A Systematic Review of Water Defluoridation usingNatural Adsorbents

Rakshitha Rajashekara[1], Chaithra Nagaraju[2], Shyla Chowdareddy[1], Pallavi Nagaraju [1*]

[1]Department of Environmental Science, School of Life Science, JSS Academy of Higher Education & Research, Mysuru-570015, India.

[2]Division of Medical Statistics, School of Life Science, JSS Academy of Higher Education & Research, Mysuru – 570015, India.

ABSTRACT

Water is a vital component for every organism living on the earth, especially the human species. The good quality of water is also very much essential for drinking. Due to water scarcity and water pollution more often clean and safe water is not available for drinking to human beings worldwide. The good quality of water gets contaminated by both anthropogenic and natural activities. There are numerous pollutants that cause hazardous problems to human health and fluoride is one such contaminant with possible health issues. Fluoride is a natural pollutant known as a double edge sword as fluoride concentrations less than 1 cause dental fluorosis and greater than 1.5 causes skeletal fluorosis. Skeletal fluorosis is a major problem in most places in south Asia regions such as India, Sri Lanka, andPakistan which are highly affected. In India Rajasthan, Gujarat, Tamil Nadu, and Andhra Pradesh are most affected while Karnataka is moderately affected by high fluoride concentrations. Conventional methods for the removal of fluoride from water are ion exchange, reverse osmosis, and adsorption. While ion exchange and reverse osmosis are expensive and energy intensive. The adsorption method is considered the effective and efficient treatment technique for the removal of fluoride from an aqueous solution. Chemical adsorbents have limitations of disposal and regeneration. Natural bio sorbents are being used to defluoridate the fluoride-contaminated water to obtain maximum removal efficiency. Natural adsorbents are environmentally friendly, low cost, locally available, high efficiency, renewable, and readily available. Natural adsorbents have a few limitations such as low absorptive capacity because of their composition and low complex activation process. In the present study, a systematic review of De fluoridation from natural adsorbents provides the baseline data for further research or study.

Keywords: De fluoridation, natural adsorbent, ion exchange, Reverse osmosis, Adsorption.

INTRODUCTION

It is well known that fluoride is a natural contaminant present in groundwater resources all over the world. Numerous countries in North and South America, including India, China, Sri Lanka, the West Indies, Spain, Holland, Italy, and Mexico, have reported having high fluoride levels in their groundwater. In India, 60% of families receive their water needs from groundwater, which is the main source. Consequently, over 100 million households, both wealthy and poor, urban residents and peasants, could be impacted by the quality of groundwater (Sakthi Thesai et al. 2020). There are many shreds of evidence to prove the rocks bear fluoride, due to natural activities it leaches out and contaminates the underground water.

The World health organization (WHO) has already set the permissible limit for fluoride in drinking water as 1.5 mg/L. The Chinese Ministry of Water Resources suggested a guideline for fluoride ions in drinking water as 1.0 mg/L based on economic, practical, and technical considerations. Excessive fluoride in the body leads to a problem called fluorosis. Thus, fluorosis affects the teeth, the skeleton, and the non-skeletal parts of the human body. Anthropogenic activities such as the disposal of waste from semiconductors, steels, fertilizers,bricks, ceramics, glass, and electroplating industries add fluoride ions to the drinking water (Dobaradaran et al. 2015). Fluoride is an electronegative toxic element its toxicity can cause adverse health effects for both human beings and animals.(Bhaumik et al. 2017).

For the removal of excess fluoride ions from drinking water and industrial effluent, traditional treatment technologies such as precipitation, electrolysis, membranes, adsorption, ion exchange, electrodialysis, coagulation/precipitation, dialysis, reverse osmosis, nanofiltration, ultrafiltration, and others have been developed and tested. (Yao et al. 2009) However, these procedures have several drawbacks, such as incomplete removal, a complicated treatment process, high cost, high energy and operational costs, the use of chemicals and the formation of hazardous sludge or other waste products, which must be disposed of again. (T. Getachew, et.al., 2014).

