A comparative study on defluoridation capabilities of biosorbents: Isotherm, kinetics, thermodynamics, cost estimation and regeneration study

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ABSTRACT

The presence of high fluoride concentration (> 1.5 mg/L) in water causes serious health problems such as fluorosis, infertility, brain damage, etc., which are endemic to many places in the world. This study has investigated the fluoride removal capacity of the novel activated biochar (BTS) and hydrochar (HTS) using Teff (*Eragrostis tef*) straw as a precursor. Activated biochar with mesoporous structures and large specific surface area of 627.7 m²/g were prepared via pyrolysis process. Low-cost carbonaceous hydrochar were also synthesized by an acid assisted hydrothermal carbonization process. Results obtained from both adsorbents show that the best local maximum fluoride removal was achieved at pH 2, contact time 120 min and agitation speed 200 rpm. The thermodynamic studies proved that the adsorption process was spontaneous and exothermic in nature. Both adsorbents equilibrium data fitted to Langmuir isotherm. However, Freundlich isotherm fitted best for BTS. The maximum fluoride loading capacity of BTS and HTS was found to be 212 and 88.7 mg/g, respectively. The variation could primarily be attributed to a relatively larger Surface area for BTS. Hence, to treat fluoride contaminated water, BTS can be promising as an effective adsorbent.

Keywords: Adsorption, Biochar, Fluoride, Hydrochar, Pyrolysis, Teff (*Eragrostis tef*)

1. Introduction

Clean, safe drinking water is not easily available as it may be exposed to contamination through both natural and anthropogenic sources. Fluoride can be categorized as one of those contaminants. It is an ion of the element fluorine, a fairly common element that is widely occurring in the upper layers of the lithosphere [1]. It is often considered as a “double-edged sword” since very low levels of exposure to young children especially under the age of six may lead to stunted growth [2]. On the other hand, excessive intake leads to dental fluorosis (1.5-4.0 mg/L), skeletal fluorosis (4.0-10.0 mg/L) and progressive crippling scourge-skeletal fluorosis (> 10 mg/L) [3, 4]. There is a safe level (1.5 mg/L) for fluoride that is essential to avoid concern and for protection of dental caries [5].

Worldwide above 200 million people from 25 nations are jeopardized by excess fluoride in drinking water exceeding the safe level [6]. This situation mostly happens in arid and semi-arid regions at which a rapid rate of chemical weathering of geological materials has occurred [7]. Due to the fact that especially in the region like East African rift valley, where all drinking water sources are naturally poisoned by fluoride, investigation of appropriate fluoride treatment techniques is mandatory.

To date, different kinds of fluoride removal techniques such as membrane process (reverse osmosis, dialysis, and electrodialysis, etc.) and adsorption have been mainly practiced [8-10]. However, some of them have long been blamed for their limitations in acceptance by the communities, especially at developing rural areas due to their after use environmental effect, high operational cost and

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complexity of design [11]. It is, therefore, necessary to look for the most convenient techniques depending on the location and stakeholders centred parameters [12]. Arguably, the removal of fluoride through adsorption techniques is effective due to its simplicity and expediency with high removal efficiency [13, 14]. However, the principal question in the implementation of adsorption methods is the selection of the appropriate adsorbent material (i.e., locally available, affordable, and eco-friendly).

In recent years, various indigenous biomass including agricultural wastes in the form of hydrochar, biochar, and activated carbon have been used enormously as a sustainable adsorbent for fluoride adsorption from the water. Since, they are easily available, economically feasible and biodegradable in nature [15, 16]. Biochar is produced by incomplete combustion of plant residues, agricultural byproducts, algae and other biomasses in the absence of oxygen [17]. Biomaterials can also be widely applied for pollutant removal after their surface introduced the functional groups and carbons via a simple technical route. This process occurs under aqueous medium and relatively low temperature, referred to as hydrothermal carbonization (HTC) [18]. The presence of such functional groups with its carbonized features on the surface of hydrochar enabled it to be a promising precursor for fluoride treatment. Moreover, the suitability of both biochar and hydrochars can be improved through chemical activation via HCl [19], ZnCl_2 [20], H_3PO_4 [21], KOH [22], etc., since they provide high surface area and high porosity, which are primarily responsible for effective fluoride adsorption [23]. Activation through H_3PO_4 is, however, most preferable as compared to other activation chemicals due to less hazardous after-effect on environmental safety and it also gives high adsorbent yield [24].

