

Research Article

Defluoridation of Water Using Aluminum Hydroxide Activated Carbon Biosorbents

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This study was aimed to investigate the efficiency of locally available low-cost and eco-friendly activated agricultural biosorbents produced from corncob and sorghum husk for the removal of fluoride from aqueous solution using batch adsorption. The activated biosorbents were characterized using SEM, XRD and FTIR spectroscopy. Effects of particle size (0.063–1.0 mm), contact time (15–120 min), pH (2–12), dose (2–10 g), and initial concentration (0.5–5.0 mg/L) were investigated. The morphology analysis revealed that biosorbents showed the presence of a high binding capacity for fluoride adsorption. The maximum adsorption was attained; size of the adsorbent 0.063 mm, pH 7, contact time 60 min, and 6 g dose of the biosorbents. Moreover, the adsorption kinetics followed the pseudo-second-order model and the adsorption isotherms fitted well to the Langmuir model. Furthermore, a field study was conducted using real water sample collected from Semema, Tigray, Ethiopia, and maximum fluoride removal was observed to be 79.44% and 77.05% for the activated carbons of Corncob and Sorghum husk at optimum conditions. Therefore, this experimental finding indicated that activated carbon of Corncob and Sorghum husk can be used as efficient, cheap, and eco-friendly biosorbents for the removal of fluoride from drinking water at community level.

1. Introduction

In developing countries, natural waters such as groundwater, surface water, and rainwater are important sources of drinking water [1]. Groundwater, which constitutes 97% of global freshwater, is consumed for drinking purposes by more than 50% of the world population [2]. In many developing communities where basic water distribution systems are unavailable, groundwater serves as the most economically viable option [3]. Access to the quality of drinking water is one of the major public health challenges for developing countries

[4]. However, groundwater often contains inorganic contaminants such as fluoride, uranium, arsenic, and boron amongst many others. Fluoride contamination of drinking water is one of the worldwide problems, and excess intake of fluoride can cause harmful effects such as dental, skeletal fluorosis, fetal cerebral function, neurotransmitters, etc. [5]. The WHO fluoride acceptable standard for drinking water is between 0.5–1.5 mg/L. However, fluoride concentration below and above the permissible limit has health effects. If fluoride is absent in the water supply it is known to cause dental caries [6].

The presence of fluoride in drinking water evokes considerable interest due to its large impact on the physiological systems of human beings [7]. The presence of an excess amount of fluoride in drinking water is often reported in many countries like Ethiopia [8], China [9], Pakistan [10], and India [11]. Ethiopia is one of the 23 countries in the world, where a significant number of its population suffers from the toxic effects of high levels of fluoride in drinking water [12]. The toxic effect of excessive amounts of fluoride in the drinking water of several towns in the Ethiopian rift valley has been in evidence since the 1970s [13]. This was because the people in these areas were familiar with drinking water that contains as much as 33 mg/L of fluoride [14].

Considering the serious health effects of fluoride, various techniques have been developed to remove fluoride from drinking water, which includes ion-exchange [15], precipitation-coagulation [16], membrane separation [17], electrolytic defluoridation [18], electrodialysis [19], etc. However, these techniques have certain disadvantages such as incomplete removal, complicated treatment process, high cost, high energy requirement, and operational cost, use of chemicals, and generation of toxic residues [20]. Hence, there is a need for the development of simple and cost-effective methods to remove excessive fluoride from the drinking water. Among these methods, adsorption has been considered to be one of the promising technologies because it was found to be simple, easy to handle, inexpensive, and less sludge producing [21].

Nowadays, several natural and low-cost adsorbents for fluoride removal from drinking water are employed such as activated alumina, activated carbon, activated alumina coated silica gel, calcite, activated sawdust, activated coconut shell carbon and activated fly ash, groundnut shell, coffee husk, rice husk, magnesite, serpentine, tricalcium phosphate, bone charcoal and activated soil sorbent [22–28], and among these the most effective adsorbent is activated carbon [29]. Thus, this work investigated the use of aluminium hydroxide activated biosorbents using corncob and sorghum husk, which are locally available, low-cost, and eco-friendly for adsorptive removal of fluoride from drinking water and aqueous solutions in batch systems and compared their adsorption efficiency for the removal of fluoride under optimum experimental conditions.

2. Materials and Methods

2.1. Materials. The chemicals and reagents used in the study were: NaF (Rankem, Indian), 37% HCl (Riedelcheim, Germany), $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ (LobaChemim, Indian), NaOH (Rankem, Indian), and deionized water. All the chemicals used were analytical grade reagents.

2.2. Preparation of Activated Carbon Biosorbents. The biosorbent of corncob and sorghum husk were collected from Semema, Tigray, Ethiopia, cut into small pieces, and allowed to be dried in sunlight. Then, the pieces of biosorbents were washed thoroughly with tap water and deionized water to remove dust and impurities that cover the surface area. After

that, the biosorbents dried in sunlight for 72 h and in an oven at 105°C. for 12 h. Finally, the biosorbents were carbonized in a muffle furnace at 400°C for 1.5 h to form activated carbon.

2.3. Formation of Aluminum Hydroxide Coated Activated Carbon. The prepared activated carbon biosorbents were washed with distilled water, dried and ground to a particle size of 4 mm, and coated using aluminum hydroxide. In brief, 500 mL of 0.6 M $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ solution was added to the conical flask, followed by slow addition 100 g of 4 mm particle size of activated carbon biosorbents to the conical flask with proper shaking by horizontal shaker to confirm the complete soaking of biosorbent in $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ solution. Thereafter, 3.0 M NaOH solution was slowly added to the conical flask while stirring at 200 rpm until the pH of the reaction mixture reaches 7. The resultant slurry mixture consisted of $\text{Al}(\text{OH})_3$ and sodium salt. The sodium salt was removed by washing with distilled water. The slurry was filtered using a vacuum filter and dried in an oven at 110°C for 2 h to get the $\text{Al}(\text{OH})_3$ coated activated carbon biosorbent. Finally, the coated biosorbent was crushed and sieved to get the different desired particle size and kept in plastic air-tied containers for further characterization and batch adsorption studies [30].

