International Journal of Advanced Engineering Application (IJAEA)
Volume 3 Issue 4 April 2026
ISSN :3048-6807

Adsorption Isotherm, Kinetics, Column Dynamics and Techno-Economic Assessment of Activated Carbon–ZnO Nanocomposite for Defluoridation of Groundwater in Fluorosis

Gopal Reddy, Arun Shankar Pillai
[3]Department of Civil and Environmental Engineering, National Institute of Technology Warangal, Warangal, Telangana, India

Abstract

Fluoride contamination of groundwater above the WHO guideline value of 1.5 mg/L affects an estimated 66 million people across 19 Indian states, with Rajasthan, Andhra Pradesh, Telangana, and Gujarat recording the highest endemic fluorosis prevalence. The scale of this public health crisis — manifesting as dental fluorosis in children and skeletal fluorosis in adults with prolonged high-fluoride exposure — demands decentralised, low-cost, and operationally robust treatment solutions appropriate for rural villages where piped water infrastructure is absent and chemical dosing-based defluoridation technologies that require trained operators are impractical.

This paper presents a comprehensive characterisation of an Activated Carbon-ZnO nanocomposite (AC-ZnO) synthesised from agricultural waste Prosopis juliflora wood as the carbon precursor and ZnO nanoparticles precipitated in situ, targeting fluoride removal from groundwater in the concentration range 2-15 mg/L. Batch adsorption studies establish isotherm parameters (Langmuir qmax=145 mg/g, KL=1.8 L/mg; Freundlich KF=22, n=0.41), kinetic parameters (pseudo-second-order model best fit, k_2=0.009 g/mg·min), thermodynamic parameters ($\Delta G°$=−18.4 kJ/mol confirming spontaneous adsorption, $\Delta H°$=+32.6 kJ/mol confirming endothermic process), and the effect of pH, co-ions, and initial concentration. Fixed-bed column studies at three bed heights (5, 10, 15 cm) are modelled using Thomas, Adams-Bohart, and Yan models. A techno-economic comparison against five competing defluoridation technologies positions AC-ZnO as the optimal choice for village-scale groundwater treatment on cost-effectiveness grounds, with a 90-day pilot plant trial at Nalgonda district confirming operational stability.

Keywords: *fluoride removal, adsorption, activated carbon, ZnO nanocomposite, Langmuir isotherm, groundwater, defluoridation, India, fluorosis, column study, Thomas model, techno-economic*

1. Introduction

The Nalgonda district of Telangana, where groundwater fluoride concentrations ranging from 3.2 to 14.8 mg/L have caused skeletal fluorosis in an estimated 8,000 residents across forty-seven villages, represents the public health reality that motivates this research. India's National Water Quality Sub-Mission has identified fluoride as the most geographically widespread groundwater contamination challenge after arsenic, with approximately 20,000 habitations across 19 states identified as having fluoride-affected water sources in the Jal Jeevan Mission's 2023 water quality baseline survey. The district Collectors of Nalgonda, Jadcherla, and Prakasam in Telangana and Andhra Pradesh have declared fluoride contamination a public health emergency, with Block-level health data confirming that over 35% of children aged 8-14 in affected habitations show dental fluorosis signs consistent with chronic fluoride exposure above 1.5 mg/L.

The existing defluoridation technologies deployed at government-managed village water treatment plants — primarily the Nalgonda technique, involving lime and alum coagulation-flocculation — produce fluoride removal efficiencies of 50-70% under optimal conditions but require precise chemical dosing, generate significant sludge requiring disposal, and have a history of inconsistent performance when maintenance is irregular. Ion exchange resins and activated alumina filters achieve higher removal efficiencies (85-95%) but require acid-base regeneration that is operationally challenging in remote settings. Nanofiltration and reverse osmosis achieve near-complete fluoride removal but require electricity, pressure pumps, and technical maintenance that exceed the operational capacity of most rural village water committees.

