Comprehensive characterization and RSM-based optimization of crystal violet adsorption using $SnCl_2$–$FeCl_3$ and $SnCl_2$–$ZnCl_2$ activated pomegranate peel biosorbents

Nada Hamrouche[ad], Chahrazed Djilani[bc], Youghourta Belhocine[ad], Nawal Bouzenad[ad], Lehtihet Boudjema Amir[g], Sabri Meradi[a], Imene Hamrouche[ef] and Djihane Slimane Ben Ali[ec*]

[a]*Department of Process Engineering, Faculty of Technology, University of 20 Août1955, El Hadaiek Road, B. O. 26 21000 Skikda, Algeria. E-mail: n.hamrouche@univ-skikda.dz*

[b]*Faculté de Technologie, University of 20 Août1955, El Hadaiek Road, B. O. 26 21000 Skikda, Algeria.*

[c]*Laboratory LRPCSI, University of 20 Août1955, El Hadaiek Road, B. O. 26 21000 Skikda, Algeria.*

[d]*Laboratory of Catalysis, Bioprocess and Environment, Department of Process Engineering, Faculty of Technology, University of 20 August 1955, Skikda 21000, Algeria.*

[e]*Department of petrochemical, Faculty of Technology, University of 20 Août1955, El Hadaiek Road, B. O. 26 21000 Skikda, Algeria.*

[f]*Laboratory of Chemical Engineering and Environment of Skikda, University of 20 August 1955 Skikda, Algeria.*

[g]*Laboratory of Chemical Process Engineering, Department of Process Engineering, Faculty of Technology, Ferhat Abbas University Setif 1, Setif 19000, Algeria.*

Table S1. Adsorption kinetics and isotherms non-linear models.

Kinetic models	Formula	Parameters	Eqs
PFO	$q_t = q_e\left(1 - exp^{-k_1 t}\right)$	q_e (mg.g^{-1}): adsorption capacity at equilibrium. q_t (mg.g^{-1}): adsorption capacity at time t. k_1 (min^{-1}): PFO rate constant. t (min): contact time.	(4)
PSO	$q_t = (q_e^2 k_2 t)/(1 + q_e k_2 t)$	k_2 (g.mg^{-1}.min^{-1}): PSO rate constant.	(5)
Inraparticle diffusion	$q_t = (k_{Int} t^{1/2} + C)$	k_{Int} (mg·g^{-1}·min$^{-1/2}$): intraparticle diffusion rate constant.	(6)
Isotherm model			
Langmuir	$q_e = (q_{max} K_L C_e)/(1 + K_L C_e)$	C_e (mg.L^{-1}): equilibrium concentration of the resting CV dye in solution. q_{max} (mg.g^{-1}): maximum adsorption capacity. K_L (L.mg^{-1}) : Langmuir constant.	(7)

Freundlich	$q_e = K_F C_e^{1/n}$	K_F (mg.g^{-1}): Freundlich constant. n: heterogeneity factor.	(8)
Temkin	$q_e = (RT/b_T)\ln(K_T C_e)$	R (8.314 J.K^{-1} .mol^{-1}): universal gas constant. T(K): the absolute temperature. b_T (J.mol^{-1}): the heat of adsorption. K_T (L.mg^{-1}): Temkin constant.	(9)

Table S2. CCD Experience Matrix (PPP/Sn-Fe).

		Factor 1	Factor 2	Factor 3	Factor 4	Response 1
Std	**Run**	**A: Concentration**	**B: pH**	**C: Temperature**	**D: Masse**	**q_t**
		mg.L^{-1}		**°C**	**g**	**mg.g^{-1}**
1	8	5	2	20	0.025	9.12
2	12	100	2	20	0.025	159.2
3	11	5	10	20	0.025	9.1
4	5	100	10	20	0.025	185.8
5	13	5	2	60	0.025	9.88
6	6	100	2	60	0.025	192.8
7	15	5	10	60	0.025	9.98
8	3	100	10	60	0.025	191.2
9	1	5	2	20	0.2	1.16
10	22	100	2	20	0.2	24.73
11	14	5	10	20	0.2	1.21
12	29	100	10	20	0.2	23.65
13	9	5	2	60	0.2	1.23

