

# Efficient Fluoride Wastewater Treatment Using Eco-Friendly Synthesized AlOOH

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## Supplementary Information

### Equation of pseudo first-order model and Langmuir isotherm model.

Equation 1 represents the pseudo-first-order kinetic equation, and Equation 2 represents the Langmuir isotherm equation.

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

$$\frac{1}{q_e} = \frac{1}{C_e K_L q_m} + \frac{1}{q_m} \quad (2)$$

Where  $q_t$  is the amount of adsorbed fluoride ion at time  $t$ .  $k_1$  is the pseudo-first-order adsorption rate constant.  $C_e$  and  $q_e$  are the fluoride ion concentration and the adsorption capacity at equilibrium, respectively.  $q_m$  is the maximum adsorption capacity.  $K_L$  is Langmuir constant.

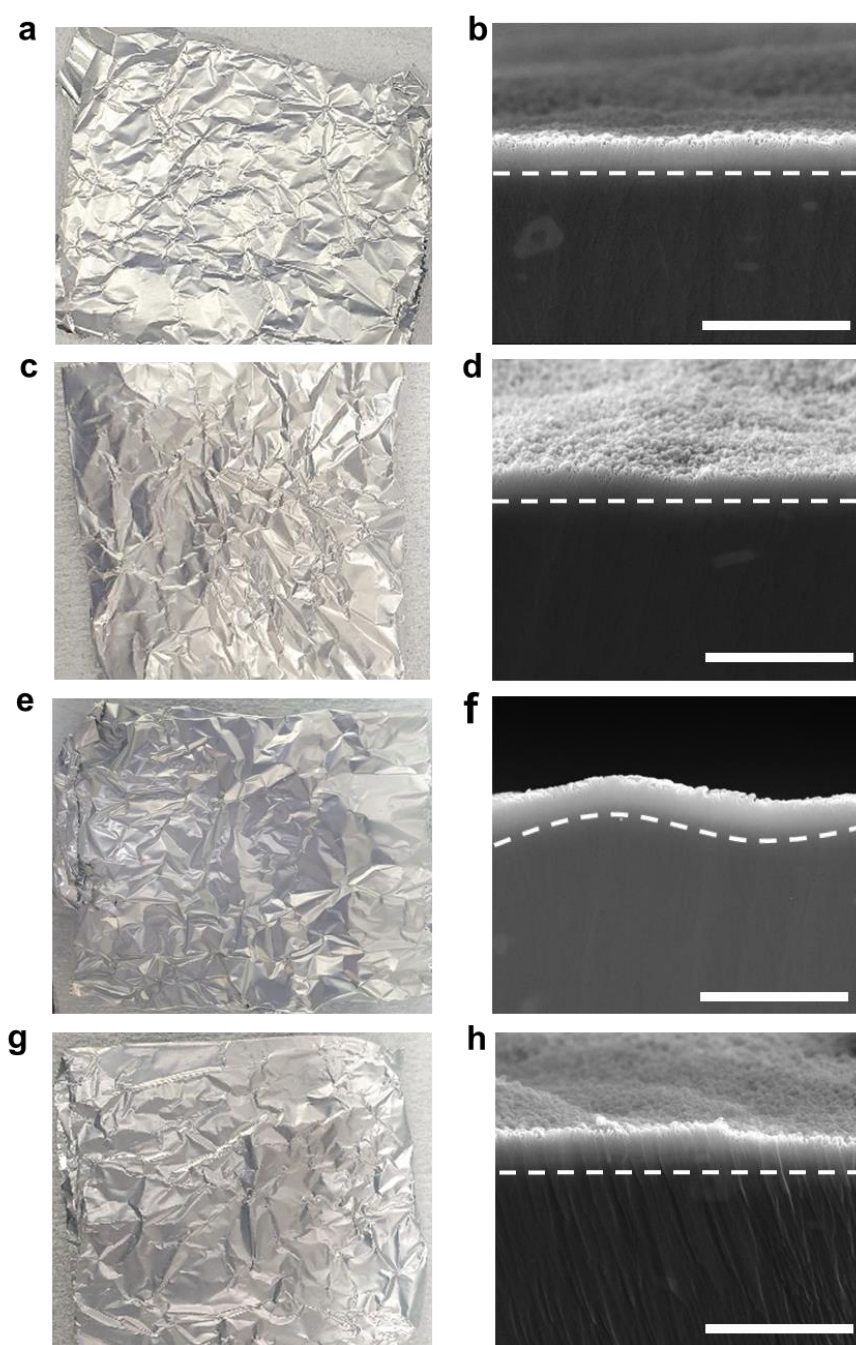
### FT-IR analysis of AlOOH-2, before and after fluoride ion removal.

