

Efficient Fluoride Adsorption by mesoporous Hierarchical Alumina microspheres

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Electronic Supplementary Material

| Adsorbent | Particle size distribution (DLS) (μm) | Surface area ($\text{m}^2 \text{g}^{-1}$) | Pore size (nm) | Pore volume ($\text{cm}^3 \text{g}^{-1}$) | pH_{zpc} |
|------------|--|---|----------------|---|--------------------------|
| HAM type A | 0.6 – 1.0 | 254.09 | 12.96 | 1.07 | 9.0 |
| HAM type B | 1.5 – 2.6 | 241.62 | 25.55 | 2.32 | 9.0 |

Table S1. Characteristics of HAM of type A and B

| Temperature (K) | Langmuir equation | | | | | Freundlich equation | | |
|-----------------|--|--------------------|-----------------|-------|-----------|---|-----------------|-------|
| | Q_{max} (mol g^{-1}) | $b(\text{M}^{-1})$ | $\log b$ | R^2 | n | $K_f(\text{L mmol}^{-1} \text{g}^{-1})$ | $\log K_f$ | R^2 |
| 298.15 | 0.022 ± 0.001 | 3308 ± 646 | 3.52 ± 0.02 | 0.997 | 4 ± 1 | 15 ± 2 | 1.18 ± 0.13 | 0.883 |

Table S2. Langmuir and Freundlich isotherm parameters for fluoride adsorption by HAM type A obtained by using the batch method with 1h as contact time.

| Mono-exponential model | | | Bi-exponential model | | | | |
|------------------------|---------------------------|-------|----------------------|---------------------------|-----------|---------------------------|-------|
| a_1 (M) | k_1 (h^{-1}) | R^2 | a_1 (M) | k_1 (h^{-1}) | a_2 (M) | k_2 (h^{-1}) | R^2 |
| 7.0 | 0.17 | 0.905 | 9.5 | 129.99 | 6.4 | 0.15 | 0.982 |

Table S3. Mono and bi-exponential parameters for the first-order kinetic model

| Adsorbent | Particle size | Initial F ⁻ (mM) | Adsorbent dosage (g L ⁻¹) | pH | Temperature (K) | Contact time (h) | Adsorption capacity (mmol g ⁻¹) | <i>b</i> (M ⁻¹) | ΔH (kJ mol ⁻¹) | Ref. |
|---------------------------------|---------------|--|---------------------------------------|-----|-----------------|------------------|---|---------------------------------------|------------------------------------|--------------|
| Nanomagnetite graphite –La | - | 0.1 – 12.9 (1.97 - 244.6 mg L ⁻¹) | 0.2 | 7.0 | 298 | 24 | 4.1 (77.12 mg g ⁻¹) | 718.2 (0.038 L mg ⁻¹) | 21.13 | 20 |
| Mixed-phase nano iron oxides | 50-200nm | 0.5 – 5.3 (10 - 100 mg L ⁻¹) | 1.2 | 7.0 | 298 | 8 | 2.8 (53.19 mg g ⁻¹) | 1.1 (0.06 L g ⁻¹) | -94.67 | 68 |
| Bone char | - | 0.1 – 1.1 (1 - 20 mg L ⁻¹) | 1.0 | 5.0 | 298 | 120-168 | 0.4 (7.74 mg g ⁻¹) | 29447.4 (1.55 L mg ⁻¹) | - | 69 |
| MgO microspheres | - | - | 1.0 | 7.0 | 298 | 12 | 6.1 (115.5 mg g ⁻¹) | 1481.9 (0.078 L mg ⁻¹) | - | 70 |
| Magnetic cationic hydrogel - La | - | 0 – 4.2 (0 - 80 mg L ⁻¹) | 0.3 | 7.0 | 298 | 0.17 | 7.9 (149.99 mg g ⁻¹) | 7219.4 (0.38 L mg ⁻¹) | - | 71 |
| UiO-66-NH ₂ | 100nm | 0.5 – 3.7 (10 - 70 mg L ⁻¹) | 0.5 | - | 293 | 2 | 3.1 (58.82 mg g ⁻¹) | 6725.4 (0.354 L mg ⁻¹) | -28.21 | 72 |
| HAM type A | 900nm | 2.0 - 16.0 | 0.5 | 5.5 | 298.15 | 12 ^a | 55.0 (1.0 g g ⁻¹) | 4820 | - | Present work |
| HAM type A | 900nm | 2.0 - 16.0 | 0.5 | 5.5 | 298.15 | 1 ^a | 26.0 (491.4 mg g ⁻¹) | 4563 | -17.7 ±0.6 | Present work |
| HAM type B | 900nm | 2.0 - 16.0 | 0.5 | 5.5 | 298.15 | 1 ^a | 20.4 (385.6 mg g ⁻¹) | 598 | -13.3 ±0.9 | Present work |

