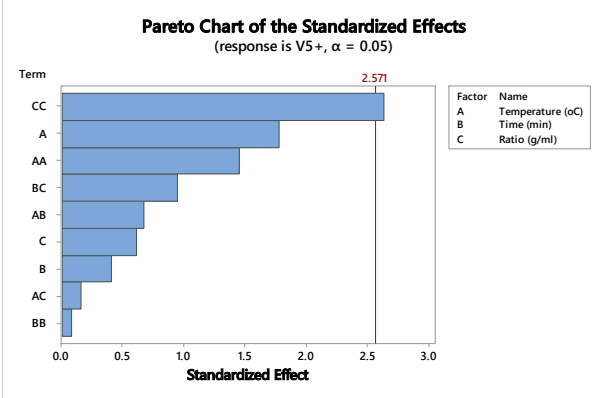
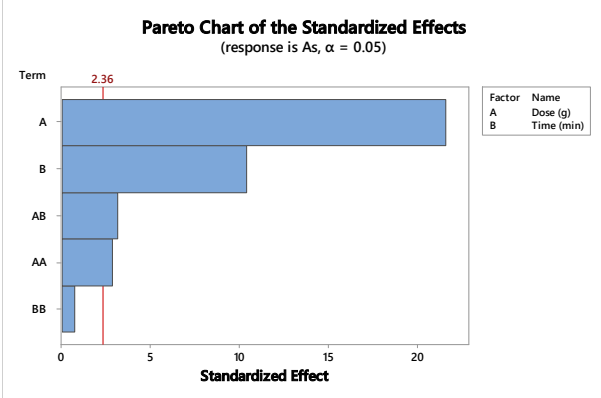
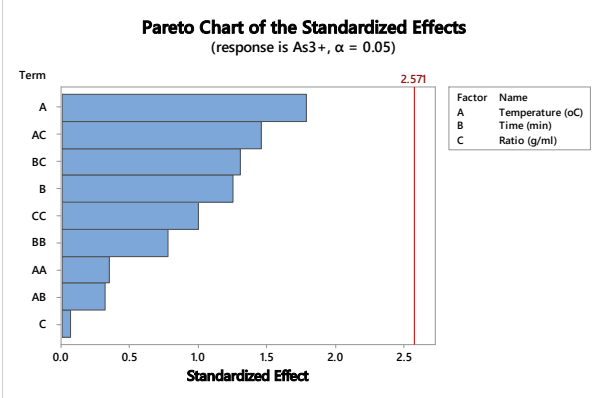
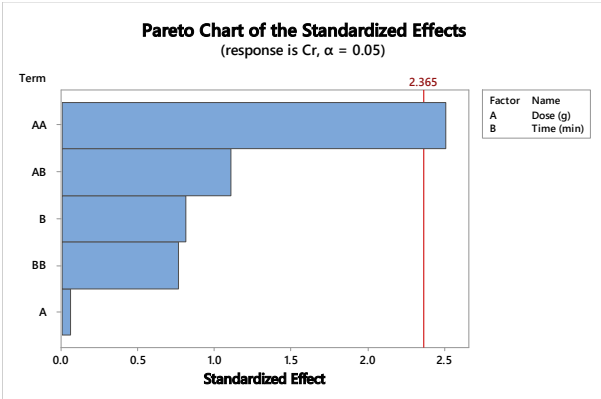
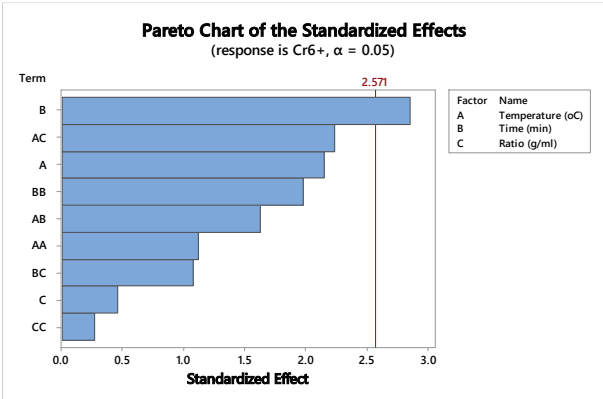


Figure-S1: Experimental data vs. model predictions for the removal efficiencies of three cations (Ni^{2+} , Co^{2+} , Cd^{2+}) and three oxyanions (V^{5+} , Cr^{6+} , As^{3+}) from MMSW (including all interactions and full factors) for Optimization-1 (higher order polynomial fit)

Optimization-1

Optimization-2



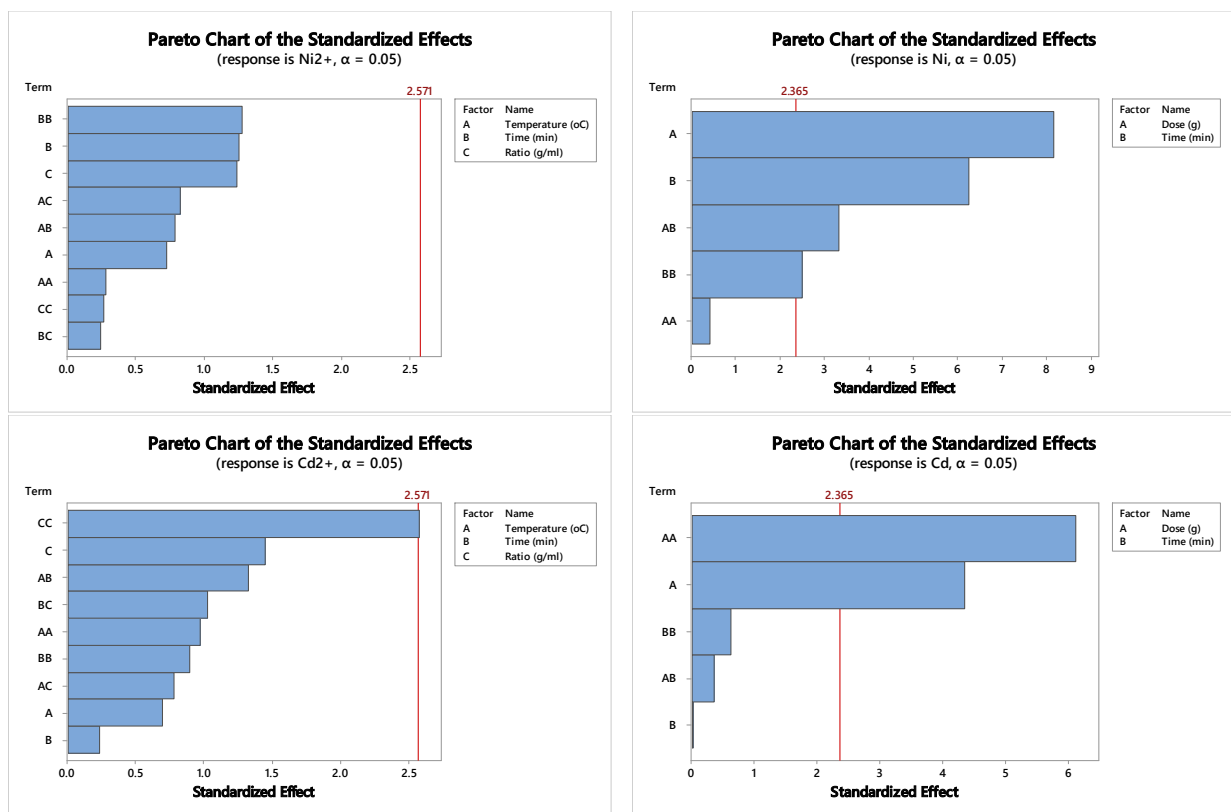


Figure-S2: Different residual plots (histogram, residual, normal probability etc.) for three cations (Ni^{2+} , Co^{2+} , Cd^{2+}) and three oxyanions (V^{5+} , Cr^{6+} , As^{3+}) for both optimizations