14	28	100	2	60	0.2	23.1
15	25	5	10	60	0.2	1.2
16	7	100	10	60	0.2	23.52
17	26	5	6	40	0.1125	2.2
18	27	100	6	40	0.1125	41.69
19	10	52.5	2	40	0.1125	21.82
20	4	52.5	10	40	0.1125	22.54
21	2	52.5	6	20	0.1125	22.46
22	17	52.5	6	60	0.1125	22.38
23	20	52.5	6	40	0.025	99.22
24	19	52.5	6	40	0.2	12.31
25	21	52.5	6	40	0.1125	22.17
26	23	52.5	6	40	0.1125	22.17
27	16	52.5	6	40	0.1125	22.17
28	18	52.5	6	40	0.1125	22.17
29	24	52.5	6	40	0.1125	22.17

Table S3. CCD Experience Matrix (PPP/Sn-Zn)

		Factor 1	**Factor 2**	**Factor 3**	**Factor 4**	**Response 1**
Std	**Run**	**A: Concentration**	**B: pH**	**C: Temperature**	**D: Masse**	**q_t**
		$mg.L^{-1}$		**°C**	**g**	**$mg.g^{-1}$**
1	8	5	2	20	0.025	9.99
2	12	100	2	20	0.025	179.48
3	11	5	10	20	0.025	9.8
4	5	100	10	20	0.025	184.78
5	13	5	2	60	0.025	9.94
6	6	100	2	60	0.025	189.36
7	15	5	10	60	0.025	9.98
8	3	100	10	60	0.025	190.92
9	1	5	2	20	0.2	1.25
10	22	100	2	20	0.2	23.95
11	14	5	10	20	0.2	1.25
12	29	100	10	20	0.2	23.26

13	9	5	2	60	0.2	1.22
14	28	100	2	60	0.2	23.87
15	25	5	10	60	0.2	1.22
16	7	100	10	60	0.2	23.8
17	26	5	6	40	0.1125	2.18
18	27	100	6	40	0.1125	42.02
19	10	52.5	2	40	0.1125	22.55
20	4	52.5	10	40	0.1125	22.62
21	2	52.5	6	20	0.1125	22.15
22	17	52.5	6	60	0.1125	22.52
23	20	52.5	6	40	0.025	102.2
24	19	52.5	6	40	0.2	12.74
25	21	52.5	6	40	0.1125	22.3
26	23	52.5	6	40	0.1125	22.3
27	16	52.5	6	40	0.1125	22.3
28	18	52.5	6	40	0.1125	22.3
29	24	52.5	6	40	0.1125	22.3

Table S4. Equations relevant to understanding the thermodynamic concepts and processes.

Thermodynamic equations	**Formula**	**Parameters**	**Eqs.**
Distribution coefficient (K_d)	$K_d = q_e/C_e$	q_e (mg.g^{-1}): adsorption capacity at equilibrium. C_e (mg.L^{-1}): equilibrium concentration of the resting CV dye.	**(12)**
Free enthalpy (ΔG°)	$\Delta G° = -RTlnK_d$	R (~ 8.314 J.mol^{-1}.K^{-1}): the universal constant of gasses. T (°K): the absolute temperature.	**(13)**
Linear fit (Van 't Hoff law)	$lnK_d = (\Delta S°/R) - (\Delta H°/RT)$	ΔS° (kJmol^{-1}.K^{-1}): standard entropy ΔH° (kJ.mol^{-1}): standard enthalpy	**(14)**

Table S5. ANOVA of Central Composite design for CV dye adsorption by PPP/Sn-Fe (Reduced Quadratic model).

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

Model	98635.54	4	24658.89	262.95	< 0.0001	significant
A-Concentration	37411.15	1	37411.15	398.93	< 0.0001	
D-Adsorbent dose	31600.14	1	31600.14	336.96	< 0.0001	
AD	22554.03	1	22554.03	240.50	< 0.0001	
D^2	7070.21	1	7070.21	75.39	< 0.0001	
Residual	2250.69	24	93.78			
Lack of Fit	2250.69	20	112.53			
Pure Error	0.0000	4	0.0000			
Cor Total	1.009E+05	28				

*df = degree of freedom

Table S6. Regression coefficient values of predicted and adjusted experimental results of CCD model (PPP/Sn-Fe).

