DETERMINATION OF FLUORIDE BIOSORPTION FROM AQUEOUS SOLUTIONS USING *ZIZIPHUS* LEAF AS AN ENVIRONMENTALLY FRIENDLY COST EFFECTIVE BIOSORBENT

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ABSTRACT: Biosorption is considered to be one of the favorite treatment technologies for fluoride ion (F) removal from aqueous solutions. The purpose of this study was to measure the efficiency of *Ziziphus* leaf in the removal of F from aqueous solutions. The biosorption experiments were performed in batch systems at room temperature. The experimental parameters studied were: (i) the initial F concentration level (3–12 mg/L), (ii) the biosorbent dose (1–10 g/L), and (iii) the contact time (5–120 min). The highest removal biosorption of 100% was observed at a biosorbent dose of 10 g/L, a contact time of 90 min, and an initial F concentration level of 12 mg/L. At an initial F concentration of 12 mg/L, the most effective and applicable biosorbent dose was 5 g/L which resulted in the removal of 95.36% of the F after 25 min with a resulting F concentration of 0.55 mg/L, which is safe for drinking water. The Langmuir model fitted better than the Frendlich model and showed a homogeneous biosorption surface with the possibility of a monolayer biosorption of F by the biosorbent. The biosorption kinetic was controlled by the pseudo-first-order model. The results showed that *Ziziphus* leaf can be used as an environmentally friendly, cost effective, and effective biosorbent for the removal of F from aqueous solutions.

Keywords: Aqueous solution; Biosorbent; Biosorption kinetic; Fluoride removal; *Ziziphus* leaf.

INTRODUCTION

The fluoride ion (F) is broadly distributed in the environment and is of particular concern because many studies have reported that an excess F intake through drinking water or food can cause a wide range of adverse health effects.[1-4] As well as F from the natural weathering of rocks, various industries, such as those producing bricks, ceramics, aluminium, glass, steel, and fertilizers, are the main sources of water pollution by F.[5-7] Many studies in Iran have reported on the occurrence of F-induced health effects and the levels of F in drinking water, air, groundwater, bottled water, tea, fish, and sea water.[8-19] Several studies have focused on F removal from waters with elevated F levels.[20-27] Among these techniques, adsorption, particularly biosorption, is arguably considered to be one of the most suitable methods for F removal from aqueous solutions.[22-27] The advantages of biosorption over

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conventional treatment methods comprise low cost, high efficiency, less sludge production, and biosorbent regeneration.[28, 29] Different biosorbents such as yeast, fungi, agricultural wastes, and algae have been used for the removal of inorganic contaminants and heavy metals from aqueous solutions.[30,31] In the present study, we aimed to determine the efficiency of *Ziziphus* leaf as a biosorbent for the removal of F from aqueous solutions. We investigated the effect of the parameters of (i) contact time, (ii) biosorbent dose, and (iii) the initial F concentration. The biosorption capacity, isotherm, and kinetics of biosorption were also determined.

MATERIALS AND METHODS

Ziziphus is a genus of about 40 species of spiny shrubs and small trees in the buckthorn family, Rhamnaceae, distributed in the warm temperate and subtropical regions throughout the world. The leaves are alternate, entire, with three prominent basal veins, and 2–7 cm long. The Bushehr Province in southwestern Iran has a warm and humid climate and *Ziziphus* trees are native to the region. The *Ziziphus* leaves used in the study were obtained from around Borazjan (Figure 1).

