Supporting Information

Functionalization of *Shorea faguetian* Biochar using Fe_2O_3 Nanoparticles and MXene for Rapid Removal of Methyl Blue and Lead from both Single and Binary Systems

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2.1. Chemicals used for this work

MAX phase powder (Ti3AlC2; Jilin Technology Co.Ltd), Hydroflouric acid (HF; 40 wt%), and Ferric Chloride salt were obtained from Merk chemical Lahore, Pakistan. Anhydrous Ferric chloride salt, methyl blue, and Ammonia solution (NH_3) were obtained from Sigma Aldrich chemical Lahore, Pakistan, and *Shorea faguetian* branches were purchased from the native market of Lahore. The botanist at the Minhaj University Lahore (department of botany) certified the *Shorea faguetian.*

2.3. Characterizations

The X-Ray (XRD) diffractograms were acquired by Rigaku TTRAX III (Cu Kα radiation). The Fourier transform infrared (FTIR) was determined using Tensor27 (Bruker, Germany) to analyze the variation of a functional group on the adsorbent's surface. The morphological feature and elemental composition of the composite were determined using a transmission electron microscope (Hitachi S3400N, Japan), scanning electron microscope (JEOL 6500F, Japan), and EDS (TM-3000 Hitachi). The distribution and valance of elements in composites were determined by X-ray photoelectron spectroscopy (ESCALAB 250, USA). The textural features of composites were determined by N2 adsorption-desorption via Quanta chrome Autosorb 1 gas analyzer. The pore volume ($cm^2\ g^{-1}$) and surface area ($m2\ g^{-1}$) of Fe_2O_3/BC/MXene composites were investigated via Brunauer-Emmett-Teller (BET) and Barret-Joyner-Hallenda (BJH) approaches, respectively. By using a vibrating sample magnetometer, the adsorbent's magnetic hysteresis loop was calculated (VSM).

2.4. Adsorption experiment

Adsorption investigation was conducted in a 250 mL flask. A total of 0.2 g of Fe_2O_3/BC/MXene adsorbent was dissolved in 200 mL of lead and MB solutions unless otherwise defined, and the resulting mixture was stirred in a rotating shaker at 200 pm. The pH of the reaction mixture was 2.0-11. The sorption investigations were performed at temperatures 293, 303, and 313 K. The lead and MB concentrations were 50-750 (mg/L), and the adsorption time was 1 -50 min. The sorption capability and rate of lead and MB removal were determined utilizing equations 1 and 2.

$$q_{e=}\left(\frac{C_O-C_e}{M}\right)V \qquad \text{* MERGEFORMAT (1)}$$

$$R=\left(\frac{C_O-C_e}{C_e}\right)\times 100 \qquad \text{* MERGEFORMAT (2)}$$

Among them, q_e represents adsorption capability in mg g^{-1}, C_o represents lead initial lead (II) and MB concentrations earlier than adsorption, R represents the remaining elimination rate (%), M represents the molecular mass of composite, and V represents the molar volume of lead (II) and solution in mL.

2.5. Isothermal study

The isotherm data were derived to determine the sorption capability of lead and MB using composite. The experimental pieces of information were separately subjected to investigation via Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich models. Here, the Langmuir and Freundlich isotherms, respectively, were employed to identify the monolayer and multilayer sorption[12]. Langmuir isotherm equation is expressed below as in eq 3

$$q_e = \frac{q_{\max} K_L C_e}{1+K_L C_e} \qquad \backslash* \text{ MERGEFORMAT (3)}$$

Here, q_e (mg g^{-1}) denotes the metal and dye sorption capability state of equilibrium, C_e denotes the pb^{2+} ions and MB dosage at equilibrium (mg/L),q_{max} denotes the single-layered sorption capability (mg/g), and K_L denotes the Langmuir rate constant (L mg^{-1}).

Freundlich isotherm equation is expressed below as in eq 4.

$$q_e = K_F C_e^{\frac{1}{n}} \qquad \backslash* \text{ MERGEFORMAT (4)}$$

Here, q_e /KF (mg/g) denotes the metal sorption capability at equilibrium, C_e denotes the Pb^{+2} ions and MB dye dosage at equilibrium (mg/L) and represents the Freundlich rate constant.

The Temkin model was utilized to measure the relationship between adsorbate and adsorbent[3]. The determination and calculation of Temkin parameters are exhibited by equation 6.

$$q_e = q_S \exp\left(-B_{\varepsilon}{}^2\right) \qquad \text{* MERGEFORMAT (5)}$$

$$q_e = \frac{RT}{b} \ln\left(AC_e\right) \qquad \text{* MERGEFORMAT (6)}$$

Among them, A (L mol^{-1}) denotes the equilibrium constant associated with the highest binding energy, R (J/mol K^{-1}) denotes the gas constant, T represents the sorption temperature (K), and b represents the Temkin isotherm coefficient.

2.6. Kinetics analysis

The Kinetics of adsorption of lead and MB on the Fe_2O_3/BC/MXene composite were explored in this work. The lead and MB concentrations were determined at 10, 20, 30, 40, and 50 min. The sorption rate (%) was guage via pseudo-first-order (PFO), pseudo-second-order reaction (PSO), and intra-particle diffusion (IPD), Elovich, and Bangham diffusion model defined as in eq 7, 8, 9. 10, and 11, respectively.