2.4. Characterization of Biosorbent Materials. The functional groups of the biosorbent involved in fluoride removal were examined using FTIR (AL.11.3.02, IRprestige21). The surface morphology of the activated carbon of the biosorbent was also determined using a scanning electron microscope (JEOL JSM-5610) at different magnifications and their crystalline structures using powder XRD (Shimadzu, XRD-7000). The radiations of Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) were generated using an X-ray generator at operating target voltage of 40 kV and the current 30 mA. The samples were powdered and scanned at a diffraction angle of 2θ ranging between 10°–80° with the scan speed of 3°/min.

2.5. Batch Adsorption Experiments. The adsorption of fluoride was investigated using batch adsorption. The working solution of fluoride ion (5 mg/L) was prepared from a stock standard solution 1000 mg/L using deionized water. The pH was adjusted with 0.1 M NaOH and 0.1 M HCl in the range from 2–12 before using the batch experiment. The experiments were carried out in a 250 mL conical flask containing 100 mL fluoride ion solutions of different concentrations and a dose of biosorbents shaking for 1 h at 250 rpm in a horizontal shaker (KS 15 B control). After the adsorption process, the mixtures were allowed to settle for 20 min and then separated from the mixture using Whatman No 42 filter paper. The collected filtrates were analyzed for fluoride ion concentration using the fluoride ion-selective electrode (HANNA, HI552202, Romania). Finally, the fluoride ion concentration before and after the sorption processes was recorded. The experiments were conducted at different experimental conditions of particle sizes

(0.063–1 mm), contact time (15–120 min), pH (2–12), adsorbent dose (2–10 g), and fluoride concentration (0.5–5.0 mg/L) to determine the optimum experimental conditions of fluoride adsorption. The amount of fluoride adsorbed per weight unit of activated carbon (mg/g) and the percentage of fluoride removal (%F) was calculated using the following equation (1) and (2), respectively [31].

$$q_e = \frac{(C_0 - C_e)V}{W}, \quad (1)$$

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100, \quad (2)$$

where q_e is the amount of adsorbed fluoride per unit weight of the adsorbent in mg/g, R is removal efficiency in %, C_0 and C_e are the fluoride concentration measured before and after adsorption (mg/L), V is the volume of aqueous solution (L), and W is a dry weight of the adsorbent (g).

3. Results and Discussion

3.1. Characterization of Aluminum Hydroxide Coated Activated Carbons

3.1.1. The FT-IR Characterization. The FTIR spectra of activated carbon of corncob (ACCC) and sorghum husk (ACSH) before and after fluoride adsorption were measured in the wave number regions of 400–4000 cm^{-1} (Figure 1). The intensity of the absorption bands was changed after the adsorption of fluoride through ACCC and ACSH. This suggests different functional groups are involved in aluminum adsorption. The band at 3444–3487 cm^{-1} was assigned to the vibration of O-H stretching indicate that water molecules was adsorbed on structure of biosorbents. Whereas the band at 2350 cm^{-1} indicates the C-H stretching of alkane. The presence of aromatic groups in the Corncob and Sorghum husk were also evidenced by the peak at 1629 cm^{-1} which may also be related to aromatic C-C vibration [32, 33]. The bands at around 1463 and 1377 cm^{-1} correspond to C-H in plane bending vibrations in methyl and methylene groups, respectively. Weak bands of Al-O are present at the range of 1050–1010 cm^{-1} , revealed aluminum bonding to the compounds of activated carbon. Generally, the presence of several functional groups indicates that the biosorbent are suitable for biosorption that could contribute to the removal of fluoride ions [34]. After fluoride adsorption, a broadening of band at 3477 and 3487 cm^{-1} indicated the fluoride adsorbed by activated carbon of Corncob and Sorghum husk which may be taken as an indication of electrostatic adsorption between the adsorbent and the fluoride [35]. Among the various functional groups, the -OH functional groups coming from the aluminium hydroxide or adsorbed water which can actively participate in the effective binding of fluoride ions through electrostatic attraction. After fluoride adsorption, the sharp peak observed around 436 and 535 cm^{-1} attributed to the adsorption of fluoride on the corncob and sorghum husk biosorbents. This might be due to the improvement of the metal oxide in the presence of fluoride onto activated carbon [36].

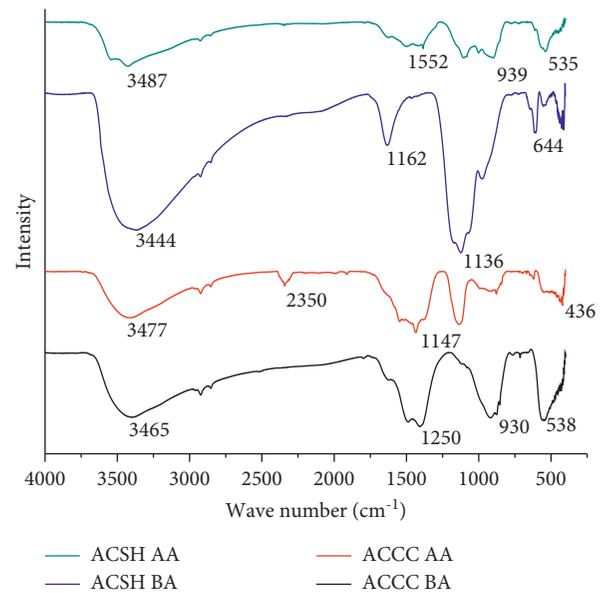


FIGURE 1: The FTIR spectra for activated carbon of corncob before adsorption (ACCC BA), activated carbon of corncob after adsorption (ACCC AA), activated carbon sorghum husk before adsorption (ACSH BA), and activated carbon sorghum husk after adsorption (ACSH AA).

3.1.2. The XRD Analysis. The XRD pattern of activated carbon of corncob and sorghum husk before and after fluoride adsorption indicated that the XRD pattern of activated carbons was mostly semicrystalline in their structures which allows better accessibility to fluoride and thus a better activity [37] (Figure 2). The peaks at $2\theta = 43.72^\circ$ and 64.28° showed the presence of aluminum hydroxide [38]. As shown in Figure 2, the XRD pattern of both biosorbents after fluoride treatment showed peaks at $2\theta = 40.94^\circ$ and 61.50° which can be assigned to aluminum fluoride formation (JCPDS 84-0943). Thus, the crystalline structures formed were due to aluminum coated on the activated carbons. Compared to the XRD pattern of before adsorption, the peaks of activated carbon after fluoride adsorption were longer indicating the increased in crystallite size due to fluoride adsorption, which is due to the high affinity of fluoride towards the crystal growth [31].

