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DEFLUORIDATION OF WATER USING *DODONAEA VISCOSA* LEAF POWDER: A STUDY OF ADSORPTION ISOTHERMS

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ABSTRACT: This study was carried out to remove excessive fluoride from drinking water through adsorption phenomenon by using *Dodonaea viscosa* leaf powder as an adsorbent. Various parameters like pH (2–8), contact time (5–145 min), adsorbent dose (1–10 g), and initial fluoride concentrations (2–10 mg/L) have been optimized. The maximum defluoridation (45%) was achieved in an acidic environment and the Langmuir isotherm model fitted well in this study. The *Dodonaea viscosa* leaf powder was found to be a very cost-effective adsorbent for fluoride ions and may be an effective and environment friendly method for the defluoridation of drinking water.

Key words: Adsorbent; Adsorption; Defluoridation; *Dodonaea viscosa* leaf powder (DLP); Water.

INTRODUCTION

Due to its widespread occurrence in nature and its ability to cause adverse health risks, the fluoride ion (F^{-}) has gained importance globally.[1, 2] Sources of F^- in water are geogenic as well as from industries such as mining and the production of chemical fertilizers.[3, 4] F^- consumption in drinking water, above the WHO recommended upper limit of 1.5 mg/L, can result in many health problems in human beings[5,6] including mild to severe dental fluorosis, skeletal fluorosis, and non-skeletal fluorosis with damage to soft tissues such as the brain and thyroid.[7, 8] Millions of people are at risk of dental, skeletal, and non-skeletal fluorosis all over the world.[9,10] Several studies have been carried out on defluoridation, the removal of excessive F^- from water.[11,12] The most common methods used for defluoridation are: ion exchange, membrane technology, chemical precipitation, and adsorption.[13] Adsorption is considered to be the most favorable technique due to its cost-effectiveness and the availability of natural material.[14,15]

In this study, we assessed the adsorption capacity for defluoridation of drinking water of a leaf powder of *Dodonaea viscosa* (DLP), a wild plant found in the hilly areas of Pakistan. Besides assessing the efficiency of DLP, the effects of other parameters, i.e., adsorbent dose, pH, initial level of F^-, and contact time, as well as isotherm models, were also studied and calculated.

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MATERIALS AND METHODS

Reagents used during the study were purchased from Merck and Sigma Aldrich with maximum available purity. F^- standard solutions of different concentrations were prepared from a stock solution (1 g/L F^-) of sodium fluoride (NaF). F^- concentrations in the media were measured by a fluoride ion meter (model ExStik FL-700).

Dodonaea viscosa plant leaves were collected, washed with distilled water (dH_2O) and dried in the sun for three days. The dried leaves were ground and sieved to get leaf powders below 0.15 cm of size. Forty g of DLP and 400 mL of 1 M HNO_3 were mixed in a 1,000 mL conical flask. After heating for 20 min, the powder was filtered and washed thoroughly with dH_2O. The DLP was then treated with 400 mL NaOH (0.5 M) in a 1,000 mL conical flask and heated again for 20 minutes. The treated biomass was washed thoroughly with dH_2O and dried for 3 hours at 110ºC in a drying oven. The treated DLP was cooled to room temperature and stored for further use.

Various doses of adsorbent were taken in conical flasks (100 mL) containing F^- solution (50 mL) of different known concentrations. The samples were shaken on a shaker (NB-205L, Korea) for 145 min (at 200 rpm and 30ºC) unless the impact of contact time was required. While studying the effects of the various parameters on the F^- adsorption, the pH of the solution was adjusted by adding HNO_3 (0.5 M) or NaOH (0.1 M). After each batch of the experiment, the adsorbent was filtered out from the solution (Whatman filter paper # 42).[16]

The defluoridation rate at pH 2, 4, 6, and 8 of the F^- solution (2 mg/L) was investigated. The contact time effect was studied, at time intervals ranging from 5 to 145 min, while keeping other parameters constant. The effect of adsorbent dose was studied in the range of 1 to 10 g/50 mL of F^- solution. The initial F^- concentrations ranged from 2 mg/L to 10 mg/L during the study.

The Freundlich and the Langmuir adsorption isotherm models were applied to the results.