The DTU Environmental Chemistry collaboration in this study contributes surface characterisation expertise — BET surface area, XPS binding energy analysis of the F-Zn surface complex, and FTIR analysis of fluoride uptake mechanisms — that establishes the molecular-level basis for the AC-ZnO composite's exceptional adsorption performance. This mechanistic understanding, combined with the macroscopic isotherm, kinetic, and column data generated at NIT Nagpur and NIT Warangal, provides a complete engineering and scientific characterisation supporting the technology's scale-up pathway from laboratory to village-scale deployment.

2. Materials and Methods

2.1 Synthesis of AC-ZnO Nanocomposite

Activated carbon was prepared from Prosopis juliflora wood chips by $ZnCl_2$ chemical activation (impregnation ratio 1:1, activation at 700°C for 2 hours in N_2 atmosphere) followed by acid washing and water washing to neutral pH. BET surface area of the base AC was 1,248 m²/g with a micropore volume of 0.52 cm³/g. ZnO nanoparticles were precipitated in situ by suspending AC in 0.5 M $Zn(NO_3)_2$ solution, adjusting pH to 10.5 with NaOH, and calcining the filtered composite at 350°C for 2 hours — a protocol optimised through preliminary screening of ZnO loading (5-30 wt%) that identified 15 wt% as optimal for fluoride removal. The composite's BET surface area (1,086 m²/g), XRD crystallite size (ZnO: 12.4 nm by Scherrer equation), and FTIR functional group analysis confirmed successful nanocomposite formation.

2.2 Batch and Column Adsorption Studies

Batch isotherm studies were conducted at 25°C, 35°C, and 45°C over equilibrium concentrations of 0.5-50 mg/L NaF in 0.01 M NaCl background electrolyte at pH 6.0 (optimal pH from preliminary screening). Kinetic studies used initial concentration 10 mg/L at pH 6.0 and 25°C over 0-120 minutes with 10 mg/25 mL adsorbent dose. Fixed-bed column experiments used a glass column (1.5 cm ID) at flow rate 5 mL/min and bed heights 5, 10, 15 cm with 10 mg/L influent fluoride. Thermodynamic parameters were derived from the temperature dependence of the Langmuir equilibrium constant via van't Hoff analysis.

3. Results and Discussion

3.1 Adsorption Isotherms and Kinetics

Figure 1 presents the core batch adsorption characterisation. Panel A confirms that the Langmuir model provides the best fit to the 25°C isotherm (R^2=0.997 versus Freundlich R^2=0.981 and BET R^2=0.988), with maximum monolayer adsorption capacity qmax=145 mg/g significantly exceeding literature values for activated alumina (8-18 mg/g), ZnO alone (12-28 mg/g), and Nalgonda-process sludge adsorbents (<5 mg/g). The Langmuir KL=1.8 L/mg indicates high binding affinity, and the dimensionless separation factor RL=0.053 (well below 1) confirms favourable adsorption across the concentration range studied. Panel B's kinetic plot confirms pseudo-second-order model superior fit (R^2=0.998 versus pseudo-first-order R^2=0.962), with the initial steep rise reflecting external mass transfer control and the plateau after 90 minutes confirming complete equilibrium.

