Dynamic Study of Multilayered Adsorption Column for Fluoride Removal Using Aspen Adsim

Junaid Korai[1,*], Imran Unar[1], Waseem Abbas[1], Masroor Abro[1], Abdul Qudoos[2],

[1]Department of Chemical Engineering, MUET, Jamshoro, Pakistan
[2]Chemical Engineering Department, University Technology Petronas, Perak, Malaysia
[*]Corresponding author: koraijunaid@gmail.com

Abstract

Groundwater is the primary drinking water source for many rural communities in Pakistan. However, it often contains natural pollutants, such as fluoride, which can be toxic. The WHO sets the safe fluoride limit in water at 1-1.5 mg/L; levels above this can lead to health issues like fluorosis. Globally, approximately 200 million people are affected by fluorosis. In Pakistan, the Tharparker and Chachro regions have fluoride concentrations as high as 28.25 mg/L. Among various techniques developed for fluoride removal, adsorption is considered the most promising due to its cost-effectiveness and simplicity in design and operation. Although numerous adsorbents have been developed, commercialization is limited as most studies remain at the laboratory scale. This study used Aspen ADSIM, a process simulation and modeling tool, to develop and optimize single and multi-layered adsorption columns for fluoride removal from groundwater. Three adsorbents were tested: activated alumina, china clay, and zeolite. Parametric investigations, including inlet feed concentration and bed column height, were conducted through several simulations. Results indicate that these parameters significantly affect the adsorption column's performance. The multi-layered adsorption column demonstrated excellent performance for large-scale applications and commercialization potential. Practical implementation requires further experimental and economic analysis.

Keywords—Fluoride Adsorption, Aspen ADSIM, Multilayered Adsorption Column, Process Simulation

1 Introduction

Survival of living species on Earth without water is impossible. Groundwater is the main source of drinking water in rural areas of Pakistan. Unfortunately, groundwater is increasingly contaminated by naturally occurring chemicals like fluoride, which seeps out from fluoride-containing rocks [1], [2]. Fluoride presence in groundwater is a severe global problem. While fluoride levels between 1-1.5 mg/L are essential for dental health, levels exceeding this limit pose serious health risks [3]. Over 260 million people globally consume water with elevated fluoride levels [4]. Fluoride is widely distributed in both natural and anthropogenic forms on the Earth's surface. It enters groundwater through the gradual dissolution of fluorine-bearing rocks. High fluoride concentrations primarily result from industrial wastewater discharge, including silicate, porcelain, and semi-conducting materials production, electro-deposition, Coal-driven power stations, brick production, and light metal smelting [5], [6], [7]. The impact of fluoride on living species depends on its concentration and the duration of exposure. Fluoride toxicity primarily affects the gastrointestinal tract upon ingestion, causing irritation resulting from the creation of hydrofluoric acid [8]. It disrupts enzymes, oxidative phosphorylation, glycolysis, and coagulation. Individuals with kidney disease are especially vulnerable. High doses of fluoride adversely impact kidney function in both animals and humans [9], [10]. Fluoride also accumulates in the pineal gland, teeth, and bones, affecting brain function and potentially increasing the risk of bladder cancer in occupational settings [11]. Developing effective technologies and scaling up to remove fluoride from drinking water is crucial due to its harmful effects on health. Researchers have developed numerous technologies for fluoride removal [12]. Among them, adsorption is widely used due to its effectiveness,

ISSN: 2523-0379 (Online), ISSN: 1605-8607 (Print)
DOI: https://doi.org/10.52584/QRJ.2201.02

cost-efficiency, and simplicity in design and operation [13]. Various adsorbents, both conventional and unconventional, have been employed, including alumina, clay, carbon, iron, and bio-based adsorbents [14], with alumina-based adsorbents showing a strong affinity for fluoride. The US EPA and WHO have recognized activated alumina as the best available technology for fluoride removal [15]. However, commercial application is limited as most studies are conducted at the laboratory scale. This is because synthesizing adsorbents on a large scale and conducting adsorption studies, along with evaluating operating parameters and optimization, incur high costs, time consumption, and complexity in process design and optimization. Additionally, ensuring maximum removal efficiency and positive results remains challenging [16]. This study developed a simulated framework of single-layer and multi-layer adsorption columns in Aspen ADSIM V10 to evaluate the performance of various adsorbents, both individually and in combination [17], for fluoride removal from groundwater. Complex mathematical models for dispersion and convection of adsorbate, simple convective equations, and Langmuir isotherms are used to optimize operating parameters, achieving successful convergence through various simulations.

