

## 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 Freundlich 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

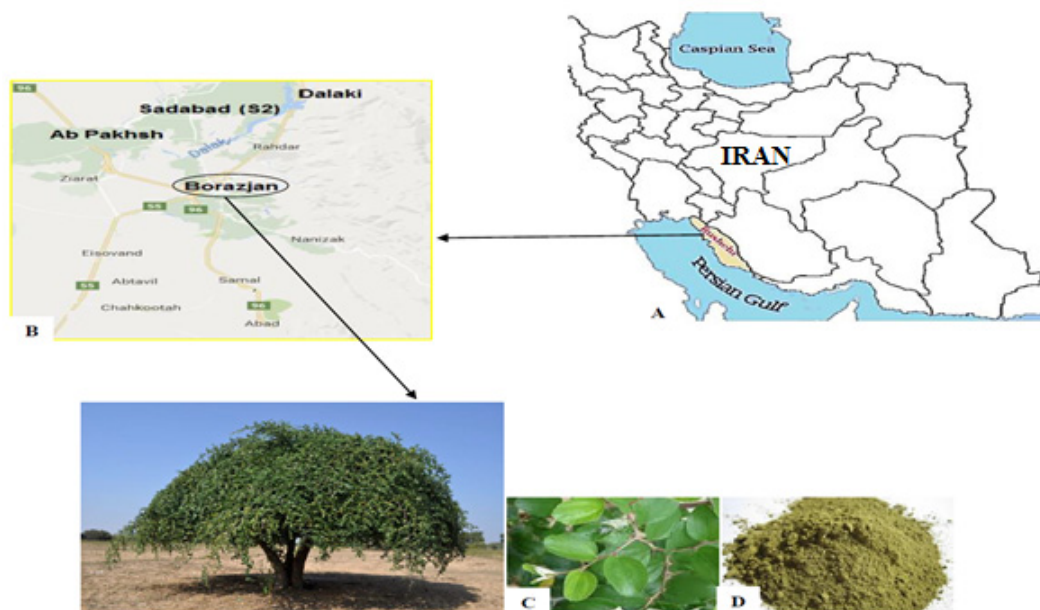
The fluoride ion (F) is broadly distributed in the environment and is of particular concern because many studies have reported that an excess F intake through drinking water or food can cause a wide range of adverse health effects.<sup>1–4</sup> As well as F from the natural weathering of rocks, various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

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conventional treatment methods comprise low cost, high efficiency, less sludge production, and biosorbent regeneration.<sup>28, 29</sup> 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.<sup>30,31</sup> 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 105°C 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±1°C). 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:

