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Research Article

An Investigation Of Fluoride Distribution In Nawa- Makrana Zone Of Nagaur District, Central Rajasthan, India And Defluoridation Of Water From Plant Material.

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Abstract
This study focuses on groundwater fluoride contamination investigations in the Nagaur district's Nawa Makrana zone, where groundwater serves as the primary supply for irrigation and drinking. In the Nawa-Kuchaman zone, 31 communities provided groundwater samples, 10 of which had fluoride amounts over the safe drinking water threshold of 1.5 mg/L. The results show that 10 of these villages have groundwater that is not suitable for consumption because of high fluoride levels. Areas of concern were outlined in a fluoride concentration map for the region. The fluoride concentration was highest in Piprali village (5.8 mg/L); and lowest in Bawali Guta (0.3 mg/L). A low-cost defluoridation technique using plant-based materials was employed to mitigate health risks associated with high Fluoride levels. Fluoride concentration in treated samples was reduced to the acceptable range (0.5 – 1.5mg/L) meeting drinking water quality standards. The importance of the development of efficient, low-cost methods of fluoride removal in affected areas is highlighted by this study.

Keywords: Carbon adsorbents, Plant byproducts, Defluoridation, fluoride, Groundwater, Central Part, Nagaur, Rajasthan.

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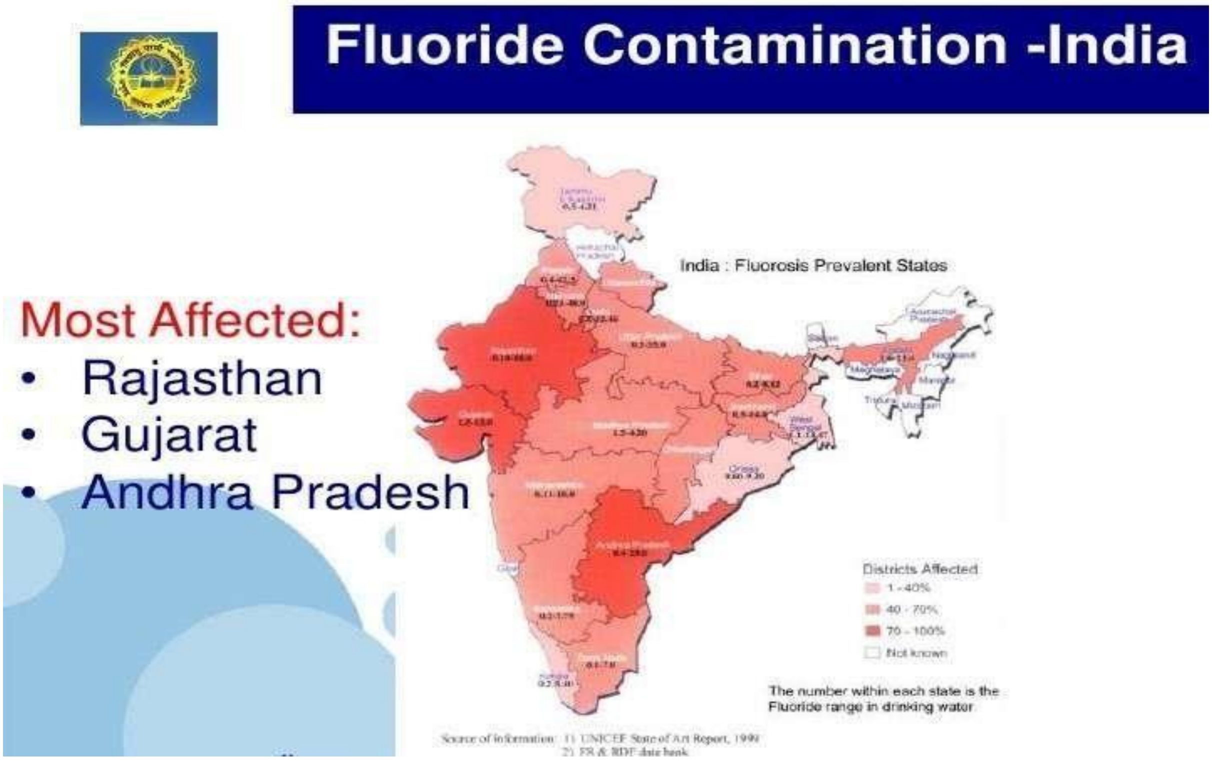
Introduction

