STUDY OF COST-EFFECTIVE NATURAL ADSORBENTS FOR THE REMOVAL OF FLUORIDE

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ABSTRACT

Contamination of fluoride in aquifer is one of the key problems in world. Fluoride is a common element, which pollutes majority of the groundwater resources in India. Fluoride, ahead of its permissible limit (1.5 mg/l), causes a various physiological troubles of which skeletal fluorosis and dental are noteworthy. So removal of fluoride from groundwater is necessary. To create a sorbent, this study compares the powdered almond tree bark, lemon leaf, and mosambi peel. Sodium fluoride anhydrous is used to create a fluoride solution (NaF). Zirconium Alizarin Reagent Preparation Almond tree bark powder has a higher percentage of fluoride removal, fluoride efficiency for optimal dose, and fluoride efficiency for optimal pH than other substances. Percentage removal of fluoride for almond bark powder is 82%, the optimum contact time for maximum removal of fluoride is 210 min.

Keywords: adsorption, fluoride, drinking water, defluoridation, natural adsorbent, pH.

AIMS AND BACKGROUND

The main sources of water pollution can be classified as municipal, industrial and agricultural. Industries dump a variety of pollutants into their wastewater, including anionic and cationic pollutants, heavy metals, organic toxins, dissolved inorganic compounds, oils, nutrients, solids, and colorants. Humic acids, hydrocarbons and pectins are among the natural organic substances present in groundwater. The presence of various dangerous pollutants such as fluoride, nitrate, pesticides, arsenic, other heavy metals, etc. in groundwater in various parts of India[1-6]. Fluoride is a potential pollutant in India and it is mainly naturally occurring in groundwater and penetrates into groundwater due to disintegration and dissolution of igneous and metamorphic rocks containing minerals such as amphiboles and micas[7].

Additionally, effluents from the chemical, metallurgical and coal mining industries also contribute to fluoride contamination in surface waters. Fluorine is a ubiquitous element and the thirteenth most naturally abundant element in the earth's crust, one of the most reactive and electronegative elements of all[8]. Fluorides are found in a wide variety of minerals, including fluorite [CaF_2], sellaite [MgF_2], rock phosphate/fluoroapatite [$Ca_5(PO_4)_3F$], cryolite [Na_3AlF_6], mica, hornblende, and others9. Fluorite (CaF_2) is a common fluoride carrier and is found in granite, granite gneiss and pegmatite[10,11] and as cryolite in igneous rocks. Fluoride is also associated with monovalent cations like NaF and KF that are soluble in water.

Fluoride contamination in the environment occurs through two different channels that are natural and anthropogenic sources[12]. During the erosion of alkaline, igneous and sedimentary rocks and the circulation of water in rocks and soils containing fluorine, it can be reached and dissolved in groundwater[13-18]. There are a large number of fluoride-contaminated areas around the world where groundwater contains higher levels of fluoride. India is the country most affected by fluoride in the world. Of the 85 million t of fluoride deposits in the earth's crust, 12 million t are in India (19). In India in 2002, 17 states were identified as endemic for fluorosis[20] and now the problem exists in more than 17 states[21-23]. In India, fluoride concentrations in drinking water in different parts of the country range from 0.5 to 50 mg/l and the degree of fluoride contamination in groundwater ranges from 1.0 to 48 mg/l (Ref. 24). In India alone, a total of 60 to 70 million people, including children, are affected by dental and skeletal fluorosis[25-27]. Several areas of the composite state of Andhra Pradesh have fluoride concentrations above the WHO limit. Fluoride has a dual meaning, namely beneficial effects on teeth at low concentrations in drinking water[28,29], but excessive exposure to fluoride in drinking water can lead to a number of negative effects.

EXPERIMENTAL

PREPARATION OF STOCK SOLUTION

Fluoride solution was prepared by using anhydrous sodium fluoride (NaF). 100 mg/l Fluoride stock solution was prepared by dissolving 221 mg anhydrous sodium fluoride in distilled water and made up to 1000 ml. Standard fluoride solution of 10 mg/l was prepared by diluting the stock solution 10 times with distilled water. The solution was stored in polyethylene bottles. All the dilutions were prepared by using the dilution formula:

C1V1=C2V2

where C1 is the concentration of available solution; V1 – the volume of available solution; C2 - the concentration of solution to be acquired, and V2 – the volume of solution to be acquired.

