DEFLUORIDATION OF GROUNDWATER USING LOW-COST ADSORBENTS

ABSTRACT

Excessive fluoride in groundwater poses significant health risks to millions of people worldwide, necessitating effective and accessible defluoridation methods. This study investigates the use of column filtration for removing fluoride from groundwater. The study employs a systematic approach to evaluate the performance of different adsorbent materials in a fixed-bed column setup. Various materials were tested as adsorbents in column, including Brick powder, Neem leaf powder, Lime, Sawdust, and Vetiver. The research examines the effects of key operational parameters such as bed depth, flow rate, and initial fluoride concentration on the overall removal efficiency. Experiments were conducted using groundwater to assess the method's effectiveness. Results indicated that column filtration can effectively reduce fluoride concentrations to below the World Health Organization's recommended limit of 1.5 mg/L. This report contributes to the development of efficient, cost-effective, and sustainable solutions for groundwater defluoridation. All adsorbents used were inexpensive materials, available easily in nature and locally at village or rural level. Some of the adsorbents were very effective in removal of fluoride ion and can be used as defluoridating agents but they impart color and turbidity to the groundwater. Among all the adsorbents used, Vetiver demonstrated higher removal efficiency of 78% followed up by limestone 77% removal but hindered by its precipitation. Sawdust and brick powder were also efficient up to a certain extent of 72% and 69% respectively in adsorbing fluoride ions. Neem leaves powder was found to be least effective in adsorbing showing about 50% removal efficiency.

Key Words: Defluoridation, Groundwater, Column filtration, Adsorbents

1.INTRODUCTION

Water is an important resource provided by the nature carry out all the metabolic activities which are essential for the living organism to sustain its lives. There are multiple sources available in ecosystem and one such the important source is Groundwater. The shortage of water is observed as an arduous challenge that the modern world is facing and even the existing water resources are affected by various contaminants and pollutants which reduces the quality of water and interferes the living system which ultimately leading to serious health complication to all the life forms existing in that contaminated water ecosystem. Groundwater also is no exception to the degradation and of all the contaminant and pollutants degrading the groundwater, one key player is Fluorine. Fluorine occurs naturally in the form of minerals such as Sellaite –MgF_2, Villiaumite - NaF, Fluorite (Fluorspar) – CaF_2, Cryolite-Na_3AlF_6, Bastnaesite - (Ce,La)(CO_3)F, Fluorapatite $Ca_3(PO4)_3F$ (Rao, Nagendra, C.R et al., 2003) and in fact is the 13th most naturally occurring element. Fluorine is an electronegative element and highly reactive, combining with all elements, except argon, helium and neon, to form ionic or covalent fluorides.

Fluoride can be useful or harmful based on the dosage in taken and processed by the human body and the allowable limit of fluoride is between (1mg/l-1.5mg/l) as establish by the World Health Organization (WHO) is beneficial for the human health, Excess intake i.e. >1.5 mg/L may cause fluorosis along with various neurological complication (Susheela, 2001). It is estimated that around 260 million people worldwide (in 30 countries) are drinking water with Fluoride content more than 1.0 mg/L. In India alone, endemic Fluorosis is thought to affect around one million people and a major problem in 17 of the 25 states, especially Rajasthan, Andhra Pradesh, Tamil Nadu, Gujarat and Uttar Pradesh. In India totally 25 states have been reported as fluoride affected areas but severe problem occurred in the states of Andhra Pradesh (Susheela, 2001, Meenakshi and Maheswari, 2006, Mohapatra et al., 2009, Chakravorti et al., 2000, Dutta et al., 2006, Das et al., 2003).

2.HEALTH IMPLICATIONS

High fluoride concentrations in drinking water can lead to various health implications, including dental fluorosis, skeletal fluorosis, and non-skeletal fluorosis. Dental fluorosis causes discoloring, mottling, and blackening of teeth, particularly in children below 8 years of age. Skeletal fluorosis is a stage of bone deformities where bones are permanently deformed, leading to pain in muscles and joints. Non-skeletal fluorosis causes gastro problems, neurological disorders, and affects the I.Q. of children.

Neurotoxicity is another potential health impact of excessive fluoride exposure, particularly in children. Studies have suggested a link between high fluoride levels in drinking water and reduced cognitive function. Children exposed to high levels of fluoride tend to have lower IQ scores compared to those in areas with lower fluoride levels. Endocrine disruption is another concern, with fluoride potentially interfering with the thyroid gland, which is crucial for regulating metabolism, growth, and development. Reproductive and developmental effects of fluoride exposure include reduced fertility, alterations in sperm morphology, decreased testosterone levels, and potential neurodevelopmental disorders. Long-term exposure to high levels of fluoride may contribute to cardiovascular problems, including hypertension and atherosclerosis. Chronic exposure to high levels of fluoride can lead to nephrotoxicity, potentially exacerbating existing kidney disease and leading to further complications. Monitoring and regulating fluoride levels in drinking water is essential for pregnant women.

