

## Removal of fluoride from drinking water using a modified fly ash adsorbent

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Received 31 May 2005; revised 19 September 2005; accepted 02 November 2005

Fly ash from a coal-fired power station was chemically modified and utilized for the removal of fluoride from drinking water. Two types of beds were used. Bed I was prepared by treatment with 12M HCl followed by neutralization with 5M NaOH solution. The reaction mass was filtered, washed, dried, and crushed to fine powder. Bed I material was mixed with alum and MgCl<sub>2</sub> solutions and treated with 0.9M Na<sub>2</sub>CO<sub>3</sub> until pH reached to 4.5. Mass was again filtered, washed, dried at 120°C for 4 h and crushed to fine powder. This bed material is Bed II, which was used for defluoridation. Bed I was used to maintain pH (7.5-8.5) of the final effluent. Fluoride (100 ppm) present in both synthetic mixtures and drinking water samples was allowed to pass through Bed II (15 g) adsorbent and effluents were found to contain no fluoride but pH of the effluent was 5.4-5.5. To maintain WHO guidelines for drinking water on pH, this effluent was again passed through Bed I. The effectiveness of the modified fly ash bed was satisfactory.

**Keywords:** Defluoridation, Drinking water, Modified fly ash bed

**IPC Code:** C02F1/00

### Introduction

Attempts have been made to remove fluoride by fly ash<sup>1</sup>, China soils<sup>2</sup>, bone char<sup>3</sup>, activated alumina<sup>4</sup> and other geomaterials like zeolite, heat treated soil, bauxite, volcanic ash, lime stone<sup>5</sup> and laterite<sup>6</sup>. The most probable path for fluoride adsorption is the formation of aluminium fluoride complex<sup>2</sup>. The fluoride adsorption on the materials depends upon pH; lower the pH, higher will be the adsorption of fluoride in all cases. Goethite<sup>7</sup> has the property to maintain a constant pH. Multielemental characterization of fly ash<sup>8</sup> and use of modified fly ash for removal of arsenic<sup>9</sup>, mercury<sup>10</sup> have been reported from present laboratory. The present work deals with the use of two beds which have been prepared from fly ash and found to be very effective not only for fluoride adsorption but also for maintenance of pH to drinking standard. The method was tested with actual fluoride containing drinking water.

### Experimental Details

#### Reagents

Standard fluoride solution (1000 ppm) was prepared from sodium fluoride (BDH, Mumbai). Lanthanum nitrate (BDH, Mumbai), alizarin

complexone (Merck) and all other reagents were AR or GR chemicals.

#### Instrumentation

A glass column fitted with a permeable glass filter (G4) was used for fluoride separation. A double beam Shimadzu (Japan) UV-visible spectrophotometer (model: UV 240) was used for spectrophotometric determination of fluoride at 600-620 nm as a blue coloured alizarin lanthanum fluoride complex. Orange solution of alizarin 3-methyl amine -N,N-diacetic acid dihydrate forms a red chelate with lanthanum(III) ion; when small quantities of F<sup>-</sup> are added, this red chelate yields the blue coloured ternary complex, whose colour intensity is proportional to the concentration of F<sup>-</sup>. With F<sup>-</sup> at 0 - 30 μg, the calibration curve forms a straight line<sup>11</sup>. An Orion-EA 940 Ion Analyzer was also used for fluoride determination. This method has been found to be effective for the quantitative determination of F<sup>-</sup> (>0.1 ppm) in water samples<sup>12</sup>.

#### Water Sampling

Drinking water sample, containing fluoride, was collected from Nashipur village, Birbhum district, West Bengal. Samples (pH: 8.2, fluoride 17.2 ppm), collected in plastic bottles (1 l), were cleaned by soap and water, followed by soaking in 1:1 HNO<sub>3</sub>. Final washing was done by demineralized water.

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Table 1— Uptake of fluoride from spiked water samples using Bed II

Nature of sample*	Inlet samples		Outlet samples		
	pH	Concentration, ppm	pH	Concentration, ppm Spectrophotometry	Ion analyser
DM	6.4	1	5.5	0.037	0.029
DM	6.45	5	5.5	0.081	0.047
DM	6.75	10	5.5	0.145	0.146
DM	6.6	20	5.5	0.307	0.147
DM	6.75	50	5.5	0.325	0.333
DM	6.80	100	5.5	0.713	0.562
DW	8.6	1	5.5	0.119	0.122
DW	8.7	5	5.5	0.169	0.142
DW	8.7	10	5.5	0.236	0.166
DW	8.7	20	5.5	0.279	0.302
DW	8.5	50	5.5	0.301	0.350
DW	8.4	100	5.5	0.824	0.612

DM = spiked fluoride in demineralized water, DW = spiked fluoride in drinking water.

