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FLUORIDE REMOVAL FROM WATER BY A NOVEL *DODONAEA VISCOSA* BARK BIOCHAR ADSORBENT

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ABSTRACT: An excess of the fluoride ion (F^-) above the recommended upper limit, such as the WHO recommended upper limit of 1.5 mgL^{-1}, may cause fluorosis in humans, as reported in several countries, e.g. Pakistan, China, and India. Various commercial adsorbents has been used for F^- removal from water but there is still a desire for an environmentally friendly and economic adsorbent. Therefore, a novel adsorbent, i.e. *Dodonaea* bark biochar (DBBC) was prepared, from *Dodonaea viscosa* under pyrolysis at 750 ºC in an inert atmosphere, to remove excessive F^- from water and studied with batch experiments involving a number of parameters: pH (2–10), contact-time (5–145 minutes), dosage of adsorbent (1–7 g/50 mL), and initial F^- concentration (2–10 mgL^{-1}). The biochar showed 90% F^- removal in the acidic range and 60% removal at neutral pH under optimized conditions. In conclusion, the adsorbent DBBC is recommended as an inexpensive sorbent material for F^- contaminated water.

Keywords: Bark; Biochar; *Dodonaea viscosa*; Fluoride; Pyrolysis; Removal of fluoride.

INTRODUCTION

The fluoride ion (F^-) may badly affect water chemistry and has achieved global importance due to its natural prevalence and its capacity to cause adverse health effects.[1-3] The existence of a high level of F^- in drinking water may lead to skeletal, dental, and non-skeletal fluorosis,[4,5] with a deterioration in the skeletal and dental structures, and in many soft tissues, including the brain and thyroid gland, with, in severe cases, the occurrence of paralysis and death.[6]

The “desirable” upper limit of F^- in drinking water recommended by the World Health Organization (WHO) is 1.5 mg/L but, as a limit of 1.5 mg/L has been seen to be unsuitable in some countries, there is also an option for countries to have their own Country Standards, and some lower country limits have been set, such as 0.6 mg/L in Senegal and 1.0 mg/L in India with the rider in India that “the lesser the fluoride the better, as fluoride is injurious to health.”[7] However, the level of F^- in drinking water in many regions of the world is higher than the recommended level and is hazardous for human health.[8] Thus, it is extremely desirable to be able to remove excessive F^- from water by following a well recommended method and, for this purpose, adsorption is a frequently used method.[9] As compared to other chemical methods, adsorption is simple to set-up, has a minimum power requirement, and is low-cost.[9] Although different adsorbents including *Eucalyptus* bark activated carbon, *Dodonaea viscosa* leaf powder, and *Ziziphus* leaf are being used for F^- removal,[10-12] there is still a need to search for and investigate novel and environmentally friendly materials for the removal of F^- from water.

Therefore in the present work, biochar was prepared from *Dodonaea viscosa* plant bark (Common name dodonaea; local Pashto name: ghorhaskay) to investigate its

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efficiency for the removal of excess F^- removal from water and to evaluate the impact on F^- removal efficiency of the factors of pH, contact-time, dosage of adsorbent, and initial F^- concentration.

MATERIALS AND METHODS

Biochar preparation: The biochar was prepared through pyrolysis in an inert atmosphere inside a furnace (purged with nitrogen gas) at 750 ºC. After pyrolysis, the biochar was allowed to cool and it was then passed through a sieve (<1.5 mm) and then stored for further use.[13,14]

Batch adsorption experiments with biochar: Different amounts (1, 2, 3, 4, 5, 6, and 7 g) of biochar were added to 50 mL of F^- solution and were shacked at 200 rpm. After each experiment, the solution was filtered and the residual F^- was measured.[11,15]

Equation (1) was used for calculating the percent removal of F^- and equation (2) was used for determining the F^- adsorbed (mg/g) q_e at equilibrium.

$$\text{Percent removal} = \left(\frac{Ci-Ce}{Ci}\right)100 \qquad \text{Equation (1)}$$

$$\text{Fluoride Adsorbed at equilibrium qe}\left(\frac{mg}{g}\right) = \left(\frac{Ci-Ce}{W}\right)v \qquad \text{Equation (2)}$$

Where, Ce and Ci (mg/L) are F^- levels at equilibrium and the initial time, W means weight (g), and volume is demoted by V in liters (L).

RESULTS AND DISCUSSION

pH effect: The results indicated that percent F^- removal decreased as the pH increased (Figure 1). The maximum adsorption (90%) was observed at the low pH of 2, which may be because of the presence of an increased number of H^+ ions at this pH. These findings are consistent with those from previous research.[11] The biochar sample was also efficient in F^- removal at pH 7, which shows its practical applicability for treating F^- containing groundwater (Figure 1).

