Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.0052

63 (2017) 87–95
February

Determination of fluoride biosorption from aqueous solutions using *Sargassum hystrix* algae

Sina Dobaradaran[a,b,c,*], Ali Akbar Babaei[d,e], Iraj Nabipour[f], Saeed Tajbakhsh[a], Sara Noshadi[b], Mozhgan Keshtkar[b], Maryam Khorsand[b], Niaz Mahdi Esfahani[g]

[a]*The Persian Gulf Marine Biotechnology Research Center, The Persian Gulf Biomedical Sciences Research Institute, Bushehr University of Medical Sciences, Bushehr, Iran, Tel./Fax: +98 7514763448; email: S.dobaradaran@bpums.ac.ir (S. Dabaradaran), tajbakhshsaeed@yahoo.com (S. Tajbakhsh)*
[b]*Department of Environmental Health Engineering, Faculty of Health, Bushehr University of Medical Sciences, Bushehr, Iran, Tel./Fax: +98 7514763448; email: S.dobaradaran@bpums.ac.ir (S. Dabaradaran), sara_noshadi@yahoo.com (S. Noshadi), keshtkar_m88@yahoo.com (M. Keshtkar), khorsand.m65@gmail.com (M. Khorsand)*
[c]*Systems Environmental Health, Oil, Gas and Energy Research Center, The Persian Gulf Biomedical Sciences Research Institute, Bushehr University of Medical Sciences, Bushehr, Iran, Tel./Fax: +98 7514763448; email: S.dobaradaran@bpums.ac.ir*
[d]*Environmental Technologies Research Center (ETRC), Ahvaz Jundishapur University of Medical Sciences, Ahvaz, Iran, email: babaei-a@ajums.ac.ir*
[e]*Department of Environmental Health Engineering, School of Public Health, Ahvaz Jundishapur University of Medical Sciences, Ahvaz, Iran, email: babaei-a@ajums.ac.ir*
[f]*The Persian Gulf Tropical Medicine Research Center, The Persian Gulf Biomedical Sciences Research Institute, Bushehr University of Medical Sciences, Bushehr, Iran, email: inabipour@gmail.com*
[g]*Department of Environmental Health Engineering, School of Public Health, Tehran University of Medical Sciences, Tehran, Iran, email: Niazmahdiesfahani@gmail.com*

Received 16 January 2016; Accepted 13 June 2016

ABSTRACT

The aim of this study was to determine *Sargassum hystrix* algae's efficiency in fluoride removal from aqueous solutions. In a series of batch experiments, the experimental parameters were studied using the dried algae: initial biosorbent dose (0.8–64 g/L), initial fluoride concentration while the mass of biosorbant dose (g/L) ratio to initial fluoride concentration (mg/L) was fixed at 5 ratios in the range of 400–8,000, contact time, pH, activation temperature and the presence of competing anions. The highest removal biosorption was at 40 g/L of biosorbent at 60 min contact time and initial fluoride concentration of 5 mg/L (100% fluoride removal); competing anions and activation temperature had no significant effect on the fluoride biosorption by biosorbent. The biosorption was found to be better fitted to the Freundlich model and follows a pseudo-second-order kinetic model. Finally, it was concluded that the *Sargassum hystrix* algae can be used as an environmental friendly, cheap and effective biosorbent from aqueous solutions.

Keywords: Biosorption isotherms; Biosorbent; Persian Gulf; *Sargassum hystrix*

1. Introduction

Fluoride naturally exists through the earth's crust and anthropogenic activities such as glass etching, electronic, and chemical industries, production of aluminum and chlorofluorocarbons, separating uranium isotopes, a catalyst in the petroleum industry, and stainless steel pickling. These industries play a significant role in water pollution to the fluoride [1–5]. Fluoride can cause a broad range of adverse health effects including teeth and bone damage, as well as adverse health consequence in soft tissues [6–14]. Because of adverse

* Corresponding author.

health potential of fluoride, the World Health Organization [15] has set a guideline value for fluoride in drinking water at 1.5 mg/L. Also U.S. Public Health Service has set a new guideline value of 0.7 mg/L for fluoride and replaced the previous recommended range of 0.7 to 1.2 mg/L [16]. Various processes [17–22], including adsorption, precipitation, ion exchange, electrodialysis and electrochemical [18], were developed to remove extra fluoride from water. Among these methods, adsorption is widely used for removal of fluoride and other contaminants [19–24]. Currently, significant interests were observed on the utilization of biosorbent materials for removal of different pollutants. Biosorption advantages over conventional treatment methods include low cost, no nutrient needs, regeneration of biosorbent, less sludge production, and high efficiency in dilute effluents, while being environmentally favorable and economically viable [25–29]. Algae is a renewable, low-cost material, available and abundant in nature, and capable of biosorbing numerous pollutants. Various types of algae have been used for biosorption of pollutants from aqueous solutions. *Sargassum*, a brown macroalgae, is broadly distributed in tropical regions and subtropical seas [30]. Many studies have been conducted in relation to adsorption of different pollutants such as cadmium, copper, and sulfur black dye by *Sargassum* [31, 32]. The objective of the present study was to determine the fluoride biosorption capacity of brown *Sargassum hystrix* algae. The effect of several important factors that can affect fluoride biosorption, such as biosorbent dosage, initial fluoride concentration, pH and contact time, was also discussed. Beside this, we determined the biosorption kinetics and modeling, sorption isotherms, and the effect of competing anions on fluoride biosorption.

2. Materials and methods

2.1. Biosorbent preparation and activation procedure

The brown algae *Sargassum hystrix* was obtained along the Persian Gulf in the Bushehr port coastal area (N 28°58′26.35″ and E 50°49′33.25″). After collection and transfer to laboratory, the algae were thoroughly washed three times by tap water and two times by distillated water in order to remove sand, clay, and other impurities. The washed algae were then dried in oven at 105°C for 24 h and finally milled and sieved through a 0.71 mm screen. All experiments were done by using dried algae as biosorbent. In order to determine the activation temperature on the biosorbent efficacy in fluoride removal and compare with dried algae (dried at 105°C) efficacy, 5 g biomass was placed in a furnace (Carbolite, England) at three different temperatures of 200°C, 400°C, and 600°C.

2.2. Fluoride sorption by batch study

A stock solution of 100 mg/L fluoride was prepared by dissolving sodium fluoride (Merck, Germany) in ultrapure water. Fluoride solutions were prepared at 2, 3, 5 and 8 mg/L concentrations. At each experiment, 100 mL of fluoride solution was agitated with specific initial fluoride concentration at 120 rpm. The effects of five contact times (5, 10, 25, 60, and 120 min), four initial fluoride concentrations (2, 3, 5, and 8 mg/L), and various mass ratios of biosorbent to the initial fluoride concentration (five ratios within the range of 400–8,000) were investigated in the batch systems. The standard SPADNS method [33] was used by using a spectrophotometer Model CAM Spec M501) for analysis of the remaining fluoride level in the aqueous solution after each experiment.

