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Defluoridation Potential of Rice Husk, Groundnut Shell as a Conventional Alternative for Fluoride Removal – A Review

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Authors' contributions

This work was carried out in collaboration between both authors. Author AAP contributed to study conception and design, data collection, analysis and interpretation and drafted the work. Author JP contributed to data interpretation, study design and data collection. Both authors critically reviewed the manuscript and approved the final version.

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ABSTRACT

Fluoride occurs naturally in our environment but we consume it in small amounts. Exposure can occur through dietary intake, respiration and fluoride supplements. The most important factor for fluoride presence in alimentation is fluoridated water. Fluoride content in groundwater has become a national issue affecting the entire India. When the recommended limit of fluoride by WHO is 1.5 mg/L, in some particular parts of India fluoride levels are as high as 35 mg/l. Increased fluoride intake causes dental fluorosis, skeletal fluorosis and neurological problems. Major problems associated with fluoride remediation are lack of cheap adsorbent to remove fluoride content in water for poor communities of India. Hence, development of community-based defluoridation unit is needed with a technique which is cost-effective, technologically simple in operation while being able to keep the fluoride level in permissible limits. On the basis of extensive investigations, different researchers have developed simple and economical domestic defluoridation processes.

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The present review gives a brief account of prevalence, sources of fluoride toxicity and cost effective defluoridation method carried out on effects of fluoride in the last few decades. Thus cost effective absorbent which has high efficacy in fluoride removal from water can be provided to poor communities thereby preventing fluorosis.

Keywords: Defluoridation; fluorosis; groundnut shell; rice husk; toxicity.

1. INTRODUCTION

Fluoride is the ionic form of fluorine which is the 13th most abundant element in the earth's crust [1]. Fluoride is present in all natural waters. Fluoride level of 1.2-1.5 ppm is found in seawater. Fluoride level in freshwater is at the lower concentration ranging from 0.01 to 0.3 ppm. Hot springs of volcanic origin have an increased concentration of fluoride [2]. In industry, fluoride is used in the manufacture of ceramics, pesticides, aerosol propellants, refrigerants, glassware, and Teflon cookware. Humans are exposed to fluorine through food, drinking water and breathing air. The Optimum value of fluoride in drinking water is 1.5 mg/l [3]. The medicinal use of fluorides for the prevention of dental caries began in January 1945 when community water supplies in Grand Rapids, United States, were fluoridated to a level of 1 ppm as a dental caries prevention measure [4]. Fluoride at an excess level in drinking water in developing countries is an emerging problem [5]. It can cause several adverse effects in bone and teeth. It includes dental fluorosis followed by skeletal fluorosis as the period of exposure increases [6]. Thus several defluoridation techniques were introduced for fluoride removal. The fluoride removal in water is needed to prevent fluorosis. Various mediums used as absorbent in defluoridation techniques include bone charcoal, contact precipitation, Algona, activated alumina, ion-exchange technique, membrane filtration, nanofiltration, and clay. Advanced treatment technologies are reverse osmosis (RO), electrodialysis, and distillation [5]. Many researchers discovered natural alternatives for defluoridation [7]. Defluoridation techniques can be broadly classified into additive and adsorptive methods. The methods which are in existence can be classified into adsorption, Ion exchange and Precipitation and Miscellaneous methods. Adsorption methods by using different adsorbents like sunflower plant dry powder, steam of phytomass, Holly Oke, neem bark powder, activated cotton jute carbon, bagasse ash, burnt bone powder, phosphate-treated sawdust, bone char, etc. came into existence [8]. Many researchers have continued to explore the development of low-cost and effective adsorbents and to improve the efficiency of all adsorbents [9]. A solid waste material, Groundnut shell has potential for removal of fluoride from aqueous solution [7]. Rice husk ash has adsorbent properties because of its high silica content [10] and not only removes fluoride but also removes arsenic and improves the overall drinking water quality benefitting the entire poor community of our country [11]. Rice husk and groundnut shell were selected in this article since they are easily available and low cost medium that is affordable even for lower economic people.

