

Defluoridation of Drinking Water by Different Techniques

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Fluoride has been reported as a health affecting substance by health organization. Fluoride in water may be beneficial and detrimental depending on their concentration and total amount ingested. The permissible limit for of fluoride is 1.0- 1.5 mg/l. Fluoride greater than limit is toxic and is associated with dental fluorosis. The flurosis is caused by oral intake of fluoride when drinking water contain more than the permitted concentration of fluoride. The amount of fluoride is increasing day by day in water samples. So, here in this research paper a comparative study has been done of the water sample containing fluoride is present in the recommended limit or not. The defluoridated is done by the mean of precipitation adsorption or ion exchange method. The comparative result is reported in the research paper.

Keywords: Fluoride, Adsorbent, Fluorosis, Defluoridation Methods.

1. INTRODUCTION

Fluoride in water may be beneficial and detrimental depending on their concentration. Fluoride is an ion of the chemical element fluorine which belongs to the halogen group. Fluoride has a significant mitigating effect against dental caries. Fluoride is beneficial for young children for calcification of dental enamel below 8 years of age when presence in permissible limit of 1.0-1.5 mg/l [1]. The fluoride is toxic at concentration greater than 1.5mg/l and is associated with dental fluorosis. The presence p of high concentration of fluoride in water resources is a major problem in almost nation in the world [2]. Excess fluoride in water multidimensional health problem including skeletal and dental fluorosis are commonly found in the rural population depend on the type of drinking water.

2. DEFLUORIDATION

Defluoridation refers to methods of water treatment that reduce the concentration of fluoride in the water, normally, in order to make it safe for human consumption. Some water treatments that have the capacity of reducing the fluoride concentration along with most other anions, or anions and cations, in the water, are not considered as defluoridation methods. Thus general demineralising methods like distillation, reverse osmosis, electro dialysis and resin de-anionisation, which are able to remove fluoride fully or partly from the water, are not considered as defluoridation methods [3]. On the other hand methods that only remove fluoride without any addition or reduction of other parameters are not yet discovered. That's why the expression "fluoride removal" lacks

precision. Defluoridation is used to characterise methods that reduce the fluoride ion specifically, without *major* other changes to the quality of the treated water.

In drinking water the natural concentration of fluoride depend on the geological, chemical and physical characteristics of the water, the porosity of soil, and action of the other chemical elements. The maximum permissible/allowable limit of fluoride in water has been laid down as 1.5 mg/l by WHO and ICMR and 0.7-1.7 mg/l by USPHS. Water containing fluoride concentration more than recommended limits, is defluoridated by means of precipitation adsorption or ion exchange methods. The effect of fluoride in drinking water has been studied in detail.

3. PHYSICOCHEMICAL PROPERTIES OF FLUORINE

Fluorine is a greenish diatomic gas, with atomic number 9, electronic configuration $2, 7$ ($1s^2, 2s^2, 2p^5$) and atomic weight 19. The great activity of the element is in part attributed to the weakness of the F-F bond in the fluorine molecule. Its ionization potential, 401 Kcal /g-atom, combined with dissociation energy, leads to the standard heat of formation of gaseous F^+ ion of 420 Kcal/g atom (Cl^+327 ; Br^+301 ; I^+268). Thus even solvated cationic species are unlikely and no evidences exist for a positive oxidation state of fluorine.

Fluorine compounds are essentially of two main types, ionic and covalent, in both of which fluorine has a complete octet. Ionic fluorides contain F^- ion. The relatively small radius of F^- 1.36 Å, is almost identical with that of the oxide O^{2-} ion (1.40 Å); consequently, many fluorides and oxides are ionic with similar formulae and crystal structure, for example CaO and NaF. Covalent fluorides of many elements exist, and in view if the high electro negativity of fluorine such bonds have considerable ionic character. Fluorine shows the lowest affinity towards oxygen due to its electro negativity. Coordination number of fluorine seldom exceeds one. An important feature in the formation of fluorides is that in reactions with fluorine, the elements usually give maximum oxidation state. Fluorine has a strong tendency to undergo reduction from zero oxidation to minus oxidation state. It is a strong oxidizing agent. Fluorine does not act on glass if it is absolutely free from all traces of hydrofluoric acid.

Fluorine compounds are used as insecticides, fungicides, fumigants and air conditioning. It is used as solvent in anesthetics and fireproofing. In nuclear physics and high voltage electricity fluoride as SF_6 finds great use.

