Synthesis of Bio-Adsorbent for Removal of Fluoride from Groundwater – A Column Study

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Abstract

High fluoride levels in ground water used for drinking have caused health concerns for millions of people across the world. Pakistan is one of the countries that have been contaminated by these toxins. However, a little amount of fluoride is required for tooth and bone strength. In any event, the presence of too much of it in drinking water can cause diseases in both people and animals. This study is focused on the synthesis of bio-adsorbent bone char to adsorbent for the removal of fluoride from groundwater obtained from Islamkot district Tharparkar. The bone char was synthesized by pyrolysis of used cow bones at temperature 550°C. The fluoride removal efficiency of bone char was optimized. The impacts of different operating parameters such as flow rates (5mL/min, 10mL/min and 15mL/min), bed height of adsorbent (2cm, 4cm and 6cm), initial fluoride concentration 7.85 mg/L, and contact time (30min, 60min, and 90min) were studied. The removal efficiency was enhanced by increasing the adsorbent bed height and decreasing contact time, and flow rate. With an initial concentration of fluoride 7.85mg/L, the maximum removal efficiency of 90.2% was obtained when the adsorbent bed height, flow rate and contact time were optimized to 6 cm, 5 mL/min and 30min, respectively. The finding showed that bone char can be used as an eco-friendly, inexpensive, and efficient adsorbent for removing fluoride from groundwater.

Keywords—Bone char, fluoride, column study, Groundwater, adsorption efficiency

1 Introduction

GROUNDWATER has been used to provide drinking water for thousands of years. Even today, a huge portion of the world's population relies on groundwater for drinking. As a result, groundwater quality is extremely important. The presence of inorganic contaminants in groundwater, such as arsenic and fluoride, is a significant quality issue [1]. A mixture of natural and anthropogenic activities has an impact on fluoride mobilization in the environment [2]. Natural actives include the breakdown, dissipation, and dissociation of fluoride-based minerals such as, cryolite, apatite, amphiboles fluorite, micas, topaz, and other fluoride-bearing minerals, sources that are anthropogenic include mining, use of pesticide and the use of brick kiln contribute fluoride aquatic system [3]. Fluoride concentrations in groundwater resources are affected by geographic location and are strongly linked to surrounding volcanic activity and fumarolic gases [4].

The World Health Organization's (WHO) recommended value of Fluoride in drinking water is 1.5 mg/L. (WHO, 2011). According to the most recent estimates, fluorosis affects almost 200 million of people live in more than 30 countries around the world [5]. Pakistan is also one of the countries facing this issue [6]. In Sindh province of Pakistan, concentration of fluoride is way above the recommended limit given by WHO. In Tharparkar city, concentration of fluoride is 0.93 ppm to 11.8 ppm [7].

Excessive amount of flouride is very harmful for health and causes many problems. Too much fluoride in the water creates health problems such as Alzheimer's disease, bone brittleness, brain damaged, arthritis, cancer, osteoporosis, thyroid malfunction, and infertility [6]. Fluorosis is a frequent sign of fluoride ingestion, and it is characterized by tooth mottling in moderate instances, neurological impairment

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in severe cases, and bone embrittlement in severe cases (Figure 1) [8]. Many methods used for defluoridation such as, Membrane process [9], co-precipitation [10], precipitation-coagulation [11], adsorption [12], and ion-exchange methods are some of the technologies available for the purpose of removing fluoride contamination from drinking water [13]. The majority of de-fluoridation processes are extremely complicated, necessitating the use of expert staff, and have a high cost [14]. Adsorption is the preferred technology for defluoridation of water at small and industrial scales due to its low price, ease of use, availability, accessibility, higher efficiency, environmental friendliness, and lack of operational expertise and electric power required conducting the process. For the removal of fluoride ions from aqueous solution, groundwater, and waste water in adsorption, carbon-based adsorbent, industrial and agricultural wastes have been investigated and employed. Activated alumina and bone char were the most effective commercial adsorbents for removing fluoride from water [15].

Adsorbents for fluoride adsorption have recently been developed, including bone char, magnetite, kaolinite, clays, biomass, activated alumina, iron oxides, activated carbon, bauxite, and serpentine [16][17][18]. Bone char adsorbent is very effective for the removal of contaminants form water. Animals are butchered all around the world to meet human need for meat. As a result, a large amount of animal bone becomes bone residue, which has an impact on the ecosystem. Animal bone, for example, has morphological qualities (surface area and pore volumes) that make it favorable for adsorption of various chemicals. The ability of hydroxyapatite and bone to remove fluoride [3].