Std. Dev.	Mean	C.V. %	R^2	Adjusted R^2	Predicted R^2	Adeq Precision
9.68	42.15	22.97	0.9777	0.9740	0.9666	50.4355

Table S7. ANOVA of Central Composite design for CV dye adsorption by PPP/Sn-Zn (Reduced Quadratic model).

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	1.031E+05	4	25779.42	370.63	< 0.0001	significant
A-Concentration	38698.55	1	38698.55	556.37	< 0.0001	
D-Adsorbent dose	33272.54	1	33272.54	478.36	< 0.0001	
AD	23630.61	1	23630.61	339.74	< 0.0001	
D^2	7516.00	1	7516.00	108.06	< 0.0001	
Residual	1669.33	24	69.56			
Lack of Fit	1669.33	20	83.47			
Pure Error	0.0000	4	0.0000			
Cor Total	1.048E+05	28				

Table S8. Regression coefficient values of predicted and adjusted experimental results of CCD model (PPP/Sn-Zn).

Std. Dev.	Mean	C.V. %	R^2	Adjusted R^2	Predicted R^2	Adeq Precision

8.34	42.92	19.43	0.9841	0.9814	0.9774	59.8724

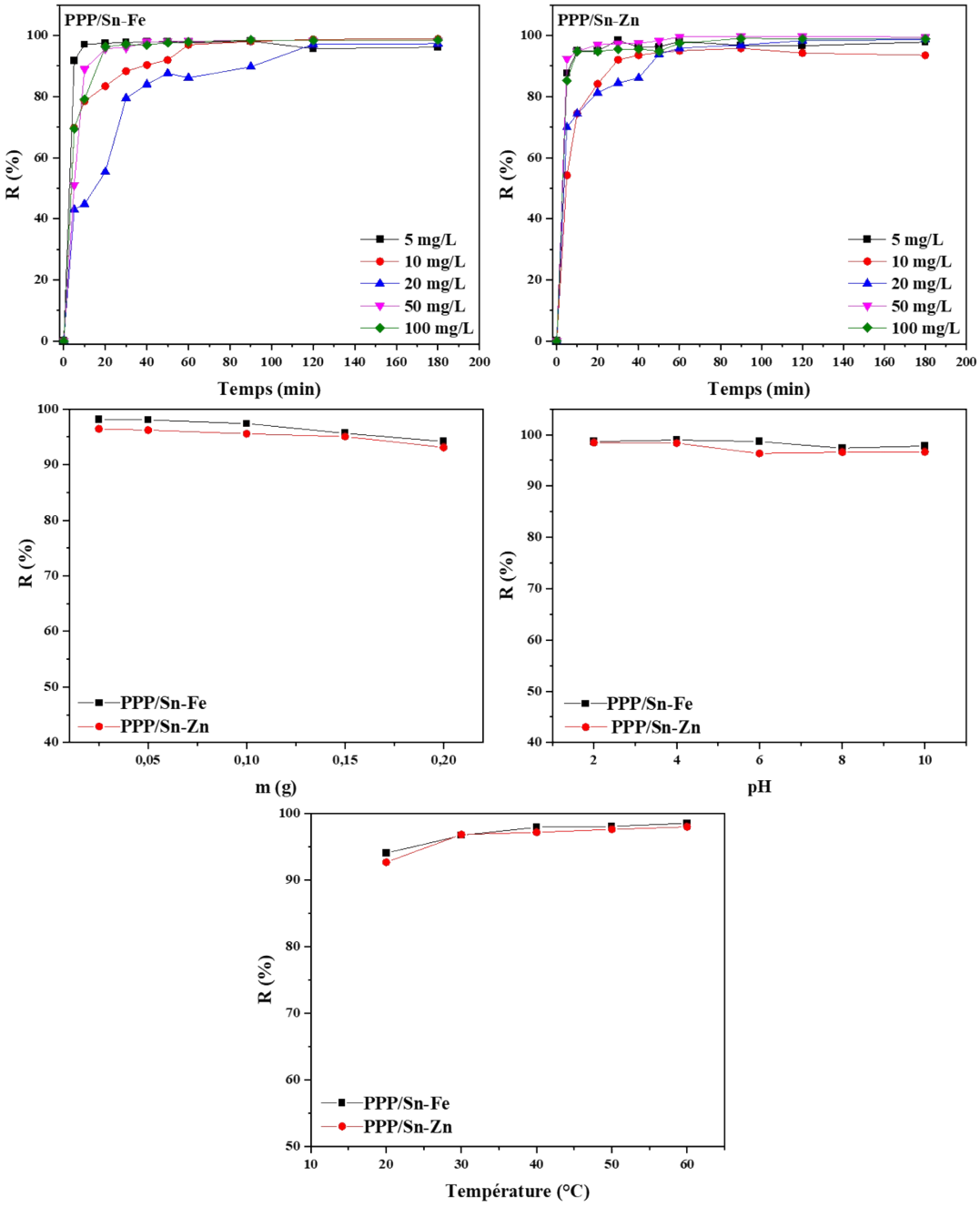

Figure S1. Effect of contact time and initial dye concentration**,** adsorbent dose, initial pH and temperature on CV dye removal by PPP/Sn-Fe and PPP/Sn-Zn.

