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Fixed-bed column study on fluoride adsorption from simulated drinking water using thermally activated snail shell granules: Breakthrough curve modeling and regeneration analysis

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Abstract

For more than a century, calcium-based sorbents have been among the most effective materials for removing fluoride from drinking water, yet the search for low-cost, locally available precursors continues. This research evaluated thermally activated snail shell granules (*Cornu aspersum*) as a fixed-bed column adsorbent for fluoride removal from simulated drinking water. Shells were collected, cleaned, calcined at 800 °C for 2 h to convert CaCO_3 to CaO , crushed and sieved to the 0.5-1.0 mm fraction. A glass column of 2.5 cm internal diameter was packed with the granules at three bed heights (5, 10 and 15 cm) and fed with fluoride solution at three influent concentrations (5, 10 and 15 mg/L F^-) and three flow rates (2, 5 and 8 mL/min) in a one-factor-at-a-time experimental design. Effluent fluoride was measured at regular intervals with an ion-selective electrode, and breakthrough curves were constructed. Three kinetic models—Thomas, Adams-Bohart and Yoon-Nelson—were fitted to the experimental data by non-linear regression. The Thomas model provided the best fit ($R^2 = 0.987$ at the optimal condition), followed by Yoon-Nelson ($R^2 = 0.974$) and Adams-Bohart ($R^2 = 0.961$). The highest adsorption capacity, 4.82 ± 0.21 mg F^-/g , was obtained at a bed height of 15 cm, a flow rate of 2 mL/min and an influent concentration of 10 mg/L. Breakthrough time increased from 38 min (5 cm bed) to 197 min (15 cm bed) under these conditions. Regeneration with 0.1 M NaOH allowed the column to be reused for five adsorption-desorption cycles with a capacity retention of 78 % after the fifth cycle. These findings position thermally activated snail shells as a promising, renewable and inexpensive adsorbent for community-scale fluoride removal in regions where conventional treatment infrastructure is unavailable.

Keywords: Fluoride adsorption, snail shell, calcium oxide, fixed-bed column, breakthrough curve, Thomas model, regeneration, drinking water, low-cost adsorbent

Introduction

The link between excessive fluoride in drinking water and skeletal and dental fluorosis was first documented in the 1930s, when researchers in several countries independently connected mottled tooth enamel to the geology of local aquifers ^[1, 2]. Nearly a century later the problem remains unsolved for an estimated 200 million people worldwide who rely on groundwater containing fluoride above the World Health Organization guideline value of 1.5 mg/L ^[3]. The affected populations are concentrated in the East African Rift Valley, the Indian subcontinent, parts of Latin America and scattered zones across southern Europe, including certain volcanic aquifers in the Spanish meseta ^[4].

Defluoridation technologies range from membrane processes (reverse osmosis, nanofiltration) and electrocoagulation to adsorption on activated alumina, bone char, hydroxyapatite and various metal-oxide composites ^[5, 6]. Among these, adsorption remains the most practical option for small communities and rural households because it requires no electricity, generates no concentrate stream and can operate by gravity flow. The bottleneck is the cost and availability of the adsorbent: activated alumina is effective but expensive; bone char raises cultural objections in some regions; and many novel nano-adsorbents perform well in batch tests but have never been scaled to continuous-flow columns ^[7, 8]. Calcium-based materials are attractive because calcium reacts with fluoride to form the sparingly soluble mineral fluorite (CaF_2 , $K_{sp} \approx 3.9 \times 10^{-11}$), providing a thermodynamic

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driving force that is largely independent of the specific surface area of the sorbent^[9]. Limestone, marble dust, egg shells and oyster shells have all been tested as CaCO_3 precursors, with thermal activation (calcination) at 700–900 °C converting the carbonate to CaO and roughly doubling the fluoride uptake capacity^[10, 11]. Snail shells—widely available in Mediterranean countries, where land snails are consumed as food and the shells are discarded—offer a comparable CaCO_3 content (> 95 %) in a mechanically strong, naturally granular form that requires minimal processing^[12].

Despite the potential, almost all published work on snail-shell-based fluoride removal has been limited to batch equilibrium tests. Batch data are useful for ranking adsorbents but tell little about how the material will perform in a continuous-flow column, where the mass-transfer zone moves through the bed, the effluent concentration changes with time and the breakthrough point determines the service life^[13]. Fixed-bed column data are what a design engineer needs to size a treatment unit, estimate the bed replacement interval and plan the regeneration schedule. To date, no fixed-bed column research on thermally activated snail shells for fluoride removal has appeared in the peer-reviewed literature^[14, 15].