In this paper, bio-adsorbent bone char was synthesized by pyrolysis process and used as an adsorbent in adsorption column for defluoridation from groundwater of Tharparkar, Sindh, Pakistan. We used bone char in column as an adsorbent and performed many experiments of groundwater and analyzed different parameter such as bed height, flow rate, initial fluoride concentrations, final fluoride concentrations and empty contact bed time to find the best fluoride adsorption efficiency.

2 Materials & Methods

2.1 Materials

All the chemicals utilized in this investigation where extremely pure grade and were acquired from Beruni Scientific Store in Hyderabad, Sindh, Pakistan. Cow bones were obtained from a butcher shop Hyderabad.

2.2 Sample Collection

The sample of ground water was collected from the well in Islamkot city, District Tharparkar, Sindh, Pakistan. The depth of that well was 14m (Figure 2).

2.3 Pretreatment of Bone Residues

The bones were washed with tap water; the undesirable material and odor was removed from the bones using a hydrogen peroxide and sodium bicarbonate combination. Additionally, the bones were treated with hydrogen peroxide and sodium bicarbonate for an hour before being cleaned with water again. Following cleaning, the bones were dried completely in the sun for 15 days before being crushed. Using a convective oven at 120 °C for 20 minutes, any remaining moisture from the bones was eliminated. The bones were crushed using a jaw crusher and sieved, and subsequently put in an oven at 105°C for removing moisture content in order to create a larger surface area for Pyrolysis.

Pyrolysis process was used to create bone char, which was then used to remove fluoride. This was accomplished by heating the bones at a rate of 4.5°C/min for 2 hours to attain 550°C temperature in the absence of air, used the bubbler at the outlet of the reactor [19]. After Pyrolysis, the temperature of the bone char was lowered to ambient, and a sample was taken, and then grinded by using a pestle and mortar and an average particle size of 0.540 mm getting after sieving (Figure 4).

2.4 Adsorption Study

The adsorption experiment was carried out in a glass adsorption column with a length of one meter and a diameter of three inches. The continuous packed bed column's design is shown in Figure 5 in column the adsorbent was fully packed and bottom of the column is supported by wool to prevent the loss of adsorbent during filtration process. After packing through the peristaltic pump, the fluoride contaminated water was pumped through the top of the column for treatment. After treatment, the water samples were collected in glass beaker and stored in plastic sample container for investigation.

2.5 Column Experiments

The experiment was conducted using an adsorption column. The de-fluoridation performance of the column is influenced by many factors. Bed height of adsorbent, flow rate, contact time, initial concentration, and final concentration are the most influential

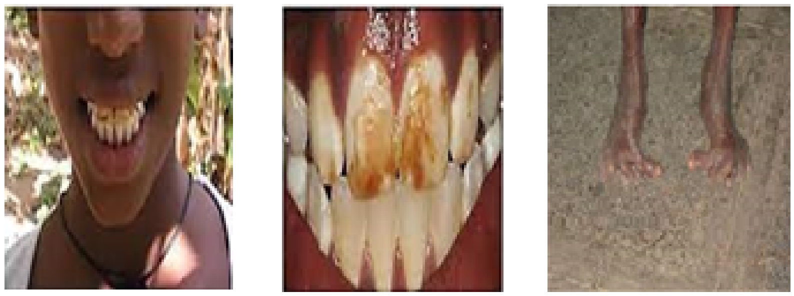

Fig. 1: Effect of Fluoride contaminates water

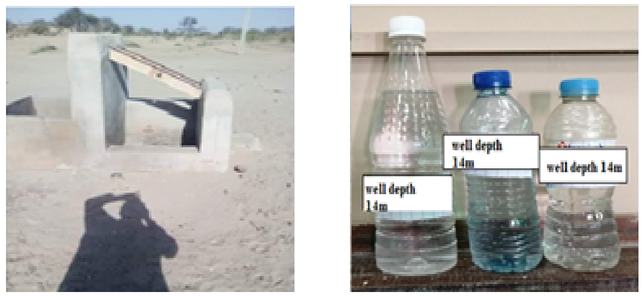

Fig. 2: (a) Islamkot well, (b) Groundwater sample

Fig. 3: (a) Bones, (b) crushing of bones using crusher, (c) pyrolysis of bones

Fig. 4: (a) Bone char, (b) sieving process of bone char, (c) after Sieving bone char

