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Case Study

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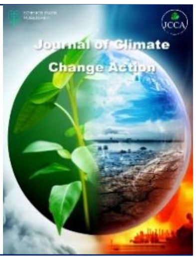

Journal of Climate Change Action

Utilizing pearl millet husk carbon as an adsorbent for groundwater defluoridation: a case study from Rajasthan, India

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Abstract

The current research focuses on the creation of an innovative and economically viable fluoride removal strategy that can be employed in developing nations rural areas. This study investigates the effectiveness of pearl millet husk, an easily accessible agricultural waste, as an inexpensive adsorbent for eliminating fluoride from groundwater. Additionally, the effects of other variables on fluoride removal were examined, including initial fluoride concentration, adsorbent dosage, contact time, and presence of different anions. A 99.42 ± 0.5% fluoride removal efficiency was achieved under optimal conditions with 0.3 g of adsorbent per 100mL of water. According to adsorption kinetics, the regression values indicate that the pseudo-second-order model was more validated compared to the pseudo-first-order model. The adsorption experiments were conducted using a fixed amount of adsorbent (0.3 g) and varying initial concentrations of adsorbate (5, 10 and 15 mg/L) solutions. The suitability of the obtained data for fitting the Langmuir adsorption isotherm was assessed. Fluoride sorption onto pearl millet husk biochar (BHB) resulted in a high R^2 value of 0.99, indicating strong correlation. The Freundlich isotherm coefficient represents the deviation from linearity in the adsorption process. The constants k and n were determined based on the gradients of the Freundlich plots. The n values lie within the range of 1–10, confirming favorable conditions for adsorption. The values of k and n were 1.48 and 1.342, respectively. The study has demonstrated that using agricultural waste from the Bajra crop to produce value-added products like bio adsorbents for fluoride adsorption results in waste minimization, water defluoridation and the development of inexpensive adsorbent that effectively removes fluoride from water, thereby reducing the risk of fluorosis.

Keywords: Groundwater defluoridation; pearl mille husk; bio-adsorbent; fluoride removal; adsorption kinetics; Rajasthan groundwater; isotherms; agricultural waste reuse

List of abbreviations

BHB	Bajra Husk Biochar
WHO	World Health Organization
RO	Reverse Osmosis
EC	Electrical Conductivity
APHA	American Public Health Association

WC	Washed and Carbonized
UC	Unwashed and Carbonized
WN	Washed and Noncarbonized
UN	Unwashed and Noncarbonized
BIS	Bureau of Indian Standards
FTIR	Fourier Transform Infrared Spectroscopy

1. Introduction

The surface of the Earth is approximately 71% covered in water, but about 97% of this water exists as saline ocean water, which is unsuitable for human consumption. Freshwater resides in soil, polar ice caps, glaciers, and the atmosphere, making up just 3% of the total water resources Earth's surface. Given that freshwater only accounts for 0.5% of the total, water is essential for life [1]. According to the United Nations International Children's Emergency Fund (UNICEF), four billion people are facing severe water scarcity for a month every year and also expected that around 700 million people will displace due to water scarcity, whereas 1 out of 4 children will face the water stress till 2040 [2].Approximately 50% of population dependent on groundwater for drinking whereas 70% of the global food production also dependent on groundwater[3]. Surface water and groundwater are the primary water sources for drinking, agriculture, and industry[4].As reported treating waste by waste considered as promising strategy; in treatment of different pollutant by agricultural waste like rice husk for fluoroquinolone removal, coconut coir dust for cationic dye removal, rice straw for tetracycline removal, walnut shell for methylene blue, rice husk ash for carboplatin, ibuprofen and diclofenac[5]. Due to the scarcity of surface water and the limited availability of high-quality groundwater, approximately one-third of the global population, mainly in arid and semi-arid nations, relies on groundwater for their daily water demands, especially for drinking [6].

Groundwater dependency is increasing rapidly as the population rises. In India, the states of Punjab, Haryana, Delhi, and Rajasthan have groundwater development levels above 100%. In these states, the annual groundwater recharge is less than groundwater outflow. In Rajasthan, groundwater resources are overexploited. Rajasthan is the largest state in the nation, covering 3.42 lakh square kilometers, accounting for 10.4% of the total land area and 5.5% of the population, but just 1% of the water resources in the nation. The lack of surface water has led to groundwater becoming the primary drinking water supply. Groundwater provides 91% of the state's drinking water needs [7].

One of the biggest problems with groundwater pollution is excess fluoride from various point and nonpoint sources contaminating groundwater [8]. Fluoride has a crucial role in preserving human health and strength. This one is the component with the greatest electronegative property. In modest amounts, it normalizes bones and aids in the development of tooth enamel. “However, human health is negatively impacted by excessive fluoride.”

The World Health Organization (WHO) [9] reported that high concentrations of fluoride and other potentially toxic elements of health concerns have rendered many groundwater sources unsuitable for drinking purposes in different parts of the world [10].

The WHO permits fluoride levels in groundwater below 1.5 mg/L. High concentrations of contaminants, such as salinity, nitrogen, phosphorus, fluoride, and arsenic, threaten groundwater quality globally, affecting areas in nations such as India, China, the United States, Canada, Spain, Iran, Pakistan, and Namibia, according to studies on groundwater geochemistry conducted across a variety of geological and climatic regions [11-13]. Particularly common in Asian and African nations, geogenic fluoride (F^-) poisoning of groundwater affects areas in Sri Lanka, India, Pakistan, China, Iran, and other countries [14-16].

Safe drinking water depends on the quality of the groundwater. Excessive fluoride exposure can result in health problems such as dental and skeletal fluorosis, which can produce symptoms like stiffness, joint discomfort, and increased bone density at concentrations of 4–8 mg/L [17]. Additionally, regions of Asia and Africa have observed "crippling fluorosis," a disorder that impacts the kidney, liver, and neurological system [18]. Researchers have also linked high fluoride levels to cognitive effects in children, including decreased IQ and reduced growth hormone production [19].

To remove excess fluoride, different methods are used, such as coagulation-precipitation adsorption [20], electro-coagulation [21], ion exchange [22], and nanofiltration [23]. For sustainable fluoride removal, more recent techniques use microalgae bio adsorbents or modified activated carbon from coconut shells [24, 25]. However, issues such as high costs and operational complexity constrain commercial adoption [26].

Utilizing agricultural waste as a bio adsorbent provides a sustainable method of waste management and fluoride mitigation. Water treatment has shown success with bio adsorbents such as millet husks, rice bran, coconut shells, soybean hulls and sugarcane bagasse [20, 27]. This study explores the potential of Pearl Millet husk (bajra -*Pennisetum glaucum*), widely grown in rural Rajasthan, as a bio adsorbent for fluoride removal. By managing agricultural waste, using bajra husks could offer farmers additional revenue while simultaneously offering a cost-effective way to mitigate fluoride [1].

2. Materials and methods

2.1. Sample collection

We obtained the bajra husk (agricultural waste) from Krishi Vigyan Kendra in Kishangarh. To remove all the dust and contaminants, the sample was carefully cleaned with reverse osmosis (RO) water. The washed sample, along with the unwashed sample, was kept separately for drying for two days. After the two sets of samples (washed and unwashed) got dried completely, they were finely ground using a mixer grinder. The groundwater samples were taken specifically from bore wells with individual grab sampling. Groundwater samples were collected from bore wells using individual grab sampling.

2.2. Preparation of stock and working fluoride solutions

All fluoride solutions were prepared using analytical grade sodium fluoride (NaF), which served as the primary source of the fluoride ion (F^-).

A stock fluoride solution of 1000 mg/L was prepared by accurately dissolving 2.21 g of NaF (calculated molecular weight 41.99 g/mol) in 1000 mL of double-distilled water in a volumetric flask. This solution was stored at 4°C to maintain stability.

