

Electronic supplementary information

Fe₃O₄-Decorated MXene for Effective Removal of ¹³³Ba and ¹³⁷Cs: Synthesis, Characterization, and Optimization via Response Surface Methodology (RSM)

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S1. Experimental

All the chemicals used in the synthesis of MXene, Fe_3O_4 , MXene- Fe_3O_4 composite and adsorption studies are of analytical grade and used as such without further purification. Barium chloride (BaCl_2 , 99.90%, M: 208.23 g/mol), cesium chloride (CsCl , 99.90%, M: 168.36 g/mol), were purchased from Merck. Radiotracer concentration was as follows: ^{133}Ba in the form of [^{133}Ba] BaCl_2 (Eurostandard CZ s.r.o., Czech Republic) with a volume activity of 2 MBq/mL and ^{137}Cs in the form of [^{137}Cs] CsCl (National Centre for Nuclear Research, Poland) with a volume activity of 55 MBq/mL.

S1.1 Synthesis of Fe_3O_4

1.3254 g of ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, AcrosOrganics, 99+ %) was stirred on magnetic stirrer in 20 mL distilled water till complete dissolution. Then 5.6 g of sodium hydroxide (NaOH , Merck, >97.0 %) in 40 mL distilled water was slowly added to this solution with vigorous stirring. The reaction mixture colour change took place within 1-2 minutes, from yellow to black with exothermic reaction, and then left to stir for 15 minutes at room temperature before its transfer to a 90 mL capacity hydrothermal autoclave reactor vessel for hydrothermal reaction at 180 °C for 12 h. After cooling down, the obtained product was washed several times with distilled water until neutral pH and dried at 60 °C.

S1.2 Synthesis of MXene

The preparation of MXene was carried out by acid-salt etching route wherein 2.94 g of ammonium fluoride (NH_4F , Merck, >98.0 %) in 20 mL hydrochloric acid (HCl , Merck, 37.0-38.0 %) was sonicated for 15 minutes, then 0.5 g of titanium aluminum carbide (Ti_3AlC_2 , Merck, >90.0 %) commercial powder (40 μm mesh size) was added slowly within 30 minutes, to avoid explosive reaction with evolution of H_2 gas. The reaction mixture kept on a magnetic

stirrer for 48 h at 25 °C, and the solution was decanted followed by ultrasonication of the reaction product in 2M HCl for 15 minutes to remove extra impurities. The obtained product was washed with distilled water until pH 6 attained and then dried using vacuum assisted filtration system.

S1.3 Synthesis of $Ti_3C_2T_x-Fe_3O_4$ (MXF-30)

To prepare this, 2.0 g of sodium acetate (CH_3COONa , Thermo Fisher scientific, 99.0 %), 0.75 g of polyethylene glycol (PEG, Fisher scientific) and stoichiometric ratio of MXene and Fe_3O_4 were added to 60 mL ethylene glycol ($C_2H_6O_2$, Fisher Scientific) as solvent in autoclave reactor. Afterwards, entire reaction mixture was ultrasonicated for 30 minutes and then subjected to solvothermal conditions at 180 °C for 12 h. The obtained black color powder was washed several times with distilled water, followed by washing with absolute ethanol at the end and dried at 40 °C.

S2 Design of Experiments

The optimal conditions for the adsorption of Ba^{2+} and Cs^+ ions were determined using BBD based on RSM. The influence of process variables, namely initial pH (A), contact time (B), and radionuclide concentration (C), on adsorption was investigated through individual experimental studies conducted separately for both Ba^{2+} and Cs^+ . The response chosen for the optimization process was adsorption capacity (q). Table S1 summarizes the levels and ranges of process variables employed in the design. Eq. (1) presents the model equation, incorporating both linear and quadratic terms to estimate the optimal response.

$$y = b_0 + b_1A + b_2B + b_3C + b_{11}A^2 + b_{22}B^2 + b_{33}C^2 + b_{12}AB + b_{13}AC + b_{23}BC \quad (1)$$

In Eq. (1), y denotes the response, which is the adsorption capacity of Ba^{2+} and Cs^+ . A , B , and C represent the coded variables. The coefficients corresponding to the intercept term, linear,

quadratic, and dual interaction effects are represented as b_0 , b_1 , b_2 , b_3 , b_{11} , b_{22} , b_{33} , and b_{12} , b_{13} , b_{23} , respectively.