characteristics. The active sites of adsorption are influenced by height of the adsorbent bed. As a result, the effect of adsorbent bed height for three different values (i.e., 2cm, 4cm and 6cm) was investigated.The contact time of given adsorbate solution with adsorbent is significantly affected by influent solution flow rates. Therefore, the effect of three different influent flow rates (i.e., 5 mL/min, 10 mL/min and 15mL/min) of fluoride solution was investigated. The empty bed contact time influences the contact of adsorbent in adsorption column. As a result; for three different values (i.e., 30min, 60min and 90min) the effect of contact time was investigated. The saturation level of active sites present on the adsorbent sample is affected by the concentration of adsorbate solution (influent). As a result, the column's performance for the inlet concentration of fluoride at 7.85 mg/L from well depth 14m was investigated . The initial and final concentrations of fluoride were analyzed through atomic absorption spectroscopy. The absorbability of

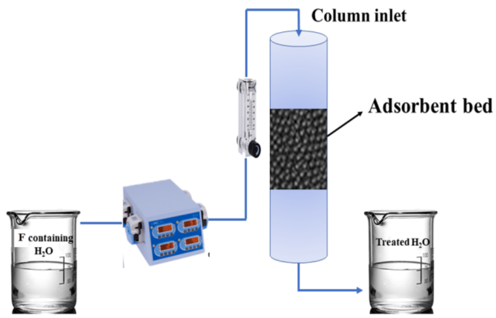

Fig. 5: Adsorption column

fluoride in column was calculated as follows,

$$\%Removal = (C_i - C_e)/C_i \times 100 \quad (1)$$

where C_i is the initial concentration of fluoride (mg/L), and C_e is the equilibrium or final concentration of fluoride (mg/L). The time duration of contact between adsorbent samples used in the column and solution of adsorbate is defined as the empty bed contact time (EBCT). The EBCT is calculated as follows,

$$EBCT = \frac{V}{Q} \quad (2)$$

where V is the volume of adsorbent sample placed in fixed bed adsorption column in cm^3, and Q is the flowrate of influent in mL/min.

3 Results & Discussion

3.1 Effect of Flow rate on Fluoride Removal Efficiency

The effect of flow rate on the removal of Fluoride adsorption was investigated by varying the flow rate from (5 mL/min, 10 mL/min and 15mL/min) at the three different bed height (2cm, 4cm and 6cm) and inlet adsorbate concentration of 7.85 mg/L, as shown in (Table 1-3). It was observed that maximum removal efficiency 90.3% occurred at a lower flow rate (5 mL/min) at the bed height (6 cm), because adsorbate has more time to interact with the surface of adsorbent [20]. At higher flow rates (15 mL/min), the removal efficiency decreased (41.2%) at (2 cm) which is due to the fast saturation of adsorbent surface (Figure 6).

3.2 Effect of Contact Time on Fluoride Removal Efficiency

The contact time refers to the amount of time the treated solution is in contact with the adsorbent. As a result, contact time can have a significant impact on

At 5 mL/min flow rate			
Initial Concentration (mg/L)	**Bed Height (cm)**	**Final Concentration (mg/L)**	**Fluoride Removal Efficiency (%)**
7.85 mg/L	2	2.19	72
	4	1.28	83.6
	6	0.76	90.3

TABLE 1: Effect of 5 mL/min flow rate on fluoride percentage removal efficiency at 7.85mg/L initial fluoride concentration

At 10 mL/min flow rate			
Initial Concentration (mg/L)	**Bed Height (cm)**	**Final Concentration (mg/L)**	**Fluoride Removal Efficiency (%)**
7.85 mg/L	2	2.85	63.6
	4	2.14	72.7
	6	01.38	82.3

TABLE 2: Effect of 10 mL/min flow rate on fluoride percentage removal efficiency at 7.85mg/L initial fluoride concentration

At 15 mL/min flow rate			
Initial Concentration (mg/L)	**Bed Height (cm)**	**Final Concentration (mg/L)**	**Fluoride Removal Efficiency (%)**
7.85 mg/L	2	3.19	59.3
	4	2.72	65.3
	6	1.73	77.9

TABLE 3: Effect of 15 mL/min flow rate on fluoride percentage removal efficiency at 7.85mg/L initial fluoride concentration