The removal efficiency was calculated using the following Eq. (1) [34]:

$$\text{Biosorption yield} = \frac{(C_i - C_e)}{C_i} \times 100 \quad (1)$$

where C_i and C_e are the concentrations of fluoride (mg/L) before and after the experiment in any time.

The equilibrium biosorption capacity of *Sargassum hystrix* algae was calculated at different fluoride concentration levels using the following Eq. (2):

$$q_e = \frac{(C_i - C_e)V}{m} \quad (2)$$

where q_e is the equilibrium biosorption capacity (mg/g); C_i is the fluoride concentration at initial time (mg/L); C_e is the concentration of fluoride in solution at equilibrium time (mg/L); V is the solution volume (L); and m is the biosorbent dosage (g).

2.3. Characterization of algal biomass

In order to determine the probable functional groups involved in the process of biosorption, characteristics of dried *Sargassum hystrix* biomass were analyzed and interpreted using Fourier transform infrared (FTIR) spectrometer (PerkinElmer FT-IR, model Spectrum RXI) over the wave number range from 4,000 to 400 cm^{-1}. Examination of *Sargassum hystrix* biomass with scanning electron microscope (SEM) with VEGA3 TESCAN model fitted with an energy dispersive X-ray analyzer (EDAX) allows a qualitative detection and localization of elements in the biosorbent.

The pH point of zero (pH_{PZC}) surface charge characteristics of *Sargassum hystrix* algae was determined using the solid addition method. 80 ml of 0.1 M NaCl solution were transferred to a series of 600 ml stoppered conical flasks. The initial pH values of the solutions were adjusted between 2 and 12 by adding either 0.2 M HCl or NaOH and were measured using a pH meter (Metrohum 744). The initial pH values of the solutions were then accurately noted. 1 g of *Sargassum hystrix* algae was added to each flask. The suspensions were then kept shaking for 24 h. The final pH values of the solutions were noted. The difference between the initial and final pH values (ΔpH) was plotted against the initial pH value. The point of decussating of the resulting curve with the initial pH axis, that is at ΔpH = 0, gave the pH_{PZC}.

3. Results and discussion

3.1. Characterization of the biosorbent

The functional responsible groups for fluoride ion biosorption on *Sargassum hystrix* algae was confirmed by FTIR spectra. The FTIR spectra of algal biomass (Fig. 1) indicated the presence of amino, carboxylic, hydroxyl and carbonyl groups. Strong broad O–H stretch carboxylic bands in the

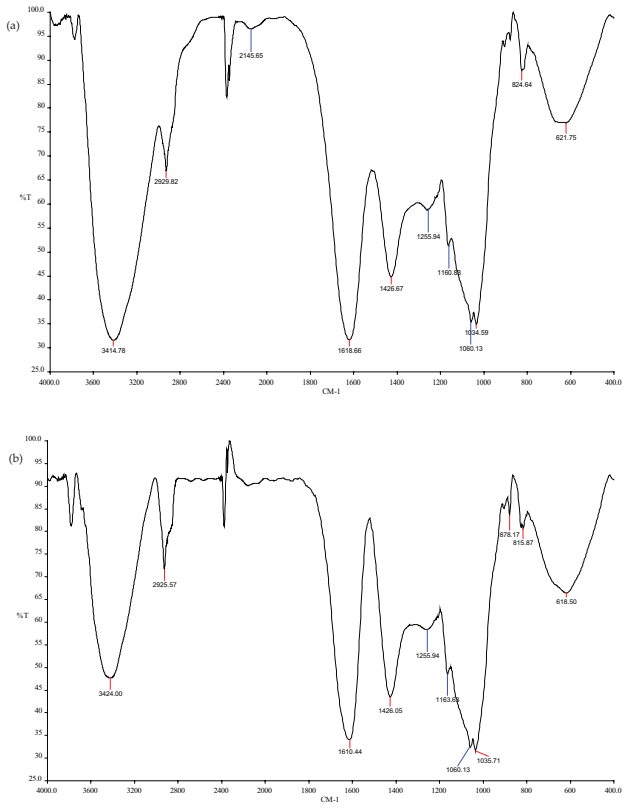
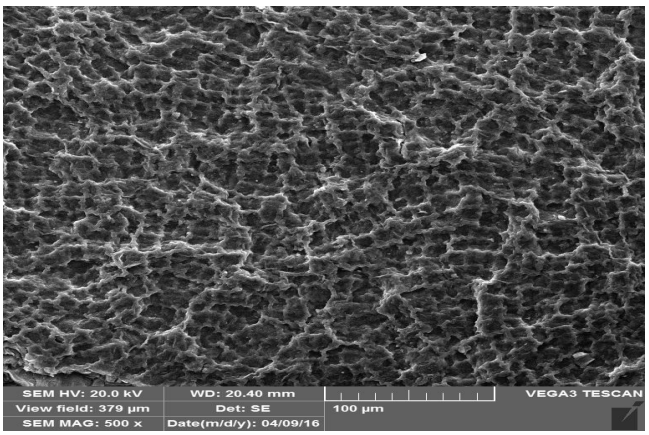


Fig. 1. FTIR spectra of *Sargassum hystrix* algae before (a) and after (b) fluoride biosorption.

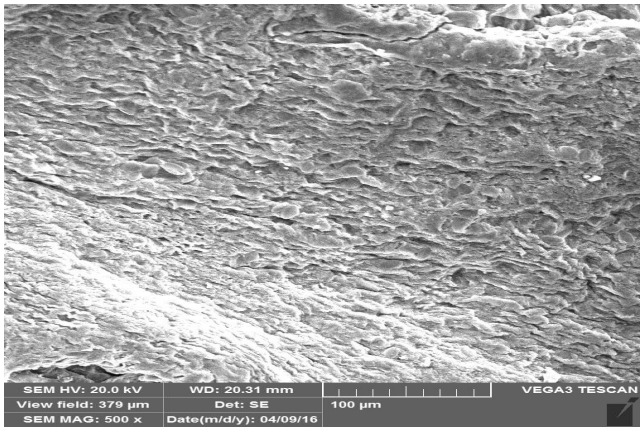
region 3,414 cm^{-1} and carboxylic stretching bands in the region of 2,929.82 cm^{-1} were observed. The peaks appearing in the region 1,618 cm^{-1} might be attributed to C=N, C=C and C = O stretch whereas the peak appearing in the region 1,426.67 cm^{-1} might represent quinine OH bond. The peaks appearing in the region 1,160.83 and 1,060.13 cm^{-1} represents N–H bending and C–O, respectively. The above-obtained results give an idea about the presence of functional groups on the algal cell surfaces. Conspicuous changes in the FTIR spectrum are observed after fluoride biosorption on the biomass, the transmittance at 3,414.78 and 1,618.66 cm^{-1} shifted to 3,424 and 1,610.44 cm^{-1}, respectively, on biosorption indicating the involvement of carboxylic groups. The observed changes in the transmittance values in the range of 1,160–1,163 and 824.64–815.87 cm^{-1} are closely related to N–H bending and S=O stretching frequencies, respectively. The shifting of these bands further indicated the involvement of S=O, N–H of amines and carboxylic groups in the biosorption process.

