

## Supplementary Information

### Eggshell-Derived Hydroxyapatite–Alkali-Activated Waste Glass Composite for Fluoride Sequestration: Characteristics and Mechanistic Insights

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Table S1. Benchmark comparison between CaO-rich AAC-P@Ca and hydroxyapatite-modified AAC-P@HAp

Parameter	AAC-P@Ca (Akorley et al., 2026 <sup>(1)</sup> )	AAC-P@HAp (This study)
Calcium phase	Free / reactive CaO-rich phase	Crystalline Ca-PO <sub>4</sub> phase (hydroxyapatite)
Primary design objective	Maximum fluoride uptake capacity	Controlled fluoride immobilization and stability
Dominant fluoride removal mechanism	Rapid Ca <sup>2+</sup> -F <sup>-</sup> precipitation and surface complexation	Hydroxyl–fluoride ion exchange and inner-sphere complexation
Maximum adsorption capacity (mg F <sup>-</sup> g <sup>-1</sup> )	> 40	< 6 (≈ 4–5.7 depending on conditions)
BET surface area (m <sup>2</sup> g <sup>-1</sup> )	82.249 m <sup>2</sup> g <sup>-1</sup> (high surface area)	Reduced (43.2 m <sup>2</sup> g <sup>-1</sup> ) due to HAp pore filling
Surface alkalinity / pH <sub>pzc</sub>	Very high, strongly alkaline (12.6)	High pH <sub>pzc</sub> (10.56) but chemically buffered
Calcium mobility / leaching tendency	High (free CaO dissolution i.e., 1430 mg L <sup>-1</sup> )	Moderate, localized Ca <sup>2+</sup> release (1043.17 mg L <sup>-1</sup> )
Nature of fluoride binding	Largely precipitation-driven, partially reversible	Chemisorptive, lattice-level incorporation (fluorapatite-like)
Regeneration behavior	Higher short-term capacity recovery	Limited regeneration due to irreversible chemisorption
Long-term fluoride stability	Moderate (risk of secondary release)	High (permanent fluoride fixation)

Parameter	AAC-P@Ca (Akorley et al., 2026 <sup>(1)</sup> )	AAC-P@HAp (This study)
Structural integrity	Highly reactive, less chemically buffered	Structurally stabilized composite
Handling and deployability	High reactivity, alkalinity concerns	Safer handling, reduced CaO reactivity
Sustainability aspect	Waste-derived but CaO-reactive	Fully waste-derived, chemically stabilized
Preferred application scenario	Capacity-driven treatment where uptake dominates	Long-term, secure fluoride sequestration and immobilization

## Statistical Evaluation of Process Parameters (Box-Behnken design)

### S1.1 Experimental Design and Model Development

A three-factor, three-level Box-Behnken design (BBD) was employed to evaluate the combined influence of adsorbent dose (A), temperature (B), and solution pH (C) on fluoride removal efficiency using AAC-P@HAp. The experimental domain was defined based on preliminary screening experiments. A total of 15 experimental runs were performed, and the response variable was fluoride removal efficiency (%).

The experimental data were fitted to a second-order quadratic model in coded variables:

$$Y(\%) = 83.3333 + 0.25A - 1.75B - 13.5C - 1.0AB + 1.5AC - 2.0BC + 0.5833A^2 + 0.58 \text{ Eqn 1}$$

### S1.2 Analysis of Variance (ANOVA)

The ANOVA results for the quadratic model are summarized in Table S2. The overall model is statistically significant ( $p < 0.001$ ), while the lack-of-fit is not significant ( $p = 0.4381$ ), indicating acceptable model adequacy within the investigated design space.

Among the tested variables, solution pH (C) exerts a dominant influence on fluoride removal ( $p \ll 0.05$ ), whereas adsorbent dose (A), temperature (B), and interaction terms are statistically insignificant within the explored domain.

**Table S2. ANOVA for the quadratic model describing fluoride removal efficiency (%)**

Source	Sum of Squares	df	Mean Square	F-value	p-value	Remark
Model	1549.2963	9	172.1440	19.9985	$2.3560 \times 10^{-7}$	Significant
A – Dose	0.5000	1	0.5000	0.0581	0.8124	Not significant
B – Temperature	24.5000	1	24.5000	2.8462	0.1098	Not significant
C – pH	1458.0000	1	1458.0000	169.3804	$2.8790 \times 10^{-10}$	Significant
AB	4.0000	1	4.0000	0.4647	0.5046	Not significant
AC	9.0000	1	9.0000	1.0456	0.3209	Not significant
BC	16.0000	1	16.0000	1.8588	0.1906	Not significant
A <sup>2</sup>	1.6667	1	1.6667	0.1936	0.6655	Not significant
B <sup>2</sup>	1.6667	1	1.6667	0.1936	0.6655	Not significant
C <sup>2</sup>	21.2585	1	21.2585	2.4697	0.1345	Not significant
Residual	146.3333	17	8.6078	—	—	—
Lack of Fit	25.0000	3	8.3333	0.9615	0.4381	Not significant
Pure Error	121.3333	14	8.6667	—	—	—
Cor Total	1695.6296	26	—	—	—	—