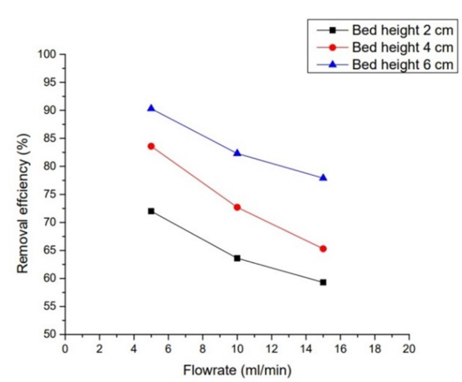

Fig. 6: Effect of flow rate on fluoride percentage removal efficiency at different bed height at 7.85mg/L initial fluoride concentration

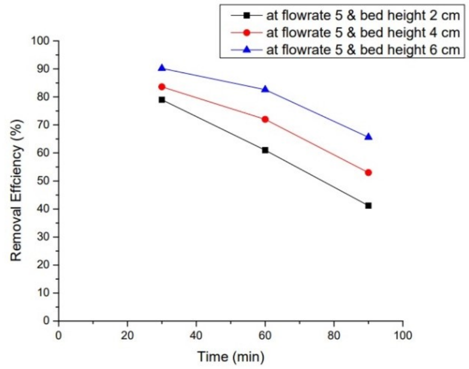

Fig. 7: Effect of time on fluoride percentage removal efficiency at different bed height at 7.85mg/L initial fluoride concentration

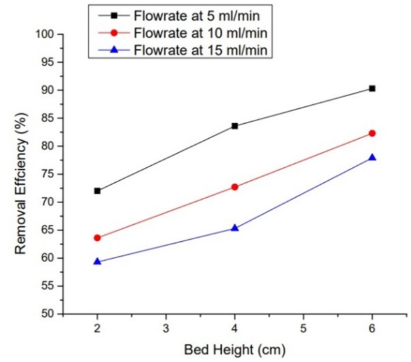

Fig. 8: Effect of bed height on fluoride percentage removal efficiency at different flow rate at 7.85mg/L initial fluoride concentration

adsorption, especially if adsorption is primarily dependent on the contact duration between the adsorbent and the adsorbate [21].

The effect of contact time was investigated by varying the flow rates and contact time, the flow rates were 5mL/min, 10mL/min and 15mL/min, corresponding to contact time of 30min, 60min and 90min, respectively (Table 4-5). The highest removal efficiency was achieved when the flow rate decreased and contact time increased due to more interaction between adsorbent and adsorbate. When the flow rate increased, the lower contact time resulted in lower column utilization [22]. It was observed that the maximum removal efficiency 90.2% occurred at a lower time adsorption (30 min) at the bed height (6 cm), at lower flow rate (5 mL/min). The removal efficiency decreased (41.2%) at at a higher time adsorption (90 min) and bed height (2 cm) which is due to the passage of time adsorption capacity of adsorbent decreases (Figure 7).

3.3 Effect of Bed height on Fluoride Removal Efficiency

Our aim was to study the effect of bed height on fluoride removal efficiency by varying bed height and flow rates. Initial concentration 7.85 mg/L of fluoride was passed through the adsorption column at flow rates of 5mL/min, 10mL/min and 15mL/min, at varying the bed height 2cm, 4cm and 6cm for investigation of fluoride removal (Table 7-9). It was observed that the maximum removal efficiency (90.3%) was observed at bed height of 6cm and at 5mL/min due more interaction between adsorbent and adsorbate, and at 2cm bed height and 15mL/min flow rate the minimum removal efficiency (59.3%) was observed. Thus, it was noticed that the removal efficiency increased with increase in bed height of adsorbent and decreased in flow rate (Figure 8). The length of the bed height strongly influenced the column performance.

4 Conclusion

In this study, the fluoride removal efficiency of bio-adsorbent bone char from cow bones was investigated. Bone char was synthesized by pyrolysis at the temperature of 550°C. After pyrolysis the bone char, particle size was reduced to 0.540 mm through grinding process. Synthetic bone char was used as an adsorbent for column study removal of fluoride from groundwater of Islamkot. Performance of column was optimized by varying different parameters such as flow rates, bed heights and contact time. The maximum fluoride removal efficiency achieved at 5 mL/min is about 90.3% at 6 cm bed height. Furthermore, it was shown that contact time has a substantial impact on fluoride removal efficiency. With a contact time of 30 minutes, the maximum fluoride removal effectiveness of 90.2% was achieved. The current study shows that bone char has a high potential for removing fluoride from water as an adsorbent. The synthetic adsorbent is safe for the environment and may be used to replace a variety of organic and inorganic coagulants. Bone char adsorbent may be manufactured to help people who use fluoride contaminated water in this area. This material is commonly accessible and has been found effective for fluoride removal.

