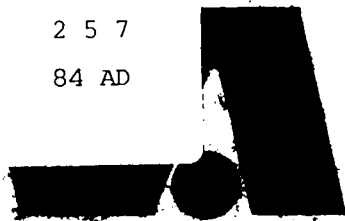


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FP-83828

Adsorption in Water Treatment Fluoride Removal

Norsk institutt for vannforskning



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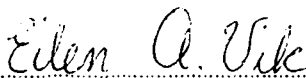
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Abstract: <p>The goal of this project has been to identify one or more adsorbents which may be suitable for low cost, low technology removal of fluoride, either for individual household use or for community water treatment systems. Experiments were performed using various types of media. The media which showed a capacity for fluoride removal were those which might have been predicted from the literature survey: superphosphate, tricalcium phosphate, aluminum sulfate, lime plus aluminum sulfate, activated alumina, and one anion exchange resin. Bone char probably would have shown a reasonable fluoride removal capacity if it had been treated with sodium hydroxide prior to testing.</p> <p>The National Environmental Engineering Research Institute, Nagpur, India, has done extensive research on fluoride removal with lime plus aluminum sulfate. It is recommended that they be contacted about their recent work on this method. Superphosphate is especially interesting because the only references to it which could be found were from 1955 and it appears quite suitable for individual household batch treatment. It is suggested that further studies on the remaining successful media being done to determine their behavior in water of various qualities. Parameters which should be varied include fluoride, alkalinity, turbidity, total dissolved solids and organics. Cost of treatment using each media should also be investigated.</p>

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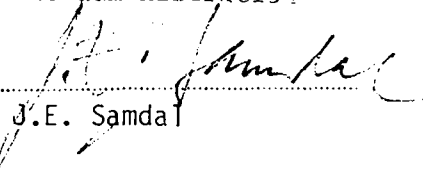
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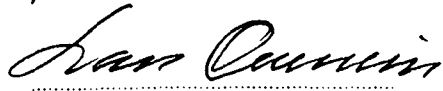

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1. PURPOSE OF STUDY

Among the method used for removal of dissolved pollutants in water, coagulation followed by flocculation, sedimentation and filtration is the traditional method. However, the adsorption process using various types of media is becoming more and more popular. The purpose of this project has been to look closer into the adsorption process, with emphasis on fluoride removal.

The Norwegian government feels a responsibility to provide technical help to developing countries. One of the basic needs of man is safe drinking water. In many rural areas, the only available water source contains a high concentration of fluoride which may cause adverse health effects. The methods of fluoride removal used in the industrialized countries require more technical support for operation and maintenance than is possible in the rural areas of developing countries. Assuring a continuous supply of treatment chemicals is often difficult.

The goal of this project has been to identify one or more adsorbents which may be suitable for low cost, low technology removal of fluoride, either for individual household use or for community water treatment systems.

2. FLUORIDE IN THE ENVIRONMENT

Fluoride in natural water is normally due to weathering or dissolution of fluoride containing minerals, mainly fluorite and fluorapatite. Fluoride concentrations in surface water are usually quite low, although Kilham and Hecky (1973) have found concentrations greater than 100 mg/l in East Africa.

Fluoride concentration in groundwater is usually less than 1 mg/l but higher concentrations have been found in many areas. In India fluoride concentration in groundwater is usually between 1 and 5 mg/l, but concentrations up to 19 mg/l have been found (Bulusu et al., 1979). High fluoride concentrations are also common in parts of Africa.

Fluoride is usually present in natural water as uncomplexed fluoride ions or as aquo complexes. In waters with relatively high concentrations of calcium, magnesium, aluminum, beryllium or iron however, metal complexes may be important (Handa, 1975).

In Norway maximum acceptable concentration in drinking water is 1.5 mg F/l.

3. HEALTH EFFECTS OF FLUORIDE

The concentration of fluoride in drinking water which causes harmful effects in humans varies in different parts of the world. A person's age, nutritional state, economic status, diet, and individual variations in fluoride absorption, as well as climate and drinking water composition all can affect the results of a given fluoride concentration (Adler, 1977). Fluoride-containing complexes are usually not absorbed by the body as well as free fluoride ions (Gitonga, 1983) so the presence of metals which form strong complexes with fluoride (Al^{3+} , Ca^{2+} , Mg^{2+}) can reduce the amount of fluoride absorbed. The presence of citrate or other species which complex Ca^{2+} ions can increase the amount of fluoride absorbed (Adler, 1977).

Small amounts of fluoride in drinking water is desirable because fluoride has been shown to reduce dental caries when ingested by children during the years of tooth formation. Too much fluoride, however, may be harmful.