Excessive fluoride and arsenic in groundwater, which is used for drinking water, constitute major public health challenges to India. About 0.06–0.09% of it is fluoride, which is the 17th most abundant element in the Earth's crust (1). The correct mineralization of bones and the formation of dental enamel depends on fluoride, yet high fluoride concentrations in groundwater pose a serious health danger (2). In general, high fluoride levels above acceptable limits can be toxic to humans and animals with metabolic disturbances such as dental and skeletal fluorosis. Water is a life-giving and changing resource, critical to the survival of all life (5-6). Without productive human endeavors like agriculture and animal management, it is hard to imagine a stable and sustained water supply. Water resource management is very much dependent upon water quality. The change is influenced by natural and human activities such as regional climate, geology, and agricultural practices. Due to high fluoride levels in their drinking water, about 200 million individuals across 25 nations are more vulnerable to poor health (7). Several researches in India have been carried out on water quality, particularly fluoride concentrations (8-10). About 177 areas of 19 states have excessive fluoride levels in groundwater. Many additional areas are likely to have high fluoride concentrations (11).



The largest state in India, Rajasthan, is 342,239 km^2 in size and has a comparatively low population density of 165 persons per km^2. While the southern, central, and eastern parts of the state make up the Peninsular Plateau, the northern and western parts are part of the Great Plain of North India (12). There is variation in the fluoride contamination levels in the groundwater across all 32 districts in Rajasthan. Traditional 'high fluoride' areas in the state's west and south have been the focus of the majority of studies assessing fluoride contamination in groundwater (13,14). The literature review indicated that no studies have been conducted in the study area of fluoride contamination and fluorosis. As a result, this study was undertaken to assess the fluoride concentrations in drinking water (groundwater) in the southwestern region of the Nagaur district. Spatial interpolation techniques using inverse distance weighting were used to map fluoride distribution. Currently, various methods are being used to remove fluoride from drinking water. The removal of fluoride from drinking water has been studied using alumina, bone char, industrial by-products, ion exchange resins, and reverse osmosis. A review of the literature, however, does not find any prior work in this field, even though the materials employed in this investigation have never been published before. There are several defluoridation methods available, but they are expensive and unsuitable for widespread use. In this study, we investigate the use of adsorbent carbon materials produced from seeds of different plants and compare the results with commercial activated carbon (CAC). Fluoride levels in drinking water are deemed safe in India when they fall between 0.6 and 1.2 mg/L; fluorosis occurs below that threshold (1.2 mg/L) (15). In the Thar Desert, which makes up almost 61% of the state's total territory, groundwater serves as the main source for irrigation, drinking, and household use (16). It lies between 26°25' and 27°40' N and 73°18' and 75°15' E on longitudes and latitudes respectively. The average elevation of the district is about 300 meters, the southern part is less than 250 meters, and the northern part to 640 meters. It includes 1,396 settlements. The Bhilwara and Delhi Supergroups of the Archaean and Proterozoic eras contain the region's main geological formations, which include gneisses, schists, quartzites, phyllites, and limestones. In the Nagaur District, groundwater is found in a variety of formations, primarily under water table conditions, and the Quaternary alluvium is a good aquifer. Secondary porosity characteristics like fractures, joints, fissures, and foliation regulate the presence and flow of groundwater in hard rock terrains. According to a survey of the literature, no research has been done on the fluoride levels in the district's groundwater.

With a focus on fluoride concentrations, this study sought to evaluate the drinking water quality in central Nagaur District, Rajasthan, India. Numerous studies have documented fluoride levels in the drinking water of various districts in Rajasthan, except Pratapgarh, a newly created district.