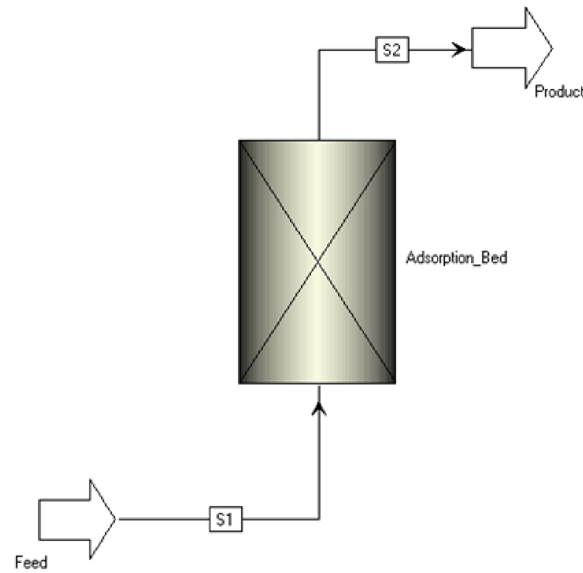


Fig. 1: Single Layer Adsorption Column in Aspen Adsim V10

2 Methodology

The adsorption column models were simulated to observe the efficiency of fluoride removal by various adsorbents, both with single and multi-layer configurations. After reviewing the literature, three adsorbents were selected for their proven affinity with fluoride: activated alumina [18], china clay [19], and zeolite [20]. The model utilized data extracted from existing published studies on fluoride uptake using these adsorbents. These studies involved making a stock solution with a constant fluoride concentration and examining the adsorbents' adsorption capacity for different conditions.

A set of equations, including algebraic equations (AEs), ordinary differential equations (ODEs), and partial differential equations (PDEs), are applied in Aspen ADSIM to model the adsorption system, using initial and final boundary conditions. The Upwind Differencing Scheme-1 (UDS-1) was chosen for simulations due to its favorable features, such as low simulation time, realistic and accurate results, and feasibility without additional conditions. This method requires minimal time to solve the equations. The column model first simulated a single adsorbent layer using Aspen ADSIM, as depicted in Figure 1. The adsorption column for each of the three adsorbents was separately configured in the Aspen simulation environment to observe their individual effects. Detailed submission guidelines can be found on the author resources Web page. All authors are responsible for understanding these guidelines before submitting their manuscript.

Polluted feed was introduced from the lower base of the adsorption column, while the purified water was collected at the upper part, typical of an adsorption column setup. Inlet feed characteristics were tailored for each adsorbent. Mass transfer coefficients were sourced from experimental studies of the selected adsorbents, and additional factors, such as isotherm standards, were computed with the conversion equations from Aspen tool (IP1 & IP2). Pressure and temperature were held steady throughout the simulations. Once individual adsorption column models were established for each adsorbent, operating parameters were tested separately to determine their fluoride ion exchange affinity.

Subsequently, the models for the three individual adsorbents were combined to form the multilayer adsorption column, the primary focus of this study. The performance of the multilayered adsorption column under varying operating parameters was evaluated, as illustrated in Figure. 2.