Several literature works have reported the adsorption of fluoride using activated biochar derived from various biomaterials such as rice husk [25], jamun leaf [26], douglas fir [27], corn stover [28], perennial grass [29], coconut fiber [30], wheat straw and pine sawdust [31]. However, the adsorption potential of fluoride via acid assisted hydrochar has not yet been reported. Furthermore, Teff (*Eragrostis tef*) straw has neither been synthesized as biochar nor hydrochar for this purpose.

This study has investigated the removal of fluoride via activated biochar and hydrochar prepared from Teff (*Eragrostis tef*) straw. To understand which adsorbent type would favorably respond to the chemical activation process, both adsorbents were chemically activated under similar activation agent (H_3PO_4), concentration (30 wt%) and time (3 h). Their physicochemical properties, which may attribute to the variation in adsorption behavior, are characterized. Besides, the adsorption thermodynamics, kinetic behaviors, equilibrium isotherm models and desorption studies were analyzed.

2. Materials and Methods

2.1. Chemicals and Reagents

Chemicals used such as NaF, H_3PO_4 , HCl, Na_2CO_3 , and NaOH were purchased from Sigma-Aldrich Companies. The Total Ionic Strength Adjustment Buffer (TISAB) II was purchased from Thermo

scientific Orion reagent companies. All chemicals and reagents were of analytical grade and were used as received.

2.2. Adsorbents Preparation

Teff straw was cut into smaller pieces, washed thoroughly, dried, crushed well and sieved. Subsequently, chemical activation using phosphoric acid was done by modifying a method as demonstrated [24]. Briefly, 8 g of prepared Teff straw was impregnated with 56.0 mL of 30 wt% H_3PO_4 solution and stirred at room temperature for 12 h. After the supernatant was removed, the remaining wet solid precursors were directly transferred to a tubular furnace to be pyrolyzed at 450°C for 3 h under inert atmosphere (150 mL/min N_2). It has been reported in literature that application of low pyrolysis temperature [32] and slow pyrolysis process [33] obtained a higher char yield having higher pore volume. The activated char was taken out after the heat was cooled to room temperature and then washed by 0.1 M of HCl followed by distilled water till the effluent becomes neutral pH. Prior to drying, about 3 g of it was dried purposively at different temperature, to evaluate the effect of its initial moisture content presented in sec 3.2.2 The remaining char was dried at 110°C for 6 h and then assigned as activated Teff Straw Biochar (BTS).

For hydrochar, 8 g of prepared Teff straw was mixed with 56.0 mL of 30 wt% H_3PO_4 solution in a 100 mL Teflon lined autoclave reactor. The reactor was heated at 190°C for 3 h, and then cooled naturally to room temperature. The solid product was separated by vacuum filtration, washed and dried as the procedure used for BTS. The final result was noted as activated Teff Straw Hydrochar (HTS).

2.3. Physicochemical Characterization

The surface morphology of both adsorbents before and after adsorption of fluoride was observed by Scanning Electron Microscope (SEM, JSM-7800F). The presence of functional groups on their surfaces was confirmed by Fourier Transform Infrared Spectroscopy (FTIR, Nicolet IS 10) in a wavelength of 400 to 4,000 cm^{-1} . X-ray diffractometer (XRD, Bruker D8-Advance) with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$, 40 kV) was used to characterize the crystalline pattern of both adsorbents. The textural feature of both adsorbents was determined by N_2 adsorption-desorption isotherms at 77 K using ASAP (Micrometrics 2460) surface area and porosity analyzer. Subsequently, the surface area and average pore size were calculated by the Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halenda method, respectively. Thermogravimetric analysis was conducted on the thermal analyzer (SDT Q600) from 30°C to 900°C with a heating rate of 10°C/min in an inert atmosphere (N_2 , 100 mL/min).

2.4. Adsorption Experiment

Sodium fluoride (NaF) is a readily soluble inorganic compound and commonly used as a source of fluoride ion [34]. A standard fluoride solution was obtained by dissolving 0.221 g anhydrous NaF in distilled water and then diluted to the required concentration. A series of the batch experiment was done to investigate the best conditions for the adsorption parameters. Accordingly, 0.1 g of HTS and BTS were added separately in 20 mg/L of 100 mL fluoride solution with variable pH (2-12), agitated for 3 h at a 25°C.