Table S1 Levels and ranges of independent variables used in BBD

Variable	Unit	Code	Level		
			-1 (low)	0 (center)	+1 (high)
Initial pH	-	A	3	5.5	8
Contact time	min	B	30	135	240
Concentration	mol/L	C	0.0001	0.05005	0.1

With the utilization of Design-Expert 13, a total of 17 experiments were designed and randomly conducted separately for Ba^{2+} and Cs^{+} . Afterwards, the acquired data underwent statistical, regression, and graphical analysis. Analysis of variance (ANOVA) was used as a diagnostic tool to assess the effectiveness of the proposed model.

S3 Adsorption studies

Adsorption of ^{133}Ba and ^{137}Cs radioisotopes on MXF-30 was investigated using a radioisotope indication method. The experimental runs were conducted using a batch method under aerobic conditions at room temperature. The influence of initial pH, initial concentration and contact time parameters on the adsorption was analysed as follows: 5 mL of the aqueous phase (containing radiotracer ^{133}Ba and ^{137}Cs), was added to 25 mg of MXF-30 (5.0 g/L). Subsequently, the mixture was agitated using a rotary laboratory mixer. Following sorption, the suspension was centrifuged at 8000 rpm for 15 minutes and an aliquot of each resulting supernatant was then collected and analysed using a Modumatic model gamma spectrometer fitted with a NaI (TI) detector. Isotherm studies were conducted using a solution of Ba^{2+} and

Cs⁺ (containing radiotracer ¹³³Ba and ¹³⁷Cs), respectively, with an initial concentration ranging from 1x10⁻⁴ to 1x10⁻¹ mol/L and 5.0 g/L of MXF-30. For Ba²⁺, the initial pH and contact time were maintained at 8.0 and 135 min, respectively. For Cs⁺, the initial pH was set at 5.5, and the contact time was also 135 min. Selectivity study and effect of coexisting ions has been carried out in the presence of Ba²⁺ and Cs⁺ ions (containing radiotracer ¹³³Ba and ¹³⁷Cs), at pH 5.5 and 8.0. Similar conditions were used for determining the effect of coexisting ions (Na⁺, K⁺, Ca²⁺, Co²⁺, and Mg²⁺) on the adsorption capacities of MXF-30. In coexisting ions study, a concentration of 5x10⁻² mol/L was used for each of the added ions (Na⁺, K⁺, Ca²⁺, Co²⁺, Mg²⁺, Ba²⁺, Cs⁺) by employing 5.0 g/L of MXF-30, (containing radiotracer ¹³³Ba and ¹³⁷Cs).

In regeneration studies, adsorption experiments were performed by using 5x10⁻² mol/L concentration of Ba²⁺ and Cs⁺ ions (containing radiotracer ¹³³Ba and ¹³⁷Cs), under optimal conditions at natural pH, while desorption experiments were conducted by employing ultrasonication conditions for 30 minutes at room temperature, using 1.0 M HCl solution as eluent.

The XPS analyses of the samples obtained after Ba²⁺ and Cs⁺ adsorption was accomplished under non-radioactive conditions.

The Eqs. (2-5), provided below were employed for the calculation of equilibrium concentration (C_{eq}), distribution coefficient (K_d), and adsorption capacity (q) and selectivity coefficient (β).

Equilibrium concentration (C_{eq})

$$C_{eq} = \frac{C_0 \times a}{a_0} \quad (\text{mol/L})$$

(2)

Distribution coefficient (K_d)

$$K_d = \frac{(a_0 - a)}{a} \times \frac{V}{m} \text{ (mL/g)} \quad (3)$$

Adsorption capacity (q)

$$q = K_d \times C_{eq} \text{ (mmol/g)} \quad (4)$$

Selectivity coefficient (β)

$$\beta_{1,2} = \frac{K_{d1}}{K_{d2}} \quad (5)$$

In the above Eqs. (2-5), C_0 is the initial concentration of the solute in aqueous phase (mol/L), C_{eq} is the equilibrium concentration of the solute in aqueous phase (mol/L), V is the volume of the aqueous phase (mL), m is the mass of sorbent (g), a_0 is the initial volume activity of solution (B_q/mL), a is the equilibrium volume activity of solution (B_q/mL), and K_d is the distribution coefficient (mL/g).

