

ADSORPTION OF FLUORIDE FROM AQUEOUS SOLUTION BY MODIFIED *AZOLLA FILICULOIDES*

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SUMMARY: This paper describes the removal of fluoride (F) from water using the water fern species *Azolla filiculoides*. This study took the form of empirical laboratory-based research. The *Azolla* plants were gathered and dried in an oven at 105°C for 24 hr. The effects of pH, contact time, adsorbent dose, and F concentration were investigated. The concentration of F was measured using a spectrophotometer in wavelengths of 570 nm. The isotherms and kinetics of adsorption were determined. The results showed that removal efficiency decreased with increasing pH and that the optimum pH was 5. The removal efficiency of *Azolla* was increased by increasing the adsorbent dose and contact time, and decreasing the initial concentration of F. The data fitted well with the Langmuir Model isotherm. There was good correlation with pseudo-second-order kinetics for the absorption of F by biomass. The results indicated that modified *Azolla filiculoides* can be used successfully as an effective adsorbent for F removal.

Keywords: Adsorption isotherm; Adsorption kinetic; *Azolla filiculoides*; Fluoride adsorption.

INTRODUCTION

Fluoride (F) is not an essential element, may adversely affect human health, and the maximum level recommended in drinking water by the World Health Organization (WHO) is 1.5 mg/L.¹⁻² Many studies have been done regarding F and its relation to health and the environment.³⁻⁵ Any excess F must be removed from drinking water. Several techniques have been investigated to remove F from water, such as reverse osmosis, nanofiltration, ultrafiltration, electro dialysis, donnan dialysis, ion exchange, and adsorption.⁶⁻⁸ Of these, adsorption is a widely used method due to its several benefits^{9,10} with activated carbon being the most widely used adsorbent. Finding a low-cost and effective adsorbent is a current concern across the world¹¹ with particular interest being taken in biosorbents for pollutant removal.¹² *Azolla filiculoides* is one such biosorbent. It is a water fern that contains blue-green algae and is found in slow-moving streams and ponds.¹³⁻¹⁵ It grows rapidly, forming dense mats over the water surface, which can have negative effects on aquatic life.¹⁶ *Azolla* in both dried and living form has been used effectively to remove heavy metals, dyes, and phenol compounds from aqueous solutions.¹⁷⁻²⁰ The aim of the present study was to investigate the ability of modified *Azolla filiculoides* to adsorb F from aqueous solutions and to apply

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kinetic modeling and isotherms. The influence of various parameters, including pH, contact time, adsorbent dose, and F concentration, were investigated.

MATERIALS AND METHODS

Azolla plants were collected from a rice paddy in the city of Sari, Iran, and dried in the oven at 105°C for 24 hr. It was crushed and sieved into particles ranging in size from 1 to 2 mm. The biomass was treated with 0.1 M HCl for a period of five hr after which it was washed with distilled water and dried in the shade.¹⁷

The specific surface area of the adsorbent was determined by the BET method using a Gemini 2357 surface area analyzer (Micromeritics Instrument Corporation, USA). Scanning electron microscopy (SEM) was carried out using a scanning microscope (Philips, Eindhoven) equipped with an energy-dispersive X-ray (EDX). The FT-IR spectra were recorded in the range of 400–4000 cm⁻¹ using a Nicolet 5700 FT-IR spectrometer (Thermo Fisher Scientific, USA) to gather data on the bending vibrations and stretching of the functional groups that are responsible for the adsorption process.

Sodium fluoride (NaF) was used to prepare the F solution. The batch experiments were carried out in 250 mL Erlenmeyer flasks (Meyer). Previous research has shown that the most effective variables on the adsorption process are pH, adsorbent dose, contact time, and pollutant concentration. The initial range of F concentration was 1 to 100 mg/L. The effect of the adsorbent dose (0.2–1.2 g), contact time (5, 15, 30, 45, 60, 75, 90, 120, and 180 minutes), and pH (3, 5, 7, 9, and 11) were investigated.