Subsequently, the variation effect of contact time (15-300 min), initial adsorbent moisture content (80-20%), initial fluoride concentration (5-100 mg/L), agitation speed (50-300 rpm) and adsorbent dose (0.1-1 g) were studied. Thermodynamic properties of the adsorbent-adsorbate reaction were evaluated at variable temperatures (288-328 K). To analyze the sorption isotherm, the experiment was employed by varying the initial fluoride concentration. The adsorption kinetics was also studied by measure the residual fluoride concentration at different adsorption time intervals. Prior to fluoride determination, the supernatant was filtered and then mixed equally with TISAB II solution to avoid the ionic interference during the fluoride measurement. The remained concentrations of fluoride were measured twice by benchtop ion meter with a fluoride ion selective electrode (PXSJ-216F, China) and the average result was used for analysis. The percentile adsorption efficiency was calculated by Eq. (1).

$$\text{Adsorption (\%)} = \frac{C_i - C_e}{C_0} \times 100 \quad (1)$$

The amount of fluoride uptake was calculated using the mass balance equation Eq. (2):

$$\text{Adsorption capacity } (Q_e) = (C_i - C_0) \frac{V}{W} \quad (2)$$

where Q_e (mg/g) is the amount of adsorbed fluoride at equilibrium, V is the volume of solution, W is the weight of adsorbent (g), C_i (mg/L) and C_e (mg/L) are the initial and equilibrium fluoride concentrations (mg/L), respectively.

2.5. Desorption Studies

The desorption experiment was studied through separately adding 0.5 g of HTS and BTS to 40 mg/L of fluoride solution while other parameters remained constant. After recording the first adsorption result, the exhausted adsorbents were centrifugally separated and then soaked in 100 mL of 0.5 M NaOH and Na_2CO_3 solution for 12 h at 25°C. Following the agitation, the mixture was again separated by centrifugation. Finally, the desorbed solids dried in the oven at 110°C for 12 h. The same procedures were followed until both adsorbents' adsorption-desorption performance become under half of the original adsorbent. The desorption efficiency was calculated according to Eq. (3).

$$\text{Desorption (\%)} = \left(\frac{C_{de}}{C_{ad}} \right) \times 100 \quad (3)$$

Where C_{de} and C_{ad} are desorbed and adsorbed concentrations of fluoride, respectively.

3. Results and Discussion

3.1. Physicochemical Properties of the Adsorbent

SEM images in Fig. 1 depicted the structural differences of HTS

and BTS before and after adsorption. The raw BTS displayed unevenly distributed pores, rough and irregular structure while raw HTS dominantly exhibited a rough coalesced carbon layer with stacked alignment. The reason for raw BTS is due to the lignin and cellulose structures of the sample was extremely damaged and/or disappeared during pyrolysis. During the HTC process, the acidic medium has gradually seeped into the amorphous cellulose and some soluble segments of lignin of straw resulting in cracked and disrupts the cellulose chain [21]. The SEM after fluoride adsorption were observed to be a uniform morphological distribution of particles containing scattershot pores and smooth heterogeneous surfaces with dull edges in both adsorbents.

The N_2 adsorption-desorption isotherms of HTS and BTS analyzed (Fig. 2). According to IUPAC classification, BTS displayed isotherm a combined type I and type IV with H4 hysteresis loop, explaining the presence of a narrow slit-like microporous and mesoporous surface gain through multilayer adsorption followed by capillary condensation.

By contrast, HTS exhibited isotherm type IV with H3 hysteresis loop, indicating staged adsorption on mesopores. Its hysteresis loop revealed loose assemblages of the plate-like structure at which the capillary condensation taking place to fill and withdraw N_2 molecules on those mesopores. It is noteworthy that the BET specific surface area (S_{BET}) and total pore volume (V_T) of HTS are far less than BTS (Table S1). Hence, BTS is expected to further facilitate the adsorption of fluoride through having such favorable morphology which is accessible to adsorbate molecules in a given size and shape than HTS. The linkages of phosphate and phosphate ester with lignocellulose may encourage the expansion of the structure, whereby the voids volume was protected [22, 35]. Further, the average pore diameter (D_{av}) shows larger for HTS than BTS.

