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**Calcium hydroxide recycled from waste eggshell resources for effective recovery of fluoride from wastewater**

Wenjing Chen[a,*], Yuanyue Wu[a], Zhiyin Xie[a], Yiyuan Li[a], Weitai Tang[a], Jinbei Yu [a]

[a] College of Resources and Environment, Chengdu University of Information Technology, Chengdu, 610225, China

Corresponding information:

*Corresponding Author:

Wenjing Chen,

E-mail: wenjingchen88@126.com, Tel.: +86 28 85966913, Fax: +86 28 85966913,

Postal address: No.24 Xuefu Road, Shuangliu District, Chengdu, 610225, PR China

## 2.1 Materials

Waste eggshells were collected from the dining hall of Chengdu University of Information Technology. Sodium fluoride (NaF, purity>99%), sodium hydroxide (NaOH, purity>98%), sodium bicarbonate ($NaHCO_3$, purity>98%), sodium sulfate ($NaSO_4$, purity>98%), potassium hydrogen phosphate ($K_2HPO_4$, purity>98%), sodium chloride (NaCl, purity>98%) and HCl were purchased from KeLong Chemical Reagent Factory (Chengdu, China). All chemical reagents were analytical grade and used without further purification. Deionized water was used throughout the whole of work. Fluoride stock solutions were prepared by deionized water with concentration of 1 g/L and 100 mg/L and stored in the polypropylene regent bottles for different adsorption experiments.

## 3.1 Screening of adsorbent

Table S1 The pH change during adsorption process with different adsorbents and the weight loss of different adsorbent in adsorption equilibrium

| Type of adsorbent | pH | | Adsorbent mass | | Weight loss | TDS/% |
|---|---|---|---|---|---|---|
| | Initial | Final | Initial | Final | | |
| ES | 6.66 | 10.51 | 0.03 | 0.0083 | 0.0217 | 72.33 |
| ES500 | | 10.56 | | 0.0113 | 0.0187 | 62.33 |
| ES600 | | 10.53 | | 0.0137 | 0.0163 | 54.33 |
| ES700 | | 10.75 | | 0.0144 | 0.0156 | 52.00 |
| ES800 | | 12.01 | | 0.0257 | 0.0043 | 14.33 |
| AES800 | | 11.94 | | 0.0286 | 0.0014 | 4.67 |
| ES900 | | 12.12 | | 0.027 | 0.003 | 10.00 |
| AES900 | | 12.04 | | 0.0291 | 0.0009 | 3.00 |

# 3.2 Batch adsorption experiments

## 3.2.3 Adsorption isotherm

$$q_t = K_{id} t^{0.5} + C1 \quad \text{(S1)}$$

Where $K_{id}$ ((mg·min$^{0.5}$)/g) is the diffusion rate constant, $q_t$ (mg/g) is the adsorption amount of fluoride at time t (min) and C1 is the thickness of boundary layer.

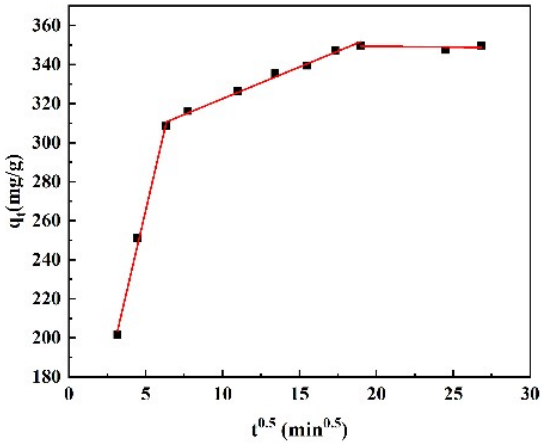


Fig. S1 The fitting results of intra-particle diffusion model

## 3.3 Adsorption mechanism analysis

Table S2 Input parameters for Visual MINTEQ 3.1.

| Parameters | Description | Reference |
|---|---|---|
| Surface complexation models | Calcite-CDM (Three Plane Model) | Wolther et al 2008 |
| Final pH | 12 | In this study |
| Solid concentration (g/L) | 1 | In this study |
| Total calcium dissolved (mg/L) | 266 | In this study |
| Specific surface area ($m^2/g$) | 2.599 | In this study |
| Fluoride concentration (mg/L) | 5-900 | In this study |

Table S3 Equilibrated mass distribution of components between dissolved and precipitated phases predicted by Visual MINTEQ 3.1.

| Initial fluoride (mg/L) | Total dissolved (mg/L) | | % Dissolved | | Total precipitated (mg/L) | | % Precipitated | |
|---|---|---|---|---|---|---|---|---|
| | Fluoride | Calcium | Fluoride | Calcium | Fluoride | Calcium | Fluoride | Calcium |
| 5 | 2.01 | 262.11 | 40.21 | 98.73 | 2.99 | 3.15 | 59.79 | 1.19 |
| 10 | 2.02 | 256.86 | 20.25 | 96.76 | 7.98 | 8.40 | 79.76 | 3.16 |
| 50 | 2.16 | 214.89 | 4.31 | 80.95 | 47.85 | 50.36 | 95.69 | 18.97 |
| 100 | 2.40 | 162.51 | 2.40 | 61.22 | 97.61 | 102.75 | 97.61 | 38.71 |
| 200 | 3.66 | 58.57 | 1.83 | 22.06 | 196.35 | 206.69 | 98.17 | 77.86 |
| 300 | 48.33 | 0.32 | 16.11 | 0.12 | 251.69 | 264.94 | 83.89 | 99.80 |
| 400 | 148.07 | 0.04 | 37.02 | 0.01 | 251.96 | 265.22 | 62.99 | 99.91 |
| 500 | 248.06 | 0.02 | 49.61 | 0.01 | 251.98 | 265.24 | 50.39 | 99.92 |
| 600 | 348.06 | 0.01 | 58.01 | 0.00 | 252.00 | 265.26 | 42.00 | 99.92 |
| 700 | 448.06 | 0.01 | 64.00 | 0.00 | 252.00 | 265.26 | 36.00 | 99.92 |
| 800 | 548.06 | 0.00 | 68.50 | 0.00 | 252.00 | 265.26 | 31.50 | 99.92 |
| 900 | 648.07 | 0.00 | 72.00 | 0.00 | 252.00 | 265.27 | 28.00 | 99.93 |

## 3.4 Evaluation of fluoride removal in real-life water

Table S4 Characteristics and treatment results of real industrial wastewater from photovoltaic industry and real groundwater sample.

| Items | Industrial wastewater | Groundwater |
|---|---|---|
| Fluoride (mg/L) | 1034.21 | 5.83 |
| pH | 1.45 | 6.8 |
| DO (mg/L) | 2043 | 4 |
| Turbidity (NTU) | 234 | 18 |
| Total hardness (mg/L) | 200 | 105 |
| Dosage (g/L) | 6 | 8 |
| Equilibrium time (h) | 12 | 24 |
| Removal rate | 99.77 | 75.54 |