Electronic Supplementary Information (ESI)

Green synthesis of a novel water-stable Sn(II)-TMA metal-organic framework (MOF): Efficient adsorbent for fluoride in the aqueous medium in the wide pH range

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Materials and Methods

Synthesis of Sn(II)-TMA MOF

1.2 mmol metal salt stannous chloride dihydrate ($SnCl_2.2H_2O$) was dissolved in 10 ml ethanol. Organic ligand solution was prepared by dissolving 0.6 mmol trimesic acid (TMA) in 10 ml ethanol under vortexing and sonicated for 10 minutes. The stannous salt solution was added dropwise to the ligand solution under constant stirring. The resultant solution was transferred to a 25 ml Teflon-lined stainless-steel autoclave and sealed. The autoclave was heated at 120 °C for 24 h in a hot air oven. After cooling down to room temperature, the yellowish-white powder precipitate was washed thoroughly with ethanol (two times) and acetone (three times) under centrifugation at 7000 rpm for 3 minutes. The final product was dried in a hot air oven at 80 °C for 3 h and kept in a tightly sealed glass vial for further characterization.

Material Characterization

The successful synthesis of Sn(II)-TMA MOF was confirmed using FT-IR (PerkinElmer Spectrum 2) and Powder X-ray diffractometer (Rigaku, Micromax-007HF). Before FT-IR analysis, the sample was grounded in a mortar pestle with KBr (1:100) and compressed in a hydraulic press for 1 min at 10 MPa to make small disc. The infrared spectrum was recorded from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1}. The PXRD pattern was recorded at a diffraction angle (2θ) ranging from 5° to 70° at a step size of 0.03°. N_2 adsorption-desorption experiment was performed at 77 K using Surface area analyzer (Quantachrome, Autosorb-IQ MP) to determine the surface area, total pore volume and pore size distribution of the synthesized material. The material was degassed at 120 °C for 6 h under vacuum before surface area analysis. The surface morphology was studied using Field Emission Scanning Electron Microscope (Zeiss, Sigma). The sample was double gold-coated under vacuum, and FESEM micrographs were captured at 20 kV, 130 eV. Netzsch (STA449F3A00) TGA analyzer was used to obtain the thermal stability data (25 °C to 800 °C) of the sample. The zeta potential of the material was analyzed using Malvern Nano ZS90 Zetasizer (Malvern, UK), while the fluoride concentration was determined with Metrohm ion meter (Basic IC 792, Switzerland) equipped with Metrosep A Supp5 (4.0 x 250 mm) anion exchange column packed with polymethacrylate with quaternary ammonium groups as stationary phase.

Aqueous stability testing

20 mg of the synthesized material was suspended in 10 ml of water and left undisturbed at room temperature for 10 days. After exposure to an aqueous solution, the material was recovered through filtration and dried at 80 ºC. To ensure that a portion of the material was not dissolved in the aqueous solution the final mass of the material was noted and via Eq. (1) the percentage of the recovered material was calculated.

$$\frac{mass_{\text{recovered}}}{mass_{\text{initial}}}\times 100 = yield\% \qquad (1)$$

After confirming the mass balance, the identity of the recovered material was verified with the pristine material using powder XRD and FT-IR.

Adsorption experiments

The effect of adsorbent dose on fluoride removal efficiency was determined by varying different doses of Sn(II)-TMA adsorbent in 12 mg L^{-1} fluoride solution (10 ml) in a 50 ml centrifuge tube. The adsorbent-adsorbate mixture was shaken in an orbital shaker at 250 rpm for 4 h at 298 K. The supernatant was collected after centrifugation at 8000 rpm for 3 min and further syringed filtered with 0.22 µm cut-off nylon membrane. The filtrate was analyzed for fluoride concentration with

Metrohm ion meter. The eluent was prepared using a mixture of 1 mM L^{-1} $NaHCO_3$ and 3.2 mM L^{-1} Na_2CO_3 in deionized water, and the flow rate was maintained at 0.7 ml min^{-1} at 10 MPa column pressure. IC Multi-element standard for anion analysis was purchased from Merck, India. The fluoride adsorption capacity was calculated using Eq. (2):

$$q_e = \frac{(C_o - C_e)V}{m} \tag{2}$$

where C_o and C_e are the initial and equilibrium fluoride concentration (mg L^{-1}), respectively, V is the volume of the fluoride solution and m the mass of the Sn(II)-TMA MOF.