The simulation of the model was conducted under several standard assumptions typical for adsorption models in tools like Aspen ADSIM®. It assumed plug flow for fluid behavior, ensuring uniform velocity profiles and incorporating axial dispersion effects. The pressure drop in the laminar liquid phase was treated

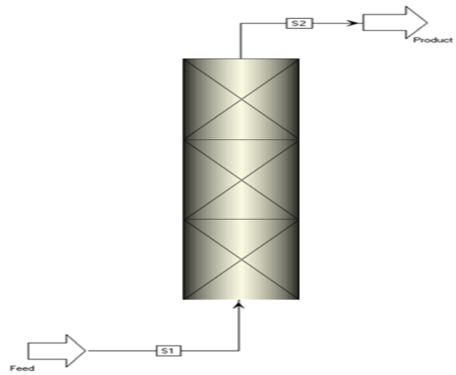


Fig. 2: Multilayered Adsorption Column in Aspen Adsim V10

as constant, maintaining momentum balance. Radial mixing within the system was considered variable, impacting overall mass transfer characteristics. The mass transfer was described using lumped resistance models, with options available for separate treatment of macro and micro pore effects. Typically, a constant mass transfer coefficient was assumed, utilizing default values provided by ASPEN Adsim®. The model also accommodated adsorption isotherms for both single and competitive multicomponent scenarios, offering flexibility in simulating diverse adsorption conditions.

Model Hypotheses

A Linear Lumped Resistance (LLR) approach was chosen, with the assumption that the force causing the mass transfer of each module varies linearly with either the concentration in the liquid or the packing in the solid phase. This assumption is stated through this correlation:

$$\rho_s \frac{\delta w_i}{\delta_t} = MTC_s(c_i - {c_i}^*) \tag{1}$$

Component Conversion

The mass balance equation in general form to liquid phase adsorption is given by:

$$-\epsilon_i E_i \frac{\delta^2 c_i}{\delta z^2} + \frac{\delta}{\delta z}(v_i c_i) + \epsilon_i \frac{\delta c_i}{\delta t} + \rho_s \frac{\delta w_i}{\delta t} = 0 \tag{2}$$

The initial term in the provided equation denotes the dispersion component, while the subsequent term indicates the convective force involved. The third term reflects accumulation, and the final term describes the mass flow from the liquid phase to the solid phase.

$$\frac{\delta w_k}{\delta} = MTC_{sk}({w_k}^* - w_k) \tag{3}$$

Convection with Constant Dispersion

The simulation utilized the Convection with Constant Dispersion option, incorporating a dispersion term in the material balance equations for the adsorption bed. A constant dispersion coefficient was applied uniformly across the bed to solve these equations for all components involved in the process.

Isotherm Selection

During the liquid separation process, equilibrium adsorption departure and isotherms play crucial roles in adsorption design. Isotherms describe how the composition of the liquid phase reaches equilibrium with the actual loading rate. By understanding the feed components and using Langmuir equations, a model can be created to predict the performance of the adsorber under specified operational conditions. Input parameters derived from the Langmuir equation are given by:

$$w_i = \frac{IP_{1i} IP_{2i} c_i}{1 + IP_{2i} c_i} \tag{4}$$

Where IP1 is isotherm parameter inverse of the product of adsorbent capacity qmax and equilibrium constant KL and IP2 is expressed in terms of inverse of the capacity of adsorbent (1/qmax). Aspen Adsim has a list of adsorption isotherm models and can be selected as per the experimental or input data available with the user.

Numerous scientists have conducted experiments on the removal of fluoride ions from water through adsorption using activated alumina, zeolite, and china clay. This research modeled the data for these three adsorbents to examine their collective impact in a multi-layered adsorption column. Table 1 provides the key values employed in the simulation, obtained from either published sources or default settings in Aspen ADSIM.

To evaluate the performance of the adsorption column, a series of dynamic simulations were conducted with varying factors, such as the adsorbent depth, initial fluoride feed concentration, and flow rate. Table 2 has a list of varying factors with values for single-layer adsorbents (activated alumina, zeolite, and china clay), while Table 3 presents the parameters for multi-layer adsorbents. ’

3 Result and Discussion

The model of a single-layer adsorption column was constructed using Aspen ADSIM to assess its effectiveness in removing fluoride ions from water. Three different adsorbents were utilized in this study, with