Table 1 presents data from all surveyed districts

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Table no. 1: Different districts of Rajasthan contain fluoride content of drinking water sources.

S No.	District	F-content groundwater	Reference
1.	Ajmer	0.1-12 0.25-16.9	Madhavan and Subramanian' 2003 Vikas et al2009
2.	Alwar	1.5-9.9 2.22-7.62	Agrawal et al.1997 Sharma et al2012
3.	Banswara	1.2-4.6	Choubisa 2001
4.	Baran	0.2-1.2	Seth et al 2005
5.	Barmer	0-10+	Ozha et a12003
6.	Bharatpur	1.5-4.9	Agrawal et aL. 1997
7.	Bhilwara	0.4-13	Hussain et atr 1010
8.	Bikaner	1.5-9.9	Agrarwal et al- 1997
9.	Bundi	0.0-5.0	Seth et al 2005
10	Chittorgarh	0.0-6.0	Seth et al 2005
11.	Churu	0.0-6.5	Seth et al 2005
12.	Dausa	1.5-9.9	Agrawal et al.l997
13.	Dholpur	1.5-4.9	Agrawal et al.l997
14.	Dungarpur	1.5-4.9 0.1-10 1.1-4.1 1.4—6.0	Agrawal et al.l997 Madhavan and Subram aniai 2004 Choubisa 200 Ayoob and Gupta 2006
15.	Hanumangarh	1.01-4.78 0.5-8.5	Suthar et al 2008 Chaudhary et al 2008
16.	Jaipur	1.5-10+ 4.5-28.1	Agrawal et al.1997 Madhavan and Subram anian 2004
17.	Jaisalmer	3.0-10+ 0.2-4.6	Agrawal et al. 1997 Madhavan and Subramanian 2004
18.	Jalor	1.5-10+	Agrawal et al. 1997
19.	Jhalawar	0.0-1.2	Seth et a|2005
20.	Jhunjhunu	0.6-8.8	Seth et a|2005
21.	Jodhpur	0.4-6.5	Seth et a|2005
22.	Karauli	0.5-4.5	Seth et a|2005
23.	Kota	1.2-4.8	Seth et a|2005
24.	Nagaur	1.5-10+ 0.0-10+ 1.1-14.62	Agrawal et al.1997 Ozha et a12003 Gautam et al2011
25.	Pali	Upto10+ 5.6 0.0-10+	Agrawal et al. 1997 Madhavan and Subram aman 2004 Ozha et a12003
26.	Pratapgarh		
27.	Raisamand	0.0-4.5	Seth et al 2005
28.	Sawai Madhopur	1.5-10+	Agrawal et al.1997
29.	Sikar	1.5-10+	Agrawal et al.1997
30.	Sirohi	1.5-9.9 <1.0-16.0	Agrawal et al.1997 Madhavan and Subramanian 2004 Maithani et al. 1998

31.	Sri Ganganaga	0.5-5.0	Chaudharv et al 2008
32.	Tonk	0.5-12.4 0.5-10.7 1.5-11.82	Seth et al 2005 Yadav and Khan, 2010 Bhargava and Bhardwaj, 2009
33.	Udaipur	0.1-11.7 0.2-4.7	Madhavan and Subram aman 2004 Choubisa 2001