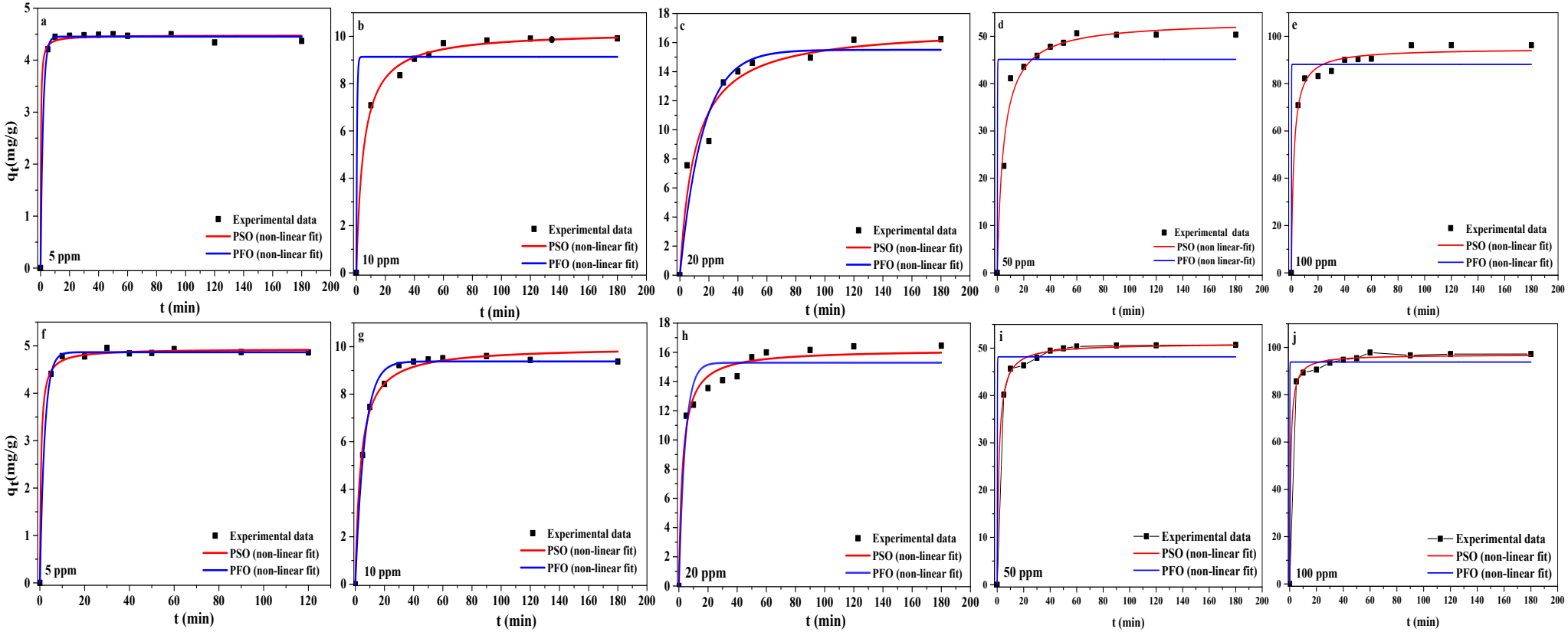

Figure S2. PFO and PSO kinetics plot for the adsorption of CV by **(a-e)** PPP/Sn-Fe and **(f-j)** PPP/Sn-Zn.