References

[1] M. K. Shahid, S. Phearom, and Y.-G. Choi, "Packed Bed column for adsorption of arsenic on mixed-valent iron [Fe (II)-Fe (III)] oxide synthesized from industrial waste," J. Hazardous, Toxic, Radioact. Waste, vol. 24, no. 2, p. 4020002, 2020.

Effect of Time at Flowrate 5mL/min & 2 cm				
Initial Concentration (mg/L)	**Flow Rate (mL/min)**	**Bed Height (cm)**	**Time (min)**	**Fluoride Removal Efficiency (%)**
7.85 mg/L	5	2	30	79
			60	61
			90	41.2

TABLE 4: Effect of Time at 5 mL/min flow rate on and 2 cm bed height on fluoride percentage removal efficiency at 7.85 mg/l initial fluoride concentration

Effect of time at flow rate 10mL/min & 4cm				
Initial Concentration (mg/L)	**Flow Rate (mL/min)**	**Bed Height (cm)**	**Time (min)**	**Fluoride Removal Efficiency (%)**
7.85 mg/L	10	4	30	83.6
			60	72
			90	53

TABLE 5: Effect of time at 10 mL/min flow rate on and 4 cm bed height on fluoride percentage removal efficiency at 7.85 mg/l initial fluoride concentration

Effect of time at flow rate 15mL/min & 6cm				
Initial Concentration (mg/L)	**Flow Rate (mL/min)**	**Bed Height (cm)**	**Time (min)**	**Fluoride Removal Efficiency (%)**
7.85 mg/L	15	6	30	90.2
			60	82.6
			90	65.6

TABLE 6: Effect of time at 15 mL/min flow rate on and 6 cm bed height on fluoride percentage removal efficiency at 7.85 mg/l initial fluoride concentration

At 2 cm Bed Height			
Initial Concentration (mg/L)	**Flow Rate (mL/min)**	**Final Concentration (mg/L)**	**Fluoride Removal Efficiency (%)**
7.85 mg/L	5	2.19	72
	10	2.85	63.6
	15	3.19	59.3

TABLE 7: Effect of bed height 2 cm on fluoride percentage removal efficiency at 7.85mg/L initial fluoride concentration

At 4 cm Bed Height			
Initial Concentration (mg/L)	**Flow Rate (mL/min)**	**Final Concentration (mg/L)**	**Fluoride Removal Efficiency (%)**
7.85 mg/L	5	1.28	83.6
	10	2.14	72.7
	15	2.72	65.3

TABLE 8: Effect of bed height 4 cm on fluoride percentage removal efficiency at 7.85mg/L initial fluoride concentration

At 6 cm Bed Height			
Initial Concentration (mg/L)	**Flow Rate (mL/min)**	**Final Concentration (mg/L)**	**Fluoride Removal Efficiency (%)**
7.85 mg/L	5	0.76	90.3
	10	1.38	82.3
	15	1.73	77.9

TABLE 9: Effect of bed height 4 cm on fluoride percentage removal efficiency at 7.85 mg/L initial fluoride concentration

[2] M. K. Shahid, J. Y. Kim, and Y. G. Choi, "Synthesis of bone char from cattle bones and its application for fluoride removal from the contaminated water," Groundw. Sustain. Dev., vol. 8, no. December 2018, pp. 324–331, 2019.

[3] M. K. Shahid, J. Y. Kim, G. Shin, and Y. Choi, "Effect of pyrolysis conditions on characteristics and fluoride adsorptive performance of bone char derived from bone residue," J. Water Process Eng., vol. 37, no. July, p. 101499, 2020.

[4] S. S. A. Alkurdi, R. A. Al-Juboori, J. Bundschuh, and I. Hamawand, "Bone char as a green sorbent for removing health threatening fluoride from drinking water," Environ. Int., vol. 127, no. April, pp. 704–719, 2019.

[5] M. O. Thompson and J. P. Kearns, "Modeling and experimental approaches for determining fluoride diffusion kinetics in bone char sorbent and prediction of packed-bed groundwater defluoridator performance," Water Res. X, vol. 12, p. 100108, 2021.

[6] T. A. Chandio, M. N. Khan, and A. Sarwar, "Fluoride estimation and its correlation with other physicochemical parameters in drinking water of some areas of Balochistan, Pakistan," Environ. Monit. Assess., vol. 187, no. 8, 2015.