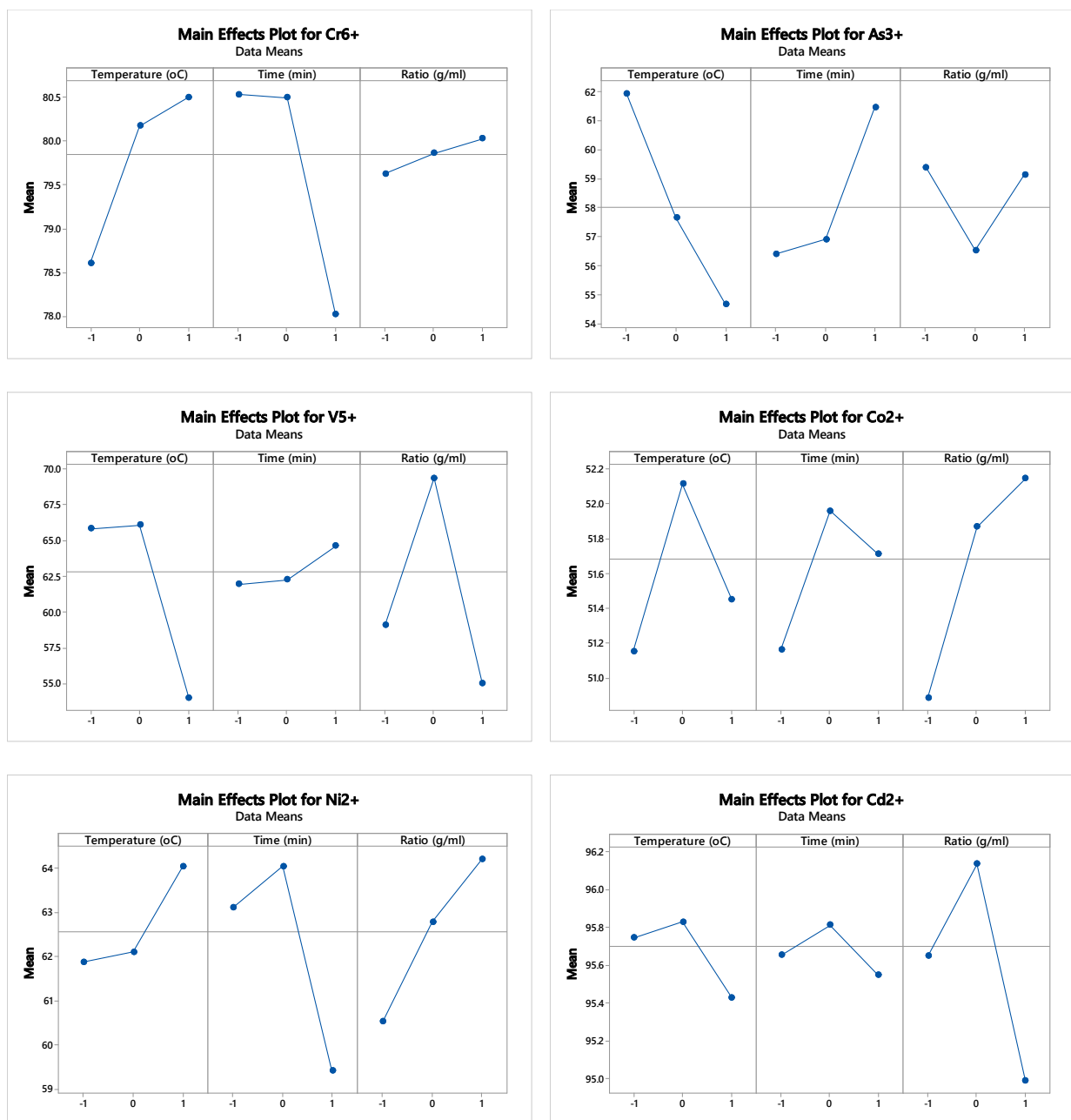
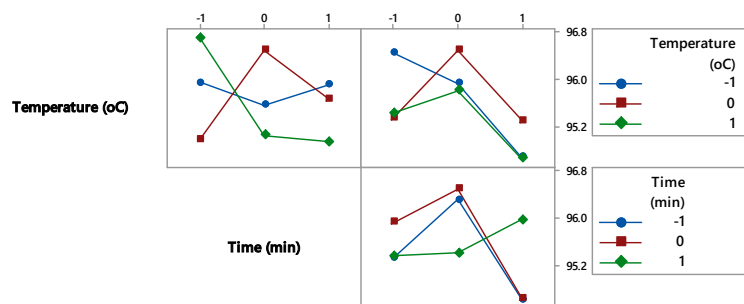


Figure S3: Main effect plots of independent parameters (e.g., Temp, time and PF/THF ratio) on the removal of three oxyanions (V^{5+} , Cr^{6+} , As^{3+}) and three cations (Ni^{2+} , Co^{2+} , Cd^{2+}) from MMSW (optimization-1)

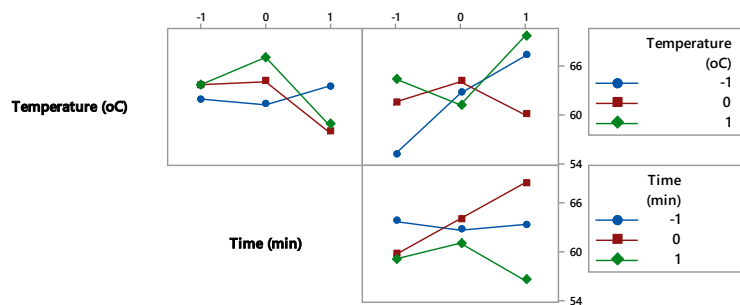
Cations

Interaction Plot for Cd2+
Data Means



Ratio (g/ml)

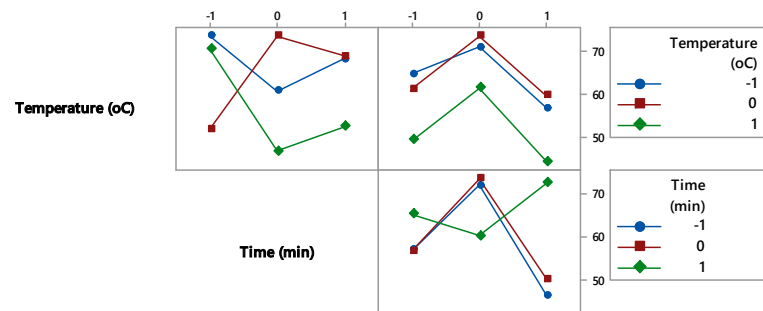
Interaction Plot for Ni2+
Data Means



Ratio (g/ml)

