BIODEFLUORIDATION OF FLUORIDE CONTAINING WATER BY A FUNGAL BIOSORBENT

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SUMMARY: Alkali-extracted mycelial biomass (biosorbent) from Aspergillus niger was effective in sequestering fluoride from fluoride-containing waters. When kept in contact overnight, the biosorbent, used at a level of 3 %, removed fluoride to an extent of 45-50% from water containing 5 mg F^-/L. 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 extent of defluoridation was dependent on the initial pH of fluoride-containing water and decreased with increasing pH. The biosorbent could bind fluoride for three successive treatments tested. The potential use of this biosorbent for biodefluoridation is being explored.

Key words: Biodefluoridation; Fungal biosorbents; Aspergillus niger.

INTRODUCTION

Excessive fluoride in drinking water causes dental and skeletal fluorosis, which is encountered in endemic proportions in several parts of the world. Due to the unavailability of effective therapeutic measures, defluoridation of drinking water appears to be the best method for combating the disease. Several methods, using a variety of materials, have been suggested from time to time. These methods are basically of two types: those based on an exchange process or adsorption, and those based on addition of chemicals to the water being treated.[1] Most of these methods have one or more short-comings with regard to the defluoridation capacity, cost effectiveness, operation at community level and quality of treated water. In view of this, search for more suitable materials and methods are still in progress.

Attempts to harness microbial biomass for the purification of polluted water from industries appear promising.[2-5] Live and inactivated fungal biomass exhibits interesting metal binding properties due to the presence of functional groups like amino, amide, carboxyl, hydroxyl, sulfhydryl etc. in the cell walls. The biosorption involves direct exchange of toxic heavy metal ions with the resident Ca^{++}/Mg^{++} ions of the biosorbent.[6] Fluoride binding by the fungal biosorbents appears possible considering their Ca^{++}/Mg^{++} content and the known affinity of Ca^{++} and Mg^{++} for fluoride ions. The following experiments demonstrate the ability of fungal biosorbent to bind fluoride which we intend to term as "biodefluoridation".

MATERIALS AND METHODS

The Aspergillus niger strain used in these experiments is a laboratory isolate[7] which exhibits resistance to toxic levels of Cd^{++} and accumulates Ca^{++} and Mg^{++}. The preparation of alkali extracted biomass of A.niger (biosorbent) was according to Akthar *et al.*[7] Finely powdered biosorbent was first washed with glass-distilled water and then

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suspended in fluoride-containing waters. After centrifugation, the fluoride content of the supernatants was determined.

Fluoride was measured using fluoride ion specific electrode (Orion model 94-09 fluoride electrode). The total ionic strength adjustment buffer (TISAB-I) contained 58 g NaCl, 300 mg trisodium citrate and 58 ml gl.acetic acid in 1 litre adjusted to pH 5.0-5.5 with 5 N NaOH. For the experiments, the following methods were used:

Fluoride binding by the biosorbent. Fluoride containing glass-distilled water was used for IA-IVA while fluoridated tap water was used for IB-IVB. The Biosorbent (3 g) was suspended in 100 mL glass-distilled water or tap water and pH adjusted to 7.8, stirred and centrifuged. The supernatant was discarded and the process repeated two more times. The final pellet was suspended in 100 mL of fluoride containing water. After specified period of exposure, the suspension was centrifuged and the fluoride content of the supernatant determined. For each subsequent transfer, the pellet was suspended again in fluoride containing water and after specified periods of exposure, the suspension was centrifuged and the fluoride content of the supernatant determined.

Time course of fluoride binding by the biosorbent. The biosorbent was washed thrice with glass-distilled water or tap water as described in the previous experiments (Table 1) and suspended in 100 mL of fluoride containing glass-distilled water or tap water. Suitable aliquots were taken at different time intervals and the fluoride content determined. The starting fluoride content of fluoridated distilled water was 5.13 mg/L and that of fluoridated tap water was 5.32 mg/L.

Effect of pH on fluoride binding by the biosorbent. The biosorbent (3 g) was suspended in 100 mL of distilled water or tap water, the pH adjusted to the specified values and fluoride stock solution (1900 mg/L) added to get the final fluoride concentration. After two hours at room temperature, the suspensions were centrifuged and the fluoride content of the supernatants determined. IA to IIIA are with glass-distilled water and IB to IIIB are with tap water.