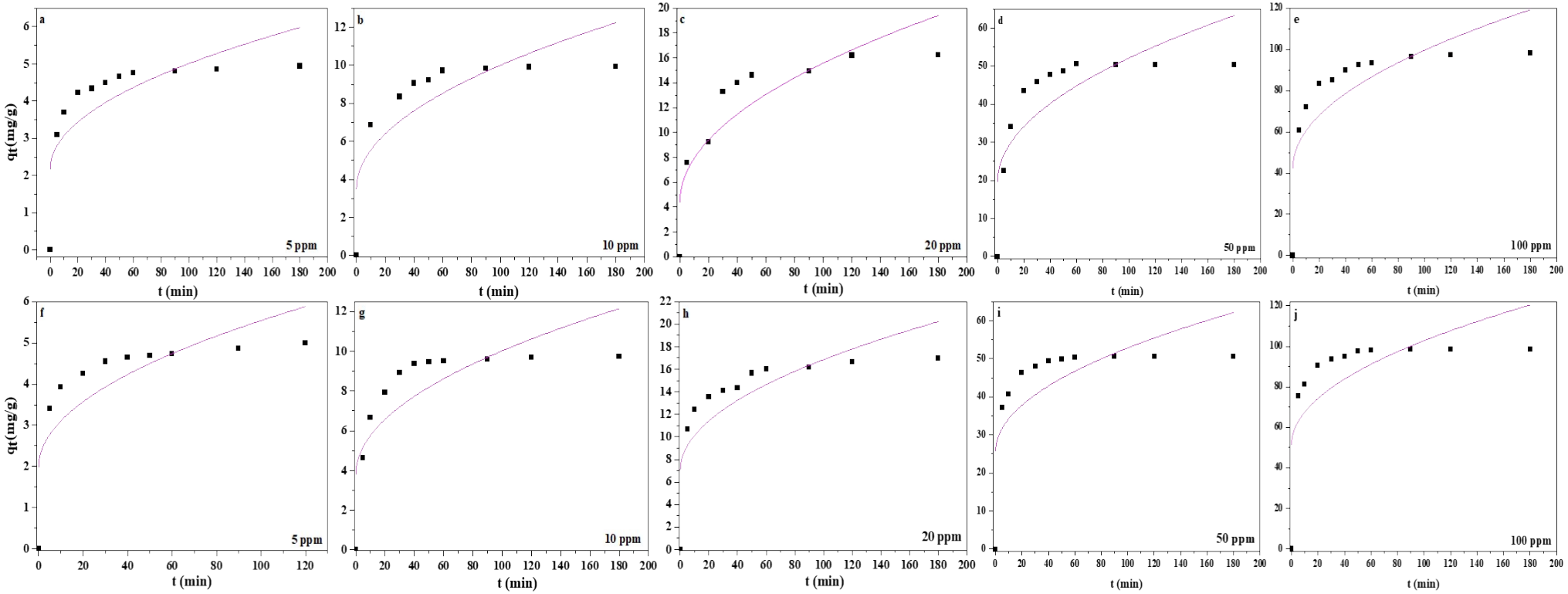

Figure S3. Intraparticle diffusion plot for the adsorption of CV by **(a-e)** PPP/Sn-Fe and **(f-j)** PPP/Sn-Zn.