PFO:

$$q_e = \left(q_e - q_t\right) = \ln q_e - K_1 t \qquad \text{* MERGEFORMAT (7)}$$

PSO:

$$q_e = \frac{t}{q_e} + \frac{1}{K_2 q_t^2} \qquad \text{* MERGEFORMAT (8)}$$

IPD

$$q_e = K_3 t^{0.5} + C \quad \text{* MERGEFORMAT (9)}$$

Elovich

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \quad \text{* MERGEFORMAT (10)}$$

Bangham diffusion model

$$\log\log\left(\frac{C_t}{C_t - q_t M}\right) = \log\left(\frac{K_j M}{2.303V}\right) + \alpha \log t \quad \text{* MERGEFORMAT (11)}$$

Among them, qt denotes sorption equilibrium (mg g^{-1}) at any time, and t (min) denotes sorption time. α denotes chemical sorption rate in mg g^{-1} min^{-1} and β represents the degree of surface area covered and activation energy in (g mg^{-1}). M expresses the concentration of the sorbent (g/L), and V defines the volume in mL. K_1, K_2, and K_3 denote the PFO, PSO, and ID kinetics rate constants, respectively. The Kj constants can be calculated by extracting them from the intercept and slope of the fitting plot. C denotes the constant which is connected to the thickness of the available boundary layers.

2.8. Thermodynamic study

Each parameter of thermodynamic sorption, such as standard entropy (ΔS; $KJmol^{-1}$), Gibbs free energy (ΔG; $KJmol^{-1}$), and standard enthalpy (ΔH; $KJmol^{-1}$), was determined via

$$K_d = \frac{q_e}{C_e} \quad \text{* MERGEFORMAT (12)}$$

$$\ln K_d = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad \text{* MERGEFORMAT (13)}$$

$$\Delta G = \Delta H + T\Delta S \quad \text{* MERGEFORMAT (14)}$$

Among them, K_d denotes the thermodynamic coefficient, and T denotes sorption temperature (K).

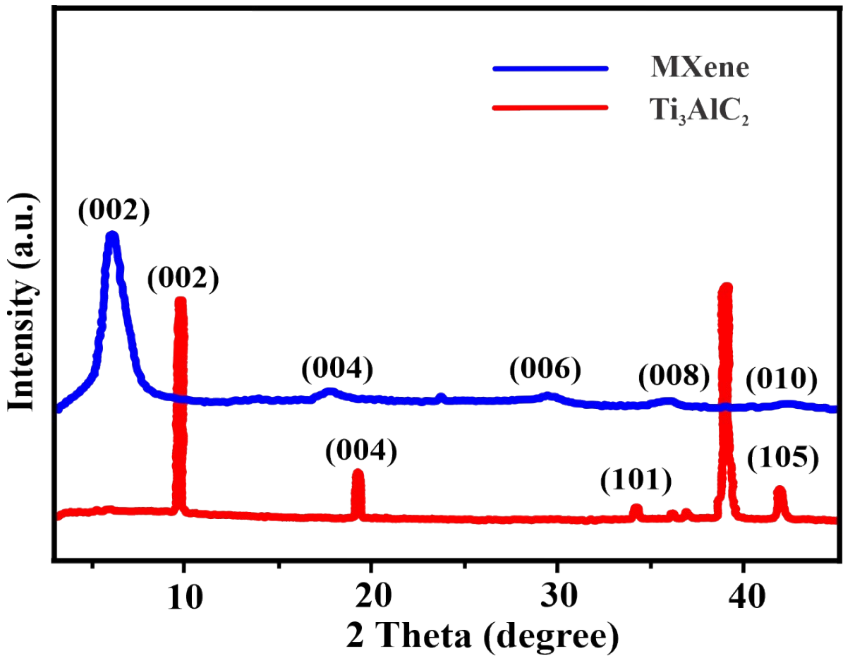


Fig. S1: XRD spectrum of MXene and Ti_3AlC_2 phase

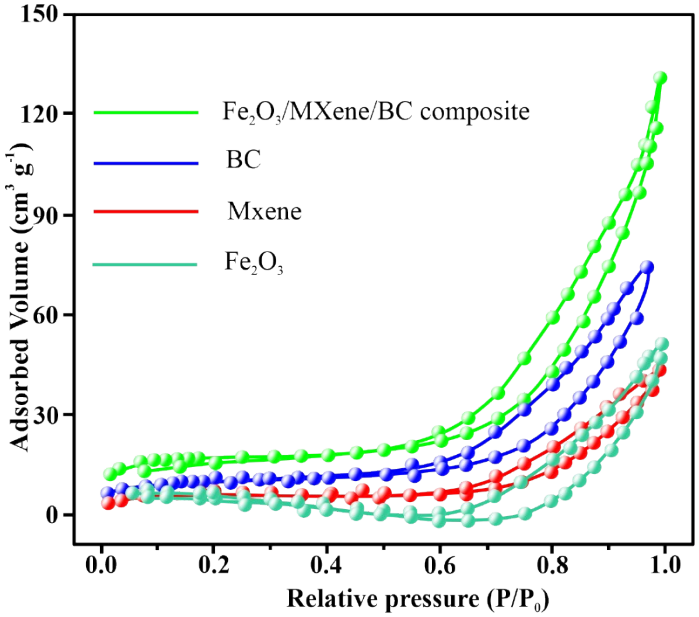


Figure.S2: N_2 adsorption/desorption isotherms of Fe_2O_3/BC/MXene, BC, MXene, and Fe_3O_4