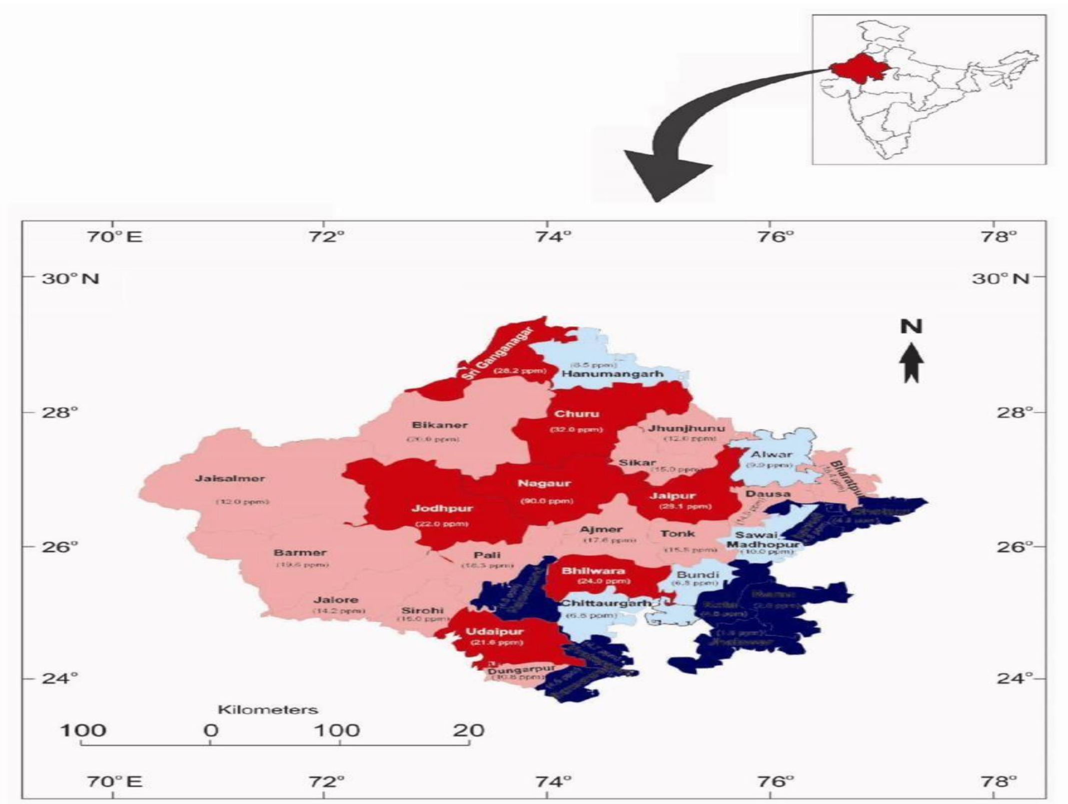
WHO guidelines and BIS standards (IS: The World Health Organization (WHO, 1991; 10500-1991) states that 1.5 mg/L of fluoride is permitted in drinking water for human use. However, individuals in a number of Rajasthani districts are consuming water that has fluoride levels up to 24 mg per liter, which is significantly more than the recommended level.

Objective:

- An examination of Rajasthan's fluoride distribution.
- An investigation into the fluoride content of groundwater in the Nagaur District's Nawa-Makrana area in Central Rajasthan, India.
- Research on the application of plant-based materials to defluoridate water.

Study Area:

Nagaur District is centrally located in Rajasthan, sharing borders with neighboring districts. It is situated between latitudes 26°25' to 27°40' N and longitudes 73°18' to 75°15' E. Approximately 17,718 square kilometers make up the district. The research area comprises Makrana, which is situated at latitudes 27°01' to 46°62' N and longitudes 74°71' to 58°76' E, and Nawa, which is located at latitudes 27°1' to 34°15' N and longitudes 75°0' E.



Material and Method

Water Sample Collection

Pre-cleaned polyethylene bottles were used to collect groundwater samples from 31 villages of the Nawa-Makrana region of Nagaur District, following necessary precautions. Samples were collected in 2022 from wells close to residential areas and manually operated public hand pumps.