TABLE 1: Adsorbents Characteristics Data

Parameter	Activation Alumina	Zeolite	China Clay
Inter Particle Porosity	0.412 m3 void/m3 bed	0.391 m3 void/m3 bed	0.451 m3 void/m3 bed
Intra Particle Porosity	0.4 m3 void/m3 bed	0.213 m3 void/m3 bed	0.28 m3 void/m3 bed
Material Mass Density	2.65 g/cm3	1.98 g/cm3	1.76 g/cm3
Mass Transfer Coefficient	0.5 sec-1	0.5 sec-1	0.5 sec-1
IP1 (Langmuir Isotherm)	0.423	0.24	0.124
IP2 (Langmuir Isotherm)	0.642	0.45	0.312

TABLE 2: Simulated Cases for different Adsorbents on Single-layered Adsorption Column

Case	Initial Concentration (mol/L)	Feed Flow (L/min)	Bed Height (cm)
1	0.001579	0.150	10
2	0.001579		20
3	0.001579		30
4	0.002632		10
5	0.002632		20
6	0.002632		30
7	0.003684		10
8	0.003684		20
9	0.003684		30

each individual adsorbent investigated under varying parameters such as bed height and initial concentration, while maintaining a constant inlet feed flow rate. Subsequently, a multi-layer adsorbent column setting was developed to examine the combined impacts of these adsorbent materials under varying parameters. The outcomes of these simulations are elaborated on in the following sections. As shown in Figure 3., a Fluoride uptake in a single-layer adsorption column using activated alumina was found to be directly proportional to the bed depth of the column. The exhaustion period of the column increased with the bed depth, particularly at lower feed concentrations. Optimal results were achieved with activated alumina, showing a saturation time of 400 minutes at a bed height of 30 cm and an initial feed concentration of 0.002632 mol/liter.

For zeolite, the bed's exhaustion time increased with the bed height, especially at low initial fluoride concentrations. Zeolite exhibited a maximum saturation time of 160 minutes at a bed height of 30 cm with an initial feed concentration of 0.001579 mol/liter as depicted in Figure 4.

China clay's performance was directly related to the bed height of the column, as shown in Figure 5, with the exhaust time increasing as bed height increased, especially at low initial fluoride concentrations. At a 30 cm bed height and an initial fluoride concentration of 0.001579 mol/liter, China Clay maintained a fluoride-free outlet for 1 hour.

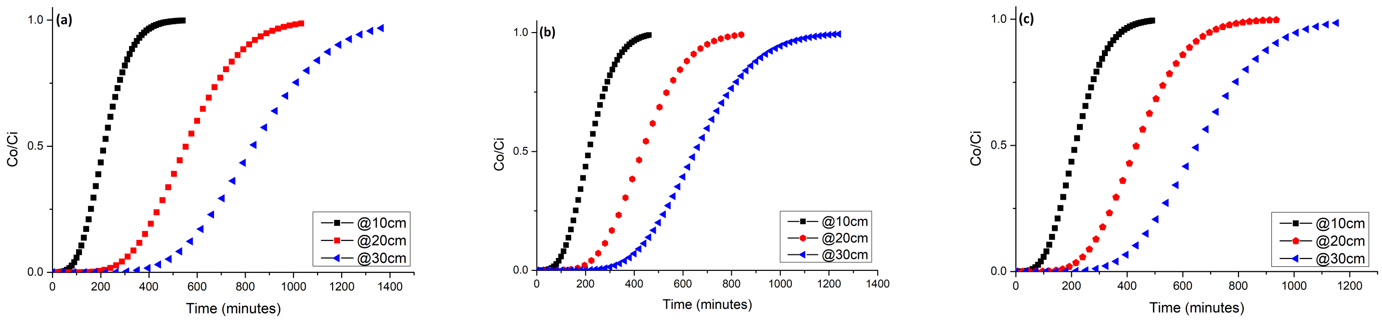
The study examined the impact of varying bed heights (10, 20, and 30 cm) and different inlet fluoride concentrations (0.001579, 0.002632, and 0.003684 mol/liter) at a constant feed flow rate (0.015 mol/liter) on the performance of a multilayered adsorption column, as shown in Figure 6. Results demonstrated a direct correlation between bed height and fluoride removal efficiency. Specifically, as the bed height increased, the exhaust time also increased, particularly at lower initial fluoride concentrations. The multilayered adsorption column exhibited peak performance, effectively removing fluoride for up to 10 hours at a 30 cm bed height and an initial concentration of 0.001579 mol/liter. Ultimately, the same bed height with an equal ratio of different adsorbents resulted in a longer time to saturate the bed, showcasing the robust impact of multilayered technology. This may be due to the varying electron affinity of fluoride with alumina, clay, and zeolite.