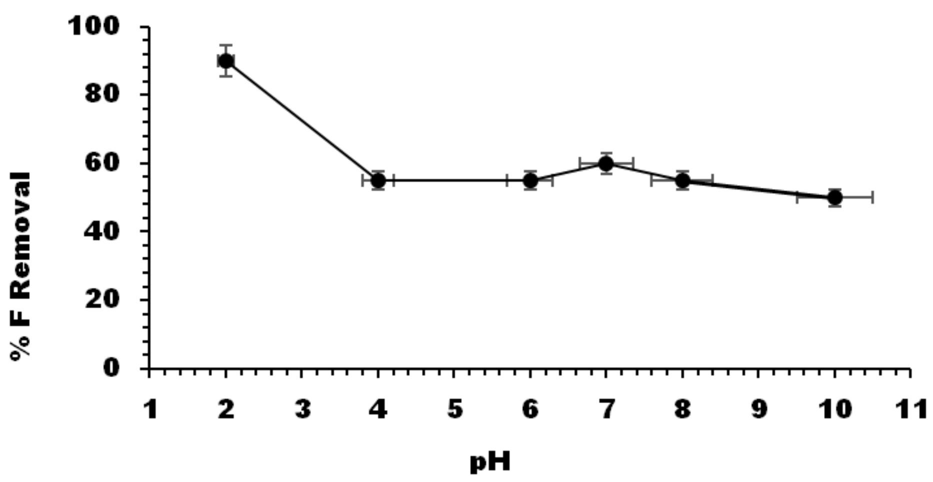

Figure 1. pH effect on F^- removal (initial F concentration: 2 mg/L, dosage of adsorbent: 5 g/50 mL, and contact time: 145 min).

Evaluation of contact time effect: The results indicated that F^- adsorption increases as the time increases (Figure 2) because with an increase in contact time the F^- find more time to catch free sites on the adsorbent.[16] By further maximizing the time interval, no more removal was noticed due to a minimal number of adsorption spaces over the surface of biochar material. Therefore, 125 minutes was selected as the optimum time. These results ware in agreement with previous findings.[17,18]

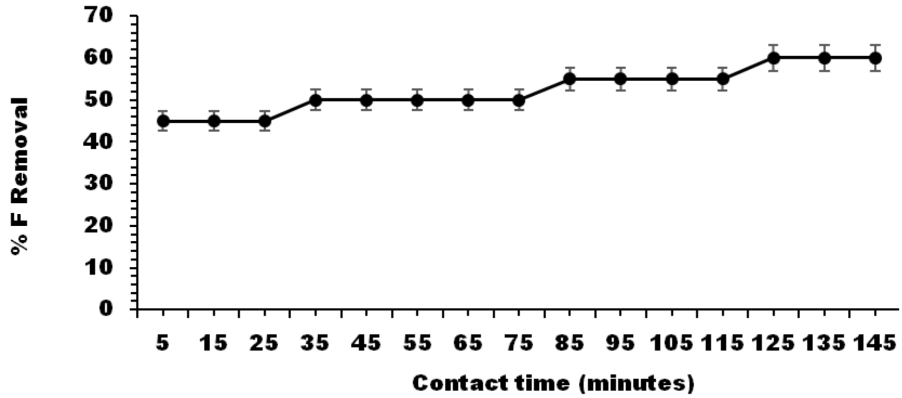

Figure 2. Effect of contact time on F^- removal from water (dosage of adsorbent: 5 g/50 mL, initial F^- concentration: 2 mg/L, and pH: 7).

Effect of adsorbent dose: The effect of sorbent quantity for F^- removal was investigated from 1 to 7 g/50 mL. The results showed that removal increased from 40% to 60% as the dose amount increased from 1 to 5. The reason for this might be that by increasing the dosage, the sum of the vacant empty spaces was also enhanced which would accelerate F^- adsorption (Figure 3). It was noticed that a further increment in dose from 5 to 7 g did not show satisfactory results; hence 5 g/L was selected as the optimum dose (Figure 3). The results are concordant with earlier work.[17,14]