Subsequent routine cleaning was done by soap and water wash, soaking for 24 h in saturated EDTA solution and final rinsing with demineralized water.

#### Preparation of Bed I and Bed II

Dried fly ash was treated with 12M HCl at 80°C for 4 h and then with 5M NaOH solution to neutralize excess acid. The mixture was then filtered, washed and dried at 110°C. The dried mass was grinded (particle size, 150 – 300  $\mu$ ) and used as Bed I material. The same material was also used for the next step of bed preparation.

Commercial grade ferric alum (100 g) and MgCl<sub>2</sub> (10 g) were dissolved in water. Now 50 g of grinded Bed I material was mixed with it and 1M Na<sub>2</sub>CO<sub>3</sub> solution was added to precipitate aluminium as its hydroxide at pH 4.5. The resulting solution was warmed to 70°C and stirred for ½ h to precipitate all aluminium hydroxide. The mixture was filtered through a vacuum pump and washed with 1% MgCl<sub>2</sub> solution and distilled water successively. The mass was dried at 120°C for 4 h, cooled and grinded to fine powder as Bed II.

#### Recommended Procedure

Bed material (15 g) was packed in a column (26.7 cm x 1.5 cm) with a bed height of 2.8 cm and washed with 1% MgCl<sub>2</sub> and demineralized water, until colourless effluent was coming out. Different standard spiked samples of fluoride in drinking water (Al < 0.1 ppm and Fe 0.2 ppm) and demineralized water were allowed to pass through Bed II. The samples after passing through Bed II were analysed for F<sup>-</sup> with ion analyzer. After defluoridation, the

effluent was again passed through Bed I for final adjustment of pH of the outlet samples.

#### Results and Discussion

The adsorption of fluoride increased at lower pH and decreased as the pH is increased. This is because adsorption of fluoride on modified fly ash Bed II occurs best at pH 4-6, like activated alumina. The modified fly ash bed with more Fe and Mg has capacity to maintain this pH range and hence the bed is capable for the adsorption of fluoride. Only activated alumina column has less capability for fluoride adsorption than hydrated alumina due to free hydroxyl group. Bed material (15 g) could remove fluoride from 2600 ml of both drinking water and demineralized water spiked with 20 ppm fluoride. Bed II (10 g) was found to remove 17.2 ppm fluoride from 220 ml drinking water. Bed II material is capable of removing fluoride from spiked demineralised and drinking water samples as determined by both spectrophotometry and Ion analyzer (Table 1). The residual fluoride in effluent is much below the WHO permissible limit.

As per WHO guideline<sup>11</sup>, pH of drinking water is 7.5-8.5, while that of effluent of Bed II is 5.5. To adjust the pH, effluent water samples from Bed II were allowed to pass through Bed I. Since Bed I and Bed II have different nature, the effluent of Bed I will maintain the pH as per WHO permissible limit for drinking water. Due to buffer action of the bed, the outlet samples always show a pH 7.5 (Table 2).

The raw materials are available free of cost and cost of production of the bed materials is cheap. Considering the cost of chemicals, manpower,

Table 2— Measurement of pH after passing through different beds

Volume of water sample, ml	Inlet sample pH	Outlet sample pH Bed II	Outlet sample pH Bed I
100	8.2	5.5	7.5
200	8.2	5.5	7.5
300	8.2	5.5	7.5
400	8.2	5.5	7.5
500	8.2	5.5	7.5
600	8.2	5.5	7.5
700	8.2	5.5	7.5
800	8.2	5.5	7.5
900	8.2	5.5	7.5
1000	8.2	5.5	7.5
1100	8.2	5.5	7.5
1200	8.2	5.5	7.5
1300	8.2	5.5	7.5
1400	8.2	5.5	7.5

infrastructure, energy consumption etc., the total expenditure for the production of modified fly ash will be Rs. 9/- per kg.

### Conclusions

Bed II made of fly ash is capable of removing fluoride concentration up to 100 ppm. Lower pH helps better fluoride adsorption, which decreases with increasing pH. The pH (5.5) of outlet of Bed II is ideal for fluoride adsorption. Since the leachate from the final bed (Bed I) maintains a pH of 7.5, there is minimum possibility to leach aluminium from bed, because aluminium is best precipitated within a pH range 6 to 7. Thus, present method of using dual bed system is capable for the removal of fluoride from drinking water and improvement of water quality.

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