Dental fluorosis is the first obvious sign of excessive fluoride in the water supply. Dental fluorosis changes the structure and appearance of tooth enamel. At low fluoride concentrations, tiny striations are formed. Higher fluoride concentrations cause irregular brown patches and at even higher concentrations the enamel becomes brittle and may chip easily. These changes occur during the years of tooth calcification, ages 1 - 12 years. The fluoride concentration which produces dental fluorosis has been reported to be 0.8 mg/l in Japan and 3 - 4 mg/l in the U.S. (Adler, 1977).

Skeletal abnormalities caused by excessive fluoride range from increased bone density to crippling fluorosis. Early harmful effects of fluoride, usually in young adults, are vague pains in the joints of the hands, feet, knees, and spine. As the person gets older, movement of the joints is limited and the spine becomes stiff (Adler, 1977). Other possible effects of long-term fluoride consumption include kidney problems and an increase in the function of the parathyroid gland which regulates calcium metabolism (Choi and Chen, 1979). Skeletal fluorosis has been identified in India where the drinking

water contains 3 - 4 mg F/l, but in areas with adequate diet and hygiene, fluoride concentrations of 8 mg/l may not be harmful (Adler, 1977).

The optimal fluoride concentration in drinking water varies with temperature since generally in warmer climates, more water is consumed, increasing the fluoride intake. The optimal fluoride concentration may be calculated based on the mean annual temperature t in $^{\circ}\text{F}$.

$$\text{optimal mg F/l} = \frac{0.212}{\tan (1.45585 t - 53.3950)} + 0.4$$

The limiting fluoride concentration above which the removal of excess fluoride is recommended, can be calculated using a similar formula.

$$\text{limiting mg F/l} = \frac{0.438}{\tan (1.45585 t - 53.3950)} + 0.4$$

The optimal and limiting fluoride concentrations calculated using these formulas are shown in Figure 1. These formulas (Adler, 1977) were derived for the temperature range 50°F to 70°F and may be less reliable outside that range.

The 1982 WHO Guidelines for Drinking Water Quality recommend that excess fluoride be removed from drinking water with more than 1.5 mg F/l.

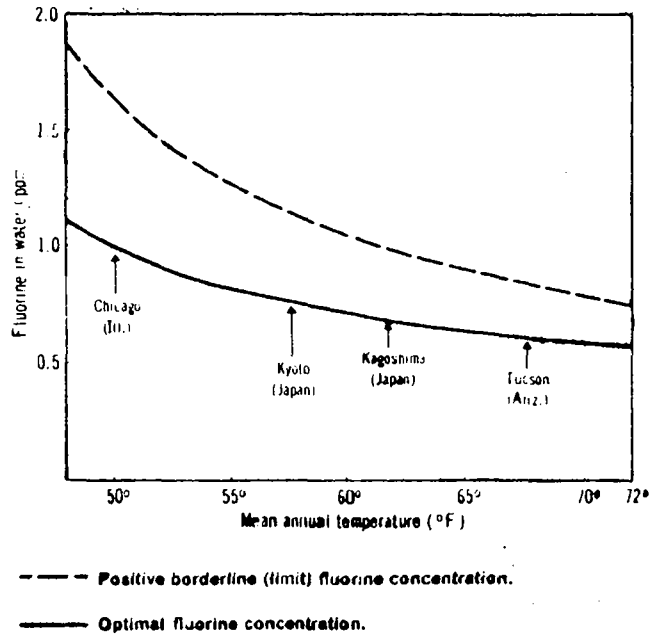


Figure 1. Calculated optimal and limit fluoride concentrations for mean annual temperatures from 50⁰F to 70⁰F (Adler, 1977).

Table 1. Fluoride Removal Methods.