The SEM (scanning electron microscope) clearly revealed the surface texture and morphology of the biosorbent. SEM images of before and after fluoride biosorption of *Sargassum hystrix* algae are shown in Figs. 2(a) and 2(b), respectively. There were apparent differences between the surfaces before and after biosorption. Many cavities before biosorption were found but such cavities were not observed after biosorption that indicated fluoride biosorption on *Sargassum hystrix* algae.

The EDAX spectra of before and after fluoride biosorption by *Sargassum hystrix a*lgae are shown in Fig. 3(a) and 3(b).



(a)



(b)

Fig. 2. SEM images of before (a) and after (b) fluoride biosorption of *Sargassum hystrix* algae.

The presence of a fluoride peak in the EDAX spectra of fluoride-sorbed *Sargassum hystrix* algae after biosorption confirms the fluoride sorption onto *Sargassum hystrix* algae which is shown in Fig. 3(b).

3.2. Biosorbent pH point of zero charge and effect of pH

The pH_{PZC} is the pH at which the total number of positive and negative charges on its surface becomes zero. The adsorption of anions is desired at pH < pH_{PZC}, while the adsorption of cations is desired at pH > pH_{PZC}. Thus, the determination of pH_{PZC} is significant for the assessment of the sorption mechanism and the probabilistic sorbent interactions. As shown in Fig. 4, the surface charge of *Sargassum hystrix* algae at pH 6.5 is zero.

The effect of pH on fluoride biosorption at a range from 3 to 11 (3, 7, 11) was investigated. The fluoride removal from aqueous solution was highly dependent on the pH of solution. Biosorption is dependent on the pH value of aqueous solution, the functional groups on the biosorbent, and their ionic states at specific pH value [35]. It was observed that by increasing the pH of solution the removal efficiency will be decreased. Biosorbent biomass contains a large quantity of polysaccharides, and some of them are associated with

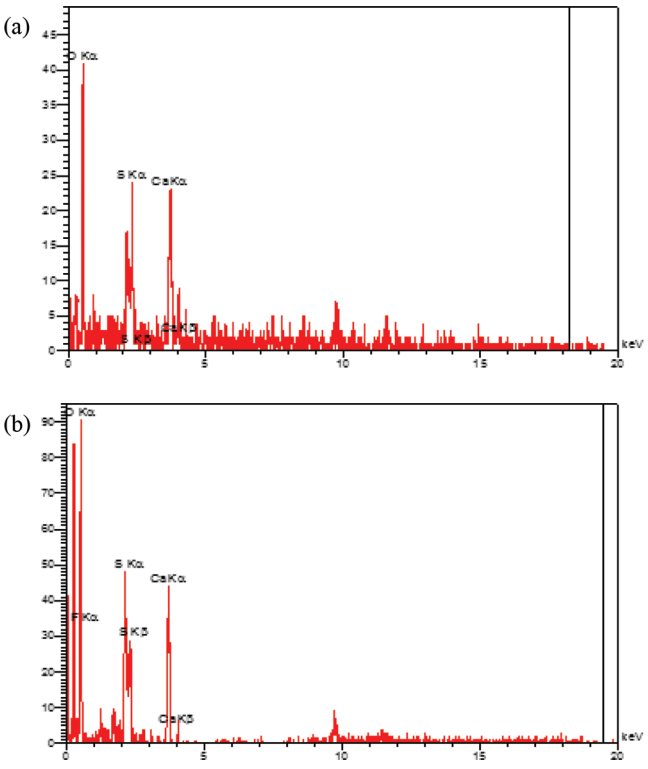


Fig. 3. EDAX spectra of before (a) and after (b) fluoride biosorption of *Sargassum hystrix* algae.

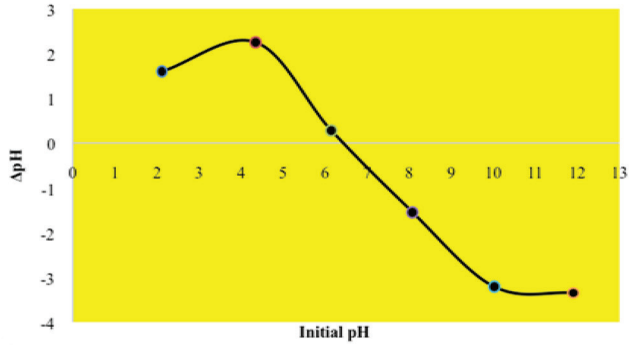


Fig. 4. pH at the point of zero charge (pH_{PZC}).

proteins and other components [36, 37]. Biomacromolecules on the biosorbent surfaces have various functional groups (such as alcohol, amino, phenol, carboxyl, thiol, sulfhydryl, and phosphate groups), and biosorption phenomena will be influenced by the protonation or deprotonation of these functional groups [36]. The ionic form of fluoride in aqueous solution and the electrical charge of the biosorbent surface might be influenced by the pH value of solution. At lower pH values, the surface of the biosorbent was turned out to be positively charged, and this facilitated sorption of fluoride ions probably was occurred by the anionic exchange sorption. At acidic, pH due to the protonated effect of surface functional groups, such as amino, carboxyl, thiol, and so on, imparts positive charge on the surface [38]. In a study, Venkata Mohan et al. examined fluoride removal by algal biosorbent, *Spirogyra sp.-IO2*, at pH values ranging from 2 to 10.5 and reported the highest fluoride removal efficiency at pH 2.0 [25]. In contrary, Dobaradaran et al. found that the removal efficiency of fluoride biosorption by shrimp shell waste increased by increasing pH value from 3 to 11 [27]. In the present study, maximum removal efficiency was observed at a pH value of 3, biosorbent dose of 8 g/L, and initial fluoride concentration of 8 mg/L (Fig. 5(a)).