Many techniques for removing fluoride from water and wastewater have been the subject of in-depth investigation in the years after it was discovered that fluoride was the cause of fluorosis. These methods are based on the principle of adsorption (Raichur and Basu, 2001), ion-exchange (Singh et al., 1999), precipitation-coagulation (Saha, 1993), membrane separation process (Dieye etal., 1998), electrodialysis (Hichour et al., 1999), etc. Among these methods, adsorption is the most effective and widely used method because it is universal, has a low maintenance cost, and is applicable for the removal of fluoride even at low concentrations. Removal of fluoride from the solution normally managed through a column set-up in which a vertical column that contains the prepared adsorbent would be used, and the solution would be run from the top through the adsorbent as pulled and guided by gravity. The treated solution collected at the bottom of a column.

3.MATERIALS AND METHODOLOGY

3.1 Adsorbent Material Collection and preparation

For this study, five materials were chosen as potential adsorbent materials which were Sawdust, Limestone, Waste Granular Brick, Neem leaf powder and Vetiver. The preparation method for each adsorbent materials before experimenting with the Column Filtration methods are as follows

1. T_1 - Saw Dust: Sawdust was collected from the nearby workshop and are dried. The dried sawdust was sieved and were preserved in different air tight covers for subsequent use as adsorbent.

2. T_2-Limestone: Limestone were obtained from the nearby locality and were then crushed, made in to a fine powder and then used as an absorbent.
3. T_3-Waste Granular Brick: Raw waste granular brick (WGB) was used for fluoride adsorption from aqueous solution as inexpensive unused substance. WGB was obtained by collecting waste bricks from different local demolition locations. The collected waste bricks were crushed into smaller size granules using manual hammer, sieved, repeatedly washed with distilled water, and then dried in oven at 105°C for 24 hours.
4. T_4-Neem leaf powder: Neem leaves were obtained from the trees in the nearby orchard and the leaves were repeatedly washed with distilled water and then alternatively sun and shade dried for 24-48 hours and then oven dried at 105^o C for 24 h and then it was crushed and made in to fine powdered form.
5. T_5-Vetiver: Vetiver roots were obtained from the locality and then washed thoroughly with distilled water and then shade dried for a day and oven dried for 24 h and placed into the column as thin root strands.

3.2 Methodology

To carry out the experiment, filter column was established by using a Borosilicate glass column. Before setting up the apparatus, the filter column was cleaned and surface sterilized and finally repeatedly rinsed with distilled waste and allow it to dry up. For filling the filter column, materials which were usually required for establishing a column i.e. Sand, Soil, Pebble and Glass wool, was also prepared by drying them to remove moisture and sieving to ensure free from debris and other contaminants. Five different columns were systematically packed, each with a distinct set of five different absorbent materials: sawdust, lime, waste granular brick, neem leaves, and vetiver root. Each column was packed with materials in a specific ratio of 1:1:3: 2:2, corresponding to Pebble, Glass Wool, Sand, Soil, and a specific adsorbent. The packing sequence for each column was Glass Wool, Sand, Soil, Pebble, Sand, Adsorbent, Soil, Adsorbent, and Sand, with each layer having a uniform depth of 3.5 cm (Fig. 1). Sample solutions were introduced into each column at a controlled flow rate of 5 ml/min to ensure optimal interaction with the absorbent materials for effective adsorption. Each column setup was replicated four times to obtain consistent and reliable results.

Fig 1 Filter Column Set up

3.3 Analysis of groundwater quality parameters and fluoride content

The physio-chemical parameters like electrical conductivity were analyzed using conductivity meter, pH using pH meter, Alkalinity was estimated by titrating with Hydrochloric acid, Chloride was estimated by standard silver nitrate, hardness by titration with standard Ethylenediame Tetraacetic acid (EDTA). Sulphate was analyzed using UV-Visible Spectrophotometer. The procedure was followed referring the American Public Health Association (APHA), 1989 standard methods. Fluoride was analyzed using Fluoride Ion Selective Electrode 9609 BNWP with Orion ion Meter, Total Ionic Strength Adjustment Buffer solution (TISAB) was prepared and added in 1:1 proportion in order to prevent the interruption of other ions while measuring fluoride. Calibration of the instrument is done with standards one with lower concentration and other with higher concentration, where the unknown lies between those two standards. Continuous stirring of standards and samples was done before measuring. The unknown concentration of fluoride was directly read from the digital display of the Orion ion meter. The advanced fluoride analysis kit can also be followed based on ion selective electrode method.