Method	Dose or Capacity	Influent pH	Estimated relative Cost	Interferences	Advantages	Disadvantages	Also Expect to Remove	References
<u>Precipitation</u>								
Alum	150 mg/mg F	ambient	high	alkalinity	well known process	large amount of alum and sludge, low pH of treated water	turbidity, colour Fe, Mn, P alkalinity	Wu & Nitya, 1979
Lime	30 mg/mg F	ambient	high		well known process	need high initial Mg, sludge disposal, high pH of effluent	hardness, turbidity	Sorg, 1978
Lime + Alum (Nalgonda)	1 mg lime/mg F 130 mg alum/mg F		high batch low-medium	alkalinity, silica	can use batch low tech method	high chemical dose, sludge disposal adequate alkalinity required	turbidity, colour alkalinity, P	Bulusu et al. 1979
CaCl ₂	3 mg/mg F	depends on flocculant	medium	ligands that complex with F		sludge disposal, need flocculant aid	turbidity	Biver & Degols, 1982
<u>Adsorption/Ion Exchange</u>								
Activated alumina	1-9 kg F/m ³	5.0-6.0	low-medium	alkalinity	effective, much experience	well trained operators, regenerant disposal, clogging	As, turbidity, alkalinity	Bishop & Sansoucy, 1978
Activated bauxite	less than activated alumina	5.5-6.8	low-medium	alkalinity	cheaper than activated alumina	less effective, higher media losses than activated alumina	turbidity, alkalinity, As	Rubel & Woosley, 1979
Bone char	100 g F/m ³	≥ 7.0	medium	As		regenerant disposal, As poisoning of media		Sorg, 1978
Tricalcium phosphate	less than bone char	≥ 7.0	medium	As		friable, less effective than bone char		Sorg, 1978
Superphosphate	3.5 g F/kg	< 6.0	medium batch low-medium		Can use batch low tech. method	acidification of source water waste disposal		Cillie, 1955a, Cillie, 1955b
Zeolites	100 mg F/kg		high			ineffective		Sorg, 1978
Activated carbon	fairly good	≤ 3.0	high	many		large pH change before and after treatment	taste, colour, odor, organics	Sorg, 1978
Charcoal	5 mg F/kg	ambient	low-medium		locally available media	low removal capacity, requires soaking in alum		Ndegwa, 1980
Plant Carbon	320 mg F/kg	7.0	low-medium		locally available media	requires soaking in KOH, alum, regenerant disposal		Ndegwa, 1980
Clay Pots	80 mg F/kg	ambient	low-medium		locally available media	low capacity, very slow	turbidity	Ndegwa, 1980
Defluoron 1	1.6 g F/kg	ambient	medium			poor hydraulic properties, attrition, losses, regenerant disposal		Bhakuni & Sastry, 1964 Bulusu et al., 1979
Defluoron 2	360 mg F/l	ambient	medium	alkalinity		regenerant disposal		Thergaonkar et al., 1969

4. FLUORIDE REMOVAL METHODS

The methods normally used or proposed for removal of fluoride from drinking water are precipitation, ion exchange and adsorption. The precipitation methods involve addition of aluminum sulfate, lime, or calcium chloride. The adsorption or ion exchange media include activated alumina, activated bauxite, bone char, tricalcium phosphate, super phosphate, zeolites, activated carbon, charcoal, plant carbon, clay pots and sulfonated sawdust and coal. A summary of these methods can be seen in Table 1. All of the methods have disadvantages of cost, efficiency, or required high technical competence.

4.1. Precipitation methods

4.1.1. Aluminum sulfate (alum)

Alum treatment to remove fluoride is similar to alum treatment for turbidity removal except the required dose is larger. Wu and Nitya (1979) found that 350 mg/l alum was needed to reduce the fluoride concentration from 3.6 mg F/l to 1.0 mg F/l. The amount of alum needed increases with alkalinity and fluoride concentration. The equipment needed is similar to that normally used for chemical precipitation; dosing system, flocculation tank, sedimentation tank, and possibly a filter. Expected problems with use of this method include the large amount of alum required, large amount of sludge produced, the low pH and increased sulfate concentration of the treated water. Well trained operators are also needed. Because of the large amounts of alum used, this method is only practical for soft water requiring turbidity removal.

4.1.2. Lime softening

During lime softening of water, fluoride coprecipitates with magnesium hydroxide. The amount of fluoride removed depends on the amount of magnesium removed. The residual fluoride can be calculated from the following formula:

$$F_r = F_i - (0.07 F_i \times Mg)$$

were F_r = residual fluoride, F_i = initial fluoride concentration, and Mg = amount of magnesium removed (Sorg, 1978). To reduce fluoride concentration from 5.0 mg/l to 1.5 mg/l would require 100 mg/l magnesium. If the amount of magnesium in the water is not sufficient for the desired fluoride removal, more must be added. If magnesium is not present, the limited solubility of calcium fluoride will reduce the fluoride concentration of high fluoride waters to about 8 mg/l (Choi and Chen, 1979). Further fluoride reduction will require an additional chemical, such as superphosphate or aluminium sulfate. The equipment needed for lime softening is similar to that needed for alum precipitation. Expected problems include sludge disposal, the high pH of the treated water and the need for magnesium or other fluoride removal reagent. Trained operators are also needed. This method would be suitable for low fluoride, high magnesium water which needs softening before use.

4.1.3. Alum and lime

In this method, often called the Nalgonda method, lime is added first, followed by aluminum sulfate. The use of lime, about 1/20 of the alum dose, reduces the amount of alum needed. Alkalinity is also required and may need to be added to the water if the initial level is too low. Predicted alum doses required for fluoride removal down to 2 mg/l (E) and 1 mg/l (P) are shown in Table 2. For water with fluoride concentrations greater than 10 mg/l two-stage treatment is recommended (Bulusu et al., 1979). Additional lime will be required in the second stage to increase the alkalinity. If this method is used for large scale treatment, the same equipment used for alum treatment will be required. Bulusu states that the treatment is also effective when done on a single family level in a 20 - 50 l bucket or drum. The amount of chemicals to be added would need to be determined for each water source since the required dose depends on the concentration of fluoride, alkalinity, and dissolved solids. For ground water sources, these parameters should change little over time. The authors also recommend adding a disinfectant with the lime and alum. Disadvantages of this method are the large amount of chemicals required and disposal of the sludge. Successful field tests have been done in rural parts of India.