3.3. Effect of biosorbent dose

The effect of biomass dosage on the fluoride removal by biosorbent was studied using different biomass doses of *Sargassum hystrix* algae in the range of 3.2–64 g/L (Fig. 5(b)). The biosorption efficiency was depended on the increasing biomass dosage in the solution. This can be attributed to the additional number of biosorption sites, which are resulted from the increase in the biosorbent dosage. Similarly, Jagtap et al. reported that fluoride removal capacity by using the metal-binding property of chitosan noticeably increased from 19% to 81.98% with the increasing biosorbent dosage from 0.2 to 1 g/L; there was no significant improvement in the fluoride removal when the biosorbent dosage reached higher than 1 g/L [39]. In another study, Dobaradaran et al. evaluated the efficiency of shrimp shell waste in removal of fluoride from aqueous solutions and determined the influence of various parameters on fluoride biosorption. They found that for an initial fluoride level of 8 mg/L, the fluoride removal percentage increased with increasing biosorbent dose from 3.2 to 64 g/L, but there were no significant differences in the fluoride removal percentage between biosorbent doses of 48 and 64 g/L [27]. Sivasankar et al. examined fluoride removal capacity with MnO_2–coated Tamarind Fruit (*Tamarindus indica*) shell at various doses and found that the removal percentage increased with increasing dosage of the biosorbent and then remained constant [17]. In contrast, Thakre et al. used lanthanum incorporated chitosan beads (LCB) for fluoride removal from drinking water and found that LCB has no significant fluoride removal capacity at doses 0.2–2 g/L [40]. In the present study, maximum removal efficiency (95%) was observed at a biosorbent dose of 64 g/L, contact time of 60 min, and initial fluoride concentration level of 8 mg/L. Also maximum capacity biosorption (1.94 mg/g) was observed at a biosorbent dose of 3.2 g/L, contact time of 60 min, and initial fluoride concentration level of 8 mg/L.

3.4. Effect of contact time and initial fluoride concentration

The effect of initial fluoride concentration on the fluoride removal is shown in Fig. 5(c). It was observed that by increasing substrate concentration from 2 to 8 mg/L, at a fixed mass ratio of biosorbent to initial fluoride concentration, the removal efficiency increased. This could be due to high biosorption capacity of *Sargassum hystrix* algae. Fluoride removal reached a maximum after 60 min and then decreased with increasing contact time which can be due to desorption and a decrease of the active surface area. The capacity of the biosorbent got exhausted after 60 min, and the total available biosorption sites were limited, which became saturated after mentioned time. Viswanathan et al. and Mahramanlioglu et al. found similar results in the defluoridation of aqueous solutions by protonated chitosan beads and poly aluminum

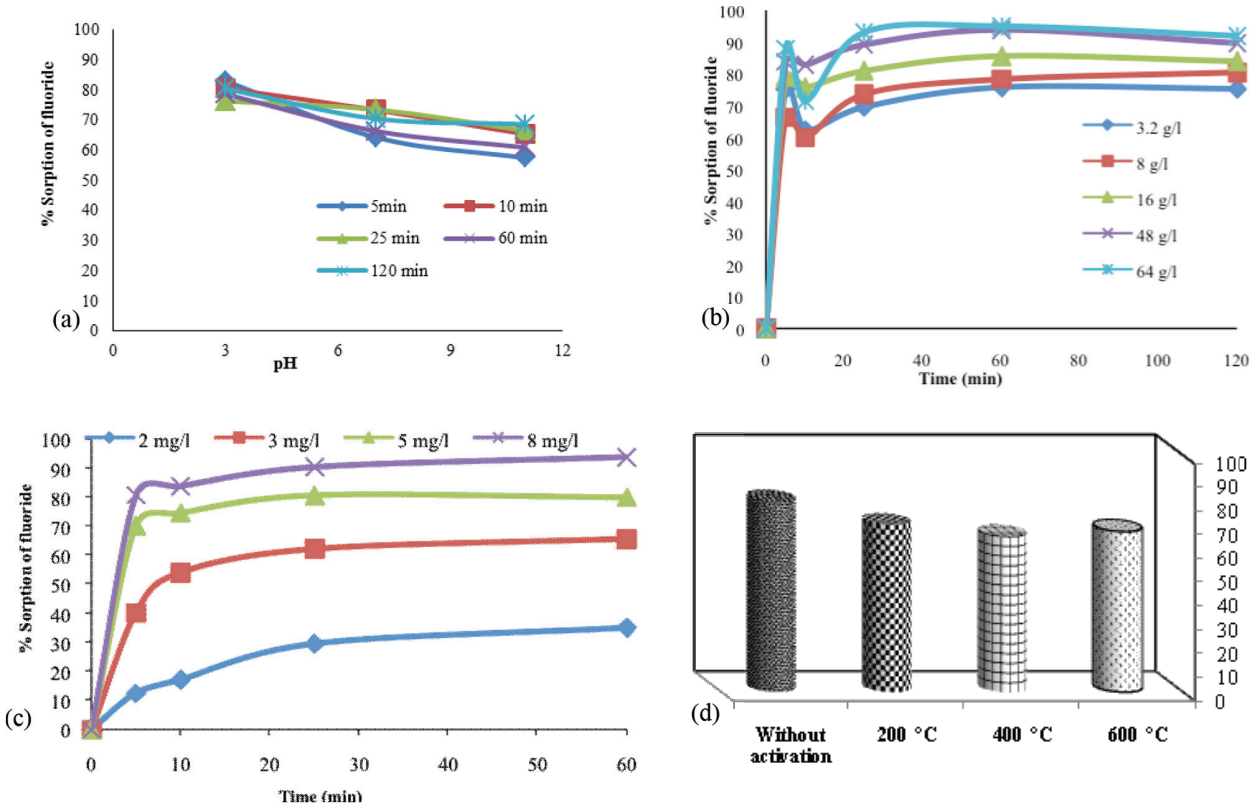


Fig. 5. Fluoride biosorption as a function of (a) pH (biosorbent dose: 8 g/L; initial fluoride concentration: 8 mg/L; room temperature), (b) biosorbent dose (initial fluoride concentration: 8 mg/L; pH: 7; room temperature), (c) initial fluoride concentration (g/L biomass/mg L fluoride: 6,000; pH: 7; room temperature), and (d) activation temperature (biosorbent: 3.2 g/L; fluoride concentration: 8 mg/L; contact time: 25 min; and pH: 7).

chloride, respectively [41, 42]. In contrast, Ramanaiah et al. performed adsorptive studies on fluoride removal using waste fungal biomass (Pleurotus ostreatus 1804) derived from laccase fermentation process and reported that the removal efficiency of fluoride by biosorbent decreases with increasing initial fluoride level [43]. In the present study, maximum removal efficiency (93.88%) and capacity biosorption (1.56 mg/g) was observed at initial fluoride concentration of 8 mg/L, contact time of 60 min, and a biosorbent dose of 48 g/L.