Adsorption techniques based on natural adsorbents or agricultural waste products are emerging as new options for removing fluoride from aqueous solutions since they are inexpensive, simple, sludge-free, regenerable, environmentally friendly, have a low initial cost, and use few chemicals. (T. Getachew, et.al., 2014). De fluoridation was researched utilizing several biosorbents such as Tamarind seed (Bharali and Bhattacharyya 2015) (M. Murugan, et.al., 2006), Waste fungus (Pleurotus ostreatus) (S.V. Ramanaiah.et.al., 2007), Moringa Oleifera (T. Getachew, et.al., 2014), Wheat straw, sawdust and activated bagasse sugarcane (Yadav et al. 2013), Tea waste (Peng et al. 2017), Chicken bones (Ismail and AbdelKareem 2015), Neem leaf (Singh and Majumder 2018), dodonea viscosa (Aziz et al. 2020) etc.,

The primary goal of the review project is to assess the efficacy of biosorbents for thedefluoridation of water. To investigate the effectiveness of bio sorbents in the removal of fluoride from water, and to evaluate the various factors influencing the defluoridation while employing bio sorbents.

MATERIALS AND METHODOLOGY

Data sources and search strategy

The literature review gives us a brief idea about the present research being carried out by scientists around the globe related to defluoridation using natural adsorbents. Systematic reviews are more crucial in many instances since they enable researchers to develop in the field, discover research gaps for additional exploration, and find research questions based on the results gained in various contexts. Systematic reviews were taken into consideration in order to obtain the answer to the research questions mentioned above and to fulfill the study's goal. This section discusses a few procedures, including study area and data selection, locating papers that can be reviewed, data extraction, statistical approaches, etc.

The study was carried out by reviewing the published articles and reports on fluoride removal and the factors affecting the removal techniques such as pH, contact time, adsorbent Dosage, and initial fluoride concentration in groundwater sources were considered as the data sources. The study searched the search engines such as PubMed, Scopus, Google Scholar, Research gate, Springer, Science Direct, and other databases for works published in the previous 20 years related to defluoridation by natural adsorbents. To select the papers in the search engines keywords such as defluoridation, adsorption, and natural adsorbent were selected and we limited the time period between 2000 -2020 i.e to 2 decades. Finally from all these search engines related to our topic, we could get around 114 papers in this database of systematic review studies. Out of 114 research papers, only 7 research papers were selected for the systematic review depending on the identification (39) screening(24), eligibility (44), and inclusion & exclusion criteria as shown in the figure below (Fig.1.1)