S4 Characterization

The purity of powder samples was estimated by using a PANalytical X-ray diffractometer equipped with CuK_α radiation and 2θ ranging from 3-70°. Morphological and structural studies was examined using scanning electron microscopy-energy dispersive spectroscopy (SEM/EDS, Tescan Lyra III) EDS, transmission electron microscopy (TEM, using JEOL JEM ARM 200 cF) including high resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) patterns. The Fourier-transform infrared spectroscopy- attenuated total reflectance (FTIR-ATR) instrument (Bruker, Tensor 27) was used to acquire spectra in the range of 650-4000 cm⁻¹. Qualitative and quantitative chemical analysis at the surface of the samples before and after adsorption studies was performed using X-ray photoelectron spectroscopy (XPS, Omicron multiprobe system) equipped with

hemispherical mirror analyzers and monochromatic Al K_{α} radiation. The surface area measurements were recorded using BET (Brunauer-Emmet-Teller) method in the range of relative pressure $p/p_0 = 0,05-0,25$ on Sorptomatic 1990 SERIES, ThermoFinnigan, Milan, Italie, with the N_2 adsorption at $T = 77.1$ K.

Table S2 ANOVA for Ba^{2+} adsorption onto MXF-30

<i>ANOVA</i>						
Source	Sum of squares	Degrees of Freedom	Mean square	F Value	P Value	R^2
Model	5.890E+05	9	65439.80	125.05	< 0.0001	0.99
A-pH	1326.75	1	1326.75	2.54	0.1553	
B-Contact time	6203.00	1	6203.00	11.85	0.0108	
C-Concentration	5.623E+05	1	5.623E+05	1074.51	< 0.0001	
AB	751.86	1	751.86	1.44	0.2697	
AC	18.90	1	18.90	0.0361	0.8547	
BC	978.92	1	978.92	1.87	0.2137	
A ²	477.19	1	477.19	0.9119	0.3714	
B ²	940.71	1	940.71	1.80	0.2219	
C ²	15087.17	1	15087.17	28.83	0.0010	
Lack of fit	2135.57	3	711.86	1.86	0.2764	

Table S3 ANOVA for Cs⁺ adsorption onto MXF-30

<i>ANOVA</i>						
Source	Sum of squares	Degrees of Freedom	Mean square	F Value	P Value	R ²
Model	1.163E+06	9	1.292E+05	48.91	< 0.0001	0.98
A-pH	1835.40	1	1835.40	0.6950	0.4320	
B-Contact time	63254.42	1	63254.42	23.95	0.0018	
C-Concentration	9.619E+05	1	9,619E+05	364.24	< 0.0001	
AB	603.80	1	603.80	0.2286	0.6471	
AC	479.30	1	479.30	0.1815	0.6829	
BC	13364.70	1	13364.70	5.06	0.0592	
A ²	38703.16	1	38703.16	14.66	0.0065	
B ²	37322.32	1	37322.32	14.13	0.0071	
C ²	32356.38	1	32356.38	12.25	0.0100	
Lack of fit	13162.85	3	4387.62	3.30	0.1396	

Table S4. Kinetic parameters for adsorption of Ba²⁺ and Cs⁺ on MXF-30 obtained by applying pseudo first order, pseudo second order and intraparticle diffusion models.

	Pseudo first order			Pseudo second order			Intraparticle diffusion		
	k_1 (1/min)	q_e (mmol/g)	R^2	k_2 (g/mmol min)	q_e (mmol/g)	R^2	Ki (mmol/gmin ^{1/2})	C (mmol/g)	R^2
Ba²⁺	0.018	0.857	0.961	1.1 x 10 ⁻¹	2.664	0.999	0.042	1.955	0.972
Cs⁺	0,032	4.501	0.927	1.2 x 10 ⁻²	4.403	0.995	0.144	2.066	0.834