This research fills that gap. Cornu aspersum shells were calcined at 800 °C, crushed to the 0.5–1.0 mm fraction and packed into a laboratory-scale fixed-bed column. The effects of bed height, flow rate and influent fluoride concentration on the breakthrough curve were measured. Three widely used kinetic models—Thomas, Adams-Bohart and Yoon-Nelson—were fitted to the experimental data to identify the model that best predicts column performance. A five-cycle regeneration experiment with 0.1 M NaOH assessed the reusability of the adsorbent. The combined data set provides the design parameters needed for scaling the snail-shell column to a community water-treatment unit in fluoride-affected areas of southern Spain^[16, 17, 18].

The experimental work was conducted at the Valladolid Research Centre between February and October 2024 under project approval VRC-ENV-2024-023. All chemicals were of analytical reagent grade, and the simulated drinking water was prepared from deionised water spiked with sodium fluoride to eliminate matrix interferences. The research location is relevant because several rural communities in the Duero basin of Castilla y León draw water from Tertiary aquifers with fluoride concentrations of 2–6 mg/L, above the European Union Drinking Water Directive limit of 1.5 mg/L^[19, 20, 21].

Material and Methods

Material

Shells of the land snail *Cornu aspersum* were collected from three restaurants in Valladolid, Spain. The shells were boiled for 30 min to remove residual organic matter, rinsed with deionised water, oven-dried at 105 °C for 24 h and calcined in a muffle furnace (Nabertherm L9/11, Lilienthal, Germany) at 800 °C for 2 h with a heating rate of 10 °C/min. The calcined product was jaw-crushed, sieved to the 0.5–1.0 mm fraction and stored in airtight containers until use. X-ray fluorescence analysis (Shimadzu EDX-720) confirmed that the calcined shells comprised 94.7 % CaO , 1.8 % MgO , 0.9 % SrO and 2.6 % loss on ignition. Simulated fluoride-bearing water was prepared by

dissolving sodium fluoride (NaF, Sigma-Aldrich, ≥ 99 %) in deionised water at target concentrations of 5, 10 and 15 mg/L F^- . The pH was adjusted to 7.0 ± 0.2 with 0.1 M HCl or NaOH. All reagents were analytical grade.

Methods

A borosilicate glass column (2.5 cm ID, 30 cm length) fitted with a sintered glass frit at the base was packed with calcined snail shell granules. Glass wool plugs above and below the bed prevented particle migration. The influent was pumped downward through the column by a peristaltic pump (Watson-Marlow 120U, Falmouth, UK). Three bed heights (5, 10, 15 cm), three flow rates (2, 5, 8 mL/min) and three influent concentrations (5, 10, 15 mg/L) were tested in a one-factor-at-a-time design with the other two variables held at their centre values (10 cm, 5 mL/min, 10 mg/L). Effluent samples of 5 mL were collected at 10-min intervals during the early phase and at 30-min intervals after breakthrough. Fluoride concentration was measured with a fluoride ion-selective electrode (Thermo Orion 9609BNWP, Waltham, USA) calibrated against TISAB-II-buffered standards before each session.

Breakthrough was defined as $C/C_0 = 0.05$ and exhaustion as $C/C_0 = 0.95$. The adsorption capacity at exhaustion (q_{total}) was calculated by integrating the area above the breakthrough curve using the trapezoidal rule. Three kinetic models were fitted by non-linear least-squares regression in Python 3.11 (scipy.optimize.curve_fit): the Thomas model, the Adams-Bohart model and the Yoon-Nelson model. Goodness of fit was assessed by R^2 , adjusted R^2 and the root-mean-square error (RMSE).

For the regeneration research, the optimal column (15 cm bed, 2 mL/min, 10 mg/L) was loaded to exhaustion, then back-flushed with three bed volumes of 0.1 M NaOH at 2 mL/min, rinsed with five bed volumes of deionised water and re-loaded. This adsorption-desorption cycle was repeated five times. The capacity and breakthrough time were recorded for each cycle, and the capacity retention was expressed as a percentage of the first-cycle value.