4. METHODS OF ESTIMATION OF FLUORIDES

The determination of the fluoride ion in water has become very important since the discovery of its importance in dental hygiene and the advent of fluoridation process. The analytical methods are given in the official British and American Compilation of methods; they give brief outlines of the main problems involved and currently accepted practice

towards reliable analysis, but improved and more rapid techniques are still being developed. Among the many methods suggested for determination of fluoride ion in water, the colorimetric and electrode methods are the most satisfactory at the present time.

4.1. Colorimetric Methods

The majority of colorimetric methods which have gained acceptance are based on the effect of fluoride in destroying the color of the Zirconium or Thorium lakes of certain dyestuffs under control conditions of pH, and in the absence of interfering substances, the effect is quantitative and accurate, visual or photometric determinations are possible. The fluoride reacts with dye-lake dissociating a portion of it into a colorless complex anion, Zirconium-hexa-fluoride, $(ZrF_6)^{-2}$ and the dye. As the amount of fluoride is increased, the color produced becomes progressively lighter or different in hue depending on the reagent (dye) used.

In one reliable technique a volumetric finish is adopted, standard fluoride is being added to a blank until the tint matches that of the test solution (I.W.E. Methods). Among dye-stuff employed, alizarin red-s is very popular but solochrome cyanin-R has been applied by E. J. Dixon (1970) [4] while standard methods also describe a procedure with dye SPADNS {2-(p-sulphophenyl-azo)- 1:8, dihydroxy naphthalene-3:6 disulphonic acid, tri-sodium salt}. The purity of dyestuff used is important and recrystallization is usual advisable in the case of alizarine red-s.

Interference in colorimetric method (shortcomings of colorimetric methods)- whenever fluoride test is under taken the interfering parameters e.g. alkalinity, aluminum, chloride, iron, phosphate and sulphate should be negligible quantity. For overcoming the interfering substances direct distillation of the samples is essential prior to the estimation of fluoride as described are standard methods.

5. EFFECTS OF FLUORIDE INGESTION IN HUMAN AND ANIMALS

The chronic toxic effects (fluorosis of excessive intake of fluoride are usually observed as skeletal abnormalities or damage [5,6]. The effects range from stiffness and rheumatism to a permanent crippling skeletal rigidity. Experimental and clinical data point to a chronic effect on the kidneys following long-term ingestion. Most thoroughly documented is an increase in function of the parathyroid glands, which regulate the metabolism of calcium. Dental fluorosis is the most common manifestation of the toxic effects of excessive fluoride in a water supply. It is characterized by an increasing mottling of teeth as the fluoride level increases. Earlier studies confirm an increase in the occurrence and severity of fluorosis of children's teeth when the fluoride level in drinking water exceeded about 1.5 mg/L.

Maclure has computed for children of various age groups the total daily intake of fluorides from food and water containing 1 mg/l of fluoride. Although with a fluoridated

water supply the average adult takes in too much fluoride, the excess is eliminated by kidneys and through the skin. McClure et al have shown that males can eliminate 5 .0 mg daily. The" Commission on chronic Illness" (an American body, 1954) investigated the excretion of 50 patients and showed that with damage kidneys their excretion of fluoride was similar to that reported by McClure for healthy young men [7].

6. AWARENESS REGARDING USE OF DEFLUORIDATION TECHNOLOGY

About 81% of respondents were found adding prescribed chemicals in drinking water but only 68% of respondents were aware of the correct amount of chemicals to be added [8].

7. TECHNIQUES OF DEFLUORIDATION

7.1. Adsorbent Formation

Most of the carbon prepared from different carbonaceous sources showed fluoride removal capacity after alum impregnation. McKee and Johnston have reported fluoride-removing capacity of various types of activated good carbons. Adsorbent was prepared from *Opuntia dilleni* by digestion in 1% KOH and soaking it overnight in 2% alum solution.

7.2. Aluminum Salts

Aluminum salts like filter alum and activated aluminum and alum treated cation exchange have shown beneficial effects. Filter alum during coagulation brings about some removal of fluorides from water. The removal efficiency is improved when used along with a coagulant aid like activated silica and clay. 300 to 500 mg/l of alum is required to bring down fluoride from 4.0 mg/l to 1.0 mg/l while with coagulant aid, the fluorides were reported to be reduced from 6.0 mg/l to 1.0 mg/l with alum dose of only 100 mg/l.