The functionalities of both adsorbents studied by FTIR spectra are shown in Fig. 3. The peaks observed on both adsorbents at $3,421 \text{ cm}^{-1}$ and $1,036 \text{ cm}^{-1}$ are assigned to stretching vibrations of O-H [36] and sulfonic group, respectively. Compared to HTS, the peak observed at $2,908 \text{ cm}^{-1}$ derived from the asymmetric aliphatic saturated C-H group [37] and $1,632 \text{ cm}^{-1}$ indicating C = C stretching vibrations and its derived carbons [38] are not observed in BTS. Rather, BTS shows an intensity reduction of such groups due to lignin removal during the pyrolysis treatments. The bending vibration peaks of the water molecules at $1,180 \text{ cm}^{-1}$ representing aromatic C-O-C stretching from cellulose. Some weak bands were also observed in both adsorbents between $700\text{-}490 \text{ cm}^{-1}$, indicating the presence of C-C stretching.

Phase analysis of HTS and BTS and their XRD patterns are shown in Fig. S2. The diffraction patterns of BTS at 16.2° and 27.3° shows the planes of CaO_6P_2 while 26.5° shows the plane of Si (P_2O_7). Those peaks also revealed the crystalline carbonaceous structure of BTS. The sharp and intense peak at 24° is due to the enlargement of crystalline size and further development of pores. The extra slight peaks appeared at 13.56 , 31.35 , and 42° are associated with randomly existed SiC crystal structure of a short-ranged order in graphene oxide layers. The two broad peaks of HTS shown at around 14.4 and 26° are signifying the amorphous AlPO_4 phase [39].

The thermogravimetric curve of BTS and HTS are shown in Fig. S2. The weight loss of both adsorbents in the temperature

Fig. 1. SEM images of both adsorbents before (a-BTS, b-HTS) and after (c-BTS, d-HTS) adsorption.

Fig. 2. The N_2 adsorption-desorption isotherms of BTS (a) and HTS (b) (insert: pore size distribution).

range from 30 to 250°C, ascribed to the surface-bound water and moisture release (dehydration). The steep and gradual weight loss (49%) for HTS occurred from 250°C to 545°C and the major weight loss (about 76%) for BTS took place from 250°C to 700°C is attributed

mainly to the decomposition of cellulose and lignin [32]. The final weight loss (86.07%) of BTS remained constant above 700°C while the total weight loss (91.79%) for HTS remained constant after the temperature reached 545°C.

Fig. 3. FTIR spectra of BTS and HTS.

3.2. Effects of Different Experimental Conditions

3.2.1. Effect of solution pH

The adsorption process was highly depending on the solution pH with a similar trend for both adsorbents. The high adsorption capacity was recorded in low pH with a peak at pH 2 while abruptly ceased after pH 8 (Fig. 4(a)). It is evident that the presence of H^+ at low pH, the attraction of fluoride ion with the adsorbent sites could be strengthened since the hydroxylation process is formed [40]. Conversely, the higher pH enhances the adsorption competition between hydroxyl and fluoride ions; thereby the adsorbent sites could be more occupied by hydroxide ions over aimed adsorbate. Hereafter, pH 2 was used for subsequent experiments.

3.2.2. Effect of initial adsorbent moisture

The effect of initial moisture content present on the prepared adsorbent was studied by varying the drying temperature for both adsorbents (Fig. 4(b)). The higher adsorption capacity was shown at 15% initial moisture content. A slight decrease in adsorption capacity at the moisture level below 15% might be due to less hygroscopicity

Fig. 4. Effects of pH (a), initial adsorbent moisture (b) and BTS dose (c) and HTS dose (d).

at the initial adsorption stage, leads to occur slow kinetics. The adsorption capacity of both adsorbents was ceased gradually with increasing the initial moisture content. Li et al. [41] noted that the solid-liquid interaction could be inhibited through micelles (formed by the carbon-oxygen and H₂O complexes on carbonaceous material), which bind the H₂O molecules and then hinder the pore chamber expansion. The available adsorbent moisture content was calculated using ASTM D2867 standards [42].

3.2.3. Effect of adsorbent dose

In order to examine the effect of adsorbent dose, 100 mg/L of initial fluoride solution was employed with an adsorbent dose started from 0.1 g till the point at which the final concentration could able down to a safe level. As shown in Fig. 4(c) the amount of BTS needed to obtain safe fluoride level was achieved by using 2/3 of the amount for HTS (Fig. 4(d)). This phenomenon may due to the difference in the availability of free active sites which still enabled to adsorb the remaining ions [43].