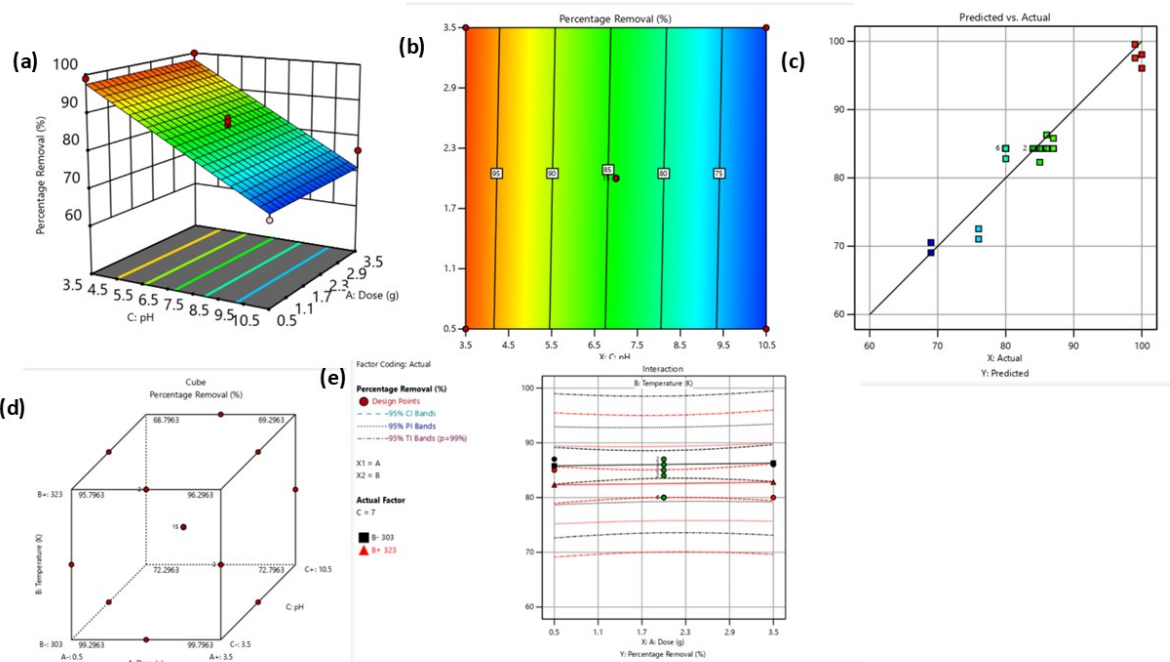
**Table S3: The Model performance statistics:**

Standard deviation	2.9339
Mean response	84.2963
C.V. (%)	3.4805
R <sup>2</sup>	0.9137
Adjusted R <sup>2</sup>	0.8680
Predicted R <sup>2</sup>	0.6820
Adeq Precision	17.9219

Although the Predicted R<sup>2</sup> is lower than the Adjusted R<sup>2</sup>, the difference remains within acceptable limits (< 0.2), indicating reasonable predictive capability within the experimental range.

### S1.3 Interpretation of Response Surface Trends

Response surface and contour plots (Figure S1a–b) show that fluoride removal efficiency varies within a relatively narrow range ( $\approx 83\text{--}87\%$ ) across the investigated factor space. This limited variation indicates that the system is relatively robust to changes in adsorbent dose and temperature under the tested conditions.



**Figure S1:** a) 3D Surface plot showing the interactive effect of adsorbent dose (A), temperature, (B) and pH (C) on fluoride removal efficiency using AAC-P@HAp adsorbent material, b) 2D contour plot showing the interactive effect of adsorbent dose (A), temperature, (B) and pH (C) on fluoride removal efficiency using AAC-P@HAp adsorbent material, c) Predicted versus actual plot of the optimization process, d) Cube plot showing the interactive effect of adsorbent dose (A), temperature, (B) and pH (C) on fluoride removal efficiency using AAC-P@HAp adsorbent material, e) interaction plot of the optimization process.

The response surfaces clearly demonstrate that decreasing pH enhances fluoride removal, consistent with the surface charge behavior and chemisorption mechanism discussed in the main manuscript. In contrast, dose and temperature produce comparatively minor changes in response.

The cube plot (Figure S1d) and interaction plot (Figure S1e) further confirm that interaction effects are weak and statistically insignificant.

#### S1.4 Model Adequacy and Practical Implications

The quadratic model provides a statistically valid representation of the system within the defined experimental domain. However, the narrow response window suggests that the adsorption process is governed primarily by surface chemistry (particularly pH-dependent mechanisms) rather than strong multivariate interactions.

Accordingly, the statistical design serves to confirm parameter hierarchy and system robustness rather than to identify a sharply defined global optimum.

**Table S4. Estimated regression coefficients for fluoride removal efficiency (%)**

Term	Coefficient	df	SE	95% CI (Low)	95% CI (High)
Intercept	83.3333	1	0.7575	81.7351	84.9316
A – Dose	0.2500	1	1.0373	-1.9385	2.4385
B – Temperature	-1.7500	1	1.0373	-3.9385	0.4385
C – pH	-13.5000	1	1.0373	-15.6885	-11.3115
AB	-1.0000	1	1.4670	-4.0950	2.0950
AC	1.5000	1	1.4670	-1.5950	4.5950
BC	-2.0000	1	1.4670	-5.0950	1.0950
A <sup>2</sup>	0.5833	1	1.3257	-2.2136	3.3803
B <sup>2</sup>	0.5833	1	1.3257	-2.2136	3.3803
C <sup>2</sup>	2.0833	1	1.3257	-0.7136	4.8803