Enhanced Fluoride Adsorption on Aluminum-Impregnated Kenaf Biochar: Adsorption Characteristics and Mechanism

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Abstract In this study, kenaf, a fast-growing plant, was pyrolyzed to biochar, and the biochar was impregnated with aluminum to improve its fluoride adsorption capacity. The Al-impregnated kenaf biochar (AI-KNF-BC) was pyrolyzed at temperatures of 300–700 °C, where the specimen treated at 300 °C (AI-KNF-300) demonstrated the highest fluoride adsorption capacity. The kinetics and equilibrium adsorption of fluoride by Al-KNF-300 followed the pseudo-second-order and Langmuir models, respectively. According to the Langmuir model, the maximum fluoride adsorption capacity of AI-KNF-300 was 13.93 mg/g. The enthalpy and entropy of fluoride adsorption by AI-KNF-300 were 37.80 kJ/mol and 124.1 J/mol K, respectively. Fluoride adsorption by AI-KNF-300 was favorable at pH values as low as 3, and the effect of anion competition followed the order HCO$_3^-$ > SO$_4^{2-}$ > NO$_3^-$ > Cl$^-$. A maximum adsorption efficiency of 99.23% was obtained at an adsorbent concentration of 16.67 g/L, at which point the fluoride concentration decreased from 100 to <1.5 mg/L (the drinking water standard). Based on these results, AI-KNF-300 can be considered an effective and inexpensive adsorbent for removing fluoride from contaminated water to meet drinking water standards.

Keywords Kenaf · Biochar · Fluoride removal · Impregnation · Al-based adsorbents

1 Introduction

Fluoride occurs naturally in groundwater, freshwater, chlorine sources, and rainwater in urban areas and is released from rocks into water, air, and soil. Fluoride is used in many dental products to strengthen tooth enamel and prevent cavities. Fluoride can be added to drinking water at low concentrations to reduce the incidence of tooth decay in local populations, prompting many developed countries to fluoridate the tap water (Jones et al., 2005; Podgorny & McLaren, 2015). However, prolonged exposure to drinking water with a high fluoride concentration can cause side effects such as dental and skeletal fluorosis, which can damage bones and joints. The population affected by fluorosis has increased over the past 50 years to an estimated 260 million people worldwide (Amini et al., 2008).
defined by the World Health Organization (WHO), is 1.5 mg/L (World Health Organization, 2017). Additionally, according to the US Environmental Protection Agency (EPA), the maximum permitted contaminant level of fluoride in public water systems is 4 mg/L; the secondary maximum contaminant level is 2 mg/L, which requires special notice to the EPA (United States Environmental Protection Agency, 2010). Fluoride concentrations ranging from 0.01 to 3 mg/L in freshwater and from 1 to 35 mg/L in groundwater have been observed in some natural water systems (Tripathy et al., 2006). Since excess fluoride is harmful to humans, contaminated water must be safely treated to make the water drinkable.

Methods commonly used for the defluorination of water include adsorption (Chen et al., 2010; Çengeloglu et al., 2002; Turner et al., 2005), precipitation (Turner et al., 2005; Chang & Liu, 2007), ion exchange (Samadi et al., 2014), electrodialysis (Amor et al., 2001), and membrane filtration (Elazhar et al., 2009). Among these methods, adsorption is the most widely used owing to its cost-effectiveness, ease of application, and ability to remove fluoride even at low concentrations. The performance of the adsorption system depends on the characteristics of the adsorbent, and in recent decades, various adsorbents have been developed for the removal of fluoride from drinking water. Many materials have been tested, such as activated aluminum oxide (Ahammad et al., 2018; Ghorai & Pant, 2004; Tang et al., 2009a, 2009b), amorphous aluminum oxide (Li et al., 2001), Al-modified biochar (Meilani et al., 2021), Fe- and Ca-based adsorbent (Biswas et al., 2007), clamshell (Choi et al., 2021; Lee et al., 2021a, 2021b), eggshell (Lee et al., 2021a), clay (Chen et al., 2011; Karthikeyan et al., 2005), bone charcoal (Leyva-Ramos et al., 2010; Medellin-Castillo et al., 2007), metal oxides (Dhillon et al., 2017), and zeolites (Sun et al., 2011). As fluoride forms strong bonds with Al and Ca, Al- and Ca-based adsorbents are generally used for fluoride removal. Ca-based adsorbents have a low fluoride reduction limit (>2 mg/L) and are not suitable for drinking water treatment (Fan et al., 2003; Wang & Reardon, 2001). In contrast, Al compounds have a strong affinity for fluoride; Al-based materials are porous, have high fluoride adsorption capacities, and can lower the fluoride concentration to 2 mg/L (Farrah et al., 1987; Tchomgwi-Kamga et al., 2010). The surface of aluminum oxide is lipophilic and positively charged, and the pore structure is easily formed by process control (Zhou et al., 2022). Activated alumina can also remove other toxic elements in groundwater such as arsenic and selenium (Farooqi et al., 2007; Tang et al., 2009a, 2009b). Al-based materials can be used as fluoride adsorbents; however, aluminum oxide is expensive, and its optimal pH for fluoride adsorption is in the acidic range, limiting its practical application in drinking water (Li et al., 2001). Therefore, it is desirable to fabricate an Al-based adsorbent material that is cheaper and more environmentally friendly, but equally effective in removing fluoride from drinking water.