RESULTS AND DISCUSSION

The results showed that F^- adsorption was better at pH 2 (Figure 1). This may be due to plenty of H^+ ions being present at a lower pH, which in turn neutralizes the OH^- ions on the adsorbed surface thereby facilitating the diffusion of F^-. The results are supported by previous work in which the maximum F^- adsorption occurred at an acidic pH. [16-18].

The results showed that F^- adsorption was quite fast in the first 5 to 25 min (Figure 2), and then, as the contact time increased, F^- adsorption decreased until 75 min. A possible reason for this pattern may be the presence of a maximum number of active sites on the adsorbent surface in the initial stages and then, with increased contact time, these sites were occupied. With a further increase in contact time beyond 75 min, F^- adsorption again increased until the maximum adsorption (45%) occurred at 145 min. With a further increase in contact time beyond 145 min, no further change occurred in the F^- uptake (not shown in Figure 2) due to fewer adsorption sites being available on the adsorbent surface. Similar findings have been reported in previous work.[17,19]

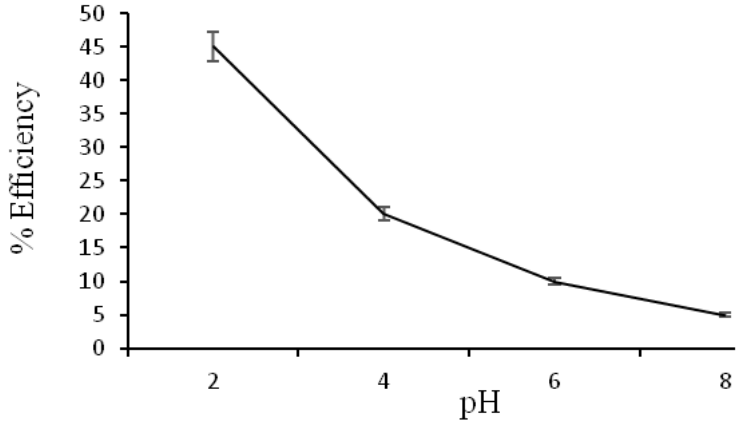

Figure 1. Influence of pH on defluoridation at an initial F^- level of 2 mg/L, an adsorbent dose of 10g/50 mL, and a contact time of 145 minutes.

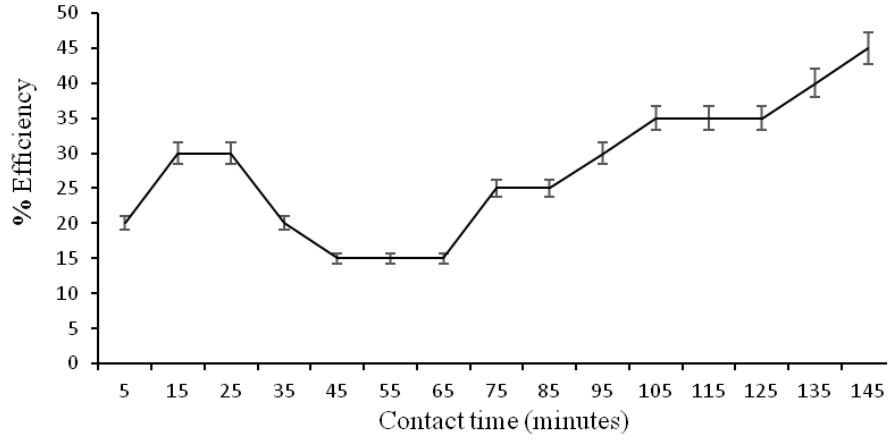

Figure 2. Influence of contact time (minutes) on defluoridation with an adsorbent dose of 10 g/50 mL, an initial F^- level of 2 mg/L, a temperature of 30ºC, and a pH of 2.

The results showed that 45% F^- was removed at an adsorbent dose of 10g/50mL (Figure 3). As the dose quantity increases, the number of pores for adsorption of F^- also increases; which provides more active sites for F^- adsorption. The results are in agreement with previous research.[20,21]

The defluoridation capacity of DLP was studied with various initial F^- concentrations (2 to 10 mg/L, Figure 4). It was noticed that as the initial F^- ion concentration increased the defluoridation capacity decreased. This may be due to the existence of more F^- ions than the adsorption capacity of the adsorbent which is also supported by other investigators.[16,19]

The linear form of the Freundlich adsorption isotherm model was plotted between $\log Q_e$ and $\log C_E$ (Figure 5 and Table 1). K_f and 1/n were calculated from the intercept (K_f) and the slope (1/n) of the fitting curve of the model (Table 2). The R^2 (regression coefficient) value with the Freundlich model was 0.706 (Table 2).