3.5. Effect of algae activation temperature

In order to determine the effect of activation temperature on the biosorbent efficacy in fluoride removal, experiments were performed at three different temperatures (200˚C, 400˚C, and 600˚C), and the efficacy of activation temperature on fluoride removal by biosorbent was compared with dried algae (dried at 105°C). As shown in Fig. 5(d), the removal efficiency of fluoride without activation is higher than fluoride biosorption when using activation process at high temperatures as by increasing activation temperature, biosorption capacities decrease from 0.2 to 0.16 mg/g. The possible reason for the decrease in biosorption efficiency was probably due to the loss of functional groups upon thermal activation [44].

3.6. Effect of anions concentration

The effects of five important natural competing anions including chloride (Cl^-), sulfate (SO_4^{2-}), carbonate (CO_3^{2-}) and nitrate (NO_3^-) at 200 and 400 mg/L were studied. As shown in Fig. 6, the results showed that the presence of competing anions did not have a significant effect on the biosorption rate as by increase the concentration of anions biosorption capacities decrease from 0.73 to 0.71, 0.7, 0.72, and 0.71 mg/g for chloride, solfate, carbonate, and nitrate, respectively.

3.7. Isotherms, kinetics, and modeling of sorption

To quantify the sorption capacity of *Sargassum hystrix* algae for the fluoride removal from aqueous solutions, three commonly used isotherms namely Freundlich, Langmuir, and Dubinin–Radushkevich (D–R) have been adopted.

The linear form of Freundlich [45] isotherm can be written as follows:

$$\text{Log}\,(q_e) = \text{Log}\,(K_f) + 1/\text{n}\,\text{Log}\,C_e \quad (3)$$

where q_e is the mass of fluoride adsorbed per unit weight of the sorbent (mg/g); K_F is the Freundlich capacity factor and a measure of biosorption capacity; and $1/n$ is the equilibrium concentration of fluoride in solution (mg/L) after biosorption.

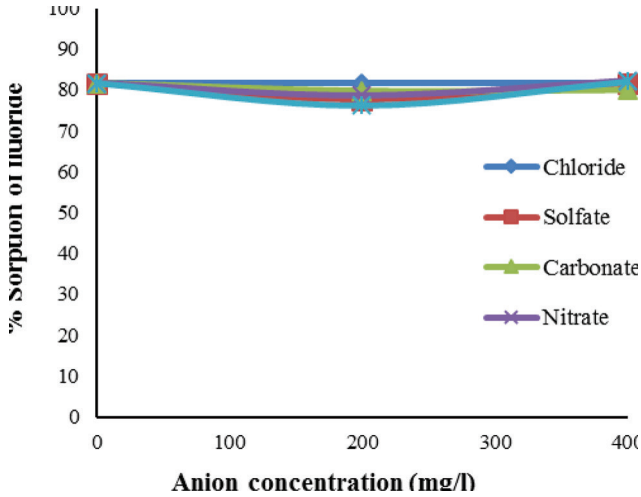


Fig. 6. Effect of competing anions concentration (200 and 400 mg/L) on fluoride biosorption (initial fluoride concentration: 5 mg/L; biosorbent dose: 5 g/L; contact time: 10 min; and pH: 7).

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 vs. log C_e.

Biosorption Freundlich isotherm parameters of fluoride onto *Sargassum hystrix* algae are shown in Table 1.

The Langmuir biosorption isotherm [46] model is defined as follows:

$$\frac{C_e}{q_e} = \frac{1}{bq_{\max}} + \frac{1}{q_{\max}} C_e \tag{4}$$

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

The Langmuir constant can be determined by plotting $\frac{C_e}{q_e}$ vs. C_e.

Biosorption Langmuir isotherm parameters of fluoride onto *Sargassum hystrix* algae are shown in Table 1.

The D–R biosorption isotherm [47] model is defined as follows:

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \tag{5}$$

where q_m is the D–R monolayer capacity (mg/g); β is a constant related to biosorption energy; and ε is the Polanyi potential which is related to the equilibrium concentration as follows:

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{6}$$

where R is the gas constant (8.314 J/mol K); T is the absolute temperature; C_e is the adsorbate equilibrium concentration (mg/L); and E is the sorption per molecule of the sorbate when it is transferred to the surface of the solid from infinity in the solution and can be calculated using the relationship:

Table 1
Biosorption isotherm parameters for fluoride sorption onto *Sargassum hystrix* algae

Isotherm	Parameter	Value
Freundlich	K_F (mg/g)	0.441
	$1/n$	0.2916
	R^2	0.9658
Langmuir	b (L/mg)	1.5185
	R_L	0.2187
	q_e (mg/g)	1.535
	R^2	0.9262
D–R	β	4×10^{-7}
	E	1107.7
	R^2	0.8741

$$E = -\frac{1}{\sqrt{(-2\beta)}} \tag{7}$$

If the value of biosorption energy E ranged between –1 to –8 kJ/mol, biosorption process is physical, and if the value of E ranged between –9 to –16 kJ/mol, it is chemical biosorption [48]. The parameters of the D–R equation were computed from the slope and intercept of the linear plot of ln q_e vs. ε^2 and are given in Table 1. The biosorption energy E value obtained –1.1 kJ/mol showed that the biosorption of fluoride on to *Sargassum hystrix* algae is a physical process.

As shown in Figs. 7(a), 7(b), and 7(c), Freundlich model was slightly better fitted than Langmuir and D–R models. Freundlich isotherm considered the heterogeneous biosorption surface and the possibility of multilayer biosorption.

