

Factors Influencing the Removal of Fluoride from Water using a Fungal Biosorbent prepared from *Fusarium moniliforme*

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Abstract: Fungal biosorbent prepared from *Fusarium moniliforme* for removal of fluoride was investigated for the various factors influencing defluoridation. Calcium and alkali treated biomass was effective in removal of fluoride. The extent of defluoridation was dependent on the initial pH of fluoride-containing water and decreased with increasing pH. Fluoride removal capacity was found to be 24% at pH 5.0 and 11% at pH 8.0. The capacity of fluoride decreased with increased bicarbonate concentration, but was independent of the presence of chloride and sulphate. The kinetics of fluoride removal exhibited a rapid phase of binding for a period of 1.0 hour and a slower phase of binding during the subsequent period. The potential use of this biosorbent for biodefluoridation is being explored. Significance of the above results are discussed in the light of existing literature.

Keywords: Fluoride, Biomass, Biosorption, *Fusarium moniliforme*.

Introduction

Excess amount of fluoride in drinking water has been known to cause adverse effects on human health. Membrane separation techniques were investigated for the effective separation of fluoride¹. Garmes et al. (2002)² have investigated a hybrid process containing adsorption and dialysis for defluoridation of water. Adsorption

process was reported to be effective, environmental friendly and economical³. Use of biosorbents/biomass from various microbial sources, leaf based sorbents, and water hyacinth, for fluoride removal was reported by various investigators^{4,5,6}. Laxmaiah et al (2002)⁷ have used fungal biosorbent for removing of fluoride from water. Apart from this report, not much

information regarding the use of fungal biosorbents for removal of fluoride are not available. Hence, the present investigation was done and the results are discussed.

Material and Methods

The *Fusarium moniliforme* strain used in these experiments was isolated from Mahatma Gandhi University Campus, Nalgonda, A.P, India. The alkali extracted biomass of *A.niger* (biosorbent) was prepared according to the method of Akthar *et al* (1995)⁸. Finely powdered biosorbent was first washed with glass-distilled water and then suspended in fluoride containing waters. The Biosorbent (1 g) was suspended in 100 mL glass-distilled water or tap water and pH adjusted to 7.0, stirred and centrifuged. The supernatant was discarded and the process repeated two more times. The final pellet was suspended in 100 mL (200µg/L) of fluoride containing water. After specified period of exposure, the suspension was centrifuged and the fluoride content of the supernatant determined. 1.0 g of dried biomass was suspended in test tubes containing 10 ml of aqueous CaCl₂, sodium bicarbonate solution in the concentration varying from 40 to 160 µg/ml and allowed to stand for 5 hours after putting it mixed for 5 minutes on rotor. Influence of the aqueous phase pH on fluoride adsorptive uptake was studied by adjusting the reaction mixture to different initial pH values from 3.0 to 8.0 and analyzed for residual fluoride after equilibrium contact time. The fluoride content of the supernatants was determined colorimetrically using SPADNS method (APHA, 1998)⁹.

Results and Discussion.

The surface characteristics of the fungus are responsible for sorptive defluoridation. The sorption is characterized under different experimental conditions and discussed. Perusal of Table 1 shows the ability of the biosorbents to bind to fluoride ions. Initially 2.0 hrs incubation was tested to check the amount of biosorbent

which would be ideal for binding to the fluoride. Biosorbent concentration at 2.0 g could bind about 15% of fluoride present in the water. More amounts of the biosorbent could not enhance the absorption of fluoride and hence 2.0 g of the biosorbent was used for further investigation. Effect of time, that is duration of exposure to the fluoride containing water was also studied. Table 2 shows the sorption profile, which clearly indicates that the sorption process attains equilibrium in 16 hrs. Sixteen hours of incubation could bind about 23% of the total fluoride present in water. Although there was a slight increase in the absorption, it was not much. Hence, 16 hrs incubation was used for further studies. The total amount of fluoride removed was found to be same even at the end of twenty hours incubation.