In Figure 7, the multilayered adsorption column exhibited optimal performance at an initial feed concentration of 0.001579 mol/L. At this concentration, the minimum saturation time was 180 minutes for a 10 cm bed height, while the maximum saturation time was 680 minutes for a 30 cm bed height. This is attributed to the rapid uptake of fluoride ions within the adsorption beds. Notably, the saturation time for the multilayered column was significantly longer than that observed for columns with individual adsorbents of similar bed height, highlighting the enhanced performance of the multilayered adsorption system.

To further evaluate the performance of the multilayered adsorption column, data were compared with that of single-layer adsorption columns at the same bed height as shown in Figure 8. The multilayered adsorption column demonstrated exceptional results, showing significantly longer saturation times at 50% bed exhaust. Peak performance was observed at a 30 cm bed height, where the multilayered bed remained unsaturated for over 610 min minutes. In contrast,

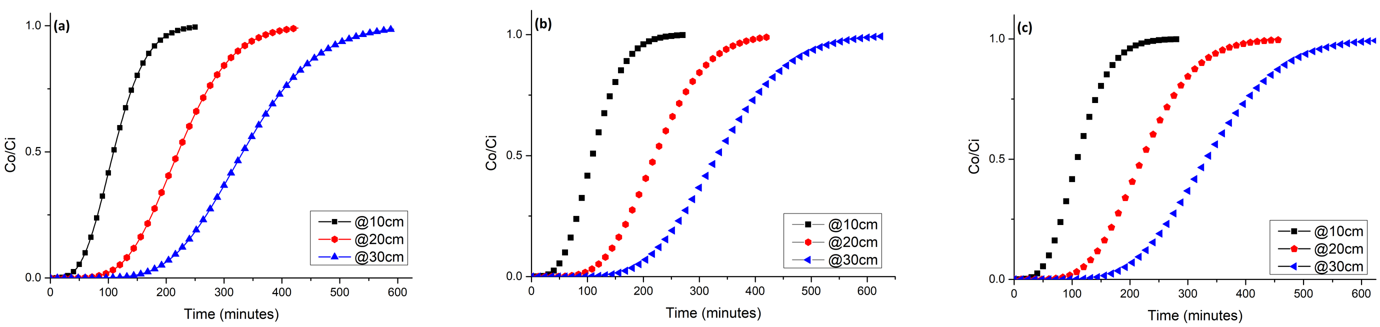
TABLE 3: Simulated Cases for Multilayered Adsorption Column

Case	Initial Concentration (mol/L)	Feed Flow (L/min)	Bed Height (cm)		
			Activated Alumina	Zeolite	China Clay
1	0.001579	0.150	3.333	3.333	3.333
2	0.001579	0.150	6.666	6.666	6.666
3	0.001579	0.150	10	10	10
4	0.002632	0.150	3.333	3.333	3.333
5	0.002632	0.150	6.666	6.666	6.666
6	0.002632	0.150	10	10	10
7	0.003684	0.150	3.333	3.333	3.333
8	0.003684	0.150	6.666	6.666	6.666
9	0.003684	0.150	10	10	10



(a) (b) (c)

Fig. 3: Breakthrough Curves of Activated Alumina at Initial Concentrations (a) 0.001579 (b) 0.002632 (c) 0.03684 mol/L