The sorption kinetics is important in the treatment of aqueous solution, as it presents significant insights into reaction and mechanisms of sorption reactions. The experimental biosorption kinetic were defined by using pseudo-first-order, pseudo-second-order, and intraparticle diffusion kinetics. This kinetics can be written in their nonlinear forms, as follows:

Pseudo-first-order model:

$$Log(q_e - q_t) = \log q_e - \frac{K_{1,}}{2.303} t, \tag{8}$$

Pseudo-second-order model:

$$\frac{t}{q} = \frac{1}{q_e^2 K_2} + \frac{1}{q_e} t, \tag{9}$$

The intraparticle diffusion model (Weber and Morris):

$$q_t = k_d t^{0.5} + C \tag{10}$$

where q_e is the mass of solute sorbed at equilibrium (mg/g); q_t is the mass of solute sorbed at time t (mg/g); K_1 is the first-order equilibrium rate constant (1/ min); and K_2 is the

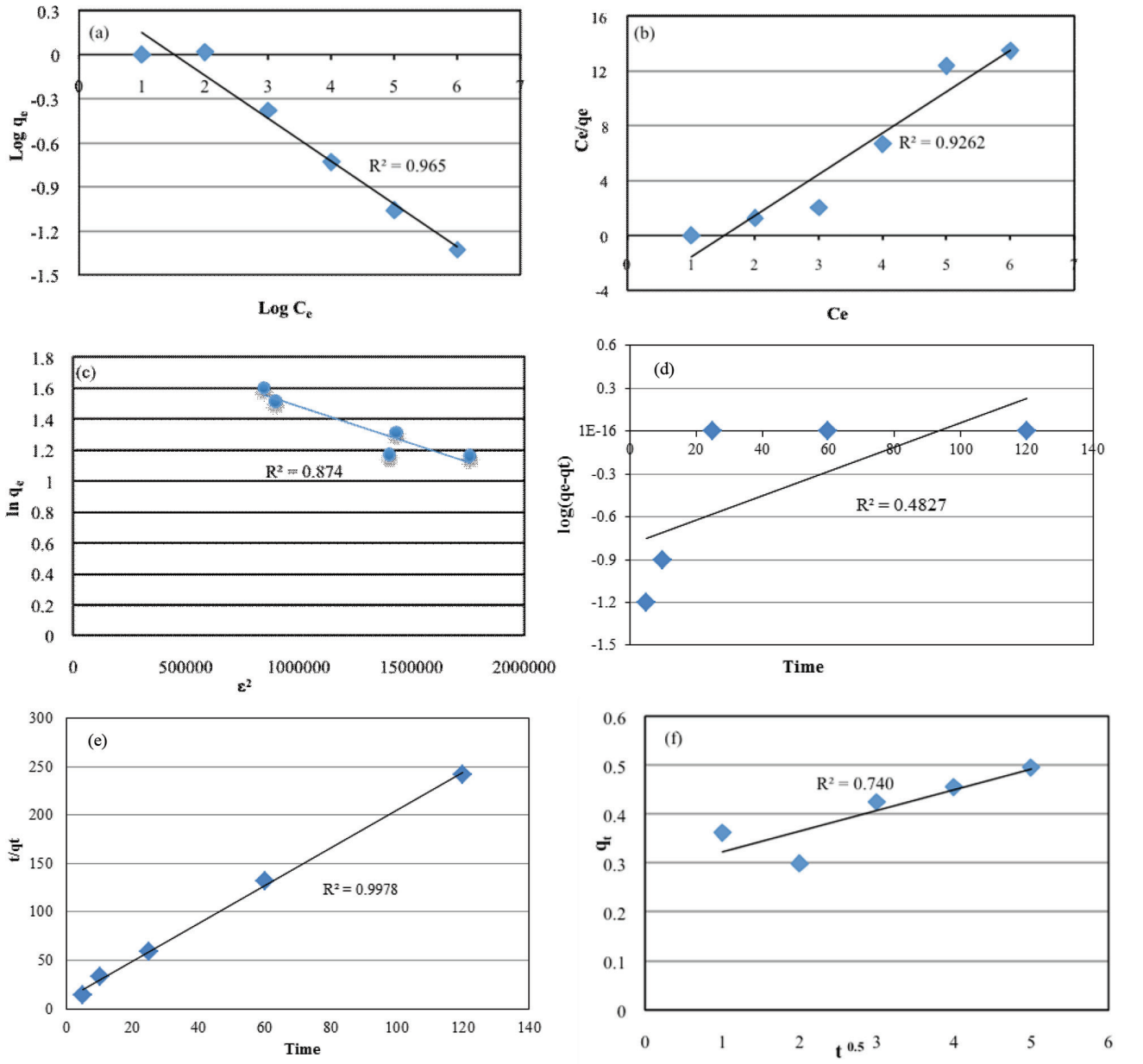


Fig. 7. Linear representation of (a) Freundlich, (b) Langmuir, (c) D–R isotherm models investigation of fluoride biosorption by *Sargassum hystrix* algae, (d) pseudo-first-order model, (e) pseudo-second-order model, and (f) intraparticle diffusion kinetics of fluoride biosorption by *Sargassum hystrix* algae.

second-order equilibrium rate constant (1/ min). K_d (mg/g. min 0.5) is the rate constant of intraparticle diffusion model; t is the time (min); and C is the intercept.

The first-order equilibrium rate constant (K_1) for fluoride sorption was calculated from the slop of the linear plot of log ($q_e - q_t$) vs. time. In the case of the second-order equilibrium rate constant (K_2), kinetic data were plotted between t/q_t against time.

The intraparticle diffusion model rate constant (K_d) and C can be measured from the slope and intercept of the linear plot of q_t vs. $t^{0.5}$, respectively.

Based on intraparticle diffusion model, the plot of q_t vs. $t^{0.5}$ should be linear (C = 0) if intraparticle diffusion is involved in the general mechanism of absorption, and in this case, the intraparticle diffusion is the only rate controlling step of the process. If this line did not through the principle (C ≠ 0), there are intraparticle diffusion and boundary layer effects in sorption process. Whatever the intercept amount (C) increase, the effect of surface sorption in the amount controlling step increases [49].

Sorption kinetic parameters for fluoride biosorption onto *Sargassum hystrix* algae are shown in Table 2. As shown in Figs. 7(d), 7(e), and 7(f) kinetics of fluoride adsorption by *Sargassum hystrix* algae followed the pseudo-second-order model, indicating that the adsorption limiting step may be chemisorption.

Table 2
Sorption kinetic parameters for fluoride biosorption onto *Sargassum hystrix* algae

Model	Parameter	Value
First-order kinetic	$q_{e,\exp}$ (mg/g)	6.2589
	K_1 (1/min)	0.0195
	$q_{e,\mathrm{cal}}$ (mg/g)	2.158
	R^2	0.4827
Second-order kinetic	$q_{e,\mathrm{cal}}$ (mg/g)	5.117
	K_2 (1/min)	0.0381
	R^2	0.9978
Intraparticle diffusion	K_d	0.0423
	C	0.28
	R^2	0.74

4. Conclusion

This study showed that *Sargassum hystrix* algae is a suitable biosorbent for the fluoride removal from aqueous solutions. The efficiency of fluoride removal was increased by increasing the biosorbent dose and initial fluoride concentration, and was decreased by increasing pH. Activation temperature and contact time did not have a significant effect on the biosorption rate. Freundlich model was slightly better fitted than Langmuir model for fluoride removal by *Sargassum hystrix* algae. The biosorption process was observed to follow a pseudo-second-order kinetic, and the presence of competing anions had not a significant effect on the biosorption rate. Finally, it should be noted that applied biosorbent in this study can be used as an effective, environmental friendly, and cost-effective biosorbent for fluoride removal from aqueous solutions especially in rural and remote areas due to its easy operation. This process may sufficiently be used for fluoride removal from industrial effluents containing high level of this pollutant.