Table S5 Literature comparison of MXene materials in removal of metal cations

Compositions	Ions	Synthesis method	Removal capacity	Ref
1D/2D hybrid MXene/AgNW composite	I ⁻ Cs ⁺	Conventional stirring of MXene with AgNW	84.70 for I ⁻ and 26.22 for Cs ⁺ mg/g in 240 min	1
PBMX-III spheres	Cs ⁺	Ultrasonication of MXene with Prussian blue sphere, followed by freeze drying to prepare aerogels	315.91 mg/g for Cs ⁺	2
Ti ₃ C ₂ T _x /POSS-NH ₂	Cs ⁺	Refluxing of MXene and POSS-NH ₂ in THF	148 mg/g at pH 7	3
Ti ₃ C ₂ T _x and Alk - Ti ₃ C ₂ T _x	Ba ²⁺	Ti ₃ C ₂ T _x using HF etching method, Alk-Ti ₃ C ₂ T _x - Immersing in 5% NaOH followed by washing and drying at RT/48 h	46.46 mg/g (three times higher than pristine Ti ₃ C ₂ T _x)	4
Ti ₃ C ₂ T _x	Ba ²⁺ Cs ⁺	Using acid + salt etching (HCl+NH ₄ F)	154.9 and 121.5 mg/g for ¹³³ Ba and ¹³⁷ Cs	5
MXF-30	Ba ²⁺ Cs ⁺	Solvothermal method by employing MXene and Fe ₃ O ₄ nanoparticles	573.8 (4.18 mmol/g) and 843.3 mg/g (6.34 mmol/g) for ¹³³ Ba and ¹³⁷ Cs	This work

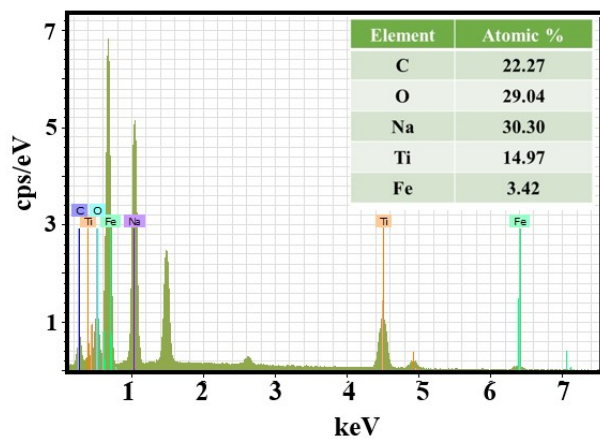


Fig. S1 SEM-EDS analysis of MXF-30.

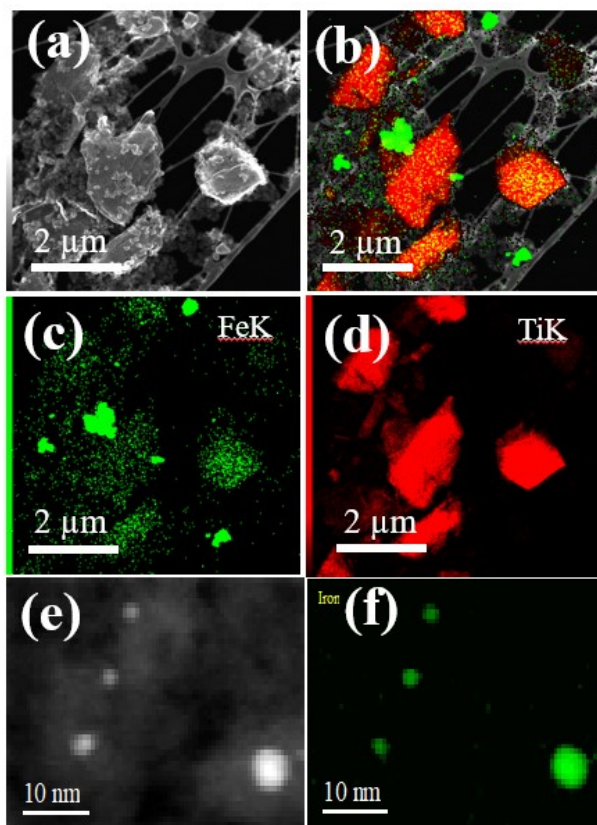


Fig. S2 (a) SEI STEM image of MXF-30 and its relevant EDS mapping of (c) Fe K and (d) Ti K. (b) overlay of FeK and TiK maps. (e) ADF STEM image of Fe_3O_4 nanoparticles (bright) in MXF-30 sample. (f) EELS STEM map of $\text{FeL}_{3,2}$ -edge.