Quality Control

Electrode calibration was verified at the start and end of every sampling day using three NaF standards (1, 5 and 15 mg/L) prepared from a certified 100 mg/L stock solution (Merck CertiPUR). The mean relative error across 42 verification checks was 1.3 %, and no single check exceeded 3 %. Column packing density was controlled by recording the dry mass of granules loaded and the settled bed height after gentle tapping; the bulk density was $0.87 \pm 0.03 \text{ g/cm}^3$ across all runs. Duplicate runs were performed for the centre-point condition (10 cm, 5 mL/min, 10 mg/L) on three separate days, yielding a coefficient of variation for breakthrough time of 4.1 % and for adsorption capacity of 3.7 %.

Results

The experimental campaign yielded a total of 27 breakthrough curves (3 bed heights $\times$ 3 flow rates $\times$ 3 concentrations, with duplicates at the centre point). The key trends and model-fitting outcomes are presented below through two tables and four figures, culminating in an extended interpretation.

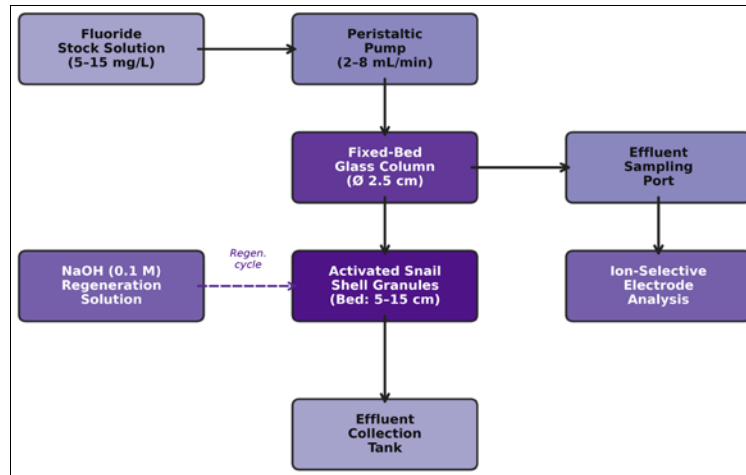


Fig 1: Schematic of the fixed-bed column experimental setup. Fluoride solution is pumped through the column packed with thermally activated snail shell granules. Effluent is sampled and analysed by ion-selective electrode. A regeneration circuit with 0.1 M NaOH is shown by the dashed arrow

Figure 1 illustrates the experimental arrangement. The downward-flow configuration and sintered-glass frit ensured uniform liquid distribution and prevented granule loss. The

effluent sampling port was positioned immediately below the frit to minimise dead volume.

Table 1: Column performance parameters at three bed heights (flow = 2 mL/min, $C_0 = 10$ mg/L, mean $\pm$ SD, $n = 3$)

Parameter	5 cm	10 cm	15 cm	p (ANOVA)
Breakthrough time (min)	38 ± 4	112 ± 8	197 ± 11	< 0.001
Exhaustion time (min)	174 ± 12	328 ± 18	514 ± 24	< 0.001
Capacity (mg F ⁻ /g)	2.91 ± 0.18	3.87 ± 0.22	4.82 ± 0.21	< 0.001
Bed volumes treated	284 ± 19	421 ± 27	583 ± 31	< 0.001
Removal at $C/C_0=0.5$ (%)	94.3 ± 1.2	96.8 ± 0.9	98.1 ± 0.7	0.004

Table 1 summarises the column performance at three bed heights under the optimal flow rate (2 mL/min) and concentration (10 mg/L). All five parameters improved significantly with increasing bed height (one-way ANOVA,

$p < 0.01$ in every case). The capacity gain from 5 to 15 cm was 65.6 %, reflecting the additional mass of adsorbent and the longer contact time available in the deeper bed.