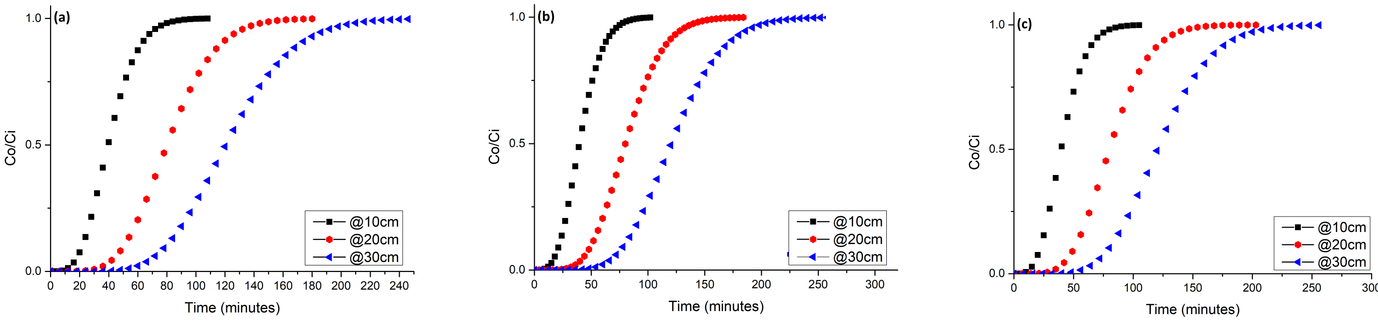
(a) (b) (c)

Fig. 4: Breakthrough Curves of Zeolite at Initial Concentrations (a) 0.001579 (b) 0.002632 (c) 0.03684 mol/L

the leading single-layer adsorbent, activated alumina, reached saturation at 390 minutes. This highlights the superior efficiency of the multilayered adsorption column.

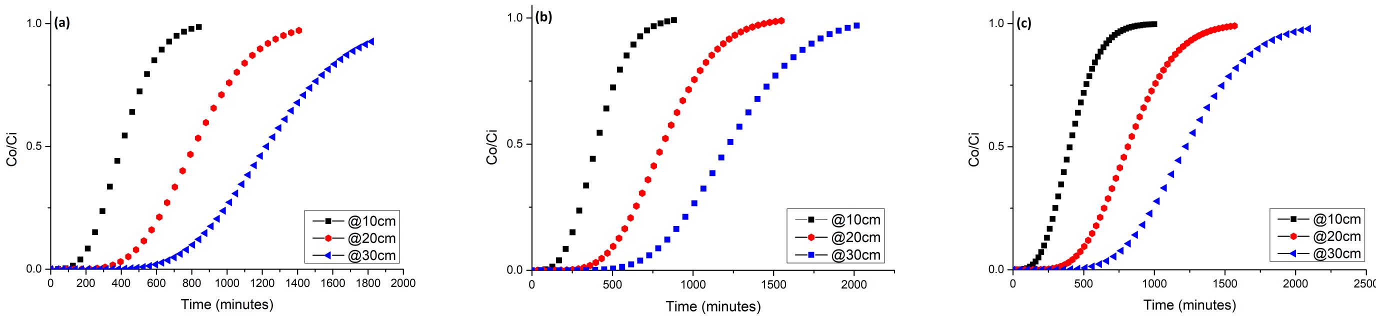
4 Conclusion

The performance of single and multilayered adsorption columns for fluoride removal from groundwater was studied. The analysis indicated that activated alumina has a strong affinity for fluoride, with a maximum unsaturated time of 390 minutes, making it the leading adsorbent. The fluoride adsorption rate significantly inclined to the porosity of the adsorbent bed, bed height, initial fluoride concentration, and contact time between the adsorbent and adsorbate. Additionally, diffusion of particles and adsorbent size also affected the removal efficiency. The bed capacity under dynamic conditions was determined using the Bohart-