Working fluoride solutions of the required concentrations (5, 10, and 15 mg/L) for batch experiments were prepared daily by precise volumetric dilution of the 1000 mg/L stock solution. The concentrations of these working solutions were routinely verified using a spectrophotometer before their use in the adsorption experiments.

2.3. Biochar preparation

Bajra husk, a finely powdered substance, was used to produce biochar. Biochar was produced via the slow pyrolysis process; a promising thermal decomposition technique [28]. The powdered and dried bajra husk was kept in a muffle furnace in a stainless-steel vessel with a tight-fitting lid. For the manufacture of biochar, an indigenously modified furnace pyrolysis; muffle furnace (model: MSW-251) was set to 500 °C at a heating rate of 20 °C/min and residence time of 4 hours with all the safety precautions. The container was thickly filled with the material to avoid the oxygen presence. The ideal pyrolysis conditions were employed, that produced the highest yield with the least amount of ash. The same method was followed for both washed and unwashed samples [29].

2.4. Groundwater sample collection

Groundwater samples were obtained from bore wells with depth of 150 m at random locations in 4 villages near the Central University of Rajasthan during March 2024. The sampling locations were;1.Mundoti (26°38'23"N; 75°2'9"E), 2. Bandar Sindri (26°36'7"N; 75°2'16"E), 3.Tilonia (26°37'32"N; 74°59'50"E), and 4.Nalu (26°39'59"N; 74°60'36"E) as shown in Figure 1. Samples were collected using the low-density polyethylene (LDPE) sampling bottles and preserved at 4 °C to ensure the integrity of the samples.

2.5. Preliminary analysis of groundwater

The sampling protocol followed the standard methods outlined by the American Public Health Association (APHA, 2023). Samples of groundwater were collected for a range of physicochemical analysis such as pH (electrometric method No. 4500 B), electrical conductivity (EC) (method No. 2510), alkalinity (titration by H_2SO_4 method No. 2320), fluoride (SPADNS method No. 4500- F^- D), hardness (titration by EDTA method No. 2340.C), chloride (argentometric method No. 4500- Cl^- - B) and sulphates (method No. 4500- S^{3-}).

Using a pump, groundwater was directly collected from the borewell's exit in one-liter bottles that had been previously sanitized and the bottles were pumped for approximately one minute. The samples were sent to the lab right away for various physicochemical analysis.

2.6. Adsorption study

Several batch tests were conducted to evaluate the BHB adsorbent's defluoridation performance and to optimise the various parameters considered for the maximum removal of fluoride levels. The research used natural local water samples with elevated fluoride content. We analyzed the fluoride levels before and after treatment. Each batch experiment involved adding weighed amounts of adsorbent BHB to 150 mL Erlenmeyer flasks containing 100 mL water sample. Afterward, a mechanical shaker (M/s. iGene labserve) was used to shake the samples at room temperature at 200 rpm. Afterwards, the optimising parameter took the aliquots in 10 mL increments at various intervals (30, 60, 90, 120, 150, 180 minutes). Before fluoride analysis, the samples were filtered using Whatman No. 1 filter paper. Plotting the graphs included the average results from all three adsorption trials carried out in duplicate. The following formula was used to determine the adsorption efficiency (%) and residual fluoride concentration (mg/L) for the adsorbent at a particular contact period (Equations 1 and 2) [30-32].

$$\textbf{Fluoride adsorption \%} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

$$q_{eq} = (C_0 - C_e) \times \frac{V}{m} \quad (2)$$

where C_0 is the initial fluoride concentration, C_t or C_e is the residual fluoride concentration (mg/L) at time in Equation 1, whereas in equation 2; q_{eq} represents the amount of adsorbate accumulated on the adsorbent surface, V is the volume of solution in Liters, and m is the mass of adsorbent in grams.

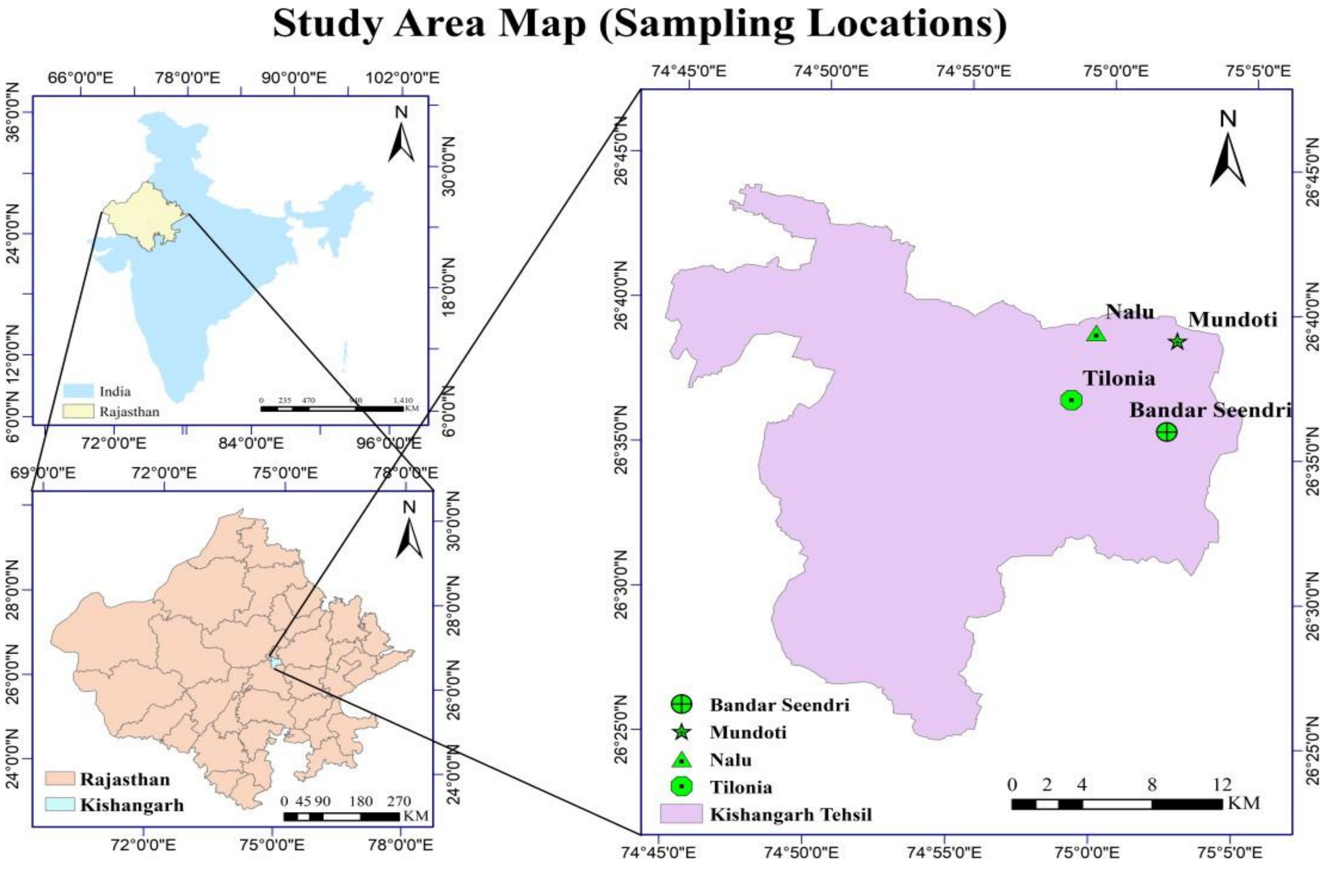

Figure 1. Study area map.