4.RESULTS & DISCCUSSION

4.1 Characteristics of the Groundwater Sample

Groundwater sample was collected from Karamadai block, Coimbatore District of Tamil Nadu and analyzed for chemical properties like pH, EC, cations and anions and the mean values of three replication were given (Table 1).

Table 1 Characteristics of Groundwater sample collected at Karamadai, Coimbatore District

Parameter	Value	Units
pH	7.79	
EC	1.47	dSm^{-1}
Ca	1.93	$m.eql^{-1}$
Mg	2.35	$m.eql^{-1}$
Na	1.57	$m.eql^{-1}$
K	0.33	$m.eql^{-1}$
Cl_2	1.04	$m.eql^{-1}$
SO_4	4.72	$m.eql^{-1}$
CO_3	0.49	$m.eql^{-1}$
HCO_3	1.00	$m.eql^{-1}$
F	2.6	mgl^{-1}

The mean pH value for the groundwater sample of three replications was 7.79. The alkalinity classification based on pH of groundwater revealed that the groundwater in the block found to have low alkalinity. Electrical conductivity value for the groundwater sample for three replications was $1.47dsm^{-1}$ thus categorised under High Salinity Class (C_3) which ranges from 0.75-2.25 ds m^{-1} (USSL Classification).

The sample was analyzed for cations such as calcium, magnesium, sodium and potassium for three replications. The mean Calcium, Magnesium, Sodium and Potassium content for three replications was 1.93 m.eql^{-1}, 2.35 m.eql^{-1}, 1.57 m.eql^{-1} and 0.33 m.eql^{-1} respectively. The calcium-to-magnesium (Ca/Mg) ratio, based on the given mean values, is approximately 1:1.22.

Anions such as carbonate, bicarbonate, chloride and sulphate were analyzed in the water sample. Bicarbonate and Carbonate content of the groundwater sample was 1.00 meql^{-1}and 0.49 meql^{-1} respectively. Mean value of Chloride content was 1.04 meql^{-1} which categorized under excellent category in the classification of irrigation water quality. Sulphate concentration in the groundwater sample was 4.72 meql^{-1}. Fluoride content of the groundwater sample was 2.6 mgl^{-1} which exceeds the permissible limit.

4.2 Effect of Adsorbent on Water's Chemical Parameters

Table 2 Parameters of the filtrate from the column containing adsorbent – Sawdust

Parameters	**Treatment with Replication**				
	T_1 (Sawdust)				
	R1	**R2**	**R3**	**R4**	**Mean Value**
pH	7.56	7.7	7.49	7.52	7.5675
EC (dSm^{-1})	1.63	1.56	1.54	1.62	1.5875
Ca(m.eql^{-1})	1.91	1.95	1.78	1.89	1.8825
Mg(m.eql^{-1})	2.29	2.37	2.29	2.31	2.315
Na (m.eql^{-1})	1.55	1.54	1.59	1.56	1.56
K (m.eql^{-1})	0.36	0.33	0.36	0.37	0.355
Cl_2(m.eql^{-1})	1.2	1.09	1.17	1.15	1.1525
SO_4 (m.eql^{-1})	4.68	4.66	4.69	4.67	4.675
CO_3(m.eql^{-1})	0.48	0.51	0.53	0.54	0.515
HCO_3 (m.eql^{-1})	1.04	1.05	1.01	1.07	1.0425
F (mgl^{-1})	0.684	0.73	0.77	0.692	0.719

The chemical characteristics of water after treatment with sawdust across four replications were analyzed and the results are shown in table 2. The pH remained slightly alkaline, averaging

7.57, while electrical conductivity (EC) was stable at 1.5875 dSm^{-1}. Calcium and magnesium levels showed minimal variation, with means of 1.88 $m.eql^{-1}$ and 2.31 $m.eql^{-1}$, respectively. The fluoride concentration significantly decreased from the initial value, averaging 0.71 mg/l post-treatment.