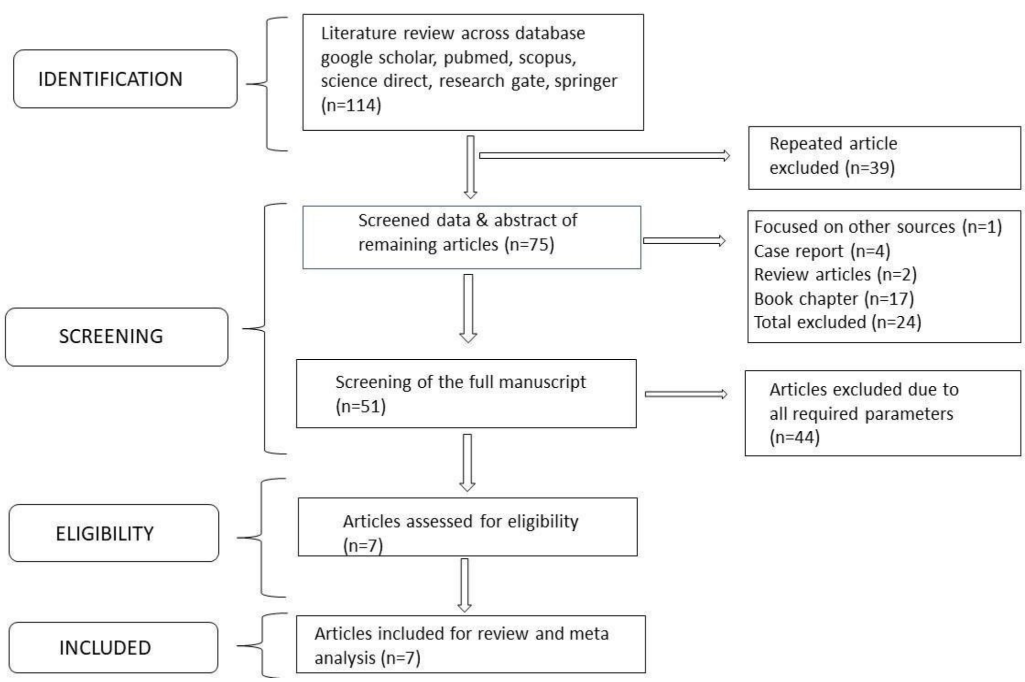


Figure1.1 Systematic review flow diagram

Inclusion and Exclusion

This is an important part of the systematic review as in this part, the research articles collected from various search engines will be checked for various criterias and accordingly selected for further study if it meets the criteria. Figure 1.1 depicts the process by which the papers for the systematic review were chosen. The amount of information that was readily available about the study title was one of the most crucial factors in the preliminary selection of a paper. In the first step, duplicate research articles (n= 39) selected from different search engines are excluded. In the next step of screening the case report(n = 4), review articles (n = 2), book chapters (n = 17), and research articles with missing data such as initial fluoride concentration, pH, adsorbent dosage, and contact time (n=44) were rejected from the study. In the third step based on our review topic and the eligibility criteria guidelines, 7 research articles with all the necessary data were selected for the final review. The final article assessed for eligibility is 7 by considering the parameters or factors which were studied by theresearcher in their research paper.

RESULTS

The study revolves around the subject of De-fluoridation for drinking water by severalnatural adsorbents. Results were obtained from seven studies and thus seek to compare the removal efficiency of different bio sorbents with certain physical and chemical factors affecting the defluoridation process. The lists of the study references taken for this study along with the bio sorbents used in those experiments are shown in Table1.1. It also displays the number of factors that were taken from those experiments like Initial Fluoride Concentration (IFC), Adsorbent Dosage (AD), Contact Time (CT), Potential of Hydrogen (pH) and Removal Efficiency (RE). These are the factors that are being taken under consideration for this systematic review study. The Mean and Standard Deviation values for IFC is 3.18 ± 2.38 (mg/L), AD is 11.86 ± 10.37 (mg/L), CT is 145.39 ± 84.94 (Mins), pH is 5.00 ± 2.65, RE is 80.66 ± 17.22 (%) shown in the Descriptive Statistics Table 2.

Table 1.1: Research articles selected for the study

SI No	Study Reference	Natural Adsorbent	IFC (mg/L)	AD (mg/L)	CT (mins)	pH	RE (%)
1	Ria Bhaumik et al. (2017)	*Carp (Catla catla)*	8.49	23	172.72	8	95
2	Juma Muhammad et al. (2020)	*Dodonea Viscosa leafpowder*	2	10	145	2	45
3	MD Nematulain Nazri et al. (2020)	*Moringa Oleifera*	2	5	160	1	97

4	Sena Dobaradaran et al.(2015)	*Moringa Oleifera Seed ash*	2.8	30	120	7	81.14
5	M.Mula et al. (2016)	*Rice husk*	3	2	100	7	80
6	Nandakishore G.Telkapallivar (2020)	*Ficus Benghalensi sleaf*	2	5	300	5	86.5
7	Sutapa Chakrabartyet al. (2012)	*Nee m leaf*	2	5	20	5	80

IFC- Initial Fluoride Concentration, AD-Adsorbent Dosage, CT- Contact Time,pH - Potential of hydrogen, RE-Removal Efficiency