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2.7. Optimization of different parameters

A variety of factors affect the ability of adsorbent to defluoridate. In order to maximize performance, optimization was conducted by varying one parameter at a time while keeping the other values constant. Eventually, they optimised the adsorbent's defluoridation efficiency one factor at a time. The most effective conditions for defluorination were found by optimising several factors, such as the initial concentration, contact time, adsorbent dose, and various adsorbent forms. All batch adsorption studies were performed at room temperature and note the lack of variable temperature experiments.

2.8. The impact of various adsorbent forms

The objective is to assess the effectiveness of various forms of the adsorbent (Bajra husk) in removing fluoride, including washed and carbonized (WC), unwashed and carbonized (UC), washed and noncarbonized (WN), and unwashed and noncarbonized (UN) forms. 0.1g of each adsorbent was added to a 100 mL ground water sample which is having high fluoride concentration taken in 150 mL conical flasks. Then the samples were incubated to 3 hours at 200 rpm. 10 mL of aliquots were withdrawn at every 30 minutes. Following incubation, each set of experiments, residual fluoride ion concentration and percentage adsorption were assessed.

2.9. Effect of adsorbent dose and contact time

The adsorbent material that exhibited the highest performance was employed to assess the effect of the adsorbent and the duration of contact on the effectiveness of defluoridation. Various doses of BHB adsorbent (0.1, 0.2, 0.3, and 0.4 g), were individually applied to separate flasks holding 100 mL of groundwater sample. Subsamples were extracted from each group of flasks containing varying amounts of adsorbent to determine the optimal contact time at certain intervals of 30, 60, 90, 120, 150, and 180 minutes. By applying the previously mentioned equations (Equation 1 and Equation 2) given earlier, the fluoride concentration and percentage of adsorption were computed for each sample.

2.10. Adsorption thermodynamics

To understand the nature and spontaneity of the adsorption process, the effect of temperature was evaluated by conducting adsorption experiments at 298 K, 308 K, and 318 K. The thermodynamic parameters, including the change in Gibbs free energy (ΔG^o), enthalpy (ΔH^o), and entropy (ΔS^o), were calculated using the following equations:

The Gibbs free energy (ΔG^o) is calculated using the distribution coefficient (K_d):

$$\Delta G^o = -RT \ln K_d \qquad (3)$$

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the absolute temperature (K), and Kd is the thermodynamic equilibrium constant (dimensionless), calculated as the ratio of equilibrium concentration in the solid phase (q_e) to the equilibrium concentration in the liquid phase (C_e):

$$K_d = q_e/C_e \qquad (4)$$

The enthalpy (ΔH^o) and entropy (ΔS^o) are determined from the van't Hoff equation:

$$\ln K_d = (\Delta S^o)/R - (\Delta H^o)/RT \qquad (5)$$

A plot of ln K_d versus 1/T yields a straight line where the slope is (ΔH^o)/R and the intercept is (ΔS^o)/R.

2.11. Effect of initial concentration and co-existing ions

100 mL each of different concentrations of 5, 10 and 15 mg/L of Fluoride solution was taken in different flasks in duplicate to estimate the impact of the starting fluoride concentration. Additionally, we included 3 genuine local environmental ground water samples with varying fluoride concentrations. The adsorbent dose for each flask was kept constant at 0.1g. Once the BHB adsorbent was added to the flasks, they were put in a shaking incubator and incubated for 3 hours at a stirring rate of 200 rpm. Residual fluoride levels and adsorption percentage were assessed at 30, 60, 90, 120, 150, and 180 minutes by collecting 10 mL samples at regular intervals.

2.12. Regeneration and reusability study

The reusability and stability of the BHB adsorbent were tested over multiple adsorption-desorption cycles to assess its practical applicability. Following the batch adsorption process, the spent BHB was separated and subjected to regeneration. A 0.1M NaOH solution was chosen as the regenerant due to its effectiveness in stripping adsorbed anions. The spent adsorbent was soaked in the NaOH solution for 24 hours, followed by repeated washing with deionized water until the washings reached a neutral pH. The regenerated adsorbent was then dried and reused for the next adsorption cycle under the optimal conditions (Adsorbent dose: 0.3 g/100 mL, initial concentration: 10 mg/L, Contact time: 120 min). This process was repeated for four consecutive cycles.

3. Results and discussion

3.1. Groundwater study of the selected villages

Groundwater from the nearby villages of Mundoti, Bandar Sindri, Tilonia, and Nalu was utilized for analysis of pH, electrical conductivity, total hardness, total alkalinity, sulphate, chloride, and fluoride. The groundwater pH ranged from 7.27 to 7.98. Total alkalinity ranged from 661.5 to 873 mg/l. Electrical conductivity varied from 0.703 to 2.03 mS/cm. Total hardness was found to be high in Bandar Sindri village and low in Mundoti, ranging from 240 to 516 mg/l. Fluoride concentration showed extremely high levels in Nalu and Mundoti (i.e., 12.5 and 10.75 mg/l, respectively), exceeding the permissible limit given by BIS. The cations magnesium and calcium ranged from 4 to 76 and from 236 to 440 ppm, respectively. Sulphate and chloride anions ranged from 21.53 to 11 and 46.48 to 307 ppm, respectively. In Nalu village, the region's fluoride concentration ranged from 3.5 to 12.5 ppm (Table 1).

This analysis proved that water sample from Nalu village has the highest fluoride content, which is 12.5 mg/l, hence selected for the further defluoridation experiments using BHB. So, more water sample has been collected from the village and conducted studies batch wise.

The research explores the use of bajra husk, an agricultural waste, as a probable bio-adsorbent for adsorbing fluoride from drinking water. Bajra cultivation is widespread in Rajasthan, and the husk currently has no commercial use. It was identified as a promising material for fluoride mitigation. The study aims to assess the effectiveness of bajra husk in defluoridation, which was obtained from the Krishi Vigyan Kendra in Kishangarh.

3.2. Characterization of biochar

3.2.1. Fourier transform infrared spectra (FTIR)

The FTIR spectra (Perkin Elmer spectrum 2400 series) of the raw BHB and the fluoride-loaded BHB are combined in Figure 2 to elucidate the mechanism of adsorption. The raw BHB spectrum shows a prominent, broad absorption band at 3200–3500 cm^{-1}, attributed to the O-H stretching of hydroxyl and N-H stretching of amine groups. These highly polar groups are identified as the primary active sites. The spectrum also features peaks characteristic of C=O stretching 1600–1650 cm^{-1} and C-O stretching 1000–1200 cm^{-1}.

After fluoride loading, the most significant change is the pronounced shift to a lower frequency and the reduction in intensity of the 3200– 3500 cm^{-1} band.

Table 1. Physico-chemical analysis of groundwater from different villages.Units of all parameters are in mg/l except EC (mS/cm) and pH.

Parameters	BIS Standards		Samples			
	Acceptable limit	Maximum limit	Mundoti Village	Bandar Sindri Village	Tilonia Village	Nalu Village
pH	6.5-9.5	No relaxation	7.27±0.28	7.98±0.42	7.35±0.35	7.48±0.40
EC	–	2500	703±24	2030±59	1562±46	1133±35
Total alkalinity	200	600	661.5±8.56	873±20	705±14	771.5±16
Total hardness	200	600	240±6.45	516±18	416±16	340±12
Chloride	250	1000	46.48±1.89	307±10.24	212.93±8.55	72.97±2.56
Sulphate	200	400	21.53±1.52	115±4.56	98.25±3.66	65±3.12
Fluoride	1	1.5	10.75±0.85	3.5±0.22	6.5±0.44	12.5±1.22

This change confirms that the O-H and N-H groups are consumed in the binding process. The observed spectral alteration provides definitive evidence that fluoride removal is a chemical adsorption process driven by a combined mechanism of strong hydrogen bonding (i.e., O-H···F$^-$) and electrostatic attraction between the protonated surface groups and the highly mobile fluoride anion. This molecular-level interaction validates BHB's high affinity for fluoride [34-35]. Additional peaks at 669, 749, 801, and 877 cm^{-1} might be due to the binding of fluoride [36]. The observation of a peak at 1385 cm^{-1} represents the presence of phenolic -OH or C-O bonds, which might be due to the adsorption of fluoride to the biochar; such functional groups shows strengthen interaction with F$^-$ ions [37].