Fluoride ion removal mechanism of AlOOH-2 was analyzed by FT-IR spectroscopy (Fig. S6). With comparison of intensity ratio of Al-O-H band at  $1063\text{ cm}^{-1}$  and Al-O band at  $594\text{ cm}^{-1}$ , their intensity ratio (Al-O-H/Al-O) were 0.99 and 0.81, before and after fluoride ion removal, respectively. After fluoride adsorption, it is found that the peak at  $1063\text{ cm}^{-1}$  compare to the peak at  $594\text{ cm}^{-1}$  corresponding to the surface hydroxyl groups decreases after fluoride adsorption, indicating that surface hydroxyl groups are involved in the fluoride adsorption process.

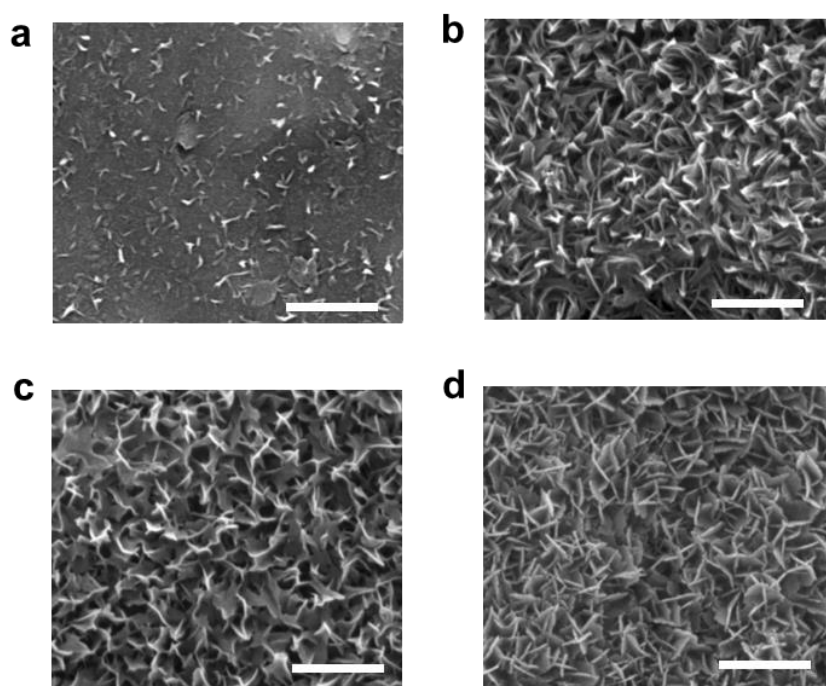
**Table S1.** Comparison of the costs of common Al salts and Al foil used as precursors for Al-based adsorbent synthesis.

Precursor	Price (USD/kg)*
Aluminum chloride	116.00
Aluminum isopropoxide	76.50
Aluminum nitrate nonahydrate	194.00
Household Al foil	2.10