Determination of fluoride concentration. The concentration of fluoride ions in the solution before and after adsorption process was determined by Zirconium Alizarin Method. The testing procedure was followed as per the zirconium alizarin method without distillation process, prescribed in IS 3025 (part 60): 2008. Principle - as the amount of fluoride increases, the colour produced becomes progressively lighter from red to yellow and hence it obeys the Beer's law in a reverse manner. The colour obtained with zirconium alizarin reagent was matched against that produced with a series of standard fluoride solutions.

CHEMICALS REQUIRED

The chemicals required were: sulphuric acid (H_2SO_4) concentrated, hydrochloric acid (HCl) concentrated; zirconyl oxychloride ($ZrOCl_2.8H_2O$); Alizarin sodium monosulphonate (alizarin red S); sodium arsenite ($NaASO_2$). All the chemicals used were of analytical reagent grade.

APPARATUS AND EQUIPMENT REQUIRED

UV-vis. double beam spectrophotometer – Path length 1 cm. For use at a wavelength of 570 nm, distilled water apparatus, pipette, measuring cylinders, beakers.

PREPARATION OF REAGENTS

Zirconium alizarin reagent. 0.3 g of zirconium oxychloride ($ZrOCl_2.8H_2O$) was dissolved in 50 ml of distilled water. 0.07 g of alizarin sodium monosulphonate (alizarin red S) was dissolved in another 50 ml quantity of distilled water and the latter solution was added slowly to the zirconium solution with continuous stirring. The resulting solution clears on standing for a few minutes.

i. 112 ml of concentrated hydrochloric acid were diluted to 500 ml with distilled water. Also 37 ml of concentrated sulphuric acid were added to 400 ml of distilled water and then diluted to 500 ml. The diluted acids were mixed once they became cool.

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ii. The clear zirconium solution prepared in (i) was diluted to 1000 ml with the mixed acid solution prepared in (ii), the reagent was red at first, but within an hour it changed to orange-yellow and it was ready for use. The solution was stored in the dark and it is stable for 2 to 3 months.

iii. Sodium Arsenite solution - 5.0 g sodium arsenite (NaAsO2) were dissolved and diluted to 1000 ml by adding distilled water.

METHODOLOGY

Clear sample of 100 ml and a series of dilutions of standard fluoride solutions in 100 ml in the range of 0 to 1.0 mg/l were taken. 5.0 ml of the zirconium alizarin reagent were added to all the solutions and were left for 1 h exactly for colour development. In order to make the solutions chlorine free, 0.05 ml of sodium arsenite solution were added. Spectrophotometer was adjusted to a wavelength of 570 nm. Blank solution was utilised as reference. After 1 h, calibration curve of absorbance versus concentration was prepared by using all standards whereas distilled water was used as reference. After the preparation of calibration curve, the samples with unknown fluoride concentrations were tested at a wavelength of 570 nm following the same procedure mentioned above with the help of calibration curve, while performing adsorption experiments. The change in colour of the solution after reacting with reagent was observed from red to yellow with increase in fluoride concentration. All the unknown fluoride samples, reagents and the standards used for calibration curve were maintained at the same temperature within 1 to 2ºC. Adsorption add almond tree bark powder dosage of 0.1, 0.2, 0.3 g, respectively in 100 ml of standard solutions and fluoride present in sample for each 2 h is determined. Similarly do it for orange peel powder and neem??? peel powder also. By comparing the results, one of the adsorbents was selected. Add 0.1 g orange peel powder in 3 beakers of 100 ml standard sample, after that by using filter paper we filter the sample and take 20 ml from each sample and make up to 100 ml and add 5 ml reagent. The sample was added to the spectrophotomer after 1 hour, and the adsorbents values were recorded for 2, 4, and 6 hours, respectively. By comparing the above values optimum contact period was fixed. After fixing contact period, the same procedure was done for the different dosages.

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RESULTS AND DISCUSSION

COMPARING REMOVAL EFFICIENCY OF FLUORIDE FOR DIFFERENT ADSORBENTS

By comparing the removal efficiencies between almond tree bark powder, mosambi peel and lemon leaf with initial concentrations of 10 mg/l, almond bark powder has highest efficiency 82% (Table 1).