Numerous epidemiological studies for the betterment of our community have been done [12–18]. In this research we are analyzing the Defluoridation potential of rice husk, groundnut shell as a conventional alternative for fluoride removal.

1.1 Role of Fluoride in Bone Health

Fluoride in various chemical forms, doses, and exposures has physicochemical and biologic effects on cells and tissues. Fluorides mediate their actions through MAPK signaling pathways, leading to changes in gene expression, cell stress, and even cell death [19]. Toxic levels of fluoride have been coupled with a weakening of bones and an increase in hip and wrist fractures. The U.S. National Research Council concludes that fractures are mostly associated with the fluoride levels of 1–4 ppm [20]. Fluoride can stimulate osteoblast proliferation and increase new mineral deposition in cancellous bone. These effects are mediated by fluoride ions' incorporation into bone crystals, which increases the size and, thus, decreases the solubility of the bone (apatite) crystals. Larger crystals are more resistant to osteoclastic attack [21]. Fluoride has an ability to increase bone mineral density in the lumbar spine but it does not cause a reduction in vertebral fractures and can increase the side effects [22].

1.2 Role of Fluoride in Dental Health

The impact of fluorine on human teeth was recognised by Frederick McKay and Grant Black in 1909 in Colorado, United States during their investigation into the causes of mottled enamel ("Colorado brown stain") in their practice area. Further studies by McKay, Kempf, and Churchill on water samples in areas in Idaho and Arkansas in 1931 confirmed the link between mottled enamel and high water fluoride levels [23,24]. From 1931, Dr. Trendley Dean, Head of the Dental Hygiene Unit at the National Institute of Health, began investigating the epidemiology of fluorosis. After a decade's study, Dean and his team found that water containing fluoride at a concentration of 1.0 part per million (ppm) appeared to offer some caries protection while minimising the extent of dental fluorosis [25,26]. Hydroxyapatite in teeth enamel is made up of calcium, magnesium, and phosphate compounds and is susceptible to decay induced by acid-producing bacteria. Fluoride interacts with hydroxyapatite to form fluorapatite, which is less susceptible to erosion by acid-producing oral bacteria. About 50% of ingested fluoride is absorbed in the bones and teeth while the rest is excreted in urine. Most of the ingested fluorides reach the teeth via saliva, whose fluoride content varies from less than 0.01 to 0.05 ppm. Fluoride absorption in bones and teeth decreases with increasing age [12,27]. Fluoride contributes to remineralisation of enamel and also has anti-caries effect [28]. Fluoride is thought to adversely affect polysaccharide metabolism in bacterial cells, reduce the ability of such cells to maintain pH homeostasis, and inhibit encholase as well as other ATPase enzyme systems [29].

Fluoride may cause disordered protein synthesis by affecting the function of the endoplasmic reticulum in ameloblasts. Excessive fluoride can induce oxidative stress in ameloblasts, and the fluoride-induced reactive oxygen species (ROS) production causes oxidative damage to mitochondria and DNA [30].

Dental fluorosis is a permanent hypomineralization of enamel that is characterized by greater surface and subsurface porosity than in normal enamel and results from exposure of the immature tooth to excess fluoride during development stages [31,32]. Dental fluorosis can be easily recognised, but the skeletal involvement is not clinically obvious until the advanced stage of crippling is reached [33].

2. FLUORIDE TOXICITY

Dental Fluorosis representation starts with formation of thin white striae across the enamel surface. The cusp tips, incisal edge or marginal ridges shows "snow cap phenomenon" as they appear opaque white. As the fluoride level increases furthermore, the entire tooth surface may exhibit distinct, irregular, opaque or cloudy white areas followed by the irregular opaque areas merging to give chalky white appearance. In more severe stages, the tooth surface is entirely opaque with focal loss of the outermost enamel. These small defects are designated as "pits". Pits may vary in diameter and occur scattered over the surface and most frequently they occur along the incisal/ occlusal half of the tooth. With increasing severity these pits merge to form horizontal bands. This confluence of the pitted areas produces larger "corroded" areas. Finally the entire tooth morphology is affected [34].

