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Research Article

REMOVAL OF FLUORIDE FROM GROUND WATER BY USING BIO-ADSORBENTS LIKE Aegle Marmelos (Bilve Patra)

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A B S T R A C T

Osteo-dental fluorosis was investigated in Fatehpura, Mewadi, Jhariyana, Indora, Deotalab, Dad, Bokedsal villages of Dungarpur and Matasula, Amlu, Dagar, Thada, Bhabrana, Dhamodar, Jhalara villages of Udaipur districts of southern Rajasthan, where fluoride concentrations in drinking waters range from 1.5 to 4.0 ppm. The aim of the present research work is to design and develop a novel, cost-effective strategy for fluoride removal from ground water. The feasibility of low-cost biomass-based adsorbent like Bilve Patra used for defluoridation of ground water at different pH and contact time the effect of this adsorbent on fluoride removal was compared with other available adsorbents. In ground water we found to be much better adsorbent with high removal efficiency at higher concentration (5 ppm) of fluoride. The effect of time for adsorbent and initial concentration of fluoride on the % removal was also studied. Adsorption was found to be pH dependent with maximum removal efficiency at pH 7.0 (in neutral medium).

INTRODUCTION

Around one million people in India are affected by endemic fluorosis [1, 2]. The incidence of high-fluoride groundwater has been reported from 23 nations around the globe. Maximum permissible limit of fluoride in drinking water has been set as 1.5 mg/ L by many regulatory authorities like WHO, US EPA, CPCB etc. Besides the natural geological sources for fluoride enrichment in groundwater, various industries are also contributing to fluoride pollution to a great extent [3] there are many processes available such as adsorption, ion exchange, electrodialysis, coagulation/ precipitation, dialysis, reverse osmosis, nano-filtration, ultra-filtration, etc., for the removal of fluoride from water [4-17]. Further, agro-based adsorbents are getting more attention now a days due to their abundant availability and low cost. Some literatures are available on the removal of fluoride from water using various agro-based adsorbents like rice husk ash, neem leaf, peepal leaf, khair leaf, tamarind fruit shell, etc. [18-20].

The "mottled enamel", occurs when the fluoride level in drinking water is marginally above 1.0 mg/l. A relationship between fluoride concentration in potable water and mottled enamel was first established in 1931. Typical manifestations of dental fluorosis are the loss of shining and development of horizontal yellow streaks on teeth. Since this is caused by high fluoride in or adjacent to developing enamel, dental fluorosis develops in children born and brought up in endemic areas of fluorosis. Fluoride levels exceeding 3 mg/l produce skeletal fluorosis which affects both adults and children and is generally manifested after consumption of water with. Typical symptoms of skeletal fluorosis are a pain in the joints and backbone. In severe cases, this can result in crippling the patient. Some studies also found have certain non-skeletal health impacts such as gastro-intestinal problems, allergies, anemia and urinary tract problems. Nutritional deficiencies can enhance the undesirable effects of fluoride.

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Defluoridation methods can be broadly divided into three categories according to the main removal mechanism

- Chemical additive methods
- Contact precipitation
- Adsorption/ion exchange methods

Adsorption/ion-exchange method

Some materials have been used for fluoride uptake like Bauxite, magnetite, kaolinite, serpentine, various types of clays and red mud are some of the naturally occurring materials studied. Rajasthan is one state where fluoride in high level is prevalent in all the 32 districts and has become a serious health hazard in 18 of them. Sarita Sansthan, Udaipur, Rajasthan is disseminating the technique with the practical assistance of UNICEF by providing a bucket (approximately 20 L capacity) fitted with a microfilter at the bottom containing 5 kg of activated alumina.

According to the survey conducted by the Public Health Engineering Department in the recent past, the drinking water sources in 9741 out of 37889 villages, 25.7 %, and 6819 out of 45311, 15 %, habitations were found to contain fluoride more than 1.5 mg/L In the absence of perennial rivers, surface sources and canal systems, groundwater, which generally contains high concentrations of fluoride, Many natural and low-cost materials such as red mud [21-22], zirconium impregnated coconut shell carbon [23], cashew nut shell carbon [24], ground nut shell carbon and clays [25] have been used as adsorbents for fluoride removal from drinking water.