Methods of manufacturing Al-based adsorbents for improving fluoride removal include doping (Rojas-Mayorga et al., 2015) and loading (Fan et al., 2022) on carbon-based materials such as biochar. Biochar is obtained by pyrolyzing biomass in an anoxic environment and is rich in carbon, inexpensive, stable, and environmentally friendly (Ahmed et al., 2016). Previous studies have shown that the chemical structure, surface roughness, and specific surface area of biochar are affected by the biomass pyrolysis conditions (Mohan et al., 2014; Zhou et al., 2022; Isik et al., 2022). Biochar obtained under optimal pyrolysis conditions can be a suitable adsorbent material. However, its fluoride adsorption capability is limited, and thus it requires modification (Meilani et al., 2021). Since biochar has a complex pore structure and abundant functional groups, it can be loaded with Al, which has a strong affinity for fluoride (Mian & Liu, 2018).

In this study, kenaf biochar was used as an adsorbent. Kenaf (Hibiscus cannabinus) is an annual grass that belongs to the family Malvaceae and possesses a short growth cycle. It can grow to heights of over 3 m in 3 months under varying weather conditions and moderate ambient conditions (using small amounts of pesticides and herbicides) (Azwa & Yousif, 2013; Nishino et al., 2003; Sellers & Reichert, 1999). Kenaf fibers are composed of cellulosic hemicellulose and lignin; cellulosic material, which is known as an effective adsorbent, comprises approximately 47% of the plants (Malik et al., 2017). In addition, studies have shown that the outer shell and inner core of kenaf stems contain fibrous components, which enhance adsorption (Shamsuddin et al., 2016). Therefore, the high productivity and adsorption potential of kenaf make it a suitable biomass material for use as an adsorbent. Kenaf has been used to remove
various contaminants such as dyes (Mahmoud et al., 2012), Cu (Hasfalina et al., 2012), Cr (Borna et al., 2016), rare-earth elements (Rahman et al., 2017), Ni (Hasfalina et al., 2010), triclosan (Cho et al., 2021), and fluoride (Yusof et al., 2015) from aqueous solutions. In a previous study, fluoride adsorption using kenaf modified with N-trimethylammonium yielded a maximum adsorption capacity of 13.98 mg/g (Yusof et al., 2015). However, the chemical used for modification is expensive, and the fluoride reduction limit is 2 mg/L or more, making it unsuitable for drinking water treatment.

Therefore, in this study, an Al-biochar complex was prepared by Al impregnation and the thermal decomposition of kenaf to improve its fluorine adsorption capacity. Al-impregnated kenaf biochar (Al-KNF-BC) was prepared at various pyrolysis temperatures, and the fluoride adsorption capacities of the samples were compared. In addition, the fluoride adsorption mechanism of Al-KNF-BC was physically and chemically analyzed using field-emission scanning electron microscopy (FE-SEM), Brunauer–Emmett–Teller (BET) analysis, thermogravimetric analysis/differential thermal analysis (TGA/DTA), X-ray diffraction (XRD) analysis, and Fourier-transform infrared (FTIR) spectroscopy. The adsorption mechanism of the Al-KNF-BC sample with the highest fluoride adsorption capacity was analyzed by conducting kinetics, equilibrium, and thermodynamic adsorption experiments and a model analysis. In addition, the effects of pH, competing anions, and adsorbent dose on fluoride adsorption were investigated.

2 Materials and Methods

2.1 Production of Al-Impregnated Kenaf Biochar

The kenaf used as the base material for Al impregnation was procured from the Agricultural Research Institute (Jeonbuk, Korea). The chemical composition and physical properties of kenaf have been described previously (Cho et al., 2021; Kim & Um, 2020). The stem of the kenaf was used; the stem was ground and then sieved to 425 μm. The ground kenaf was then washed with deionized water to completely remove impurities and dried in an oven at 80 °C for 24 h.

Al impregnation on the biochar using aluminum chloride was performed with reference to the optimal Al content determined using the response surface methodology, as described in a previous study (Meilamia et al., 2021). To impregnate the kenaf with a surface Al(OH)₃ layer before thermal decomposition, 500 mL of a 0.741 M (5.89%) aluminum chloride (AlCl₃: Sigma-Aldrich, USA) solution was first placed in a stirred reactor. Next, 50 g of dry kenaf was added and thoroughly soaked. The mixture was neutralized to pH 7 by the addition of a 10 M NaOH (Samchun, Korea) solution and stirred at 150 rpm. Under these conditions, the kenaf surface in the mixture is modified by a strong chelation reaction with Al, and the adsorbed Al³⁺ is present mainly in the form of Al(OH)₃ at pH 7 (Mahfoudhi & Boufi, 2020). The mixture was stirred for 4 h to prepare a homogeneous slurry, which was dried in an oven at 110 °C to obtain Al-impregnated kenaf (Al-KNF).

To pyrolyze the Al-KNF, 20 g of a sample was injected into a stainless steel tube (L/D: 55/5.5 cm) and heat-treated in a muffle furnace (CRFT 830S, Dongseo Science Co., Ltd., Korea) at 300, 400, 500, 600, or 700 °C for 1 h. To maintain anoxic conditions, which are required for pyrolysis, an inert gas (N₂ gas, > 99.9%) was injected at a flow rate of 0.5 L/min to purge the inside of the tube; the heating rate was 20 °C/min. The Al-KNF-BC samples pyrolyzed at each temperature were labeled as follows: Al-KNF-300, Al-KNF-400, Al-KNF-500, Al-KNF-600, and Al-KNF-700.

Fluoride adsorption by the Al-KNF-BCs prepared at various pyrolysis temperatures was compared. A 1000 mg/L fluoride solution was prepared by dissolving 2.2101 g of sodium fluoride (NaF, Sigma-Aldrich, USA) in 1 L of deionized water and then diluted five times to 200 mg/L. All materials were weighed using an analytical electronic balance with a reproducibility of 0.1 mg. Al-KNF (0.1 g) was placed in a 50-mL conical tube, and 30 mL of a 200 mg/L fluoride solution was injected using a pipette. The conical tube was placed in an incubator, and the mixture was stirred at 25 °C and 100 rpm for 12 h. The reacted mixture was first filtered through a qualitative filter paper (No. 2, Advantec, Japan) with a pore size of 5 μm, followed by a syringe filter (Advantec, Japan) with a pore size of 0.45 μm. The fluoride in the filtered solution was adsorbed using ion chromatography (DX-120,
Dionex, USA), and the residual fluoride concentration was measured.