Table 2: Descriptive Statistics for all the factors

Factors	**Minimum**	**Maximum**	**Mean**	**Standard Deviation**
IFC (mg/L)	2	8.49	3.18	2.38
AD (mg/L)	100	200000	41814.29	73477.01
CT (Mins)	20	300	145.39	84.94
pH	1	8	5.00	2.65
RE (%)	45	97	80.66	17.22

The person's correlation coefficient was indicating a small association between the variables such as: AD and IFC (r = -0.14), CT and AD (r = -0.05), pH and AD (r = -0.35), pHand CT (r = -0.09). The correlation values between CT and IFC (r = 0.09), RE and IFC (r = 0.38), RE and CT (r = 0.19), RE and pH (r = 0.31) indicates a small positive linear relationship. The correlation matrix represents a medium to a strong relationship between different variables shown in table 3**,** this indicates the extent of association between different factors involved in the study. From the result, there are two significant correlations between the factors, the first one being between pH and IFC. A correlation of r = 0.61, which falls in the medium range of correlation between two variables, indicates that there is a positive correlation between pH and IFC i.e., as IFC increases there would be an increase in pH. The second one is between Removal efficiency and Adsorbent dosage. These two factors display a correlation of r = - 0.89, which falls in the range of strong negative correlation between two variables, which indicates that as adsorbent dosage goes on increasing, there would be a significant decrease in the removal efficiency of fluoride pollutant. The visualization of the correlation matrix is displayed in figure1.

Table 3: Correlation matrix for variables

	IFC	AD	CT	pH	RE
IFC	1.00				
AD	-0.14	1.00			
	0.09	-0.05	1.00		
CT	**0.61**	-0.35	-0.09	1.00	
	0.38	**-0.89**	0.19	0.31	1.00
pH					
RE					

IFC- Initial Fluoride Concentration, AD-Adsorbent Dosage, CT- Contact Time, pH -Potentialof Hydrogen, RE-Removal Efficiency

Figure 1: Correlogram for all factors

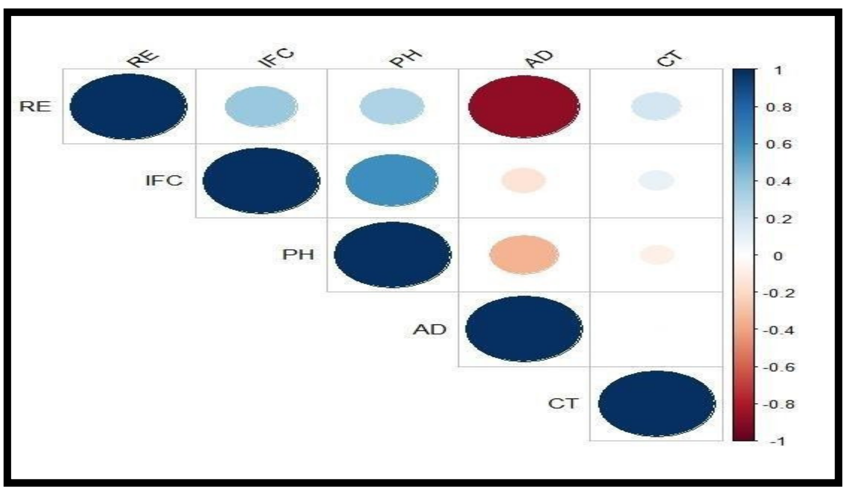
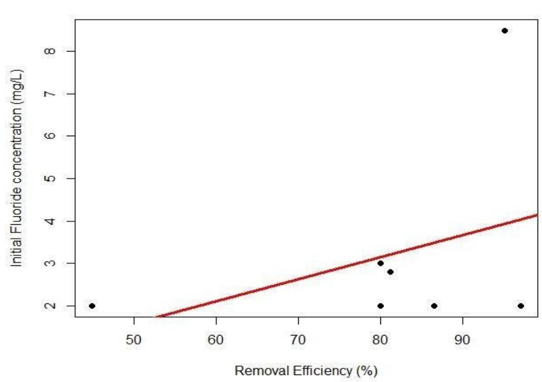