Methodology

A fluoride ion-selective electrode was used to electrochemically quantify the amount of fluoride present in water. This technique can be used to find fluoride concentrations in drinking water between 0.01 and 1000 mg/L. For the analysis, an Orion electrometer was used in conjunction with an Orion fluoride electrode. A stock solution with 100 mg/L of sodium fluoride was used to create standard fluoride solutions (0.1–10 mg/L). Ten milliliters of the sample were mixed with one milliliter of Total Ionic Strength Adjustment Buffer (TISAB III) for the experiment. The slope at which the ion meter was calibrated was -59.2 ± 2. 385.4 g of ammonium acetate, 17.3 g of cyclohexylene diamine tetraacetic acid, and 234 mL of concentrated hydrochloric acid per liter were used to make the TISAB solution. With a repeatability error of ±2%, all tests were performed in triplicate, and the results were consistent.

Preparation of TISAB-III

Combine 234 milliliters of strong hydrochloric acid with 250 milliliters of deionized water. 17.3 g of 1,2-cyclohexylene dinitroacetic acid (CDTA) and 385.4 g of ammonium acetate should be added to this. After mixing until completely dissolved, let it cool to room temperature. Finally, dilute to a total volume of 1000 mL.

Procedure

Before the instrument is ready for measurement, it is calibrated using a set of standards within the proper concentration range (0.1 mg/L, 1.0 mg/L, and 10.0 mg/L) to obtain a slope of −59.2 ± 2 mV. Sample analysis involves measuring the fluoride concentration after mixing 10 mL of the sample with 1 mL of TISAB III.

Spatial Distribution of Fluoride Using Inverse Distance Weighted Method

The dry fruits of Citrus limon (CLC) from the Rutaceae family and Enterolobium saman (ESC), Acacia arabica (AAC), and Prosopis juliflora (PJC) from the Mimosideae family were gathered in manufacturing locations and used to make defluoridating products. The materials, which are agricultural wastes, were carbonized in a muffle furnace at temperatures between 400°C and 500°C. The resultant char was chemically treated using a 0.5 M HNO_3 solution, rinsed with distilled water, and sieved to produce particles that were 75 µm in size. A computer program created to gather, store, process, evaluate, organize, and display spatial data is called a Geographic Information System (GIS). GIS effectively manages geographic data in a digital format to meet various needs. The Inverse Distance Weighted (IDW) interpolation technique is derived based on the idea that points that are close together will be more similar than those that are farther apart. Values are estimated at unmeasured locations about nearby measured values. The proximity to the prediction points of measured values affects estimates, with measured values closer to the prediction point having a stronger effect than those farther away. IDW assumes that the influence of a measured point decreases with the distance. Consequently, areas closer to the prediction location are assigned greater weights which decrease as distance increases.

CAC was used for comparison with other materials. To make the CAC, 0.5 g of adsorbent carbon was combined with 100 ml of water samples and shaken at 100 rpm for 30 minutes on a Remi shaker. Whatman No. 42 filter paper was used to filter the mixture, and an ion-selective electrode was used to evaluate the filtrate. The ideal pH range for the batch mode investigation was 6.9–9.0, the agitation time was 40 minutes, and the adsorbent concentration was 5g. The same settings were used to defluoridate drinking water samples in the batch mode investigation. For groundwater with fluoride concentrations between 3.0 and 6.0 mg/L, the adsorbent dose was 5 g/L; for samples with fluoride levels between 1.5 and 3.0 mg/L, it was 4.0 g/L. However because they believe the water from deeper wells tastes bland, locals prefer to use water from hand pumps or shallow wells instead of drinking from deeper wells or open water sources. Many of the surveyed residents in the chosen communities have bone abnormalities, early tooth decay, and dental erosion. Local medical professionals also validated these findings.