Table 1. Removal efficiency of fluoride for different adsorbents

Adsorbents powder	Initial concentration(mg/l)	Final concentration (mg/l)	Removal efficiency (%)
Almond bark powder	10	2.8	82
Mosambi peel powder	10	3.0	70
Lemon leaf powder	10	3.7	63

EFFECT OF ADSORBENT DOSE

Adsorbent dosage is an important parameter due to its strong effect on the capacity of an adsorbent at given initial concentration of adsorbate. Dosage varies from 0.1 to 2 mg/100 ml. Maximum removal efficiency is at 0.5 mg/100 ml dosage of almond tree bark powder (Tables 2 – 4 and Figs 1 - 3).

Table 2. Removal efficiency of fluoride for optimum dosage (for almond bark powder)

Dosage (mg/100 ml)	Initial concentration (mg/l)	Final concentration (mg/l)	Removal efficiency (%)
0.1	10	3.0	70
0.2	10	2.9	71

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0.3	10	2.6	74
0.4	10	2.5	75
0.5	10	2.2	79
1.0	10	2.1	78
1.5	10	2.3	76
2.0	10	2.4	74

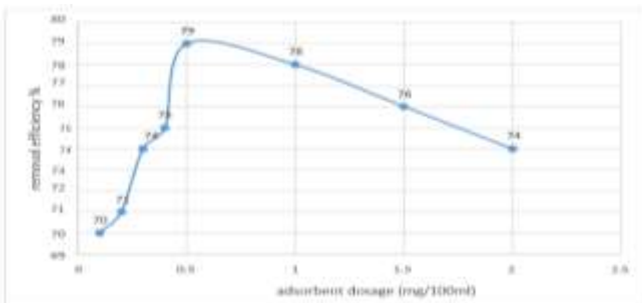

Fig. 1. Effect of removal of fluoride for optimum dosage (almond bark powder)

Table 3. Removal efficiency of fluoride for optimum dosage (for mosambi peel powder)

Dosage (mg/100 ml)	Initial concentration (mg/l)	Final concentration (mg/l)	Removal efficiency (%)
0.1	10	3.4	60
0.2	10	3.2	63
0.3	10	3.1	65
0.4	10	3.9	69
0.5	10	2.7	72
1.0	10	3.0	73
1.5	10	3.2	68
2.0	10	3.3	67

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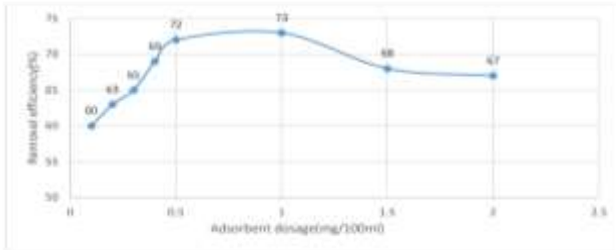

Fig. 2. Effect of removal of fluoride for optimum dosage (mosambi peel powder)

Table 4. Removal efficiency of fluoride for optimum dosage (for lemon leaf powder)

Dosage (mg/100 ml)	Initial concentration (mg/l)	Final concentration (mg/l)	Removal efficiency (%)
0.1	10	4.0	60
0.2	10	3.8	62
0.3	10	3.6	64
0.4	10	3.5	65
0.5	10	3.3	67
1.0	10	3.2	68
1.5	10	3.0	70
2.0	10	3.4	66

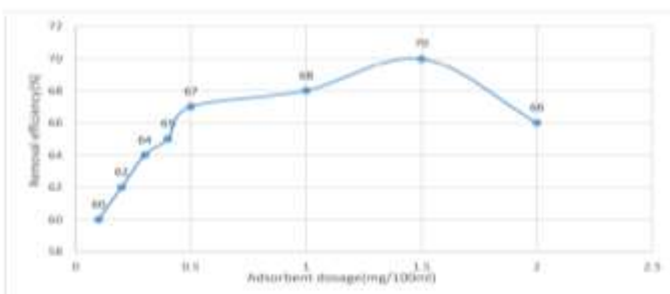

Fig. 3. Effect of removal of fluoride for optimum dosage (lemon leaf powder)

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EFFECT OF pH

After selecting optimum time, optimum dosage, pH can varied and the maximum efficiency achieved for pH 6 for almond bark powder and pH 8 for lemon leaf and mosambi powder is shown in Tables 5 – 7 and Figs 4 - 6.