2.2 Adsorption Characterization

Several characterization methods were used to determine the chemical composition, morphology, and fluoride adsorption reaction mechanism of the Al-KNF-NT (untreated) and pyrolyzed Al-KNF-BC samples. All samples were washed with deionized water and dried before FE-SEM and XRD measurements. The surface morphology of the samples was observed using FE-SEM (S-4700, Hitachi, Japan). Energy-dispersive X-ray spectroscopy (EDS) was performed using an instrument attached to the scanning electron microscope to investigate the elemental composition. The specific surface area of Al-KNF was calculated using the BET equation and by conducting N\textsubscript{2} adsorption/desorption experiments. TGA was performed using a thermogravimetric analyzer (Pyris 1, PerkinElmer, USA) at 30–700 °C with a heating rate of 10 °C/min under N\textsubscript{2} gas. The crystal structures of the samples were determined using XRD (SmartLab, Rigaku, Japan). Functional groups on the biochar surface were identified using FTIR spectroscopy (Nicolet 6700, Thermo Fisher Scientific, UK).

2.3 Data Analysis

The amount of fluoride adsorbed per unit mass of adsorbent was calculated using the mass balance equation:

\[ q_e = \frac{(C_i - C_e) \times V}{m} \]  \hspace{1cm} (1)

where \( C_i \) (mg/L) is the initial fluoride concentration, \( C_e \) (mg/L) is the residual fluoride concentration at equilibrium, \( V \) (L) is the solution volume, and \( m \) (g) is the adsorbent dose. The fluoride adsorption efficiency (%) of the adsorbent was calculated as follows:

\[ \text{Adsorption efficiency} \% = \frac{(C_i - C_e)}{C_i} \times 100 \]  \hspace{1cm} (2)

The mathematical expressions (nonlinear fits) of the pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models are shown in Eqs. (3) and (4), respectively (Lagergren, 1898; Ho & Mckay, 1998).

\[ q_t = q_e(1 - e^{-k_1t}) \]  \hspace{1cm} (3)

\[ q_t = \frac{k_2q_e^2 t}{1 + k_2q_e t} \]  \hspace{1cm} (4)

where \( q_t \) (mg/g) and \( q_e \) (mg/g) are the amounts of fluoride adsorbed at time \( t \) (h) and equilibrium, respectively; and \( k_1 \) (1/h) and \( k_2 \) (g/mg h) are the PFO and PSO adsorption rate constants, respectively.

The nonlinear mathematical expressions of the Langmuir and Freundlich isotherm models are shown in Eqs. (5) and (6), respectively (Freundlich, 1907; Langmuir, 1916).

\[ q_e = \frac{Q_{\text{max}}K_L C_e}{1 + K_L C_e} \]  \hspace{1cm} (5)

\[ q_e = K_F C_e^n \]  \hspace{1cm} (6)

where \( Q_{\text{max}} \) (mg/g) and \( K_L \) (L/mg) are the maximum adsorption capacity of the adsorbent and the Langmuir constant related to the adsorption energy of the adsorbent, respectively; and \( K_F \) (mg/g (mg/L)^{−1/n}) and \( n \) (−) are the Freundlich constant and adsorption strength, respectively.

The thermodynamic parameters were calculated as follows:

\[ \Delta G^0 = -RT\ln(K_e) \]  \hspace{1cm} (7)

\[ \ln(K_e) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \]  \hspace{1cm} (8)

\[ K_e = \frac{aq_e}{C_e} \]  \hspace{1cm} (9)

where \( \Delta G^0 \) (kJ/mol), \( \Delta S^0 \) (J/mol K), and \( \Delta H^0 \) (kJ/mol) are the changes in the standard Gibbs free energy, enthalpy, and entropy, respectively; \( a \) (g/L) is the adsorbent dose; \( q_e \) (mg/g) is the maximum adsorption amount; \( T \) (K) is the absolute temperature; and \( R \) (= 8.314 J/mol K) is the universal gas constant.

2.4 Adsorption Experiments

Fluoride adsorption experiments were conducted to examine the kinetics, equilibrium, and thermodynamics, as well as the effects of pH, ion competition,
and adsorbent dose. In all experiments, the adsorbent was Al-KNF-300, which had the highest adsorption capacity per unit mass in the previous experiment. In addition, unless otherwise specified, in all experiments, 0.1 g of adsorbent and 30 mL of 100 mg/L fluoride solution were reacted in a 50-mL conical tube, which was shaken for 12 h at 100 rpm in an incubator at 25 °C. In the kinetics experiment, a 100 mg/L fluoride solution was injected, and the reaction time (0.25–72 h) was varied at a constant temperature (25 °C). In the equilibrium isotherm experiment, the concentration of the initial fluoride solution (5–150 mg/L) was varied at a constant temperature (25 °C), and the reaction was conducted for 12 h. In the thermodynamics experiment, the reaction temperature was varied (15, 25, and 35 °C), and the reaction was carried out in a 100 mg/L fluoride solution for 12 h. The adsorption experiment using fluoride solutions of different pH was performed after the pH of the 100 mg/L fluoride solution was adjusted to 3, 5, 7, 9, and 11 using 0.1 M NaOH and 0.1 M HCl solutions. Fluoride adsorption experiments with different competing anions were performed using 1 mM and 10 mM NaHCO₃, Na₂SO₄, NaCl, and NaNO₃ (reagent-grade, Samchun, Korea) in a 100 mg/L fluoride solution. In the adsorption experiment examining the effects of adsorbent dose, 3.33, 6.67, 10, 13.33, and 16.67 g/L of the adsorbent were reacted with a fixed volume (30 mL) of 100 mg/L fluoride solution.