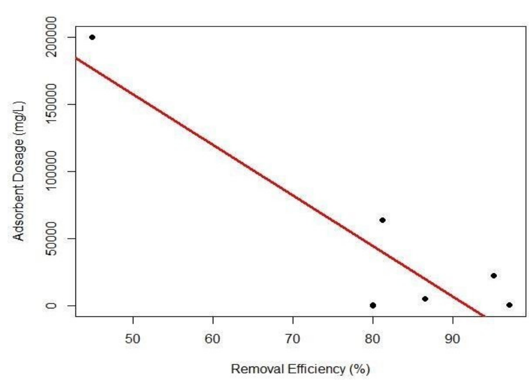
Table 4: Relationship of Removal Efficiency with factors

Factors	r- value	p-value	Remarks
IFC	0.38	0.403	Result is not significant ($p>0.05$)
AD	-0.89	**0.007***	**Result is significant** ($p<0.05$)
CT	0.19	0.687	Result is not significant ($p>0.05$)
pH	0.31	0.501	Result is not significant ($p>0.05$)

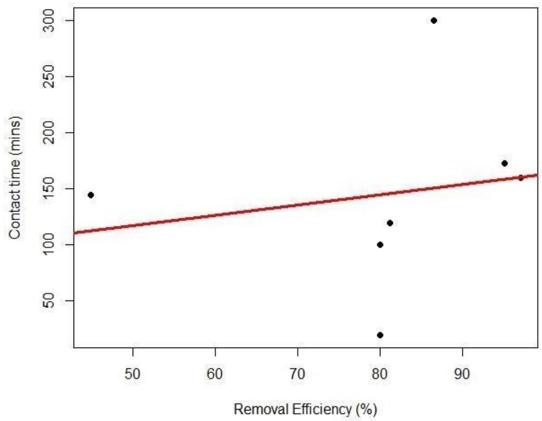
Table 4 illustrates the correlation between Removal efficiency and all other factors along with their values and p - values at a 5 % level of significance. The results shows that the insignificant relationship between Removal efficiency with IFC (r = 0.38, p = 0.403), CT (r = 0.19, p = 0.687) and PH (r = 31, p = 501) respectively. The only adsorbent dosage has a highly negative correlation with Removal efficiency i.e., r = -0.89 and significant with p- value = 0.007.



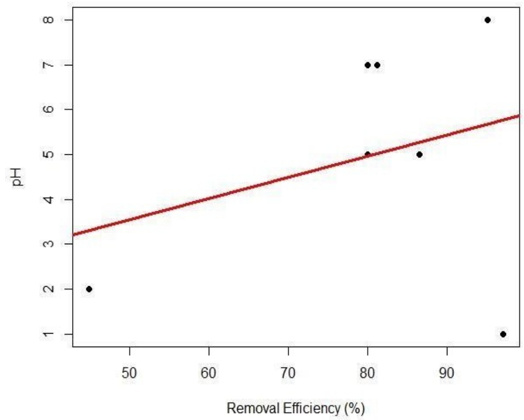
2(a): $\hat{y}$ = -1.02+0.052(X); RSQUARED= 0.142 0.788