In each experiment, a particular volume of F solution with a particular concentration was added to an Erlenmeyer flask and a particular adsorbent dose added. The solution was mixed with shaker at 180 rpm for 60 min. The samples were then centrifuged at 3600 rpm for 10 min. The data were analyzed using SPSS 16 statistics software. The standard curve was provided by using the different concentrations of F, prepared from stock solution (100 mg/L). The pH was regulated by 0.1 M HCl and 0.1 M NaOH. For the measurement of the F, 1 mL of ZrOCl₂.8H₂O and 1 mL SPADNS F reagent solution were added to the prepared samples and each measured by spectrophotometer in λ_{max}=570 nm.¹⁸ The equilibrium adsorption capacity was calculated using the following equation:¹⁸

$$q_e = \frac{(C_0 - C_e)V}{M}$$

Where C₀, C_e (mg/L) are the initial and the equilibrium concentration of F, q_e (mg/g) the amount of F adsorbed at equilibrium, M (g) the adsorbent mass, and V (L) the volume of solution.

The experiments to determine the adsorption isotherms were performed with an adsorbent amount of 10 g/L at pH 5. The important parameter in designing the absorption system is the prediction of the adsorption capacity. This can be obtained by analyzing the isotherm data. The obtained data were fitted on the first- and second-order models to find the best chemical removal model for describing

the experimental kinetic data. The equations of isotherms and kinetics are shown in Table 1.

Table 1. The equations of isotherms and kinetics.¹⁸

Model Langmuir	$\frac{C_e}{q_e} = \frac{1}{q_e k_l} + \frac{C_e}{q_m}$
Model Freundlich	$\text{Log } q_e = \frac{1}{n} \log C_e + \log K_F$
Model Tempkin	$q_e = B_1 \ln(k_1) + B_1 \ln(C_e)$
Model BET	$\frac{C_e}{(c_i - c_e)q} = \frac{1}{A q_m} + \frac{A-1}{A q_m}$
Pseudo-first-order kinetic	$\text{Log } \frac{(q_e - q)}{t} = \log q_e - \frac{k_1 t}{2.3}$
Pseudo-second-order kinetic	$\frac{1}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}$

RESULTS AND DISCUSSION

The specific surface area is related to the number of active adsorption sites of dried *A. filiculoides*. Adsorption increased with increased specific surface area and pore volume of the adsorbent. The specific surface area of modified *Azolla* was determined to be 36 m²/g indicating that the modified *Azolla* had a relatively good ability to remove the pollutants.

SEM images were used to analyze the surface structure of *A. filiculoides* (Figures 1 and 2).

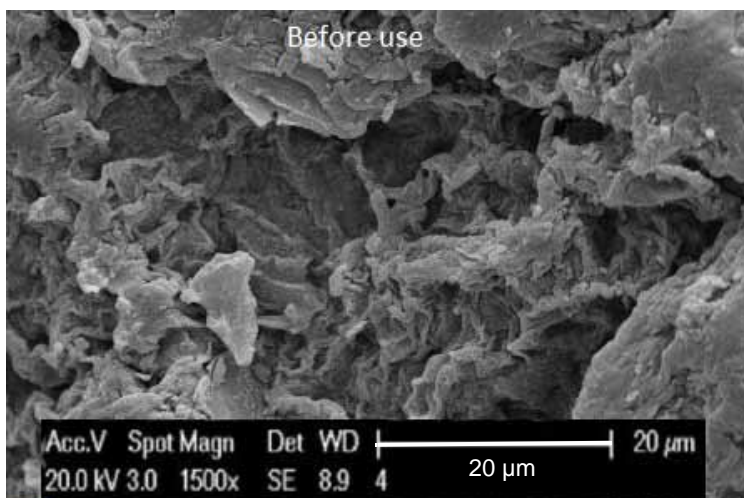


Figure 1. SEM image of *Azolla filiculoides* before use.

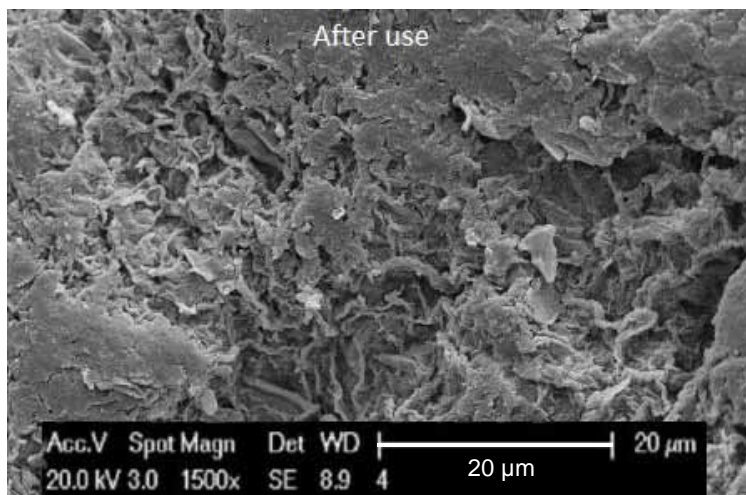


Figure 2. SEM image of *Azolla filiculoides* after use.