3.2.2. Scanning Electron Microscopy (SEM)

The surface morphology of the raw BHB was examined using SEM (Q 150R S plus of Thermo Fisher Scientific), with the images presented in Figure 3(a). Raw BHB reveals a highly heterogeneous and porous surface structure. The material exhibits numerous irregular pores, channels, and crevices, which are characteristic features of pyrolyzed agricultural waste. This high degree of surface roughness and porosity is crucial, as it provides a significantly high surface area and a multitude of accessible channels and adsorption sites, directly contributing to the material's high adsorption capacity.

The image of the adsorbent after fluoride adsorption (BHB) in Figure 3(b) shows subtle changes to the morphology. While the primary carbon structure remains intact, some of the smaller pores appear less defined or partially filled, suggesting the successful deposition and lodging of the fluoride species onto the interior and exterior surfaces of the material.

3.2.3. Energy-dispersive X-ray (EDX)

EDX spectroscopy (PAN analytical (Empyrean)) was performed on both the raw and spent adsorbents to confirm elemental composition and provide semi-quantitative evidence of fluoride binding [37]. The results are summarized in Table 2 and correspond to the elemental maps presented alongside the SEM images.

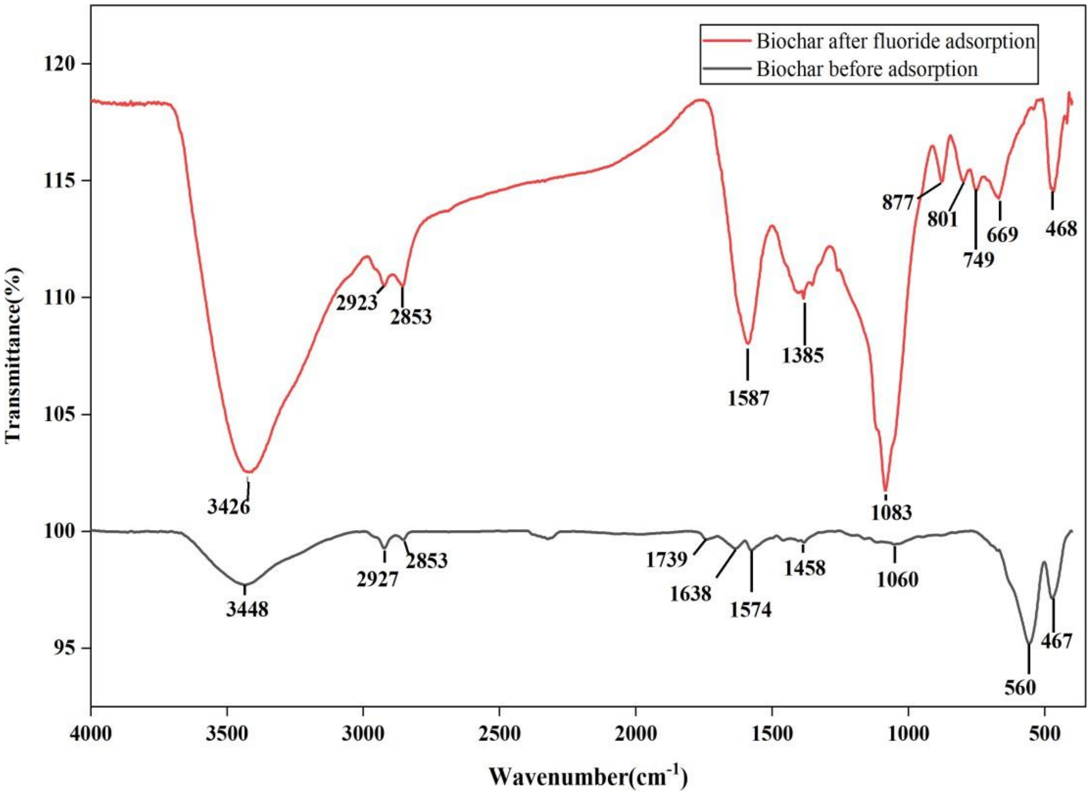

Figure 2. FTIR spectra Biochar before adsorption and Biochar after fluoride adsorption.

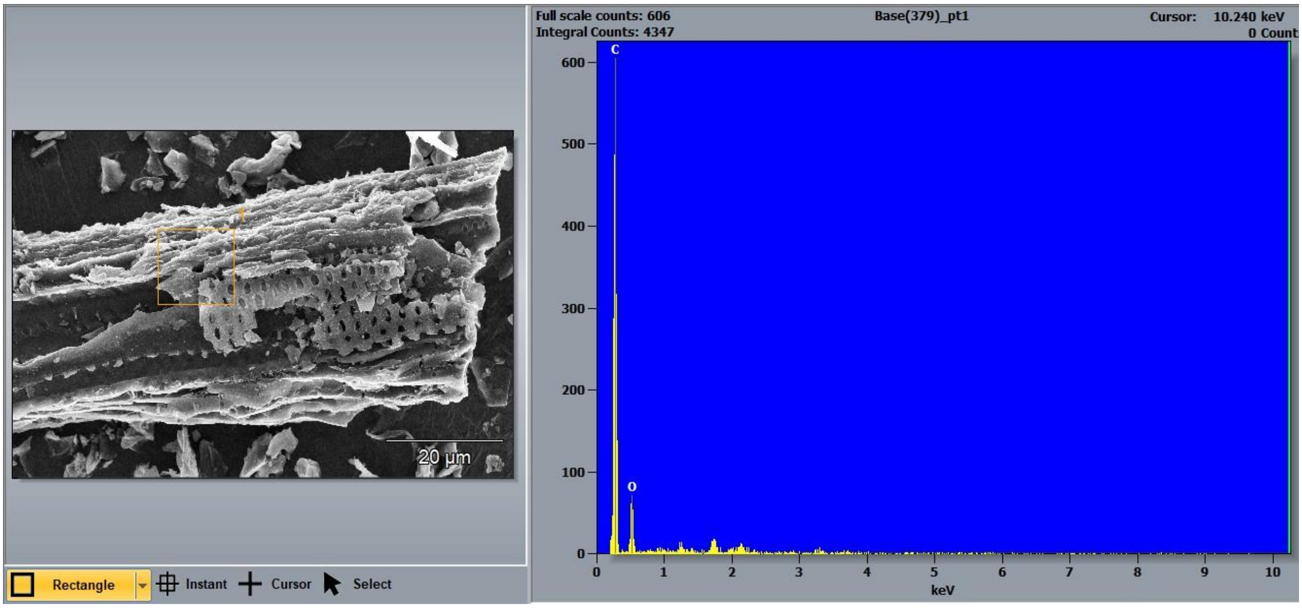

Figure 3. (a) SEM images of BHB (Before).