[7] S. K. Alvi, U. Asghar, F. Perveen, F. A. Khan, and T. H. Usmani, "Groundwater quality of district Tharparkar, Sindh, Pakistan: Focus on fluoride and fluorosis," J. Chem. Soc. Pakistan, vol. 30, no. 3, pp. 372–376, 2008.

[8] Y. Zhou, C. Yu, and Y. Shan, "Adsorption of fluoride from aqueous solution on La 3 + -impregnated cross-linked gelatin," vol. 36, pp. 89–94, 2004.

[9] A. Jeihanipour, J. Shen, G. Abbt-Braun, S. A. Huber, G. Mkongo, and A. I. Schäfer, "Seasonal variation of organic matter characteristics and fluoride concentration in the Maji ya Chai River (Tanzania): Impact on treatability by nanofiltration/reverse osmosis," Sci. Total Environ., vol. 637–638, pp. 1209–1220, 2018.

[10] M. Chigondo, H. K. Paumo, M. Bhaumik, K. Pillay, and A. Maity, "Rapid high adsorption performance of hydrous cerium-magnesium oxides for removal of fluoride from water," J. Mol. Liq., vol. 265, pp. 496–509, 2018.

[11] M. Changmai, M. Pasawan, and M. K. Purkait, "A hybrid method for the removal of fluoride from drinking water: Parametric study and cost estimation," Sep. Purif. Technol., vol. 206, no. May, pp. 140–148, 2018.

[12] M. Mourabet, A. El Rhilassi, H. El Boujaady, M. Bennani-Ziatni, R. El Hamri, and A. Taitai, "Removal of fluoride from aqueous solution by adsorption on hydroxyapatite (HAp) using response surface methodology," J. Saudi Chem. Soc., vol. 19, no. 6, pp. 603–615, 2015.

[13] P. Miretzky and A. F. Cirelli, "Fluoride removal from water by chitosan derivatives and composites: A review," J. Fluor. Chem., vol. 132, no. 4, pp. 231–240, 2011.

[14] L. Chen, K. S. Zhang, J. Y. He, W. H. Xu, X. J. Huang, and J. H. Liu, "Enhanced fluoride removal from water by sulfate-doped hydroxyapatite hierarchical hollow microspheres," Chem. Eng. J., vol. 285, pp. 616–624, 2016.

[15] R. Tovar-Gómez, M. R. Moreno-Virgen, J. A. Dena-Aguilar, V. Hernández-Montoya, A. Bonilla-Petriciolet, and M. A. Montes-Morán, "Modeling of fixed-bed adsorption of fluoride on bone char using a hybrid neural network approach," Chem. Eng. J., vol. 228, pp. 1098–1109, 2013.

[16] J. Cai, X. Zhao, Y. Zhang, Q. Zhang, and B. Pan, "Enhanced fluoride removal by La-doped Li/Al layered double hydroxides," J. Colloid Interface Sci., vol. 509, pp. 353–359, 2018.

[17] E. E. Merodio-Morales, H. E. Reynel-Ávila, D. I. Mendoza-Castillo, C. J. Duran-Valle, and A. Bonilla-Petriciolet, "Lanthanum- and cerium-based functionalization of chars and activated carbons for the adsorption of fluoride and arsenic ions," Int. J. Environ. Sci. Technol., vol. 17, no. 1, pp. 115–128, 2020.

[18] W. Jia et al., "Identification for the capability of Cd-tolerance, accumulation and translocation of 96 sorghum genotypes," Ecotoxicol. Environ. Saf., vol. 145, no. July, pp. 391–397, 2017.

[19] L. N. Côrtes et al., "Biochars from animal wastes as alternative materials to treat colored effluents containing basic red 9," J. Environ. Chem. Eng., vol. 7, no. 6, p. 103446, 2019.

[20] S. Charola, R. Yadav, P. Das, and S. Maiti, "Fixed-bed adsorption of Reactive Orange 84 dye onto activated carbon prepared from empty cotton flower agro-waste," Sustain. Environ. Res., vol. 28, no. 6, pp. 298–308, 2018.

[21] Y. Shan and H. Guo, "Fluoride adsorption on modified natural siderite: Optimization and performance," Chem. Eng. J., vol. 223, pp. 183–191, 2013.

[22] S. Ghorai and K. K. Pant, "Investigations on the column Performance of fluoride adsorption by activated alumina in a fixed- bed," Chem. Eng. J., vol. 98, no. 1–2, pp. 165–173, 2004.