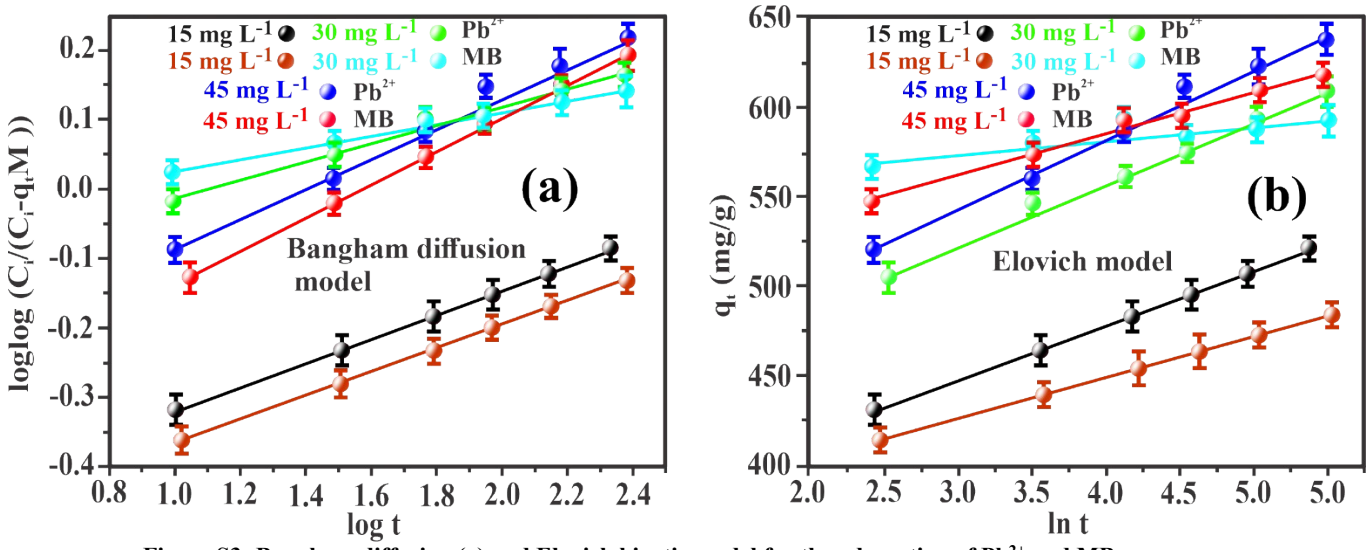


Figure.S3: Bangham diffusion (a) and Elovich kinetic model for the adsorption of Pb^{2+} and MB.

