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Adsorption of Dicamba and MCPA onto MIL-53(Al) Metal-organic Framework: Response Surface Methodology and Artificial Neural Network Model Studies

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Table S1: Coded range for independent variables for the CCD-RSM factor levels

Variables	Units	Range and levels				
		–α	**–1**	**0**	**+1**	**+α**
Contact time	min	35	5	15	25	45
Initial concentration	mg/L	40	10	20	30	50
Adsorbent dosage	g/L	0.04	0.01	0.02	0.03	0.05
pH		8	2	4	6	10
Temperature	°C	40	25	30	35	45

Table S2**:** Experimental design data matrix for predicting adsorption capacity of dicamba and MCPA

Runs	Contact time (min)	Initial concentration (mg/L)	Adsorbent dosage (g/L)	pH	Temperature (°C)
1	15	20	0.02	4	30
2	5	10	0.03	2	35
3	15	20	0.04	4	30
4	15	20	0.02	8	30
5	25	40	0.02	4	30
6	25	10	0.01	2	35
7	15	20	0.02	4	45
8	5	30	0.01	2	35
9	5	30	0.01	6	25
10	5	30	0.03	2	25
11	5	10	0.03	6	35
12	25	10	0.01	6	35
13	25	30	0.03	6	35
14	25	30	0.01	2	35
15	5	10	0.01	2	25
16	5	30	0.01	6	35
17	35	20	0.02	4	30
18	5	30	0.03	6	35
19	5	30	0.03	6	25
20	25	10	0.03	2	25
21	25	30	0.01	6	35
22	15	20	0.02	10	30
23	25	10	0.03	6	25
24	25	10	0.03	6	35
25	45	20	0.02	4	30
26	25	20	0.01	4	40
27	5	10	0.01	6	25
28	5	10	0.03	6	25
29	25	30	0.03	2	35
30	5	30	0.01	2	25
31	25	30	0.03	2	25
32	5	10	0.01	2	35
33	5	30	0.03	2	35
34	25	30	0.01	6	25
35	5	10	0.03	2	25
36	25	10	0.01	6	25
37	15	20	0.05	4	30

38	15	20	0.02	4	30
39	25	50	0.01	4	40
40	5	10	0.01	6	35
41	15	10	0.01	2	25
42	25	30	0.03	6	25
43	25	30	0.01	2	25
44	25	20	0.01	4	35

Table S3: Analysis of variance (ANOVA) for dicamba and MCPA adsorption by RSM

	Dicamba					**MCPA**				**P-value**
Source	**Sum of square**	**df**	**mean square**	**F-value**	**P-value**	**Sum of square**	**df**	**mean square**	**F-value**	< 0.0001
Model	419.1	17	24.6	73.4	< 0.0	439.5	17	25.8	70.8	0.0
A-Time	4.4	1	4.4	13.2	0.0	5.4	1	5.4	14.8	< 0.0
B-Concentration	324.1	1	324.1	965.8	< 0.0	337.3	1	337.3	924.3	0.0
C-Dosage	2.6	1	2.6	7.7	0.0	2.7	1	2.7	7.5	0.1
D-pH	0.6	1	0.6	1.8	0.1	0.7	1	0.7	2.1	0.0
E-Temperature	2.1	1	2.1	6.2	0.0	2.3	1	2.3	6.4	0.0
AB	2.1	1	2.1	6.3	0.0	2.1	1	2.1	5.8	0.0
AC	4.6	1	4.6	13.8	0.0	5.2	1	5.2	14.4	0.0
AD	5.4	1	5.4	16.9	0.0	5.7	1	5.7	15.7	0.0
BC	3.7	1	3.7	11.1	0.0	3.9	1	3.9	10.9	0.0
BD	2.3	1	2.3	7.0	0.0	2.7	1	2.7	7.4	0.0
BE	1.3	1	1.3	3.8	0.1	1.4	1	1.4	3.9	0.0
CD	5.3	1	5.3	16.1	0.0	6.1	1	6.1	16.6	0.0
CE	3.2	1	3.2	9.7	0.0	3.5	1	3.5	9.7	0.0
DE	2.9	1	2.9	8.7	0.0	2.8	1	2.8	7.7	0.0
BÂ²	5.7	1	5.7	17.1	0.0	7.5	1	7.5	20.5	0.0
CÂ²	3.8	1	3.8	11.4	0.0	5.1	1	5.1	14.0	0.0
EÂ²	2.5	1	2.5	7.5	0.0	2.4	1	2.4	6.7	
Residual	4.3	26	0.3			4.7	26	0.3		
Lack of Fit	4.3	1	0.5			4.7	1	0.5		
Pure Error	0.0	25	0.0			0.0	25	0.0		
Cor Total	423.5	43				444.2	43			
	Dicamba					**MCPA**				
R^2	0.988					0.987				
R^2adj	0.974					0.976				
Predicted R^2	0.866					0.870				
Adeq Precision	24.519					24.761				