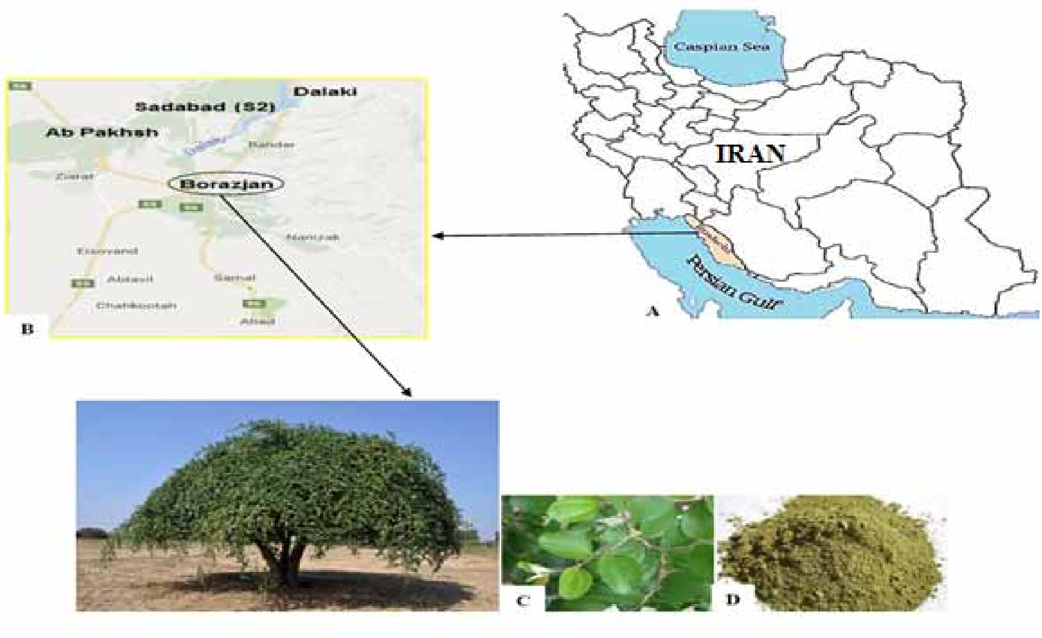


Figure 1. A and B: location of the site for the collection of the *Ziziphus* leaf; C: *Ziziphus* leaves before preparation as a biosorbent; D: *Ziziphus* leaves after preparation as a biosorbent.

and then with distilled water, several times in order to remove all the impurities such as clay and sand. The washed leaves were then dried in an oven at 105ºC for 6 hours and afterwards ground and sieved with 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 the 3, 5, 8, and 12 mg/L concentration levels. In each experiment, 100 mL of a F solution with a particular initial F concentration level was agitated at 120 rpm. The effects of five contact times (5, 25, 60, 90, and 120 min), four initial F concentration levels (3, 5, 8, and 12 mg/L), and four biosorbent doses (1, 3, 5, and 10 g/L) were examined in batch systems at room temperature (25±1ºC). All the experiments were performed at a pH level of 7. For the analysis of the remaining F concentration level in the aqueous solution after each experiment, the standard SPADNS method was used by applying a Spectrophotometer (model CAM Spec M501) and the efficiency of each experiment was calculated by using the following equation:

$$\text{Biosorption yield} = \frac{(C_i - C)}{C_i} \times 100$$

where:

C_i = the concentration level of fluoride (mg/L) before the experiment
C = the concentration level of fluoride (mg/L) after the experiment

The equilibrium biosorption capacity of Ziziphus leaves at different F concentration levels was also calculated by using the following equation:

$$q_e = \frac{(C_i - C_e)\,V}{m}$$

where:

q_e = the equilibrium biosorption capacity (mg/L)
C_i = the initial fluoride concentration (mg/L)
C_e = the fluoride concentration level in the solution at equilibrium (mg/L)
V = the solution volume (L)
m = the biosorbent dosage (g)

RESULTS AND DISCUSSION

The effect of the biosorbent dose on the removal of F is presented in Figures 2A and 2B.