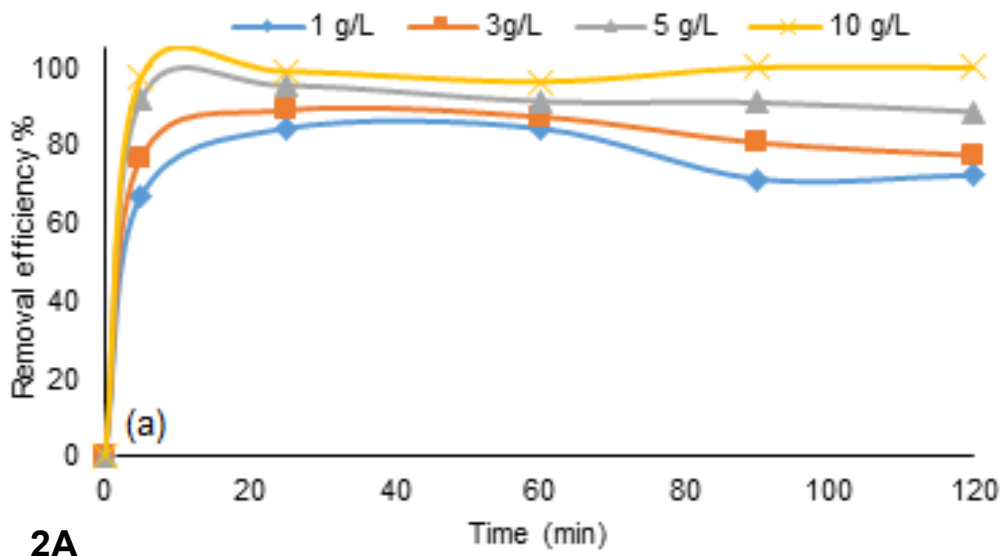
$$q_e = \frac{(C_i - C_e) V}{m}$$

where:

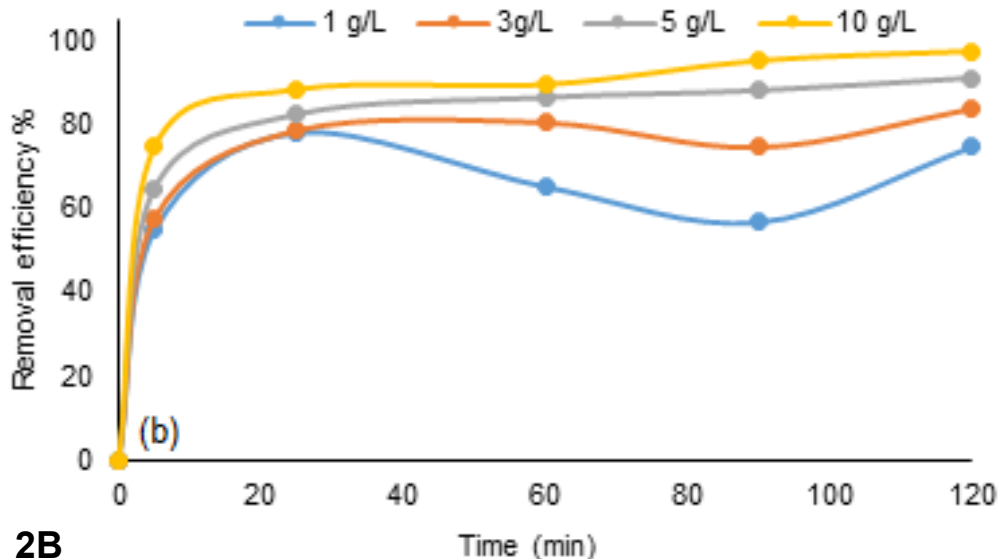
- $q_e$  = the equilibrium biosorption capacity (mg/L)
- $C_i$  = the initial fluoride concentration (mg/L)
- $C_e$  = the fluoride concentration level in the solution at equilibrium (mg/L)
- $V$  = the solution volume (L)
- $m$  = the biosorbent dosage (g)

## RESULTS AND DISCUSSION

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



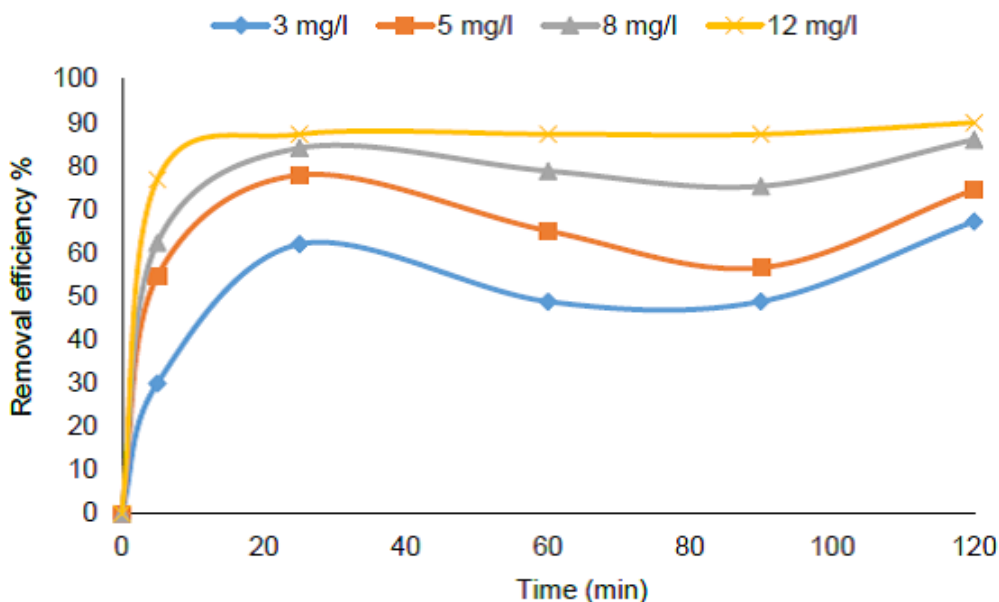
**Figure 2A.** Fluoride (F) adsorption as a function of the adsorbent dose at the initial F concentration of 12 mg/L (pH: 7).