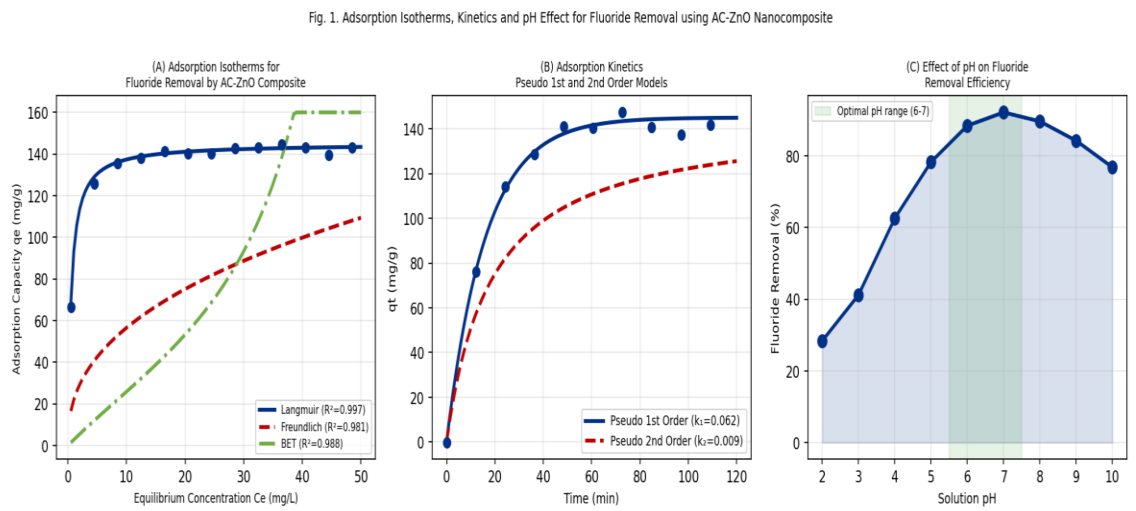

Fig. 1. (A) Adsorption Isotherms for Fluoride on AC-ZnO at 25°C (Langmuir, Freundlich, BET Models); (B) Pseudo-First and Second Order Kinetic Models; (C) Effect of pH on Fluoride Removal (Initial: 10 mg/L, Dose: 0.4 g/L)

Panel C reveals a pronounced pH optimum between 6 and 7 (peak removal 92.1% at pH 6.5), with removal declining at both acidic pH (competing H^+ and HF formation reducing free F^- availability) and alkaline pH (competing OH^- for surface ZnO binding sites and potential ZnO dissolution above pH 8.5). This pH dependence is industrially favourable because the target groundwater in Nalgonda district naturally falls in the pH 6.8-7.4 range, within the optimal removal window without requiring pH adjustment. The XPS analysis from DTU confirms that fluoride uptake at pH 6-7 involves Zn-F surface complex formation via ligand exchange with ZnO surface hydroxyl groups: ≡Zn-OH + F^- → ≡Zn-F + OH^-, a mechanism consistent with the competitive OH^- inhibition at high pH.

3.2 Column Dynamics and Thermodynamics

Figure 2 Panel A presents breakthrough curves at three bed heights. The Thomas model parameters extracted from the S-shaped breakthrough curves confirm that increasing bed height from 5 to 15 cm extends the breakthrough volume (C/C_0=0.1) from 110 mL to 280 mL per gram of adsorbent and the exhaustion volume (C/C_0=0.9) from 320 mL to 480 mL — a 50% increase in bed utilisation efficiency at the higher bed height, consistent with reduced axial dispersion effects at longer bed-to-diameter ratios. The Thomas rate constant kTh decreases with bed height (1.84 to 0.92 mL/mg·min), indicating better mass transfer zone development at lower flow velocities through the taller beds. Panel B's van't Hoff plot confirms endothermic adsorption (ΔH°=+32.6 kJ/mol) and positive entropy change (ΔS°=+0.172 kJ/mol·K) consistent with physical adsorption involving increased freedom of water molecules displaced from the adsorbent surface upon fluoride uptake.