Table 3 Parameters of the filtrate from the column containing adsorbent - Limestone

Parameters	**Treatment with Replication**				
	T2 (Limestone)				
	R1	**R2**	**R3**	**R4**	**Mean Value**
pH	8.3	8.4	7.99	8.2	8.22
EC (dSm^{-1})	1.33	1.24	1.31	1.40	1.32
Ca($m.eql^{-1}$)	2.20	2.43	2.21	2.09	2.23
Mg($m.eql^{-1}$)	2.43	2.41	2.39	2.41	2.41
Na ($m.eql^{-1}$)	1.54	1.59	1.61	1.55	1.57
K ($m.eql^{-1}$)	0.31	0.29	0.36	0.34	0.32
Cl_2($m.eql^{-1}$)	0.93	0.94	0.85	0.79	0.87
SO_4 ($m.eql^{-1}$)	4.73	4.74	4.71	4.74	4.73
CO_3($m.eql^{-1}$)	0.51	0.48	0.54	0.52	0.51
HCO_3 ($m.eql^{-1}$)	1.10	1.09	1.13	1.14	1.11
F (mgl^{-1})	0.57	0.61	0.56	0.57	0.58

The filtrate from Limestone had its pH slightly alkaline with a mean value of 8.22, while EC averaged 1.32 dSm^{-1}. Calcium and magnesium concentrations were consistent across replications (Table 3), with means of 2.23 $m.eql^{-1}$ and 2.41 $m.eql^{-1}$, respectively but there was slight increase in calcium content indicating the precipitation of calcium content in the limestone. **(**Nath, S. K., and Dutta, R. K., 2010) from their study inferred nearly the same results. Fluoride levels were reduced to a mean of 0.58 mg/l, reflecting a high removal efficiency.

Table 4 Parameters of the filtrate from the column containing adsorbent – Waste Granular Brick Powder

Parameters	Treatment with Replication				
	T3 (Waste Granular Brick)				
	R1	**R2**	**R3**	**R4**	**Mean Value**
pH	7.63	7.59	7.87	7.58	7.66
EC (dSm^{-1})	1.42	1.52	1.45	1.51	1.47
Ca($m.eql^{-1}$)	2.07	2.03	1.97	1.91	1.99
Mg($m.eql^{-1}$)	2.41	2.43	2.39	2.41	2.41
Na ($m.eql^{-1}$)	1.61	1.59	1.58	1.63	1.60
K ($m.eql^{-1}$)	0.38	0.33	0.38	0.41	0.37
Cl_2 ($m.eql^{-1}$)	1.08	1.07	1.08	1.10	1.08
SO_4 ($m.eql^{-1}$)	4.74	4.77	4.72	4.76	4.74
CO_3 ($m.eql^{-1}$)	0.52	0.49	0.55	0.51	0.51
HCO_3 ($m.eql^{-1}$)	1.06	1.05	1.04	1.05	1.05
F (mgl^{-1})	0.72	0.85	0.83	0.81	0.80

In case of Waste Granular Brick powder, the pH ranged from 7.58 to 7.87, averaging 7.66. EC showed a slight increase, averaging 1.47 dS/m. Calcium and magnesium levels were relatively stable, with mean values of 1.99 $m.eql^{-1}$ and 2.41 $m.eql^{-1}$ (Table 4), respectively. (Abd Ali, Z. T., and Ismail, Z., Z.2021) report has shown a similar result. The fluoride concentration was reduced to an average of 0.80 mg/l, with a removal efficiency of approximately 69.03%, indicating moderate effectiveness.

Table 5 Parameters of filtrate from the column containing adsorbent – Neem leaf Powder

Parameters	Treatment with Replication

	T4 (Neem leaf Powder)				
	R1	R2	R3	R4	Mean value
pH	7.97	7.93	7.70	7.80	7.85
EC (dS/m)	1.35	1.41	1.37	1.38	1.37
Ca (m.eql^{-1})	1.89	1.85	1.87	1.91	1.88
Mg (m.eql^{-1})	2.37	2.41	2.43	2.44	2.41
Na (m.eql^{-1})	1.56	1.60	1.55	1.57	1.57
K (m.eql^{-1})	0.37	0.36	0.35	0.34	0.35
Cl_2 (m.eql^{-1})	0.97	1.03	1.02	0.99	1.00
SO_4(m.eql^{-1})	4.69	4.67	4.73	4.7	4.69
CO_3(m.eql^{-1})	0.54	0.51	0.52	0.49	0.51
HCO_3(m.eql^{-1})	1.07	1.06	1.08	1.06	1.06
F (mgl^{-1})	1.24	1.33	1.34	1.26	1.29

The chemical properties of water after treatment with neem powder were analyzed (Table 5). (R.S.Dave and M.T. Machhar's) report a similar result was obtained. The pH was slightly alkaline, averaging 7.85, with an EC of 1.37 dS/m. Calcium and magnesium levels remained stable, with means of 1.88 m.eql^{-1} and 2.41 m.eql^{-1}, respectively. The fluoride concentration was reduced to an average of 1.29 mg/l.