Acknowledgments

The authors are grateful to the Bushehr University of Medical Sciences for their financial support (Grant no.: 20/71/1864) and the laboratory staff of the Environmental Health Engineering Department for their cooperation. This project was partly supported by Iran National Science Foundation (Research Chair Award No. 95/INSF/44913).

References

[1] Agency for Toxic Substances and Disease Registry (ATSDR), Toxicological profile for fluorides, hydrogen fluoride and fluorine, U.S. Public Health Service, U.S. Department of Health and Human Services, Atlanta, GA (1993).
[2] U.S. Environmental Protection Agency, Health issue assessment: summary review of health effects associated with hydrogen fluoride and related compounds, EPA/600/8-89/002F. Environmental Criteria and Assessment Office, Office of Health and Environmental Assessment, Office of Research and Development, Cincinnati, OH (1989).
[3] M. Sittig, *Handbook of toxic and hazardous chemicals and carcinogens*, 2nd ed. Noyes Publications, Park Ridge, NJ (1985).
[4] California Environmental Protection Agency (CalEPA), Technical support document for the determination of noncancer chronic reference exposure levels. Draft for Public Comment, Office of Environmental Health Hazard Assessment, Berkeley, CA (1997).
[5] N. Kalinic, J. Hršak, V. Vadjic, Z. Lambaša-Belak, V. Mihelčić, B. Perković, Fluoride content in soil and vegetation, Bull. Environ. Contam. Toxicol. l5 (2005) 157–162.
[6] Y.M. Shivarajashankara, A.R. Shivashankara, S.H. Rao, P.G. Bhat, Oxidative stress in children with endemic skeletal fluorosis, Fluoride, 34 (2001) 103–107.
[7] S. Dobaradaran, A.H. Mahvi, S. Dehdashti, D.R.V. Abadi, Drinking water fluoride and child dental caries in Dashtestan, Iran, Fluoride, 41 (2008) 220–226.
[8] A. Rahmani, K. Rahmani, S. Dobaradaran, A.M. Mahvi, R. Mohamadjani, H. Rahmani, Child dental caries in relation to fluoride and some inorganic constituents in drinking water in Arsanjan, Iran, Fluoride, 43 (2010) 179–186.
[9] A. Ostovar, S. Dobaradaran, M. Ravanipour, A. Khajeian, Correlation between fluoride level in drinking water and the prevalence of hypertension: an ecological correlation study, Int. J. Occup. Med. Environ. Health, 49 (2013) 216–217.
[10] S. Dobaradaran, A.H. Mahvi, S. Dehdashti, Fluoride content of bottled drinking water available in Iran, Fluoride, 41(2008) 93–94.
[11] S. Dobaradaran, A.H. Mahvi, S. Dehdashti, S. Dobaradaran, R. Shoara, Correlation of fluoride with some inorganic constituents in groundwater of Dashtestan, Iran, Fluoride, 42 (2009) 50–53.
[12] S. Dobaradaran, D.R.V. Abadi, A.H. Mahvi, A. Javid, Fluoride in skin and muscle of two commercial species of fish harvested off the Bushehr shores of the Persian Gulf, Fluoride, 44 (2011) 143–146.
[13] S. Dobaradaran, F. Fazelinia, A.H. Mahvi, S.S. Hosseini, Particulate airborne fluoride from an aluminium production plant in Arak, Iran, Fluoride, 42 (2009) 228–232.
[14] M. Shams, S. Dobaradaran, S. Mazloomi, M. Afsharnia, M. Ghasemi, M. Bahreini, Drinking water in Gonabad, Iran: fluoride levels in bottled, distribution network, point of use desalinator, and decentralized municipal desalination plant water, Fluoride, 45 (2012) 138–141.
[15] Water, Sanitation, and World Health Organization. "Guidelines for drinking-water quality [electronic resource]: incorporating first addendum. Vol. 1, Recommendations." (2006).
[16] U.S. Department of Health and Human Services Federal Panel on Community Water Fluoridation. U.S. Public Health Service Recommendation for Fluoride Concentration in Drinking Water for the Prevention of Dental Caries. Public Health Reports. 2015; 130(4):318-331.
[17] V. Sivasankar, T. Ramachandramoorthy, A. Chandramohan, Fluoride removal from water using activated and MnO_2-coated Tamarind Fruit (Tamarindus indica) shell: batch and column studies, J. Hazard. Mater., 177 (2010) 719–729.
[18] F. Shen, X. Chen, P. Gao, G. Chen, Electrochemical removal of fluoride ions from industrial wastewater, Chem. Eng. Sci., 58 (2003) 987–993.
[19] M.A. Zazouli, A.H. Mahvi, S. Dobaradaran, M. Barafrashtehpour, Y. Mahdavi, D. Balarak, Adsorption of fluoride from aqueous solution by modified Azolla filiculoides, Fluoride, 47 (2014) 349–358.
[20] S. Dobaradaran, M. Kakuee, A.R. Pazira, M. Keshtkar, M. Khorsand, Fluoride removal from aqueous solutions using Moringa oleifera seed ash as an environmental friendly and cheap biosorbent, Fresenius Environ Bull., 24 (2015) 1269–1274.
[21] M. Rahmani Boldaji, A.H. Mahvi, S. Dobaradaran, S.S. Hosseini, Evaluating the effectiveness of a hybrid sorbent resin in removing fluoride from water, Int. J. Environ. Sci. Technol., 6 (2009) 629–632.
[22] M. Shams, M. Qasemi, S. Dobaradaran, A.H. Mahvi, Evaluation of waste aluminum filling in removal of fluoride from aqueous solutions, Fresenius Environ. Bull., 22 (2013) 2604–2609.
[23] M. Keshtkar, S. Dobaradaran, I. Nabipour, S. Tajbakhsh, F. Soleimani, H. Darabi, H. Ghaedi, Removal of manganese from aqueous phase using Padina sanctae crucis obtained from Persian Gulf, J. Mazandaran Univ. Med. Sci., 26 (2016) 103–107.

