FLUORIDE REMOVAL FROM AQUEOUS SOLUTIONS USING SHRIMP SHELL WASTE AS A CHEAP BIOSORBENT

Sina Dobaradaran,^{a,b} Iraj Nabipour,^c Amir Hossein Mahvi,^{d,e} Mozhgan Keshtkar,^f Farzaneh Elmi,^f Fatemeh Amanollahzade,^f Maryam Khorsand^f

Bushehr, Iran

SUMMARY: The aim of this study was to determine the efficiency of shrimp shell waste for the removal of fluoride (F) from aqueous solutions by adsorption, the most promising treatment technology for this purpose. In a series of batch experiments at room temperature, the experimental parameters studied were: initial adsorbent dose (3.2-64 g/L), initial F concentration (2-8 mg/L) while the mass ratio of biosorbant dose (g/L) to initial F concentration (mg/L) was fixed at 5 ratios in the range 400–8000, contact time (5-120 min), pH (3-11), and the presence of competing anions (bicarbonate, nitrate, carbonate, sulfate, and chloride at 200–400 mg/L). We concluded that shrimp shell waste can be a cheap, effective, and environmentally friendly adsorbent of F from aqueous solutions.

Keywords: Adsorption; Biosorbent; Persian Gulf; Shrimp shell waste.

INTRODUCTION

Fluoride (F) is widely distributed in the environment and is therefore of special concern. Besides natural weathering, anthropogenic activities, such as aluminium, steel, fertilizer, bricks, ceramics, and glass industries as well as nuclear applications, play an important role in increasing water pollution by F.¹⁻³ F can cause a wide range of adverse health effects.⁴⁻⁷ In this regard, various studies in Iran have reported the occurrence of elevated F concentrations in drinking water, air, fish, tea, and sea as well as in connection with its removal from high F waters.⁶⁻²⁰ Adsorption of F is considered as the most effective treatment method for F removal from aqueous solutions. Biosorption advantages over conventional treatment methods include low cost, high efficiency, less sludge production, and regeneration of biosorbent.²¹⁻²² The aim of this study was to determine the efficiency of shrimp shell waste as a biosorbent in the removal of F from aqueous solutions.

MATERIALS AND METHODS

The shrimp shell wastes were obtained from local fishery waste along the Persian Gulf in the Bushehr port coastal area. Shrimp shell wastes were washed thoroughly with distilled water several times. The washed materials were then dried in an oven at 60°C for 2 hours and 40°C for 20 hr, and then ground and

^aFor correspondence: Assistant Professor, The Persian Gulf Marine Biotechnology Research Medical Centre. Bushehr Universitv of Sciences. Bushehr. Iran. E-mail: sina dobaradaran@yahoo.com; ^bDepartment of Environmental Health Engineering, Faculty of Health, Bushehr University of Medical Sciences, Bushehr, Iran; ^cThe Persian Gulf Tropical Medicine Research Center, Bushehr University of Medical Sciences, Bushehr, Iran; ^dDepartment of Environmental Health Engineering, School of Public Health, Tehran University of Medical Sciences, Tehran, Iran; eCenter for Solid Waste Research, Institute for Environmental Research, Tehran University of Medical Sciences, Tehran, Iran; ^fStudent Research Committee, Bushehr University of Medical Sciences, Bushehr, Iran.

sieved through a 0.71 mm screen. A stock solution of 100 mg/L F was prepared by dissolving sodium fluoride (NaF) in ultrapure water. F solutions were prepared at 2, 3, 5, and 8 mg/L concentrations. At each run, 100 mL of F solution with a specific initial F concentration was agitated at 120 rpm. The effects of five contact times (5, 10, 25, 60, and 120 min), four initial F concentrations (2, 3, 5, and 8 mg/L), three different pHs (3, 7, and 11), and different mass ratios of biosorbent to the F level (five ratios within the range of 400–8000) were investigated in the batch experiments. The standard SPADNS method was used by using a Spectrophotometer (model CAM Spec M501) for analysis of the remaining F concentration in the aqueous solution after each run.

RESULTS AND DISCUSSION

F removal as a function of contact time and adsorbent dose has been studied. In our study, for an initial F concentration of 8 mg/L, the removal percentage of F increased with increasing adsorbent dose from 3.2 g/L to 64 g/L but there were no significant differences in the F removal between adsorbent doses of 48 g/L and 64 g/L (Figure 1). The adsorption rate was fast initially with F removal reaching a maximum after 15 min and it then decreased with increasing contact time, especially for lower adsorbent doses which can be due to desorption and a decrease of the active surface area.

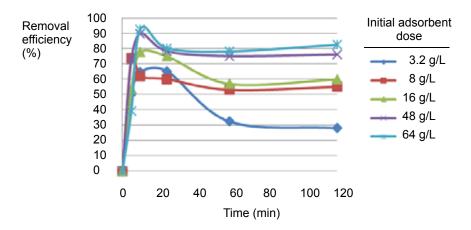


Figure 1. F adsorption as a function of adsorbent dose (initial F concentration = 8 mg/L).