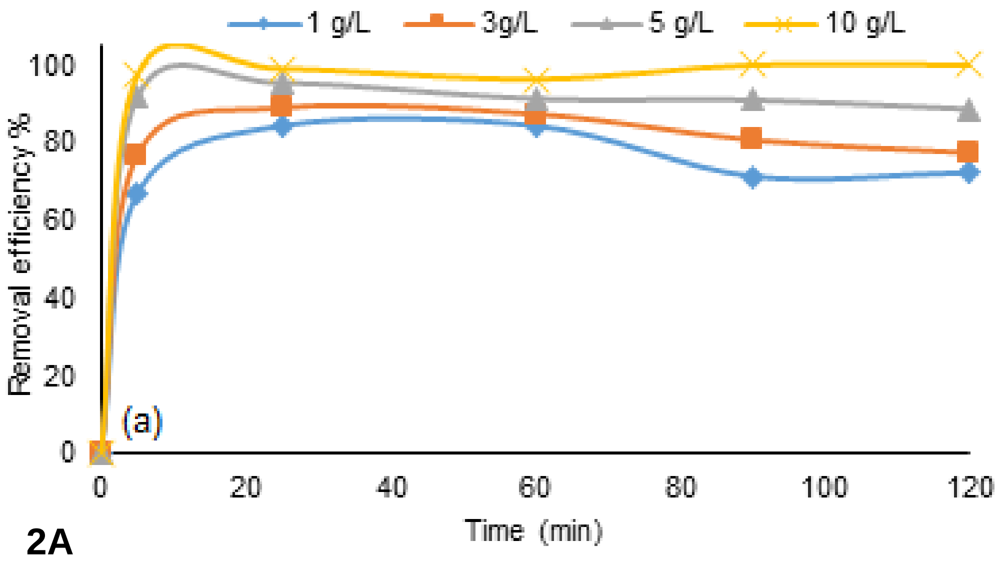


Figure 2A. Fluoride (F) adsorption as a function of the adsorbent dose at the initial F concentration of 12 mg/L (pH: 7).

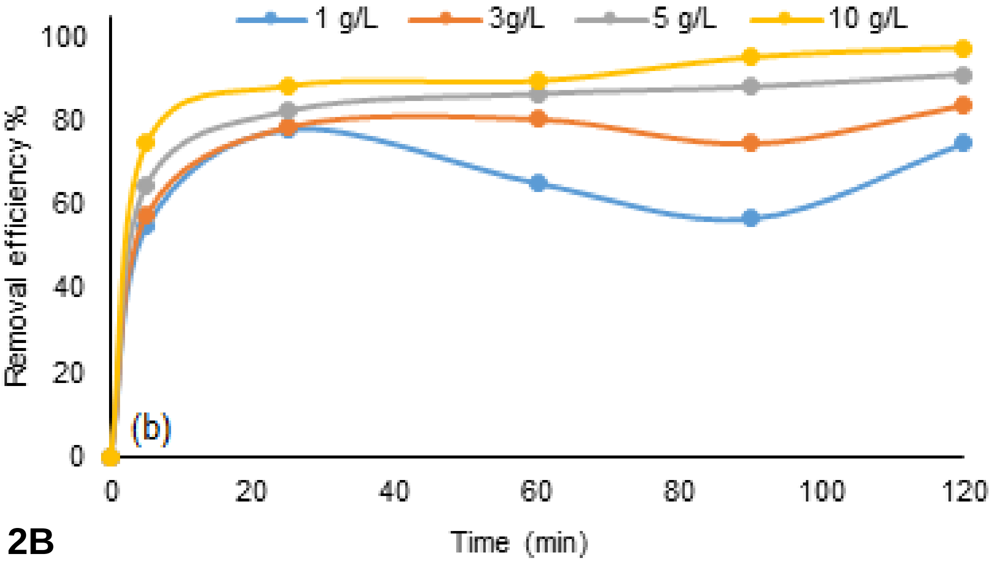


Figure 2B. Fluoride (F) adsorption as a function of the adsorbent dose at the initial F concentration of 5 mg/L (pH: 7).

The amount of biosorbent influenced the extent of F biosorption. As presented in Figures 2A and 2B, once the biosorbent dose increased from 1 to 10 g/L at initial F concentration levels of 12 and 5 mg/L, the F removal increased from 72.36% to 100% and 74.51% to 97.35%, respectively. The most effective and applicable adsorbent dose was 5 g/L at an initial F concentration level of 12 mg/L which resulted in 95.36% removal at 25 min time when the F concentration was 0.55 mg/L which is safe for drinking water. This may be due to the extra number of biosorption sites resulting from the increase in the biosorbent amount. Defluoridation of aqueous solutions by using *Moringa oleifera* seed ash and shrimp shell waste showed similar results.[23,25] Mourabet et al. also reported that by increasing the biomass dosage of apatitic tricalcium phosphate, the rate of F adsorption rate increased.[32] However, in a study in which lanthanum incorporated chitosan beads (LCB) were used for the removal of F from drinking water, it was reported that variations in the quantity of LCB in the dosage range of 0.2–2 g/L had no significant effect on the F removal capacity.[33]