Table 2. Doses of filter alum required in Nalgonda technique for defluoridation (Bulusu et al., 1979).

Raw water Fluorides mg F/l	80		125		200		310		400		510		600		820		1070	
	E*	P**	E	P	E	P	E	P	E	P	E	P	E	P	E	P	E	P
2	0	104	0	143	0	221	0	273	0	312	0	351	0	403	0	468	0	520
3	78	***	117	221	156	299	200	351	260	403	312	507	351	520	377	585	429	767
4	143		195	***	208	403	286	416	299	468	390	559	403	598	481	689	559	936
5	***		247		286	***	338	507	377	598	468	689	471	715	650	884	663	1010
6			***		403		390	611	455	715	520	780	598	936	702	1066	767	1209
8					***		598	***	663	***	624	986	741	1118	871	1300	936	1430
10							***		***		767	***	832	***	1014	1508	1157	1690

Note: Filter alum (16 - 17 % alumina) required to obtain excessive and permissive values of fluoride in treated water at various raw water alkalinity and fluoride levels are given. The doses (mg/l) are approximate and can serve as a guideline. The values given in italics are not generally recommended. The line required is one-twentieth of filter alum.

Conditions comprising high fluoride and low alkalinity are not usual in India. When such conditions prevail the alkalinity of the raw water can be increased by lime.

* E-excessive limit, 2 mg F/l, ** P-permissive limit, 1 mg F/l, *** Not possible to attain the limit at the test water alkalinity.

4.1.4. Calcium chloride

The addition of calcium chloride to precipitate calcium fluoride has also been proposed as a fluoride removal method (Biver and Degols, 1982). An inorganic flocculation aid (Al, Fe, Si) is helpful. Optimal pH for the process depends on the flocculation aid used; pH of 9 - 10 for aluminum, and pH of 1 - 9 for iron. The calcium dose rate is about twice that stoichiometrically needed for the calcium fluoride, about 12 mg/l calcium chloride would be needed to remove 4 mg F/l. Fluoride can be removed to a residual level of about 1 mg/l. Equipment needed would be similar to that for alum precipitation. Disadvantages of this method are possible difficulties in flocculation and sludge disposal, and the need for well trained operators.

4.2. Adsorption and ion exchange

4.2.1. Activated alumina

Activated alumina, calcined granules of hydrated aluminum oxide, has been used in several commercial fluoride removal plants. Water flows through contact filters with a residence time of at least five minutes.

Optimal pH is 5.0 to 6.0. The fluoride concentration is reduced from an initial level of 4.5 - 7.5 mg/l to less than 1.0 mg/l. The capacity of the media is 1 - 9 kg/m³ (Bishop and Sansoucy, 1978, Rubel and Woosley, 1979). The media is regenerated using 1 % sodium hydroxide, then neutralized with sulfuric acid (Rubel and Woosley, 1979). Arsenic is also removed by the activated alumina. If arsenic is present in the source water, 4 % sodium hydroxide should be used for regeneration to avoid losses in media capacity (Rubel and Williams, 1980).

Problems with this method are the need for well trained operators, hazardous chemicals used in regeneration, disposal of waste regenerant, and possible clogging of the filter bed. The activated alumina has a high capacity for fluoride and this method is quite suitable for municipal plants in developed countries.

4.2.2. Fluidized activated alumina

This variation of the preceding method uses fluidized media rather than a contact filter. Because the available surface area is larger, the fluoride removal is greater. Regeneration can be done with more concentrated sodium hydroxide, producing a smaller volume of waste (Bishop and Sansoucy, 1978). This variation may reduce the cost of activated alumina treatment for fluoride removal in developed countries.

4.2.3. Activated bauxite

Activated bauxite, mainly Al₂O₃, may be used instead of activated alumina for fluoride removal. The capacity of activated bauxite for fluoride is less than that of activated alumina and the media losses during regeneration are greater but the purchase price is much lower than the price of activated alumina. It may be economically feasible for some plants to use activated bauxite rather than activated alumina.

4.2.4. Bone char (hydroxyapatite)

Bone char is ground animal bones which have been charred to remove organics. This media was originally developed for decoloring sugar cane syrups. It was used commercially in Britton, South Dakota, USA, from 1953 to 1971 to remove fluoride from drinking water. The capacity

of bone char is 100 g F/m³ when removing 5 mg F/l. The media also removes arsenic which is not released during regeneration, poisoning the media. Influent pH should be 7.0 or greater because the media is soluble in acid. The media is regenerated by sodium hydroxide. Disadvantages of this method include the need for skilled operators, disposal of waste regenerant and media poisoning by arsenic (Sorg, 1978).