It was found that the adsorbent had a heterogeneous surface structure with deep pores. The elemental composition analysis showed that the adsorbent in the sample contained: C (57.57%), O (35.7%), Ca (4.40%), Mg (1.2%), K (0.075%), Cl (0.017%), and Al (0.045%) (Figure 3).

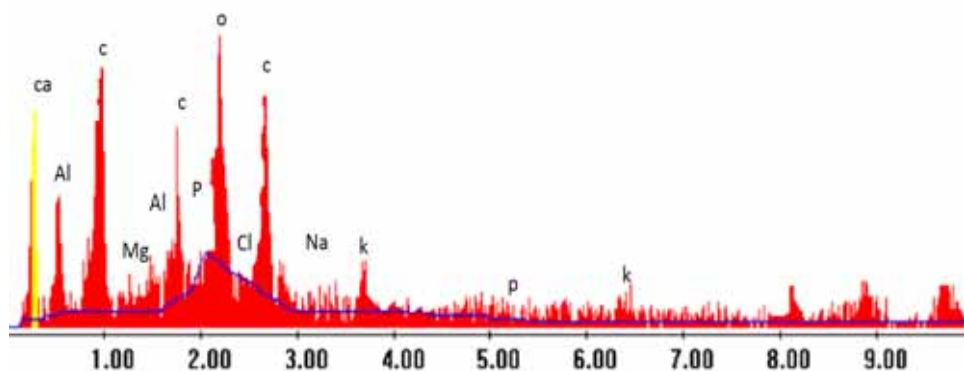


Figure 3. EDX spectrum of modified *Azolla filiculoides*.

To understand the interaction between functional groups on the surface of dried *A. filiculoides* and fluorine cations, samples of dried *A. filiculoides* both before and after use were examined using FT-IR spectroscopy. As shown in Figures 4 and 5, the dried *A. filiculoides* both before and after use showed a similar pattern and the same number of observed peaks in the FT-IR spectra. Intense absorption peaks at around $3410\text{--}3430\text{ cm}^{-1}$ correspond to the O–H stretching vibrations due to inter- and intra-molecular hydrogen bonding of polymeric compounds, thus showing the presence of ‘free’ hydroxyl groups on the adsorbent surface. The peaks at 2928 cm^{-1} are attributed to the symmetric and asymmetric C–H stretching vibration of aliphatic acids. The peak observed at 1744 cm^{-1} is the stretching vibration of bonds due to non-ionic carboxyl groups (--COOH , --COOCH_3), and may be

assigned to carboxylic acids or their esters. The peaks at 1638 and at 1413–1418 cm^{-1} are due to asymmetric and symmetric stretching vibrations of C=O in ionic carboxylic groups ($-\text{COO}-$). Aliphatic acid group vibration at 1262 cm^{-1} may be assigned to the deformation, vibration of C=O and stretching formation of $-\text{OH}$.