Natural adsorbents

Many natural adsorbents from various trees were tried as defluoridation agents. Seeds of the Drumstick tree, roots of Vetiver grass and Tamarind seeds were few among them. The seeds of the drumstick tree (*Moringa oleifera*) adsorb fluoride from water. Drumstick seeds act as a coagulant. They have long been a traditional method for purification of turbid water in both India and Africa. The Researchers of M. S. Swaminathan Research Foundation" (MSSRF) had shown drumstick seeds to have remarkable defluoridation efficiency, which was higher than that of activated alumina. Many adsorbent materials have been tried in the past to find out an efficient and economical defluoridating agent. The process is highly selective but it has low adsorption capacity, poor physical integrity, requires acidification and pretreatment and its effectiveness for fluoride removal reduces after each regeneration. The use of powdered activated carbon for fluoride removal and achieved good results [26]. New ideas about the removal of fluoride in aqueous and synthetic solutions by adsorption technique that has been given by various researchers in the field of fluoride removal [27].

Advantages of Adsorption Process

Cheap: The cost of adsorbent is low since they are often made from locally, abundantly and easily available materials.

Metal Selective: The metal sorbing performance of different types of bio-mass can be more or less selective on different metals.

***Regenerative*:** Sorbent material can be possible to reuse after regeneration

No Sludge Generation: Unlike the problems in other techniques (ex: precipitation), there is no issue of sludge generation in adsorption process.

Performance: Performance of adsorption process in terms of efficiency and cost is comparable with the other methods available.

MATERIAL AND METHODS

Preparation of Standard fluoride solution (5ppm solution)

A stock solution of 100mg/ liter (100 ppm) of fluoride was prepared by dissolving 221 mg of anhydrous sodium fluoride (NaF) in 1000 ml distilled water. Now 5 ppm solution prepared from stock solution by suitable dilution.

Prepration of adsorbent Aegle Marmelos (bilva patra)

*Aegle Marmelos (*Bilva patra) leaves easily available at a tree, collect and washed with distilled water several times then dried in sunlight for 3-4 days. Now grind this dry leaves with mixer & sieved with suitable mesh size (30 bss size) taken for analysis

Measurement

To observe fluoride Removal used Fluoride Ion Meter Panamax Model PX/IMC/321. First Calibrate with 100 ppm & 10 ppm solution prepared by the stock solution. Now check 5 ppm fluoride solution for system response Washed Plastic beaker with tap water then distilled water Take 100 ml of 5 ppm solution of water in 250ml plastic beaker weigh 1.0 gm of adsorbent hold for 30 minutes after 30 min filter the solution take reading using various parameter like pH, dose of adsorbent and contact time of adsorbent.

RESULTS AND DISCUSSION

(i) Effect of pH

pH	Initial concentration (ppm)	After Four Hour (ppm)	Removal in ppm	% Removal
2.0	5.0	2.9	2.1	42
3.0	5.0	2.8	2.2	44
4.0	5.0	3.0	2.0	40
5.0	5.0	2.9	2.1	42
6.0	5.0	2.5	2.5	50
7.0	**5.0**	**1.9**	**3.1**	**62**
8.0	5.0	2.1	2.9	58
9.0	5.0	2.6	2.4	48
10.0	5.0	2.8	2.2	44
11.0	5.0	2.7	2.3	46

The pH can influence the surface charge of the adsorbent, the degree of ionization also the species of adsorbate. In a particular pH range, most metal sorption is enhanced with pH, increasing to a certain value followed by a reduction when further pH increases. The dependence of the metal uptake on pH can be associated with both the surface functional groups on the biomass' cell walls and also the metal chemistry of the solution [28]. The effect of pH on the removal of fluoride was studies in the range of 2-11 and results are illustrated in the Fig-1. pH plays an important role in adsorption process on bio adsorbents. The results confirm a strong dependence between the adsorption of fluoride and pH, whereby adsorption appears to increases with increasing pH, within a pH range of 1–7. Maximum adsorption was observed at a pH of 7 and 8 for Aegle Marmelos in 1 hr. the pH of the solution governed the ionic form of fluoride in solution and the electrical charge (i.e. functional groups carrying polysaccharides and proteins) on the bioadsorbent.