Table 6 Parameters of the filtrate from the column containing adsorbent - Vetiver

Parameters	Treatment with Replication				
	T5 (Vetiver)				
	R1	R2	R3	R4	Mean Value
pH	8.05	7.86	7.89	7.81	7.90
EC (dS/m)	1.37	1.42	1.43	1.38	1.40
Ca (m.eql^{-1})	1.85	1.91	1.86	1.87	1.87
Mg (m.eql^{-1})	2.39	2.45	2.39	2.42	2.41
Na (m.eql^{-1})	1.54	1.57	1.58	1.55	1.56

K (m.eql^{-1})	0.34	0.35	0.32	0.35	0.34
Cl_2 (m.eql^{-1})	1.03	1.04	1.05	1.04	1.04
SO_4 (m.eql^{-1})	4.74	4.75	4.74	4.71	4.73
CO_3 (m.eql^{-1})	0.52	0.51	0.51	0.54	0.52
HCO_3(m.eql^{-1})	1.03	1.00	1.02	1.01	1.01
F (mgl^{-1})	0.57	0.56	0.54	0.56	0.56

For the filtrate from the column containing vetiver as adsorbent the parameters were evaluated (table 6). The pH averaged 7.90, while the EC was relatively stable at 1.4 dS/m. Calcium and magnesium levels showed little variation, with means of 1.87 m.eql^{-1} and 2.41 m.eql^{-1}, respectively. From the report of (Puthenveedu Sadasivan Pillai Harikumar, Chonattu Jaseela, Tharayil Megha,2012), nearly similar results were obtained. The fluoride concentration was significantly reduced to an average of 0.56 mg/l, resulting in the highest removal efficiency among the tested materials.

Table 7 Mean value of all the five treatments

Parameters	**Treatment with various adsorbents**				
	T1 SAWDUST	**T2 LIMESTONE**	**T3 GRANULAR BRICK**	**T4 NEEM LEAF POWDER**	**T5 VETIVER**
pH	7.56	8.22	7.66	7.85	7.90
EC (dS/m)	1.58	1.32	1.47	1.38	1.40
Ca (m.eql^{-1})	1.88	2.23	1.99	1.88	1.87
Mg (m.eql^{-1})	2.31	2.41	2.41	2.42	2.41
Na (m.eql^{-1})	1.56	1.57	1.40	1.57	1.56
K (m.eql^{-1})	0.34	0.32	0.37	0.35	0.34
Cl_2 (m.eql^{-1})	1.15	0.87	1.08	1.00	1.04
SO_4 (m.eql^{-1})	4.67	4.73	4.74	4.69	4.73
CO_3 (m.eql^{-1})	0.51	0.51	0.51	0.51	0.52
HCO_3(m.eql^{-1})	1.04	1.11	1.05	1.06	1.01

F (mgl^{-1})	0.71	0.58	0.80	1.29	0.56

Table 8 Analysis of Fluoride Removal Efficiency for Various adsorbents

Fluoride Concentration	**T1 (Sawdust)**				
	R1	**R2**	**R3**	**R4**	**Mean value**
Initial (Ci)	2.60	2.60	2.60	2.60	2.60
Final (Cf)	0.68	0.73	0.77	0.69	0.71
Removal Efficiency (%)	73.6	71.9	70.4	73.3	72.3

Fluoride Concentration	**T2 (Limestone)**				
	R1	**R2**	**R3**	**R4**	**Mean value**
Initial (Ci)	2.60	2.60	2.60	2.60	2.60
Final (Cf)	0.57	0.61	0.56	0.57	0.58
Removal Efficiency (%)	77.8	76.57	78.3	77.9	77.64

Fluoride Concentration	**T3 (Waste Granular Brick)**				
	R1	**R2**	**R3**	**R4**	**Mean value**
Initial (Ci)	2.60	2.60	2.60	2.60	2.60
Final (Cf)	0.72	0.85	0.83	0.81	0.80
Removal Efficiency (%)	72	67	68.4	68.7	69.025

