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A Novel adsorbent for the removal of fluoride using Arenthrmum leaves

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Abstract: Fluorine is the most electronegative element in periodic table, due to which, it has highest electron affinity and readily combines with any metal to form simple as well as complex compounds. Fluoride is naturally as well as artificially present in soil and water, the basic natural resources. Presence of fluoride in water, an essential resource for not only human beings, but also flora as well as fauna is proving out to be a serious issue from few decades as it causes Fluorosis. Various methods are applied to defluoridise the drinking water and bring fluoride concentration up to prescribed levels as depicted by different organizations. Adsorption method has proven to be having considerable effect on fluoride removal. The study on the novel adsorbent prepared from arenthrmum leaves was carried out to analyse fluoride removal in contrast with neem leaves, tamarind seeds and charcoal adsorbents. Efficiency was calculated based on fluoride removal including parameters as flow rate and time. Despite this, saturation period was calculated for the efficient adsorbent.

Keywords: Fluoride, Fluorosis, Adsorbent, Adsorption, defluoridise, saturation.

I. INTRODUCTION

I. Fluoride:
Occurrence: -Fluorine is the thirteenth most abundant naturally occurring element in the Earth's crust and is lightest member of the halogens. Fluorine is the most electronegative element and is extremely reactive, it has found in nature as fluoride mineral complex and not in elemental form. It occurs in crust as fluorspar(CaF_2), rock phosphate, cryolite(Na_3AlF_6), apatite($Ca_5(PO_4)_3F$), mica and hornblende. Fluoride leaches off into ground water from these minerals. Despite these minerals, man-made causes such as mining and use of pesticides contaminates water resource with fluoride. There are numerous fluoride belts throughout the world where ground water contains unsafe levels of fluoride. Due to rapid urbanization and growth of modern industries (anthropogenic source of fluoride) as well as geo chemical dissolution of fluoride bearing minerals (natural source of fluoride), its concentration is increasing in the environment including water resources. Hence, fluoride is present naturally as well as artificially in water resources contaminating it despite other inorganic elements like chloride, Sulphate, cyanide, arsenic, calcium, magnesium and many more.

II. Fluorosis: -Increase in fluoride consumption causes disease known as Fluorosis which is being highlighted all over the world. It has attained alarming dimensions all over the world, in India, it is one of the serious health problem.

A. Dental Fluorosis: It is loss of luster and shine of the dental enamel. The discoloration starts from white yellow, brown to black. Enamel matrix is laid down on incremental lines before and after birth. Hence dental fluorosis is invariably seen on horizontal lines or on bands on surface of teeth. The minimal daily intake of fluoride causing mild fluorosis is estimated to be about 0.1 mg/kg body weight.

B. Skeletal Fluorosis: Excessive quantity of fluoride deposited in the skeleton, which is more in cancellous bone than cortical bone. Fluoride presence leads to severe pain associated with rigidity and restricted movements of cervical and lumbar spine, knee and pelvic joints as well as shoulder joints.

C. Non-Skeletal Fluorosis: Despite teeth and bone, excess of fluoride can cause several other kind of manifestations. It includes neurological, muscular, allergic, gastro-intestinal as well as urinary tract issues.

D. Drug Induced Fluorosis: Prolonged consumption of drugs containing sodium fluoride is known to cause skeletal fluorosis. Fluoridated toothpaste and mouth rinses may cause drug induced fluorosis.

E. Industrial Fluorosis: A number of industries use hydrofluoric acid and fluoride containing salts, in the different sections of an industry for several reasons as such. Industries like aluminium, steel, enamel, pottery, glass and many more.