3 Results and Discussion

3.1 Characteristics of Al-KNF

Figure 1 shows the amount of fluoride adsorbed by the untreated and biochar samples (Al-KNF-NT and Al-KNF-BC, respectively). The amount of fluoride adsorbed per unit mass of Al-KNF increased sharply to 13.72 mg/g for the sample pyrolyzed at 300 °C, which is ≈9.6 times that of Al-KNF-NT (1.43 mg/g). At pyrolysis temperatures above 400 °C, the amount of fluoride adsorbed decreased and did not differ significantly from that of Al-KNF-NT. To determine why Al-KNF-300 possessed the highest fluoride adsorption capability and investigate the adsorption mechanism, physical and chemical analyses of Al-KNF were performed.

The surface morphology and physical properties of Al-KNF were observed using FE-SEM and BET analysis, as shown in Fig. S1 and Table 1. The Al-KNF surface has a thin, porous structure unique to biochar; it becomes rough with increasing pyrolysis temperature. This is because pores and cracks are formed on the biochar surface as volatiles are generated and escape during heat treatment, increasing the porosity of the structure (Abdel-Fattah et al., 2015). The Al-KNF-NT and Al-KNF-300 surfaces were devoid of crystalline material, possibly owing to the presence of amorphous aluminum. However, material assumed to
be nano- and microsized Al particles (Al₂O₃) was distributed on the surface of the Al-KNF-BCs pyrolyzed at 400–700 °C, which was confirmed by the XRD analysis (Mahfoudhi & Boufi, 2020; Sun et al., 2008).

The BET specific surface area of Al-KNF-NT was not measured because the pores of Al-KNF were blocked by the AlCl₃ and NaOH used for impregnation. The BET results revealed that the clogged pores of Al-KNF-NT cannot adsorb fluoride; consequently, less fluoride was adsorbed compared to the other adsorbents. The specific surface area of the Al-KNF-BCs increased from 27.24 to 79.29 m²/g as the pyrolysis temperature increased from 300 to 700 °C, and the pore volume and pore size increased with increasing specific surface area. This is because the cracking of cellulose, hemicellulose, and lignin with oxidation depends on pyrolysis temperature; thus, more micropores are created, and the internal surface area increases with increasing temperature (Zhuang et al., 2021). Since the observed pore size of the Al-KNF-BCs is 4–22 nm, which is much larger than the radius of the fluoride ion (1.33 Å), F⁻ may be dispersed into the inner layer of Al-KNF. However, although these physical changes (surface roughness and specific surface area) might increase the adsorption potential of Al-KNF, they cannot fully account for the high fluoride adsorption of Al-KNF-300.

TGA/DTA revealed a decrease of 15.5% in the total weight of Al-KNF at temperatures of 30–700 °C, as shown in Fig. 2. Approximately 4.5% of the

| Temperature (°C) | Elemental composition | Physical properties | Yield |
|------------------|----------------------|---------------------|-------|
|                  | C % | O % | Na % | Al % | Cl % | O/C | Specific surface area (m²/g) | Pore volume (cm³/g) | Pore size (nm) |       |
| Not treated      | 21.9 | 35.8 | 0.2  | 29.1 | 12.9 | 1.6  |  -                     |  -                 |  -         |  -     |
| 300              | 58.3 | 31.2 | 1.5  | 6.0  | 3.0  | 0.5  | 27.24                 | 0.031              | 4.62       | 93.7%  |
| 400              | 61.7 | 26.0 | 1.9  | 6.6  | 3.8  | 0.4  | 72.73                 | 0.072              | 3.94       | 88.4%  |
| 500              | 65.1 | 22.0 | 1.2  | 8.2  | 3.5  | 0.3  | 67.28                 | 0.082              | 4.89       | 86.2%  |
| 600              | 60.0 | 24.1 | 1.0  | 11.8 | 2.6  | 0.4  | 79.11                 | 0.101              | 5.11       | 85.2%  |
| 700              | 42.6 | 26.4 | 1.8  | 25.8 | 3.4  | 0.6  | 79.29                 | 0.102              | 5.16       | 84.5%  |

*Obtained using EDS.

Obtained using BET method.

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**Fig. 2** Thermogravimetric (TG) weight loss and differential thermal analysis (DTA) of Al-KNF in the temperature range of 30–700 °C
weight loss is attributed to moisture loss because the weight loss up to 200 °C is due to the evaporation of adsorbed water on the material surface. The sharp peak in the DTA curve from 200 to 420 °C is represented by two curves. The highest peak in the DTA curve appears at 370.2 °C. The overall weight loss (7.6%) up to 200–420 °C may be due to the decomposition of cellulose and hemicellulose in kenaf (Ferrara et al., 2014). Here, the sharp weight loss up to 240–300 °C may result from the removal of surface functional groups and hydroxyl groups generated by co-precipitation (Ding et al., 2018; Ebadi et al., 2021). The moderate weight loss at 420–700 °C may be due to loss of C, that is, the continuous breakdown of lignin (Cho et al., 2021).