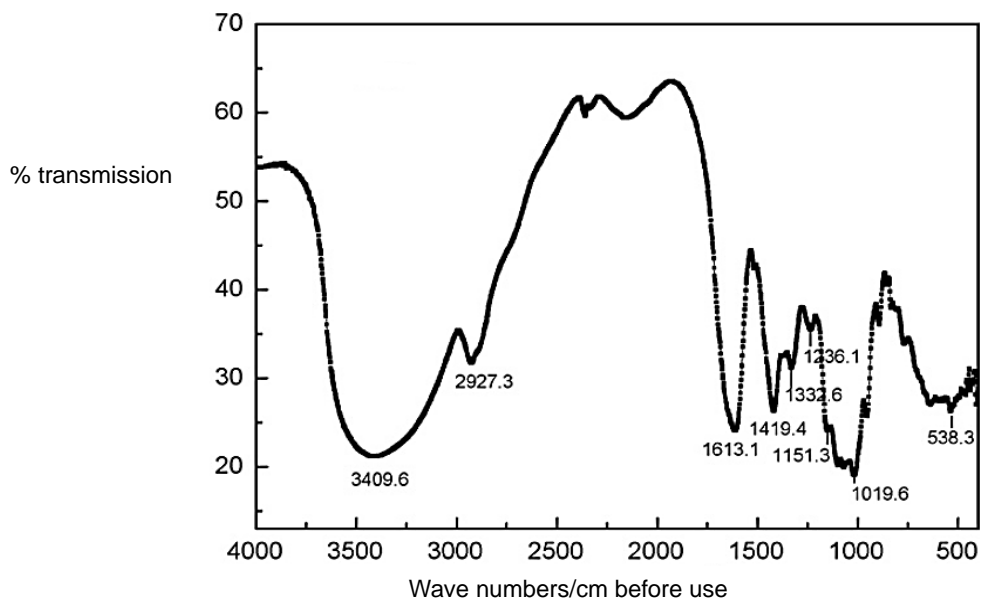


Figure 4. FT-IR spectra of modified *Azolla filiculoides* before use.

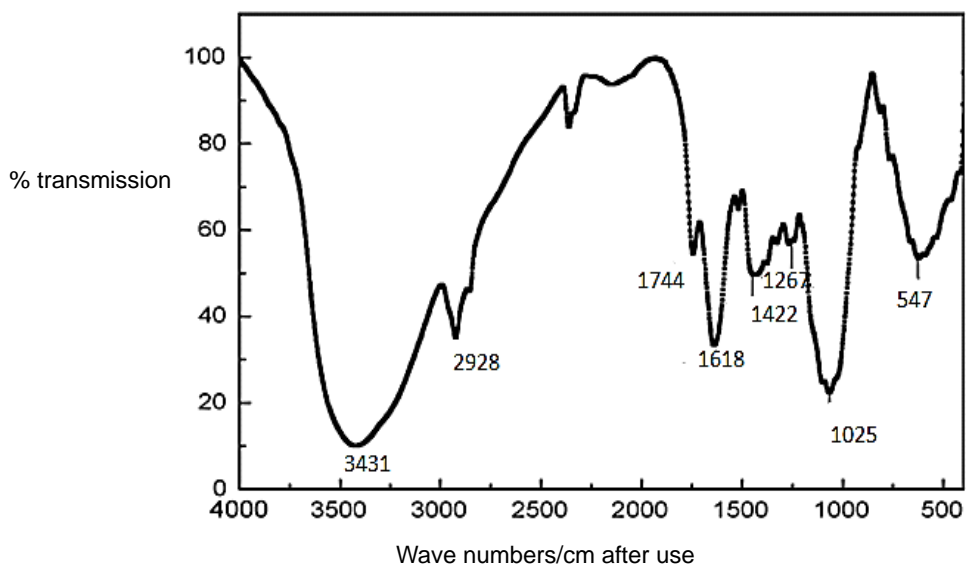


Figure 5. FT-IR spectra of modified *Azolla filiculoides* after use.

The influence of contact time on F removal efficiency was investigated by varying the experiment time between 10 and 180 min using the adsorbent dose of

6 g/L and an initial F concentration of 10 mg/L. The effect of contact time on F removal efficiency is shown in Figure 6.

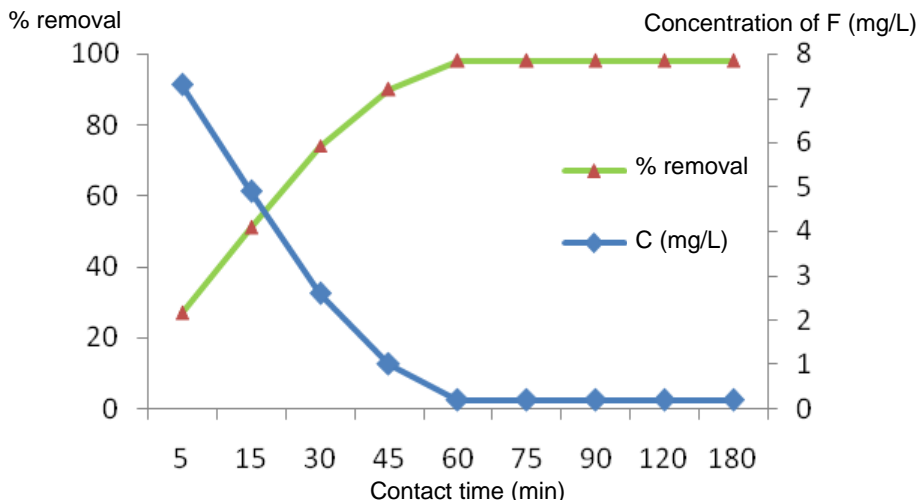


Figure 6. The effect of contact time on fluoride removal efficiency. The figure shows the % removal and concentration of F. C: concentration of F in the solution in mg/L.