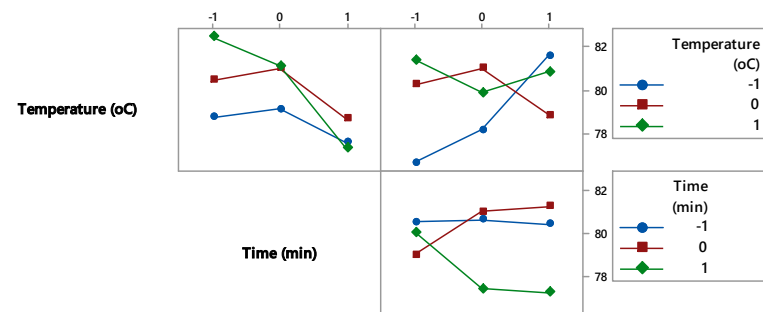
Oxyanions

Interaction Plot for V5+
Data Means



Ratio (g/ml)

Interaction Plot for Cr6+
Data Means



Ratio (g/ml)

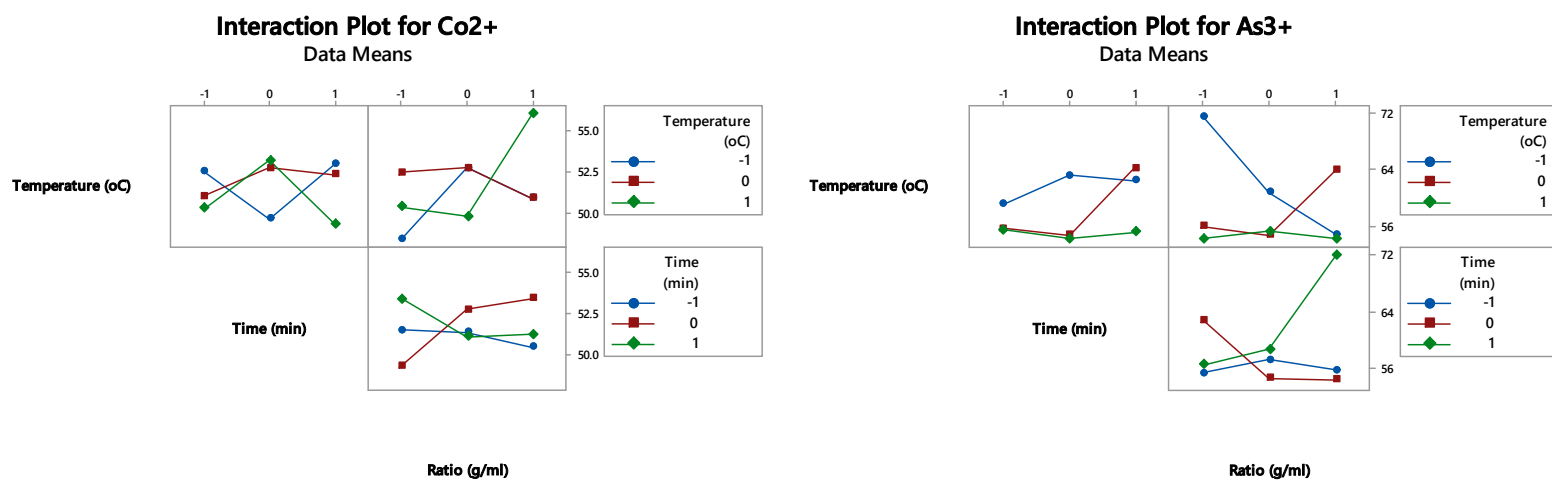
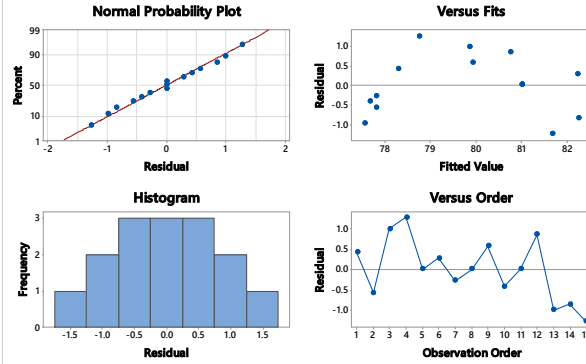


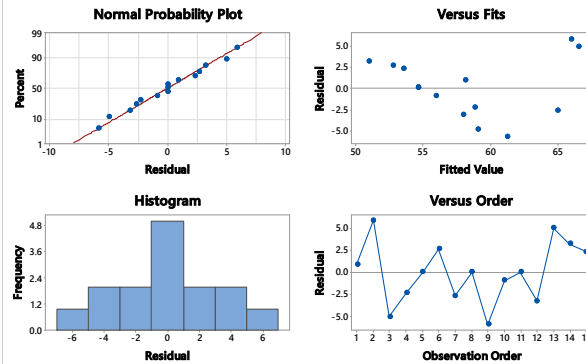
Figure S4: Interaction plots of independent parameters (e.g., Temp, time and PF/THF ratio) on the removal of three oxyanions (V^{5+} , Cr^{6+} , As^{3+}) and three cations (Ni^{2+} , Co^{2+} , Cd^{2+}) from MMSW (optimization-1)