Jamode et al. found F removal from water using fresh leaves of trees increased from 20 to 85 percent with increasing adsorbent doses from 0.5 to 12 g/L.²³ Mahramanlioglu et al. and Rani et al. reported similar results in the defluoridation of aqueous solutions with increasing adsorbent doses.²⁴⁻²⁵ We found that, at a fixed mass ratio of biosorbent to initial F concentration, the efficiency of F removal increased when the initial F concentration was increased (Figure 2). By increasing the F concentration from 2 to 8 mg/L, the removal efficiency increased from 33 to 81 percent. In contrast, Jamode et al. and Mahramanlioglu et al., using different adsorbents, reported lower adsorption rates at higher initial F concentrations.²³⁻²⁴ Our study found that for the removal of F from aqueous

solutions, shrimp shell waste had a higher adsorption capacity than that reported for other adsorbents.²³⁻²⁴

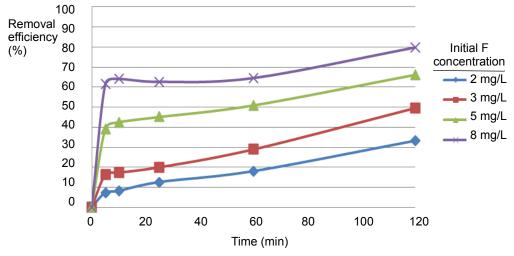
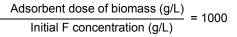


Figure 2. F adsorption, using a fixed mass ratio of biosorbent to initial F concentration, as a function of initial F concentration.



The removal efficiency for F adsorption by shrimp shell waste increased as the pH increased from 3 to 11 (Figure 3).

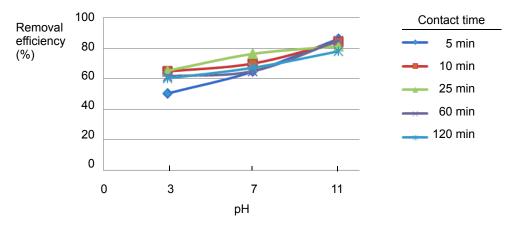


Figure 3. Effect of pH on F removal by shrimp shell waste (biosorbent dose = 3.2 g/L, initial F concentration = 8 mg/L).

Similarly, Shams et al. found that granular ferric hydroxide (GFH) was most efficient in removing F at the highest pH studied (pH 8).¹⁵ Gupta et al. examined F removal with waste carbon slurry at pH values ranging from 2 to 12 and observed that the highest F removal efficiency occurred at pH 8.²⁶ However, Kermer et

al.²⁷ and Nigussie et al.²⁸ reported that pH had no effect on F removal by waste residues from waste mud and alum manufacturing process, respectively.

The presence of competing anions, including HCO_3^- , NO_3^- , Cl^- , CO_3^{2-} , and SO_4^{2-} , at 200 and 400 mg/L levels, had no significant effect on F adsorption by the biosorbent (Figure 4).

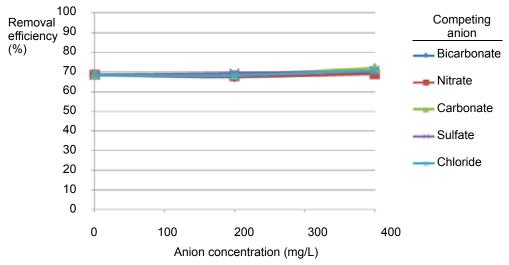


Figure 4. Effect of competing anions (concentrations of 200 and 400 mg/L) on F adsorption onto biosorbent (initial F concentration = 8 mg/L, biosorbent dose = 8 g/L, contact time = 5 min).

In this study, we found that shrimp shell waste was effective in removing F from aqueous solutions. Our results showed that increasing the contact time did not have a significant effect on the adsorption rate but that the removal efficiency increased with increasing the adsorbent dose. When the mass ratio of the dose of biosorbent to the initial F level was fixed, the F removal efficiency also increased with increasing the initial F concentration. Shrimp shell waste exhibited a high defluoridation efficiency and most of the adsorption occurred within a few minutes of contact time. The adsorbent applied in this study, shrimp shell waste, was easy to source and inexpensive. Finally, it should be noted that shrimp shell waste can be used as an environmentally friendly, effective, and cheap adsorbent for the removal of F from aqueous solutions, especially from industrial wastewaters.

ACKNOWLEDGMENTS

The authors are grateful to the Bushehr University of Medical Sciences for their financial support.

REFERENCES

- 1 Toma S, Kreidman J, Vedina O, Veliksar S. Some observations on fluoride problems in the Moldova Republic. Fluoride 1999;32(2):67-70.
- 2 Jezierska-Madziar M, Pińskwar P, Przybył A. Reduction in fluoride levels in the old Warta reservoir near Luboń, Poland. Fluoride 2001;34(1):51-4.
- 3 Morra P, Lisi R, Spadoni G, Maschio G. The assessment of human health impact caused by industrial and civil activities in the Pace Valley of Messina. Sci Total Environ 2009;407(12):3712-20.