Table S4. Fluoride removal parameters for several absorbing materials (data relative to the HAM prepared in this work are also recalled for comparison). In parentheses the original values reported in the references. ^aDelay time between fluoride solution additions.

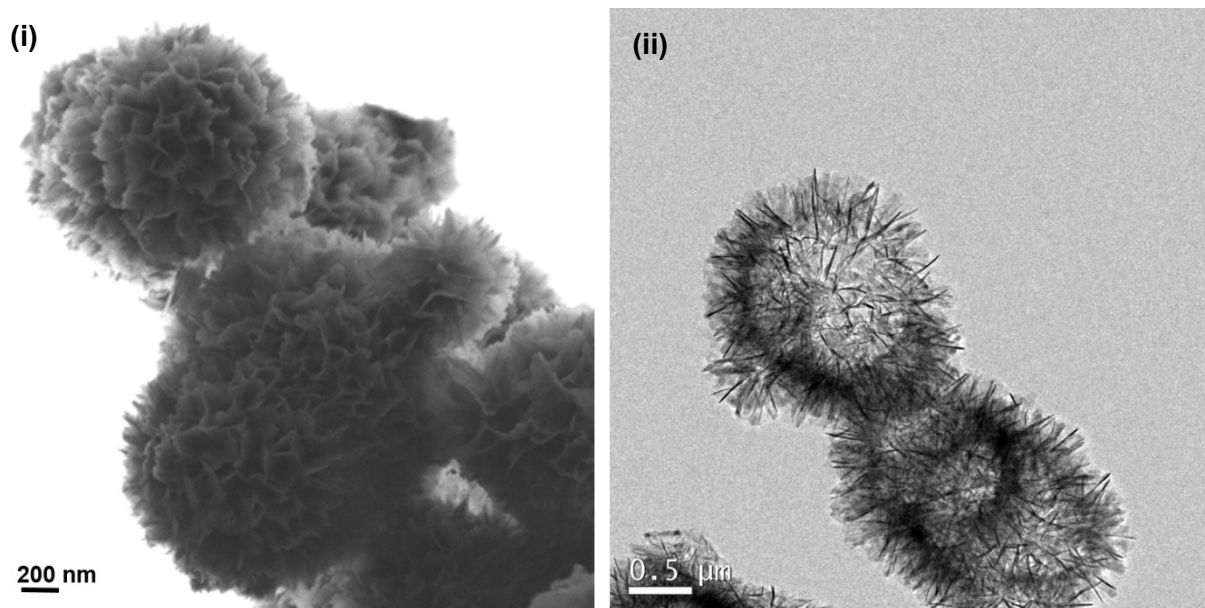


Figure S1. SEM (i) TEM (ii) images of synthesized type B HAM, before calcination process.