Where it shows that the overall charge on the surface of bioadsorbent is positive. Positive charge binds the negatively charged fluoride ions. In the case of *Aegle Marmelos*, no effect of pH was observed because it shows the adsorption at neutral pH of 7. At the lower value of pH (< 7) the surface of the adsorbent gets positively charged and sorption of fluoride occurred, probably anionic exchange sorption. In acidic medium because of the protonation, action on the surface functional groups such as amino, carboxyl, thiol, etc., imparts a positive charge on the surface. Relative sorption inhibition occurred at basic pH (>7) range, might be assigned to the increase of hydroxyl ion leading to formation of aqua-complexes; thereby, desorption occurred According to the study of pH optimization, adsorption of bio adsorbent mostly observed in the acidic range of the pH But removal of fluoride in our case has observed in less acidic or neutral range which is more beneficial and cost-effective for the removal.

(ii) Dose of Adsorbent (Aegle Marmelos (**Bilva patra) leaves powder**)

S. No.	wt of adsorbent (gm)	Amount of water 5.0 ppm (ml)	initial concentration before treatment (ppm)	after 4.0 hrs (ppm)	ppm removal	% Fluoride Removal
1	0.2501 gm	100 ml	5.00	2.8	2.20	44
2	0.5012 gm	100 ml	5.00	2.6	2.40	48
3	1.010 gm	100 ml	5.00	1.9	3.10	62
4	**2.010 gm**	**100 ml**	**5.00**	**1.4**	**3.60**	**72**

3. Effect of Contact Time

(a)

Dose gm/100ml	Contact time (minute)	Initial Concentration	Final Fluoride (Mg/L) ppm	Reduction Of Fluoride	% Removal Efficiency
0.2501	30	5.00	4.6	0.40	8
0.2501	60	5.00	3.8	1.20	24
0.2501	120	5.00	3.6	1.40	28
0.2501	180	5.00	3	2.00	40
0.2501	240	5.00	2.8	2.20	44
0.2501	**300**	**5.00**	**2.5**	**2.50**	**50**

(b)

Dose gm/100ml	Contact time(minute)	Initial Concentration	Final Fluoride (Mg/L) ppm	Reduction Of Fluoride	% Removal Efficiency
0.5012	30	5.00	4.1	0.90	18
0.5012	60	5.00	3.4	1.60	32
0.5012	120	5.00	3	2.00	40
0.5012	180	5.00	2.4	2.60	52
0.5012	240	5.00	2.6	2.40	48
0.5012	**300**	**5.00**	**2.3**	**2.70**	**54**

(c)

Dosegm/100ml	Contact time (min)	Initial Concentration	final fluoride (Mg/l)	Reduction of fluoride	% removal efficiency
1.01	30	5.00	3.6	1.40	28
1.01	60	5.00	2.6	2.40	48
1.01	120	5.00	2.4	2.60	52
1.01	180	5.00	2	3.00	60
1.01	240	5.00	1.9	3.10	62
1.01	300	5.00	1.6	3.40	68

(d)

Dose gm/100ml	Contact time (min)	Initial Concentration	Final Fluoride (Mg/L) ppm	Reduction of fluoride	% removal efficiency
2.01	30	5.00	3.4	1.60	32
2.01	60	5.00	2.4	2.60	52
2.01	120	5.00	2.2	2.80	56
2.01	180	5.00	1.6	3.40	68
2.01	240	5.00	1.4	3.60	72
2.01	**300**	**5.00**	**1.2**	**3.80**	**76**

The metal removal efficiency of fluoride through a combination of factors such as the availability of specific surface functional groups and the ability of surface functional groups to bind metal ions.