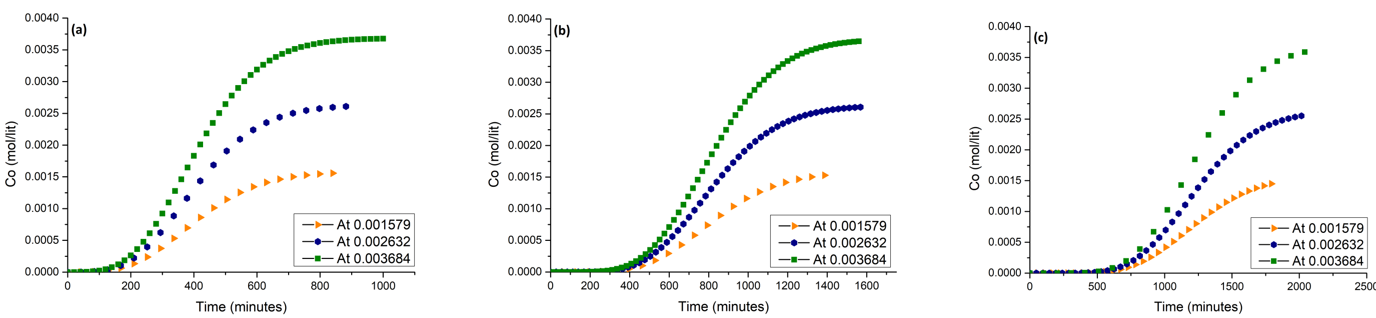
(a) (b) (c)

Fig. 5: Breakthrough Curves of China Clay at Initial Concentrations (a) 0.001579 (b) 0.002632 (c) 0.03684 mol/L



(a) (b) (c)

Fig. 6: Breakthrough Curves of Multilayered Adsorption Column at Initial Concentrations (a) 0.001579 (b) 0.002632 (c) 0.03684 mol/L



(a) (b) (c)

Fig. 7: Breakthrough Curves of Multilayered Adsorption Column at Initial Concentrations at (a) 10 (b) 20 (c) 30 cm

Adams equation, with constant values predicted from breakthrough points via plots of ln[(Co/Ct)-1] against time (t). The multilayered adsorption column showcased a superior fluoride removal capacity compared to its single-layer counterpart, with the bed achieving saturation after a significantly prolonged duration. This extended saturation period underscores the column's enhanced efficiency in fluoride ion sequestration. Notably, the multilayered adsorption column exhibited remarkable performance, with substantially longer saturation times observed at 50% bed exhaust. Optimal results were achieved with a 30 cm bed height, where the multilayered configuration remained unsaturated for over 610 minutes, highlighting its robust fluoride removal capability. This study successfully developed a model for fluoride removal using a multilayered adsorption column, demonstrating significant potential for real-world applications. The simulation results indicate that the proposed model could efficiently treat real water samples, suggesting its viability for practical

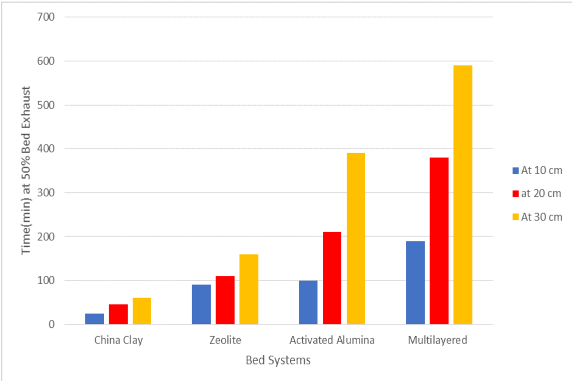


Fig. 8: Performance comparison of the multilayered adsorption column, with single-layer adsorption columns

use.

To advance this research, a pilot-scale facility should be established to verify the simulation results and conduct further experiments. This facility would allow for the performance evaluation of the newly designed multilayered ad-sorption column under real-world conditions. Experimental analysis on the multilayered adsorption column is necessary to validate the simulation results, as no experimental work has been conducted on an adsorption column with multilayered adsorbents to date. The outcomes of this study can be instrumental in developing a comprehensive computational model for adsorption, which would be beneficial for advanced research and practical applications in fluoride removal from groundwater.

References

[1] Z. U. Rahman, "A Review of Groundwater Fluoride Contamination in Pakistan and an Assessment of the Risk of Fluorosis," Fluoride, 2018.