2(b): $\hat{y}$ = 347- 3.78(X); R SQUARED=



2(C): $\hat{y}$ = 70.6855+0.9261(X); R SQUARED= 0.0352



2(d): $\hat{y}$ = 1.179+0.047(X); R SQUARED= 0.0950

Figure2: Regression analysis of Removal Efficiency (RE) with factors

The Removal efficiency (RE) showed a positive linear trend with IFC in figure 2(a) and PH infigure 2(d) respectively, these indicate that an increase in IFC and PH led to an increase in Removal efficiency with the fitted linear equation for IFC i.e., $\hat{y}$ = -1.02+0.052(X) with R square = 0.142 and for PH: $\hat{y}$ = 1.179+0.047(X); R square = 0.0950, which are 14.2% and 9.5 % of the change in an independent variable to be explained by the dependent variable. There is a negative linear trend between Adsorbent dosage and Removal efficiency in figure 2(b) with a fitted linear equation i.e., $\hat{y}$ = 347-3.78 (X); R SQUARED = 0.788. which is 78.83%of the change in Removal efficiency to be explained by Adsorbent dosage. Contact time and removal efficiency showed a slightly positive trend. This indicates that an increase in Contact time led to a slight increase in removal efficiency. Here $\hat{y}$ = 70.6855+0.9261 (X); R square= 0.0352, which is 3.52% of the change in removal efficiency to be explained by contact time, which is comparatively lower.

Conclusions

In recent years, there has been an increase in interest in using an adsorption technique to remove fluoride from aqueous media, according to the literature that has been reviewed here. Natural sorbents have drawn attention to the defluoridation process even though a wide variety of chemical adsorbents have been used during the past ten years. In many cases, the methodologies of systematic reviews and meta-analyses are more important since they allow researchers to advance in their field, identify knowledge gaps for further investigation, and propose research questions based on the findings in diverse situations. The Pearson correlation values indicates a small positive linear relationship between CT and IFC (r = 0.09), RE and IFC (r = 0.38), RE and CT (r = 0.19), RE and pH (r = 0.31). The Adsorbent Dosage (AD) has a highly negative correlation with Removal Efficiency (RE) i.e., r = - 0.89 indicating that as Adsorbent Dosage (AD) goes on increasing, there would be a significant decrease in the Removal Efficiency (RE) of fluoride from water and the p-value = 0.007 also indicates that the result is significant. The regression analysis of Removal efficiency (RE) showed a positive linear trend with Initial Fluoride Concentration (IFC) and pH indicating an increase in pH and IFC will increase the removal efficiency. Contact time (CT) and Removal Efficiency (RE) slightly showed a positive trend indicating a slight increase in contact time increases the RE. This analysis has been successful in explaining the development of defluoridation by natural adsorbents. Adsorption is a useful method for reducing fluoride contamination in aqueous media, it can be inferred. Additionally, using natural adsorbents and green synthesis techniques can be recommended when choosing environmentally friendlyapproaches.

REFERENCE

Amin F, Talpur FN, Balouch A, et al (2015) Biosorption of fluoride from aqueous solution bywhite - rot fungus Pleurotus eryngii ATCC 90888. Environmental Nanotechnology, Monitoring and Management 3:30–37. https://doi.org/10.1016/j.enmm.2014.11.003

Ayinde WB, Gitari WM, Munkombwe M, et al (2020) Journal of Environmental Chemical Engineering Green synthesis of AgMgOnHaP nanoparticles supported on chitosan matrix : Defluoridation and antibacterial effects in groundwater. 8:. https://doi.org/10.1016/j.jece.2020.104026

Aziz F, Din I, Khan S, et al (2020) Defluoridation of water using dodonaea viscosa leafpowder: A study of adsorption isotherms. Fluoride 53:90–96

Balouch A, Kolachi M, Talpur FN, et al (2013) Sorption Kinetics, Isotherm and Thermodynamic Modeling of Defluoridation of Ground Water Using Natural Adsorbents. American Journal of Analytical Chemistry 04:221–228. https://doi.org/10.4236/ajac.2013.45028

Balouch A, Kolachi M, Talpur FN, et al (2013) Sorption Kinetics, Isotherm and Thermodynamic Modeling of Defluoridation of Ground Water Using Natural Adsorbents. American Journal of Analytical Chemistry 04:221–228. https://doi.org/10.4236/ajac.2013.45028

Ben Amor T, Kassem M, Hajjaji W, et al (2018) Study of defluoridation of water using natural clayminerals. Clays and Clay Minerals 66:493–499. https://doi.org/10.1346/CCMN.2018.064117

Bharali RK, Bhattacharyya KG (2015) Biosorption of fluoride on Neem (Azadirachta indica)leaf powder. J Environ Chem Eng 3:662–669. https://doi.org/10.1016/j.jece.2015.02.007

Bhaumik R, Mondal NK, Chattoraj S (2017) An optimization study for defluoridation fromsynthetic fluoride solution using scale of Indian major carp Catla (Catla catla)

Cai HM, Chen GJ, Peng CY, et al (2015) Removal of fluoride from drinking water using tea wasteloaded with Al/Fe oxides: A novel, safe and efficient biosorbent. Elsevier B.V.