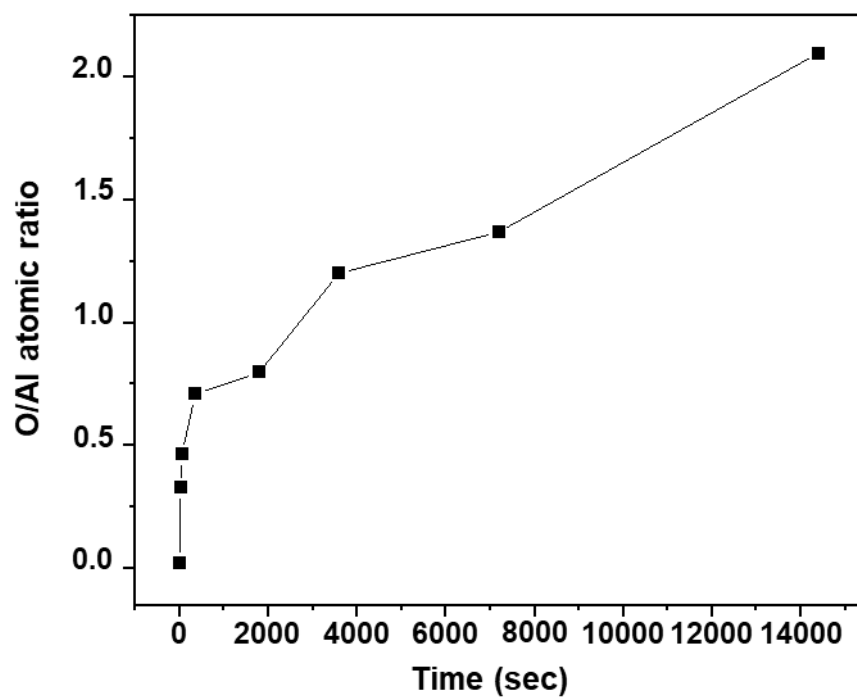
\* Prices are compared based on the listings provided by Alibaba.com (Alibaba Group Holding Ltd.) for aluminum foil, and Sigma-Aldrich Inc. for the other precursors.



**Figure S1.** (a, c, e, g) Photographs and (b, d, f, h) cross-sectional view FE-SEM images of AlOOH on Al foil which were fabricated by immersing Al foil in boiling DI water with different immersing time. (a, b : 0.5 h, c, d: 1.0 h, e, f: 2.0h and g, h: 4.0h, white scale bar is 3  $\mu\text{m}$ )).



**Figure S2.** FE-SEM images of AlOOH on Al foil, synthesized by immersing in boiling DI water for (a) 10 sec, (b) 30 sec, (c) 1 min, (d) 5min (refer to AlOOH-10s, AlOOH-30s, AlOOH-1m, AlOOH-5m, white scale bar is 500 nm).



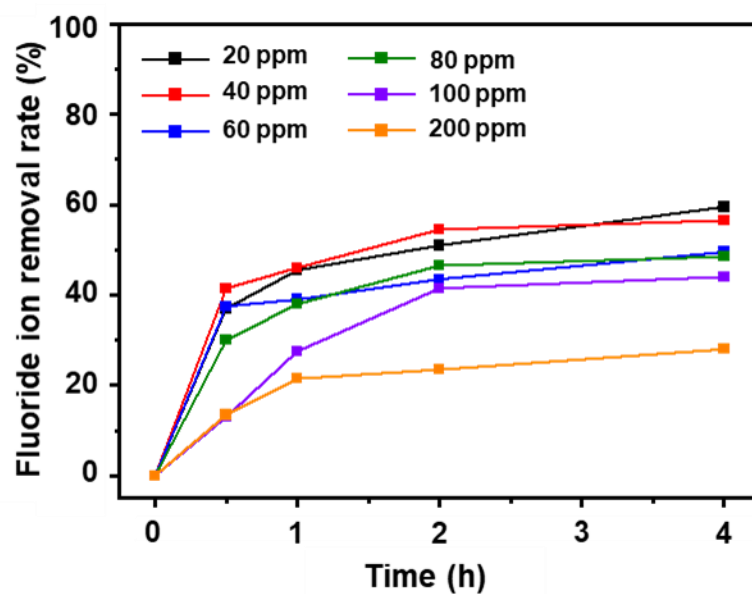
**Figure S3.** Atomic ratio of Al and O of AlOOH on Al foil with different immersing time in boiling DI water, from EDS analysis.

**Table S2.** Atomic percent of Al and O of AlOOH on Al foil with different immersing time in boiling DI water by EDS analysis.