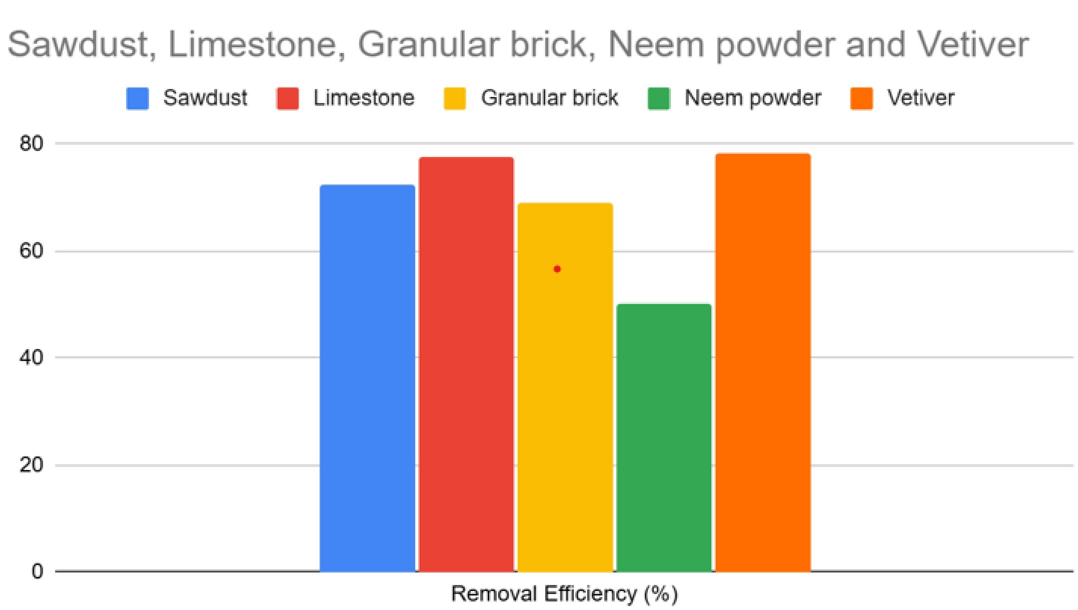
Fluoride Concentration	**T4 (Neem Powder)**				
	R1	**R2**	**R3**	**R4**	**Mean value**
Initial (Ci)	2.60	2.60	2.60	2.60	2.60
Final (Cf)	1.24	1.33	1.34	1.26	1.29
Removal Efficiency (%)	52	48.8	49	51.5	50.32

Fluoride Concentration	T5 (Vetiver)				
	R1	**R2**	**R3**	**R4**	**Mean value**
Initial (Ci)	2.60	2.60	2.60	2.60	2.60
Final (Cf)	0.57	0.56	0.54	0.56	0.56
Removal Efficiency (%)	77.9	78.4	79	78.1	78.35

4.3 Comparative Analysis of Treatment Efficacy on Fluoride Removal

Table 9 Analysis of Fluoride Removal Efficiency for all the absorbents

Fluoride Concentration	Mean value of all five replications				
	Sawdust	**Limestone**	**Granular brick**	**Neem powder**	**Vetiver**
Initial (Ci)	2.60	2.60	2.60	2.60	2.60
Final (Cf)	0.71	0.58	0.80	1.29	0.56
Removal Efficiency (%)	72.3	77.7	69.02	50.32	78.35



Fluoride removal efficiency of adsorbents

Fig – 1 Comparison of Fluoride Removal Efficiency Using Sawdust, Limestone, Granular brick powder, Neem leaf Powder, and Vetiver

The results for Fluoride ion (F^-) removal using the adsorbents in the Column Filtration method are shown in Table 9 and the mean removal efficiency of the adsorbents are compared in Fig 1. For the Sawdust adsorbent the removal efficiency being at a maximum of 73.6% with an average of about 72% with a pH range of 7.5-7.8. The values validate with the findings of (Suman Mann, Dr Anubha Mandal, 2014) who had a removal efficiency of about (70-75.2%) at an optimal condition of pH 6-8 (average of 7-7.5) in batch sorption method.

Limestone had a much higher efficiency rate with a range of 76-78% with an average of about 77% under optimal conditions. This shows a higher adsorption of fluoride onto the surface of the limestone. (Turner et.al.,41) have shown that limestone can precipitate as well as adsorb fluoride. As the acidic ions reacts with limestone generated Ca^{2+} and it precipitates as CaF_2. At the same time new surfaces of limestone are created and fluoride also gets adsorbed onto the surface. (Nath, S. K., & Dutta, R. K 2010) had a similar efficacy for the removal of fluoride using crushed limestone where in their indicated that the fluoride removal at initial stages showed about a change from an initial concentration of 10mg/l to a lower value up to 2mg/l.

For brick powder adsorbent the removal efficiency is high i.e. around 72% at pH 7.5 and optimum conditions with an average of about 69% with a pH range of 7.5-7.8 (Ziad T.Abd Ali, Zainab Z. Ismail, concluded nearly the same results upon using granular brick powder i.e. around 80% removal efficiency). Their Batch test results demonstrated that the maximum removal efficiency of fluoride was found to be 82% using pH 8 and optimum conditions.