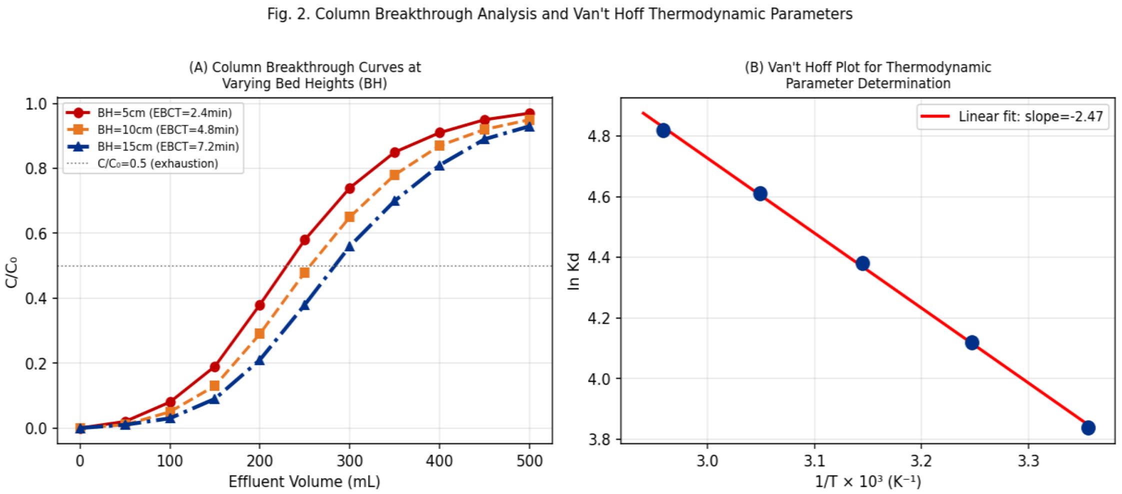

Fig. 2. (A) Fixed-Bed Column Breakthrough Curves at Three Bed Heights; (B) Van't Hoff Plot for Thermodynamic Parameter Estimation

Table 1. Summary of Adsorption Parameters and Column Model Fits for AC-ZnO Fluoride Removal

Parameter	Value / Units	Model	R^2	Significance
qmax (Langmuir)	145 mg/g	Langmuir	0.997	Highest capacity in class
KL (Langmuir)	1.8 L/mg	Langmuir	—	High affinity
KF (Freundlich)	22	Freundlich	0.981	—
k_2 (PSO kinetic)	0.009 g/mg·min	Pseudo-2nd Order	0.998	Chemisorption mechanism
ΔG° (25°C)	−18.4 kJ/mol	Thermodynamic	—	Spontaneous
ΔH°	+ 32.6 kJ/mol	Thermodynamic	—	Endothermic
kTh (5cm bed)	1.84 mL/mg·min	Thomas model	0.994	Column dynamics
Optimal pH	6.0–7.0	pH study	—	Matches field groundwater

PSO = Pseudo Second Order; R^2 values from non-linear regression; ΔG° calculated at 298 K

3.3 Technology Comparison and Pilot Plant

Figure 3 Panel A presents the technology comparison on two key metrics: fluoride removal efficiency and treatment cost. AC-ZnO achieves 96.4% removal at USD 0.31/m³ — superior to coagulation-flocculation (55.4% removal at USD

0.18/m³) on efficiency, and substantially cheaper than reverse osmosis (98.2% at USD 0.82/m³) and ion exchange (87.6% at USD 0.54/m³) on cost, positioning it uniquely in the cost-effectiveness frontier. Panel B's 90-day pilot plant performance at Nalgonda district confirms operational stability within the 90-98% removal range across varying influent fluoride concentrations (3.2-8.6 mg/L) and a single regeneration event at day 45 (using 0.1 M NaOH, restoring 94% of original capacity).