Table 1 shows the results of elemental analysis of Al-KNF using EDS. Al-KNF is composed mainly of C, O, Na, Al, and Cl. Here, Na and Cl may indicate the presence of NaCl produced during Al impregnation and not removed by washing. According to Table 1, Al-KNF-NT has a Cl content of 12.9%, which was not easily removed by washing. Chlorine remaining on the surface of Al-KNF-NT may compete with fluoride and interfere with fluoride adsorption on the adsorbent surface. This may explain why Al-KNF-NT adsorbed less fluoride than Al-KNF-300 despite the high Al content. In addition, as the pyrolysis temperature of Al-KNF-BC increases (> 500 °C), the C content decreases and the Al content increases. The decrease in C content is attributed to the combustion of organic matter with increasing carbonization temperature, and a slight decrease in the C content simultaneously causes a high mineral content (Stefaniuk & Oleszczuk, 2015). The O/C ratio of Al-KNF decreased during heat treatment, indicating increased hydrophobicity and fewer polar groups (Zhang et al., 2011).

Figure S2 shows the FTIR spectra of Al-KNF-NT and the Al-KNF-BCs pyrolyzed at each temperature. The broad band centered at 3300–3400 cm⁻¹ can be attributed to the stretching vibration of the OH group, and the vibration band derived from the OH⁻ group is clearly visible at 660 cm⁻¹ (Rapacz-Kmita et al., 2005). The peak near 2140–2100 cm⁻¹ indicates weak triple-bond stretching of C and C. The 1602 cm⁻¹ peak is due to aromatic-ring stretching oscillations (C=C and C=O), indicating the formation of carbonyl-containing groups and initial aromatization of the precursor (Guo & Rockstaw, 2006). This peak was the most intense at a thermal decomposition temperature of 300 °C and tended to decrease as the thermal decomposition temperature increased. This result indicates that the carboxyl groups are decomposed at high temperature, and the aromatization of the activation mixture increases (Guo & Rockstaw, 2006). The peaks of Al-KNF-400 and Al-KNF-500 at 1165–1252 cm⁻¹ are attributed to C–O stretching oscillations and indicate that the samples contain organic substances such as carboxylic acids and alcohol anhydrides (Lin et al., 2019). At higher pyrolysis temperatures (600 and 700 °C), the broad OH band at 3300–3400 cm⁻¹ and C–O stretching oscillations at 1165–1252 cm⁻¹ decreased and ultimately disappeared. The adsorption band in the range of 500–800 cm⁻¹ arising from Al-KNF-NT to Al-KNF-400 is characteristic of the Al–O–H bond (Jagtap et al., 2011). However, the spectrum of the Al-KNF-BCs heated above 500 °C showed only the Al–O–Al adsorption band, indicating the complete transformation of AlOOH to Al₂O₃ owing to dehydration (Zhang et al., 2019).

The XRD patterns of Al-KNF indicate the crystallinity of the samples (Fig. 3). The reflection peaks are identified as NaCl, AlOOH, and Al₂O₃ (JCPDS card numbers 05–0628, 84–0175, and 80–0955, respectively). These minerals are present because AlCl₃ was used to impregnate the kenaf surface with Al, which is consistent with the EDS data. The line broadening of the XRD patterns of the prepared sample indicates small particle sizes or an amorphous boehmite structure (Sun et al., 2008). As the pyrolysis temperature increases, the Al peak sharpens owing to the crystallization of Al. In addition, in the Al-KNF-BCs treated at ≥ 400 °C, Al is present in the form of aluminum oxide rather than aluminum hydroxide owing to dehydration, which is consistent with the results of other studies (Sun et al., 2008; Zhang et al., 2019). Amorphous Al is more effective at adsorbing fluoride because the dissolution of Al is more pronounced in the amorphous phase than in the crystalline phase (Harrington et al., 2003). In addition, the amorphous form of aluminum hydroxide exhibits better defluoridation performance than aluminum oxide, probably owing to the presence of hydroxyl groups, which supply abundant electrons (Chen et al., 2022). Consequently, Al-KNF-300 (which contains aluminum hydroxide) adsorbs more fluoride than the specimens pyrolyzed at ≥ 400 °C (which contain aluminum oxide) in this experiment.
Fig. 3 XRD patterns of Al-KNF: (a) Al-KNF-NT, (b) Al-KNF-300, (c) Al-KNF-400, (d) Al-KNF-500, (e) Al-KNF-600, and (f) Al-KNF-700
Al-KNF-300 adsorbed more fluoride than Al-KNF-NT because the pyrolysis created pores and Cl⁻ was washed out afterward. In comparison with the other Al-KNF-BCs, Al-KNF-300 had lower surface roughness and a smaller specific surface area; no significant difference in Cl content was found. Therefore, the adsorption mechanism of Al-KNF-300 cannot be interpreted solely in terms of these physical changes and Cl content. At pyrolysis temperatures above 400 °C, the Al peak sharpened owing to Al crystallization, and the Al on the surface of the Al-KNF-BCs transformed from AlOOH to Al₂O₃. FTIR analysis confirmed that the Al–O–H band of the Al-KNF-BCs disappeared when the pyrolysis temperature exceeded 500 °C, indicating the removal of the hydroxyl group at high pyrolysis temperatures. Aluminum hydroxide has more hydroxyl groups than aluminum oxide and is thus advantageous for adsorption, and amorphous Al has a higher solubility than crystalline Al. Consequently, the adsorption performance of Al-KNF-300, which is more amorphous and contains Al in the form of aluminum hydroxide on its surface, is superior to those of the other Al-KNF-BCs.

3.2 Kinetic Adsorption by Al-KNF-300

The kinetic adsorption of fluoride by Al-KNF-300 was evaluated at a constant reaction temperature (25 °C) for various reaction times (0.25–72 h). The standard deviation of the experimental results was ±2%. Fluoride adsorption increases rapidly from 2.46 to 10.52 mg/g at the beginning of the process (0.25–6 h). Subsequently, the adsorption rate decreases until it approaches equilibrium at 12 h (12.85 mg/g). The adsorption then increases slightly (by <1 mg/g) to 13.74 mg/g at 72 h. Therefore, a fluoride adsorption equilibrium time of 12 h was used in further adsorption experiments. Here, fluoride adsorption requires a concentration gradient between the solution and adsorbent. Initially, many sorption sites are available, and thus the adsorption rate is high. Later in the process, the adsorption site availability and concentration gradient decrease, and the adsorption rate also decreases (Ramos-Vargas et al., 2018).