Optimization -1

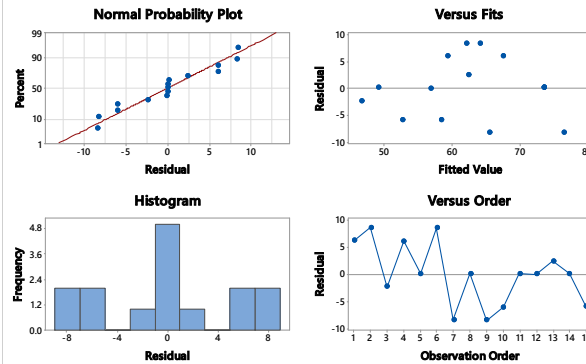
Residual Plots for Cr6+



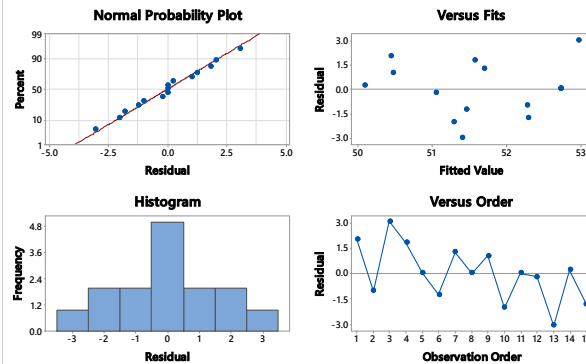
Residual Plots for As3+



Residual Plots for V5+

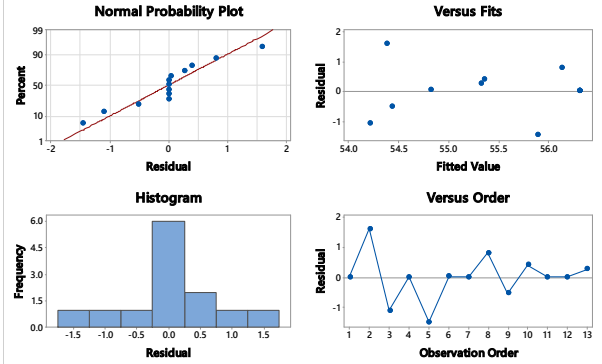


Residual Plots for Co2+

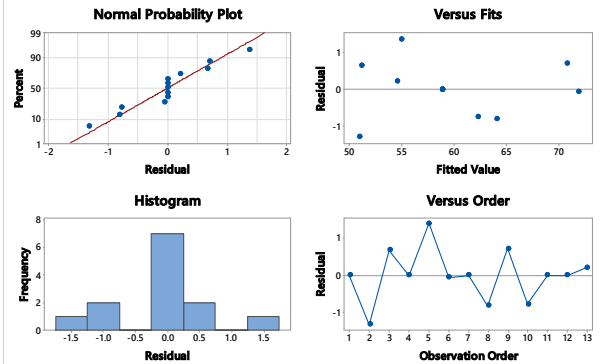


Optimization -2

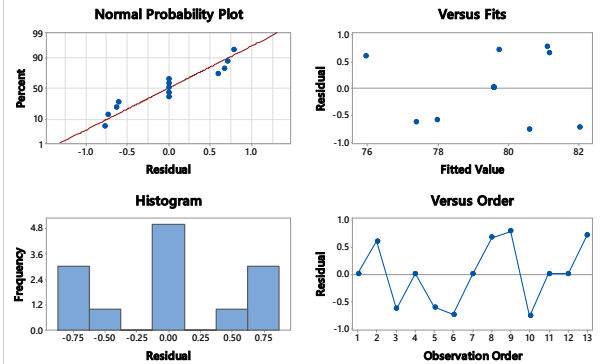
Residual Plots for Cr



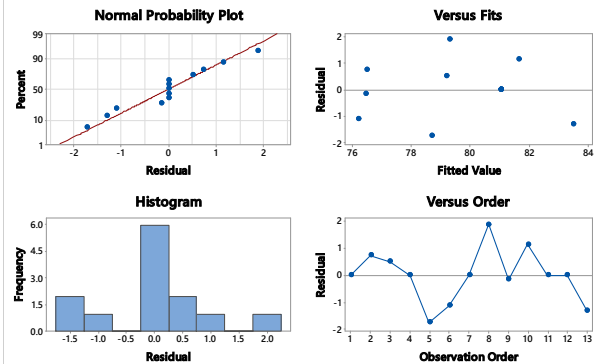
Residual Plots for As



Residual Plots for V



Residual Plots for Co



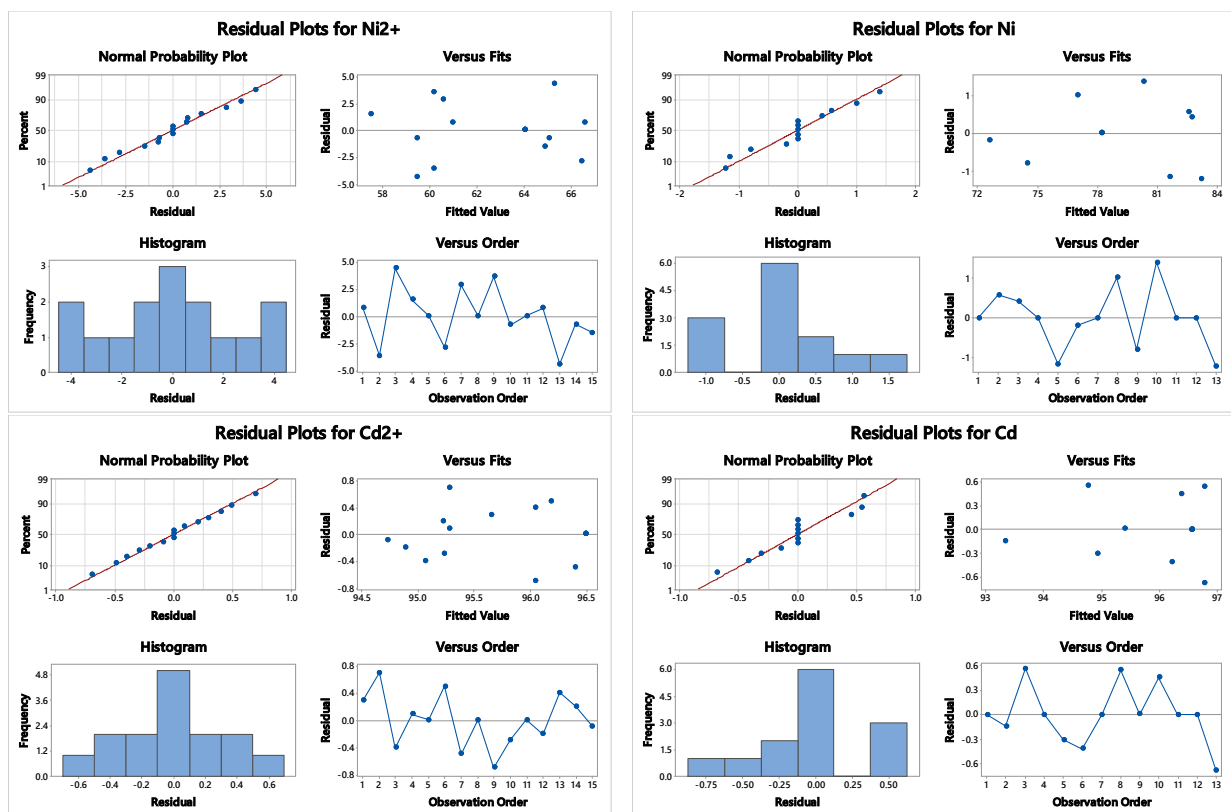