[24] S. Dobaradaran, I. Nabipour, S. Tajbakhsh, M. Khorsand, M. Keshtkar, A. Khaledi, F. Babaahmadi, Biosorption of cadmium from aqueous solution onto cuttle bone obtained along the Persian Gulf coast as a cheap and effective biosorbent: evaluation of adsorption isotherms and kinetics, Int. J. Pharm. Technol., 7 (2015) 9975–9984.
[25] S. Venkata Mohan, S.V. Ramanaiah, B. Rajkumar, P.N. Sarma, Removal of fluoride from aqueous phase by biosorption onto algal biosorbent Spirogyra sp.-IO2: sorption mechanism elucidation, J. Hazard. Mater., 141 (2007) 465–474.
[26] B. Volesky, Z.R. Holan, Biosorption of heavy metals, Biotechnol. Prog., 11 (1995) 235–250.
[27] S. Dobaradaran, I. Nabipour, A.H. Mahvi, M. Keshtkar, F. Elmi, F. Amanollahzade, M. Khorsand, Fluoride removal from aqueous solutions using Shrimp Shell waste as a cheap biosorbent, Fluoride, 47 (2014) 253–257.
[28] M.A. Zazouli, A.H. Mahvi, S. Dobaradaran, M. Barafrashtehpour, Y. Mahdavi, D. Balarak, Adsorption of fluoride from aqueous solution by modified Azolla Filiculoides, Fluoride, 47 (2014) 349–358.
[29] S. Dobaradaran, M.A. Zazuli, M. Keshtkar, S. Noshadi, M. Khorsand, F. Faraji Ghasemi, V. Noroozi Karbasdehi, et al., Biosorption of fluoride from aqueous phase onto Padina sanctae crucis algae: evaluation of biosorption kinetics and isotherms, Desal. Water Treat. (2016) 1–12, doi:10.1080/19443994.2016.1182081.
[30] C. Hu, L. Feng, R.F. Hardy, E.J. Hochberg, Spectral and spatial requirements of remote measurements of pelagic Sargassum macroalgae, Remote Sens. Environ., 167 (2015) 229–246.
[31] K. Vijayaraghavan, D. Prabu, Potential of Sargassum wightii biomass for copper(II) removal from aqueous solutions: application of different mathematical models to batch and continuous biosorption data, J. Hazard. Mater., 137 (2006) 558–564.
[32] G. Vijayaraghavan, S. Shanthakumar, Removal of sulphur black dye from its aqueous solution using alginate from Sargassum sp. (Brown algae) as a coagulant, Environ. Prog. Sustain. Energy., 34 (2015) 1427–1434.
[33] American Public Health Association, American Water Works Association, Water Environment Federation, *Standard methods for the examination of water and wastewater*, 21st ed, Washington D.C., AWWA. (2005).
[34] R. Bharali, K. Bhattacharyya, Kinetic and thermodynamic studies on fluoride biosorption by Devdaru (polyalthia longifolia) leaf powder, Oct. Jour. Env. Res., 2 (2014) 22–31.
[35] S.V. Mohan, Y.V. Bhaskar, J. Karthikeyan, Biological decolorization of simulated azo dye in aqueous phase by algae Spirogyra species, Int. J. Environ. Pollut., 21 (2003) 211–222.
[36] T. Ilhami, B. Gulay, Y. Emine, B. Gokben, Equilibrium and kinetic studies on biosorption of Hg(II), Cd(II) and Pb(II) ions onto micro algae Chlamydomonas reinhardtii, J. Environ. Manag., 77 (2005) 85–92.
[37] S. Panumati, K. Chudecha, P. Vankhaew, V. Choolert, L. Chuenchom, W. Innajitara, O. Sirichote, Adsorption of phenol from diluted aqueous solutions by activated carbons obtained from bagasse, oil palm shell and pericarp of rubber fruit, Songklanakarin J. Sci. Technol., 30 (2008), 185–189.
[38] S. Venkata Mohan, S.V. Ramanaiah, B. Rajkumar, P.N. Sarma, Biosorption of fluoride from aqueous phase onto algal Spirogyra IO1 and evaluation of adsorption kinetics, Bioresour. Technol., 98 (2007) 1006–1011.
[39] S. Jagtap, D. Thakre, S. Wanjari, S. Kamble, N. Labhsetwar, S. Rayalu, New modified chitosan-based adsorbent for defluoridation of water, J. Colloid Interface Sci., 332 (2009) 280–290.
[40] D. Thakre, S. Jagtap, A. Bansiwal, N. Labhsetwar, S. Rayalu, Synthesis of La-incorporated chitosan beads for fluoride removal from water, J. Fluorine Chem., 131 (2010) 373–377.
[41] N. Viswanathan, C. Sairam Sundaram, S. Meenakshi, Removal of fluoride from aqueous solution using protonated chitosan beads, J. Hazard Mater., 161 (2009) 423–430.
[42] M. Mahramanlioglu, I. Kizilcikli, I.O. Bicer, Adsorption of fluoride from aqueous solution by acid treated spent bleaching earth, J. Fluorine Chem., 115 (2002) 41–47.
[43] S.V. Ramanaiah, S. Venkata Mohan, P.N. Sarma, Adsorptive removal of fluoride from aqueous phase using waste fungus (Pleurotus ostreatus 1804) biosorbent: kinetics evaluation, Ecol. Eng., 31 (2007) 47–56.
[44] F. Banat, S. Al-Asheh, L. Al-Makhadmeh, Evaluation of the use of raw and activated date pits as potential adsorbents for dye containing waters, Process Biochem., 39 (2003) 193–202.
[45] H.M.F. Freundlich, Uber die adsorption in losungen, Z. Phys. Chem., 57 (1906) 385–470.
[46] I. Langmuir, The constitution and fundamental properties of solids and liquids, J. Am. Chem. Soc., 38 (1916) 2221–2295.
[47] M.M. Dubinin, L.V. Radushkevich, The equation of the characteristic curve of the activated charcoal, Proc. Acad. Sci. USSR Phys. Chem. Sect., 55 (1947) 331–337.
[48] R.O. Ajemba, Adsorption of malachite green from aqueous solution using activated ntezi clay: optimization, isotherm and kinetic studies, IJE C: Aspects, 27 (2013) 839.
[49] A. Murugesan, L. Ravikumar, V.S.S. Bala, P.S. Kumar, T. Vidhyadevi, S. Dinesh, S.S. Kiruphaa, et al.,Removal of Pb(II), Cu(II) and Cd(II) ions from aqueous solution using polyazomethineamides: equilibrium and kinetic approach, Desalination, 271 (2011) 199–208.