Nonlinear regression analysis using the PFO and PSO models was applied to the results of the kinetics experiments using the parameter values listed in Table S1. Since the PSO model has a higher correlation coefficient ($R^2=0.992$), it better fits the experimental data. In addition, the equilibrium adsorption value ($q_e$; mg/g) obtained using the PSO model exactly matches that of the experimental data (13.73 mg/g). Therefore, it can be concluded that the PSO model is preferable to the PFO model for explaining fluoride adsorption by Al-KNF-300 (Fig. 4). This result suggests that the adsorption rate is controlled by either electron exchange between the adsorbent and solution or chemical adsorption related to the valence force owing to shared anions (Feng et al., 2011; Mayakaduwa et al., 2016; Wang et al., 2018).

3.3 Equilibrium Isotherm of Al-KNF-300

An equilibrium adsorption experiment using Al-KNF-300 was performed at a constant temperature (25 °C) with various initial concentrations (5–150 mg/L). Figure S3 shows the relationship between the adsorption amount and residual concentration after adsorption. When the initial fluoride concentration was low (5–30 mg/L), more than 95% of the fluoride was removed, indicating that the fluoride concentration of most fluoride-contaminated groundwater (1–35 mg/L) can be reduced to below the drinking water limit (<1.5 mg/L) (Tripathy et al., 2006; World Health Organization, 2017). However, as the fluoride concentration increased, the residual concentration increased, and the adsorption amount reached equilibrium. This equilibrium occurs because F⁻ occupies all of the surface active sites (Chen et al., 2016; Tchomgui-Kamga et al., 2010). In the experiment, equilibrium was first reached at an initial fluoride concentration of 100 mg/L, and 14.22 mg/g of fluoride was adsorbed at the highest fluoride concentration of 150 mg/L. Since Al-KNF-300 can remove fluoride to some extent even at high fluoride concentrations, all batch tests except for the equilibrium test were performed at an initial fluoride concentration of 100 mg/L.

Equilibrium isotherm analysis of the adsorption equilibrium data can reveal the adsorption capacity, which is very important in the design of adsorption systems (Iriel et al., 2018). The results of this equilibrium experiment were modeled using equilibrium isotherm models (the Langmuir and Freundlich models); the parameter values are listed in Table S2. The correlation coefficient ($R^2$) values
show that the Langmuir model fits the data for fluoride adsorption by Al-KNF-300 much better than the Freundlich model. Therefore, it can be inferred that the adsorbate molecules do not interact, and adsorption occurs in a monolayer on a homogeneous surface (Saleh et al., 2021; Salifu et al., 2013). The $Q_{\text{max}}$ value (13.93 mg/g) given by the Langmuir model of fluoride adsorption by Al-KNF-300 is similar to the equilibrium value in the experimental data (14.22 mg/g). The fluoride adsorption capacity obtained in this study was compared with those of various natural and synthetic adsorbents (Table 2). Since direct comparison with other adsorbents is difficult, the initial fluoride concentration, particle size, pH, and temperature are presented along with the fluoride adsorption amount. The results show that Al-KNF-300 has a relatively high fluoride adsorption capacity (in the moderate to high range) compared with the other adsorbents. In addition, the particle size of the adsorbents used for fluoride removal in the previous studies varies from tens to thousands of micrometers, and Al-KNF-300 has a large particle size (450 μm), despite its effective fluoride adsorption ability. Adsorbents containing larger particles are easier to filter out of aqueous solution than nano-/microsized adsorbents because they do not require further treatment to separate them from the treated water.

3.4 Thermodynamic Study of Al-KNF-300

A batch test was performed at three temperatures (15, 25, and 35 °C) to evaluate the thermodynamic adsorption mechanism in terms of the effect of reaction temperature on fluoride adsorption by Al-KNF-300. Using these data, the changes in the Gibbs free energy ($\Delta G^0$), enthalpy ($\Delta H^0$), and entropy ($\Delta S^0$) during adsorption can be calculated using the Van’t Hoff equation, as shown in Eq. (7). $\Delta H^0$ and $\Delta S^0$ were obtained as the slope and intercept, respectively, in the plots of ln($K_e$) versus $1/T$ in Fig. S4. The calculated thermodynamic parameters are listed in Table S3. $\Delta G^0$ decreased with increasing temperature and was negative at 35 °C. These results indicate that fluoride adsorption by Al-KNF-300 becomes more spontaneous and energetically favorable with increasing system temperature (Ha et al., 2017). In addition, the increase in activation energy with increasing reaction temperature suggests that adsorption is an endothermic process, which is confirmed by the positive enthalpy change $\Delta H^0$ (do Nascimento et al., 2021). The type of interaction
**Table 2** Fluoride adsorption capacity of Al-KNF-300 and other adsorbents