The fluoride adsorption kinetics was investigated at 298 K with 12 mg L^{-1} initial fluoride concentration. After a specified time interval (15-300 min) an appropriate volume of sample was collected and filtered with 0.22 µm filter paper for fluoride determination.

Adsorption isotherm study was conducted with the different initial concentrations of fluoride (5-150 mg L^{-1}) at 298 K. The effect of coexisting anions (50 mg L^{-1} each) and ionic strength of solution on the fluoride removal efficiency was also investigated.

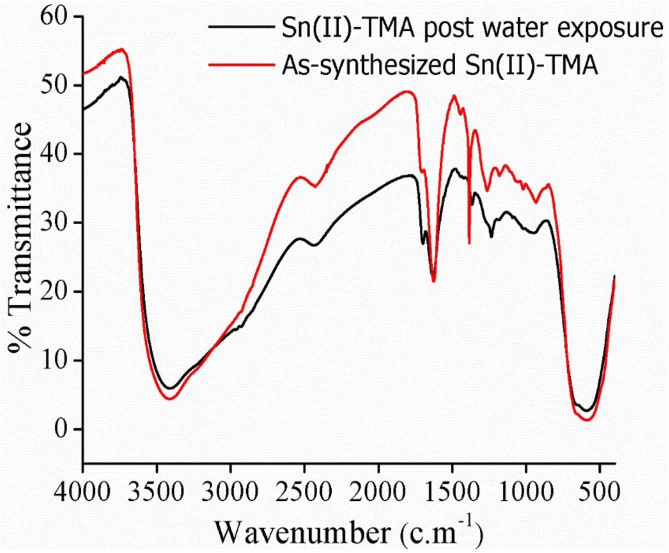

Figure S1. FTIR spectrum of Sn(II)-TMA MOF pre and post water exposure.

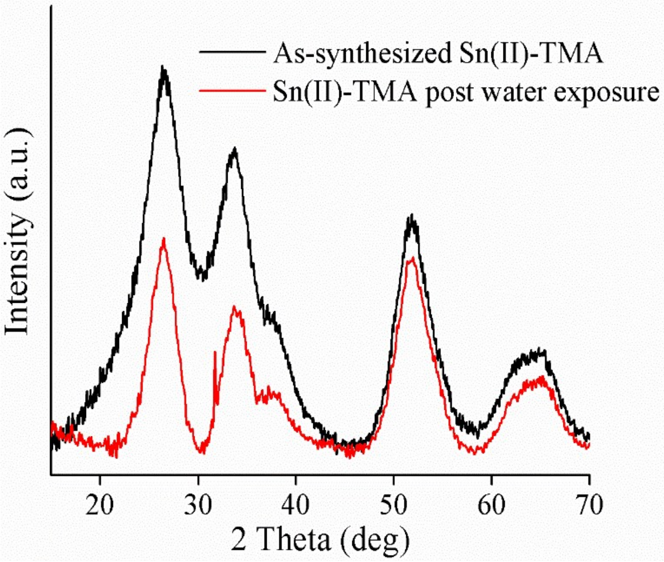

Figure S2. PXRD pattern of Sn(II)-TMA MOF pre and post water exposure.