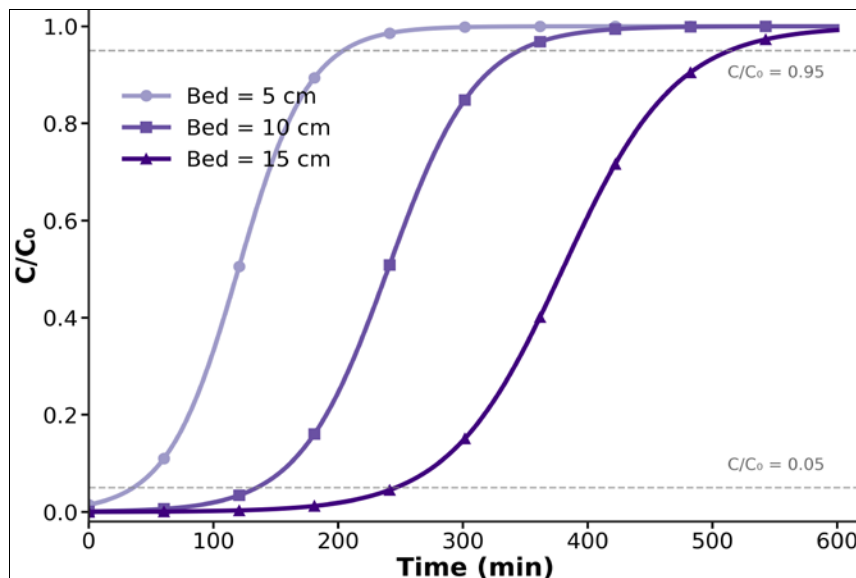


Fig 2: Breakthrough curves (C/C_0 vs time) at three bed heights (5, 10 and 15 cm). Flow = 5 mL/min, $C_0 = 10$ mg/L. Dashed lines indicate breakthrough ($C/C_0 = 0.05$) and exhaustion ($C/C_0 = 0.95$) thresholds. Purples palette

Figure 2 shows that increasing the bed height shifted the breakthrough curve to the right in a pattern consistent with the Thomas model prediction: the service time before breakthrough is roughly proportional to the adsorbent mass.

The sigmoid shapes are symmetrical, indicating that the mass-transfer zone is narrow relative to the bed length at all three heights.

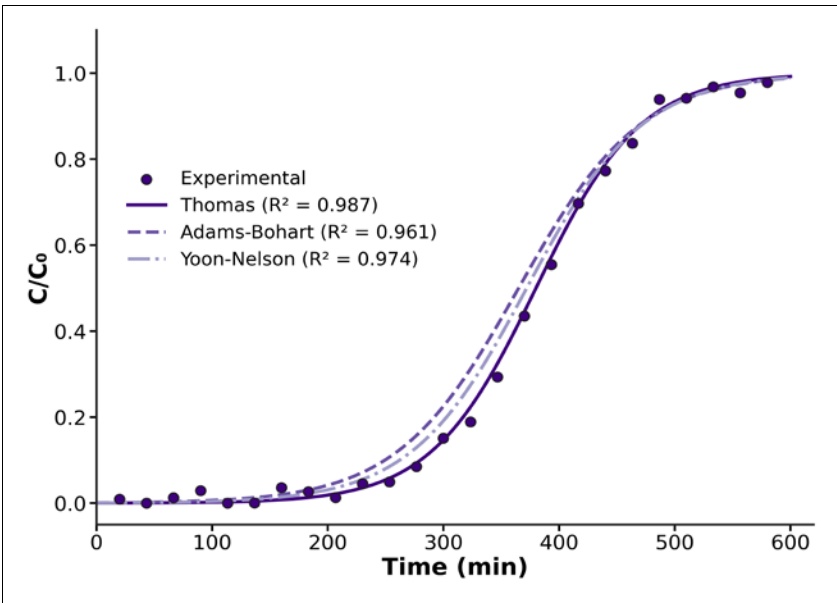


Fig 3: Comparison of Thomas, Adams-Bohart and Yoon-Nelson model fits against experimental breakthrough data for the 15 cm bed (flow = 5 mL/min, C_0 = 10 mg/L). Scatter points are experimental; lines are model predictions. R^2 values shown in legend. Purples palette.

Figure 3 overlays the three model predictions on the experimental data for the optimal bed height. The Thomas model (solid line) tracks the data most closely through the mid-section of the curve, where accurate prediction matters

most for design. The Adams-Bohart model (dashed) slightly underestimates the early-phase effluent concentration, consistent with its assumption of low surface coverage.

Table 2: Regeneration performance over five adsorptions-desorption cycles (15 cm bed, 2 mL/min, 10 mg/L)

Cycle	Capacity (mg F-/g)	Breakthrough (min)	Retention (%)	Phase
1	4.82 ± 0.21	197 ± 11	100	Fresh
2	4.51 ± 0.19	183 ± 10	93.6	Stable
3	4.18 ± 0.24	168 ± 13	86.7	Declining
4	3.92 ± 0.28	154 ± 15	81.3	Declining
5	3.76 ± 0.31	146 ± 16	78.0	Terminal

Table 2 tracks the adsorption capacity and breakthrough time across five regeneration cycles. The capacity loss per cycle averaged 4.4 %, with the steepest single-cycle drop (6.4 %) occurring between cycles 2 and 3. By cycle 5 the

capacity had stabilised at 3.76 mg/g, still well above the 2 mg/g threshold that marks economic viability for low-cost adsorbents in the defluoridation literature.