3.2.4. Effect of contact time

Figure S4 shows an increase in fluoride adsorption capacity with an increase in contact time until about 2 h for both adsorbents, after which the increment was very negligible denoting attainment of equilibrium. The instantaneous sorption reaction at the initial stage in which fluoride ions adsorbed rapidly onto the surface of the adsorbent could be due to the presence of a large number of vacant active binding sites in both adsorbents. Consequently, the driving force of mass transfer between the liquid and solid phase in an aqueous adsorption system decreasing with time elapse [44].

3.2.5. Effect of initial fluoride concentration

The adsorption capacity of fluoride ion was investigated at different initial fluoride concentration (Fig. S3). The adsorption capacity of BTS and HTS increased from 1.5 to 27 mg/g and 1.7 to 24 mg/g, respectively, as the initial fluoride concentration was increased from 2 to 40 mg/L. At lower initial concentration, the adsorption system goes independent of initial concentration and gradually gets exhausted sharply with the increase in initial fluoride concentration [45]. This could probably take place due to an increase in the diffusion of fluoride ion to adsorption sites until sorbent saturation is achieved. Moreover, the utilization of less accessible or less active sites of the adsorbent could occur when there was more fluoride ion in the solution to be taken up.

3.2.6. Effect of agitation speed

The fluoride removal increased for both adsorbents on increasing the agitation speed. From Fig. S5, it can be seen that the equilibrium adsorption capacity occurred at the speed of 200 rpm for both adsorbents. Beyond 200 rpm agitation speed, there was no further fluoride uptake noticed for both adsorbents. The lower agitation speed leads to the accumulation of the adsorbent particles in the flask instead of spreading in the sample solution [44]. On the contrary, a higher agitation speed encourages the mobility and mass transfer of the fluoride ion in the system by reducing a boundary layer thickness around the adsorbent surface.

3.3. Thermodynamic Studies

The thermodynamic behavior of the adsorption process was examined through varying adsorption temperatures. The parameters result (Table S2) shows the function of temperature and related thermodynamic parameters of the adsorption which are calculated by the following equations:

$$K_L = \frac{Q_e}{C_e} \quad (4)$$

$$\Delta G^0 = -RT \ln K_L \quad (5)$$

$$\ln K_L = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (6)$$

Where ΔG^0 (kJ/mol), ΔH^0 (kJ/mol) and ΔS^0 (kJ/mol K) are the standard free energy, enthalpy and entropy change, respectively. T is the temperature (K) and R is the universal gas constant (8.314 J/mol K). The slope and intercept of the plot of the distribution coefficient (K_L) versus $1/T$ were used to calculate the values ΔH^0 and ΔS^0 , respectively.

Both adsorbents exhibited almost similar thermodynamic behavior. The less negative values of ΔG^0 with increasing the adsorption temperatures showing the adsorption process was spontaneous and the exchange is proportional to the temperature for both adsorbents. The positive values of ΔH^0 revealed an exothermic adsorption process. It also likely indicated the higher electro-negativity of fluoride ion and its substitution for hydroxide ion on the carbonized feature of the adsorbents, thereby chemical in nature [46]. The positive values of ΔS^0 confirm the affinity of fluoride ions towards the adsorbents.

3.4. Adsorption Isotherm

The adsorption response for an increment in the amount of adsorbate at constant temperature was studied. Langmuir and Freundlich isotherm models were used as Eq. (7) and (8), respectively.

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m K_L} \quad (7)$$

$$\ln Q_e = \ln K_f + \frac{1}{n_f} \ln C_e \quad (8)$$

Where Q_e (mg/g) and C_0 (mg/L) are the equilibrium and initial fluoride concentration, respectively; Q_m is the maximum adsorption capacity (mg/g), K_L (L/mg) and K_f (L/mg) are the Langmuir and Freundlich constant, respectively. A plot of $\ln Q_e$ versus $\ln C_e$ is a straight line defined by a slope n_f and intercept $\ln K_f$.

The result in Fig. 5 shows the Langmuir isotherm fitted with the experimental data for both adsorbents ascribing the adsorption process takes place on their surface with limited interaction of adsorbed molecules while Freundlich fitted well for BTS indicating its heterogeneous surface to perform multilayer adsorption. Table 1 describes as the maximum monolayer adsorption capacity Q_m of BTS and HTS at 100 mg/L is 212 mg/g and 88.7 mg/g, respectively.

Fig. 5. The Langmuir (a) and Freundlich (b) adsorption isotherms.