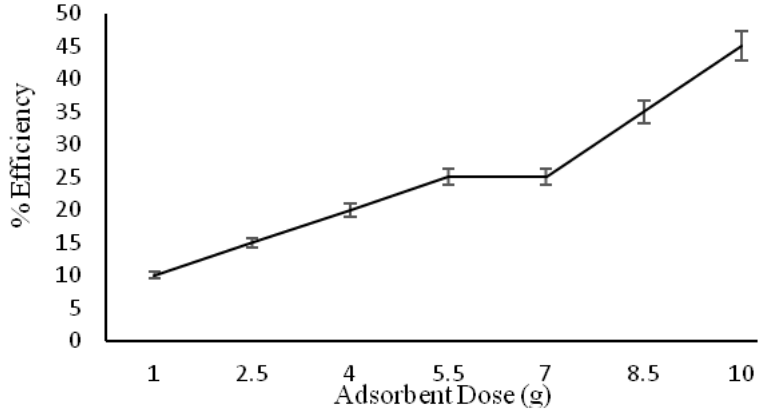

Figure 3. Effect of adsorbent dose (g) on defluoridation at an initial F^- level of 2 mg/L, a temperature of 30ºC, a pH of 2, and a contact time of 145 minutes.

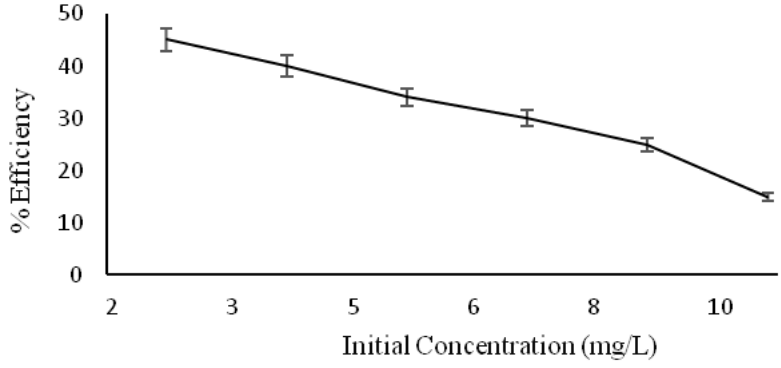

Figure 4. Effect of initial F^- level on defluoridation at an adsorbent dose of 10g/50mL, a temperature of 30ºC, a pH of 2, and a contact time of 145 minutes.

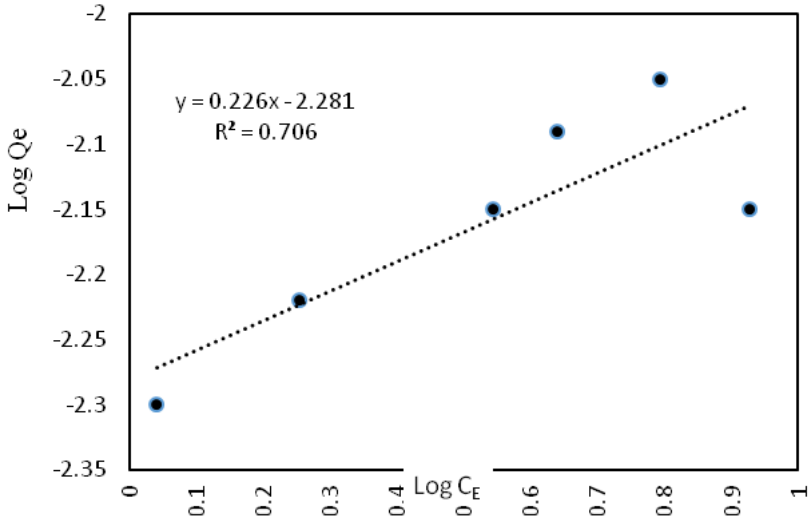

Figure 5. Freundlich model for the removal of F at pH 2, temperature 30ºC, weight of adsorbent 10 g, volume 50 mL, contact time 145 minutes, and varied initial levels of adsorbate.