Mass dependence and pH influence on the biodefluoridation by the biosorbent was investigated (Table 3). At pH 5.5, 24 % of fluoride was bound to the biosorbent while at pH 8.0 11% of the biosorbent was bound. With increase in pH the ability of the sorbent to bind to the fluoride ions gradually decreased. Overall acidic pH was amenable than basic pH for removal of fluoride. Lower binding at higher pH could be due to competition between F⁻ and OH⁻ for fluoride binding sites. The mechanism of fluoride binding by the biosorbent is not clear and may be due to the protonation of primary amino groups at acidic pH which could bind to fluoride.

Temperature can also effect the rates of defluoridation. Temperature at 35°C was found to bind more amounts of fluoride. About 28% of the fluoride was absorbed at this temperature. Increase in temperature above 35°C resulted in decrease in the rates of defluoridation. Only 19% of fluoride could be removed with increase in the temperature upto 50°C. The effects of coexisting anions such as chloride, sulphate and bicarbonate on fluoride adsorption by the fungal adsorbent were examined and the results are given in Table 5. Chloride and sulphate did not perceptibly interfere with fluoride removal at a concentration of 160 µg/L. However, bicarbonate showed great competitive adsorption with fluoride. The

fluoride adsorption amount decreased quickly from 24 to 12% with the increase of bicarbonate concentration from 40 to 160 $\mu\text{g/L}$. This may be due to the competition of bicarbonate ions with the fluoride ions at the active site present on the surface of the sorbents. The order of interference for fluoride removal observed as in the following order, $\text{HCO}_3^- > \text{SO}_4^{2-}$, Cl^- for the adsorbent. The present results indicated that the addition of

co-ions, in the concentration ranges investigated had no appreciable effect on the amount of fluoride ions removed by these adsorbents except for bicarbonates. Almost 50% reduction in binding was seen when bicarbonate concentration was increased to 160 $\mu\text{g/L}$.

Table 1; Effect of adsorbent concentration on binding of fluoride

| Biosorbent (conc in g) | pH | Duration of exposure (hours) | Fluoride in water ($\mu\text{g/L}$) | Capacity ($\mu\text{g F-g}$ biosorbent) |
|---------------------------|-----|------------------------------------|---|--|
| 0.25 | 7.0 | 2.0 | 200 | 16 |
| 0.50 | 7.0 | 2.0 | 200 | 22 |
| 0.75 | 7.0 | 2.0 | 200 | 24 |
| 1.0 | 7.0 | 2.0 | 200 | 24 |
| 1.5 | 7.0 | 2.0 | 200 | 28 |
| 2.0 | 7.0 | 2.0 | 200 | 30 |
| 2.5 | 7.0 | 2.0 | 200 | 30 |
| 3.0 | 7.0 | 2.0 | 200 | 30 |

Table 2: Time course of fluoride binding by the biosorbent

| Biosorbent (conc in g) | pH | Duration of exposure (hours) | Fluoride in water ($\mu\text{g/L}$) | Capacity ($\mu\text{g F-g}$ biosorbent) |
|---------------------------|-----|------------------------------------|---|--|
| 2.0 | 7.0 | 1.0 | 200 | 20 |
| 2.0 | 7.0 | 2.0 | 200 | 22 |
| 2.0 | 7.0 | 4.0 | 200 | 26 |
| 2.0 | 7.0 | 6.0 | 200 | 30 |
| 2.0 | 7.0 | 8.0 | 200 | 32 |
| 2.0 | 7.0 | 10.0 | 200 | 38 |
| 2.0 | 7.0 | 12.0 | 200 | 40 |
| 2.0 | 7.0 | 14.0 | 200 | 42 |
| 2.0 | 7.0 | 16.0 | 200 | 46 |
| 2.0 | 7.0 | 18.0 | 200 | 46 |
| 2.0 | 7.0 | 20.0 | 200 | 46 |