3.1.3. The SEM Analysis. The SEM micrographs of the activated carbons of corncob and sorghum husk before and after the adsorption result indicated little variation in the surface structure of the SEM micrographs before and after the adsorption of the fluoride ions (Figures 3(a)–3(d)). The SEM micrographs of biosorbents before adsorption of fluoride showed the distribution of heterogeneous porous and irregular surface structures providing a large exposed surface area for the adsorption of fluoride. The formation of pores might be attributed due to the aluminum activation of the biosorbent and these pores provide active centers for the adsorption of the fluoride ions [39]. After the fluoride adsorption, decreasing pore sizes and morphological features of the adsorbent slightly changed which were likely due to

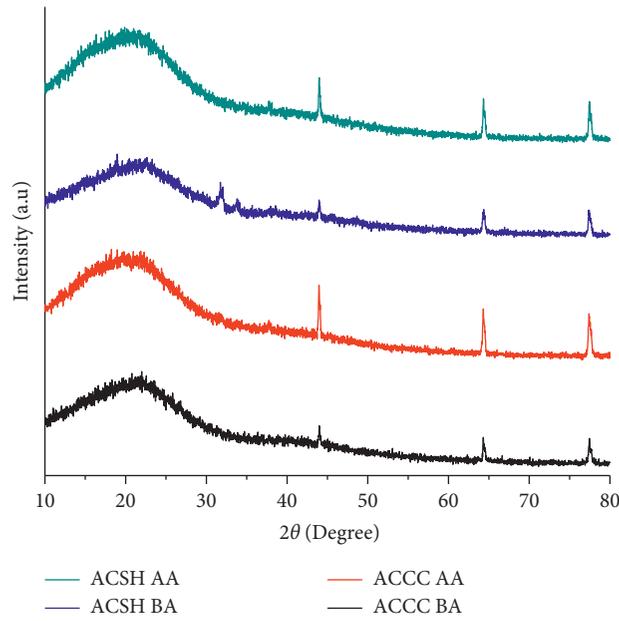


FIGURE 2: The XRD pattern for activated carbon of corncob before adsorption (ACCC BA), activated carbon of corncob after adsorption (ACCC AA), activated carbon sorghum husk before adsorption (ACSH BA), and activated carbon sorghum husk after adsorption (ACSH AA).

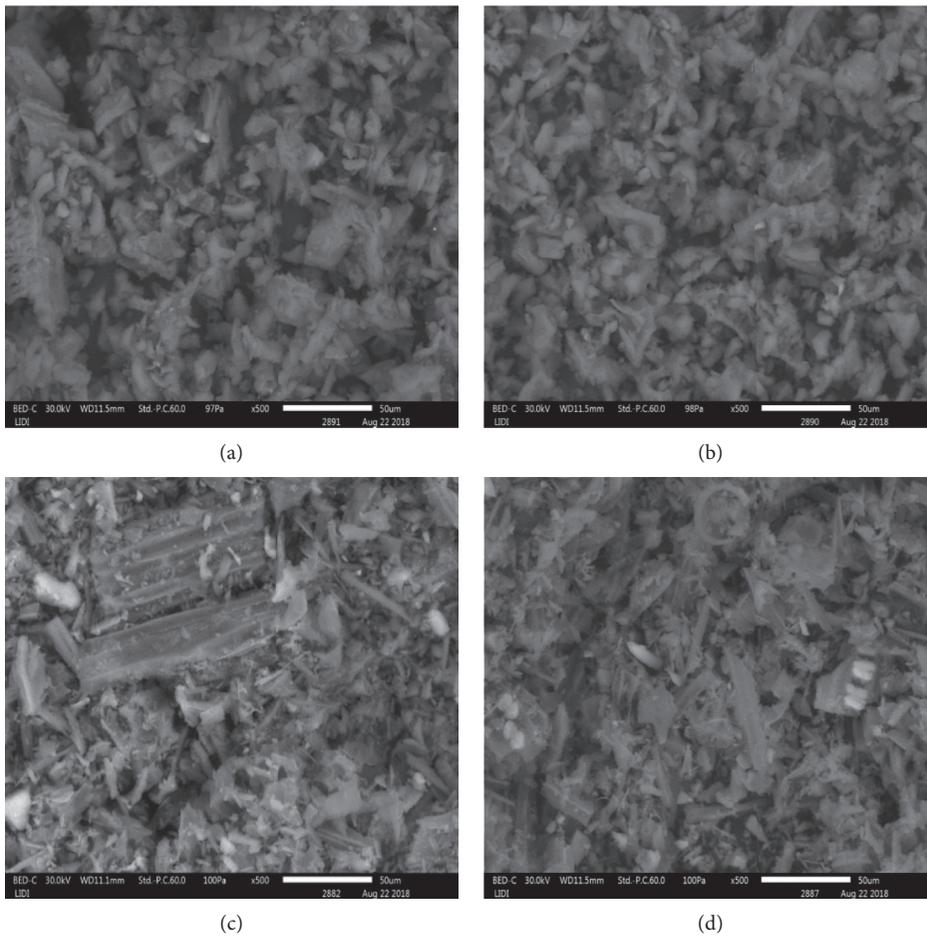


FIGURE 3: The SEM for activated carbon of (a) before adsorption for corncob and (b) after adsorption for corncob; (c) before adsorption for sorghum husk and (d) after adsorption for sorghum husk.

the deposition of fluoride ion on the surface [30] as confirmed by FTIR. This concludes that fluoride was adsorbed onto the surface of the biosorbents.

3.2. Effect of Contact Time. The effect of contact time for the removal of fluoride using aluminum hydroxide coated activated biosorbents of ACCC and ACSH were studied by varying the contact time in the range of 15–120 min, keeping other parameters constant (pH 7, dose 6 g, the particle size of adsorbent 0.063 mm and initial fluoride concentration 5 mg/L). As the contact time increased the removal efficiency of the fluoride using activated biosorbent of corncob and sorghum husk increased reaching saturation at 60 min (Figure 4). The rapid increase in adsorption up to 60 min might be due to the presence of functional groups and a large number of available active sites for the initial fluoride adsorption [40]. However, it slowly approached a constant value indicated that it reaches a steady state. As a result, a further increase in contact time did not increase the uptake of fluoride due to the deposition of fluoride ions on the available adsorption sites of adsorbent material [41]. Accordingly, at the optimal adsorption time of 60 min, a maximum of 95.8% and 93% of the defluoridation efficiency of the aluminum-coated activated carbons of corncob and sorghum husk were obtained, respectively.