Effect of biosorbent concentration on fluoride binding. The indicated amounts of biosorbent were first suspended in 100 mL glass-distilled water, pH adjusted to 7.0, centrifuged and the supernatant discarded. The pellet was then suspended rapidly in 50 mL of fluoride solution (5.13 mg F^-/L in glass-distilled water), allowed to stay for 2 hours at room temperature, centrifuged and the fluoride content of the supernatant determined.

TABLE 1. Fluoride binding by the sorbent

Subsequent No. of transfers	Duration of exposure (hours)	Fluoride in water (mg/L)	Capacity (µg F^-/g biosorbent)	Binding (%)
I A	18.0	4.94	82.1	50.0
II A	18.0	5.13	75.8	44.4
III A	18.0	5.13	67.8	39.8
IV A	90.0	5.13	87.6	51.4
I B	18.0	5.32	90.3	50.9
II B	18.0	5.32	58.6	33.0
III B	18.0	5.32	38.0	21.4
IV B	90.0	5.32	103.0	58.0

RESULTS

Fluoride binding by the biosorbent. The fluoride binding ability of the biosorbent with successive transfers is shown in Table 1. Overnight exposure for a period of 18 hours was considered convenient for application at community level. With successive transfers the per cent binding diminished from 50 % to 40 % in glass-distilled water and 51 % to 21 % in tap water. The duration of exposure for the last transfer (IV A & IVB) was 90 hours which resulted in higher binding due to longer period of exposure. **Time course of fluoride binding by the biosorbent.** The kinetics of fluoride binding by the biosorbent from the medium exhibited a rapid phase in which 31 % binding was complete within one hour in glass-distilled water and 24 % in tap water. Subsequent binding was slow and much less as shown in Table 2.

Effect of pH on fluoride binding by biosorbent. The effect of initial pH on fluoride uptake by the fungal biosorbent is shown in Table 3. Over the pH range tested (pH 5.5 to pH 10.0) the extent of binding decreased with increase in the initial pH. The decrease in binding was from 52 % to 17 % in glass-distilled water and from 45 % to 26 % in tap water.

Effect of biosorbent concentration on fluoride binding. The extent of fluoride binding was linearly related to the amount of biosorbent over a range of 0.25 g to 4.00 g, cf. Table 4.

TABLE 2. Time course of fluoride binding by the biosorbent

Duration of Exposure	Capacity (µg F^-/g biosorbent)		Binding (%)	
(hours)	Distil.	Tap	Distil.	Tap
1.0	52.2	42.6	30.6	24.1
2.0	52.2	50.3	30.6	28.4
4.0	52.2	55.2	30.6	31.2
7.0	57.0	62.2	33.5	35.1
12.0	57.0	62.2	33.5	35.1
24.0	65.8	76.2	38.6	43.0

TABLE 3. Effect of pH on fluoride binding by the biosorbent

No.	F^- conc. (mg/L)	Adjusted initial pH	Binding (%)	Capacity (µg F^-/g biosorbent)
IA	5.01	5.54	51.9	86.7
IIA	4.75	8.06	38.0	59.9
IIIA	5.0	10.00	17.0	28.4
IB	4.5	5.62	45.4	68.2
IIB	4.9	8.08	39.7	64.9
IIIB	5.2	10.10	26.3	45.5

DISCUSSION

There has been considerable research activity in recent years on the use of biosorbents (bacterial, algal and fungal) for scavenging heavy metal cations from polluted waters. Reports regarding the use of biosorbents for removal of hazardous anions like fluorides, nitrates etc. are not available. The results reported here clearly demonstrate the ability of alkali-treated Aspergillus niger to bind fluoride (biodefluoridation). The biodefluoridation is rapid and diminishes with repeated cycles. Mass dependence and pH influence further substantiate the authenticity of the observed biodefluoridation by the biosorbent. 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. The organic matrix of the biosorbent contains Ca^{++} and Mg^{++} ions. It is possible that the Ca^{++} and Mg^{++} ions are responsible for binding fluoride. The primary amino groups could also get protonated at

acidic pH and bind fluoride. Further work is needed on the mechanism of binding which would enable genetic and chemical manipulation of the fungal and other biosorbents for large scale defluoridation of water supplies.

TABLE 4. Effect of biosorbent concentration on fluoride binding.

No.	Biosorbent (g/50 mL)	F^- conc. (mg/L)	Removal (µg F^-)	Binding (%)
1	0.25	5.13	20.25	7.89
2	0.50	5.13	33.25	12.96
3	1.00	5.13	52.25	20.37
4	1.50	5.13	76.95	30.00
5	2.00	5.13	87.60	34.15
6	4.00	5.13	171.0	66.66

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