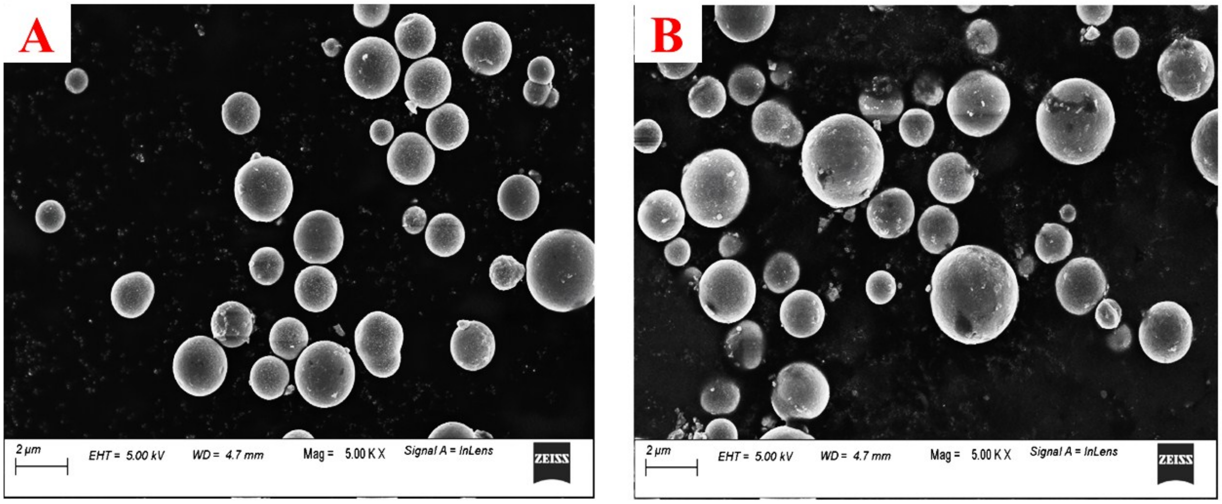

Figure S3. FESEM image of (A) as-synthesized Sn(II)-TMA MOF, and (B) Sn(II)-TMA MOF after water exposure

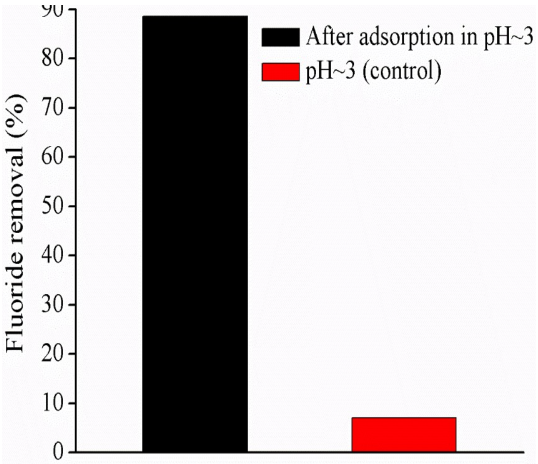

Figure S4. Fluoride removal (%) in pH~3 (control) and after adsorption with Sn(II)-TMA MOF in pH~3 solution.

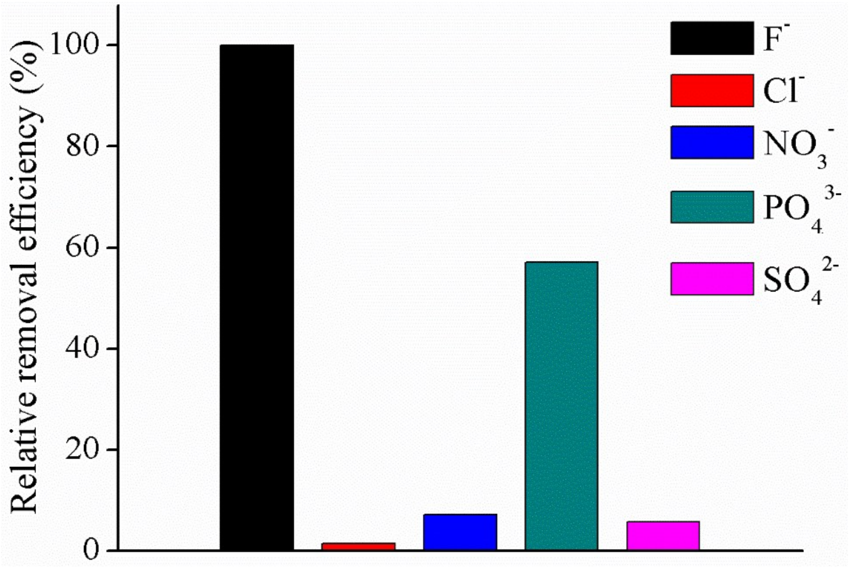

Figure S5. Preferential fluoride removal in the presence of a five-times concentration of co-existing anions (50 mg L^{-1} each) compared to fluoride concentration (10 mg L^{-1}).