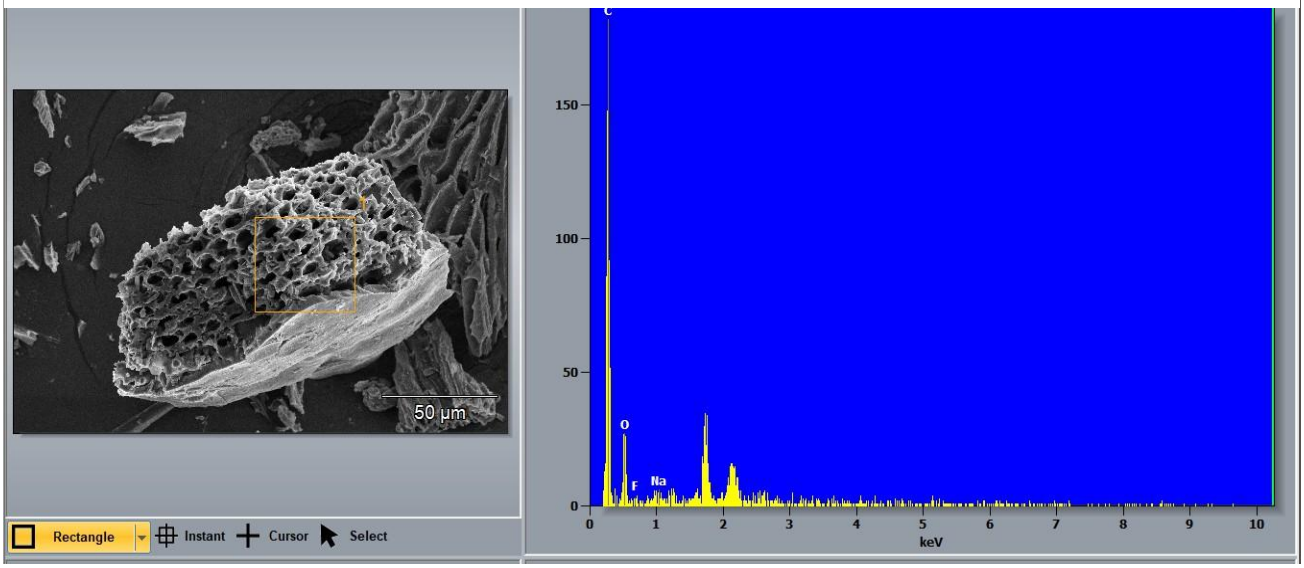

Figure 3. **(b)** SEM images of BHB with fluoride adsorbent (After).

Table 2. EDX Analysis.

Element	BHB (Weight%)	BHB -F (Weight%)	BHB (Atomic%)	BHB -F (Atomic%)
C	70.3	63.7	75.9	70.5
O	29.7	33.3	24.1	27.6
Na	ND	1.8	ND	1.1
F	ND	1.1	ND	0.8

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The EDX data presented in Table 2 are critically important for confirming the successful adsorption of fluoride. The spectrum of the raw BHB showed no detectable (ND) signal for the fluoride element. Conversely, spectrum of the spent adsorbent (BHB-F) clearly shows the presence of weight 1.1% and atomic 0.8% of the fluoride element. The corresponding decrease in the percentage of Carbon (C) and Oxygen (O) in the BHB-F sample, when compared to the raw BHB; due to successful mass loading of heavier fluoride species onto the surface. This elemental change is consistent with the F-binding demonstrated by the FTIR analysis. The results from EDX analysis thus provide unambiguous semi-quantitative evidence of the physical adsorption and retention of fluoride ions on the surface of the BHB Carbon.

3.3. Effect of different forms of adsorbents

To find out the defluoridation efficiency of different forms of bajra husk, 0.1 g of each adsorbent such as WC, UC, WN, and UN was used for 100 mL groundwater samples and treated for 3 hours, and aliquots were removed every 30 minutes. After the analysis, findings revealed that UC has more adsorption efficiency compared to washed samples (Table 3). Unwashed bajra husk likely retains more of its natural surface properties, including pores, affinity for fluoride ions and active sites, which are crucial for adsorption processes. Washing may remove some of these surface features, diminishing the adsorption capacity. Unwashed bajra husk contains organic matter that can enhance fluoride adsorption. Organic compounds in the husk may form complexes with fluoride ions, increasing their affinity for the adsorbent surface. Also, compared to carbonized and non-carbonized bajra husk adsorbents, the carbonized sample has higher adsorption efficiency than the noncarbonized bajra husk. Carbonization usually brings a material with a greater surface area by removing volatile components. The enhanced surface area increases the efficacy of fluoride adsorption by making more active sites available.

Activated carbon's ability to remove fluoride from water depends on several variables, including solution pH, solubility, polarity, pore size distribution, adsorbate molecular size, surface area, surface functional groups, and other ions. The adsorption capacity of microporous activated carbons for molecules with low molecular weight is high due to their vast surface areas [35].

3.4. Impact of adsorbent dosage and contact time

The impact of fluoride adsorption was dependent on the adsorbent's dosage. Adjusting the adsorbent dose from 0.1 to 0.4 g BHB per 100 mL of water sample with a primary fluoride level of 5 ppm changed the adsorption ability of fluoride particles. Results (Figure 4) demonstrate that increased adsorbent dosage and incubation period increased the fluoride removal capacity. The enhanced adsorption capacity for fluoride can be attributed to the augmentation of surface area and active sites resulting from the higher dosage of BHB adsorbent.

Table 3. Effect of different forms of adsorbent.

Types of Adsorbents	% Adsorption of Fluoride					
	30 min	60 min	90 min	120 min	150 min	180 min
WC	25.43±0.5%	34.68±0.5%	36.41±0.5%	40.46±0.5%	41.04±0.5%	42.19±0.5%
UC	30.63±0.5%	42.24±0.5%	53.75±0.5%	57.80±0.5%	58.38±0.5%	59.53±0.5%
WN	11.56±0.5%	15.60±0.5%	19.07±0.5%	24.85±0.5%	24.97±0.5%	25.08±0.5%
UN	14.45±0.5%	19.65±0.5%	26.01±0.5%	28.90±0.5%	29.47±0.5%	30.06±0.5%

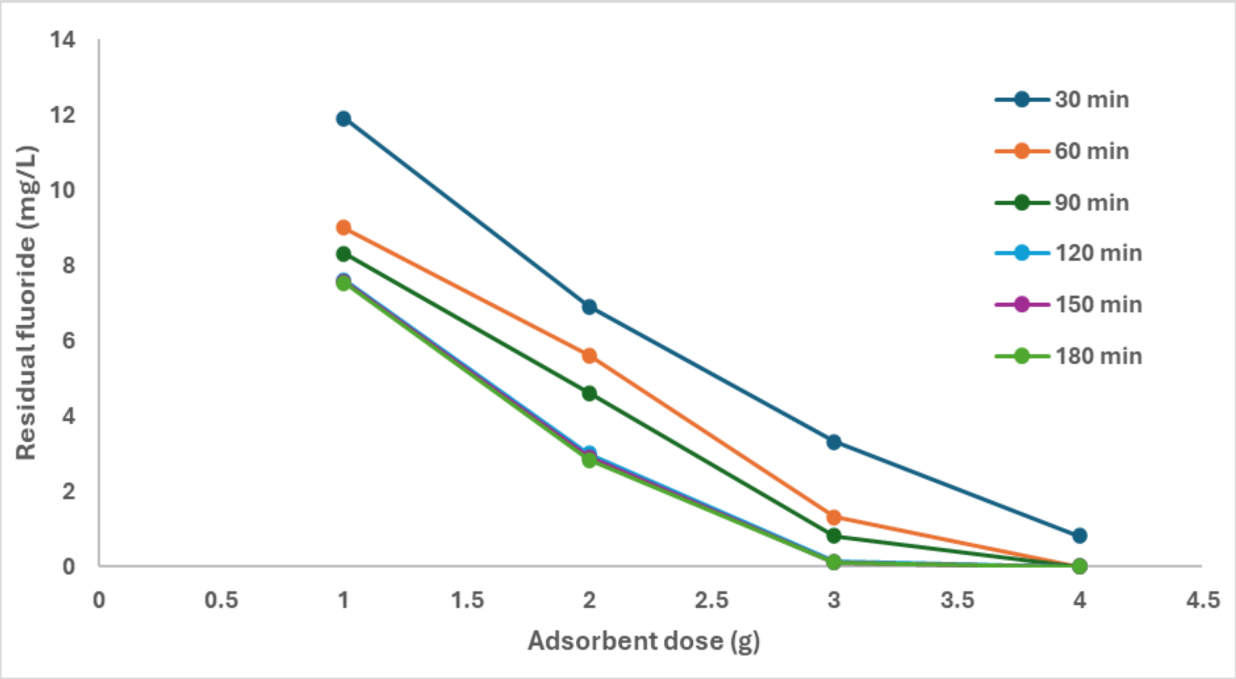

Figure 4. Fluoride removal capacities with respect to the BHB adsorbent dose and incubation time.