**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.<sup>23,25</sup> Mourabet et al. also reported that by increasing the biomass dosage of apatitic tricalcium phosphate, the rate of F adsorption rate increased.<sup>32</sup> 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.<sup>33</sup>

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.<sup>25</sup> 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.<sup>23</sup>



**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.<sup>34</sup> Also, Jamode et al. and Mahramanlioglu et al., using different adsorbents, found lower adsorption rates at higher initial F concentration levels.<sup>35,36</sup> 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.<sup>37,38</sup>

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  $\text{log } q_e$  against  $\text{log } C_e$ .

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:

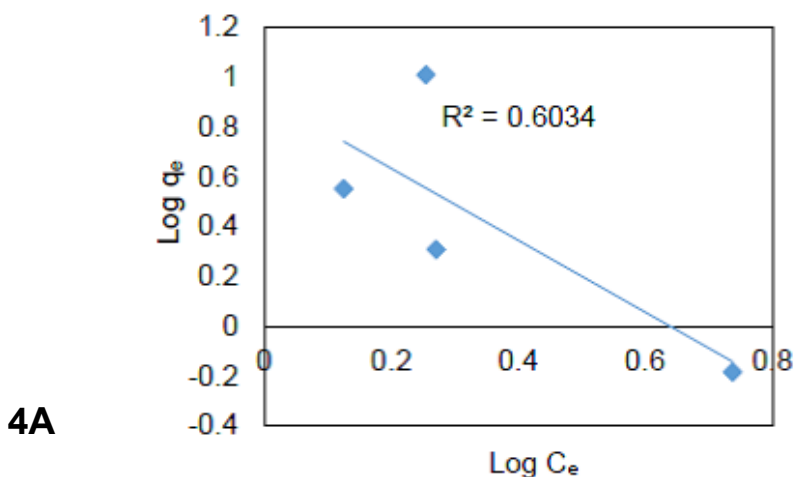
- $q_e$  = the mass of fluoride per unit mass of sorbent (mg/g)
- $q_{max}$  = the monolayer sorption capacity
- $b$  = the Langmuir constant related to the free energy of sorption equilibrium concentration of fluoride in the solution (mg/L) after biosorption