III. Effects of Fluoride content: -
Table1: Effect of fluoride on the basis of its concentration in intake medium.

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Concentration of Fluorides	Medium	Effects
1 ppm	Water	Dental caries reduction
2 ppm or < 2 ppm	Water	Mottled enamel (dental fluorosis)
8ppm	Water	10% osteosclerosis
20-80 mg/day	Water or food	Crippling skeletal fluorosis
50 ppm	Water or food	Thyroid changes
100 ppm	Water or food	Growth retardation
125 ppm	Water or food	Kidney changes
2.5-5.0 g	Acute dose	Death

IV. Prevention and Control: - Fluoride contamination can be prevented or minimized by using alternative water resources, these can be as

1) Surface Water
2) Rain Water
3) Low- Fluoride Groundwater

V. Scenario: - In India, many states are affected by fluoride contamination which includes Andhra Pradesh, Assam, Bihar, Delhi, Gujarat, Kerala, Maharashtra, Madhya Pradesh, Punjab and many more states. Several districts of all these states are at risk.
Despite in India, fluoride has spread its effect internationally which includes UK, US, Australia and many more as such.

VI. Permissible limits for fluoride:

1) Bureau of Indian Standards (BIS)- 0.6 to 1.2 mg/lit
2) World Health Organization (WHO-1984) for drinking water- 1 to 1.5 mg/lit
3) Indian Council of Medical Research (ICMR-1975)- 1 mg/lit
4) World Health Organization (WHO) European standards- 0.7 to 1.7 mg/lit

VII. Defluoridise techniques: Defluoridisation is simply removal of fluoride. Fluoride removal is must because of its effects. Techniques used for defluoridisation are as:

A. Precipitation- Coagulation: Lime and alum are the most commonly used coagulants, addition of lime leads precipitation of fluoride as insoluble calcium fluoride and raise pH value up to 11-12. Alum causes coagulation by forming insoluble aluminium hydroxide. The best fluoride removal is accomplished at pH range of 5.5-7.5.

B. Electrochemical Method: The process utilizes 0.3 to 0.6kwh of Electricity per 1000litre of water containing 5-10 mg/L of fluoride. The anode is continuously consumed and needs to be replenished. The process generates sludge at the rate of 80-100g/1000L (on dry basis).

C. Ion-Exchange Mechanism: It is classified as
a) Anion exchange resin: Strong base exchange resins remove fluorides either on hydroxyl cycle or chloride cycle along with anions. Some inorganic ion-exchangers e.g. complex metal chloride silicates, formed from barium or ferric chloride with silicic acid, also exchange fluoride for chloride. Polystyrene anion exchange resins and strongly basic quartnery ammonium type resins are well known to remove fluorides from water along with other anions.
b) Cation exchange resin: Cation exchange resins impregnated with alum solution have been found to act as defluoridating agents. "Avaram bark" based cation exchange resin works effectively in removing fluoride from water.

D. Membrane Process: Although various conventional techniques are present to be used but none of them are user-friendly and cost-effective due to some limitations. Reverse Osmosis(RO) membrane process has emerged as a preferred alternative to purify water.

E. Adsorption Method:
a) What is it?
Adsorption is the phenomenon of accumulation of large number of molecular species at the surface of liquid or solid phase in comparison to the bulk.

b) How it occurs?
The process of adsorption arises due to presence of unbalanced or residual forces at the surface, while absorption means uniform distribution of the substance throughout the bulk, adsorption essentially happens at the surface of the substance. When both Adsorption and Absorption processes take place simultaneously, the process is called sorption.
Adsorption process involves two components Adsorbent and Adsorbate. Adsorbent is the substance on the surface of which adsorption takes place. Adsorbate is the substance which is being adsorbed on the surface of adsorbent.

Adsorbate + Adsorbent ↔ Adsorption + Desorption

c) Features of Process: -
Adsorption is a spontaneous process: - For reaction or process to be spontaneous, there must be decreases in free energy of the system i.e. ΔG of the system must have negative value.Also we know,

$$\Delta G = \Delta H - T\Delta S$$

And during this process of adsorption, randomness of the molecule decreases which ΔS is negative. We can rewrite above equation as

$$\Delta G = \Delta H + T\Delta S$$

Therefore, for a reaction to be spontaneous ΔH has to be negative and

$$|\Delta H| > |T\Delta S|$$

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Adsorption is an exothermic process: -Adsorption process takes place by adsorbate getting adsorbed on adsorbent. Forces of attraction exist between adsorbate and adsorbent and due to these forces of attraction, heat energy is released during adsorption. So adsorption is an exothermic process. [1]