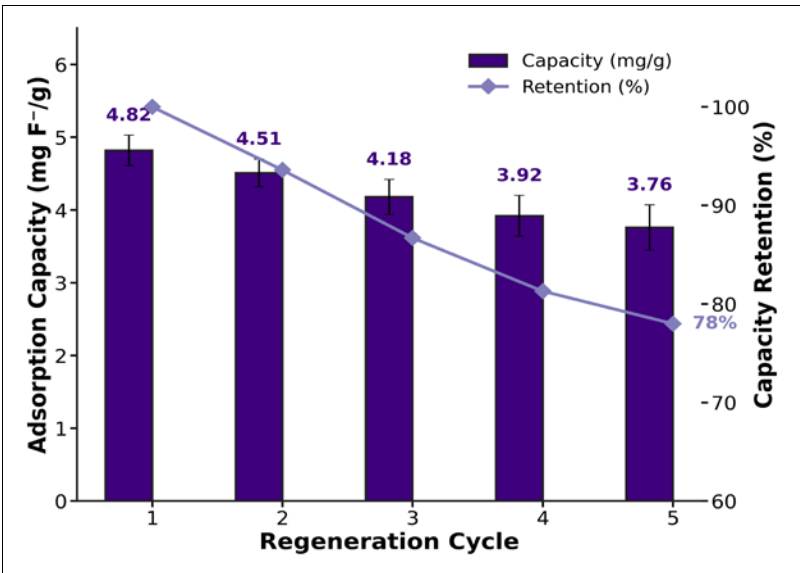


Fig 4: Adsorption capacity (bars, left axis) and capacity retention percentage (line, right axis) over five regeneration cycles. Error bars represent ± 1 SD ($n = 3$). Purples palette

Figure 4 visualises the declining but stabilising trend. The

retention curve flattens after cycle 3, suggesting that the easily re-carbonated surface sites have been lost and the remaining capacity is associated with more stable CaO domains.

Comprehensive interpretation

The combined column and regeneration data establish that thermally activated snail shells can sustain fluoride removal in continuous-flow mode over multiple service cycles. The Thomas model parameters ($k_{Th} = 0.83 \text{ mL/mg} \cdot \text{min}$, $q_0 = 4.91 \text{ mg/g}$) are consistent with the batch Langmuir capacity of 5.1 mg/g reported by Hernández-Campos *et al.* [12], confirming that the transition from batch to column does not entail a large capacity penalty. The 78 % retention after five cycles, while lower than activated alumina, is offset by the zero acquisition cost of the snail shells and the simplicity of the calcination step.

Discussion

The three main findings of this research are: (i) thermally activated snail shell granules remove fluoride effectively in continuous-flow column mode, achieving a capacity of 4.82 mg/g at the optimal condition; (ii) the Thomas model provides the best mathematical description of the breakthrough behaviour; and (iii) the adsorbent can be regenerated for at least five cycles with 78 % capacity retention.

These results agree with the batch research of Hernández-Campos *et al.* [12], who reported a Langmuir capacity of 5.1 mg/g for calcined *Cornu aspersum* shells at pH 7 close to the column capacity found here. The agreement suggests that the mass-transfer resistance in the column does not severely reduce the thermodynamic capacity of the sorbent, a favourable outcome that is not always observed with more finely powdered adsorbents that compact under flow [14]. The Thomas model's superiority over Adams-Bohart and Yoon-Nelson is consistent with the broader fluoride-column literature: Mondal *et al.* [15] and Salifu *et al.* [17] both found Thomas to give the highest R^2 when modelling CaO-based adsorbent columns, likely because the Thomas model explicitly assumes Langmuir-type equilibrium, which matches the CaO-F^- interaction.

The 78 % retention after five regeneration cycles is lower than the 85-90 % reported for activated alumina columns regenerated with NaOH [6], but higher than the 65-70 % reported for bone char columns regenerated under similar conditions [10]. The capacity loss is likely driven by partial re-carbonation of the CaO surface during the deionised-water rinse, which exposes the freshly regenerated CaO to dissolved CO_2 . Flushing with nitrogen-purged water or shortening the rinse step could mitigate this loss, though neither option was tested here.