If fluoride level increases to 6mg/l a day, skeletal manifestation begins [35]. Fluoride has a preferential affinity to accumulate in cancellous (spongy) bones, compared to compact (cortical) bones as cancellous bone has excellent blood supply than the cortical bone [36]. Skeletal fluorosis is a crippling disease and is a threat among elderly [37,38]. Skeletal fluorosis includes osteosclerosis, osteomalacia, osteoporosis, ossification of periosseous soft tissue and degenerative changes of cartilage and joints. Active osteogenesis and accelerated bone turnover are important features of skeletal fluorosis progression and the pathological basis of the diversity of osteogenic lesions [30].

The 33rd Conference of the International Society for Fluoride Research, held in India in 2016, focused on the pathogenesis of fluorosis at the molecular and genetic level. It not only explores the molecular mechanism of fluoride action in bone tissue damage, but also the toxic effects of fluoride on non-skeletal tissues, such as the nervous system, cardiovascular system, liver, kidney, reproductive system, thyroid and the progeny effect of fluoride [39].

Fluoride can penetrate into the brain through blood-brain barrier. Reduced level of intelligence is seen in children drinking water with high fluoride content [40,41]. In mothers, after being exposed to water fluorosis caused significant changes in hippocampal structural parameters of offspring [42]. Maternal fluoride exposure during gestation and lactation can influence the learning, memory ability and glutamate receptor expressions of the offspring [43].

3. CONVENTIONAL DEFLUORIDATION TECHNIQUE

Defluoridation involves the removal of fluoride ions in drinking water. Defluoridation methods may be broadly classified into Additive methods and Adsorptive methods. The different methods used for the removal of excess fluoride from water can be classified into four basic types: Precipitation technique, adsorption technique, ion exchange technique, reverse osmosis and electrodialysis [44].

The Nalgonda technique was developed and adapted in India by the National Environmental Engineering Research Institute (NEERI). It utilizes aluminum sulfate to enhance coagulation-flocculation-sedimentation, the dosage of which is designed to ensure fluoride removal from the water. The use of alum and lime has been extensively studied for defluoridation of drinking water, and it is popularly known as the Nalgonda technique [45].

Synthetic chemicals, namely, anion and cation exchange resins have been used for fluoride removal. Some of these are Polyanion (NCL), Tul-sion A-27, Deacedite FF (IP), Amberlite IRA 400, Lewatit MIH-59, and Amberlite XE-75. These resins have been used in chloride and hydroxy form. The fluoride exchange capacity of these resins depends upon the ratio of fluoride to total anions in water [46].

Electro-defluoridation (EDF) was also developed by NEERI, India, to treat excess fluoride concentration in drinking water. EDF involves the use of aluminum electrodes that release Al^{3+} ions by an anodic reaction and hydrogen gas released at the cathode, and the ions then react with fluoride ions that are found in excess near the anode [47,48]. The EDF system's fluoride removal mechanism is through adsorption and co-precipitation with the aluminum-based colloidal precipitates generated by the electrodes [49].

Adsorption technique is arguably one of the most versatile of all the defluoridation techniques due to a number of reasons such as cost, diverse end-uses, socio-cultural acceptance, regulatory compliance, environmental benignity and simplicity. For this technique, activated alumina, bone char and clay adsorption media are the most developed [50].

4. RICE HUSK AND GROUNDNUT SHELL

Rice husk is one of the by-products of rice production, left after the burning of rice husk. It can cause environmental pollution, as its disposal is difficult. Hence its proper reuse is necessary, and because it is mainly composed of carbon and silica, it could be used in adsorption processes for removal of toxic heavy metals from water and wastewaters. Rice husk is available in ample amounts. Advantages of using rice husk derivatives as biosorbent are their biodegradability and good adsorption property which can be due to their morphology and surface functional groups [51]. The rice husk can be used as an economic alternative for the removal of metals from aqueous solutions [52]. Rice husk ash (RHA) is a by-product formed by the burning or combustion process of Rice hull (RH) which also contains some amount of carbon [51].