The effect of the initial F concentration level on the removal of F is presented in Figure 3. It was seen that by increasing the initial F concentration level from 3 to 12 mg/L the efficiency of F biosorption increased. This shows the high adsorption capacity of *Ziziphus* leaves for the removal of F. Similarly, Dobaradaran et al. found that the biosorption efficiency of F when using shrimp shell waste increased with increasing the initial F concentration levels.[25] In another study, it was reported that the efficiency of *Moringa oleifera* seed ash for removing F from aqueous solutions increased from 33% to 81% when the initial F concentration level was increased from 2 to 8 mg/L.[23]

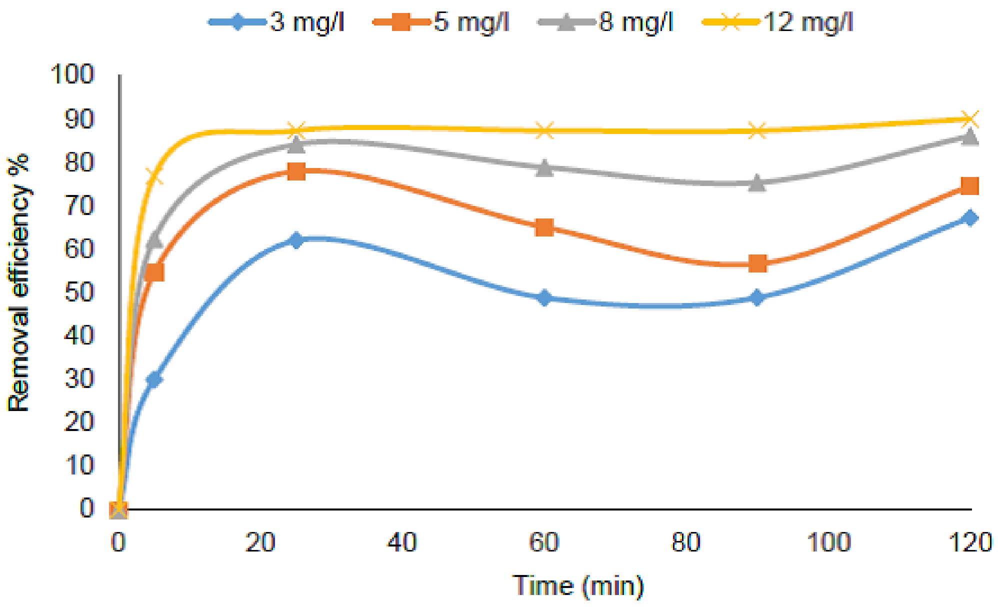


Figure 3. Fluoride (F) biosorption as a function of the initial F concentration level (pH: 7; biosorbent dose: 1 g/L).

In contrast, Ramanaiah et al. studied F biosorption in experiments using waste fungal biomass derived from the Laccase fermentation process and reported that the biosorption efficiency of F by the biosorbent decreased with increasing the initial F concentration level.[34] Also, Jamode et al. and Mahramanlioglu et al., using different adsorbents, found lower adsorption rates at higher initial F concentration levels.[35,36] As is clear in Figures 2A, 2B, and 3, the highest biosorption rates were took place in the first 25 min. To measure the bisorption capacity of *Ziziphus* leaf in the removal of F from aqueous solutions, the isotherm parameters of F onto *Ziziphus* leaf were calculated for two commonly used isotherms, the Freundlich and Langmuir models.[37,38]

The Freundlich equation can be represented as follows:

$$\text{Log}\,(q_e) = \text{Log}\,(K_f) + \frac{1}{n}\,\text{Log}\,C_e$$

where:

q_e = the amount of fluoride adsorbed per unit weight of the sorbent (mg/g)
K_f = the Freundlich capacity factor and a measure of biosorption capacity
$1/n$ = the equilibrium concentration of fluoride in the solution (mg/L) after biosorption

The values of $1/n$ and K_f for the sorbent were calculated from the slope and the intercept of the linear plot of log q_e against log C_e.

The Langmuir biosorption isotherm model can be written as follows:

$$\frac{C_e}{q_e} = \frac{1}{bq_{max}} + \frac{1}{q_{max}} C_e$$

where:

q_e = the mass of fluoride per unit mass of sorbent (mg/g)
q_{max} = the monolayer sorption capacity
b = the Langmuir constant related to the free energy of sorption equilibrium concentration of fluoride in the solution (mg/L) after biosorption

The Langmuir constant can be determined by plotting C_e/q_e vs. C_e.