Immersing time  Atoms (at %)	10 sec	30 sec	1 min	5 min	0.5 h	1.0 h	2.0 h	4.0 h
O	2.14	24.61	31.63	41.45	44.28	54.53	57.73	67.67
Al	97.86	75.39	68.37	58.55	55.72	45.47	42.27	32.33

**Table S3.** Atomic percent of Al and O of AlOOH-0.5, AlOOH-1, AlOOH-2, and AlOOH-4 by spot EDS analysis from cross-sectional view.

Sample Atoms (at %)	AlOOH-0.5	AlOOH-1	AlOOH-2	AlOOH-4
O	65.55	65.40	66.27	66.39
Al	34.45	34.60	33.73	33.61



**Figure S4.** Fluoride ion removal rates of AlOOH-2 with different adsorption time and initial fluoride ion concentration (initial fluoride ion concentration: 20 ppm - 200 ppm, sample loading: 0.25 g, and adsorption time: 4.0 h).

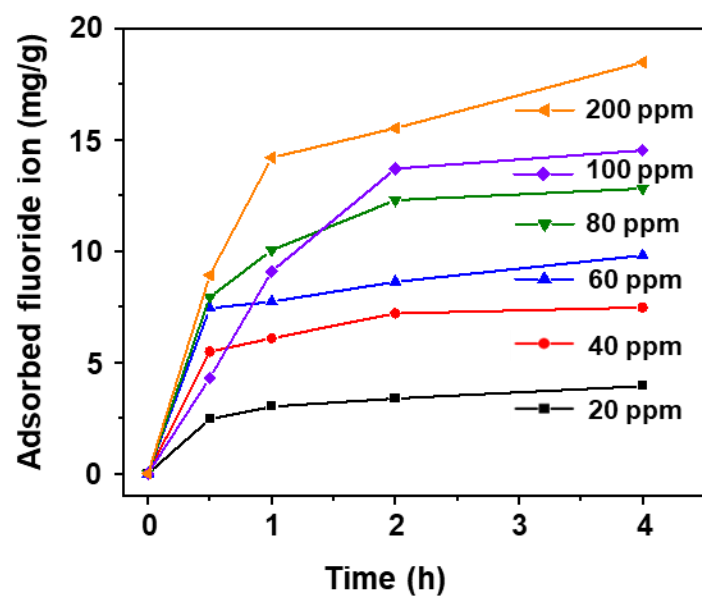


**Table S4.** Kinetic model parameters of AlOOH-2 for pseudo first-order obtained from sorption experiments with different initial fluoride ion concentration.

Initial concentration (mg/L)	Pseudo first-order model		
	$q_e$ (mg/g)	$k_1$ (1/h)	$R^2$
20	0.28	1.04	0.87
40	0.54	1.76	0.95
60	0.68	1.35	0.94
80	0.96	1.49	0.98
100	1.18	0.85	0.98
200	1.35	1.41	0.98