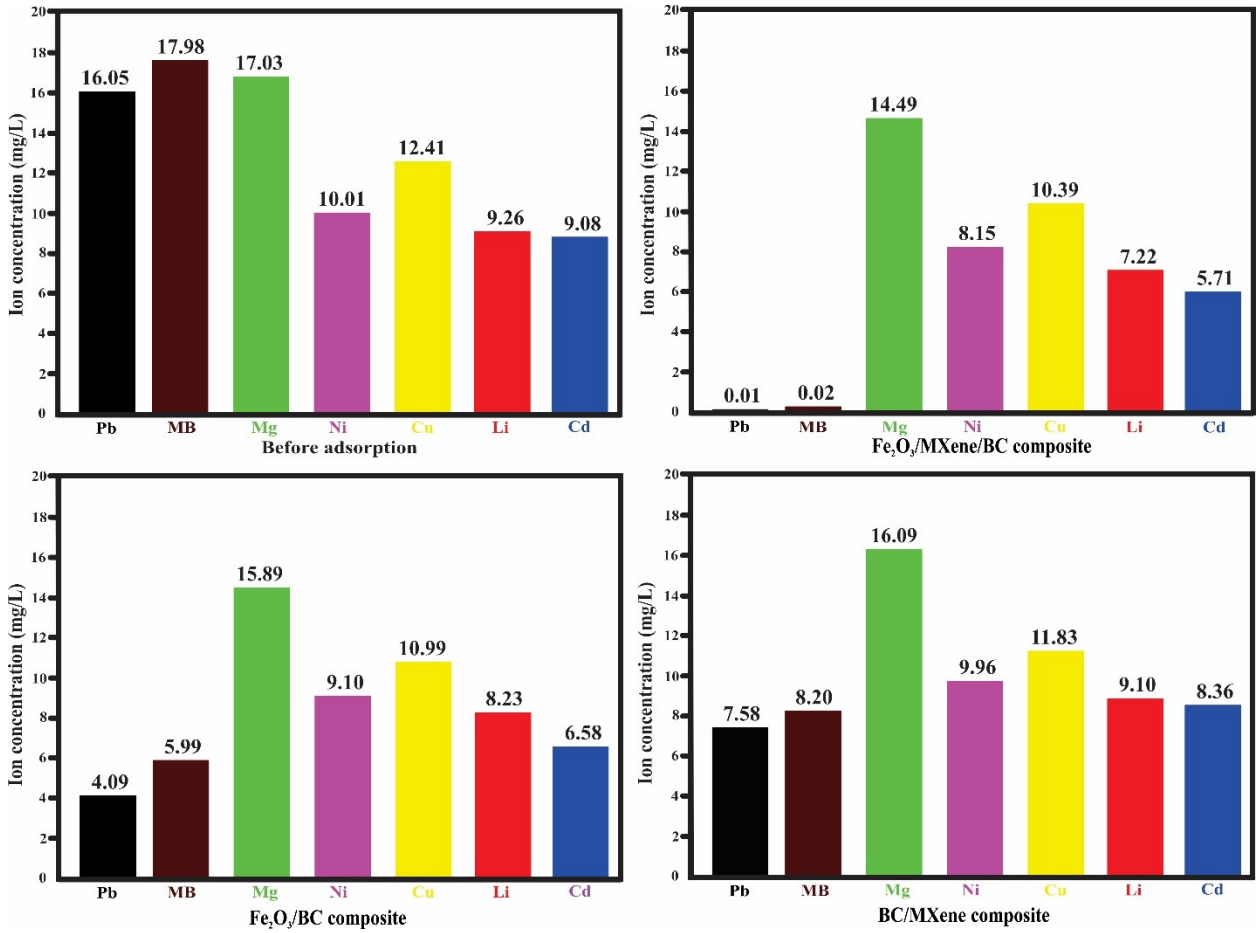
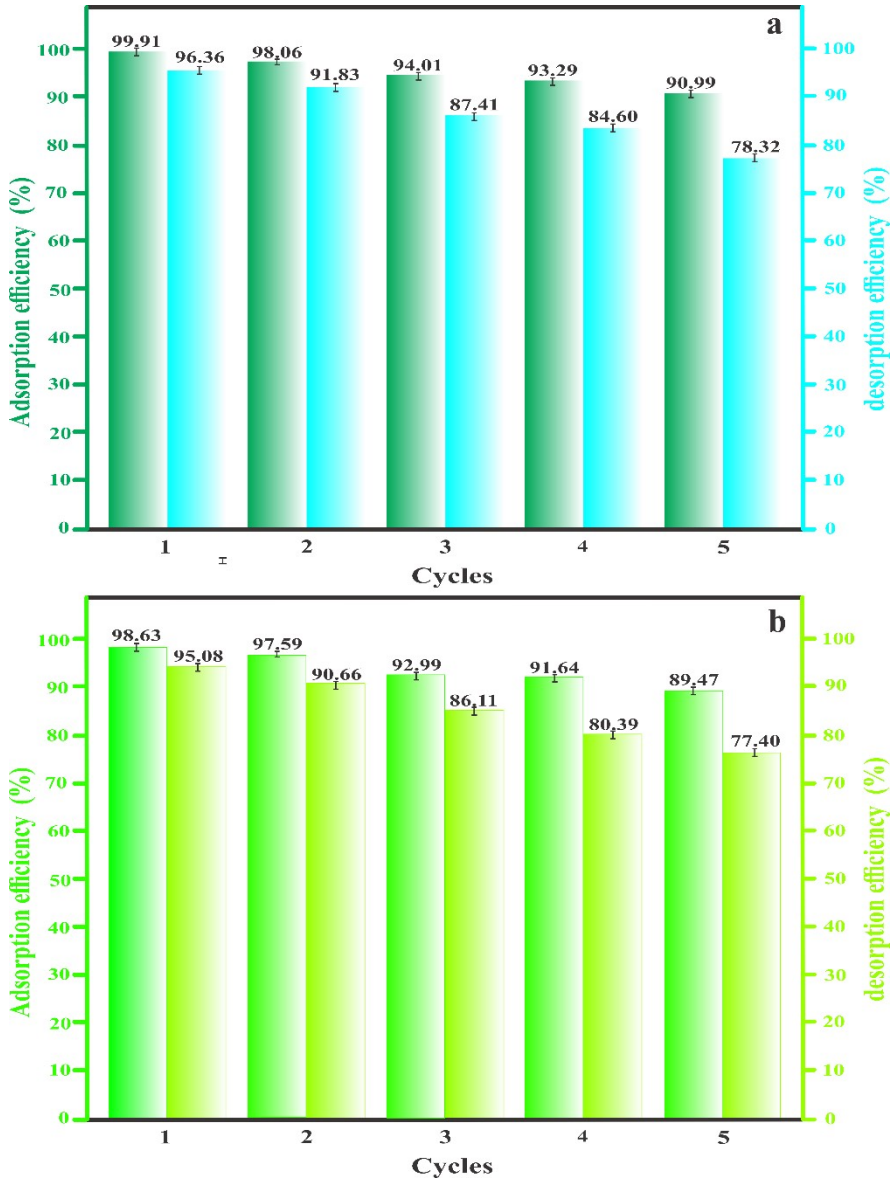