[2] E. Shaji, "Fluoride Contamination in Groundwater: A Global Review of the Status, Processes, Challenges, and Remedial Measures," Geoscience Frontiers, vol. 15, no. 2, p. 101734, 2024.

[3] A. Malik, "Health Risk Assessment of Nitrates and Fluorides Ingestion and Geochemical Evaluation of Groundwater Characteristics in Semi-Arid Regions," International Journal of Environmental Science and Technology, pp. 1-28, 2024.

[4] A. Kerketta, "Groundwater Fluoride Prediction Modeling Using Physicochemical Parameters in Punjab, India: A Machine-Learning Approach," Frontiers in Soil Science, vol. 4, p. 1407502, 2024.

[5] J. Wei, "A Novel Hybrid Approach for Revealing the Genesis and Spatiotemporal Variation of High Fluoride Groundwater Under Natural and Anthropogenic Influences," Journal of Hydrology, p. 131782, 2024.

[6] E. D. Sunkari, "Hydrogeochemistry, Sources, Enrichment Mechanism and Human Health Risk Assessment of Groundwater Fluoride in Saboba District in the Oti Sub-Basin of the Volta River Basin, Northern Ghana," Groundwater for Sustainable Development, vol. 25, p. 101132, 2024.

[7] M. O. Awaleh, "Spatial Distribution, Geochemical Processes of High-Content Fluoride and Nitrate Groundwater, and an Associated Probabilistic Human Health Risk Appraisal in the Republic of Djibouti," Science of The Total Environment, vol. 927, p. 171968, 2024.

[8] J. Zhou, D. Sun, and W. Wei, "Necessity to pay attention to the effects of low fluoride on human health: an overview of skeletal and non-skeletal damages in epidemiologic investigations and laboratory studies," Biological Trace Element Research, vol. 201, no. 4, pp. 1627-1638, 2023.

[9] F. A. Dar, "Fluoride in Drinking Water: An In-Depth Analysis of Its Prevalence, Health Effects, Advances in Detection and Treatment," Materials Today: Proceedings, 2023.

[10] K. K. Tiwari, "Recent Advancements in Fluoride Impact on Human Health: A Critical Review," Environmental and Sustainability Indicators, p. 100305, 2023.

[11] L. Valdez-Jiménez, "Effects of Fluoride on the Central Nervous System," Neurología (English Edition), vol. 26, no. 5, pp. 297-300, 2011.

[12] N. Arab, "Approaches for the Efficient Removal of Fluoride from Groundwater: A Comprehensive Review," Toxics, vol. 12, no. 5, p. 306, 2024.

[13] Z. Zeng, "The Model and Mechanism of Adsorptive Technologies for Wastewater Containing Fluoride: A Review," Chemosphere, p. 139808, 2023.

[14] W. Z. Gai, "A Comprehensive Review of Adsorbents for Fluoride Removal from Water: Performance, Water Quality Assessment and Mechanism," Environmental Science: Water Research & Technology, vol. 7, no. 8, pp. 1362-1386, 2021.

[15] L. R. Brunson, "Methods for Optimizing Activated Materials for Removing Fluoride from Drinking Water Sources," Journal of Environmental Engineering, vol. 142, no. 2, p. 04015078, 2016.

[16] J. Singh, "Fluoride Ions vs Removal Technologies: A Study," Arabian Journal of Chemistry, vol. 9, no. 6, pp. 815-824, 2016.

[17] J. Haydary, Chemical Process Design and Simulation: Aspen Plus and Aspen Hysys Applications. John Wiley & Sons, 2019.

[18] U. Kumari, "A Novel Acid Modified Alumina Adsorbent with Enhanced Defluoridation Property: Kinetics, Isotherm Study and Applicability on Industrial Wastewater," Journal of Hazardous Materials, vol. 365, pp. 868-882, 2019.

[19] P. K. Gogoi, "Fluoride Removal from Water by Adsorption on Acid Activated Kaolinite Clay," 2008.

[20] Y. Sun, "Removal of Fluoride from Drinking Water by Natural Stilbite Zeolite Modified with Fe (III)," Desalination, vol. 277, no. 1-3, pp. 121-127, 2011.