**Table S5.** Calculated parameters for Langmuir isotherm models obtained from equilibrium sorption experiments.

Langmuir model		
qm (mg/g)	KL (L/mg)	R <sup>2</sup>
1.98	0.02	0.99

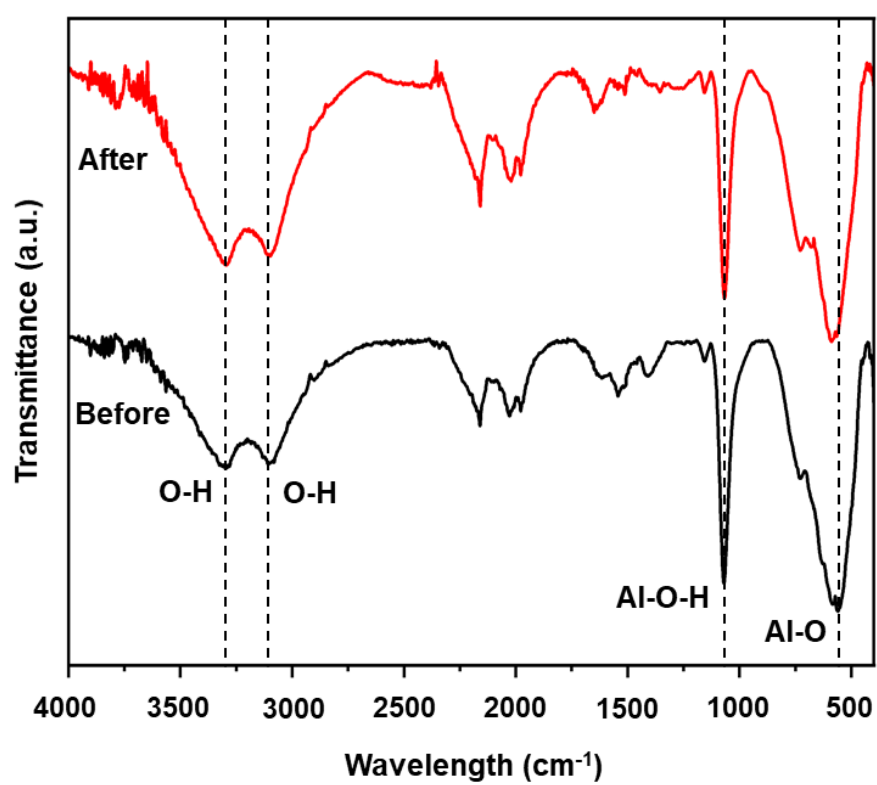


**Figure S5.** Adsorbed fluoride ion with different adsorption time and initial fluoride ion concentration by A IOOH-2 (This adsorbed fluoride ion value was calculated by the volume ratio calculated from the thickness for the AlOOH-only portion of the AlOOH on Al sample, initial fluoride ion concentration: 20 ppm - 200 ppm, sample loading: 0.25 g, and adsorption time: 4.0 h).

**Table S6.** Adsorption capacities of various Al-based adsorbents for fluoride ions.

Adsorbents	Adsorption Capacity (mg/g)	references
Al-modified magnetite ore	1.51	[50]
Al/Fe oxide-loaded tea waste	18.52	[51]
Al <sub>2</sub> O <sub>3</sub> -modified expanded graphite	5.75	[52]
$\gamma$ -AlOOH@chitosan shell@Fe <sub>3</sub> O <sub>4</sub>	67.5	[53]
mesoporous CoAl <sub>2</sub> O <sub>4</sub>	14.8	[54]
Al <sub>2</sub> O <sub>3</sub> nanoparticles	9.73	[55]
MgO-loaded Al <sub>2</sub> O <sub>3</sub>	37.35	[56]
bayerite/boehmite	56.8	[57]
amorphous AlOOH	41.9	[3]
Activated alumina	16.34	[58]
Hydrous-manganese oxide-coated alumina	7.09	[59]
Nano-AlOOH	3.259	[22]
Aluminium hydroxide impregnated macroporous polymeric resin adsorbent	36.61	[45]
Al-Zr loaded tea waste adsorbent	17.54	[46]
AlOOH-2	1.98 26.12*	This study

\* This value was calculated based on the volumetric ratio, calculated from the height of the AlOOH film in the sample.



**Figure S6.** FT-IR spectra of AlOOH-2 (black: before fluoride ion removal, red: after fluoride ion removal).

**Table S7.** Concentrations of dissolved Al in the simulated wastewater with different pH conditions measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) after removal of fluoride ion. (Relative weight percentage of the initial sample dosing amount)