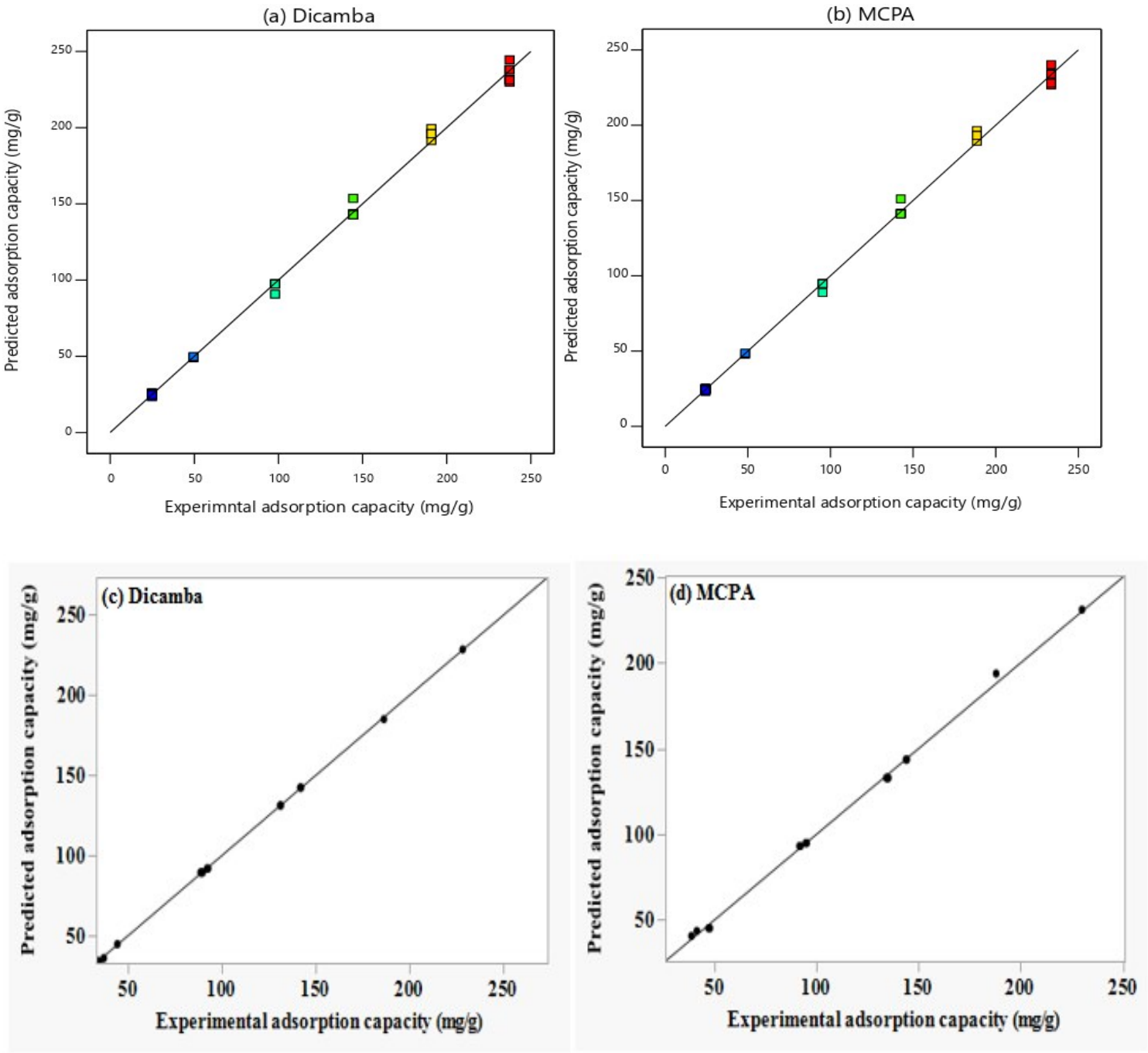


Fig. S1: RSM prediction scatter plots (a) dicamba (b) MCPA and ANN prediction scatter plots (c) dicamba (d) MCPA

Adsorption Kinetics

Adsorption kinetics was applied to understand the rate of adsorbate uptake, reaction mechanism and equilibrium time required for the adsorption process. It is a fundamental factor that was used to determine the effectiveness and efficiency of the adsorbent as well as the mass transfer which explains the rate-limiting steps in designing the adsorption system [1]. In this study, the pseudo-first order, pseudo second order and intraparticle diffusion model were used to ascertain the best fitting for the experimental data. Using these models, criteria such as coefficient of determination (R^2), adjusted R^2 (R^2adj), root mean square error (RMSE), alkaike information criteria (AIC) are considered as the best fit to judge the performance of our adsorption process by regression analysis [2] .

The following equations were used for this study [1]. The equations for the models were given as:

Lagergren pseudo-first-order model

$$q_t = q_e(1 - e^{-k_1 t}) \quad (11)$$

Pseudo-second-order model

$$q_t = \frac{K_2 q_e^2 t}{1 + K_2 q_e t} \quad (12)$$

Intraparticle diffusion model

$$q_t = K_P t^{0.5} + C \quad (13)$$

Where q_t and q_e are the amount of dicamba and MCPA adsorbed at certain equilibrium and time t (mg/g), K_1 (min^{-1}) is the pseudo-first-order rate constant, K_2 (g mg/g min^{-1}) is the equilibrium rate constant of the pseudo-second-order and the intra-particle diffusion rate constant is represented as K_p (mg/g min^{-1}).

Adsorption isotherms