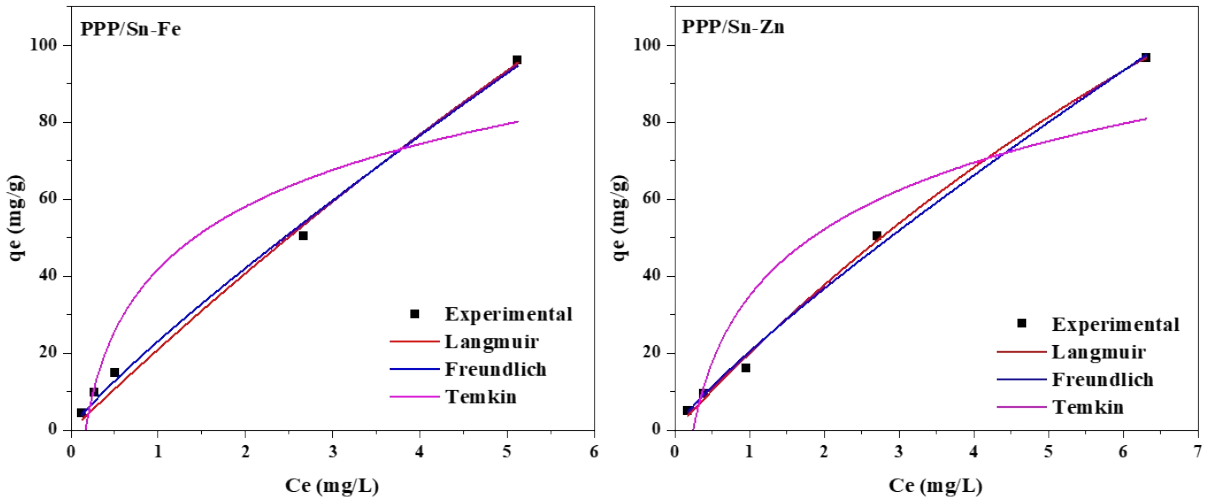

Figure S4. Isotherm plot of PPP/Sn-Fe and PPP/Sn-Zn for adsorption of CV dye.

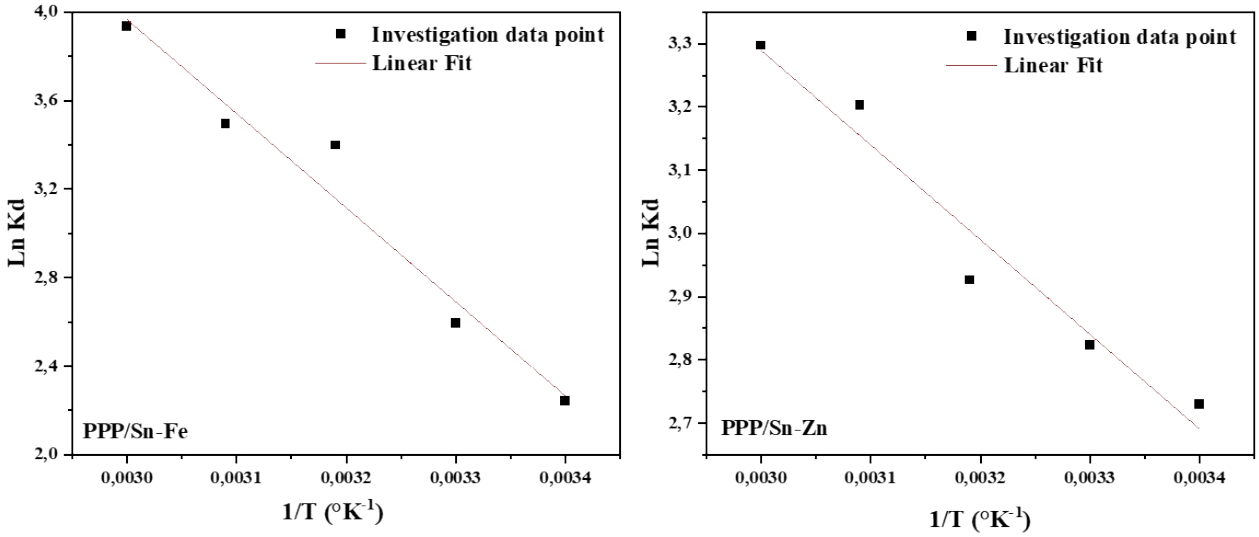

Figure S5. Plot of the Van't Hoff equation.