After 3.0 hrs1 gm adsorbent taken in 100 ml 5.0 ppm water

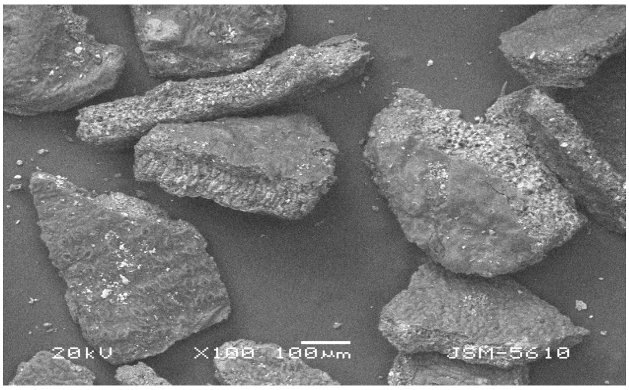
Temperature- °C	Initial Concentration	After 3. Hrs	% Removal of Fluoride
22	5	2.4	52
30	5	2.2	56
40	5	1.8	64
50	**5**	**1.7**	**66**

5. Particle Size of Adsorbent1 gm adsorbent taken in 100 ml 5.0 ppm water

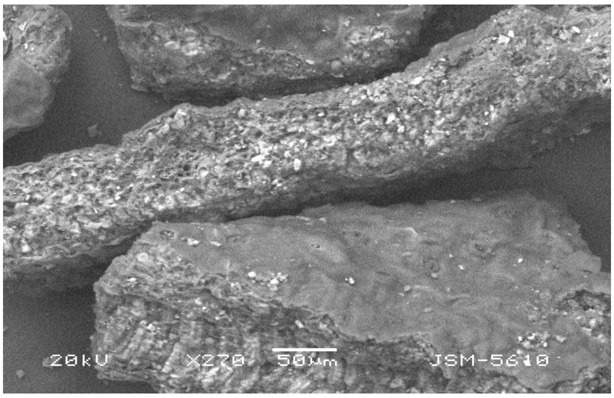
Concentration	60 BSS	52 BSS	36 BSS	30 BSS
Initial	5	5	5	5
After 4 Hour	3.2	3	2.4	1.9
Ppm Removal	1.8	2	2.6	3.1
% Removal	**36**	**40**	**52**	**62**

The initial concentration of a solution can provide an important driving force to overcome the mass transfer resistance of metal between the aqueous and solid phases [28]. The removal efficiency of fluoride is strongly dependent on concentration of adsorbent dose in test sample. Removal of fluoride increases as increasing dose of adsorbent in the sample as shown in Fig-2. At the starting, removal of fluoride increases as increasing the dose until some extent after that very slight change in the removal of fluoride itmeans, the curve indicating the higher fluoride adsorption occurs at their maximum dose and the removal remains constant. Adsorption increases after that adsorption of fluoride is constant at higher dose because of saturation of pore volume and surface. Efficiency for Aegle Marmelos leaves powder from 2.8 ppm to 1.4 ppm, for the dose range 0.25-2.01 gm/100 ml.