Adsorption isotherms provide information on the adsorption capacity and the type of interaction mechanism that exist between MIL-53(Al) and the studied herbicides. The Langmuir, Freundlich and Temkin isotherms were used to describe the adsorption of dicamba and MCPA onto MIL-53(Al). The models are described by the following equations [2]:

Langmuir model

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (14)$$

$$R_L = \frac{1}{1 + C_o K_L} \quad (15)$$

Where C_e is the concentration at equilibrium (mg/g), q_e is the quantity of dicamba and MCPA adsorbed at equilibrium (mg/g), q_m and K_L are the constant representing adsorption capacity and adsorption energy, respectively. R_L depict the favourability of the adsorption process (R_L>1, unfavourable; 0 < R_L< 1, favourable; R_L = 1, linear).

Freundlich model

$$\log(q_e) = log\ K_F + \frac{1}{n}\ log\ C_e \quad (16)$$

Where K_F is the Freundlich constant of adsorption capacity, n is the adsorption intensity and C_e is the equilibrium concentration of dicamba and MCPA (mg/g).

Temkin model

$$q_e = BlnA_T + BlnC_e \quad (17)$$

Where B is the heat of adsorption (J/mol) and A_T is the Temkin equilibrium binding constant corresponding with the maximum binding energy (L/g).

Thermodynamics studies

The basic thermodynamic parameters were used in this study to assess the feasibility of adsorption process based on temperature changes. They include the Gibbs free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°). This helps to determine whether the adsorption process is spontaneous, exothermic or endothermic. The equations are given as [3]:

$$\Delta G^{\circ} = -RTInK_C \quad (18)$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \quad (19)$$

Where ΔG° is the free energy (J K mol^{-1}), T (K) and R (J K mol^{-1}) are the temperature and universal gas constant for the adsorption, respectively and K_c is the equilibrium constant.