3.3. Effect of pH. The pH alters the surface charge on the biosorbent and is considered as one of the main factors in controlling the adsorption of fluoride ions on the surfaces of biosorbents in aqueous solution [36]. Figure 5 showed the percent removal of fluoride ions by the aluminum-coated activated carbon of the studied biosorbent of ACCC and ACSH at different pH values ranging from 2–12, keeping other parameters constant (contact time 60 min, particle size of biosorbent 0.063 mm, dose 6 g and initial concentration of 5 mg/L). The result revealed an initial increase in fluoride ion removal near to pH 7 with maximum defluoridation efficiency of 96% and 93% for the studied biosorbents of corncob (ACCC) and sorghum husk (ACSH), respectively. The lower adsorption efficiency of fluoride ion at low pH levels could be due to the formation of weak hydrofluoric acid and the complexation of fluoride ions with aluminum [42] but the low level of fluoride removal at higher pH could be due to the deprotonated and negatively charge of the biosorbents and high competitive effects of the OH^- ions [43].

3.4. Effect of Particle Size. The influence of adsorbent particle size on the removal of fluoride ions was conducted through batch experiments. Particle size analysis was conducted on the aluminum-coated activated carbons of the biosorbents of corncob (ACCC) and sorghum husk (ACSH) in the range of 0.063–1 mm, keeping other parameters constant (pH 7, dose 6 g, contact time 60 min and initial fluoride ion concentration 5 mg/L). The result of the batch experiment showed a decrease in the removal of fluoride ion concentration from 96% to 65% for ACCC and 93.5% to 58.8% for ACSH with the increase of particle size from 0.063 to 1.0 mm (Figure 6).

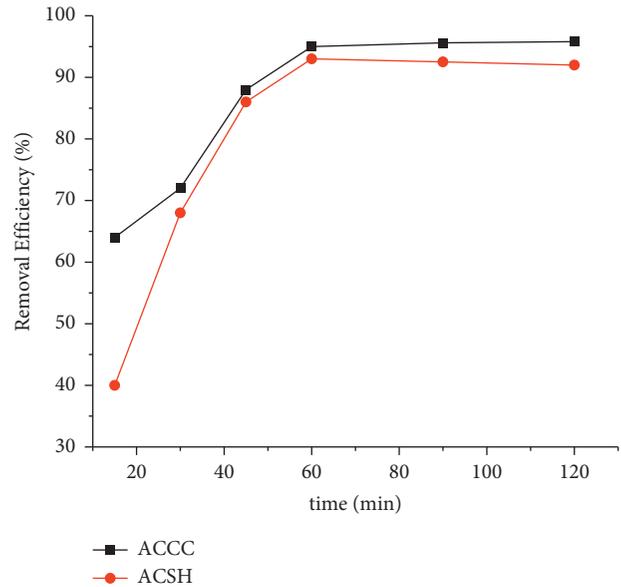


FIGURE 4: Effect of contact time on the removal of fluoride using activated carbon of corncob and sorghum husk (dose = 6 g, with an initial fluoride concentration of 5.0 mg/L).

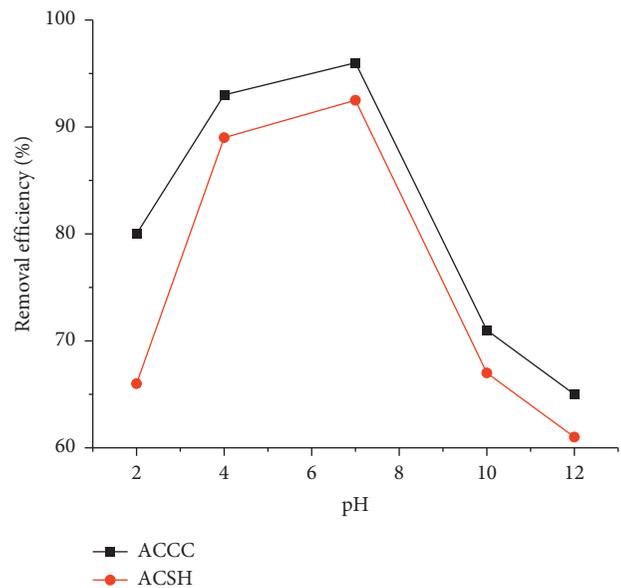


FIGURE 5: Effect of pH on fluoride removal efficiency of activated carbon of corncob, and sorghum husk (dose = 6 g contact time = 1 h) with an initial fluoride concentration of 5.0 mg/L.

The highest removal efficiency of the two biosorbents was obtained with a particle size of 0.063 mm which is similar with Amalraj and Pius [36]. The increased uptake of fluoride ions at lower particle sizes of the biosorbents was contributed due to the increased surface area and the number of active pores of the biosorbents [44].

3.5. Effect of Adsorbent Dose. To optimize the dosage of activated carbon of the studied activated carbons (ACCC and ACSH), the adsorption of fluoride ion was studied by

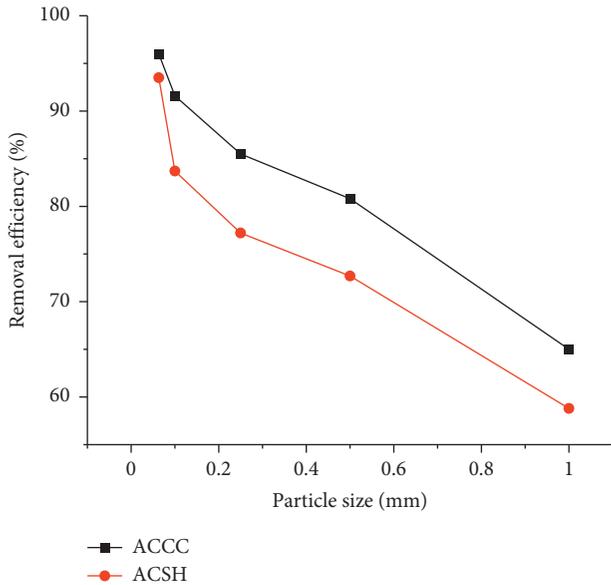


FIGURE 6: Effect of particle sizes on adsorption efficiency of activated carbon of corncob, and sorghum husk (dose = 6 g, rpm = 250, and 5.0 mg/L concentration).