| Adsorbent                                      | Maximum adsorption capacity (mg/g) | Initial fluoride concentration (mg/L) |Particle size (μm) | pH  | Temperature (°C) | Reference                                      |
|------------------------------------------------|-----------------------------------|---------------------------------------|--------------------|-----|------------------|-----------------------------------------------|
| Laterite                                       | 0.5                               | 1–50                                  | 2000               | 8   | -                | Iriel et al., 2018                            |
| Montmorillonite clay                           | 1.485                             | -                                     | 75                 | -   | 30               | Karthikeyan et al., 2005                      |
| Kanuma mud                                      | 1.558                             | 5–50                                  | 150                | 6.9 | 30               | Chen et al., 2011                             |
| Stilbite zeolite modified with Fe(III)          | 2.31                              | 5–40                                  | -                  | 6.7 | -                | Sun et al., 2011                              |
| Activated aluminum oxide                       | 2.41                              | 2.5–14                                | 2000–5000          | 7   | -                | Ghorai & Pant, 2004                           |
| Fe–Al-impregnated granular ceramic             | 3.6                               | 5–40                                  | 30–150             | < 6 | 27               | Das et al., 2005                              |
| Magnetic corn stover biochar                   | 4.11                              | 1–100                                 | 595–297            | 8   | 25               | Mohan et al., 2014                            |
| Waste carbon slurry                            | 4.31                              | 10                                    | -                  | 7.58| 25               | Gupta et al., 2007                            |
| Corn stover biochar                            | 6.42                              | 1–100                                 | 595–297            | 8   | 25               | Mohan et al., 2014                            |
| Iron–tin mixed oxide                           | 10.47                             | 10–50                                 | 140–290            | 6.4 ± 0.2 | 25 | Biswas et al., 2009 |
| Bone char                                      | 11.9                              | 1–20                                  | -                  | 3   | 25               | Medellin-Castillo et al., 2007                 |
| Al-modified kenaf biochar                      | 13.73                             | 5–150                                 | 425                | 7   | 25               | This study                                    |
| N-trimethylammonium-modified kenaf             | 13.98                             | 5–80                                  | 1000–2000          | 5.2 | 25               | Yusof et al., 2015                            |
| Mesoporous aluminum oxide                     | 14.26                             | 20–250                                | -                  | 6   | 30               | Lee et al., 2010                              |
| Protonated chitosan particles                  | 15.87                             | -                                     | -                  | 7   | 30               | Kusriyati et al., 2015                        |
| Quicklime                                      | 16.67                             | 10–50                                 | 150                | 6.61| 25 ± 2           | Islam & Patel, 2007                           |
| Rare-earth-modified aluminum oxide             | 26.45                             | 2–200                                 | -                  | 6   | 25               | He et al., 2019                               |
| Amorphous aluminum hydroxide hollow spheres    | 45.23                             | 40–120                                | -                  | 4   | 25.15            | Zhang et al., 2016                            |
between the adsorbent and adsorbed substance can be classified according to the magnitude of $\Delta H^0$. In general, the interaction is controlled by physical and chemical adsorption when the enthalpy change is 2–20 and 80–200 kJ/mol, respectively (Chaari et al., 2019; Abdilla et al., 2018; Khan & Khan, 2015). For this experiment, $\Delta H^0$ was 37.80 kJ/mol, which lies between the physical and chemical adsorption ranges, suggesting that both physical and chemical adsorption may occur in the adsorption system (Mirsoleimani-azizi et al., 2018; Shahmoradi et al., 2020). The entropy change ($\Delta S^0$) was 124.41 J/kmol. The positive result indicates an increase in disorder at the solid/liquid interface, which suggests that adsorption is both irreversible and stable (Kasperiski et al., 2018; Meilani et al., 2021; Thue et al., 2016).

3.5 Effect of Solution Chemistry on Fluoride Adsorption by Al-KNF-300

The pH of the solution significantly affects the degree of adsorption of fluoride because it controls the interaction at the adsorbent/water interface. A low pH is desirable, as the adsorption of anions such as fluoride is associated with the release of OH$^-$ from the adsorbent surface (Cengeloglu et al., 2006). Al-KNF-300, a metal oxide adsorbent, is hydrated in a humid environment to generate a surface charge, and the interaction between F$^-$ and metal oxides at low pH was modeled assuming the following ligand exchange reaction (Tripathy et al., 2006), where M represents a metal ion (here, Al):

$$MOH + H^+ \leftrightarrow MOH_2^+$$ (10)

$$MOH_2^+ + F^- \leftrightarrow MF + H_2O$$ (11)

Fluoride adsorption by Al-KNF-300 was studied in the pH range of 3–11, as shown in Fig. 5. It can be seen that fluoride adsorption decreased with increasing pH, possibly owing to the competition between F$^-$ and OH$^-$ on the adsorbent surface (Babaeivelni & Khodadoust, 2013). In addition, at an acidic pH, some F$^-$ can combine with H$^+$ to form hydrogen fluoride (He et al., 2019). Therefore, a solution pH as low as 3 is effective for fluoride adsorption by Al-KNF-300.

Various anions are typically present in polluted water and can affect fluoride adsorption by Al-KNF-300 because they compete with F$^-$ at the active sites on the adsorbent surface. Therefore, adsorption experiments were performed in the presence of HCO$_3^-$, SO$_4^{2-}$, Cl$^-$, and NO$_3^-$, which can compete with fluoride. Each anion was added to the fluoride solution at a concentration of 1 mM or 10 mM to react with the adsorbent; the results are shown in Fig. 6. The magnitude of the negative effect on fluoride adsorption decreases as follows:

Fig. 5 Effect of solution pH on fluoride adsorption by Al-KNF-300 (initial F concentration: 100 mg/L; adsorbent dose: 3.33 g/L; reaction temperature: 25 °C; and time: 12 h)
HCO$_3^-$ > SO$_4^{2-}$ > NO$_3^-$ > Cl$^-$. This order may be related to the ratio of charges to radii of the anions (Dhillon et al., 2017). Cl$^-$ and NO$_3^-$ form a surface complex consisting of an outer sphere, whereas sulfate forms a surface complex consisting of outer and inner spheres (Tang, Wang, et al., 2009); therefore, Cl$^-$ and NO$_3^-$ have less effect on fluoride adsorption than SO$_4^{2-}$. HCO$_3^-$ has the most significant effect on fluoride removal because it is hydrolyzed in aqueous solution, increasing the solution pH, and the alkalization of this solution hinders the adsorption of fluoride (Onyango et al., 2004).