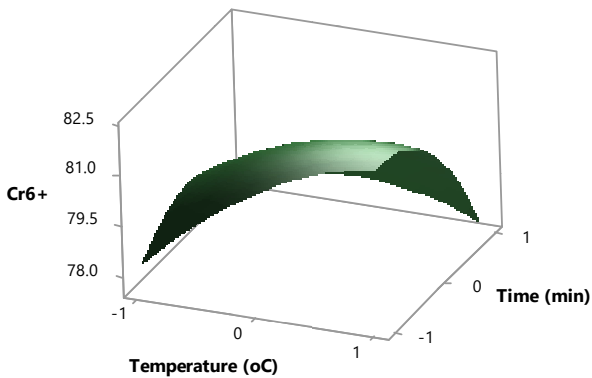
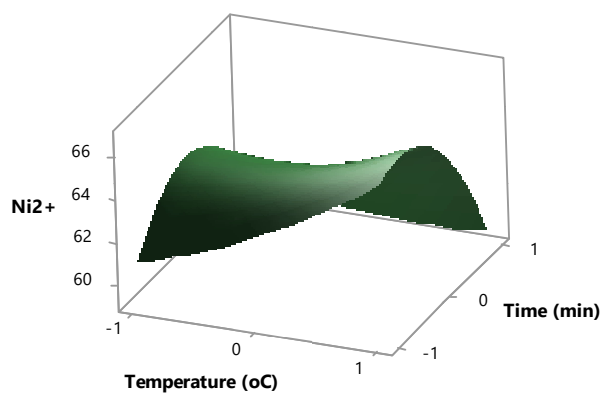
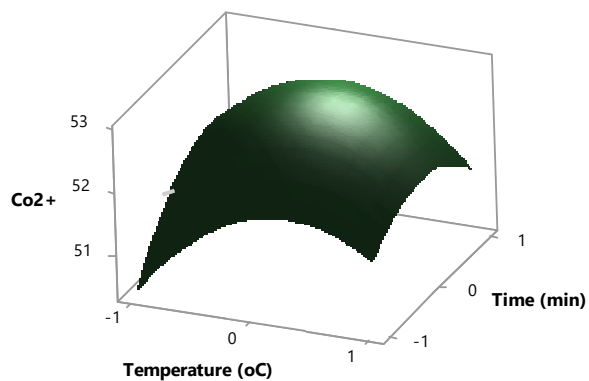
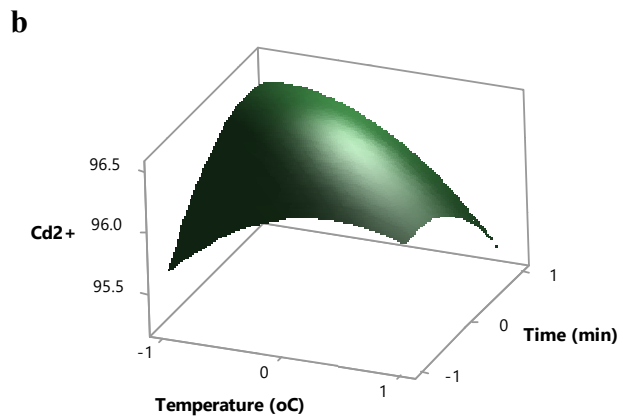
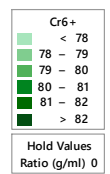
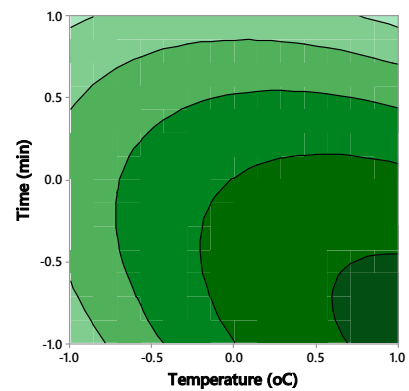
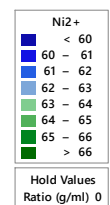
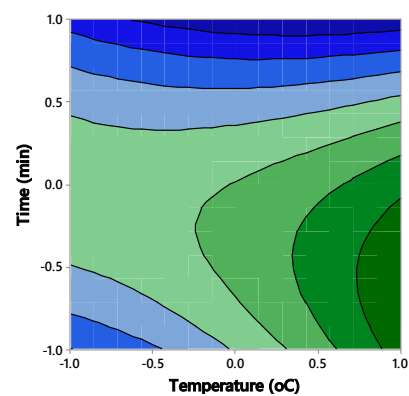
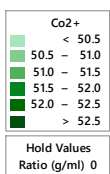
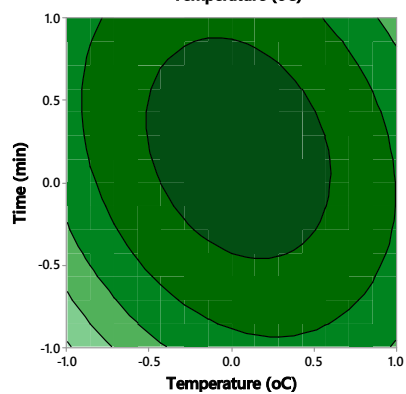
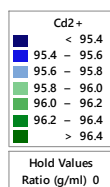
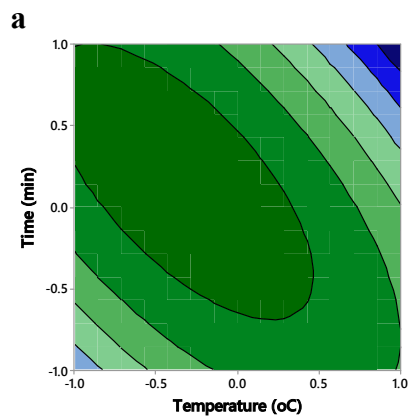