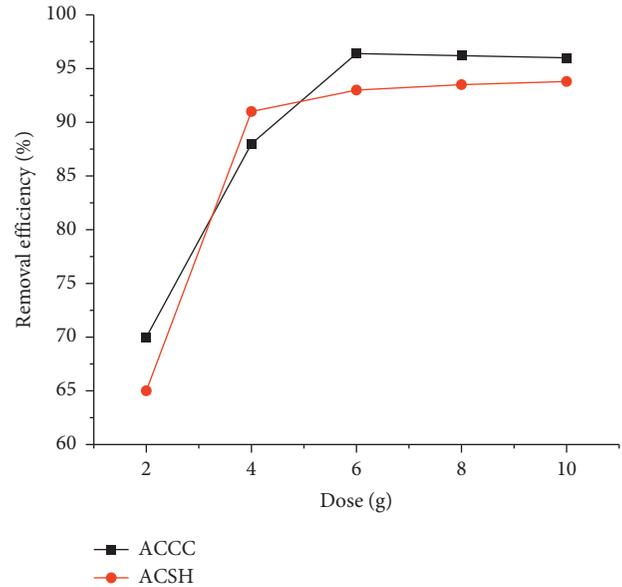


FIGURE 7: Effect of dose on fluoride removal efficiency of activated carbon of corncob and sorghum husk (contact time = 1 h) with an initial fluoride concentration of 5.0 mg/L at pH 7.

varying the dose of the biosorbent in the ranges of 2.0–10.0 g, keeping other parameters constant (pH 7, contact time 60 min, particle size 0.063 mm and initial concentration 5 mg/L). The percentage removal of fluoride ion was increased up to 96% for ACCC and 93% for ACSH until the optimum dosage of 6 g/100 mL and becomes saturated (Figure 7). The initial increase in percentage removal might be attributed to the large availability of active sites with increasing dosage of the biosorbents up to 6 g/100 mL. Then, there was no significant change in percentage removal of fluoride ions which could be attributed due to the overlapping of active sites at a higher dosage and hence reducing the net surface area [45] to be saturated. Therefore, 6 g/100 mL was taken as the optimum dose for the removal of fluoride ion using ACCC and ACSH.

3.6. Effect of Initial fluoride Ion Concentration. The fluoride removal efficiency was investigated by varying initial fluoride ion concentration by varying the concentration from 0.5–5 mg/L, keeping other parameters their optimum values (pH 7, dose 6 g, contact time 60 min, and particle size 0.063 mm). The percentage removal efficiency of fluoride ions decreased with increasing the initial fluoride ion concentration (Figure 8). This was because of the low concentration ratio of the available active surface of the biosorbents to the initial fluoride ion concentration and hence maximum adsorption was obtained at the fluoride ion concentration of 0.5 mg/L [46]. This was because at higher concentrations of fluoride ion more fluoride ions were left unadsorbed because of the limited number of active sites and the availability of competing ions in the solution [14, 47].

3.7. Adsorption Isotherm. The adsorption isotherm is useful to study for the feasibility of removal of ions from the bulk of

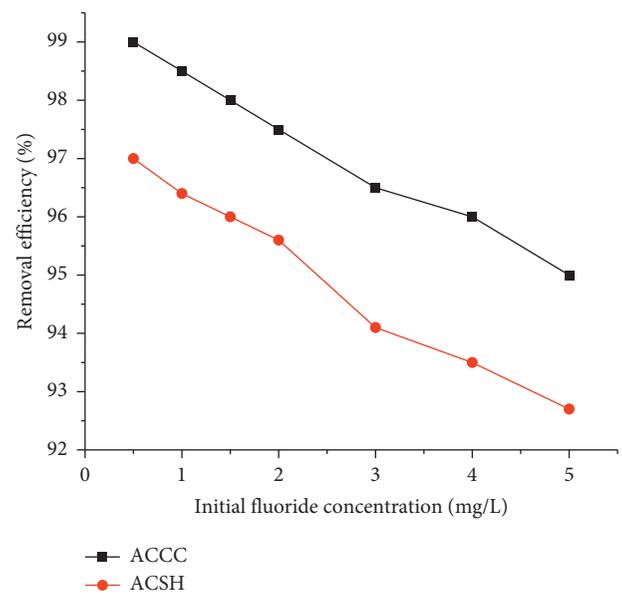


FIGURE 8: Effect of concentration on fluoride removal efficiency of activated carbon of corncob and sorghum husk (dose = 6 g contact time = 1 h) with an initial fluoride concentration of 5.0 mg/L at pH 7.

solutions. Among the different adsorption isotherms, Langmuir and Freundlich isotherm models are commonly used to study the nature of the adsorption process. Therefore, Langmuir and Freundlich isotherm models were used to investigate the adsorption equilibrium between the fluoride solutions and activated biosorbents of ACCC and ACSH. The correlation coefficient of Langmuir ($R^2 = 0.9396$ for ACCC and $R^2 = 0.9597$ for ACSH) was higher than that of Freundlich ($R^2 = 0.9049$ for ACSH and $R^2 = 0.9325$ for ACCC) indicating that the adsorption was more favorable to

Langmuir isotherm model for both biosorbents (Figures 9 & 10, Table 1). This indicated that the formation of a monolayer of fluoride was favorable on the surface of the studied activated biosorbents. Moreover, the result showed the process of adsorption was mainly controlled by chemisorptions [48]. To find out the probability of isotherm, the important characteristics of Langmuir isotherm was expressed in terms of a dimensionless constant separation factor, R_L [49].

$$R_L = \frac{1}{1 + bC_o} \quad (3)$$

where C_o is the initial fluoride ion concentration (mg/L) and b is the Langmuir constant. The value of R_L indicates the shape of the isotherms. In this study, the values of R_L computed were in the range of 0.0169–0.0467, indicating that the adsorption process was favorable for the removal of fluoride (Table 2).

3.8. Adsorption Kinetic Study. Two kinetic models such as the pseudo-first-order rate equation and pseudo-second-order rate equation were used to understand the dynamics of the adsorption process due to their simplicity [21]. The pseudo-first-order model is expressed as

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (4)$$

And the pseudo-second-order kinetic model is also expressed as

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e} \quad (5)$$

where q_e and q_t are the amounts of fluoride adsorbed (mg/g) at equilibrium and at different time intervals, respectively; k_1 and k_2 are equilibrium rate constant of first-order (in min^{-1}) and second-order (in $\text{g mg}^{-1}\text{min}^{-1}$).