Table 3: Effect of pH on fluoride binding by the biosorbent

| Biosorbent (conc in g) | pH | Duration of Exposure (hours) | Fluoride in water ($\mu\text{g/L}$) | Capacity ($\mu\text{g F-}/\text{g biosorbent}$) |
|------------------------|-----|------------------------------|---------------------------------------|---|
| 2.0 | 3.0 | 16 | 200 | 26 |
| 2.0 | 3.5 | 16 | 200 | 30 |
| 2.0 | 4.0 | 16 | 200 | 34 |
| 2.0 | 4.5 | 16 | 200 | 40 |
| 2.0 | 5.0 | 16 | 200 | 44 |
| 2.0 | 5.5 | 16 | 200 | 48 |
| 2.0 | 6.0 | 16 | 200 | 38 |
| 2.0 | 6.5 | 16 | 200 | 32 |
| 2.0 | 7.0 | 16 | 200 | 26 |
| 2.0 | 7.5 | 16 | 200 | 24 |
| 2.0 | 8.0 | 16 | 200 | 22 |

Table 4: Effect of temperature on removal of fluoride

| Biosorbent (conc in g) | Temp ($^{\circ}\text{C}$) | pH | Duration of Exposure (hours) | Fluoride in water ($\mu\text{g/L}$) | Capacity ($\mu\text{g F-}/\text{g biosorbent}$) |
|------------------------|-----------------------------|-----|------------------------------|---------------------------------------|---|
| 2.0 | 25 | 5.0 | 16 | 200 | 40 |
| 2.0 | 30 | 5.0 | 16 | 200 | 52 |
| 2.0 | 35 | 5.0 | 16 | 200 | 56 |
| 2.0 | 40 | 5.0 | 16 | 200 | 52 |
| 2.0 | 45 | 5.0 | 16 | 200 | 46 |
| 2.0 | 50 | 5.0 | 16 | 200 | 38 |

Table 5: Effect of chloride, sulphate and bicarbonate on fluoride removal of water

| Biosorbent (conc in g) | cations | Duration of Exposure (hours) | Fluoride in water ($\mu\text{g/L}$) | Capacity ($\mu\text{g F-}/\text{g biosorbent}$) |
|------------------------|--------------|------------------------------|---------------------------------------|---|
| | Chloride | | | |
| 2.0 | 40 | 16 | 200 | 52 |
| 2.0 | 80 | 16 | 200 | 52 |
| 2.0 | 120 | 16 | 200 | 50 |
| 2.0 | 160 | 16 | 200 | 52 |
| | Sulphates | | | |
| 2.0 | 40 | 16 | 200 | 50 |
| 2.0 | 80 | 16 | 200 | 52 |
| 2.0 | 120 | 16 | 200 | 50 |
| 2.0 | 160 | 16 | 200 | 52 |
| | Bicarbonates | | | |
| 2.0 | 40 | 16 | 200 | 48 |
| 2.0 | 80 | 16 | 200 | 40 |
| 2.0 | 120 | 16 | 200 | 32 |
| 2.0 | 160 | 16 | 200 | 24 |

Conclusions:

Fusarium moniliforme used in this study could clearly remove fluoride at a rate of 36%. The present results reported here agree with those of Laxmiah et al (2002)⁷ where alkali-treated fungal biosorbent was used for defluoridation. The organic matrix of the biosorbent contains Ca⁺⁺ ions after treatment with calcium. It is possible that the Ca⁺⁺ ions are responsible for binding fluoride. It may be possible that cations

on the surface of biomass may be used to removal anions that are not usually removed as the cell envelopes carry negative charges or their surface. The mechanism of binding is not clear and further work is required to understand the molecular aspects for large scale defluoridation of water supplies. Hence, biosorption can therefore provide a solution to control fluoride pollution.

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