Figure.S4: Selectivity of Pb^{2+} and MB adsorption before adsorption (a), on Fe_2O_3/BC/MXene (b), BC/Fe_2O_3 (c), and BC/MXene (d)



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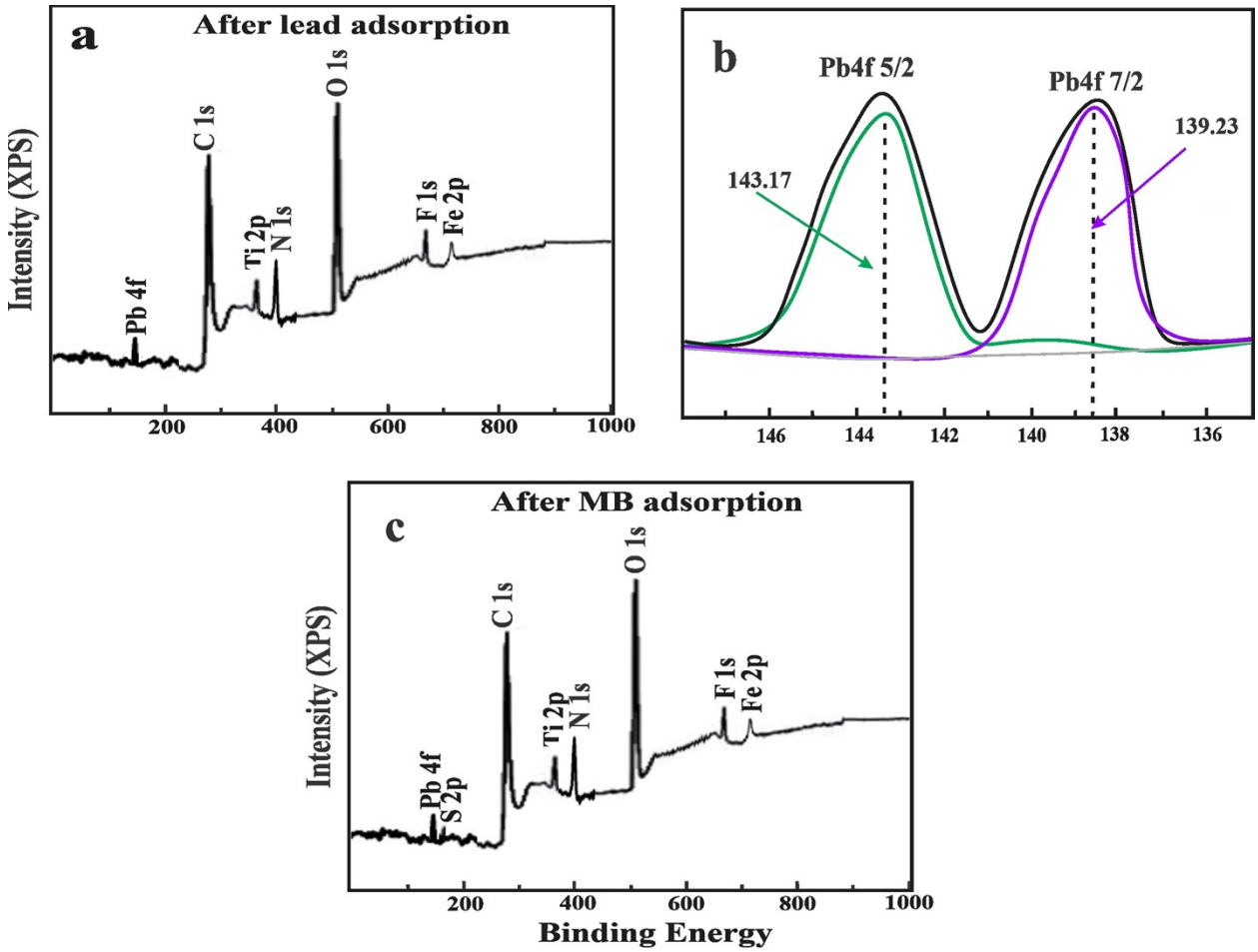
115 **Figure.S5: Reusability of Fe_2O_3/BC/MXene composite for sorption of Pb^{2+} (a) and MB (b)**