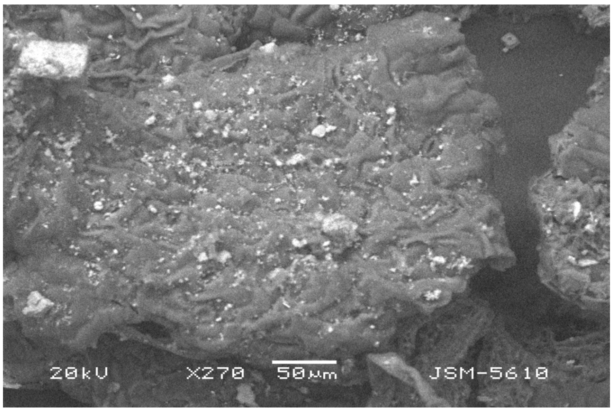
It is observed that the exclusion of fluoride ions increases with increase in contact time to some level at optimum pH and dose. Further increase in contact time does not increase the Fig-3 explains the optimum percentage removal of fluoride by three considered bio adsorbents at different contact times. The adsorption of the metal ion by adsorbent also depends on the interactions of functional groups between the solution and the surface of the adsorbent. Adsorptions can be assumed to be complete when equilibrium is achieved between the solute of the solution and the adsorbent. However, a specific time is needed to maintain the equilibrium interactions to ensure that the adsorption process is complete [29]. However, it progressively approached an almost steady value, denoting accomplishment of equilibrium, these similar trends also observed in Effects of stirring rate and temperature on fluoride removal by fishbone charcoal [30].



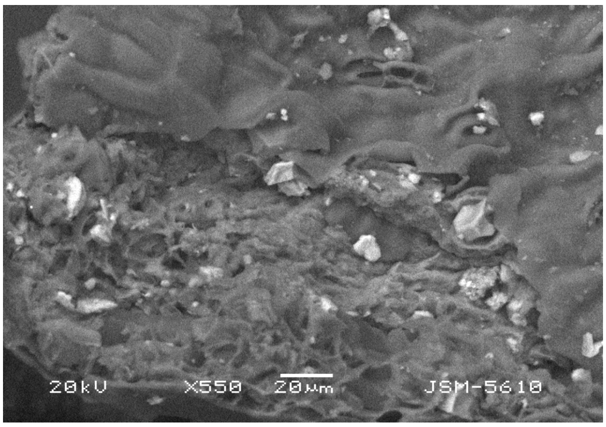
1SEM Image of Bilve Patra Powder (Aegle Marmelos) before treating



2 SEM Image of Bilve Patra Powder (Aegle Marmelos) before treating



3 SEM Image of Bilve Patra Powder (Aegle Marmelos) after treating



4 SEM Image of Bilve Patra Powder (Aegle Marmelos) after treating

Fluoride removal efficiency was decreased by increasing the initial fluoride concentration because of the fixed dose of adsorbent capacity adsorbents gets saturated at high concentration. Pore volume and active sites of the adsorbents filled by the fluoride finally its removal is decreased. The similar trend has been reported for fluoride removal by using Neem charcoal [31].

The defluoridation methods depend on hot climates, for sorption capacities attained under room temperature conditions may be higher than in the field as a result of increased temperatures [32]. Temperature can impact the physical binding processes of fluoride to a sorbent. However, temperature also can have a direct impact on the physical properties of a sorbent, if thermally treated prior to exposure, so that sorption capacities can be significantly altered. As temperature increased, sorption was shown to be less favored most likely due to increased deprotonation or hydroxylation of the surface causing more negatively charges sorbent surfaces. It is clear that smaller the particle size increase the % removal of fluoride in ground water. The Smaller particle sizes reduce internal diffusion and mass transfer limitation to the penetration of the adsorbate inside the adsorbent. Addition of the powdered adsorbent must be followed by their removal.

***Analysis of Sample*: -** The EDS and SEM analysis of the sample of Bilve Patra (Aegle Marmelos) powder after treated with fluoride water attached to this file in figure form.

CONCLUSIONS

The paper briefly highlighted the importance of adsorption process and its benefits. Also, the overview of various papers publishes in various journals on the removal of fluoride ions from water or wastewater by adsorption using various low-cost adsorbents instead of expensive commercial adsorbents. The efficiency of different adsorbents in the removal of fluoride depends on the dose of adsorbate, characteristics of adsorbent, pH, temperature, contact time, etc. The study of various low-cost adsorbents presented here shows a great potential for the fluoride removal. The use of commercially available adsorbents can be replaced by the inexpensive and effective low-cost adsorbents. There is a need for more studies to better understand the process of low-cost adsorption and to demonstrate the technology effectively.

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