To understand the kinetics of fluoride adsorption on the studied activated biosorbents (ACCC and ACSH), the pseudo-first-order and pseudo-second-order kinetic models were applied to simulate the adsorption data. Figure 11 showed the linear plot of the pseudo-second-order model for the biosorption of fluoride on the activated Biosorbent. By comparing the kinetic parameters for the two rate models, the pseudo-second-order model fitted the experimental data well with a R^2 close to one (Table 2 and Figure 11) than to that of the first-order model (Figure 12). Based on the correlation coefficients, the biosorption of fluoride follows a second-order reaction pathway indicating that the pseudo-second-order model was more suitable for the studied activated biosorbents. Moreover, the kinetic model of adsorption supported that the process of adsorption was mainly controlled by the chemisorptions process which involves

chemical bonding between adsorbent active sites and adsorbate valance forces [50].

3.9. Desorption Study. To be cost-effective, the reuse of biosorbent helps to decrease environmental pollution-related to biosorbent disposal. the fluoride desorption studies were carried out by varying pH values (2–11) using fluoride loaded ACCC and ACSH with 0.1 M NaOH and 0.1 M HCl, small fluoride was leached until pH 7 (Figure 13). However, desorption of fluoride enhanced at pH greater than 10 and reached a maximum of 88%, and 74% at pH 11 for ACCC and ACSH its comparative to other reports [30]. According to the results of desorption, the biosorbents can be reused through further optimization of parametric conditions.

3.10. Field Study. For selection of efficient and locally available sorbents for removal of fluoride; field study is crucial. The fluoride concentration before and after the treatment of the real sample via the activated carbon are shown in Table 3. The fluoride adsorption efficiency of activated corncob (ACCC) and sorghum husk (ACSH) was tested using drinking water samples collected from Semema, Tigray, Ethiopia, which is rich in fluoride ion concentrations. Accordingly, the experimental results indicated 6 g of activated carbon at room temperature effectively reduced the level of fluoride ions in a real water sample from 5.01 mg/L to 1.03 mg/L and 1.15 mg/L for ACCC and ACSH, respectively which is below the permissible limit of fluoride (<1.5 mg/L) in drinking water [51]. The amount of fluoride removed in lab scale is higher than the real water sample, this might be due to some ions such as sulfate, chloride, nitrate, hydroxide, and others may present in real water sample which is expected to interfere with fluoride ions during adsorption. Therefore, the activated carbon of corncob and sorghum husk can be used for removal of fluoride from drinking at the local community level (Table 4).

3.11. Possible Mechanism of Fluoride Adsorption. Several researchers have reported the possible adsorption mechanism of fluoride on aluminium-coated activated carbon through hydrogen bonding, ligand exchange reaction and electrostatic adsorption [53, 54]. Based up on the experimental data we proposed the possible mechanism of fluoride ion adsorption. When aluminum coated activated carbon become hydrated, the dissociative of water results in the formation of surface hydroxyl groups [55]. The surface hydroxyl ions, coordinated with aluminum cations, constitute the functional groups (Al-OH) and are responsible for the electrostatic interaction of aluminium and fluoride as described by the following equation:



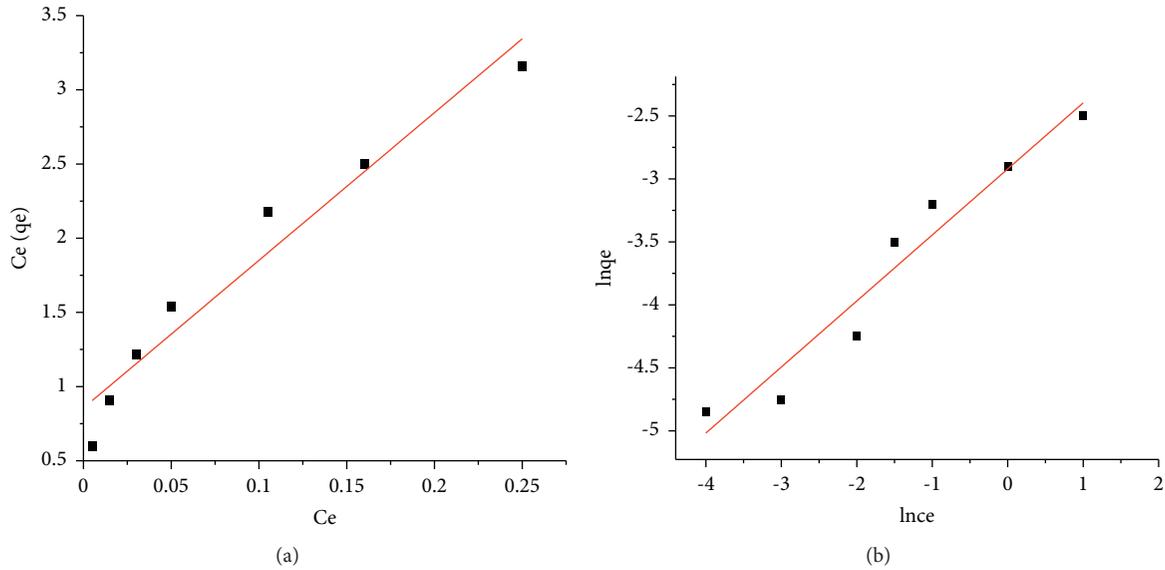


FIGURE 9: Adsorption isotherm of activated carbon of corncob for adsorption of fluoride: (a) Langmuir isotherm; (b) Freundlich isotherm.