Neem showed a comparatively lower removal efficiency of 50% maximizing at efficiency of 52% under the pH of range 7.7-8 and optimum conditions. Neem is not much effective in removal of fluoride as indicated in the studies of (Dave and Macchar, 2015) where in the removal efficiency of the bio adsorbent decreases with increase in the pH and increase in the adsorbent dose and time. The analysis shows a similar efficiency to that of (Dave and Macchar, 2015) where at pH of 8 only about 50% of efficiency could be achieved.

Vetiver showed a promising removal efficiency of the range 77-79% with a maximum removal at a 79% reducing the initial concentration of 2.6 mg/L to 0.546 mg/L. The analysis shows a similar result to the research of (Puthenveedu Sadasivan Pillai Harikumar, Chonattu Jaseela, Tharayil Megha, 2012) where their study shows a potential efficiency of 90% in a column of an ordinary household water filter (7.5 cm height and 8 cm diameter) was packed with four materials in five layers-sand, activated Vetiver root, activated carbon and pebbles are in a ratio of 1:2:4:6.

From table 9, for effective fluoride removal, Vetiver appears to be the best option, especially where high efficiency is required. Sawdust and limestone, both having similar and relatively high efficiencies, offer sustainable, natural alternatives. These materials could be considered where environmental impact and availability are concerns. Granular brick and neem powder might be more suitable for supplementary use rather than as primary materials for fluoride removal, given their moderate and low efficiencies, respectively. This study highlights limestone as the superior material for fluoride removal, followed closely by sawdust and vetiver. Neem powder's low performance suggests limited use in fluoride removal applications. These findings can help guide the selection of materials for effective water treatment, particularly in areas where fluoride contamination is a concern.

CONCLUSION

The research results indicate a clear variation in the efficiency of fluoride removal depending on the adsorbent used. Among the materials tested, Vetiver emerged as the most effective, with a fluoride removal efficiency of approximately 78.35%. Limestone also performed well, achieving an average removal efficiency of around 77.64%. Sawdust and waste granular brick demonstrated moderate effectiveness, with efficiencies of 72.3% and 69.03%, respectively. Neem leaves, however, showed the least efficacy, with only about 50.33% fluoride removal. These findings underscore the importance of selecting the appropriate adsorbent material for groundwater treatment based on specific local conditions and resource availability. For example, vetiver roots and limestone not only showed high removal efficiencies but are also relatively inexpensive and readily available in many regions, making them practical options for widespread use, especially in rural areas.

The results of this study align with previous research in the field, confirming the potential of certain natural and low-cost materials for defluoridation. Vetiver roots high efficiency i.e. can be attributed to their significant surface area and porosity, which enhance their adsorption capacity. This finding corroborates studies by (Puthenveedu Sadasivan Pillai et al. 2012), who highlighted vetiver's effectiveness in similar applications. Limestone's efficiency is also well-documented, with the material facilitating both adsorption and precipitation processes to remove fluoride from water, as noted in studies by (Nath and Dutta, 2010).Sawdust and waste granular brick, while slightly less effective of 72.3% and 69.02% respectively still present viable options, particularly where vetiver or limestone may not be available. Sawdust, being a by-product of wood processing, offers a sustainable and economical solution, though its efficiency could be further optimized through chemical modification or by combining it with other adsorbents. Similarly, waste granular brick, an often-overlooked material, has shown promise in removing fluoride, especially when considering its low cost and abundance in areas where construction debris is prevalent.

The relatively poor performance of neem leaves in this study, with only about 50% fluoride removal, is noteworthy. This result suggests that while neem leaves may have some potential as a bio-adsorbent, their application in defluoridation might require enhancement through chemical treatments or by combining them with other, more effective materials. The study by (Dave and Machhar, 2015) supports this conclusion, indicating that neem's adsorption capacity might be limited by its surface properties and the interaction between fluoride ions and the active sites on the neem powder. The outcomes of this study have significant implications for water treatment practices, particularly in regions where access to clean water is limited. The use of natural and low-cost materials such as vetiver roots and limestone provide a promising approach to mitigating the health risks associated with fluoride-contaminated groundwater. These materials not only meet the criteria of efficiency and cost-effectiveness but also offer sustainability, which is crucial for long-term water management strategies.

Disclaimer (Artificial intelligence)

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Author(s) hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc.) and text-to-image generators have been used during the writing or editing of this manuscript.