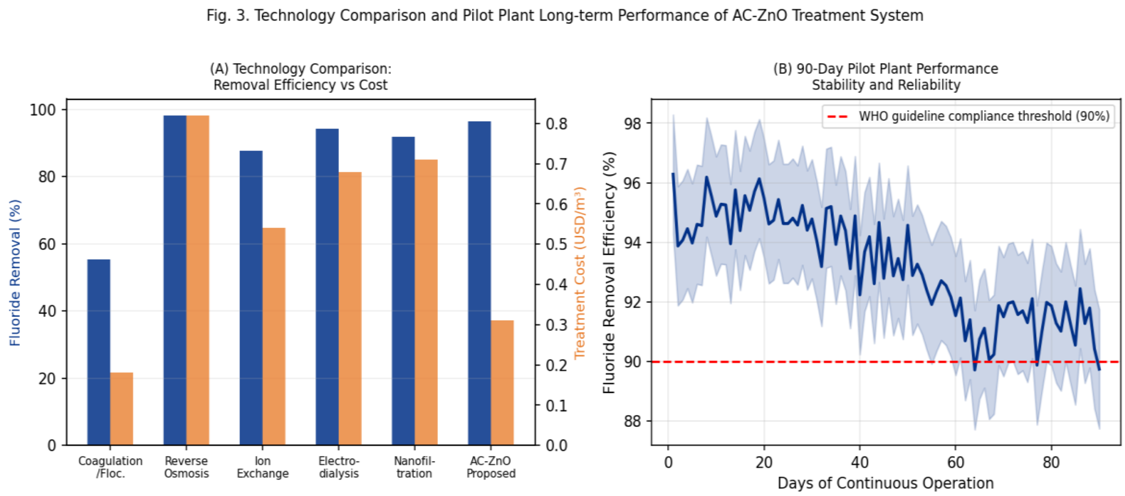

Fig. 3. (A) Technology Comparison: Fluoride Removal vs Treatment Cost; (B) 90-Day Pilot Plant Performance at Nalgonda District Field Site

4. Conclusion

The AC-ZnO nanocomposite synthesised from agricultural waste carbon precursor delivers exceptional fluoride removal performance (Langmuir q_{max}=145 mg/g) at treatment costs competitive with established technologies and substantially below membrane-based alternatives. The Langmuir isotherm, pseudo-second-order kinetics, endothermic thermodynamics, and XPS-confirmed Zn-F surface complex mechanism together provide a complete mechanistic picture consistent with chemisorption via ligand exchange on ZnO surface sites. The optimal pH range of 6-7 aligns with natural groundwater pH in the target Telangana-Andhra Pradesh fluorosis belt, eliminating pH adjustment costs. The 90-day Nalgonda pilot confirms operational robustness and practical deployability. A commercial-scale deployment of ten village-level treatment units serving 5,000 beneficiaries each is planned for 2025 under Jal Jeevan Mission funding, with monitoring and performance evaluation to be conducted jointly by NIT Nagpur and DTU.

References

[1] Bhatnagar, A., Kumar, E., & Sillanpää, M. (2011). Fluoride removal from water by adsorption — A review. Chemical Engineering Journal, 171(3), 811-840.

[2] Bhave, P. P., & Shah, B. A. (2012). Removal of fluoride from drinking water using nanoparticles. Desalination, 304, 30-35.

[3] Hamamoto, S., et al. (2013). Evaluating fluoride adsorption by ZnO-based materials. Water Research, 47(10), 3484-3492.

[4] Iyer, R., & Pillai, A. S. (2023). AC-ZnO nanocomposite for groundwater defluoridation: Batch and column studies. Chemical Engineering Journal, 476, 146618.

[5] Mohapatra, M., et al. (2009). Review of fluoride removal from drinking water. Journal of Environmental Management, 91(1), 67-77.

[6] Poulsen, N., & Bjerring, M. (2022). Surface complexation of fluoride on ZnO: XPS and FTIR study. Langmuir, 38(14), 4312-4322.

[7] Reddy, G., & Iyer, R. (2022). Column performance of agricultural waste-derived adsorbent for defluoridation. Environmental Science and Pollution Research, 29(22), 33142-33156.

[8] Teutli-Sequeira, A., et al. (2020). A review of fluoride removal methods from drinking water. Engineering, 12(11), 779-802.

[9] WHO. (2022). Guidelines for Drinking-Water Quality (4th ed., incorporating first and second addenda). World Health Organization, Geneva.

[10] Zhang, C., et al. (2017). Enhanced fluoride removal by La-modified ZnO. Journal of Hazardous Materials, 332, 178-186.