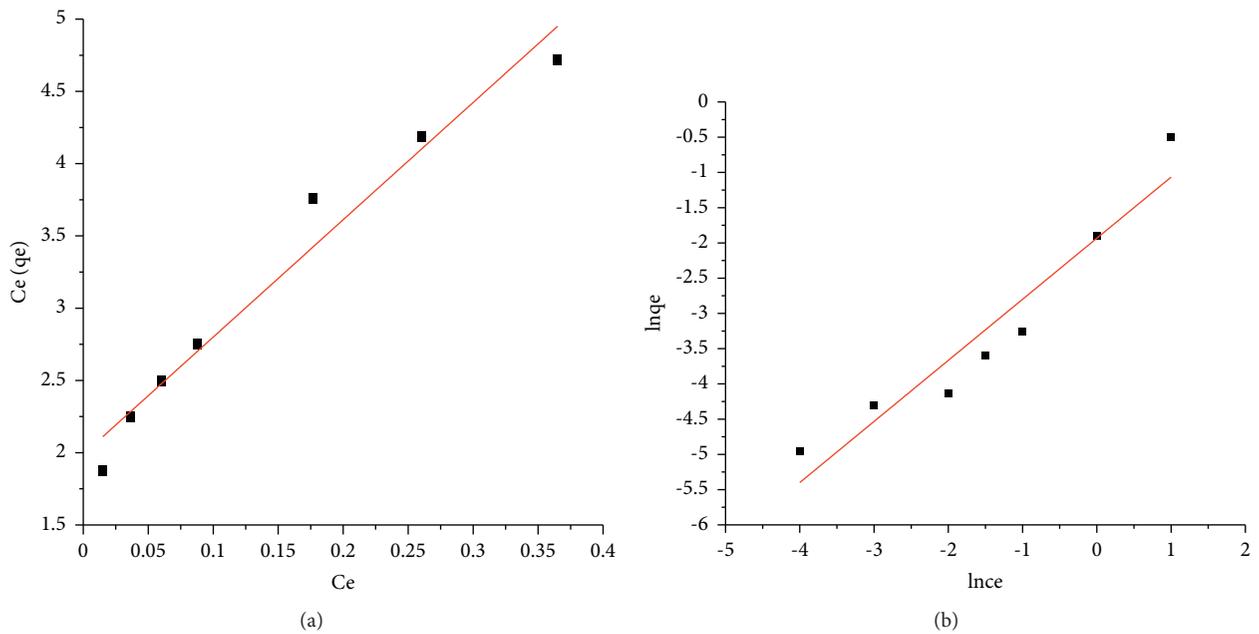


FIGURE 10: Adsorption isotherm of activated carbon of sorghum husk for adsorption of fluoride: (a) Langmuir isotherm; (b) Freundlich isotherm.

TABLE 1: The parameters of isotherms models for fluoride adsorption using activated carbon of corncob and sorghum husk.

Adsorption isotherm models	Equation	Parameters	Biosorbents	
			Corncob	Sorghum husk
Langmuir	$C_e/q_e = C_e/Q_0 + 1/bQ_0$	Q_0 (mg/g)	1.1689	0.5027
		b (lt/mg)	11.649	4.0778
		R^2	0.9396	0.9597
		R_L	0.0169	0.0467
Freundlich	$\log q_e = \log K_F + (1/n)\log C_e$	K_F	0.0012	0.0117
		n	1.9073	1.1539
		R^2	0.9325	0.9049

TABLE 2: Adsorption kinetic parameters.

Biosorbent	Adsorption kinetic models	Slope	Intercept	R^2
ACCC	Pseudo-first-order	-0.0205	-1.4222	0.9664
	Pseudo-second order	1.13886	11.53324	0.99483
ACSH	Pseudo-first-order	-0.2586	-0.9432	0.94071
	Pseudo-second order	1.08375	20.07029	0.97068

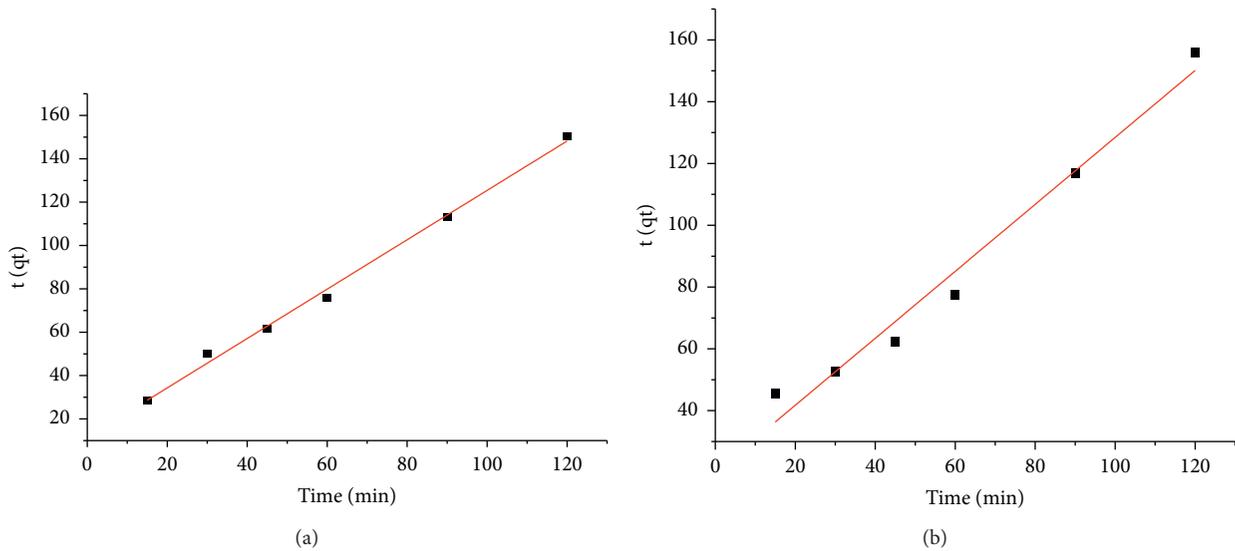


FIGURE 11: Pseudo-second order kinetic model fitting for activated carbon of corncob and Sorghum husk.