The adsorption capacity of all treatment dosages gradually increased during the initial two hours. However, there was no notable variation in the percentage of fluoride adsorbed after this period. After two hours, the complete saturation of each active site on the adsorbent's surface is demonstrated. 0.4 g of fluoride was 100% removed after three hours of incubation. Increasing the dose did not improve the percentage of fluoride removed by the adsorbent beyond a particular point, and that was the point at which the optimal dose was determined. It is also necessary to reduce the fluoride concentration in water to the allowable range of 0.5–1.5 ppm, requiring a minimum dose of 0.3 grams and a 2-hour contact time. Up to 95.37 ± 0.5 % fluoride can be removed by combining the adsorbent dosage and contact duration. As a result, it was determined that the ideal adsorbent dosage for BHB was 0.3 g per 100 mL, and the perfect incubation time was two hours. Acacia catechu wild khair, pipal (Ficus religiosa), neem (A. indica) leaves, and activated charcoal [38] all produced comparable results. The adsorption capacity per unit of adsorbent remained constant, and increasing the adsorbent dose did not result in additional adsorption, indicating the presence of excess adsorption sites already saturated with fluoride ions.

The absence of further adsorption at high adsorbent doses can be attributed to the initial fluoride concentration and the increasing amount of solid added for the constant solute load. In addition, there was a reduction in the concentration of fluoride ions per unit mass of adsorbent [34, 39].

3.5. Effect of initial concentration and co-existing ions

The BHB defluoridation efficiency was also influenced by the original fluoride concentration in the test solution. Figure 5 shows the impact of the initial fluoride levels on the ability of natural and synthetic water samples, with varying fluoride concentrations, to remove fluoride using BHB defluoridation. An increase in the original levels of fluoride decreased the efficacy of fluoride removal by the adsorbent. The synthetic samples achieved a maximum proficiency of 39.40 ± 0.5% in removing fluoride, whereas the actual water samples achieved a higher proficiency of 94.64 ± 0.5%. These results were obtained when the beginning fluoride concentrations were 5 ppm for the synthetic samples and 5.6 ppm for the actual water samples. Real water samples often contain a variety of ions and organic matter that can influence the defluoridation process in several ways, leading to higher adsorption efficiency compared to prepared fluoride solutions. It contains various ions like chloride, sulphate, bicarbonate, and etc.

Specific ions on the bio-adsorbent material may interact with fluoride ions for adsorption sites. Fluoride adsorption efficiency in natural water samples can be increased when other ions are present because there is less electrostatic repulsion between the fluoride ions and the adsorbent surface. Natural local water samples contain organic debris and other components that can alter the surface characteristics of the bio adsorbent material to improve fluoride adsorption. Gradually increasing the concentration from 5 to 15 mg/L also resulted in a decline in removal effectiveness. Similarly, in the natural local water sample, the fluoride adsorption percentage declined as the preliminary concentration enhanced from 5 to 10.6 ppm. This is due to the presence of both positive and negative charges on the BHB surface, the efficiency of removing fluoride ions decreased as the initial concentration of fluoride ions in the solution rose. The material's ability to remove fluoride ions from a solution was significantly diminished due to insufficient charges and surface area to effectively modify additional fluoride elements and trap them at higher levels [38]. The fluoride removal of using coconut shells carbon, wheat straw, activated bagasse carbon, and moringa oleifera has been reported as 6.7, 1.93, 1.15, and 2.06 mg/g, respectively, whereas bajra husk carbon has been found to be 7.6 mg/g [39]. Thus, the underlying concentration of the material affects its ability to adsorb fluoride. Therefore, it is essential to ascertain the initial fluoride attachment before releasing it. Thus, the sample's initial fluoride content, contact time, and adsorbent dose are several factors that affect BHB's defluoridation capacity.

3.6. Adsorption kinetics

The mechanism of fluoride adsorption on the examined adsorbents was investigated by testing adsorption kinetics. In this study, both pseudo-first order (PFO) and pseudo-second-order (PSO) kinetic models were employed. The rate constant (k) for the fluoride sorption by all the adsorbents under consideration was determined using the Lagergren rate equation [40].

Investigating adsorption kinetics is essential as it offers a valuable understanding of the chemical pathway and the mechanism of fluoride sorption. The sorption mechanism is contingent upon the physical and chemical properties of the adsorbent, as well as the mass-transfer process. Intraparticle diffusion rate evaluates the mass transfer process; piecewise diffusion governs the pore diffusion of the adsorbent significantly [41].

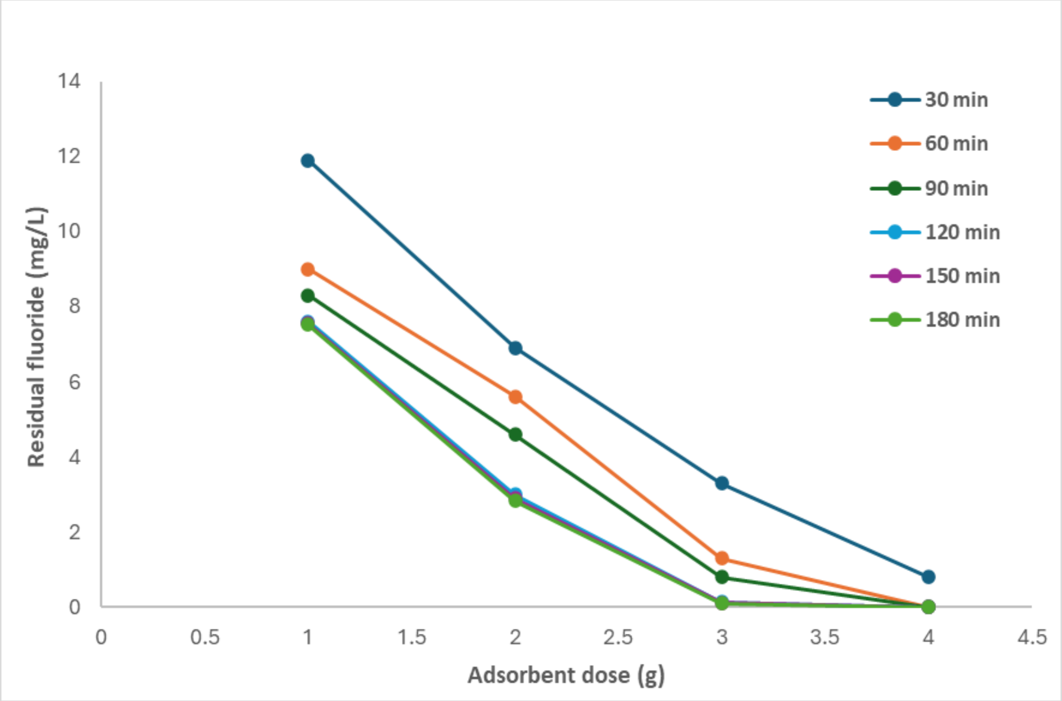

Figure 4. The amount of residual fluoride (ppm) concerning the adsorbent's time and dose.