Figure-S5: Different pareto charts for three cations (Ni^{2+} , Co^{2+} , Cd^{2+}) and three oxyanions (V^{5+} , Cr^{6+} , As^{3+}) for both optimizations



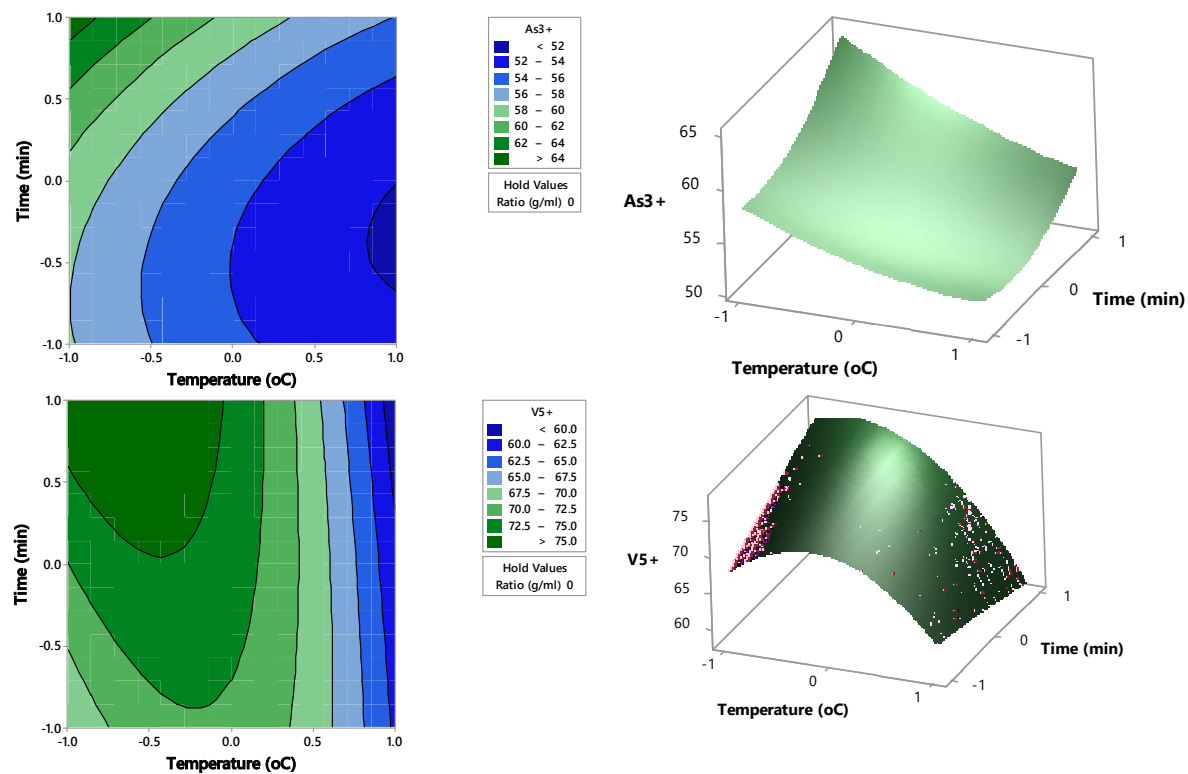
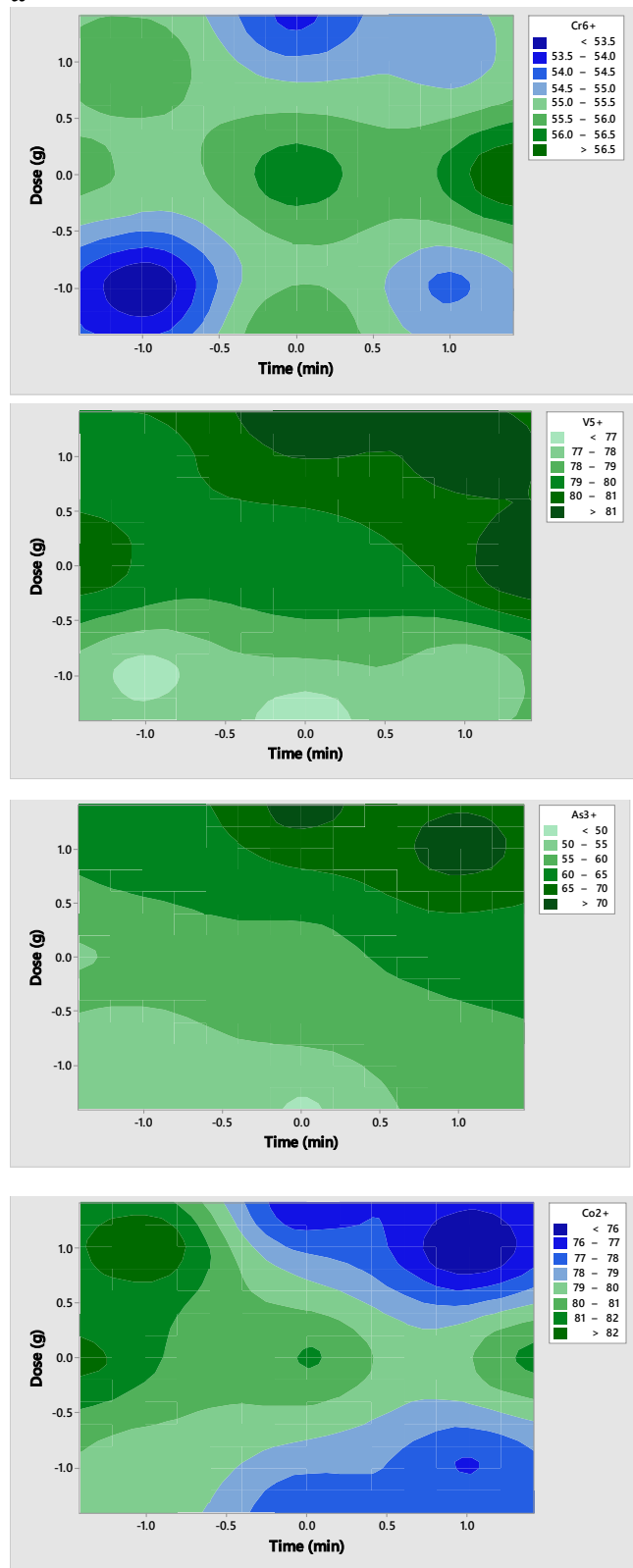
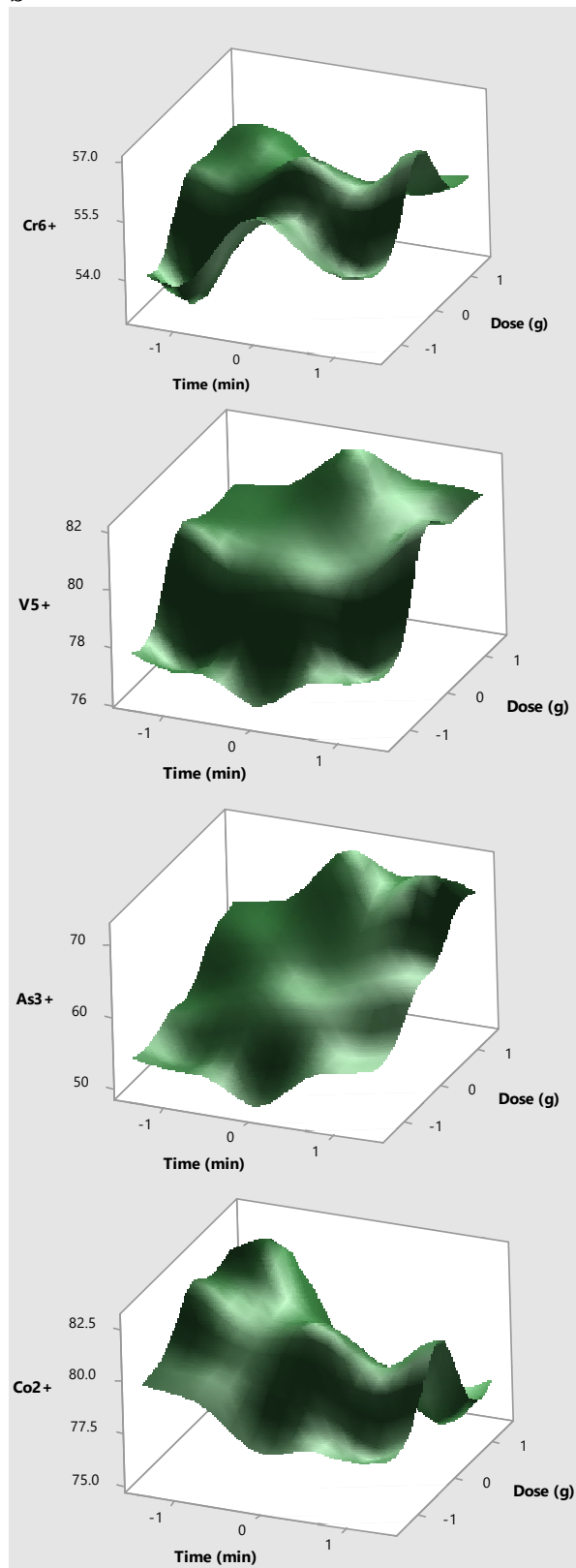


Figure-S6: (a) 2D contour plots and (b) 3D surface plots for three cations (Ni^{2+} , Co^{2+} , Cd^{2+}) and three oxyanions (V^{5+} , Cr^{6+} , As^{3+}) for optimization-1 (Temperature vs. Time holding PF/THF ratio at 0).