4.2.5. Tricalcium phosphate (synthetic bone, synthetic hydroxyapatite)

This media is similar to bone char but it is more friable. It was used in the Britton defluoridation plant from 1948 to 1951 when it was replaced because of high media losses, 42 % per year. It is not as effective as bone char and requires more frequent regeneration (Sorg, 1978).

4.2.6. Superphosphate (Calcium tetrahydrogen di-orthophosphate)

The superphosphate is activated by being soaked in 5 % sodium hydroxide before use. Granular superphosphate is used in a conventional ion exchange column. Regeneration is accomplished with 1 % sodium hydroxide. Influent pH should be 6.0 or lower. Most source water will require acidification before treatment. Capacity is 3.5 g F/kg media for influent fluoride concentration of 10 mg/l (Cillie, 1955a). Use of powdered superphosphate is possible in a small scale batch process (Cillie, 1955b). Either form of superphosphate produces treated water with a residual fluoride concentration of about 1.0 mg/l. Disadvantages of using superphosphate are the need for acidification of source water prior to treatment and, for the column method, the need for well trained operators and the disposal of waste regenerant.

4.2.7. Zeolites

Zeolites were tested by Boruff in 1934 and found to be impractical for fluoride removal treatment (Sorg, 1978). Different zeolites are selective for different ions, however, and it is possible that a zeolite which more effectively removes fluoride may exist. Zeolites generally have little resistance to abrasion (Weber, 1972) which may cause excessive media losses. Although a naturally occurring or synthetic zeolite which selectively removes fluoride may be found, the search does not appear to be promising.

4.2.8. Activated carbon

Activated carbon effectively removes fluoride at pH 3.0 or less (Sorg, 1978). Thermal regeneration would produce a fluorine containing gas. Effectiveness of fluorine removal is expected to be affected by other components of the water. This method is not practical because of the large change in pH required before and after treatment.

4.2.9. Charcoal

Charcoal, prepared by burning wood under natural conditions followed by soaking in alum before use, has been reported to remove fluoride from water (Ndegwa, 1980). The capacity is relatively small, 5 mg F/kg media, perhaps due to the low surface area. Although regeneration was not tested, soaking in alum may restore removal capacity.

Disadvantages of this method are low removal capacity and possible contamination problems if the charcoal is later used as fuel for cooking or heating. Many of the areas where the groundwater contains excess fluoride are arid or semi-arid with limited availability of wood.

4.2.10. Plant carbon

Treatment of paddy husks by digestion in 1 % potassium hydroxide followed by soaking in 2 % alum also produces a media which will remove fluoride (Ndegwa, 1980). The material may be regenerated using 2 % alum. Optimal influent pH is 7.0. The removal capacity is reported to be 320 mg F/kg of media at pH 7.0. Although other plant sources apparently were not tested, other crop wastes may also be suitable. Disadvantages include disposal of waste regenerant.

4.2.11. Clay pots

Clay pots have also been tested for removal of fluoride. Water is poured into the pot, it flows through the walls and out. Reported capacity is 80 mg F/kg clay (Ndegwa, 1980) but this probably varies with the type of clay used. The time required for the water to flow through the pot may be quite long; a 400 g pot produced about 100 ml per day (Ndegwa, 1980). Disadvantages of this method are the low removal capacity and the excessive time required. Clay pot chips in a column were also tested. Although the time required was much less, the removal capacity was also very small.

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4.2.12. Defluoron 1

This media is prepared by treating dried sawdust with concentrated sulfuric acid, washing with sodium carbonate or sodium chloride, followed by 1 % aluminum sulfate. A capacity of 1 600 mg F/kg media is reported from column tests for an initial fluoride concentration of 4.3 mg/l. The media may be regenerated with 1 % alum (Bhakuni and Sastry, 1964). This media has been reported to have poor hydraulic properties and high attritional losses (Bulusu, et al., 1979). Trained technical operators are also required for media regeneration.

4.2.13. Defluoron 2

This patented media is a sulfonated coal regenerated with alum. A capacity of 360 mg F/l media is reported from column tests with initial fluoride concentration of 5.0 mg/l. Hydraulic properties and attrition losses are said to be good (Thergaonkar et al., 1969). Capacity of the media decreases with increasing alkalinity and decreasing initial fluoride concentration (Bulusu et al., 1979). A disadvantage of this method is the need for skilled operators for plant operation and media regeneration, and waste regenerant disposal.

5. MATERIALS AND METHODS

A variety of media were chosen for testing of fluoride removal ability. To provide adequate contact time for fluoride removal, a batch process was used rather than column tests. Some media were treated before testing. A description of the pretreatment of these media is given in Table 3. If possible, the particle size of each media was adjusted to greater than 0.85 mm and less than 2 mm. Media which were initially smaller than this are indicated in the results.