Table 5**.** Removal efficiency of fluoride for optimum pH (almond bark powder)

pH	Initial concentration (mg/l)	Final concentration (mg/l)	Percentage removal (%)
2	10	2.2	78
4	10	2.1	79
6	10	2	80
8	10	2.3	77
10	10	2.3	77

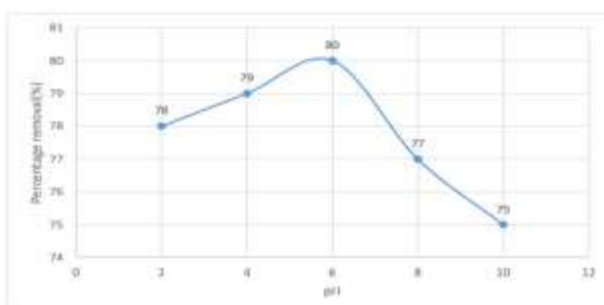

Fig. 4. Effect of removal of fluoride for optimum pH (almond bark powder)

Table 6. Removal efficiency of fluoride for optimum pH (mosambi peel powder)

pH	Initial concentration (mg/l)	Final concentration (mg/l)	Percentage removal (%)
2	10	3	70

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4	10	2.7	73
6	10	2.4	76
8	10	2.2	78
10	10	3.1	69

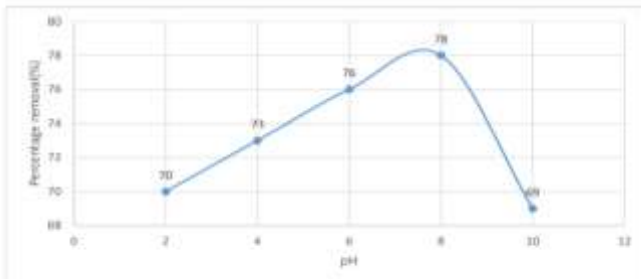

Fig. 5. Effect of removal of fluoride for optimum pH (mosambi peel powder)

Table 7. Removal efficiency of fluoride for optimum pH (lemon leaf powder)

pH	Initial concentration (mg/l)	Final concentration (mg/l)	Percentage removal (%)
2	10	3.1	69
4	10	2.9	71
6	10	2.8	72
8	10	2.6	74
10	10	3.2	68

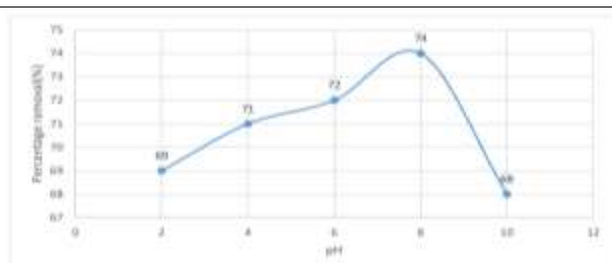

Fig. 6. Effect of removal of fluoride for optimum pH (lemon leaf powder)

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EFFECT OF CONTACT TIME

The sample was analysed at various time intervals for total duration of 5 h (Tables 8–10 and Figs 7-9) . The maximum removal efficiency was achieved at duration 210 min for almond bark powder (Table 8, Fig. 7).

Table 8. Removal efficiency of fluoride for optimum contact time (almond bark powder)

Time (min)	Initial concentration (mg/l)	Final concentration (mg/l)	Percentage removal (%)
30	10	4.8	52
60	10	4.3	57
90	10	3.7	63
120	10	3.7	63
150	10	2.7	73
180	10	2.2	78
210	10	1.8	82
240	10	2	80
270	10	2.5	75
300	10	2.7	73

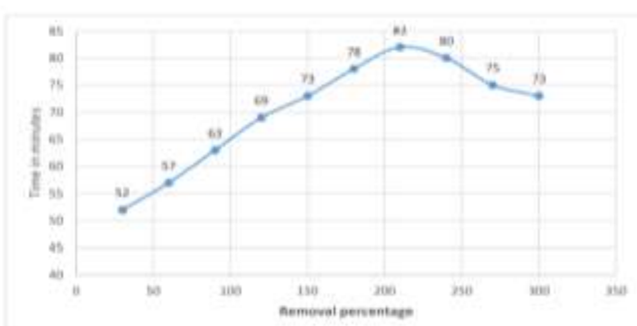

Fig. 7. Effect of removal of fluoride for optimum contact time (almond tree bark powder)