Kinetics model

Kinetics parameters were studied using the pseudo-first-order, pseudo-second-order and intra-particle diffusion models to ascertain the best fitting model that describe the adsorption process. From all the values obtained for the various models, the pseudo-second-order kinetics (Fig. S2 (a) and (b)) has the best fitting between the experimental and the theoretical values with the coefficient of determination R^2 > 0.99% for both dicamba and MCPA; R^2adj > 0.99%, lowest RMSE = 0.005, least AIC = - 133.830 values. The q_e values calculated for the pseudo-second-order kinetic model for dicamba and MCPA are in agreement with the experimental results in Table S4. The maximum q_e values for dicamba and MCPA were determined as q_e exp. 228.5, 231.9 mg/g and q_e cal. 227.2, 232.5 mg/g respectively at the equilibrium points which represent the adsorption capacity of MIL-53(Al). These values are in strong agreement with the RSM and ANN prediction models, which indicate that the simulated adsorption capacity by RSM and ANN is well validated by the experimental findings. Thus, the result further explain that the adsorption is a chemisorption process since it follows the pseudo-second-order kinetics. The intraparticle diffusion mechanism was used to describe the interaction and the movement of the molecules inside the particles of the adsorbent. Fig S3 (a) and b)) indicate two major stages that represent an external diffusion of herbicides to the surface of the adsorbent and the penetration of the molecules inside the pore of the MOF.

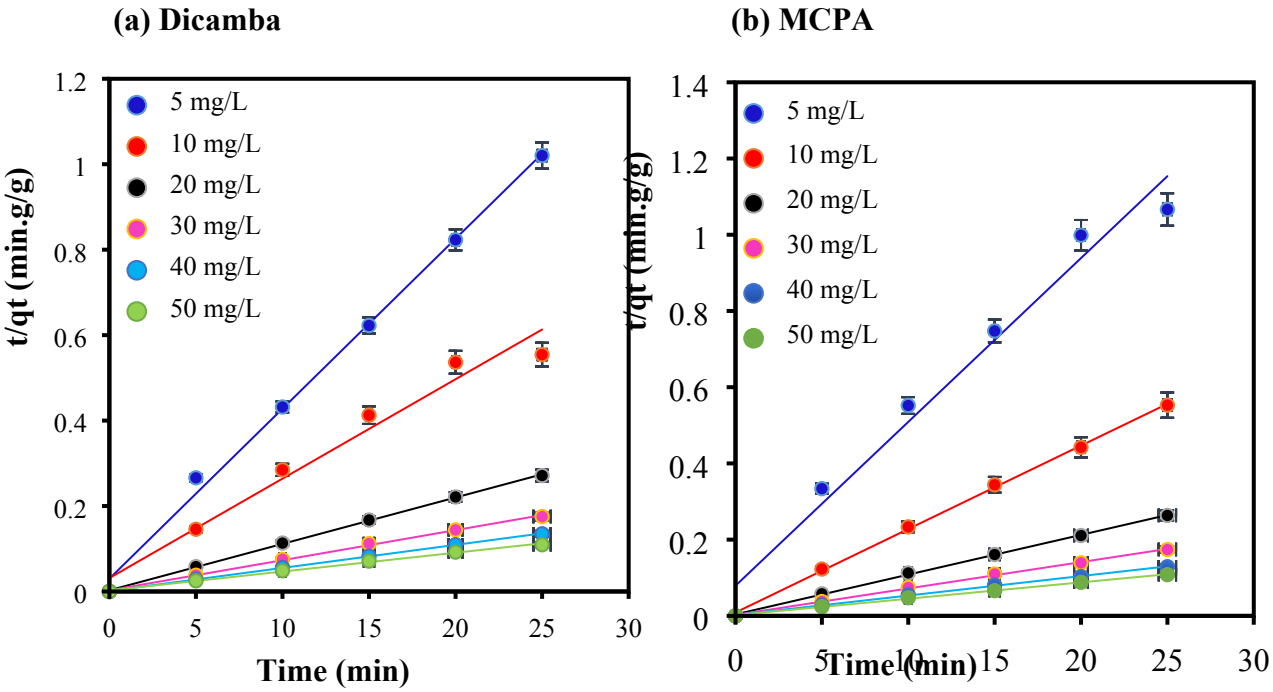
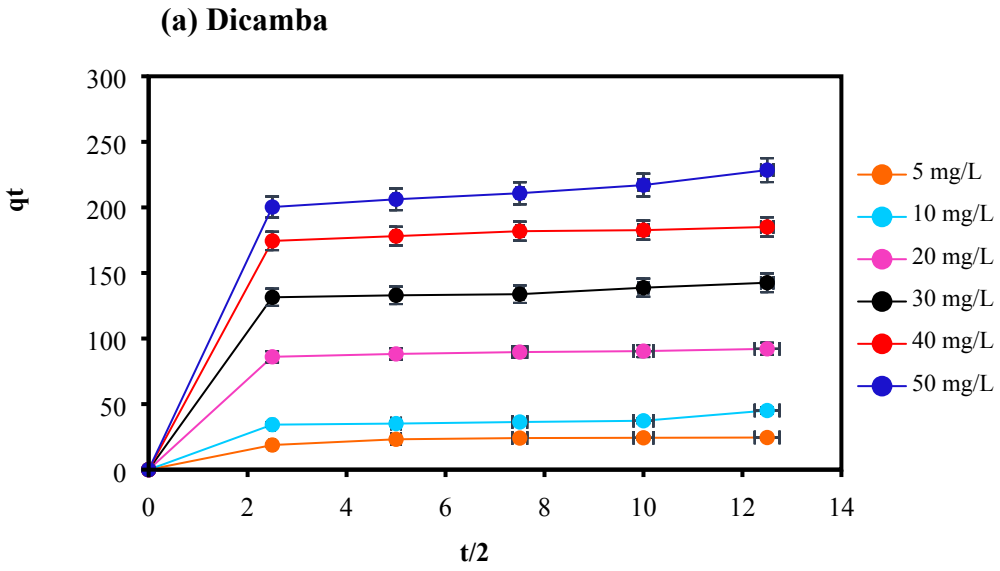