George AM, Tembhurkar AR (2019) Optimization of defluoridation using Ficus benghalensis leaf biosorbent through Taguchi's method. Water Environment Research 91:340–350.https://doi.org/10.1002/wer.1051

Getachew T, Hussen A, Rao VM (2015) Defluoridation of water by activated carbon prepared frombanana (Musa paradisiaca) peel and coffee (Coffea arabica) husk. International Journal of Environmental Science and Technology 12:1857–1866. https://doi.org/10.1007/s13762-014- 0545-8

Ismail ZZ, AbdelKareem HN (2015) Sustainable approach for recycling waste lamb andchicken bones for fluoride removal from water followed by reusing fluoride-bearingwaste in concrete. Waste Manag 45:66–75.
https://doi.org/10.1016/j.wasman.2015.06.039

Kigga M (2020) Bio-inspired materials for defluoridation of water: A review. ECSN 126657. https://doi.org/10.1016/j.chemosphere.2020.126657

Kumar P, Saraswat C, Mishra BK, et al (2017) Batch technique to evaluate the efficiency of different natural adsorbents for defluoridation from groundwater. Applied Water Science 7:2597–2606. https://doi.org/10.1007/s13201-016-0473-5

Li Y, Yang S, Jiang Q, et al (2018) The adsorptive removal of fluoride from aqueous solution by modified sludge: Optimization using response surface methodology. International Journal of Environmental Research and Public Health 15:. https://doi.org/10.3390/ijerph15040826

Mandal S, Mayadevi S (2009) Defluoridation of water using as-synthesized Zn/Al/Cl anionic clay adsorbent: Equilibrium and regeneration studies. Journal of Hazardous Materials 167:873– 878. https://doi.org/10.1016/j.jhazmat.2009.01.069

Manna S, Roy D, Saha P, Adhikari B (2015) Defluoridation of aqueous solution using alkali-steam treated water hyacinth and elephant grass. Journal of the Taiwan Institute of Chemical Engineers 50:215–222. https://doi.org/10.1016/j.jtice.2014.12.003

Miretzky P, Cirelli AF (2011) Fluoride removal from water by chitosan derivatives and composites: A review. Journal of Fluorine Chemistry 132:231–240. https://doi.org/10.1016/j.jfluchem.2011.02.001

Mohan R, Dutta RK (2020) Journal of Environmental Chemical Engineering Continuous fi xed-bed column assessment for de fl uoridation of water using. Journal of Environmental Chemical Engineering 8:103840. https://doi.org/10.1016/j.jece.2020.103840

Mouelhi M, Giraudet S, Amrane A, Hamrouni B (2016) Competitive adsorption of fluoride and natural organic matter onto activated alumina. Environmental Technology (United Kingdom) 37:2326–2336. https://doi.org/10.1080/09593330.2016.1149521

Murugan M, Subramanian E (2006) Studies on defluoridation of water by Tamarind seed, an unconventional biosorbent. Journal of Water and Health 4:453–461.https://doi.org/10.2166/wh.2006.014

Pandi K, Viswanathan N, Meenakshi S (2019) Hydrothermal synthesis of magnetic iron oxide encrusted hydrocalumite-chitosan composite for defluoridation studies. International Journal of Biological Macromolecules 132:600–605. https://doi.org/10.1016/j.ijbiomac.2019.03.115