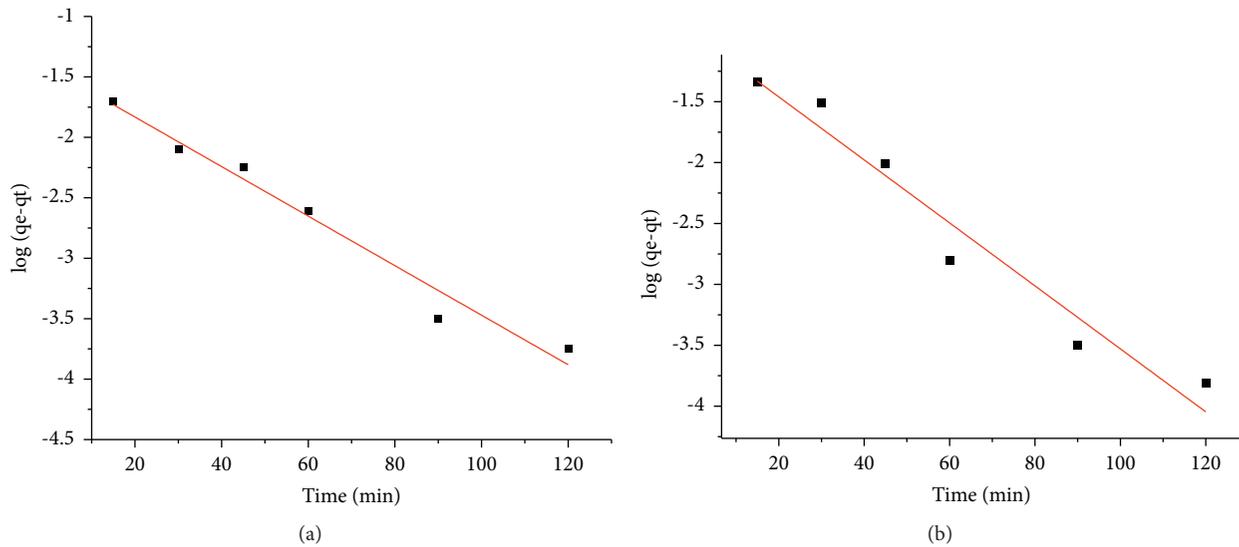


FIGURE 12: Pseudo-first order kinetic model fitting for activated carbon of corncob (a) and sorghum husk (b).

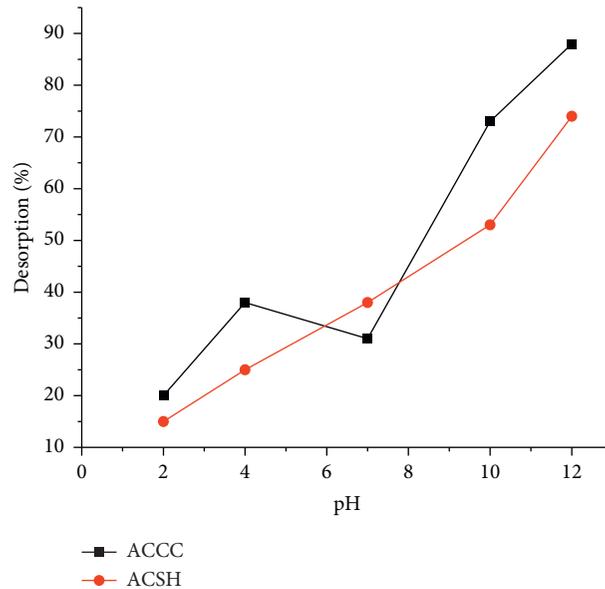


FIGURE 13: Regeneration of activated carbon of corncob (ACCC) and sorghum husk (ACSH) at different pH.

TABLE 3: Fluoride removal from the real water samples using the adsorbents prepared from corncob and sorghum husk at optimized conditions (pH 7 contact time 1 h, dose 6 g, particle size 0.063 mm).

Biosorbents	Parameters	Before treatment	After treatment	Removal (%)
Corncob	F (mg/L)	5.01	1.03	79.44
	pH	8.17	7.31	
Sorghum husk	F (mg/L)	5.01	1.15	77.05
	pH	7.14	6.9	

TABLE 4: Comparison of the adsorption efficiency with literature studies.

Biosorbents	Adsorption (%)	Reference
Activated biochar of <i>Colocasia esculenta</i> stem	40.2	[52]
Coffee (<i>Coffea arabica</i>) husk	84	[14]
Rice husk	75	[41]
Corncob	96	Current study
Sorghum husk	93	

3.12. *Performance Comparison with Literature.* The adsorption efficiency of biosorbents towards fluoride; compared with literature studies, the biosorbents are effective as compared with activated *Colocasia esculenta*, coffee (*Coffea Arabica*) husk, and rice husk (Table 4).

4. Conclusion

The activated carbon corncob and sorghum husk have favorable for removal of fluoride from aqueous solution by modifying their surface by aluminium hydroxide at size of the adsorbent 0.063 mm, pH 7, contact time 60 min and 6 g dose of the biosorbent. According to the biosorbents FTIR characterization, The FTIR studies provides the evidence of interaction between activated carbon and fluoride and was found that the mechanism of removing fluoride from aqueous solutions are related to electrostatic interactions. The adsorption equilibrium better described by Langmuir models and pseudo-

second-order rate equation, this suggests the sorption mechanism of fluoride is chemisorption on a biosorbents. Moreover, the desorption study indicated that 88% of the initially bound fluoride ion was desorbed from the activated carbon of corncob. There is a difference between the fluoride removal at lab scale and real water samples due to the presence of anions that enable to interfere the adsorption. The column study also efficiently removed the fluoride ion to the level of below WHO standard limit using both aluminium coated activated carbon of corncob and sorghum husk. Therefore, the locally available and low-cost biosorbents are promising and could also possibly be a useful alternative for the removal of fluoride from drinking water at the household level in developing countries to minimize the negative impacts of fluoride on human health.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare no conflicts of interest.

Authors' Contributions

Azmera Mezgebo took part in conceptualization, methodology, formal analysis, original draft preparation and

manuscript preparation, sorting and analyzing data, validation, and investigation. Mengstu Etay took part in collecting resources, data curation, and reviewing. Abraha Gebrekidan reviewed and edited the manuscript. Kebede Nigussie contributed to visualization and project administration, funding acquisition, and supervision. Zenebe Hailu took part in sorting and analyzing data. Kassa Amare was responsible for reviewing and validation.

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Supplementary Materials

Supplementary Figure 1: adsorption isotherm of activated carbon of corncob for adsorption of fluoride: (a) Langmuir isotherm; (b) Freundlich isotherm. Supplementary Figure 2: adsorption isotherm of activated carbon of sorghum husk for adsorption of fluoride: (a) Langmuir isotherm; (b) Freundlich isotherm. Supplementary Figure 3: pseudo-second order kinetic model fitting for activated carbon of corncob and sorghum husk. Supplementary Figure 4: pseudo-first order kinetic model fitting for activated carbon of corncob (a) and sorghum husk (b). (*Supplementary Materials*)

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