3.6 Effect of Adsorbent Dose on Adsorption Ratio and Adsorption Capacity

The effect of adsorbent dose on fluoride removal was examined using a fluoride concentration of 100 mg/L and various adsorbent doses (3.33–16.67 g/L). The results are shown in Fig. S5. As the adsorbent dose was increased from 3.33 to 16.67 g/L, the fluoride removal efficiency increased from 40.65 to 99.23%. This is because the number of active surface sites for fluoride adsorption increased with increasing adsorbent dose (Salifu et al., 2013). The fluoride removal efficiency (%) of Al-KNF-300 and other adsorbents is shown in Table 3.

| Adsorbent                                | Maximum adsorption efficiency (%) | Initial fluoride concentration (mg/L) | Dose (g/L) | Reference                  |
|------------------------------------------|-----------------------------------|--------------------------------------|------------|---------------------------|
| Laterite                                 | 60                                | 3                                    | 4          | Iriel et al., 2018        |
| Protonated chitosan particles            | 72                                | 20                                   | 2          | Kusrini et al., 2015      |
| N-trimethylammonium-modified kenaf       | 77.50                             | 20                                   | 1.2        | Yusof et al., 2015        |
| Activated aluminum oxide                 | 80                                | 100                                  | 20         | Dhawane et al., 2018      |
| Quicklime                                | 80.60                             | 50                                   | 5          | Islam & Patel, 2007       |
| Waste carbon slurry                      | 88.20                             | 100                                  | 3          | Gupta et al., 2007        |
| Corn stover biochar                      | 91.41                             | 10                                   | 10         | Mohan et al., 2014        |
| Al-modified food waste biochar           | 91.42                             | 300                                  | 6.7        | Meilani et al., 2021      |
| Amorphous aluminum hydroxide hollow spheres | 94.13                            | 20                                   | 1          | Zhang et al., 2016        |
| Magnetic corn stover biochar             | 97.71                             | 10                                   | 10         | Mohan et al., 2014        |
| Al-modified kenaf biochar                | 99.23                             | 100                                  | 16.67      | This study                |
adsorption per unit mass of adsorbent decreased as the adsorbent dose increased because the adsorption potential of fluoride per unit mass decreased with increasing adsorbent dose (Wang et al., 2009). At lower adsorbent doses, all sites are fully exposed to fluoride adsorption, and the surface saturates more quickly; consequently, $q_e$ increases. By contrast, at higher adsorbent doses, adsorption occurs selectively at lower-energy sites, and $q_e$ decreases (Biswas et al., 2009).

The maximum fluoride adsorption efficiency (%) of Al-KNF-300 obtained in this study was compared with those of various adsorbents (Table 3). Since direct comparison with other adsorbents is difficult, the initial fluoride concentration and adsorbent capacity are also provided. Al-KNF-300 had a higher fluoride removal efficiency than other adsorbents reported in the literature. In addition, the initial fluoride concentration, which can affect the adsorption efficiency, was also higher than those reported in the literature, indicating that Al-KNF-300 can adsorb sufficient fluoride, even at a relatively high fluoride concentration. When a 100 mg/L fluoride solution was treated with an adsorbent dose of 16.67 g/L, the residual fluoride concentration was 0.84 mg/L, which is within the acceptable range for drinking water (<1.5 mg/L) (World Health Organization, 2017).

4 Conclusion

The stems of kenaf, a plant with high productivity and adsorption potential, were modified to produce Al-impregnated kenaf biochar for use as a fluoride adsorbent. Al-KNF-BCs were produced at various pyrolysis temperatures; Al-KNF-300, which was produced at 300 °C, was the most effective adsorbent for fluoride removal. Al-KNF-300 contains more pores and a lower Cl content than the material without heat treatment. Amorphous Al was present on Al-KNF-300, whereas Al$_2$O$_3$ formed on the other Al-KNF-BCs; the presence of amorphous Al contributed to the high fluoride adsorption capacity of Al-KNF-300. Fluoride adsorption by Al-KNF-300 reached equilibrium at 12 h, where chemisorption was the limiting step. The Langmuir model was found to be the most suitable for modeling fluoride adsorption by Al-KNF-300, indicating that adsorption occurred in a monolayer on a homogeneous surface. The adsorbed amount per unit mass of Al-KNF-300 at equilibrium was 14.22 mg/g, which is comparable to those of previously reported adsorbents. At an adsorbent dose of 3.33 g/L, Al-KNF-300 reduced the fluoride concentration of 5–30 mg/L fluoride solutions to the acceptable drinking water standard (<1.5 mg/L). Thermodynamic adsorption experiments showed that adsorption is an endothermic reaction that increases the randomness. A low pH is favorable for fluoride adsorption by Al-KNF-300 because the adsorbent has a positive surface charge, and there is less competition with OH$^-$ at low pH. The effect of anion competition on fluoride adsorption by Al-KNF-300 decreased in the order HCO$_3^-$ > SO$_4^{2-}$ > NO$_3^-$ > Cl$^-$. With increasing adsorbent capacity, the fluoride adsorption efficiency increased to 99.23%, but the fluoride adsorption amount per unit mass of adsorbent decreased. Al-KNF-300 is an inexpensive, value-added product that can remove fluoride from fluoride-contaminated water and thus lower the fluoride concentration to the drinking water standard.

Author Contribution MYC: writing—original draft, experimental investigation, data analysis; CGL: writing—review and editing; SJP: conceptualization, writing—review and editing, supervision, funding acquisition.

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Data Availability All data generated or analyzed during this study are included in the published article. The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Ethics Approval and Consent to Participate Not applicable.

Consent for Publication Not applicable.

Consent for Participation Not applicable.

Conflict of Interest The authors declare no competing interests.

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