II. LITERATURE SURVEY

I. Neem leaves powder as a low-cost adsorbent and its characteristic by Ghanshyam Pandhare and S.D Dawande: In the above paper, the detailed process for the preparation of adsorbent from neem leaves using chemical treatment is depicted finely for the removal of fluoride. The characterization of the adsorbent was done using BET method in order to determine the surface area which was found to be 421m^2/g for particle size of 5micrometer. Chemical treatment was using both acid and base to adjust pH and the activated carbon was prepared in crucible at 260^{o}C for about 20minutes. It was concluded that it can be used to remove impurity from waste water besides its medicinal utility. It followed Langmuir adsorption theory and removal increased with increased adsorbent dose.

II. Studies on defluoridation of water by tamarind seed, an unconventional biosorbent by M. Murugan and E. Subramanian: -
In the above paper, the detailed process for the preparation of adsorbent from tamarind seeds using chemical treatment is depicted finely for the removal of fluoride. Tamarind seeds was soaked in water, dried in oven at 110^{o}C for an hour then was powdered succeeded by sieving. Desorption of the adsorbed fluoride was carried out using HCL solution of known normality. It was observed that it follows first order kinetics and Langmuir type behavior.

III. Defluoridisation of drinking water: Efficacy and need by Anurag Tewari and Ashutosh Dubey
In the above paper, the detailed effect of fluoride contamination was depicted along with its symptoms and remedial measures. Fluorosis types including skeletal, non-skeletal, drugs induced, dental and industrial are covered in this paper.

III. MATERIALS & METHODS

I. Materials: -
Raw Materials: -
A. Neem Leaves

Fig 1. Neem Leaves

B. Tamarind Seeds

Fig 2. Tamarind Seeds

C. Activated Charcoal

Fig 3. Activated Charcoal

D. Arenthrmum Leaves

Fig 4. Arenthrmum Leaves

Chemicals Procurements: -
1. Distilled water
2. Potassium Hydroxide (KOH)
3. Sodium Hydroxide (NaOH)
4. Sodium Fluoride (NaF)

II. Methods for Adsorbent Preparation: -
1) Physical treatment: Fresh Leaves were chosen and was cleaned succeeded by crushing manually so as to save energy while, tamarind seeds were washed, dried and then powdered manually.
2) Chemical Treatment: The powdered leaves were treated with 2N NaOH solution while, the powdered tamarind solution was treated with 4N KOH solution. On the contrast, activated charcoal was readily brought from chemical shop (was not synthesized).
3) Stock Preparation: Stock is prepared using Sodium fluoride (NaF) in distilled water to make a solution of 9.25ppm.

IV. EXPERIMENTATION

I. Setup: -
It consists of cylindrical column with conical end, Inlet is at the top while outlet is collected from bottom end. The column is filled with the adsorbents prepared simultaneously of fixed dimension (30.4x27.66) cm

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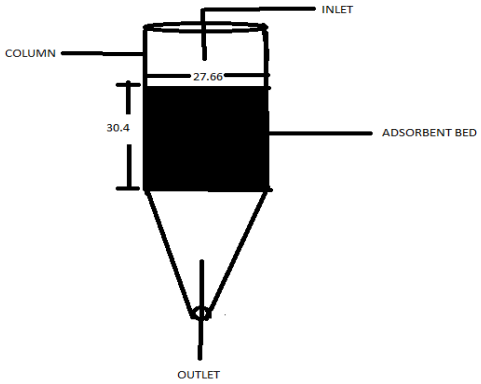

Fig 5: Adsorption Column

II. Procedure: -

1) The cylindrical column is filled with adsorbent simultaneously of specified dimension (30.4x27.66) cm.

2) The stock prepared is flowed through the bed of adsorbent.

3) As it passes through the bed, the fluoride content of stock solution is removed as it gets adsorbed at the pores of adsorbent (Adsorption).

4) The fluoride removed is calculated by marking difference in final and initial concentrations.

5) Final concentration of fluoride is calculated using fluoride selective electrode method, while the initial concentration is known.

6) The most efficient fluoride removal adsorbent was further used to calculate the saturation period.