Table 1. Values of different parameters used in adsorption isotherm of *Dodonaea viscosa* leaf powder (DLP)

C_i mg/L	C_E mg/L	X mg/L	X% mg/L	w g	Qe mg/g	C_E/Qe	log C_E	log Qe	$1/C_E$	1/Qe
2	1.1	0.9	45	10	0.005	220	0.041	–2.30	0.909	200
3	1.8	1.2	40	10	0.006	300	0.255	–2.22	0.555	166
5	3.5	1.5	30	10	0.007	500	0.544	–2.15	0.286	142
6	4.38	1.62	27	10	0.008	548	0.641	–2.09	0.228	125
8	6.24	1.76	22	10	0.009	693	0.795	–2.05	0.160	111
10	8.5	1.5	15	10	0.007	1214	0.929	–2.15	0.118	142

X* Removal

Table 2. The values of the Freundlich and Langmuir adsorption isotherm model parameters

Isotherm model	Values of parameters
Freundlich	K_f (Intercept) = 0.00524
	1/n (Slope) = 0.226
	n = 4.425
	R^2 = 0.706
Langmuir	$1/Q_0$ (Intercept) = 111.31
	Q_0 = 0.008
	1/b = 0.868
	b = 1.151
	R^2 = 0.859
	$1/b.Q_0$ (Slope) = 96.705

For the Langmuir adsorption isotherm model, the values of $1/Q_e$ were plotted against the values of $1/C_e$ where the slope and intercept were represented by $1/bQ_0$ and $1/Q_0$, respectively. The values of b and Q_0 were calculated from the slope and intercept of the line (Figure 6 and Table 2). The value of R^2 (0.859) showed that the Langmuir model fitted the data better than the Freundlich model in which the R2 was

0.706 (Table 2 and Figures 5 & 6). The Langmuir model is best suited for single layer adsorption and it suggests that all the adsorption sites have equal attraction for adsorbate molecules and no transmigration of adsorbate molecules occurs.

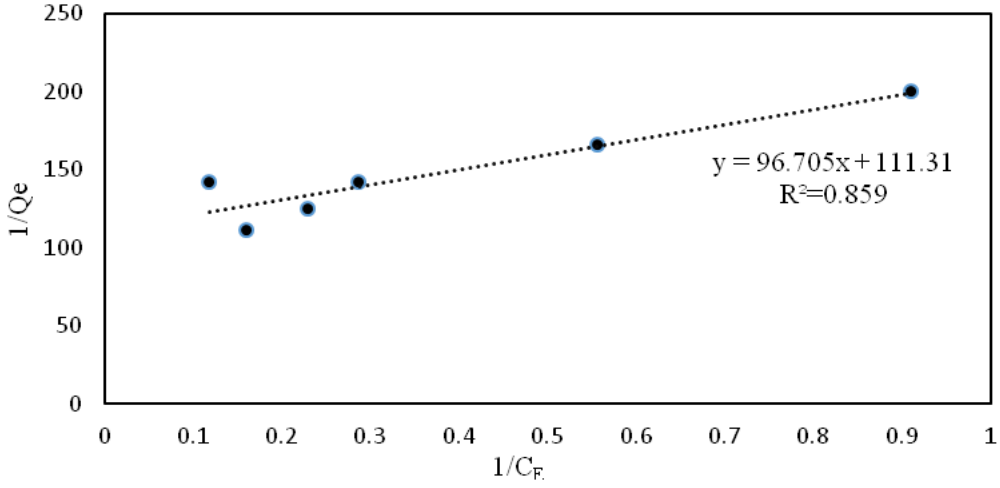

Figure 6. Langmuir model linear form for defluoridation at 10g adsorbent weight, volume of 50mL, pH of 2, temperature of 30ºC, contact time of 145 minutes, and varied initial concentrations of adsorbate.

CONCLUSIONS

The study concluded that the highest F^- removal occurred at pH 2, initial adsorbate dose of 10g, initial fluoride concentration of 2 mg/L, and a contact time of 145 minutes The removal capacity of the prepared adsorbent increased with the increase in adsorbent dose and contact time. Similarly, the removal capacity of the adsorbent decreased with the increase in F^- concentration and pH. The adsorption process of F^- by DLP adsorbent followed more strictly the Langmuir isotherm model than the Freundlich model. The present study also concluded that the DLP as an adsorbent can be effectively utilized for the defluoridation of water on an industrial basis. Further studies on the chemical modification of the adsorbent are recommended.

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