The results showed that the Langmuir model fitted the data better than the Freundlich model (Table 1 and Figures 4A and 4B). The Langmuir isotherm assumes a monolayer adsorption on a homogenous flat surface, due to the greater tendency of F to be adsorbed onto the adsorbent surface instead of undergoing heterogeneous adsorption.

Table 1. Biosorption isotherm parameters for fluoride (F) biosorption onto *Ziziphus* leaves

Isotherm	Parameter	Value
Freundlich	K_f (mg/g)	8.298
	1/n	1.439
	R^2	0.6034
Langmuir	b (mg/L)	0.707
	R_L	0.105
	q_{max} (mg/g)	0.4882
	R^2	0.9858

4A

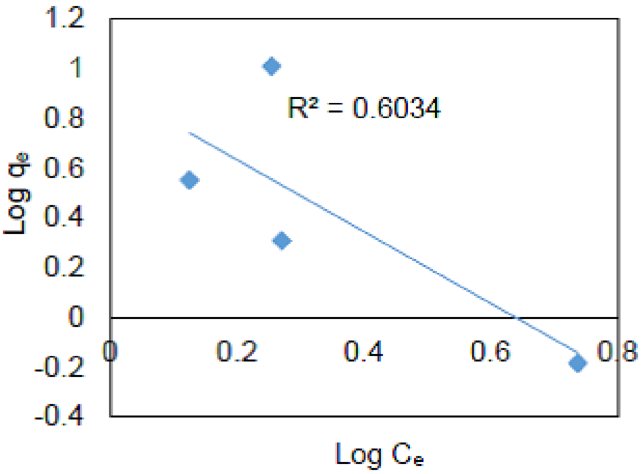


Figure 4A. Linear representation of the Freundlich model of the investigation of fluoride (F) biosorption by *Ziziphus* leaf.

4B

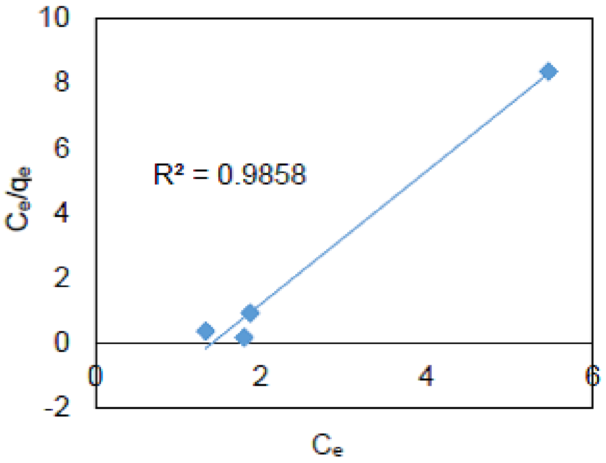
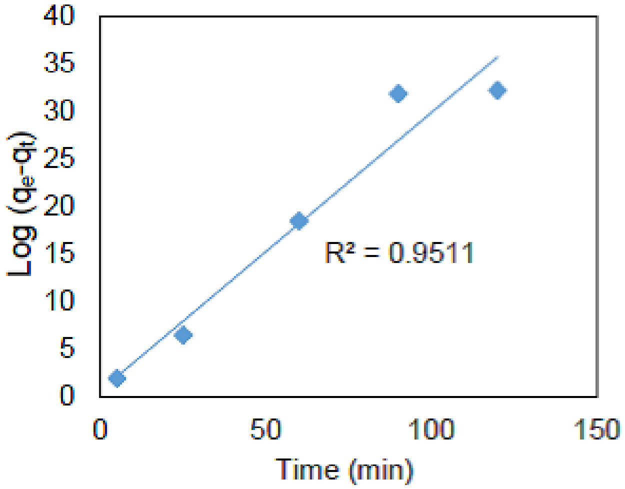


Figure 4B. Linear representation of the Langmuir model of the investigation of fluoride (F) biosorption by *Ziziphus* leaf.