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Table 9. Removal efficiency of fluoride for optimum contact time (mosambi peel powder)

Time (min)	Initial concentration (mg/l)	Final concentration (mg/l)	Percentage removal (%)
30	10	5	50
60	10	4.5	55
90	10	4.3	57
120	10	4	60
150	10	3.8	62
180	10	3.4	66
210	10	3.2	68
240	10	3	70
270	10	3.2	68
300	10	3.5	65

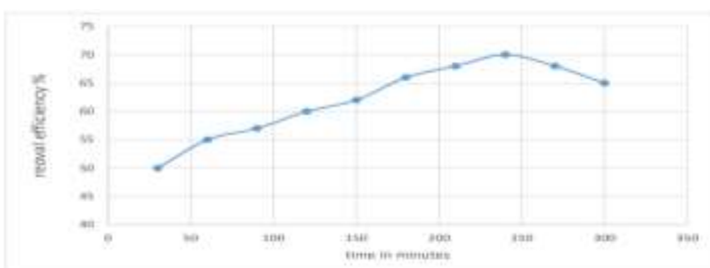

Fig. 8. Effect of removal of fluoride for optimum contact time (mosambi peel powder)

Table 10. Removal efficiency of fluoride for optimum contact time (lemon leaf powder)

Time (min)	Initial concentration (mg/l)	Final concentration (mg/l)	Percentage removal (%)
30	10	5.6	44
60	10	5.3	47

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90	10	5.2	48
120	10	4.8	52
150	10	4.6	54
180	10	4.5	55
210	10	4.1	59
240	10	3.9	61
270	10	3.7	63
300	10	4	60

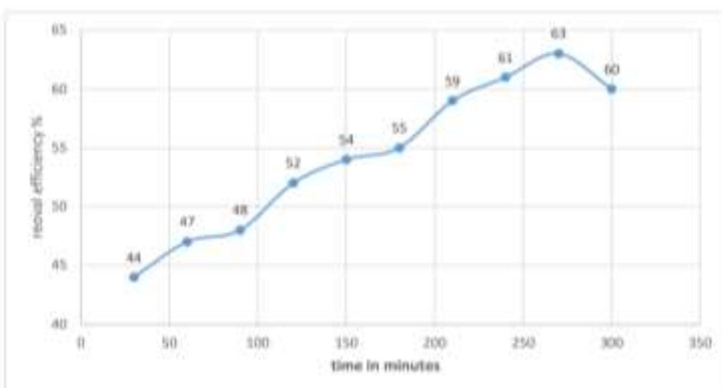

Fig. 9. Effect of removal of fluoride for optimum contact time (lemon leaf powder)

Optimum contact time for maximum removal of fluoride for almond bark powder is 210 min and the removal of fluoride is 82%. Optimum contact time for maximum removal of fluoride for lemon leaf powder is 270 min and 59% of fluoride are removed. Optimum contact time for maximum removal of fluoride for mosambi powder is 240 min and 70% of fluoride are removed. 82% percentage of fluoride removed in 210 minutes contact time. English??? After 210 min the efficiency decreases for almond bark powder. While comparing optimum contact time, the almond bark powder has more efficiency than lemon leaf and mosambi powder. Optimum dosage for maximum removal of fluoride for almond bark powder is 0.5 g/100 ml and 79% fluoride removal. Optimum dosage for maximum removal of fluoride for mosambi powder is 1.0 g/100 ml and 73% fluoride removal efficiency. Optimum dosage for maximum removal of fluoride for lemon leaf powder is 1.5 g/100 ml and 70% percentage fluoride

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removed. Optimum pH for maximum removal of fluoride is 6 for almond bark powder and 80% of fluoride removed. Optimum pH for maximum removal of fluoride is 8 for mosambi powder and 78% of fluoride removed. Optimum pH for maximum removal of fluoride is 8 for lemon leaf powder and 74% of fluoride removed. The efficiency of removal of fluoride by using almond tree bark powder was greater than mosambi peel powder and lemon leaves. Contaminant of fluoride in aquifer especially in India can be removed efficiently by naturally available absorbents like almond tree bark powder and it is ecofriendly.

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