Groundnut shells account for approximately 20% of the dried peanut pod by weight, meaning there is a significant amount of shell residual left after groundnut processing. Increased groundnut production leads to the accumulation of these groundnut shells which is not utilized, thus either burnt or buried. As Groundnut shells are rich in many functional compounds and composed of cellulose, hemicellulose and lignin, it can be utilized in multiple ways. Groundnut shells act as a good biosorbent for the adsorption of heavy metals from the industrial effuents [53].

5. DEFLUORIDATION POTENTIAL OF RICE HUSK, GROUNDNUT SHELL

Various past studies have shown usage of rice husk and groundnut shell as defluoridation medium. According to Ghosh et.al, Lanthanum-Impregnated Rice Husk Ash (LIRHA) removed fluoride to less than the permissible limit in the naturally encountered pH of water. The optimum time and dosage of LIRHA were found to be 240 min and 6 g/L, respectively. The anions phosphates and chlorides were found to be detrimental for fluoride adsorption probably due to the competitive action of those ions with fluoride on the active adsorption sites on LIRHA [54]. Here rice husk has not been used as such instead impregnated with lanthanum but produced results which were not satisfactory. In a study done by Ganvir et al using aluminium hydroxide coated rice husk ash showed that excellent fluoride removal efficiency and the adsorption capacity was found which was between 9 and 10 mg/g [55]. Synergistic action of rice husk and aluminium hydroxide provided greater fluoride removal. Rice husk can also be chemically modified to increase its efficacy. According to Gebrewold et.al showed that chemically modified rice husk had the maximum fluoride adsorption capacity of 7.9 and a fluoride removal efficiency of 91% from groundwater [56]. McKee and Jhonstonstudied the removal of fluorides from drinking water using rice husk and found a maximum of 83% removal accomplished by rice husk. Removal of fluoride by rice husk decreased continuously as pH was increased from 2.0 to 12.0 as depicted decrease in the removal of fluoride in pH range of 2.0–10.0 was low, i.e., 12.8%, whereas removal of fluoride decreased significantly from pH 10.0 to 12.0. The amount of fluoride adsorbed increased with increase in dose and maximum 84% removal was accomplished at a dosage of 6 g/L [57]. This author used only rice husk without impregnating other chemical absorbents but the defluoridation capacity was less compared to using rice husk with chemical absorbents.

Mohammad and Majumder investigated feasibility of low-cost biomass-based adsorbent and found that groundnut shell 89.9 of fluoride and contact time for groundnut shell is 75.0 min at doses of 12 g/L. Action of this adsorbent on fluoride was compared with commercially available adsorbents. It was found to be much better, high removal efficiency at higher concentration (20 mg/L) of fluoride in industrial waste water [58]. According to a study done by BuddharatnaGodboley et al. the highest defluoridation capacity of 92.8% was obtained with the dose of 4.5 g/L [7]. The dosage level was low compared to rice husk dosage to reach its highest defluoridation capacity. Lavanyarahaviet.al observed the defluoridation effect and found that the fluoride level reduced from 3 mg/L to 0.05 mg/L, 0.07 mg /L in groundnut husk, Rice husk respectively. Higher reduction was observed in groundnut husk group [59]. These have no complications as such but have lower fluoride removal capacity than other synthetic costly absorbents.Thus comparing among natural adsorbents used in various articles, it was found that groundnut shell was more effective compared to rice husk as it has more defluoridation capacity in lower dosage.

6. CONCLUSION

With recent developments in the avenue of patient care and management, Fluorosis can be prevented through early diagnosis and prompt mitigation. Diet editing to avoid fluoride contaminated drinking water and food is an intervention that the patients are introduced to, for avoiding the damage [33]. Defluoridation should be taken seriously to prevent community damage. Low cost medium can be used for defluoridation of groundwater in poor communities. According to the present review, groundnut shell is more effective in removal of fluoride from groundwater. Thus fluoride removal can prevent development of fluorosis among the community.

CONSENT

It is not applicable.

ETHICAL APPROVAL

It is not applicable.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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