pH	4	5	7	9	11
Al Conc. (wt%)	0.0191	0.0079	0.0002	0.0035	0.0115

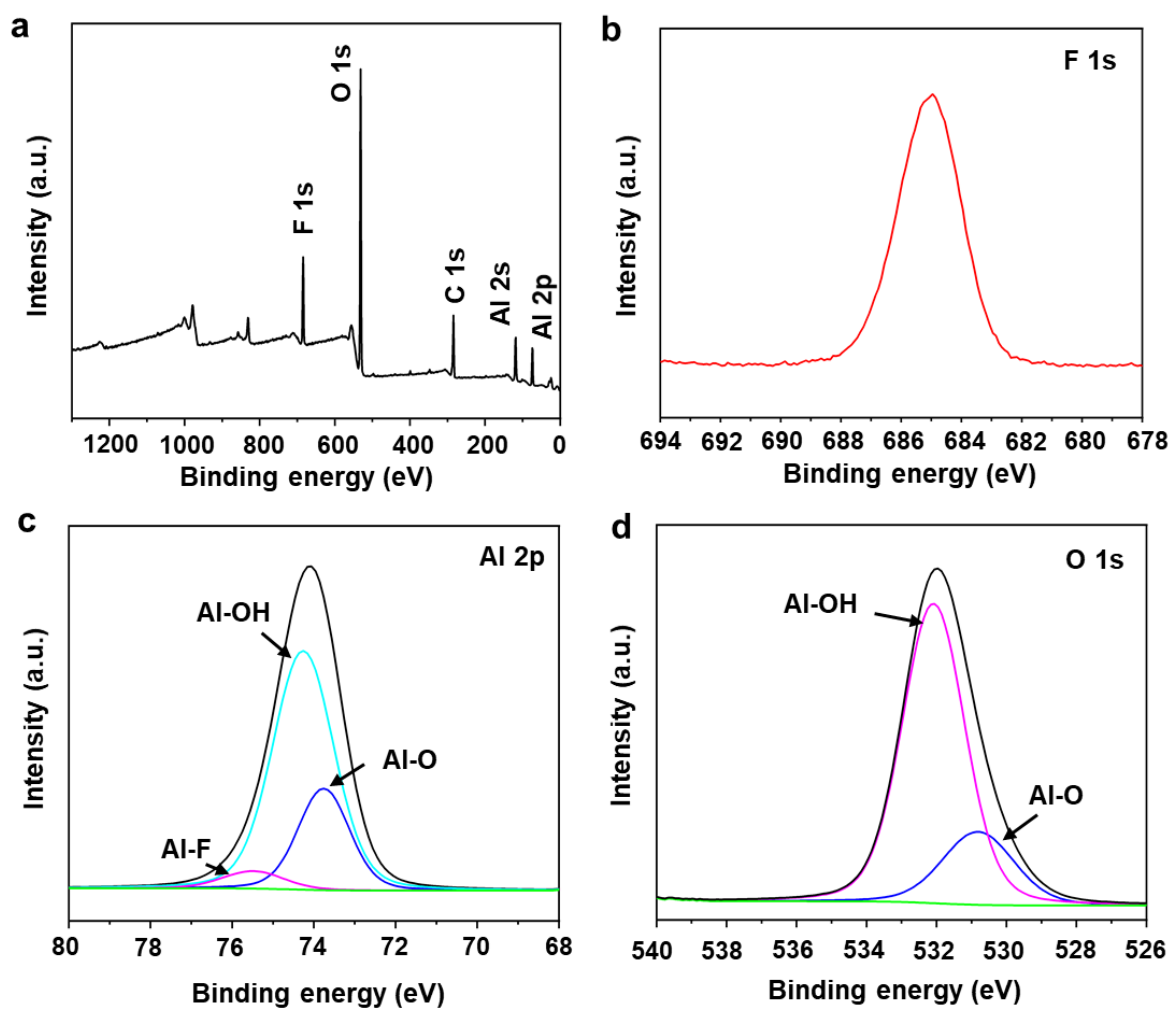


Figure S7. (a) XPS survey spectra and XPS spectra of (b) F 1s, (c) Al 2p and (d) O 1s of regenerated AlOOH-2.

**Table S8.** Al 2p and O 1s Peak Parameters for the regenerated AlOOH-2.

Electrons	Peak	Binding energy (eV)	Concentration (%)
Al 2p	Al-O	73.5	24.98
	Al-OH	74.1	69.89
	Al-F	75.3	5.13
O 1s	Al-O-Al	530.6	21.78
	Al-OH	532.0	78.22