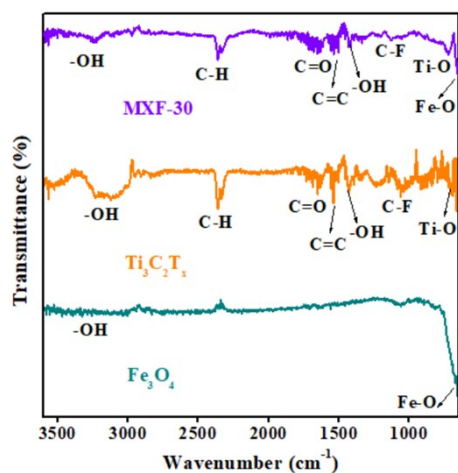


Fig. S3 FTIR spectra of Fe_3O_4 , $\text{Ti}_3\text{C}_2\text{T}_x$ and MXF-30.

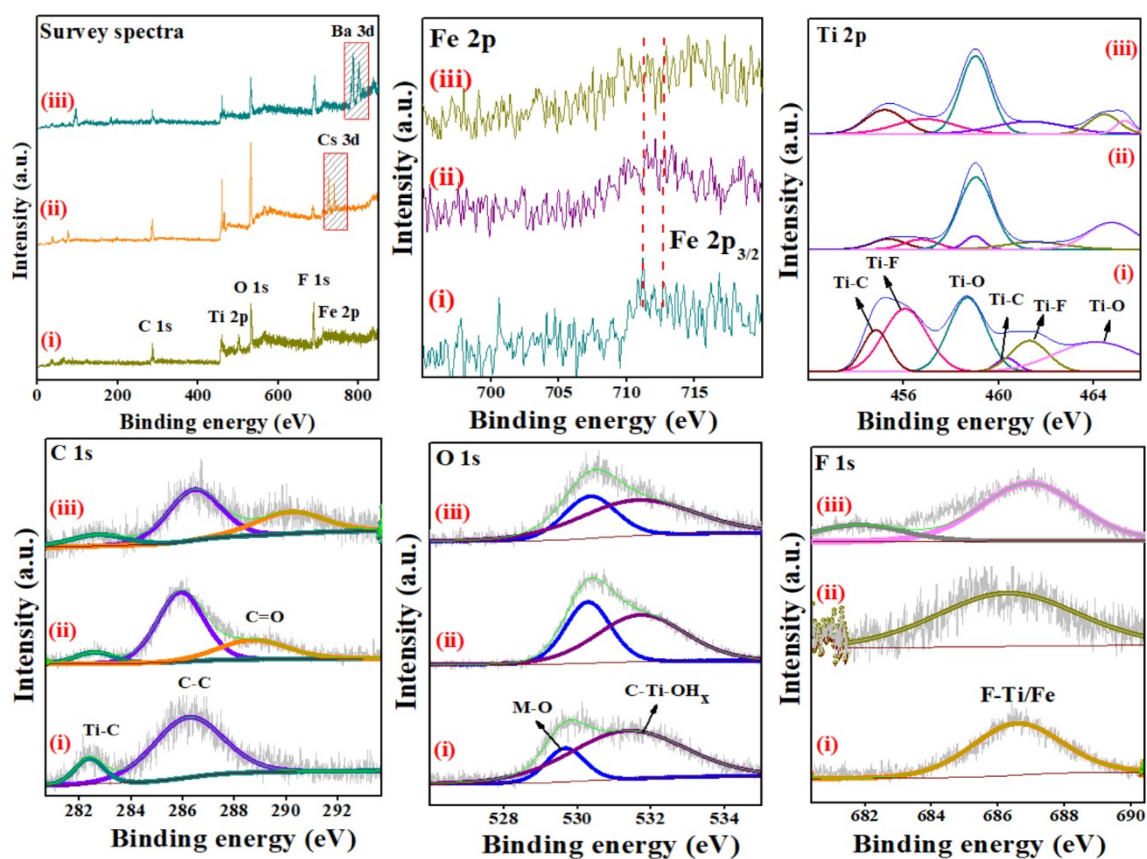


Fig. S4 XPS survey and high-resolution spectra of Fe 2p, Ti 2p, C 1s, O 1s and F 1s for (i) MXF-30, (ii)MXF-30-Ba and (iii) MXF-30-Cs.