a



b



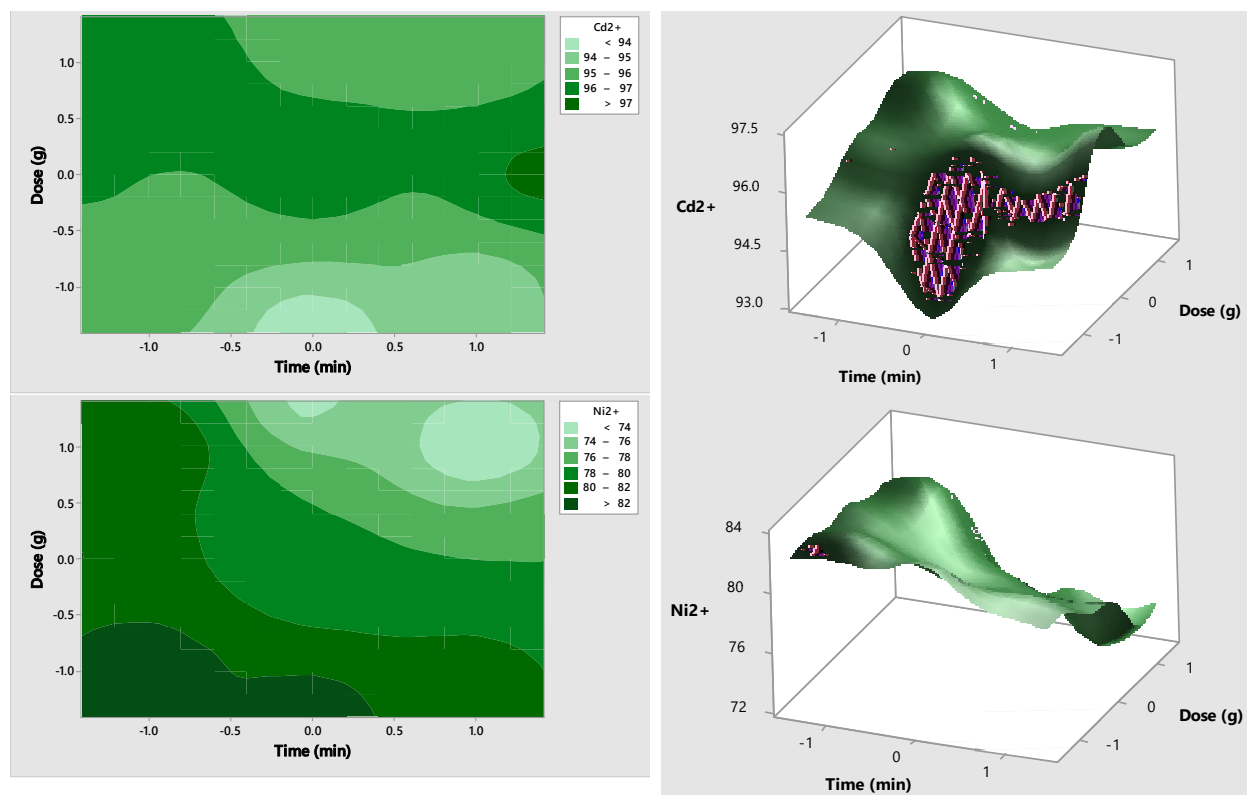


Figure-S7: (a) 2D contour plots and (b) 3D surface plots for three cations (Ni²⁺, Co²⁺, Cd²⁺) and three oxyanions (V⁵⁺, Cr⁶⁺, As³⁺) for optimization-2 (Dose vs. Time).

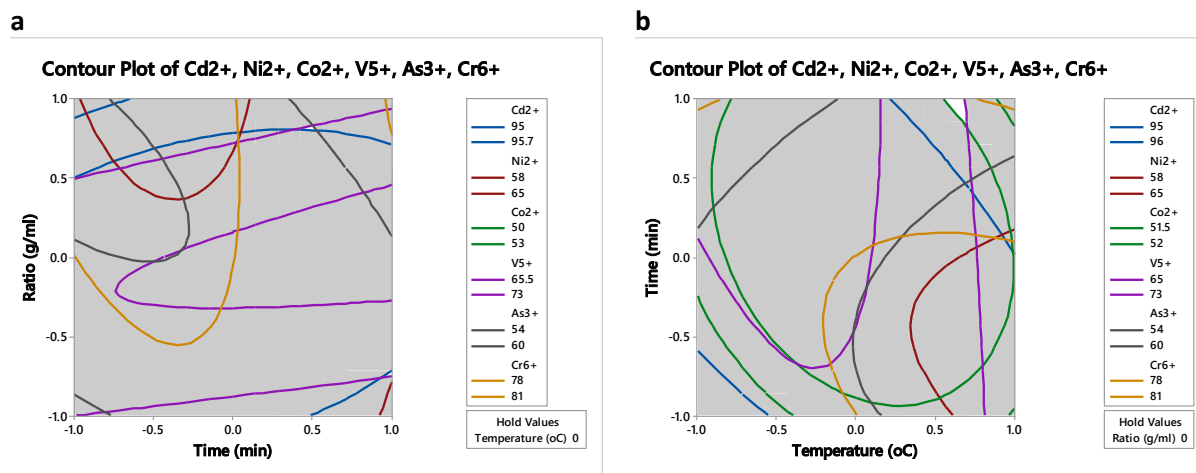


Figure-S8: Other combinations of overlaid contour plots for the removal of oxyanions and cations in multi-objective optimization (a) PF:THF ratio vs. time for optimization-1 (b) Time vs. temperature for optimization-1

FTIR analysis

The FTIR spectra of PF before and after the biosorption of trace metals show (**Figure S9**) that some sorption peaks have shifted or disappeared, and new peaks have formed due to THF treatment and metal adsorption. A broad range of peaks around the 3000 cm^{-1} region corresponds to =C-H , O-H , and C-H stretching vibrations of alkanes, aromatic, and carboxylic acids, indicating the presence of free hydroxyl groups on the biosorbent surface. The figure also shows that after THF treatment, the peaks at 2850 and 2918 cm^{-1} disappeared, exposing additional functional groups. It is evident that after biosorption with the treated THF, there is a shift of the peak from 2962 to 2957 cm^{-1} , indicating a decrease in free hydroxyl group content (O-H stretching vibration), likely due to the interaction between metal ions and the -OH groups of the biosorbent (Chakrabarty et al. 2020). This also suggests that the O-H group is involved in the biosorption process. Additionally, a new peak appeared at 1740 cm^{-1} , indicating the possible involvement of the amide I group (carbonyl and amide stretching) in the biosorption process during the adsorption of metal ions onto the biosorbent surface. A detailed mechanistic study of keratin involved in the biosorption process has been discussed in our previous study (Zahara et al. 2023).