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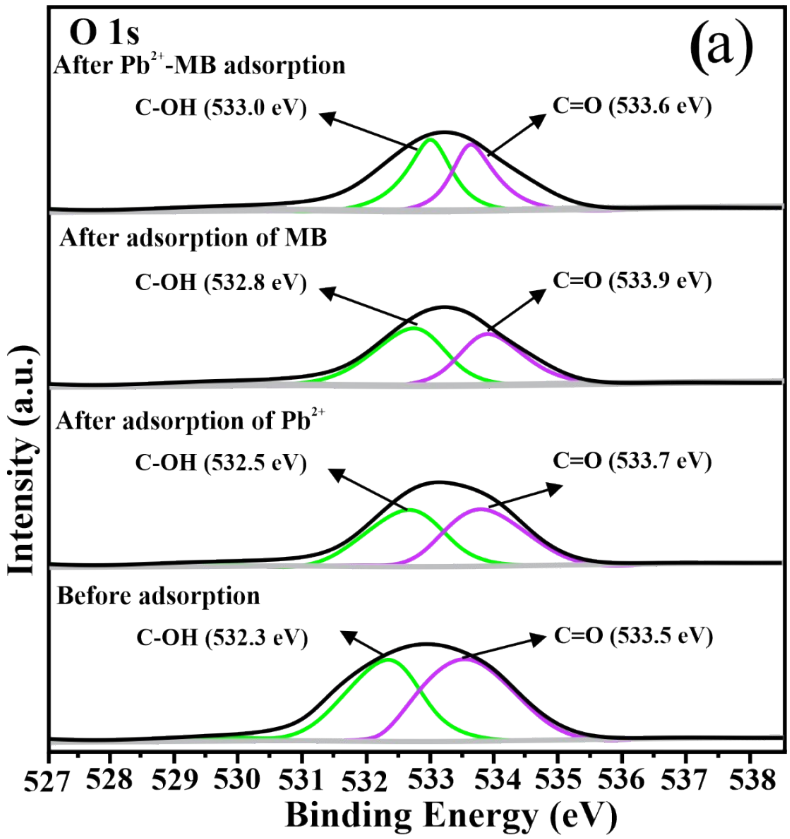
117 **Figure.S6: XPS survey patterns of Fe_2O_3/BC/MXene composite after adsorption of lead (a-b) and MB (c)**


O 1s
(a)
After Pb2+-MB adsorption
C-OH (533.0 eV)
C=O (533.6 eV)
After adsorption of MB
C-OH (532.8 eV)
C=O (533.9 eV)
After adsorption of Pb2+
C-OH (532.5 eV)
C=O (533.7 eV)
Before adsorption
C-OH (532.3 eV)
C=O (533.5 eV)
Intensity (a.u.)
527 528 529 530 531 532 533 534 535 536 537 538
Binding Energy (eV)

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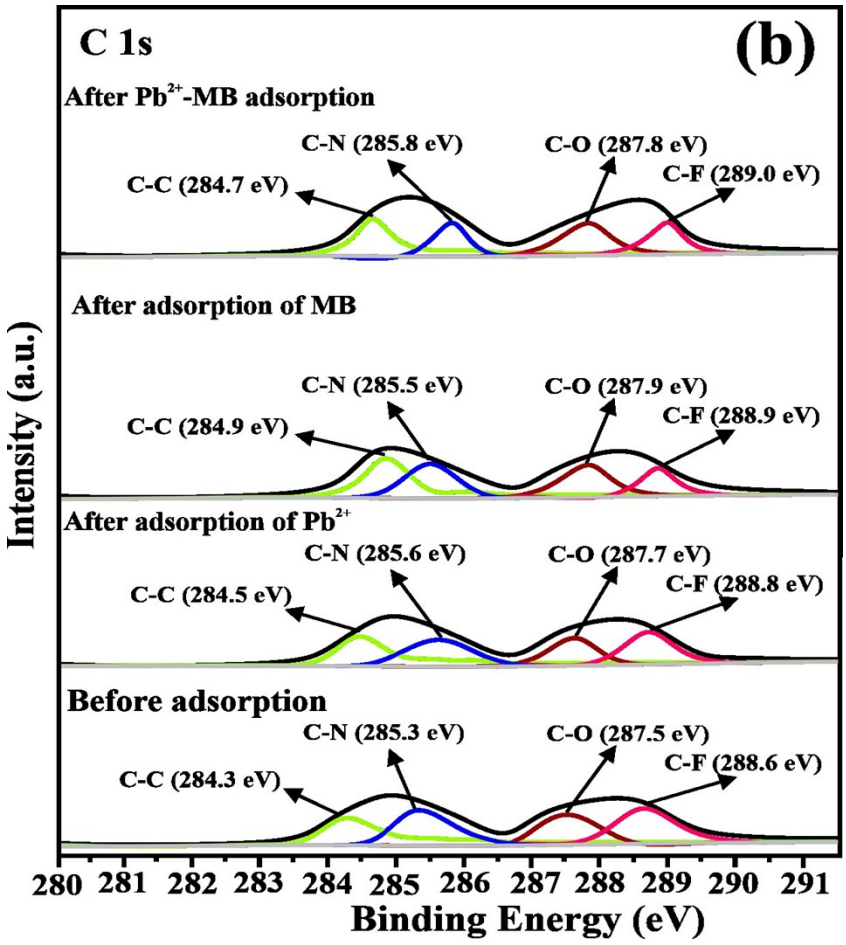
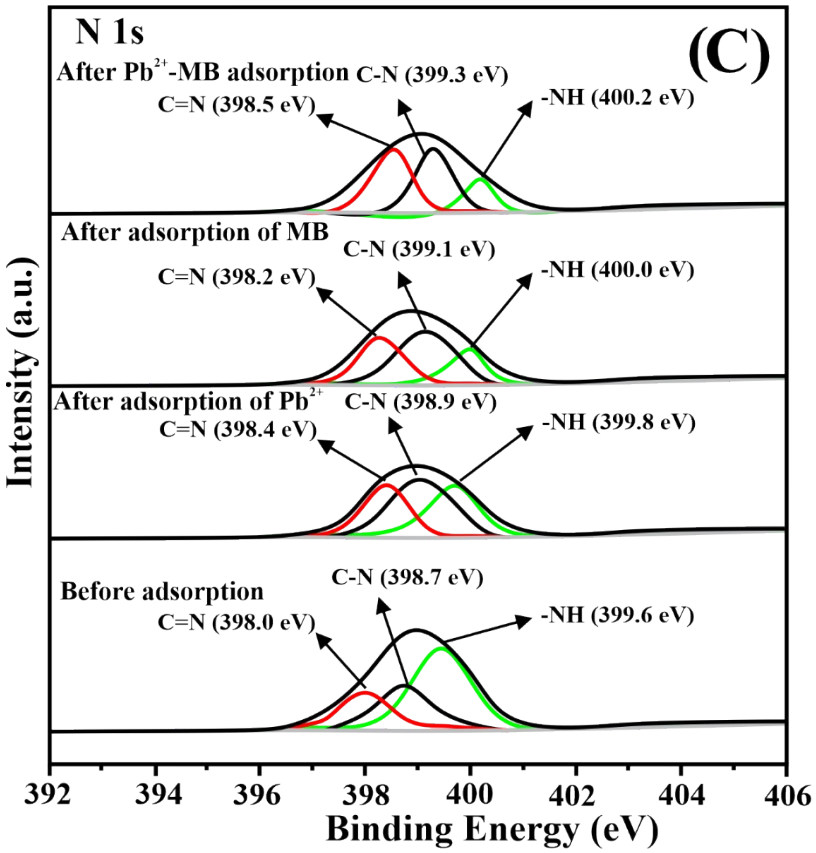