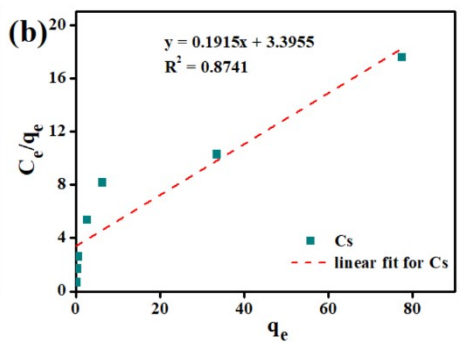
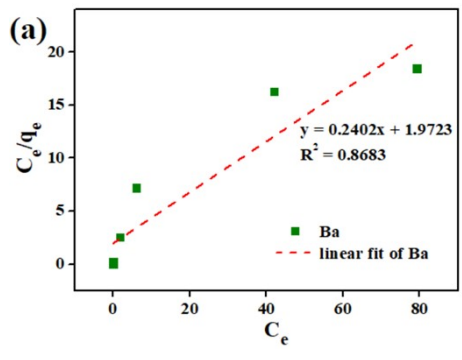


Fig. S5 Langmuir adsorption isotherm for Ba²⁺ and Cs⁺ adsorption.

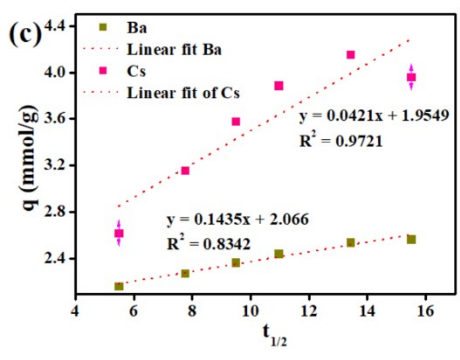
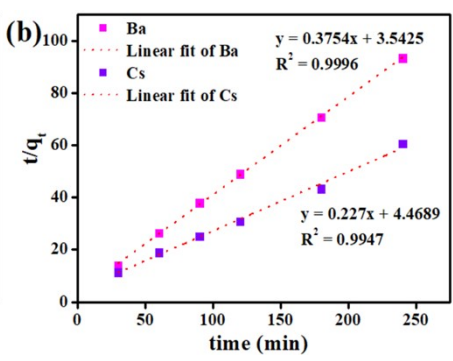
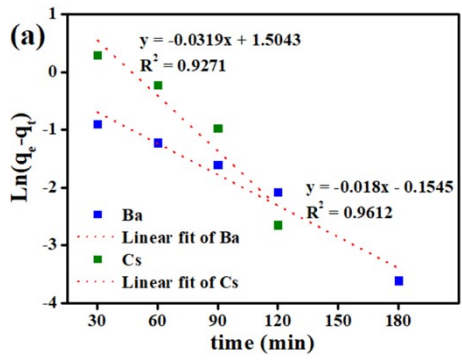


Fig. S6 Kinetic models for Ba^{2+} and Cs^+ removal (a) pseudo first order model (b) pseudo second order model (c) intraparticle diffusion model.

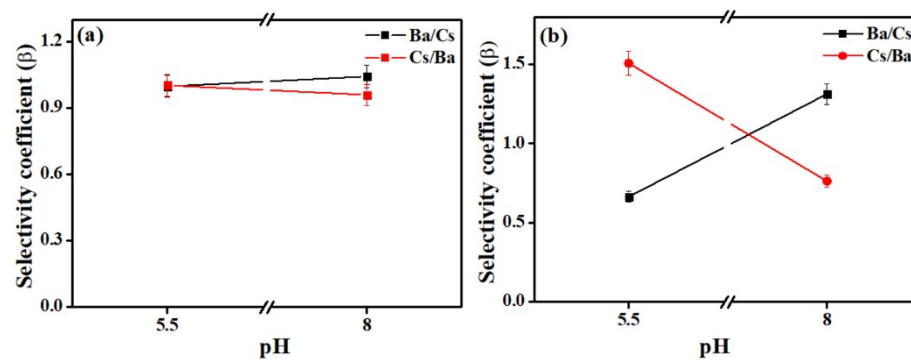


Fig. S7 Selectivity coefficient (β) values in (a) binary solutions (b) complex ion solutions.