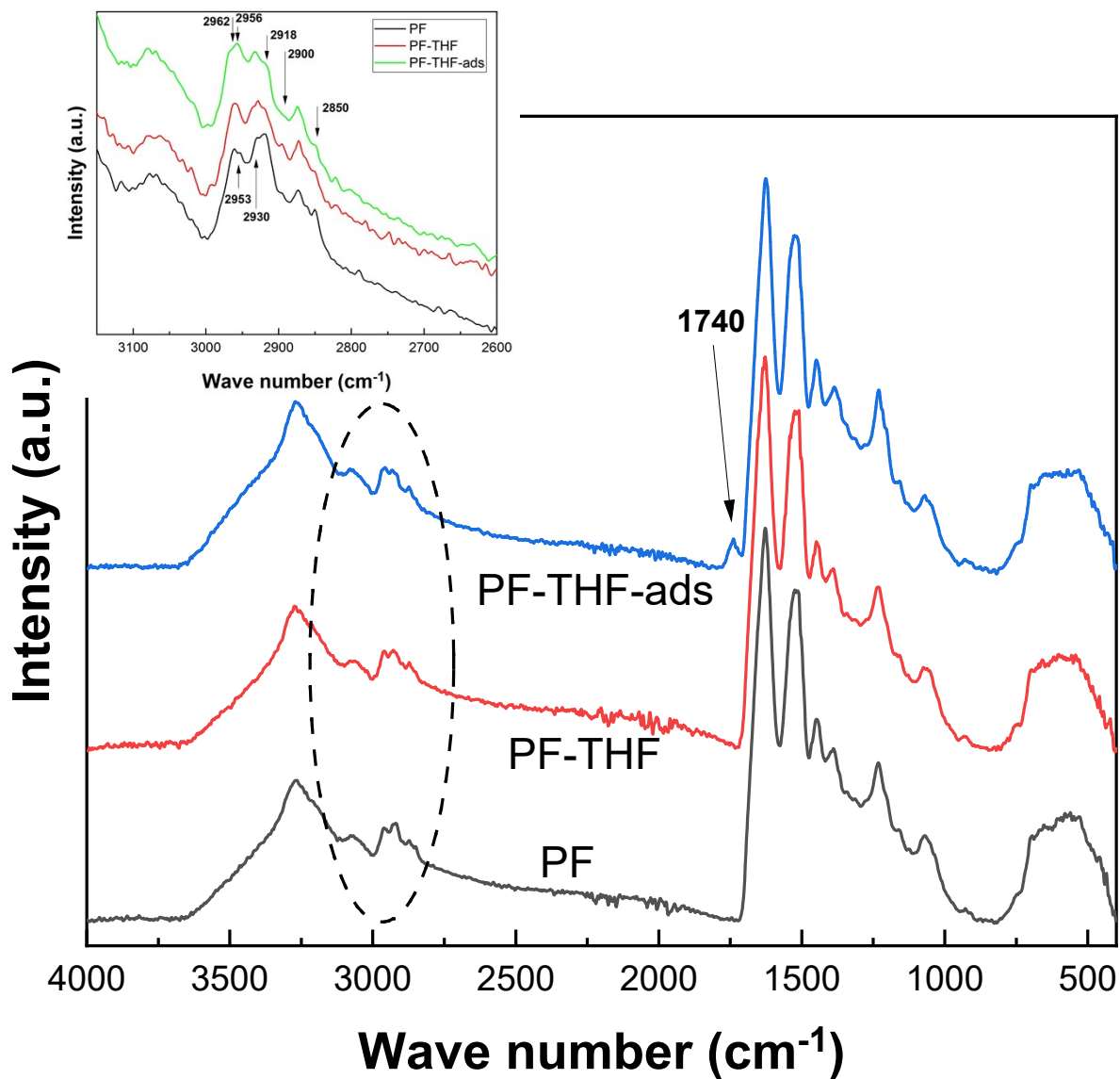
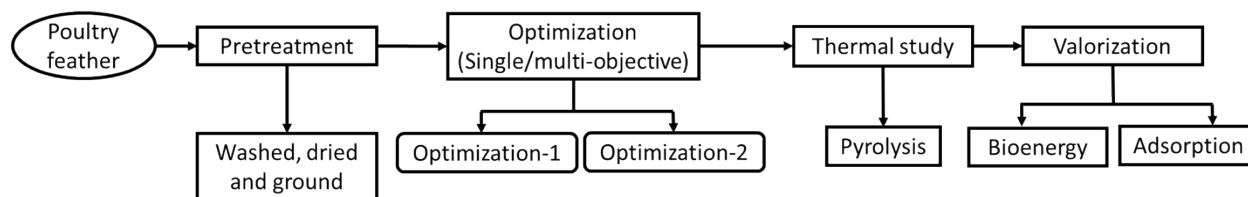


Figure S9: FTIR spectra of parent poultry feather, THF treated poultry feather before and after adsorption from 4000 to 500 cm⁻¹



Scheme-S1: A flowchart outlining the overall experimental approach

Description and mathematical forms of different models

Model-free methods

Model-free kinetic methods are primarily iso-conversional in approach. They allow for accurate determination of activation energy (E_a) using both isothermal and non-isothermal data and are frequently applied in the study of biomass pyrolysis kinetics (Opfermann et al., 2002). These methods are capable of addressing complex reactions and are based on the principle that, at a constant level of conversion (α), the reaction rate under a given heating rate (β) depends solely on the temperature, with the function $f(\alpha)$ remaining unchanged. Without requiring prior knowledge of the reaction mechanism, model-free methods enable comprehensive kinetic analysis and can reveal the presence of multiple processes when E_a significantly changes with α (Vyazovkin et al., 2011). Depending on the kinetic equation's formulation, these methods are categorized as either differential or integral. The Friedman method is the most widely used differential approach, whereas the Kissinger-Akahira-Sunose (KAS) method is a commonly adopted integral technique. Compared to differential methods, integral methods are generally less affected by data noise and yield more consistent E_a results.

1- Friedman method

The mathematical form of Friedman method is presented below:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln\left(\beta \frac{d\alpha}{dT}\right) = \ln(k_0) - \frac{E}{RT} + \ln(f(\alpha))$$

This approach uses the logarithm of the conversion rate $\left(\frac{d\alpha}{dt}\right)$ as a reciprocal function of temperature which gives straight line. E at a particular conversion is estimated from the slope of the straight line.

2- KAS method

The mathematical form of KAS method is presented below:

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{Rk_0}{E g(\alpha)}\right) - \frac{E}{RT}$$

E can be calculated from the slope of straight line of $\ln\left(\frac{\beta}{T^2}\right)$ versus reciprocal function of temperature at particular conversion for different heating rates.

Model-fitting method

Model-fitting method is traditionally employed to evaluate the pyrolysis behavior of biomass by analyzing their devolatilization weight loss data. This is typically done using a first-order single-step reaction model or by combining the contributions of multiple pseudo-components such as

cellulose, hemicellulose, lignin, and others (Aboyade et al., 2012). The kinetic analysis using model-fitting methods provides detailed simulations that closely replicate experimental biomass pyrolysis data. Furthermore, more accurate simulations can be achieved by applying n th-order reaction models for specific mechanisms, where optimization of unknown parameters is required (Osman et al., 2017). Therefore, in model-fitting approaches (Coats-Redfern), various kinetic models (e.g. first order, diffusion, nucleation etc.) are tested against experimental data to determine the best fit and extract the corresponding kinetic parameters (Ali and Bahadar, 2019).

Coats-Redfern Method

$$\ln(g(\alpha)) = -\frac{E}{RT} + \ln\left(\frac{Rk_0}{\beta E}\right)$$

where

$$g(\alpha) = \frac{\ln(1 - \alpha)}{T^2} \quad \text{for } n=1$$

$$g(\alpha) = \frac{1 - (1 - \alpha)^{1-n}}{(1 - n) T^2} \quad \text{for } n \neq 1$$

The plot of left-hand side of expression (given in Table) versus $1/T$ for different reaction mechanisms gives straight line from where kinetic parameters and rate determining steps can be evaluated.

Basic thermodynamic relations

Further parameters which include enthalpy, entropy and Gibbs free energy were determined using basic thermodynamic equations as follows: [Palmay et al., 2021; Patidar et al., 2022].

$$\Delta H^\ddagger = E - RT_m$$

$$\Delta G^\ddagger = E + RT \ln\left(\frac{K_B T_m}{h k_0}\right)$$

$$\Delta S^\ddagger = \frac{\Delta H^\ddagger - \Delta G^\ddagger}{T_m}$$

where, h is the Plank constant (6.626×10^{-34} J/s), K_B is the Boltzmann constant (1.381×10^{-23} J/K) and T_m is maximum decomposition temperature for each phase.

Performance Indicators

Coefficient of determination:

$$R^2 = 1 - \frac{\sum_{i=1}^M (Y_E - Y_P)^2}{\sum_{i=1}^M (Y_E - \bar{Y}_E)^2}$$

Percent relative error:

$$RE(\%) = \left| \frac{Y_E - Y_P}{Y_E} \right| \times 100$$

Root mean square error:

$$RMSE = \sqrt{\frac{\sum_{i=1}^M (Y_E - Y_P)^2}{M}}$$

Mean absolute error:

$$MAE = \frac{\sum_{i=1}^M |Y_E - Y_P|}{M}$$

where, M is the total number of runs, Y_P is the predicted value, Y_E is the experimental value and $\bar{Y}_E$ is the average of experimental values.

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