Sodium fluoride solution was prepared by adding reagent grade sodium fluoride to tap water from Maridalsvann. The water quality of the tap water are listed in Table 4. The fluoride concentration was approximately 10 mg F/l except for one run in which the concentration was about 50 mg F/l. The pH of the solution was adjusted to approximately 5.0, 7.0 or 9.0 using hydrochloric acid or sodium hydroxide. The solution was prepared at least 24 hours before use to assure that it was at room temperature when used.

A weighed amount (according to table 5) of the media was placed in a 500 ml plastic flask. Two hundred ml of sodium fluoride solution were added, and the flask was placed on a shaker table for three hours. At the end of the mixing period the pH of the solution was measured. Eighteen hours later, a sample for fluoride measurement was removed from the flask. if the solution was not clear, it was filtered through a 0.45 μ m filter before sample removal.

Fluoride was measured using an Orion fluoride specific ion electrode following Orion's recommended procedure.

Table 3. Media pretreated prior to fluoride removal tests.

Media	Pretreatment
<u>Superphosphate</u>	Soak in 5 % NaOH with mixing for 24 hours. Wash and dry.
<u>Cation exchange resin</u>	Soak in 2 % alum overnight. Wash and dry.
<u>Activated carbon</u>	Soak in 2 % alum overnight. Wash and dry.
<u>Charcoal</u>	Crush. Soak in 2 % alum overnight. Wash and dry.
<u>Bark</u>	Add conc. H_2SO_4 and heat for 2 hours. Wash until neutral. Soak ⁴ in 2 % alum overnight. Wash and dry.
<u>Sawdust</u>	Add conc. H_2SO_4 . Let react several minutes. Wash. Soak ² in 2 % alum overnight. Wash and dry.
<u>Peat</u>	Add conc. H_2SO_4 and heat for 2 hours. Wash until neutral. Soak ⁴ in 2 % alum overnight. Wash and dry.
<u>Zeolite</u>	Soak in 2 % alum overnight. Wash and dry.

Table 4. Water quality of tap water from Maridalsvann. (Vik, 1983).

pH	6.5
turbidity	0.60 FTU
colour	10 mg Pt/l
conductivity	3.5 mS/m
alkalinity	0.12 mmol/l
calcium	2.5 mg Ca/l
magnesium	0.5 mg Mg/l
chloride	2.0 mg Cl/l
sulfate	6.5 mg SO_4 /l
sodium	1.4 mg Na/l

6. RESULTS AND DISCUSSION

Results of the fluoride removal experiments are shown in Table 5. The apparent removal capacity of each media was calculated by dividing the amount of fluoride removed during the test by the amount of media used. For most media the capacity would be expected to vary with the initial fluoride concentration, but this calculation provides a quick method for comparing the tested media. Based on these initial tests, the following media show significant fluoride removal; superphosphate (after sodium hydroxide treatment), tricalcium phosphate, aluminum sulfate, lime plus aluminum sulfate, amberlite IRA-47 anion exchange resin, and most forms of activated alumina.

The pH of the fluoride solutions adjusted to pH 5 and pH 9 decreased when the solutions were stored in the laboratory at room temperature. The pH 9 solution was readjusted to pH 9.0 one day after initial pH adjustment. The following day the pH of the blank samples was below 8.0. The pH of the pH 5 solution decreased to 4.2. The actual pH values of the solutions tested, although lower than planned, still bracket the pH range of most natural waters.

The test conditions were chosen to maximize the fluoride removal of most media. The conditions were not ideal for flocculation, however. The aluminum sulfate and lime plus aluminum sulfate samples did not have obvious sediment at the end of the tests. In the absence of a solid which could be separated from the remainder of the sample, there is some doubt as to how the fluoride was removed from solution. It is not expected that the presence of aluminum fluoride complexes reduced the measured free fluoride concentration. The addition of TISAB buffer is reported to eliminate the aluminum interference (APHA, 1981).

Generally, the test results correspond to the results expected based on the literature survey. The media most effective for removing fluoride are those which have been identified as fluoride - removal agents in the past. The aluminum sulfate and lime plus aluminum sulfate show fluoride removal results better than expected from reported literature values. This is especially surprising because no floc was

Table 5. Results from fluoride removal experiments.