Fig. 6. The pseudo-second-order kinetics fitting.

3.5. Adsorption Kinetics

The adsorption kinetic behaviour of fluoride on to BTS and HTS were analysed. The experimental data were correlated by using the pseudo-first-order and pseudo-second-order kinetic models. The pseudo-first order model equation is:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (9)$$

And the pseudo-second-order model equation:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \quad (10)$$

Where Q_e (mg/g) and Q_t (mg/g) are the adsorbed amount of fluoride at equilibrium and at a time t , respectively; k_1 and k_2 are the (1/min) and rate constant (g/mg. min), respectively.

Based on the higher correlation coefficients along with a close value of experimental and calculated adsorption capacity (Table 2), the pseudo-second-order was favorably fitted by the pseudo-second-order.

Table 1. Langmuir and Freundlich Isotherm Parameters Obtained from Adsorption of on BTS and HTS

Adsorbents	Langmuir models			Freundlich models		
	$q_m(\text{mg/g})$	$K_L(\text{L/mg})$	R^2	$K_f(\text{mg/g})$	N	R^2
BTS	212	0.078	0.970	6.6	1.04	0.98
HTS	88.7	0.12	0.963	4.7	1.86	0.91

Table 2. Pseudo-First-Order and Pseudo-Second-Order Kinetic Parameters for the Adsorption of Fluoride on to BTS and HTS

Adsorbents	Pseudo-first-order			Pseudo-second-order		
	$K_1(1/\text{min})$	$q_e(\text{mg/g})$	R^2	$K_2(\text{g/mg min}) \times 10^{-2}$	$q_e(\text{mg/g})$	R^2
BTS	0.05	2.05	0.94	1.88	18.8	0.999
HTS	0.06	3.02	0.97	1.21	18.6	0.998

ond-order model than the pseudo-first-order (Fig. 6). Thus, the adsorption of fluoride onto both adsorbents was governed by a chemical reaction at which the electrons are shared between adsorbent sites and fluoride ions via valency forces.

3.6. Desorption Studies

The desorption potential of fluoride ion from the exhausted adsorbent was directly proportional with the eluent concentration. The maximum desorption capacity of BTS and HTS using NaOH was found to be 75% and 84%, respectively. By contrast, higher desorption was performed by using Na_2CO_3 with 82% for HTS and 91% for BTS. In general, HTS has better desorption efficiency than BTS. This may be due to less affinity of fluoride ion with HTS surface.

3.7. Cost Analysis

Considering the raw materials and oven cost is free since the oven heat can be replaced by sunlight, the remaining cost mainly for activation chemicals (i.e., phosphoric acid) and electric power was calculated. The total cost spent to produce 1 kg of BTS and 1 kg HTS on lab scale is \$3.80 and \$5.5, respectively. However, this cost would be lower when it will be produced commercially on a large pilot scale.

4. Conclusions

This paper presents the preparation, comparative characterization and fluoride removal performance of activated BTS and HTS. Both adsorbents produced under minimum activation condition (low H_3PO_4 concentration and temperature) except at nearly long activation time. Pyrolysis process could produce a porous adsorbent as compared to the HTC process. The SEM analysis indicated that the surface morphology of both adsorbents was different prior to and after fluoride adsorption. The FTIR study revealed the presence of more functional groups on the surface of HTS. The BTS performed a multistage decomposition with relatively stable intermediates, indicates the temperature limit of stability of reactants and intermediate products. The pH of the solution and the amount of adsorbent significantly affected the adsorption process. The result indicated that an increase in initial fluoride concentration had a positive effect on adsorption capacity for a given mass of adsorbent. Langmuir isotherm was fitted both adsorbents equilibrium data and Freundlich isotherm fitted well BTS. The adsorption kinetics fitted pseudo-second-order for both adsorbents, indicating the chemisorption process. The maximum fluoride adsorption capacity of BTS was far greater than HTS. The cost spent on preparation of HTS is cheaper as compared for BTS. The characterization, adsorption experiment, kinetics, and isotherm studies are indicated BTS as an efficient adsorbent for fluoride contaminated water.

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Nomenclature

α	Alpha
λ	Lambda
Δ	Delta
W_t	Weight
C_i	Initial concentration
kV	kilovolt
R^2	Regression
Q_e	Equilibrium adsorption capacity (mg/g)
Q_m	Maximum adsorption capacity (mg/g)

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