Fig. S2: Pseudo-second-order kinetics for the removal of (a) dicamba and (b) MCPA (Dosage: 0.01 g/L; 40°C; equilibrium time: 25 min; rpm: 150).



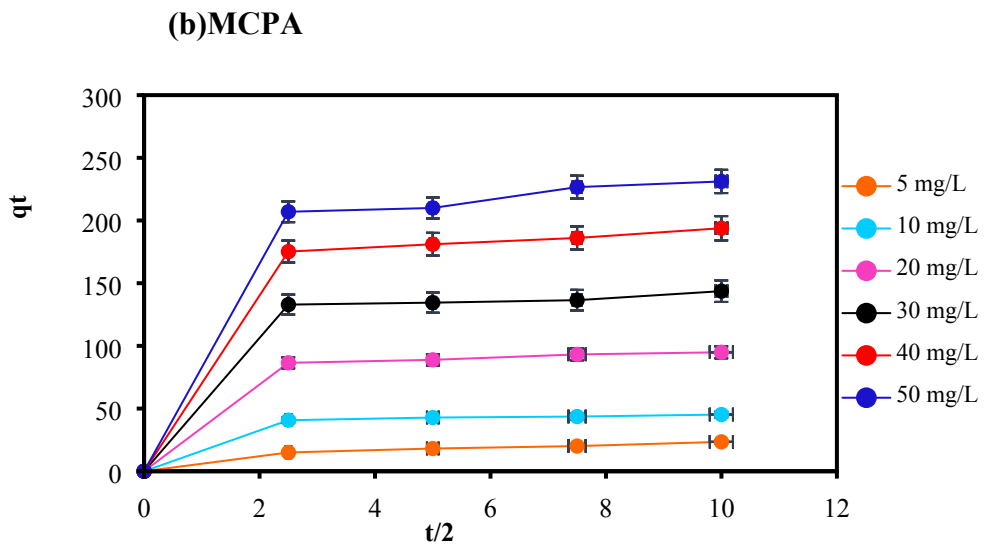


Fig. S3: Intraparticle diffusion model kinetics (a) dicamba and (b) MCPA
(Dosage: 0.01 g/L; 40°C; equilibrium time: 25 min, rpm: 150)