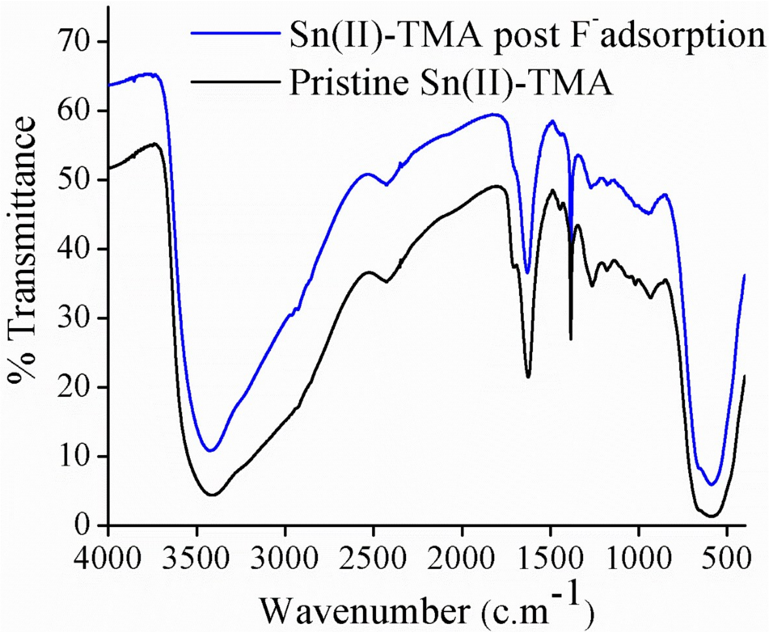

Figure S6. The FT-IR spectrum of Sn(II)-TMA MOF pre and post fluoride adsorption.

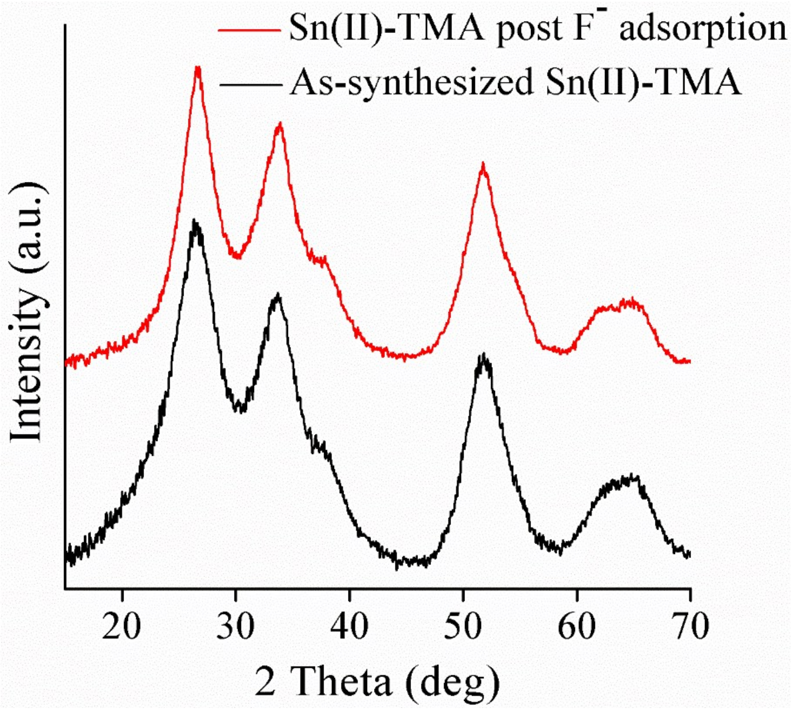

Figure S7. PXRD pattern of Sn(II)-TMA MOF pre and post fluoride adsorption.

Table S1. Calculated R_L values based on the Langmuir model at different fluoride initial concentrations (C_o)

C_o (mg L^{-1})	5	10	20	40	60	80	100	150
R_L	0.93	0.49	0.32	0.193	0.13	0.1	0.08	0.06

Table S2. Comparative adsorption capacities (Q_e) of different MOF based adsorbents for fluoride removal.

Sl No.	MOF based adsorbent	pH	T (K)	t (min)	Qe (mg g^{-1})	Reference
1	MOF-801 (Zr)	2-10	303	120	40	[1]
2	La MOF (Ce)	3-7	298	120	103.95	[2]
3	AlFu (Al)	7	303	1440	550	[3]
4	UiO-66-NH_2 (Zr)	3-7	303	30	55.70	[4]
5	UiO-66 (Zr)	7	298	360	41.5	[5]
6	UiO-66 (Zr)	6.8	303	80	41.36	[6]
7	MIL-96 (Al)	3-10	298	240	31.69	[7]
8	Sn(II)-TMA (Sn)	3-10	298	150	30.86	Present work

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