257 Research report Fluoride 47(3)253–257 July-September 2014

- 4 Spittle B. Dyspepsia associated with fluoridated water. Fluoride 2008;41(1):89-92.
- 5 Shivarajashankara YM, Shivashankara AR, Rao SH, Bhat PG. Oxidative stress in children with endemic skeletal fluorosis. Fluoride 2001;34(2):103-7.
- 6 Dobaradaran S, Mahvi AH, Dehdashti S, Abadi DRV. Drinking water fluoride and child dental caries in Dashtestan, Iran. Fluoride 2008;41(3):220-6.
- 7 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.
- 8 Dobaradaran S, Mahvi AH, Dehdashti S. Fluoride content of bottled drinking water available in Iran. Fluoride 2008;41(1):93-4.
- 9 Dobaradaran S, Mahvi AH, Dehdashti S, Dobaradaran S, Shoara R. Correlation of fluoride with some inorganic constituents in groundwater of Dashtestan, Iran. Fluoride 2009;42(1):50-3.
- 10 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.
- 11 Dobaradaran S, Fazelinia F, Mahvi AH, Hosseini SS. Particulate airborne fluoride from an aluminium production plant in Arak, Iran. Fluoride 2009;42(3):228-32.
- 12 Mahvi AH, Zazoli MA, Younecian M, Esfandiari Y. Fluoride content of Iranian black tea and tea liquor. Fluoride 2006;39(4):266-8.
- 13 Boldaji MR, Mahvi A, Dobaradaran S, Hosseini S. Evaluating the effectiveness of a hybrid sorbent resin in removing fluoride from water. Int J Environ Sci Technol 2009;6(4):629-32.
- 14 Dobaradaran S, Abadi DRV, Mahvi AH, Javid A. Fluoride in skin and muscle of two commercial species of fish harvested off the Bushehr shores of the Persian Gulf. Fluoride 2011;44(3):143-6.
- 15 Shams M, Nodehi RN, Dehghani MH, Younesian M, Mahvi AH. Efficiency of granular ferric hydroxide (GFH) for removal of fluoride from water. Fluoride 2010;43(1):61-6.
- 16 Shams M, Qasemi M, Dobaradaran S, Mahvi AH. Evaluation of waste aluminum filling in removal of fluoride from aqueous solutions. Fresen Environ Bull 2013;22(9):2604-9.
- 17 Nabipour I, Dobaradaran S. Fluoride and chloride levels in the Bushehr coastal seawater of the Persian Gulf. Fluoride 2010;46(4):204-7.
- 18 Nabipour I, Dobaradaran S. Fluoride concentrations of bottled drinking water available in Bushehr, Iran. Fluoride 2013;46(2):63-4.
- 19 Ostovar A, Dobaradaran S, Ravanipour M, Khajeian A. Correlation between fluoride level in drinking water and the prevalence of hypertension: an ecological correlation study. Int J Occup Environ Med 2013;494):216-7.
- 20 Shams M, Dobaradaran S, Mazloomi S, Afsharnia M, Ghasemi M, Bahreini M. Drinking water in Gonabad, Iran: fluoride levels in bottled, distribution network, point of use desalinator, and decentralized municipal desalination plant water. Fluoride 2012;45(2):138-41.
- 21 Ayoob S, Gupta A, Bhakat P, Bhat VT. Investigations on the kinetics and mechanisms of sorptive removal of fluoride from water using alumina cement granules. Chem Eng J 2008;140(1):6-14.
- 22 Onyango MS, Kojima Y, Aoyi O, Bernardo EC, Matsuda H. Adsorption equilibrium modeling and solution chemistry dependence of fluoride removal from water by trivalent-cationexchanged zeolite F-9. J Colloid Interface Sci 2004;279(2):341-50.
- 23 Jamode A, Sapkal V, Jamode V. Defluoridation of water using inexpensive adsorbents. J Indian Inst Sci 2013;84(5):163.
- 24 Mahramanlioglu M, Kizilcikli I, Bicer I. Adsorption of fluoride from aqueous solution by acid treated spent bleaching earth. J Fluor Chem 2002;115(1):41-7.
- 25 Rani B, Maheshwari R, Chauhan AK, Bhaskar NS. Defluoridation of contaminated water employing brick powder as an adsorbent. Int J Sci Nat 2012;3(1):78-82.
- 26 Gupta VK, Ali I, Saini VK. Defluoridation of wastewaters using waste carbon slurry. Water Res 2007;41(15):3307-16.
- 27 Kemer B, Ozdes D, Gundogdu A, Bulut VN, Duran C, Soylak M. Removal of fluoride ions from aqueous solution by waste mud. J Hazard Mater 2009;168(2):888-94.
- 28 Nigussie W, Zewge F, Chandravanshi BS. Removal of excess fluoride from water using waste residue from alum manufacturing process. J Hazard Mater 2007;147(3):954-63.