Table S4: Kinetics parameters for the adsorption of dicamba and MCPA onto MIL-53(Al)

Kinetic Models		Dicamba						MCPA					
		5	10	20	30	40	50	5	10	20	30	40	50
Pseudo-first-order	q_e exp (mg/g)	24.5	45.1	92.1	142.5	185.1	228.4	23.4	45.2	94.8	143.6	193.8	231.1
	q_e cal (mg/g)	11.0	35.0	31.1	66.4	64.5	150.4	8.3	27.4	29.8	48.1	51.5	110.3
	K_1 (min)$^{-1}$	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	R^2	0.56	0.66	0.78	0.74	0.81	0.76	0.42	0.37	0.45	0.29	0.37	0.55
	R^2adj	0.52	0.55	0.71	0.66	0.75	0.69	0.37	0.31	0.40	0.23	0.31	0.43
	RMSE	1.07	0.47	0.84	0.79	0.85	0.64	10.04	0.78	0.91	0.72	0.74	0.89
	AIC	3.5	-5.9	-0.2	-0.8	-0.1	-2.9	61.8	-4.6	-0.6	-6.5	-5.7	-1.1
Pseudo-second-order	q_e cal (g mg/g)	25.1	42.9	91.7	142.8	185.1	227.2	20.7	45.2	95.2	142.8	192.3	232.5
	K_2 (g mg/ min^{-1})	0.1	0.0	0.0	0.0	0.0	0.1	0.1	0.1	0.0	0.0	0.1	0.1
	R^2	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99
	R^2adj	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99
	RMSE	0.02	0.03	0.00	0.01	0.01	0.01	0.06	0.02	0.01	0.01	0.01	0.01
	AIC	-87.1	-87.1	-121.5	-109.5	-127.4	-133.8	-69.6	-90.1	-109.5	-121.1	-128.3	-131.5
Intra-particle diffusion	K_p (mg/g min$^{1/2}$)	1.5	2.6	5.4	8.4	10.9	13.6	2.1	3.7	7.8	11.6	15.9	19.2
	C	9.1	14.5	40.4	60.7	82.2	91.6	4.9	15.8	33.3	51.3	67.5	78.5
	R^2	0.33	0.48	0.26	0.29	0.25	0.33	0.47	0.28	0.27	0.27	0.28	0.29
	R^2adj	0.26	0.43	0.19	0.22	0.19	0.27	0.42	0.21	0.21	0.21	0.22	0.22
	RMSE	5.81	9.33	22.64	34.30	45.828	53.24	5.05	10.99	23.18	34.94	46.94	55.79
	AIC	47.61	59.8	82.9	93.7	101.2	105.1	43.9	64.1	83.5	95.3	101.9	106.3

Adsorption Isotherms

The equilibrium interaction between the analytes and the MIL-53(Al) MOF was studied based on the isotherm models. The values obtained are highlighted in Table S5. Based on the various results calculated, the Freundlich isotherm model (Fig. S4) best fit the adsorption process with the highest R^2 = 0.974%, 0.962%; R^2adj = 0.955, 0.953%; lowest RMSE < 0.079, 0.918; and the least AIC < -28.875, -18.279 values for dicamba and MCPA, respectively. The Freundlich isotherms implies a multilayer interaction on a heterogeneous surface with different adsorption sites.