The biosorption kinetics are important in the treatment of aqueous solutions, as they present important understandings into the mechanisms of biosorption reactions. In order to recognize the mechanism of F biosorption onto *Ziziphus* leaf the experimental biosorption kinetics were defined by using the pseudo-first-order and pseudo-second-order models. The biosorption kinetic was controlled by the pseudo-first-order model (Table 2 and Figures 5A and 5B). In the pseudo-first-order model it is assumed that the rate of change in the solute amount over time is logarithmically proportional to the changes in the saturation concentration and the amount of adsorbent over time.

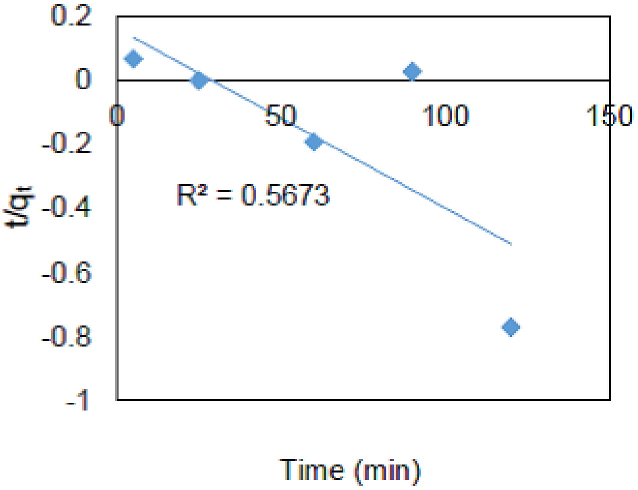
Table 2. Biosorption kinetic parameters for fluoride (F) biosorption onto *Ziziphus* leaf

Model	Parameter	Value
First-order kinetic	q_e (mg/g)	3.808
	K_1 (1/min)	0.6742
	R^2	0.9511
Second-order kinetic	q_e (mg/g)	178.571
	K_2 (g/mg min)	0.00017
	R^2	0.5673



5A

Figure 5A. Linear representation of the pseudo-first-order model of fluoride (F) biosorption by *Ziziphus* leaf.



5B

Figure 5B. Linear representation of the pseudo-second-order model of fluoride (F) biosorption by *Ziziphus* leaf.

CONCLUSIONS

In the present study we used *Ziziphus* leaf as a local biosorbent for the removal of F from aqueous solution. The parameters that affected the F biosorption efficiency were the initial F concentration level, the biosorbent dosage, and the contact time. The results showed that, by increasing the biosorbent dose and the initial F concentration level, the removal efficiency increased. The Langmuir model fitted the data better than the Freundlich model indicating that there was a homogeneous biosorption surface and the possibility of a monolayer biosorption of F by the biosorbent. The kinetic data indicated that the biosorption of F ions onto *Ziziphus* leaf followed the pseudo-first-order kinetic model best. Finally, according to the existing findings, it can be stated that *Ziziphus* leaf is an effective, cheap, and environmentally friendly biosorbent for the F removal from aqueous solutions, particularly in remote and rural areas where the *Ziziphus* leaf is available.

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REFERENCES

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

2 Shivarajashankara YM, Shivashankara AR, Rao SH, Bhat PG. Oxidative stress in children with endemic skeletal fluorosis. Fluoride 2001;34(2):103-7.

3 Dobaradaran S, Mahvi AH, Dehdashti S, Abadi DRV. Drinking water fluoride and child dental caries in Dashtestan, Iran. Fluoride 2008;41(3):220-6.

4 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.

5 Toma S, Kreidman J, Vedina O, Veliksar S. Some observations on fluoride problems in the Moldova Republic. Fluoride 1999;32(2):67-70.

6 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.

7 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.

8 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;4(4):216-7.

9 Dobaradaran S, Mahvi AH, Dehdashti S. Fluoride content of bottled drinking water available in Iran. Fluoride 2008;41(1):93-4.

10 Nabipour I, Dobaradaran S. Fluoride concentrations of bottled drinking water available in Bushehr, Iran. Fluoride 2013;46(2):63-4.

11 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.

12 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.

13 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.

14 Mahvi AH, Zazoli MA, Younecian M, Esfandiari Y. Fluoride content of Iranian black tea and tea liquor. Fluoride 2006;39(4):266-8.

15 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.

16 Nabipour I, Dobaradaran S. Fluoride and chloride levels in the Bushehr coastal seawater of the Persian Gulf. Fluoride 2013;46(4):204-7.