The removal efficiency increased with an increase of contact time up to 75 minutes. This is known as equilibrium time. The removal rate in the early part of process was observed to be faster, which is consistent with several other studies.^{21,22} This is probably due to the large available surface area of the adsorbent at beginning of the adsorption process. The F removal efficiency at equilibrium time was 98%.

The effect of pH on F removal efficiency was investigated by varying the pH between 3 and 11 (Figure 7).

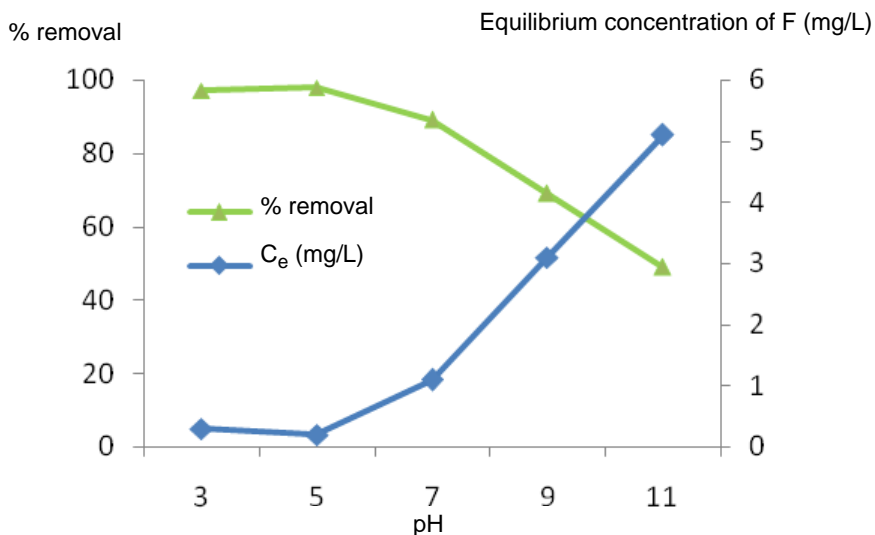


Figure 7. The effect of pH on fluoride removal efficiency. The figure shows the % removal and concentration of F. C_e : equilibrium concentration of F in the solution in mg/L.

Maximum F removal was obtained at pH 5, which concurs with several previous studies.^{22,23} At pH levels above 5, the adsorption capacity decreased. This is probably due to inappropriate surface charge and competition for adsorption sites because of the excess of anions in alkaline conditions.²¹ However, there is no significant difference in the percentage of F removal between pH 3 and 5, being only 2%.

The effect of initial F concentration was investigated by varying the concentration range between 1 and 100 mg/L. The relationship between initial F concentration and removal efficiency is shown in Figure 8.

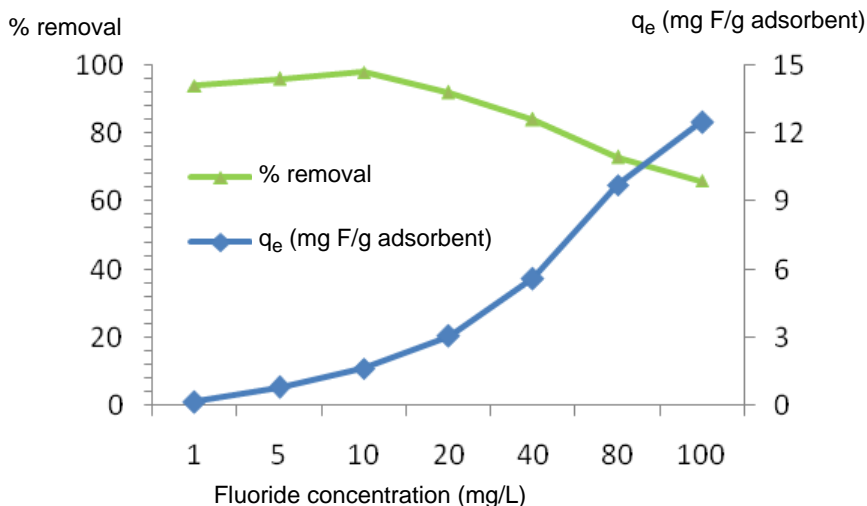


Figure 8. The effect of fluoride concentration on fluoride removal efficiency. The figure shows the % removal and quantity of F adsorbed on the adsorbent at equilibrium. q_e : quantity of F adsorbed on the adsorbent in mg F/g of adsorbent at equilibrium.