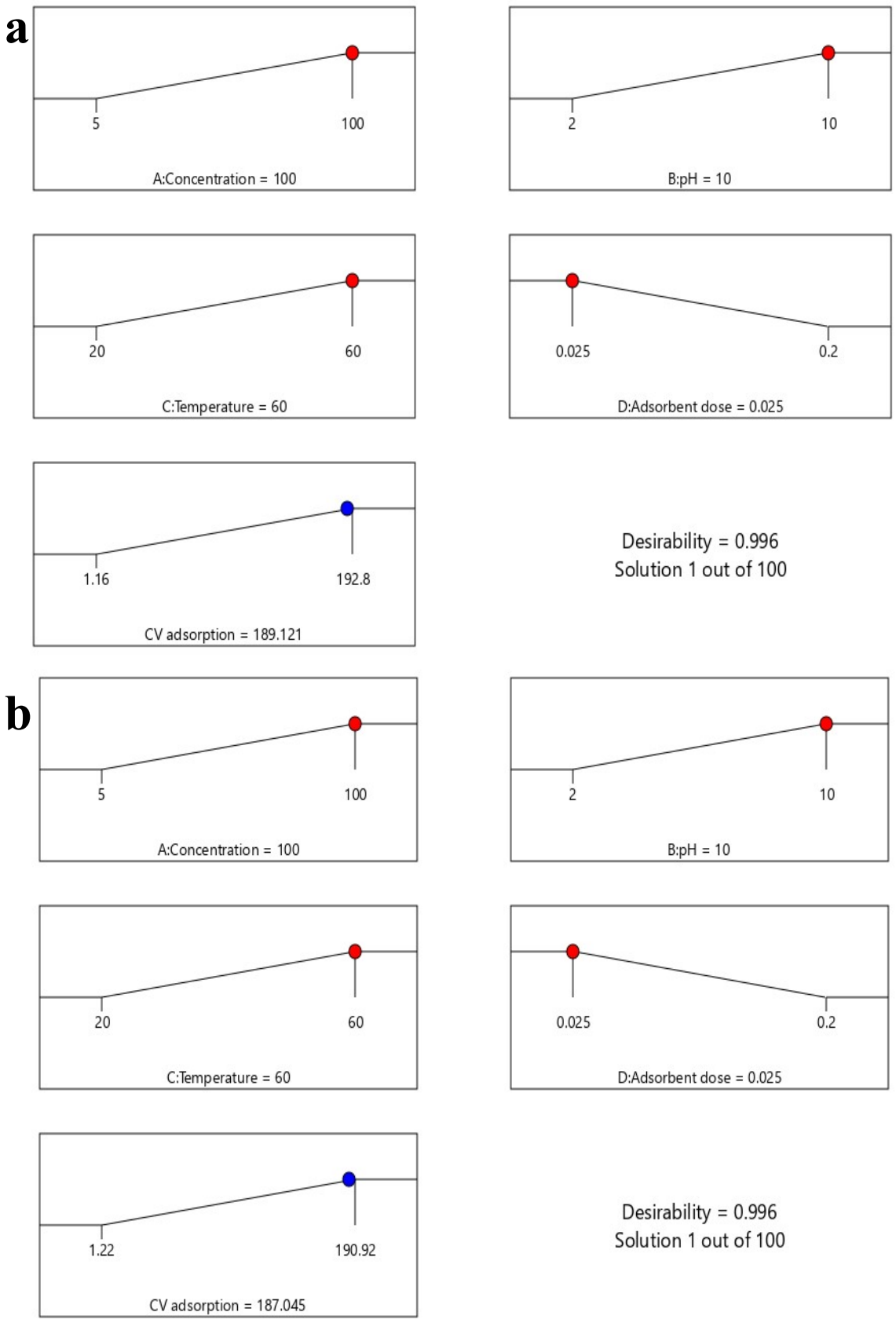

Figure S6. Optimization of CV biosorption capacity responses on a) PPP/Sn-Fe and b) PPP/Sn-Zn and desirability function (CCD model).