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

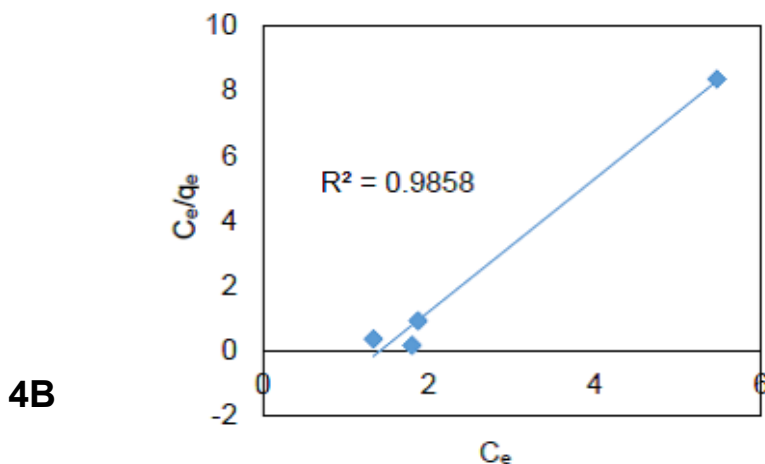
The results showed that the Langmuir model fitted the data better than the Freundlich model (Table 1 and Figures 4A and 4B). The Langmuir isotherm assumes a monolayer adsorption on a homogenous flat surface, due to the greater tendency of F to be adsorbed onto the adsorbent surface instead of undergoing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



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

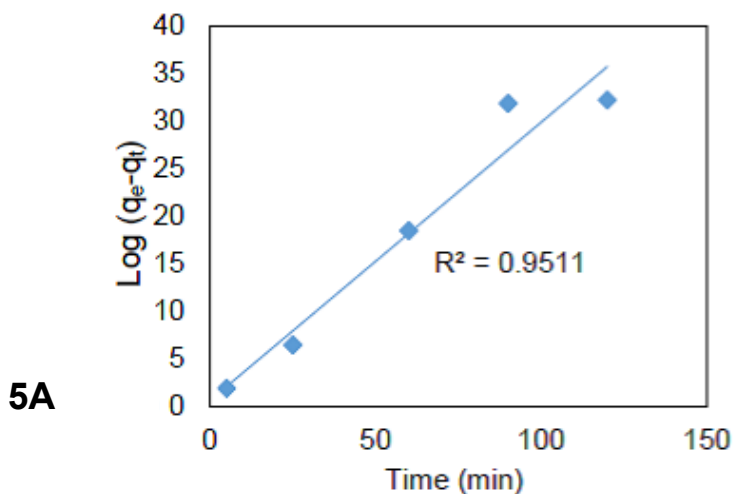


**Figure 4B.** Linear representation of the Langmuir model of the investigation of fluoride (F) biosorption by *Ziziphus* leaf.

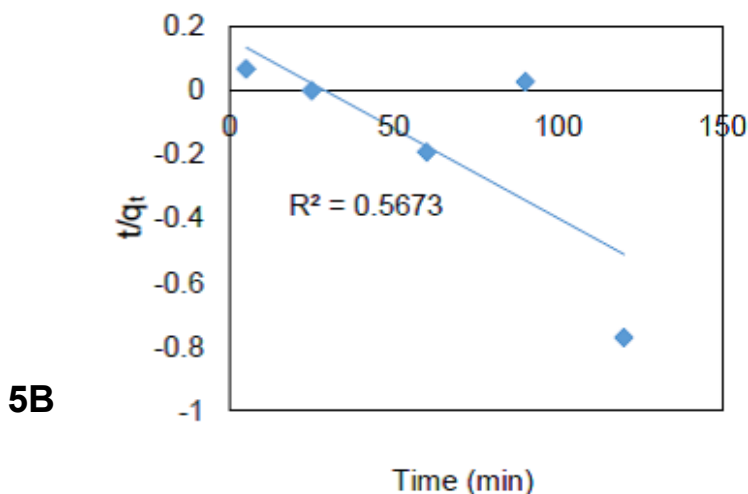
The biosorption kinetics are important in the treatment of aqueous solutions, as they present important understandings into the mechanisms of biosorption reactions. In order to recognize the mechanism of F biosorption onto *Ziziphus* leaf the experimental biosorption kinetics were defined by using the 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



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



**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.

#### ACKNOWLEDGEMENTS

The authors are grateful to the Bushehr University of Medical Sciences for their financial support and to the laboratory staff of the Environmental Health Engineering Department of the University for their cooperation.

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