Parlikar a S, Mokashi SS (2013) Defluoridation Of Water by Moringa Oleifera- A Natural Adsorbent. International Journal of Engineering Science and Innovative Technology (IJESIT) 2:245–252

Peng C, Xi J, Chen G, et al (2017) Highly selective defluoridation of brick tea infusion by tea waste supported aluminum oxides. J Sci Food Agric 97:1509–1516. https://doi.org/10.1002/jsfa.7893

Pillai P, Dharaskar S, Shah M, Sultania R (2020) Determination of fluoride removal using silica nano adsorbent modified by rice husk from water. Groundwater for Sustainable Development 11:100423. https://doi.org/10.1016/j.gsd.2020.100423

Rajkumar S, Murugesh S, Sivasankar V, Chaabane T (2015) Low-cost fluoride adsorbents preparedfrom a renewable biowaste : Syntheses , characterization and modeling studies. ARABIAN JOURNAL OF CHEMISTRY. https://doi.org/10.1016/j.arabjc.2015.06.028

Ramanaiah S V., Venkata Mohan S, Sarma PN (2007) Adsorptive removal of fluoride fromaqueous phase using waste fungus (Pleurotus ostreatus 1804) biosorbent: Kinetics evaluation. Ecological Engineering 31:47–56. https://doi.org/10.1016/j.ecoleng.2007.05.006

Sakthi Thesai A, Rajakumar S, Ayyasamy PM (2020) Removal of fluoride in aqueous mediumunder the optimum conditions through intracellular accumulation in Bacillus flexus (PN4). Environ Technol (United Kingdom) 41:1185–1198. https://doi.org/10.1080/09593330.2018.1523951

Samarghandi MR, Khiadani M, Foroughi M, Zolghadr Nasab H (2016) Defluoridation of water using activated alumina in presence of natural organic matter via response surface methodology. Environmental Science and Pollution Research 23:887–897. https://doi.org/10.1007/s11356-015-5293-x

Sharma R, Sharma R, Parveen K, et al (2021) Comprehensive and critical appraisal of plant-based defluoridation from environmental matrices. Chemosphere 281:130892. https://doi.org/10.1016/j.chemosphere.2021.130892

Singh TP, Majumder CB (2018) Batch and Column Performance of Fluoride Adsorption by Java Plum Seeds. Journal of Hazardous, Toxic, and Radioactive Waste 22:1–10. https://doi.org/10.1061/(asce)hz.2153-5515.0000394

Tomar V, Prasad S, Kumar D (2014) Adsorptive removal of fluoride from aqueous media using citrus limonum (lemon) leaf. Microchemical Journal 112:97–103. https://doi.org/10.1016/j.microc.2013.09.010

Wirtu YD, Melak F, Yitbarek M, Astatkie H (2021) Aluminum coated natural zeolite for water defluoridation: A mechanistic insight. Groundwater for Sustainable Development 12:100525. https://doi.org/10.1016/j.gsd.2020.100525

Xia Y, Huang X, Li W, et al (2018) Facile Defluoridation of Drinking Water by Forming Shell@Fluorapatite Nanoarray during Boiling Egg Shell. Journal of Hazardous Materials. https://doi.org/10.1016/j.jhazmat.2018.09.007

Yadav AK, Abbassi R, Gupta A, Dadashzadeh M (2013) Removal of fluoride from aqueous solution and groundwater by wheat straw, Sawdust and activated bagasse carbon of sugarcane. Ecol Eng 52:211–218. https://doi.org/10.1016/j.ecoleng.2012.12.069

Yadav AK, Kaushik CP, Haritash AK, et al (2006) Defluoridation of groundwater using brick powder as an adsorbent. Journal of Hazardous Materials 128:289–293. https://doi.org/10.1016/j.jhazmat.2005.08.006

Yao R, Meng F, Zhang L, et al (2009) Defluoridation of water using neodymium-modified chitosan. J Hazard Mater 165:454–460. https://doi.org/10.1016/j.jhazmat.2008.10.052