Results and Discussion

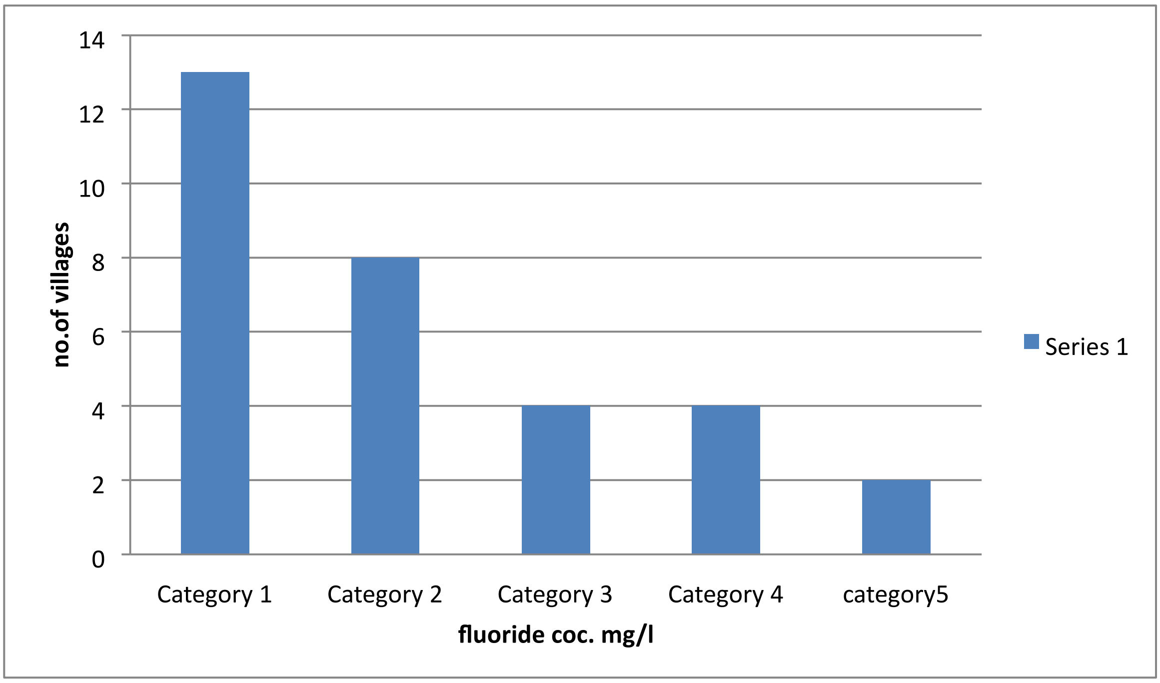
Fluoride levels in groundwater were examined in 31 communities in the Nawa-Makrana zone. The following concentration ranges were used to classify the settlements (Table 1): Less than 1.0 mg/L of fluoride is classified as Order I; 1.0 to 1.5 mg/L as Order II; 1.5 to 3.0 mg/L as Order III; 3.0 to 5.0 mg/L as Order IV; and more than 5.0 mg/L as Order V. The distribution of fluoride in the Nawa-Makrana zone's groundwater is depicted in Figure 1, where levels range from 0.3 to 5.8 mg/L. Piprali village had the greatest levels (5.8 mg/L), whereas Bawali Guta village had the lowest. The fluoride levels are generally below 1.0 mg/L in most of the settlements that are recommended safe limit for drinking water by WHO guidelines. In these areas, the fluoride levels are not high enough to cause fluorosis, but are good for the calcification of dental enamel, especially for children less than 10 years of age. Among these 31 habitations in the Nawa Makrana zone, 8 habitations (25%) are of order II with a fluoride concentration of 1.0 to 1.5 mg/l. WHO recommends the maximum limit of fluoride in drinking water is 1.5 mg/L. Twenty-five percent of people in these eight communities drink water that contains more fluoride than four milligrams per day, which can lead to first and second-degree dental fluorosis. In addition, around 12% of people in 4 communities drink water with fluoride concentrations between 1.5 and 3.0 mg/L, which is greater than the WHO's recommended upper limit. Dental fluorosis is a characteristic of these communities. Teeth with this fluoride concentration become less shiny and have mottled enamel with white, silver, black, or chalky patches. Four habitations (12%) have groundwater fluoride readings that fall into order IV and range from 3.0 to 5.0 mg/L.