The study investigated the process of fluoride sorption onto BHB at an optimized pH of 7.5 and adsorbent concentration of 0.3 g/L. The experiment examined the effects of different initial fluoride concentrations, ranging from 5 to 15 mg/L in synthetic fluoride samples and high fluoride concentrations of 5.6 to 10.6 mg/L in natural groundwater samples. The experiments were conducted at room temperature. The validity of the results was assessed using kinetic models, specifically the pseudo-first order and pseudo-second-order models (Table 4). The mechanism of fluoride sorption onto BHB can be elucidated using pseudo-first order and pseudo- second-order models, which identify the rate-controlling phases in the adsorption process.

PFO model: $$\mathrm{Ln}\,(q_e - q_t) = \mathrm{Ln}(q_e) - k_1 t \qquad (6)$$

PSO model: $$\frac{t}{q_t} = \frac{1}{k_2\, q_e^2} - \frac{1}{q_e\, t} \qquad (7)$$

The PFO model is a basic adsorption kinetic model proposed by Lagergren in 1898. The regression results demonstrated that the PFO was applicable for the synthetic fluoride samples at concentrations of 5, 10, and 15 mg/L, with values of 0.782, 0.856, and 0.902 (Table 5).

Similarly, for the natural fluoride samples at concentrations of 5.6, 9.0, and 10.6 mg/L, the regression values were 0.994, 0.986, and 0.996. The PSO model was used to determine the R^2 values for synthetic fluoride water samples, which were found to be 0.856, 0.92, and 0.98. Similarly, natural groundwater samples had R^2 values of 0.956, 0.998, and 0.999. Based on the principles of pseudo-second-order kinetics, the adsorption rate is directly proportional to the quantity of active sites on the surface of the adsorbent. The compliance of the PSO model is satisfactory, with regression coefficients of R^2 = 0.98 for synthetic data and 0.99 for natural samples. According to the regression values, it can be determined that the PSO model was more validated compared to the PFO model, as previously found by Yadav et al in 2013.

Table 4. Effect of initial concentration and co-existing ions.

Initial fluoride concentration (ppm)	Residual fluoride concentration (ppm)		
	60 min	120 min	180 min
Synthetic water samples			
5	3.4±0.29	3.13±0.26	3.03±0.18
10	7.96±0.36	7.3±0.32	7.2±0.29
15	13.3±058	12.66±0.85	12.3±0.86
Natural ground water samples			
5.6	0.9±0.06	0.43±0.02	0.3±0.02
9	2.1±0.22	1.68±0.38	1.56±0.33
10.6	3.6±0.35	2.6±0.26	2.4±0.24

Table 5. Data of various kinetic models at various fluoride concentrations.

Parameter	Synthetic samples: Initial fluoride concentration (mg/L)			Natural ground water samples : Initial fluoride concentration (mg/L)		
	5	10	15	5.6	9	10.6
Pseudo-first-order model						
q_e	1.825	2.623	3.645	0.138	0.269	0.426
K_1 ($\times 10^{-2}$)	0.144	0.256	0.691	0.152	0.356	0.756
R^2	0.782	0.856	0.902	0.994	0.986	0.996
q_m	3.645			0.426		
Δq_e, (%)	75.0	75.8	85.0	1.45	41.3	10.8
Pseudo-second-order model						
q_e	0.456	0.635	0.545	0.14	0.158	0.38
K_2 ($\times 10^{-3}$)	1.98	16.32	46.52	1.92	18.26	35.66
R^2	0.856	0.92	0.983	0.956	0.998	0.999
q_m	0.545			0.38		

3.7. Adsorption isotherms

The adsorption experiments were conducted using a fixed amount of adsorbent (0.3 g) and varying initial concentrations of the adsorbate (5, 10, 15, 5.6, 9, and 10.6 mg/L) solutions. The suitability of the obtained data for fitting the Langmuir adsorption isotherm was assessed. The tests were conducted for a duration that allowed for establishing equilibrium at the ideal pH of 7. The 2 hours of incubation period, with the samples being agitated at 200 revolutions per minute were used. The data were calibrated to the Langmuir model [44], as Volesky described [45].

$$\frac{c_e}{q_e} = \frac{1}{q_{max}\, K_L} + \frac{c_e}{q_{max}} \qquad \textbf{(8)}$$

The variables in the Equation 8 are as follows: q_e represents the amount of fluoride taken up by the biomass at equilibrium (measured in mg/g); q_{max} represents the maximum amount of fluoride that can be adsorbed onto the biomass (measured in mg/g); C_e represents the final concentration of fluoride in the solution at equilibrium (measured in mg/L); and b represents the Langmuir affinity constant, which is a measure of the energy of adsorption (measured in L/mg of fluoride). The values of q_{max} and b were obtained from the slope and intercept of the linear plot of C_e/q_e vs C_e, as depicted in Figure 7.

The fluoride sorption onto BHB resulted in a high R^2 value of 0.99, indicating a strong correlation. The necessary characteristics of the Langmuir isotherms can be articulated in terms of a dimensionless constant separation factor or equilibrium parameters.

To determine the isotherm's viability (R_L), the Langmuir isotherm's fundamental properties can be described using a dimensionless separation factor or equilibrium parameter, R_L, as defined in Equation 9.

In Equation 9, b represents the Langmuir isotherm constant, and C_0 represents the initial fluoride concentration (mg/L). The R_L value was calculated to be 0.617 for an initial fluoride content of 5 mg/L.

$$R_L = \frac{1}{(1+b\, C_0)} \qquad \textbf{(9)}$$

The obtained R_L values for fluoride adsorption are below 1. McKay et al. [46] said that R_L values ranging from 0 to 1 indicate favorable adsorption. The R_L values for all concentrations were consistently below 1, indicating a good adsorption process.

The Langmuir isotherm is formulated based on the following assumptions as proposed by Langmuir in 1918. Fluoride ions are chemically attracted and attached to a specific and limited number of clearly defined locations. Each site has a capacity for only one ion. All sites have the same energy level, and the ions have no interaction between them.

As the initial fluoride concentration increases, the adsorption increases since the binding sites are not yet saturated. The Langmuir adsorption model is followed by the adsorption, as seen by the linear plot of C_e/q_e versus C_e (Figure 6). The correlation coefficient is 0.99.

The Freundlich isotherm is represented by Equation 10 [47]:

$$Ln(\, q_e) = Ln(K_F) + \frac{1}{n\, Ln\,(C_e)} \qquad \textbf{(10)}$$

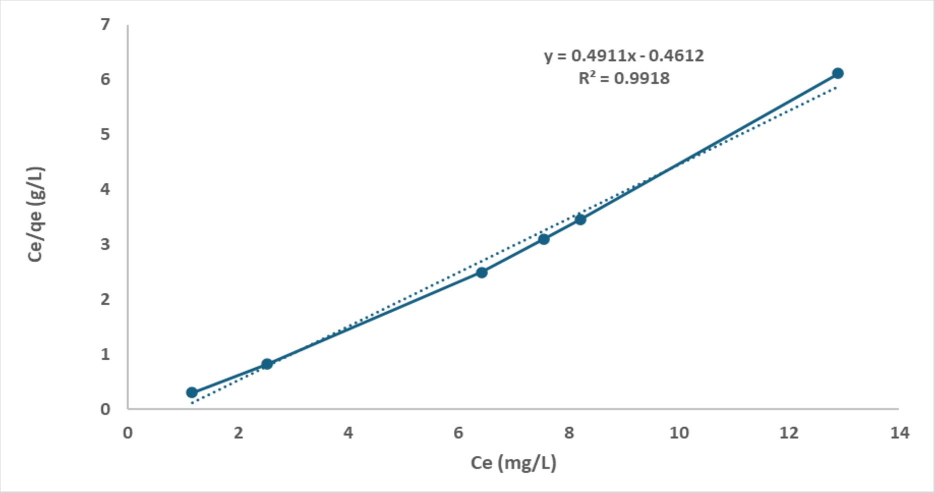

Figure 6. Langmuir adsorption isotherm for the variation of concentration of fluoride.