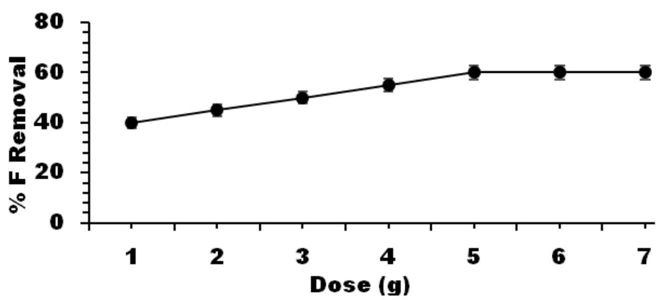

Figure 3. Adsorbent dose effect on F^- removal (initial F^- concentration: 2 mg/L, pH: 7, and contact time: 145 min)

Fluoride initial concentration effect: The F^- removal efficiency of biochar was calculated at various levels ranging from 2–10 mg/L, and it was observed that with a high F^- quantity, the defluoridation efficiency of the adsorbent decreased (Figure 4). The basis of for this may the relative abundance of F^- ions relative to the sorption ability of the studied material.[17,18] The results indicate that the percent F^- removal is greatly dependent on the F^- initial concentration in the solution.[19]

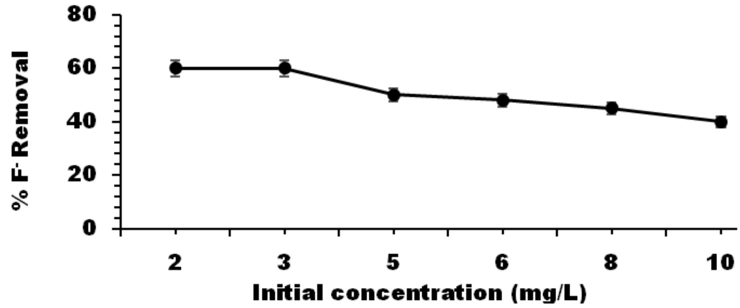

Figure 4. Effect of initial F^-concentration (dosage of adsorbent: 5 g/L dose, pH:7, and contact time:145 min).

Reusability and regeneration study of biochar: The spent adsorbent (biochar) was assessed for its reusability characteristic and it was recycled for 5 repeated cycles (Figure 5). If an adsorbent has a recycling ability, this minimizes the cost and the production of secondary pollutants. The biochar after each batch experiment was washed with distilled water for adsorbed F^- desorption. Significant adsorption-desorption capacity was sustained up to and including the 5th cycle. The results showed that the biochar was very efficient and able to remove 60% of the F^- with the 3rd cycle. The adsorption ability decreased after the 3rd cycle and was 55% with the 5th cycle. The reusability study showed that the biochar adsorbent can be successfully and periodically used in the treatment of F^- contaminated waters at neutral pH.

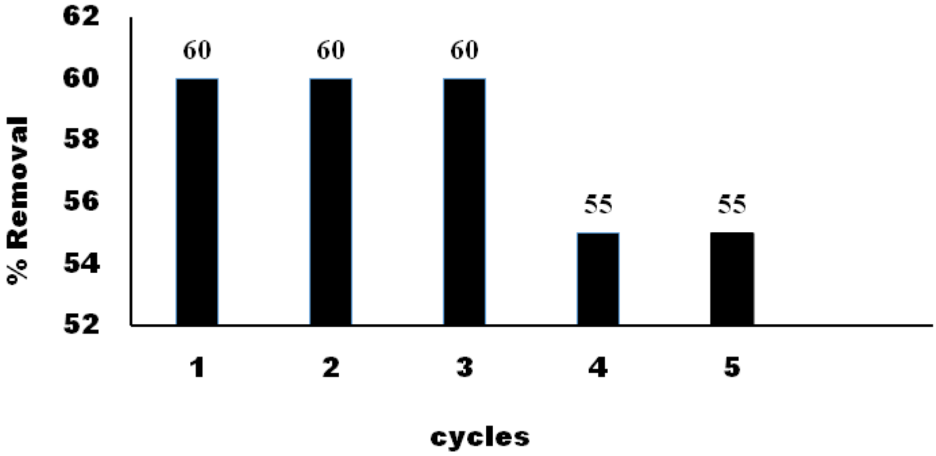

Figure 5. Reusability study of biochar.

CONCLUSIONS

F^- removal was investigated using *Dodonaea* bark biochar (DBBC) and the highest F^- removal (90%) was observed in acidic range. The removal capacity was increased by increasing the dose and the duration of the contact time and decreased with a rise in amount of F^- in the solution and the pH level. We concluded that DBBC could be successfully used as an inexpensive and efficient adsorbent for F^- adsorption and it is recommended that further studies be carried out on the possibility that the removal efficiency of the DBBC adsorbent may be enhanced by further chemical or physical activation.