C 1s
(b)
After Pb2+-MB adsorption
C-N (285.8 eV)
C-O (287.8 eV)
C-C (284.7 eV)
C-F (289.0 eV)
After adsorption of MB
C-N (285.5 eV)
C-O (287.9 eV)
C-C (284.9 eV)
C-F (288.9 eV)
After adsorption of Pb2+
C-N (285.6 eV)
C-O (287.7 eV)
C-C (284.5 eV)
C-F (288.8 eV)
Before adsorption
C-N (285.3 eV)
C-O (287.5 eV)
C-C (284.3 eV)
C-F (288.6 eV)
Intensity (a.u.)
280 281 282 283 284 285 286 287 288 289 290 291
Binding Energy (eV)

119



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121 **Figure.S7: O 1 s XPS spectra before adsorption and after adsorption of Pb^{2+}, MB, and Pb^{2+}-MB (a). C 1 s XPS spectra**
122 **before adsorption and after adsorption of Pb^{2+}, MB, and Pb^{2+}-MB (b). N 1 s XPS spectra before adsorption and after**
123 **adsorption of Pb^{2+}, MB, and Pb^{2+}-MB (c).**

124 **Table.S1: PFO, PSO, Elovich, and Bangham kinetic models' parameters**

Kinetic models used	Lead concentrations (mg L^{-1})	Variables or Parameters				
		$\ln(q_e-q_t)$	K_1	R^2	$\chi 2$	SSE
Lead (II)						
PFO	15	0.237	0.935	0.8950	4.768	8.587
	30	7.905	1.035	0.9326	9.250	16.025
	45	8.091	1.650	0.8791	15.255	22.291

MB						
PFO	15	0.203	0.713	0.8521	2.396	3.985
	30	4.369	0.906	0.9183	6.575	8.577
	45	8.091	1.650	0.8791	13.951	15.368
Lead (II)						
PSO	15	181.088	0.999	1.000	0.425	0.789
	30	179.631	0.073	0.999	0.634	0.923
	45	66.476	0.059	0.999	0.991	0.992
MB						
PSO	15	180.233	0.917	0.997	0.163	0.130
	30	153.891	0.063	0.993	0.149	0.228
	45	47.568	0.031	0.993	0.173	0.421
Lead (II)						
Elovich		**β_{El}**	**α_{El}**	**R^2**	**$\chi 2$**	**SSE**
	15	0.1327	1.831×10^{28}	0.996	9.816	10.990
	30	0.0635	4.608×10^{9}	0.980	26.558	14.584
	45	0.0356	$2.9\ 7\times 10^{5}$	0.926	44.002	59.287
MB						

Elovich		**β_{El}**	**α_{El}**	**R^2**	**$\chi 2$**	**SSE**
	15	0.1067	1.531×10^{25}	0.981	8.367	10.058
	30	0.0425	3.256 × 107	0.973	24.458	35.583
	45	0.0219	1.95 × 104	0.918	21.781	31.177
Lead (II)						
Bangham		**K_j**	**α**	**R^2**	**$\chi 2$**	**SSE**
	15	523.65	0.0739	0.969	7.905	11.208
	30	613.51	0.3215	0.921	28.318	39.986
	45	640.83	0.0751	0.955	55.258	68.828
MB						
Bangham	15	460.39	0.0522	0.952	5.571	8.890
	30	593.85	0.2293	0.939	19.507	22.515
	45	624.47	0.0425	0.946	25.879	31.025