Media	Amount tested	pH = 5			pH = 7			pH = 7, 50 mg F/l			pH = 9			Comments
		pH	mg F/l	removal capacity mg F/g media	pH	mg F/l	removal capacity mg F/g media	pH	mg F/l	removal capacity mg F/g media	pH	mg F/l	removal capacity mg F/g media	
Blank		4.20	10.8		6.89	10.7		6.87	52.1		7.65	10.6		
Blank		4.16	11.6		6.89	10.8		6.85	51.4	7.36	10.6			
Bone char	5.0	7.17	10.7	0.02				7.58	53.3		7.90	10.7	0.12	Carbo Animals BPC 1934, Evans medical Ltd, Liverpool
Shell sand	5.0	9.02	10.1	0.14				9.36	50.4	0.28	9.55	10.0	0.16	
Zeolite (Treated)	5.0	6.30	9.52	0.26				7.00	49.9	0.38	8.27	10.1	0.14	
	5.0	4.61	7.47	0.67	5.11	7.38	0.68				5.84	7.48	0.66	
Perlite Norcem No. 30	0.3	4.36	10.7	0.33				6.79	53.1		7.45	10.6	0.67	
Perlite Norcem No. 65	0.5	4.34	10.6	0.40				7.10	53.8		7.85	10.5	0.60	
Perlite Norcem Ekopert	0.3	4.37	10.8	0							7.72	10.5	1.0	
	0.5							6.65	54.1					
Superphosphate " (treated)	0.5	3.95	10.7	0.70										Powder
	0.5	5.82	2.09	17.4	6.13	0.69	20				6.66	2.41	16.8	
Tricalcium phosphate	0.5	6.97	2.26	17	7.34	2.72	16	7.64	38.1	25	7.61	3.45	14.7	Powder
Dolomite	5.0	10.85	4.93	1.7	10.76	4.95	1.2	10.83	36.1	3.1	10.73	7.12	0.74	Neodote German type GJE
Filtercarb	5.0	10.95	4.36	1.3	10.86	4.27	1.3	10.55	33.9	3.6	10.77	4.51	1.3	1.2 mm < size < 1.8 mm
Hustad Marmor N2	0.1	8.7	10.6	2.0							9.38	11.1		Powder
	0.5		0.05		9.13	10.5	0.60			9.15				
Hustad Marmor N5	0.1		10.5	3.0							9.42	11.0		
	0.5				9.24	10.5	0.6							
Aluminum sulfate	0.2	4.07	3.48	37	4.16	3.44	37	4.40	23.2	143	4.20	3.48	37	Little or no solid on bottom
	0.1													
Ca(OH) ₂ + alum	0.01	4.21	3.82		4.26	3.92					4.25	3.90		
	0.1			35			34						35	
CaCl ₂	0.1	4.87	10.0	8.0	7.29	10.6	2.0	7.2	28.8	230	8.92	10.7	1.0	
Anion Exchange Resin Lewatit MP 62	0.5	5.53	10.8					7.0	50.5	2.6	7.54	10.5	0.6	Size < 0.85 mm OH ⁻ form Bayer
Lewatit M 500	0.5	4.50	7.83	5.9	7.0	6.12	9.4	7.15	39.2	25	7.17	6.61	8.4	Size < 0.85 mm, Ce ⁻ form Bayer Type 1

Table 5. Results from fluoride removal experiments (cont.).