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Details of the AI usage are given below:

1.

2.

3.

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APPENDIX

WHO STANDARDS FOR DRINKING WATER

WHO produces international norms on water quality and human health in the form of guidelines that are used as the basis for regulation and standard setting, in developing and developed countries worldwide. The quality of drinking water is a powerful environmental determinant of health. Assurance of drinking water safety is a foundation for the prevention and control of waterborne diseases. The guidelines developed by WHO are prepared through a vast global consultative process involving WHO member, national authorities and international agencies, in consultation with the WHO Expert Advisory Panel.

Table 10.WHO STANDARDS FOR DRINKING WATER

Parameters	**Standard limits as per WHO guidelines (mg/L)**
Acrylamide	0.0005
Alachor	0.02
Aldicarb	0.01
Aldrin and Dieldrin	0.00003

Ammonia	1.5
Antimony	0.02
Arsenic	0.01
Atrazine	0.002
Barium	0.7
Benzene	0.01
Benzo(?)pyrene	0.0007
Boron	0.5
Bromate	0.01
Bromodichloromethane (BDCM)	0.06
Bromoform	0.1
Cadmium	0.003
Carbofuran	0.007
Carbon tetrachloride	0.004
Chlorate	0.7
Chlordane	0.0002
Chloramines	0.5 - 1.5
Chloride	200 - 300
Chlorine	5
Chlorite	0.7
Chloroform	0.3
Chlorotoluron	0.03
Chlorpyrifos	0.03
Chromium	0.05
Colour in drinking water	No visible colour
Copper	2.0
Cyanazine	0.0006
Cyanide	0.07
1,2-Dichlorobenzene	1.0
1,4-Dichlorobenzene	0.3

1,2-Dichloroethane	0.03
Dichloromethane	0.02
2,4-Dichlorophenoxyacetic acid	0.03
DDT and metabolites	0.001
Di(2-ethylhexyl)phthalate	0.008
1,2-Dichloroethylene	0.05
1,2-Dichloropropane	0.04
Dimethonate	0.006
1,4-Dioxane	0.05
Dissolved oxygen	No health-based guideline value is recommended
Edetic acid (EDTA)	0.6
Endrin	0.0006
Epichlorohydrin	0.0004
Ethylbenzene	0.3
Fenoprop	0.009
Fluoride	1.5
Hexachlorobutadiene	0.0006
Iron	No health-based guideline value is proposed
Isoproturon	0.009
Lead	0.01
Lindane	0.002
Manganese	0.4
Mercury	0.006
Methoxychlor	0.02
Metolachlor	0.01
Microcystin-LR	0.001
Molinate	0.006
Molybdenum	0.07
Monochloroacetate	0.02
N-Nitrosodimethylamine	0.0001

Nickel	0.07
Nitrate	50
Nitrilotriacetic acid (NTA)	0.2
Nitrite	3
Pendimethalin	0.02
Pentachlorophenol	0.009
Permethrin	0.3
pH	No health-based guideline value is proposed
Pyriproxyfen	0.3
Selenium	0.01
Simazine	0.002
Sulphate	No health-based guideline value has been derived
Styrene	0.02
Terbuthylazine	0.007
Tetrachloroethylene	0.04
Toluene	0.7
Total dissolved solids (TDS)	No health-based guideline value is proposed
Trichloroacetate	0.2
Trichloroethylene	0.02
2,4,6,-Trichlorophenol	0.2
Trifluralin	0.02
Trutuim	10000 Bq/L
Uranium	0.015
Vinyl chloride	0.0003
Xylenes-total	0.5
Zinc	No health-based guideline value is proposed

Table 11. GENERAL WATER QUALITY STANDARDS PRESCRIBED BY CPCB

Quality parameter	For discharge into inland surface water	For discharge into public sewers	For discharge into land for irrigation
pH	5.5 – 9.0	5.5 – 9.0	5.5 – 9.0
Temperature (^{0}C)	Not to exceed 5^{0}C above receiving water temperature		--
TSS (mg l^{-1})	100	600	200
TDS (mg l^{-1})	2100	2100	2100
Total hardness (mg l-1)	500 or less, but < 100 desirable		--
BOD (mg l^{-1})	30	350	100
COD (mg l^{-1})	250	--	--
Chlorides (mg l^{-1})	1000	1000	600
Sulphates (mg l^{-1})	1000	1000	1000
Total Cr (mg l^{-1})	2.0	2.0	--
Cr (VI) (mg l^{-1})	0.1	2.0	--
Fluoride (mg l^{-1})	2.0	15	--
Faecal coliforms	Absent in drinking water	--	--