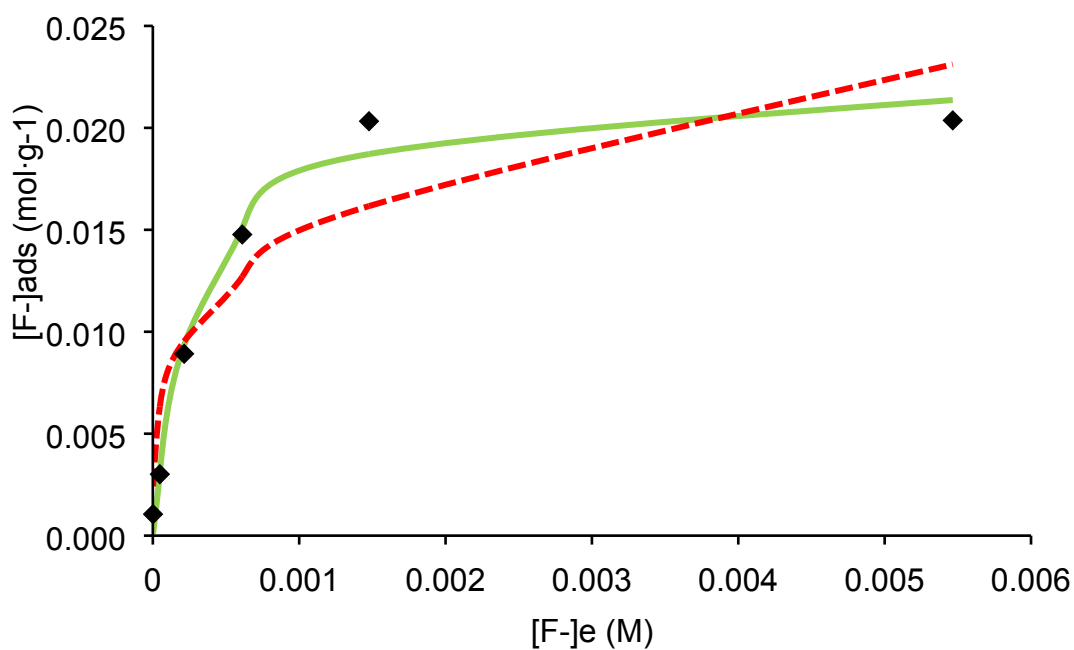


Figure S2. Experimental fluoride adsorption data (batch method) fitted with Langmuir (green line) and Freundlich (dashed red line) models with 1h of contact time (type A sample).

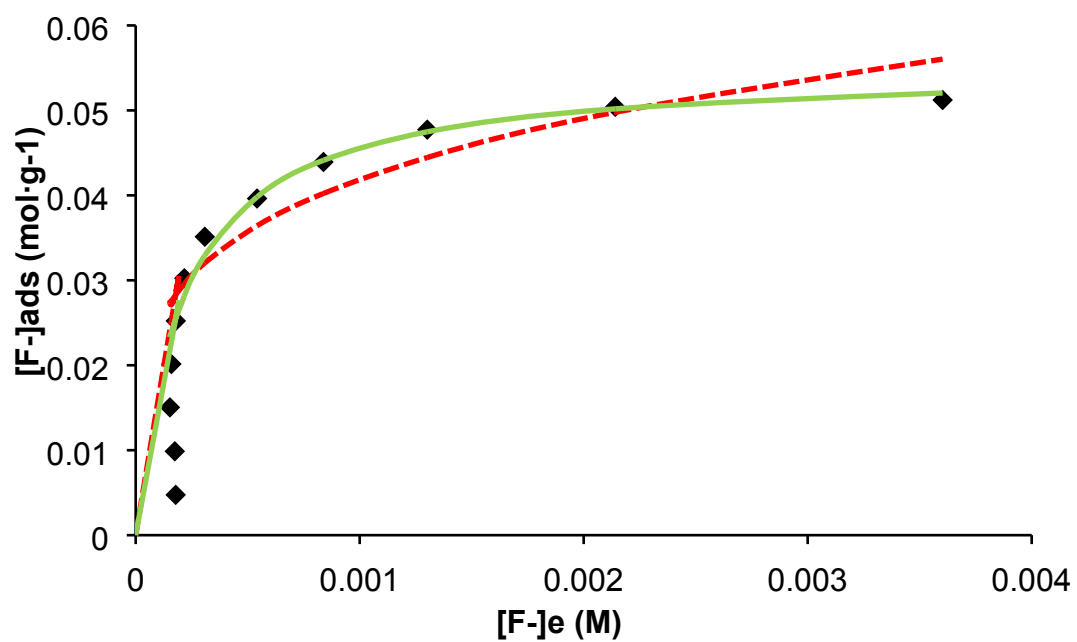


Figure S3. Fluoride adsorption data fitted with Langmuir (green line) and Freundlich (dashed red line) models with 12h delay between injections (type A sample).