The removal efficiency decreases with increasing F concentration. This is thought to be because there are not enough available active sites on the adsorbent surface in comparison with the large number of active sites which are required for a high concentration of F.²⁴ Removal efficiency increases up to a concentration of 10 mg/L and then decreases as concentration rises. This concurs with several previous studies.^{6,21}

The impact of the adsorbent dose on F removal efficiency was investigated by varying the adsorbent dose between 2 and 14 g/L using an initial F concentration of 10 mg/L and a contact time of 75 min. The effect of the adsorbent dose on F removal is shown in Figure 9. It was observed that F removal efficiency increases on increasing the adsorbent dose. However, the adsorption capacity (q_e) decreases. The maximum F removal efficiency was obtained at an adsorbent dose of 6 g/L, and there was no significant difference in removal percentage in levels higher than 8 g/L. This concurs with other studies^{10,25} and may be due to the overlapping of active sites of the adsorbent at higher dosages.^{6, 21}

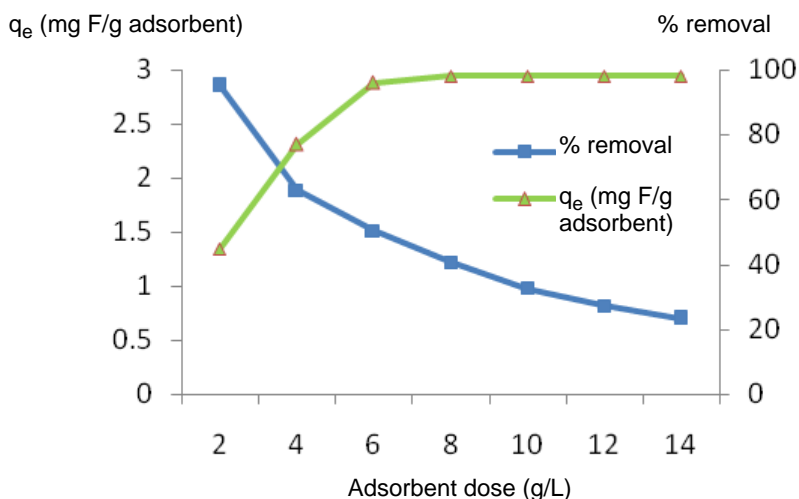


Figure 9. The effect of adsorbent dose on fluoride removal efficiency. The figure shows the % removal and quantity of F adsorbed on the adsorbent at equilibrium. q_e : quantity of F adsorbed on the adsorbent in mg F/g of adsorbent at equilibrium.

The obtained values of these isotherms and kinetics are presented in Table 2.

Table 2. Obtained values of isotherms and kinetics

Langmuir Model			Freundlich Model			Tempkin Model			BET Model		
q_m	b	R^2	n	K	R^2	B_1	k_t	R^2	A	q_m	R^2
11.2	0.95	0.998	0.34	0.225	0.912	61.4	4.45	0.943	22.4	0.181	0.967
Pseudo Second-order Model			Pseudo First-order Model								
c_0 (mg/l)	k_2	R^2	q_e	K_1	R^2	q_e					
10	0.095	0.995	2.1	0.079	0.924	1.75					
25	0.11	0.997	5.4	0.092	0.936	4.3					
50	0.124	0.999	9.6	0.113	0.949	8.1					

The results of the isotherm study indicate that although the value of R^2 for most models is more than 0.9, the F adsorption isotherm most closely followed the Langmuir Model with $R^2=0.998$. Kinetics of adsorption were well described by the pseudo second-order model. The results of this study are consistent with other studies.^{3,4}

CONCLUSION

F removal in the study was found to be 98%. This indicates that modified *Azolla* can be used as an effective and inexpensive adsorbent for F removal. The removal

efficiency decreased with increasing of pH and initial concentration of F. It increased with an increase in adsorbent dose and contact time. Adsorption isotherm data showed that F sorption followed the Langmuir Model. Kinetics of sorption were well described by the pseudo second-order model.

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