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COMPETING INTEREST

The authors declares no competing interest

REFERENCES

[1] Shivarajashankara Y, Shivashankara A, Rao SH, Bhat, PG. Oxidative stress in children with endemic skeletal fluorosis. Fluoride 2001;34:103-7.

[2] Spittle B. Dyspepsia associated with fluoridated water. Fluoride 2008;41(1):89-92.

[3] Rahmani A, Rahmani K, Dobaradaran S, Mahvi AH. Mohamadjani R, Rahmani H. Child dental caries in relation to fluoride and some inorganic constituents in drinking water in Arsanjan, Iran. Fluoride 2010;43(3):179-86.

[4] Igwegbe C, Rahdar S, Rahdar A, Mahvi A, Ahmadi S, Banach A. Removal of fluoride from aqueous solution by Nikel oxide nanoparticles: Equilibrium and kinetic studies.Fluoride 2019;52(4):569-79.

[5] Aziz F, Din I, Khan S, Khan M, Mustafa G, Nawab F, Khan F, Ahmad K. Fluorides in drinking water and its health risk assessment in district Malakand, Khyber Pakhtunkhwa, Pakistan.Arabian Journal of Geosciences 2021;14(9):1-9.

[6] Nouri J, Mahvi AH, Babaei A, Ahmadpour E. Regional pattern distribution of groundwater fluoride in the Shush aquifer of Khuzestan County, Iran. Fluoride 2006;39(4):321-5.

[7] Spittle B. A step in the right direction [editorial]. Fluoride2015;48(2):91-2.

[8] Aghaei M, Derakhshani R, Raoof M, Dehghani M, Mahvi AH. Effect of fluoride in drinking water on birth height and weight: an ecological study in Kerman Province, Zarand County, Iran. Fluoride 2015;48(2):160-8.

[9] Bazrafshan E, Balarak D, Panahi AH, Kamani H, Mahvi AH. Fluoride removal from aqueous solutions by cupricoxide nanoparticles. Fluoride 2016;49(3):233-44.

[10] Mahvi AH, Mostafapour FK, Balarak D. Adsorption of fluoride from aqueous solution by eucalyptus bark activated carbon: Thermodynamic analysis. Fluoride 2019;52(4);562-8.

[11] Aziz F, Din I, Khan S, Mustafa G, Khan M, Muhammad J, Jalal A. Defluoridation of water using *Dodonaea viscosa* leaf powder: A study Of adsorption isotherms. Fluoride 2020; 53(1 Pt 1):92-6.

[12] Mahvi AH, Dobaradaran S, Saeedi R, Mohammadi MJ, Keshtkar M, Hosseini A, Moradi M, Ghasemi F F. Determination of fluoride biosorption from aqueous solutions using *Ziziphus* leaf as an environmentally friendly cost effective biosorbent. Fluoride 2018; 51(3):220-9.

[13] Choudhary B, Paul D, Singh A, Gupta T. Removal of hexavalent chromium upon interaction with biochar under acidic conditions: mechanistic insights and application. Environmental Science and Pollution Research 2017; 24(20):16786-97.

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[14] Wang J, Chen N, Li M, Feng C. Efficient removal of fluoride using polypyrrole-modified biochar derived from slow pyrolysis of pomelo peel: sorption capacity and mechanism. Journal of Polymers and the Environment 2018;26(4):1559-72.

[15] Tomar V, Prasad S, Kumar D. Adsorptive removal of fluoride from aqueous media using *Citrus limonum* (lemon) leaf. Microchemical Journal 2014;112:97-103.

[16] Khosravi R, Fazlzadehdavil M, Barikbin B, Taghizadeh AA. Removal of hexavalent chromium from aqueous solution by granular and powdered Peganum Harmala. Applied Surface Science 2014;292:670-7.

[17] Papari F, Najafabadi PR, Ramavandi B. Fluoride ion removal from aqueous solution, groundwater, and seawater by granular and powdered *Conocarpus erectus* biochar. Desal Water Treat 2017;65:375-86.

[18] Wu S, Zhang K, He J, Cai X, Chen K, Li Y, Sun B, Kong L, Liu J. High efficient removal of fluoride from aqueous solution by a novel hydroxyl aluminum oxalate adsorbent. Journal of Colloid and Interface science 2016;464:238-45.

[19] Tirkey P, Bhattacharya T, Chakraborty S. Optimization of fluoride removal from aqueous solution using Jamun (*Syzygium cumini*) leaf ash. Process Safety and Environmental Protection 2018;115:125-38.