Table S5: Isotherm parameters for dicamba and MCPA adsorption onto MIL-53(Al)

Isotherm Model	Parameter	Dicamba	MCPA
Langmuir	q_m (mg/g)	322.5	454.5
	K_L (L mg/g)	0.4	0.3
	R_L	0.1	0.1
	R^2	0.23	0.40
	R^2adj	0.04	0.20
	RMSE	0.01	0.01
	AIC	59.3	59.6
Freundlich	K_F (mg/g)	5.9	7.7
	n	1.1	0.7
	R^2	0.97	0.96
	R^2adj	0.95	0.95
	RMSE	0.07	0.19
	AIC	-28.8	-18.2
Temkin	A (mg/g)	8.8	3.5
	bT (kJ mol^{-1})	110.6	113.3
	R^2	0.71	0.74
	R^2adj	0.63	0.68
	RMSE	48.16	46.48
	AIC	48.1	47.6

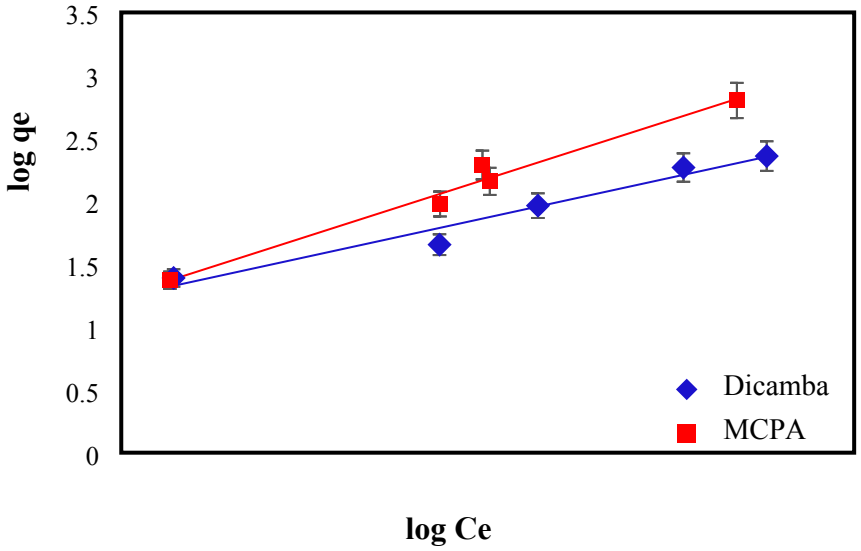


Fig. S4: Freundlich isotherms for the removal of (a) dicamba and (b) MCPA
(Dosage: 0.01 g/L; 40°C; equilibrium time: 25 min**;** rpm: 150)

Thermodynamic studies

The thermodynamics values obtained are summarised in Table S6. The increase in temperature can impact on the pore capacity of the adsorbent as well as facilitate the number of cavity bubbles formed in the liquid bulk for easy dispersion. The ΔG° show negative values that indicate the spontaneous nature of the adoption process. The values obtained for ΔH° are positive (ΔH° =55.57 and 49.12 KJ mol^{-1}) suggested that the adsorption of dicamba and MCPA on MIL-53(Al) follows an endothermic process. This depict an increased randomness at the liquid-solid interface during the adsorption process.

Table S6: Thermodynamic parameters for the adsorption of dicamba and MCPA onto MIL-53(Al)

	Dicamba			**MCPA**		
Temp (K)	ΔG°(KJ mol^{-1})	ΔH°(KJ mol^{-1})	ΔS°(KJ mol^{-1} K^{-1})	ΔG°(KJ/ mol^{-1})	ΔH°(KJ/ mol^{-1})	ΔS°(J /mol^{-1} K^{-1})
298	-51.5	55.5	172.6	-38.5	49.1	129.1
303	-52.3			-39.1		
308	-53.2			-39.8		
313	-54.1			-40.4		
318	-54.9			-41.1		
323	-55.8			-41.7		

References

1 Z. U. Zango, N. S. Sambudi, K. Jumbri, N. Hana, H. Abu, N. Ain, F. Abdullah, E. M. Negim and B. Saad, *Chem. Eng. Sci.*, 2020, **66**, 115608.

2 N. Delgado, A. Capparelli, A. Navarro and D. Marino, *J. Environ. Manage.*, 2019, **236**, 301–308.

3 Z. U. Zango, K. Jumbri, N. S. Sambudi, N. H. Hanif Abu Bakar, N. A. Fathihah Abdullah, C. Basheer and B. Saad, *RSC Adv.*, 2019, **9**, 41490–41501.