17 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.

18 Izadi A, Dobaradaran S, Nabipour I, Mahvi AH, Abedi E, Keshtkar M. Fluoride and chloride levels in seawater along northern part of the Persian Gulf in Bushehr province. Fluoride. Accepted.

19 Soleimani F, Dobaradaran S, Mahvi AH, Parhizkar G, Ghaderi M, Keshtkar M, et al. Fluoride and chloride levels in ballast water in commercial ships entering Bushehr port on the Persian Gulf. Fluoride 2017;50(1 Pt 2):121-6.

20 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.

21 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.

22 Zazouli MA, Mahvi AH, Dobaradaran S, Barafrashtehpour M, Mahdavi Y, Balarak D. Adsorption of fluoride from aqueous solution by modified Azolla filiculoides. Fluoride 2014:47(4):349-58.

2 Dobaradaran S, Kakuee M, Pazira AR, Keshtkar M, Khorsand M. Fluoride removal from aqueous solutions using Moringa oleifera seed ash as an environmental friendly and cheap biosorbent. Fresen Environ Bull 2015; 24:1269-74.

24 Keshtkar M, Dobaradaran S, Nabipour I, Mahvi AH, Ghasemi FF, Ahmadi Z, et al. Isotherm and kinetic studies on fluoride biosorption from aqueous solution by using cuttlebone obtained from the Persian Gulf. Fluoride 2016:49(1):319-27.

25 Dobaradaran S, Nabipour I, Mahvi AH, Keshtkar M, Elmi F, Amanollahzade F, Khorsand M.Fluoride removal from aqueous solutions using shrimp shell waste as a cheap biosorbent. Fluoride 2014;47(3):253-7.

26 Dobaradaran S, Ali Zazuli M, Keshtkar M, Noshadi S, Khorsand M, Faraji Ghasemi F, et al. Biosorption of fluoride from aqueous phase onto *Padina sanctae crucis* algae: evaluation of biosorption kinetics and isotherms. Desalination Water Treat 2016; 57(58):28405-16.

27 Dobaradaran S, Babaei AK, Nabipour I, Tajbakhsh S, Noshadi S, Keshtkar M, et al. Determination of fluoride biosorption from aqueous solutions using Sargassum hystrix algae. Desalination Water Treat 2017;63:87-95

28 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.

29 Onyango MS, Kojima Y, Aoyi O, Bernardo EC, Matsuda H. Adsorption equilibrium modeling and solution chemistry dependence of fluoride removal from water by trivalent-cation exchanged zeolite F-9. J Colloid Interface Sci 2004; 279(2):341-50.

30 Maleki A, Mahvi AH, Zazouli MA, Izanloo H, Barati AH. Aqueous cadmium removal by adsorption on barley hull and barley hull ash. Asian J Chem 2011; 23(3):1373-6.

31 Mahvi AH, Gholami F, Nazmara S. Cadmium biosorption from wastewater by *Ulmus* leaves and their ash. Eur J Sci Res 2008; 23(2):197-203.

32 Mourabet M, El Rhilassi A, El Boujaady H, Bennani-Ziatni M, El Hamri R, Taitai A. Removal of fluoride from aqueous solution by adsorption on Apatitic tricalcium phosphate using Box–Behnken design and desirability function. Appl Surf Sci 2012; 258:4402-10.

33 Thakre D, Jagtap S, Bansiwal A, Labhsetwar N, Rayalu S. Synthesis of La-incorporated chitosan beads for fluoride removal from water. J Fluor Chem 2010; 131(3):373-7.

34 Ramanaiah SV, Venkata Mohan S, Sarma PN. Adsorptive removal of fluoride from aqueous phase using waste fungus (*Pleurotus ostreatus* 1804) biosorbent: kinetics evaluation. Ecol Eng 2007;31:47-56.

35 Jamode AV, Sapkal VS, Jamode VS. Defluoridation of water using inexpensive adsorbents. Journal of the Indian Institute of Science 2013;84(5):163-71.

36 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.

37 Freundlich HMF. Uber die adsorption in losungen. Zeitschrift für Physikalische Chemie 1906;57:385-470. [in German].

38 Langmuir I. The constitution and fundamental properties of solids and liquids. J Am Chem Soc. 1916;38(11):2221–95.