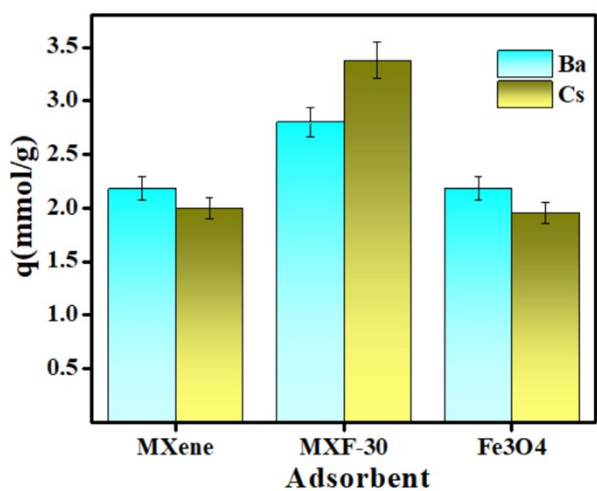


Fig. S8 Adsorption performance of $Ti_3C_2T_x$, Fe_3O_4 and MXF-30 in removal of Ba^{2+} and Cs^+ at pH 8.0 and pH 5.5.

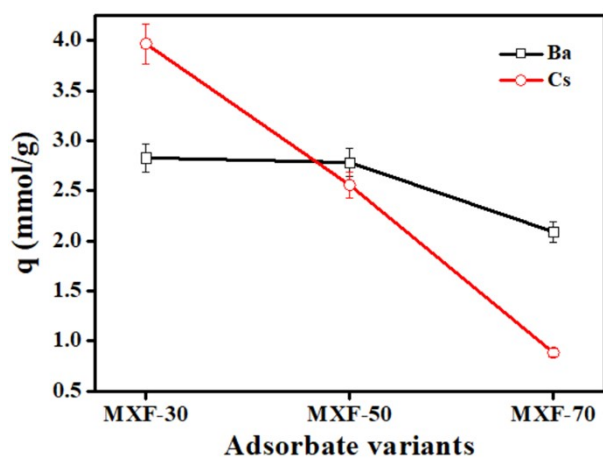


Fig. S9 Adsorption performance of MXF-30, MXF-50 and MXF-70 in removal of Ba^{2+} and Cs^+ at natural pH of water.

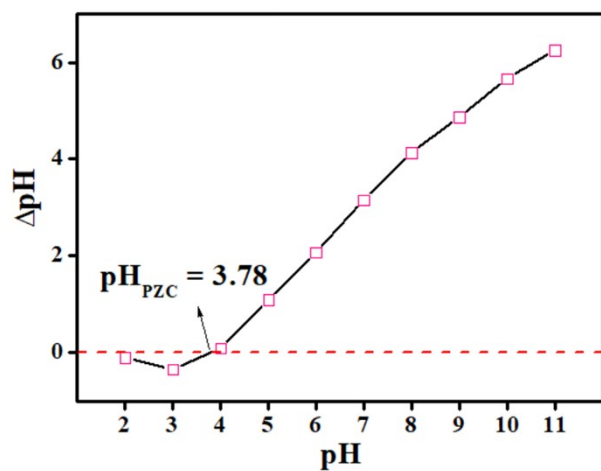


Fig. S10 Assessment of pH of zero-point charge (pH_{PZC}) of MXF-30 using the drift method.

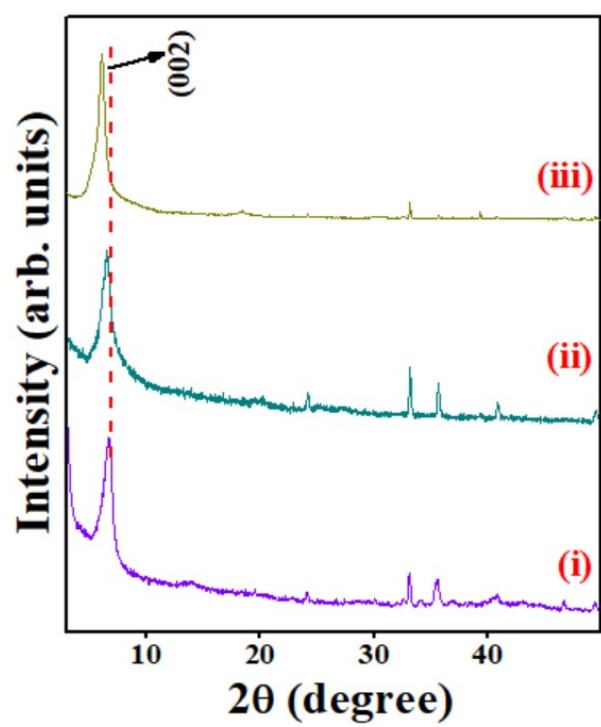


Fig. S11 PXRD patterns for the (i) MXF-30, (ii)MXF-30-Ba and (iii) MXF-30-Cs.

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