Alum treated polystyrene cation exchangers and sulphonated coals have also been used successfully [9]. A cation exchanger prepared from extract of *Avaram* bark and formaldehyde when soaked in alum solution has been found to have good fluoride removal capacity (800 mg/Kg).

Calcinated or activated alumina in granular form can be used for fluoride removal and the spent material regenerated with alkali, acid or by both alternately (removal efficiently 1.2 kg of fluoride/m³). A dilute solution of aluminium sulphate used as the regenerate for the spent material makes the alumina four times more efficient [10].

7.3. Treatment Of Synthetic Wastewater Containing Fluoride

The treatment of synthetic wastewater containing different concentration of fluoride ion viz: 15 ppm, 20 ppm and 25 ppm using batch experiment. The known amount of adsorbent were mixed and shaken vigorously for different contact time ranging 0 to 700 minute. The concentration of fluoride ion synthetic drinking water was measured of different time interval and percentage adsorbance of fluoride removal were studied using below formula:

$$\% \text{ Adsorbance} = \frac{\text{Initial conc. of fluoride} - \text{Final conc. of fluoride}}{\text{Initial conc. of fluoride}} \times 100$$

The experimental data were studied kinetically using integrated form of first order rate constant.

Table 1: Adsorbance of Fluoride varying Contact Time at pH 6 by Adsorbent (Opuntia Dilleni).

Time	% Adsorbance (5 ppm)	% Adsorbance (4 ppm)	% Adsorbance (3 ppm)
50	12.6	15.1	16.8
100	23.1	27.8	27.2
150	30.2	30.4	35.8
200	35.2	43.2	42.4
250	39.7	50.4	50.8
300	47.2	59.6	59.4
350	51.7	59.9	64.6
400	52.8	62.9	66.3
450	53.1	64.6	70.1
500	55.4	68.3	74.7
550	56.2	69.2	74.9
600	56.8	69.4	75.8.
650	58.4	69.8.	76.4
700	58.9	70.1	75.9

Table 2: Adsorbance of Fluoride varying Contact Time at pH 7 by Adsorbent (Opuntia Dilleni).

Time	% Adsorbance (5 ppm)	% Adsorbance (4 ppm)	% Adsorbance (3 ppm)
50	17.4	18.2	19.1
100	24.6	29.3	33.9
150	36.8	40.5	45.8
200	43.5	43.4	55.7
250	50.2	52.4	63.6
300	54.7	59.1	69.9
350	59.2	64.2	75.8
400	64.6	68.6	80.5
450	67.3	70.8	84.4
500	69.4	74.5	86.5
550	70.6	76.4	87.4
600	70.9	76.8	87.6
650	72.3	78.3	87.9
700	72.8	78.5	88.2

Table 3: Adsorbance of Fluoride varying Contact Time at pH 8 by Adsorbent (Opuntia Dilleni).

Time	% Adsorbance (5 ppm)	% Adsorbance (4 ppm)	% Adsorbance (3 ppm)
50	9.5	13.2	16.2
100	15.2	23.1	22.0
150	23.4	34.6	36.4
200	32.1	38.2	42.1
250	39.6	45.6	49.6
300	45.7	53.2	56.4
350	52.6	55.1	60.1
400	54.7	59.8	65.4
450	55.6	62.3	66.2
500	58.5	63.8	70.9
550	58.9	63.9	71.1
600	59.2	64.4	71.4
650	59.7	64.8	72.5
700	57.2	70.1	73.7

8. RESULT AND CONCLUSION

Fluorosis is an important public health problem in India. Drinking water is one main source of ingestion of fluoride. All the three tables and diagram show the effect of contact time on the percentage adsorbance of fluoride at different concentration of 5, 4, 3, ppm at the different concentration of (6, 7, 8 pH) used adsorbent prepared from Opuntia Dilleni. It has observed that with the increase in contact time the percentage rate of adsorption of fluoride also increases rapidly up to 450 minutes and then increases very slowly with the increase in contact time up to 700 minutes the Maximum adsorption was observed at the pH 7. The investigation and result reveal excellent performance of adsorbent for removal

of fluoride from drinking water. So, by applying the process mention we can remove the excess fluoride content from the water sample.

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