Adults in these regions consume large amounts of fluoride every day. However, about 6% of people living in these communities may have mild, moderate, severe, or very severe dental fluorosis, and after the age of 30, skeletal fluorosis. The risk of getting severe skeletal fluorosis can increase to approximately 17% beyond the age of 45, and it typically affects the majority of people. Piprali and Sirsi villages have 1 % of the population in the Nawa zone but in whole study. These settlements have fluoride values above 5.0 mg/L, which might cause fluorosis of various kinds in the residents. Later on, people may suffer from increased calcification in ligaments causing bone pain. For Nawa area, a thorough study on health risks, especially symptoms associated with fluorosis and complete data on the affected population is necessary.

Fluoride categorization of villages of Nawa and makrana tehsil

Order I (Below 1.0 mg/l)	Order II (Between 1.0 and 1.5 mg/l)	Order III (Between 1.5 and 3.0 mg/l)	Order IV (Between 3.0 and 5.0 mg/l)	Order V (Above 5.0 mg/l)
Adaksar 0.8	Panchota 1.3	Kooni 2.3	Prempura 3.0	sirsi 5.6
Muwana 0.4	Bhatipura 1.1	Mindha 1.6	Padampura 4.0	Piprali 5.8
Jeenwar 0.9	Kasari 1.2	Joosri 2.4	Nimbani 3.3	
Ulana 0.5	Lalas 1.3	Khardiya 2.2	Raithaliya 4.1	
Nalot 0.8	Parewadi 1.4			
Chitawa 0.8	Githala 1.3			
Kukanwali 0.9	Laroli 1.1			
Nagwara 0.8	Indokha 1.3			
Maroth 0.7				
Bawali guta 0.3				
Bajoli 0.8				
Barwala 0.5				
Devangar 0.8				

Categorization of villages as per their fluoride concentration range.



Fluoride when consumed or inhaled in excess (more than 1 ppm) can cause several health problems. It affects young and old alike

: Relation between concentration of fluorides and biological effects [17-19]

Concentration of fluoride in mg/l	Medium	Effect
0.002	Air	Injury to vegetation
1	Water	Dental carries reduce
2 or more	Water	Mottled enamel
8	Water	100% osteosclerosis
50	Foods and water	Thyroid changes
100	Foods and water	Growth retardation
120	Foods and water	Kidney changes

Defluoridation studies of potable water samples

Eight samples from hand pumps, eighteen samples from bore wells, and four samples from open wells were found to have fluoride levels over the allowable limit of 1.5 mg/L in water samples taken from different villages in the Nawa and Makrana tehsils (Tables 1 and 2). Consequently, defluoridation investigations were conducted on the particular samples utilizing adsorbents from ESC, AAC, PJC, and CLC. It was discovered that 40 minutes of stirring at a steady 200 rpm was the ideal contact time. Following defluoridation, the fluoride ion concentration in the samples was also recorded in the tables. Before and after defluoridation utilizing several absorbents like ESC, AAC, PJC, CLC, and CAC, the minor but insignificant increases in some physicochemical parameters, such as pH, EC, TDS, PO_4^{3-}, SO_4^{2-}, Cl^-, and K, were compared. The most successful adsorbents in lowering the fluoride level in drinking water without going above the allowable limits of other water quality criteria were ESC, AAC, and PJC. The adsorption capacity order for the removal of fluoride was determined to be ESC > AAC > PJC > CLC > CAC.

Conclusions

Effective fluoride and fluorosis control strategies are limited in developing nations by a lack of funding and accessible technologies. The construction of piped water networks is one potential remedy. Water sources should be identified when fluoride levels are below recommended levels. Rainwater can be used to dilute high fluoride water, extending the supply. A fluoride public health campaign should take dietary fluoride into account. Low-cost adsorbents like ESC, AAC, and PJC may be more efficient than CLC at lowering fluoride levels in drinking water. This means that ESC, AAC, and PJC can be used for defluoridation at the home level. The results also show that the water is unsafe to drink and that fluoride contamination is extremely high in the area. As a result, local inhabitants will need to take the necessary safeguards.

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