The equilibrium concentration (C_e) is the concentration of the substance in (mg/L) at equilibrium. The amount adsorbed (q) is the quantity of the substance adsorbed in (mg/g). The Freundlich constant (K_F) is a parameter that characterizes the adsorption process. The heterogeneity factor (n), the Freundlich coefficient, represents the divergence from linearity in the adsorption process. k and n were determined based on the gradients of the Freundlich plots. The values of k and n are 1.48 and 1.342, respectively (Figure 7). If the value of n falls between the range of 1 to 10, it indicates a favourable adsorption process [48]. As the adsorbent dose increases, fluoride adsorption improves due to the higher number of adsorption sites and the larger surface area available [33, 47, 49].

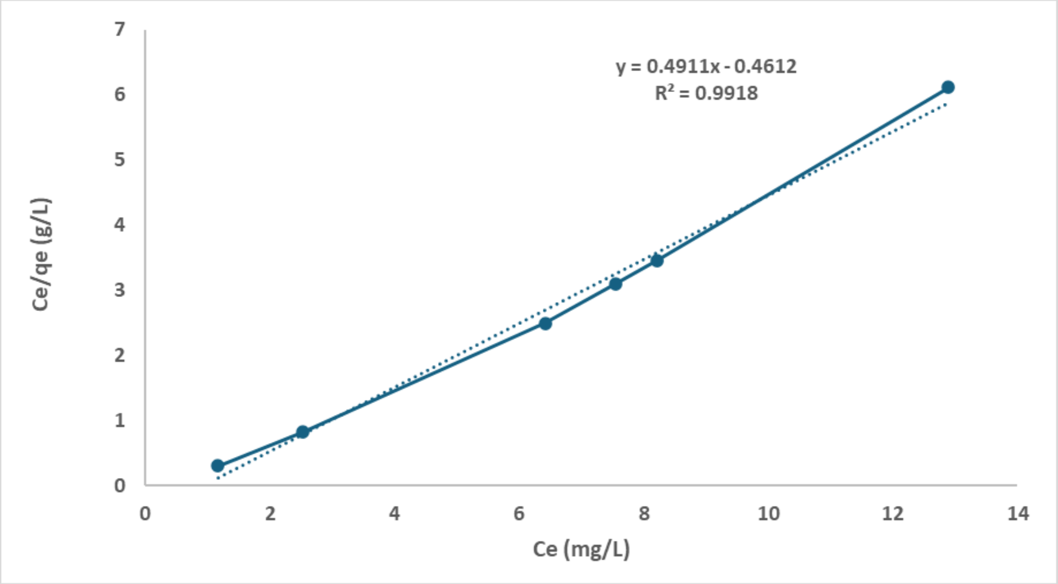

Figure 7. Freundlich adsorption isotherm for the variation of concentration of fluoride.

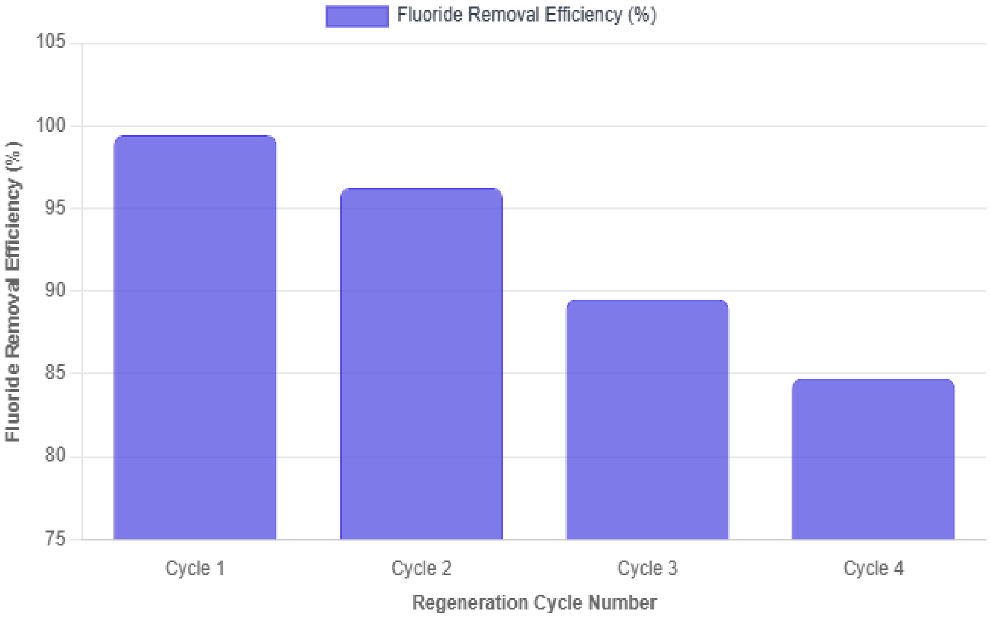

Figure 8. Adsorption-desorption cycles.

3.8. Reusability and regeneration efficiency of BHB

The practical and economic viability of the BHB adsorbent was confirmed through a series of four consecutive adsorption-desorption cycles. The results, visually represented in Figure 8, demonstrated the adsorbent's high stability and excellent reusability. After the initial cycle (Cycle 1), which achieved the maximum removal efficiency, the regenerated BHB retained 96.8% of its original capacity. Even following the fourth complete regeneration cycle using an alkaline eluent, the material maintained a high removal performance, exhibiting 85.2% of its original fluoride removal efficiency. This small, gradual decline in capacity is typical for bio-adsorbents and can be attributed to minimal irreversible site blocking or slight material loss during the regeneration process. Crucially, the sustained high retention rate of over 85% after multiple uses strongly validates BHB as a cost-effective and sustainable solution for practical, long-term defluoridation in rural water treatment applications.

4. Conclusion

- The study demonstrates that BHB is a low-cost and efficient adsorbent capable of reducing fluoride concentrations in groundwater to within permissible drinking water limits.
- Among the tested materials, unwashed BHB exhibited the highest fluoride adsorption efficiency, making it suitable for further optimization and practical application.
- The optimum defluoridation conditions were achieved at an adsorbent dosage of 0.3 g/100 mL, with 2 hours of contact time and 200 rpm stirring, resulting in up to 100% fluoride removal efficiency.
- The process is cost-effective and sustainable, utilizing agricultural waste (bajra husk) to treat contaminated water, thereby promoting waste-to-resource conversion and supporting rural and semi- arid communities.
- The developed biochar-based defluoridation system is scalable, biodegradable, and easily adoptable for village-level implementation. Co-existing ions in real samples were found to enhance fluoride removal, and further research is recommended to explore other agricultural wastes for similar applications.

Authors' contributions

Raghavendra T., Validation, Resources, Data curation, Writing—original draft. Akshay B Thomas., Formal analysis, Investigation. Jagriti Dadhwal., Writing—review and editing, Data curation, Visualization, Garima Kaushik., Investigation, Writing—review and editing, Pramod N Kamble., Methodology, Investigation, Writing—review and editing. Ritu Singh., Writing—review and editing, Visualisation. Himabindu V., Methodology, Investigation, Writing—review. Bhagawan D., Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Data curation, Writing—review and editing, Supervision.

Conflict of interest statement

All authors have seen and approved the manuscript being submitted. Hence, on behalf of all authors, the corresponding author states that there is no conflict of interest.

Funding statement

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Compliance with Ethical Standards

Not applicable

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Data availability

All data generated or analyzed during this study are included in this article.

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