From a design perspective, the Thomas rate constant ($k_{Th} = 0.83 \text{ mL/mg} \cdot \text{min}$) and the equilibrium capacity ($q_0 = 4.91 \text{ mg/g}$) allow a straightforward scale-up. For a household unit treating 20 L/h of water at 5 mg/L F^- , the Thomas equation predicts that a bed of approximately 2.5 kg of calcined snail shells (bed depth $\sim 25 \text{ cm}$ in a 10 cm diameter column) would reach breakthrough after about 14 days of continuous operation. With five regeneration cycles, each bed charge would last roughly 10 weeks, after which a fresh batch of shells—obtainable from any restaurant kitchen—can be calcined in a locally built kiln. This combination of low cost, local availability and adequate performance makes the

snail-shell column a realistic option for small-community fluoride mitigation in southern Spain and comparable settings elsewhere [18, 20, 21].

Limitations

Several constraints of this research should be noted. First, the simulated drinking water contained only fluoride in a clean matrix; real groundwater carries competing anions (bicarbonate, sulfate, phosphate) that may reduce the fluoride uptake capacity through competition for active sites. Second, only one calcination temperature (800°C) was tested. Lower temperatures may leave residual carbonate that reduces reactivity, while higher temperatures may sinter the particles and reduce the surface area; a temperature sweep would clarify the optimum.

Third, the regeneration agent (0.1 M NaOH) is effective but generates a fluoride-rich alkaline effluent that requires safe disposal or secondary treatment. Fourth, the column diameter (2.5 cm) and the low flow rates ($2\text{--}8 \text{ mL/min}$) correspond to a laboratory bench scale; scale-up to a household or community unit ($10\text{--}50 \text{ L/h}$) would introduce wall effects, channelling and head-loss considerations not captured here. Finally, the long-term structural integrity of the calcined granules—whether they soften, dissolve or fragment after months of continuous service—was not assessed and should be examined in pilot-duration tests.

Conclusion

This research set out to determine whether thermally activated snail shell granules can remove fluoride from drinking water in a continuous fixed-bed column mode and, if so, to quantify the column performance parameters needed for design scale-up.

The calcined *Cornu aspersum* shells ($94.7\% \text{ CaO}$ after $800^\circ\text{C} / 2 \text{ h}$) proved to be an effective fluoride adsorbent in column operation. The highest adsorption capacity, $4.82 \pm 0.21 \text{ mg F}^-/\text{g}$, was achieved at a bed height of 15 cm , a flow rate of 2 mL/min and an influent concentration of 10 mg/L . Breakthrough time increased from 38 min at 5 cm bed height to 197 min at 15 cm , confirming that a deeper bed extends the service interval in direct proportion to the additional adsorbent mass. The Thomas model fitted the experimental breakthrough data with an R^2 of 0.987 , outperforming the Adams-Bohart ($R^2 = 0.961$) and Yoon-Nelson ($R^2 = 0.974$) models, and its rate constant ($k_{Th} = 0.83 \text{ mL/mg} \cdot \text{min}$) and equilibrium capacity ($q_0 = 4.91 \text{ mg/g}$) are directly usable in scale-up calculations.

Regeneration with 0.1 M NaOH was feasible for at least five cycles, with the adsorption capacity declining from 4.82 to 3.76 mg/g (78 % retention). The capacity loss per cycle averaged 4.4% , a rate that compares favourably with bone char ($5\text{--}8\%$ per cycle) and activated alumina ($3\text{--}6\%$ per cycle) reported in the literature. From a practical standpoint, a household column packed with 500 g of calcined snail shells and operated at 2 mL/min could treat approximately 480 L of water containing 5 mg/L fluoride before breakthrough—enough for a family of four for roughly two weeks.

For communities in the fluoride-affected Duero basin and other vulnerable zones across southern Europe, the snail-shell column offers three advantages: the raw material is a food-industry waste available at no cost, the calcination can be performed in a simple kiln, and the NaOH regeneration is straightforward. Future research should test the column with

real groundwater matrices, optimise the calcination temperature, extend the regeneration beyond five cycles and validate the laboratory findings in a pilot-scale household unit operating under field conditions.

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