Media	Amount tested	pH = 5			pH = 7			pH = 7, 50 mg F/l			pH = 9			Comments
		pH	mg F/l	removal capacity mg F/g media	pH	mg F/l	removal capacity mg F/g media	pH	mg F/l	removal capacity mg F/g media	pH	mg F/l	removal capacity mg F/g media	
Lewatit Vers Prod	0.5	4.21	10.8					6.4	49.3	5.0	6.96	9.86	1.9	Size < 0.85 mm OC ⁻ form Bayer 1014
Amberlite IRA-47	0.5	5.06	5.57	11	5.10	4.27	13	6.60	33.1	37	6.16	4.91	12	Size < 0.85 mm, OH ⁻ form
Amberlite IRA-400	0.5	5.10	7.78	6.0	7.12	6.14	9.3	6.86	39.9	24	7.53	6.72	8.2	14-52 mesh, Cl ⁻ form
IMAC A 205	0.5	6.53	10.7	0.20				7.70	50.0	3.6	8.05	9.75	2.1	Size < 0.85, Akzo Chemie, Netherland
Cation Exchange Resin														
Dowex 50w-x8	0.5	4.68	10.8					6.93	52.5		7.90	10.2	1.2	18-52 mesh, Na form
" (treated)	0.5	5.24	6.45	8.7	6.71	5.88	9.8				7.24	7.11	7.4	
Flitton	0.5	4.22	10.9					7.4	53.1		8.25	10.6	0.4	Size < 0.85 mm
"	0.5							7.0	53.7					
Activated Carbon Atlas Granular	0.5	5.66	7.94	5.7				7.43	47.2	9.2	6.98	8.13	5.3	Hydrodarco 12 x 20
" (treated)	0.5	4.42	9.10	3.4	6.04	8.00	5.6				6.66	7.76	6.1	
Darco HD3000	0.5	4.86	8.70	4.2				7.61	47.6	8.4	7.25	8.42	4.8	
" (treated)	0.5	4.71	9.30	3.0	6.01	7.73	6.1				6.65	8.08	5.4	
Noritt A1603	0.5	9.96	10.5	0.6				9.94	51.0	1.6	10.24	9.95	1.7	
" (treated)	0.5	4.51	8.75	4.1	5.89	6.51	8.6				6.58	6.81	8.0	
Activated Alumina Granalox HHN/Q812	0.2	5.17	10.2	3.0	7.54	9.62	5.9	7.56	46.7	26	8.08	9.95	4.3	Martinsverk
Compalox AN/V801	0.2	6.37	9.48	6.6				7.62	48.3	18	8.88	9.90	4.5	Martinsverk
AX	0.2	6.96	8.20	13	7.84	7.89	15	8.08	46.6	26	8.17	8.85	9.8	Powder, Martinsverk
GX	0.2	6.58	8.46	12				8.12	46.9	25	8.28	8.77	10	Powder, Martinsverk
HN	0.2	7.57	6.85	20	8.36	6.67	21	8.69	42.0	49	8.48	7.33	17	Powder, Martinsverk
SAP, 350 Stand	0.2	7.95	5.69	26	8.76	5.70	26	9.14	37.8	70	8.84	5.79	25	Size < 0.85 Rhône-Poulenc
Alumina Woelm B	0.2	6.5	8.0	14				8.08	48.7	16	8.24	9.12	8.4	Size < 0.85
Charcoal	0.5	5.25	10.7	0.2				7.54	54.2		8.16	10.4	0.8	
" (treated)	0.5	4.46	9.98	1.6	6.28	10.1	1.4				7.27	10.4	0.8	
Bark	0.2										7.08	10.1	3.5	
"	0.5							6.37	52.0					
" (treated)	0.5										2.94	9.12	3.4	
Sawdust	0.4	4.65	10.9					6.58	52.3		7.26	10.4	1.0	
" (treated)	0.4				3.31	8.05	6.9							
Peat	0.4	4.95	10.9					5.15	52.7		5.42	10.3	1.3	Size < 0.85 mm
" (treated)	0.4				5.83	10.9								
Alginates Protanol LF 40	0.5	5.76	11.6					6.5	57.6		7.13	12.4		Size < 0.85 mm pr. No. 164
Protanal HF 40	0.5	5.63	11.3					6.4	54.6		6.64	10.4	0.8	Size < 0.85 mm pr. No. 165
Bolfloc L	0.5	6.33	10.1	1.4				7.5	55.1		7.30	10.3	1.0	pr. No. 163

formed. Super phosphate powder also removed more fluoride than expected, possibly because of the low concentration of other constituents in the fluoride solution. The superphosphate was effective in the high pH solution even without prior acidification of the solution as recommended by Cillie (1955a). A better buffered solution may, however, require prior acidification.

The bone char showed very little fluoride removal capacity. It should have been treated with sodium hydroxide, the recommended regenerant, prior to use. Fluoride removal ability is then expected to be slightly better than that of tricalcium phosphate.

The dolomite and filtercarb samples showed some fluoride removal ability but the amount of media needed was relatively high. The pH of the treated solution was also very high.

The anion exchange resins displayed a wide range of apparent capacities for fluoride removal. The most effective was an OH^- form resin but the other two OH^- form resins were among the least effective. It is expected that competition with other ions will significantly reduce the fluoride removal in water with greater dissolved solids and organics.

There is also a fairly large range of fluoride removals among the activated alumina samples tested. The removal shows little change due to influent pH although the recommended influent pH is 5.0 - 6.0. The apparent capacity is much larger for the samples with higher initial fluoride concentration.

The treated sawdust and bark showed some fluoride removal capacity. The final pH of the treated solutions was very low which may indicate insufficient washing of the media. The treated peat showed no fluoride removal. Not all tests were run on the treated sawdust, bark, and peat due to media losses during preparation.

The shell sand, zeolite, perlites, alginates, filton, charcoal, untreated bark, sawdust and peat showed little or no capacity for fluoride removal.

7. CONCLUSIONS

The media which showed a capacity for fluoride removal are those which might have been predicted from the literature survey: superphosphate, tricalcium phosphate, aluminum sulfate, lime plus aluminum sulfate, activated alumina, and one anion exchange resin. Bone char probably would have shown a reasonable fluoride removal capacity if it had been treated with sodium hydroxide prior to testing.

The National Environmental Engineering Research Institute, Nagpur, India, has done extensive research on fluoride removal with lime plus aluminum sulfate. It is recommended that they be contacted about their recent work on this method.

It is suggested that further studies on the remaining successful media be done to determine their behavior in water of various qualities. Parameters which should be varied include fluoride, alkalinity, turbidity, total dissolved solids and organics. Cost of treatment using each media should also be investigated.

Superphosphate is especially interesting because the only references to it which could be found were from 1955 and it appears quite suitable for individual household batch treatment.

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