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126 **Table .S2: The fitting parameters of IPD**

Adsorbent cons (mg L^{-1})	**R^2**	**C (mg/g)**	**K (mg/g-$min^{0.5}$)**
Lead (II)			

	$1R^2$	$2R^2$	$3R^2$	C_1	C_2	C_3	K_1	K_2	K_3
15 mg L^{-1}	1.0	0.81	0.76	9.65	8.67	7.36	0.39	0.27	0.22
30 mg L^{-1}	1.0	0.96	0.61	15.32	9.90	8.06	0.35	0.19	0.15
45 mg L^{-1}	1.0	0.98	0.59	16.43	10.76	9.62	0.29	0.14	0.07
MB									
15 mg L^{-1}	1.0	0.79	0.70	8.19	7.39	5.03	0.37	0.30	0.24
30 mg L^{-1}	1.0	0.93	0.57	13.61	11.31	8.61	0.36	0.15	0.13
45 mg L^{-1}	1.0	0.96	0.49	14.90	10.69	6.62	0.29	0.11	0.09

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128 **Table.S3: Adsorption isotherm parameters of $Pb^{2+}$and MBadsorption time on Fe_2O_3/BC/Mxene**

Isothermal model	**Para meters**	**293 K**	**303 K**	**313K**
Lead (II)				
Langmuir	$q_{m\,exp}$ (mg g^{-1})	1003	625	325
	$q_{m\,cal}$ (mg g^{-1})	992.76	623.37	319.06
	K_L	0.065	0.041	0.033
	R^2	0.999	0.997	0.995
	$\chi 2$	1.18	2.07	4.62
	SSE	3.06	4.25	5.51
MB				
Langmuir	$q_{m\,exp}$ (mg g^{-1})	995	565	300

	$q_{m\ cal}$ (mg g^{-1})	899.03	562.91	296.88
	K_L	0.055	0.036	0.017
	R^2	0.998	0.996	0.993
	$\chi 2$	2.72	3.68	6.90
	SSE	4.81	6.37	8.02
Lead (II)				
Freundlich				
	$K_{F\ exp}$ (mg g^{-1})	820	626	419
	$K_{F\ cal}$ (mg g^{-1})	809.41	600.05	401.99
	n	3.68	3.39	3.27
	R^2	0.853	0.846	0.839
	$\chi 2$	7.27	13.00	25.68
	SSE	10.21	19.68	31.01
MB				
Freundlich				
	$K_{F\ exp}$ (mg g^{-1})	805	515	320
	$K_{F\ cal}$ (mg g^{-1})	791.74	507.61	311.54
	n	3.55	3.31	2.99
	R^2	0.816	0.879	0.799
	$\chi 2$	11.62	15.85	39.25

	SSE	14.33	21.84	45.39
Lead (II)				
Temkin				
	K_T	783.09	608.58	497.69
	B	0.856	0.456	0.409
	R^2	0.975	0.859	0.921
	$\chi 2$	19.56	27.35	44.28
	SSE	33.45	56.24	70.69
MB				
Temkin				
	K_T	701.04	553.18	398.99
	B	0.789	0.398	0.307
	R^2	0.935	0.813	0.889
	$\chi 2$	25.17	38.69	51.28
	SSE	33.45	56.24	70.69

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130 **Table.S4: Thermodynamic parameters of $Pb^{2+}$and MB adsorption on Fe_2O_3/BC/MXene**

Temperature (K)	**ΔG(KJ mol^{-1})**	**ΔH(KJ $mol^{-1}K^{-1}$)**	**ΔS(K mol^{-1})**
Lead (II)			
393 K	-8.362	-39.319	-0.110

303 K	-5.395		
313 K	-3.287		
MB			
393 K	-6.929	-25.179	-0.103
303 K	4.081		
313 K	-2.731		

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132 **Table.S5: Selectivity parameters of $Pb^{2+}$and MB adsorption on Fe_2O_3/BC/MXene, BC/Fe_2O_3 (c), and BC/MXene**

	Fe_2O_3/BC/MXene composite		**BC/F_e2O_3.**		**BC/MXene**	
Heavy metals ion	**K_d(mL g^{-1})**	**K**	**K_d(mL g^{-1})**	**K**	**K_d(mL g^{-1})**	**K**
Pb (II)	19303.88	-	743.50	-	355.89	-
MB	16976.03	-	556.81	-	237.59	-
Mg (II)	80.43	230.8	80.39	11.28	32.02	54.80
Ni(I)	298.6	51.01	389.87	3.99	177.15	89.63
Cu (II)	3.75	6127.85	40.62	19.36	23.50	75.38
Cd (II)	176.09	100.21	7.52	141.73	85.38	133.90
Li (I)	19.51	985.67	41.52	23.63	102.61	3.63

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134 **References**

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