III. Analysis: -

- Fluoride Selective Electrode: It is most important electro analytic method for determination of fluoride ion in water and is sensitive. Temperature ranges from 0 to 50^{o}C. The electrode used is fluoride lantana (LaF_3).
- Other methods that can be used to find fluoride content in the solution is titration method using thorium nitrate titrant and Alizarin Red S. indicator in a nesseler cylinder.

IV. Cost Estimation: -

1) Chemicals : Rs. 660
2) Charcoal (10 Kg) : Rs. 100
3) Tamarind seeds : Rs. 500
4) Neem Leaves : Rs. 100
5) Arenthrmum Leaves : 189 per plant

For 200g of adsorbent, the cost estimated for different adsorbent using:

- Neem :Rs. 50
- Tamarind :Rs 242
- Charcoal :10 per kg
- Arenthrmum :Rs.50

V. RESULT AND DISCUSSION

Experimental results on Run: -

Table 2. Actual experimental results

Adsorbent	Inlet (ppm)	Flow Rate (ml/ min)	Outlet (ppm)	Time for Collection (hrs.)
Arenthrmum (Arum Maclatum)	9.25	4	7.87	4.5
Activated Charcoal (Physiculus nematopus)	9.25	16	8.04	1.0
Tamarind (Tamarindus Indica)	9.25	3	8.96	5.5
Neem (Azadirachta Indica)	9.25	8	9.04	2.5

1) After experimentation, it is concluded that Arenthrmum is the most efficient adsorbent.
2) The experimentation holds parameters like flow rate of stock through the bed and the time taken for collection of stock through the bed.
3)The fluoride concentration was calculated using fluoride selective electrode method.
The efficiency for all the above named adsorbents are calculated based on the tabular data and it is given as in table below:

Table 3 Efficiency of Adsorbents

Sr. No.	Adsorbent	Adsorption efficiency (%)
1	Neem	2.27
2	Tamarind	3.14
3	Activated Charcoal	13.08
4	Arenthrmum	15

The most efficient adsorbent that is arenthrmum was further used up to calculate the saturation period by constantly passing stock solution through the bed and frequently measuring fluoride concentration. It is given as below in observation table:

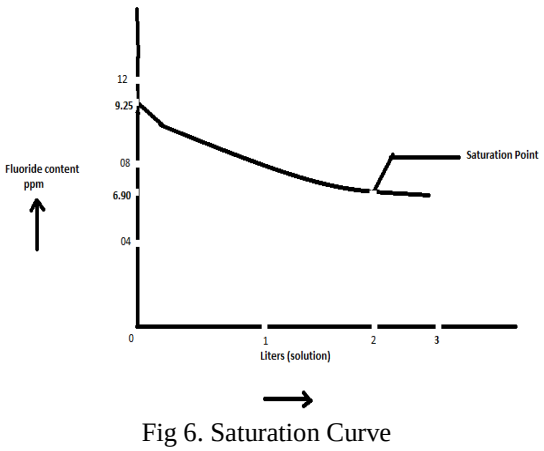

Fig 6. Saturation Curve

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Table 4 Fluoride Concentration per lit solution

Volume of Solution (litres)	Fluoride Concentration (ppm)
0	9.25
1	7.87
2	6.9
3	6.9

VI. CONCLUSION

We studied different methods of defluoridisation out of which our focus was on adsorption method using different adsorbent prepared from neem, tamarind, activated charcoal and arenthrmum. The adsorbent prepared from arenthrmum leaves was found to be efficient among all the four adsorbents and saturation period was calculated for it. The adsorbent was prepared using physical and chemical treatment along with the stock preparation using sodium fluoride. The obtained result for arenthrmum was found to be good enough in comparison with other three adsorbents. Despite, the result for arenthrmum could be expected to be raised by undergoing pyrolysis or by altering the chemical quantity used for activation. The filtrate obtained was colored and viscous. The expected reason could be presence of particles of adsorbent or due to the excess presence of the chemical used for treatment. Thus, it can be concluded that adsorption despite being complex phenomenon due to the recovery issues of adsorbent used yet it has found its application in almost several sectors. Adsorption, thus is a rising technique for the development too.

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