A novel core-shell bimetallic ZrAl-MOF simultaneously boosting electrostatic attraction and ion exchange to eliminate excessive fluoride

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Table S1 Fitted results by Langmuir model at different temperatures

Temperature	Parameter			Linear equation
(K)	b	q^0(mg F/g)	R^2	$\frac{c_e}{q_e} = \frac{c_e}{q^0} + \frac{1}{q^0 b}$
298k	0.4301	83.33	0.9989	Ce/qe=0.012Ce+0.0279
308k	0.1859	111.11	0.9953	Ce/qe=0.009Ce+0.04842
318k	0.2182	109. 89	0.9913	Ce/qe=0.0091Ce+0.0417

Table S2 Fitted result by Freundlich model at different temperatures

Temperature	Parameter			Linear equation
(K)	K	1/n	R^2	$lgqe = \frac{1}{n} lgCe + lgK$
298	41.59	0.175	0.8361	lgqe=0.175lgC_e+1.619
308	31.70	0.257	0.9736	lgqe=0.257lgC_e+1.501
318	42.76	0.291	0.9551	lgqe=0.219lgC_e+1.631

Table S3 Pseudo-first order and pseudo-second order kinetic models for fluoride removal

Model	k	R2
primary	-0.0703	0. 9206
secondary	0.01463	0.9994

Table S3 Comparison studies of ZrAl-MOF with reported adsorbent materials in literature.

S.no	Name of the adsorbents	Adsorption capacity (mg g-1)
1	present study	109.2
2	Alumina supported on carbon nanotubes[1]	9.6
3	Ce-TDC[2]	94.9
4	Zr-TDC[2]	97.0
5	(Ce)-UiO-66[3]	66.1
6	Zr@Fu MOF composite[4]	4.92
7	La@Fu MOF composite[4]	4.92
8	Fe@Fu MOF composite[4]	4.85
9	Ce-Al bimetallic oxide[5]	146.73
10	Ce@Fe1:1[6]	101.3
11	Ce@Al1:1[6]	99.3
12	Ce@La1:1[6]	90.9
13	UiO-66 (Hf)[7]	33.35
14	Ce-MIL-96[8]	38.65
15	Sn (II)-TMA MOFs[9]	30.86

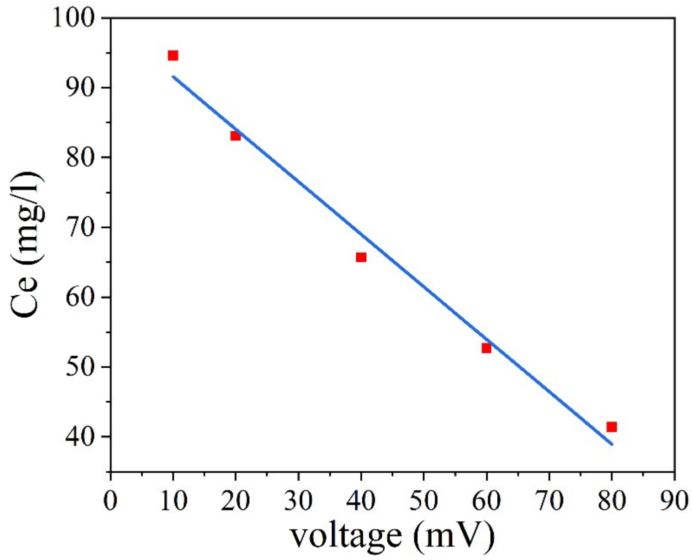

Fig.S1 Fluoride ion measurement standard curve

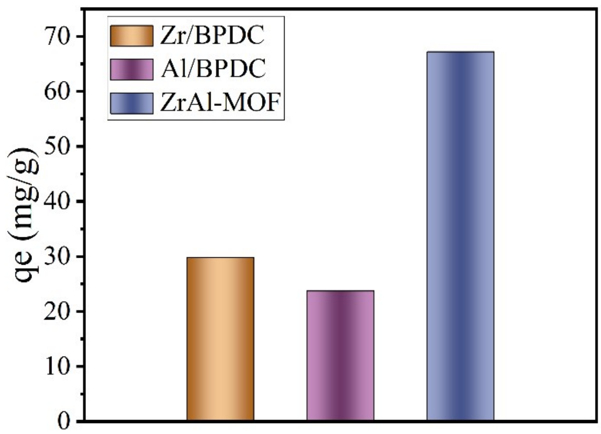

Fig.S2 Chart of Performance Comparison

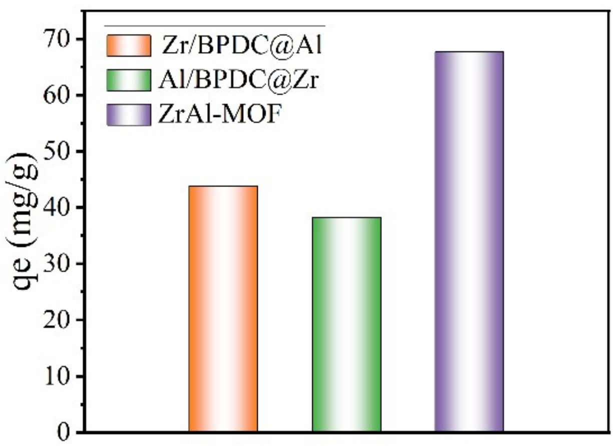

Fig.S3 Comparative performance graph of doped MOF

Validation of the optimized method

The limit of detection (LOD) and limit of quantification (LOQ) can be derived as 9.48 μg/l and

31.6 μg/l, respectively, based on the signal ratios ($3 \times {}^{SD}/_{S}$) and ($10 \times {}^{SD}/_{S}$). The results demonstrate that the method exhibits high sensitivity and reproducibility for both LOD and LOQ.[10]

Quality Assurance/Quality Control (QA/QC)

Quality assurance (QA) measures.

About the adsorbent: ZrAl-MOFs accurately measured the specific surface area and pore size distribution of the adsorbent using the nitrogen adsorption-desorption test (BET method). After several measurements and validations, the specific surface area of the selected adsorbent reached 342 m^2/g and the pore size distribution was concentrated at 3.58 nm, which provided sufficient sites and suitable channels for effective adsorption of fluoride ions. The size and shape of the adsorbent particles were analysed using a scanning electron microscope (SEM) to ensure that the particles were uniform in size and regular in shape, which is conducive to the formation of a stable adsorption environment in the adsorption device.

Fluoride ion solution: High-purity sodium fluoride (≥99%) was used as the raw material for the preparation of the fluoride ion solution, which was prepared on the basis of accurate weighing and volume adjustment.

Experimental apparatus and methods: The experimental apparatus was carefully selected to ensure that the material of the apparatus had good chemical compatibility with fluoride ions and adsorbents, the structure of the apparatus could meet the experimental requirements, and it was equipped with temperature control equipment and stirring equipment to ensure that the temperature control accuracy was within ±0.5℃.

Quality control (QC) measures

Adsorption monitoring: For static adsorption experiments, the fluoride ion concentration in the adsorbed solution was measured at preset time intervals (every 10 minutes) using the ion-selective electrode method, and the amount of adsorption was calculated based on the change in concentration.

Data processing and analysis: Repeatability was performed to assess the quality of the data. In the repeatability test, three experiments were conducted under the same conditions, and the standard deviations of the key data were calculated, which indicated that the experimental data had good repeatability.

In addition, the experimental data were compared and analysed with common theoretical models of fluoride ion adsorption (e.g. Langmuir and Freundlich isotherm models), and the experimental data were consistent with the theoretical models within a reasonable error range, which further verified the reliability of the experimental results.

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