Defluoridation of water through the application of carbonised bone as a green adsorbent: A review

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Flouride contamination of water is recognised as a serious challenge facing humanity. Consumption of water that contains excessive amounts of fluoride can result in fluorosis. Consequently, concerted efforts have been made to develop cheap, effective and green techniques/materials to remove fluoride from water, particularly potable water. Bone char prepared from bovine, swine, and equine bones has been used extensively in this regard, and is the most promising, cheap and green material for treating drinking water with high fluoride concentration, particularly in developing countries. However, research on bone char prepared from bones of animals in the wild, as well as those from domestic and semi-wild animals treated with antibiotics to enhance growth, has been scanty. Such research is important as the use of antibiotics may alter the composition of bones, and thus their potential as a green adsorbent to remove fluoride may be impaired. Furthermore, little attempt has been made so far to package char bones for easy application domestically, particularly in rural communities.

Significance:

- Contamination of water by fluoride is a major problem globally.
- Various techniques and materials have been employed for water defluoridation, including the use of bone char, which has several advantages.
- Bone char prepared from bones of animals in the wild and those from domestic and semi-wild animals treated with antibiotics to enhance growth should be further investigated.
- Cheaper and less elaborate processes and packaging are required to scale down the use of bone char at domestic level.

Introduction

Covering approximately 75% of the surface of the earth, water is the most common substance on earth and one of the major elements that are essential for sustaining all life forms on earth.[1] Water has the ability to dissolve almost all substances with which it comes into contact, hence it is frequently referred to as a universal solvent.[2] About 60% of the available fresh water is found in just nine countries and the distribution of water is still uneven within these countries.[3] The shortage of water is observed as an arduous challenge that the modern world is facing. Fluoride (F) in water affects millions of people worldwide and hence is a major contributor to the world's water crisis.[4] Arid and semi-arid regions are ideal sites for contamination of drinking water by fluoride.[5] Groundwater is one of the primary sources of water for daily needs in many regions of the world.[6] Around 200 million people from 25 nations in the world, including highly populated countries like China and India, and a significant population from East Africa, are worst affected by the presence of excess fluoride in their drinking water.[7-10]

South Africa is a water-stressed country. However, like other areas of the globe facing severe water stress have demonstrated, there are solutions available to cultivate a more secure water future for South Africa.[11] These solutions include using groundwater more frequently in areas where the supply is sustainable.[12] Most rural communities in Africa, including South Africa, depend on groundwater as the foremost water reservoir. However, groundwater is prone to contamination by chemicals that occur in nature, including fluoride.[13-15] Fluorine is a highly reactive element of fluoride which is found naturally as calcium fluoride (CaF_2).[16] Due to geogenic causes, the distribution of fluoride in the environment is unbalanced.[17] Fluoride has a strong liking for the acquisition of electrons, hence the formation of negative fluoride ions (F^-). As a result, fluoride forms composites with numerous positively charged ions, which constitute about 0.75% of the earth's crust. Seawater contains fluoride that is about 1 mg/L in concentration, while lakes and rivers, and groundwater have fluoride concentrations of 0.5 mg/L and 1–35 mg/L, respectively.[18,19]

Origins of fluoride

Fluoride originates from both natural sources, such as volcanic activities, as well as anthropogenic sources, such as pesticides and industrial waste. The origins of fluoride are discussed below.[20]

Natural sources

Typical natural sources of fluoride are soil, water, forage and grasses, and volcanic activity. Soil normally has a fluoride content that ranges from 150 mg/kg to 400 mg/kg[21,22], and this content varies in other natural sources based on alkalinity and temperature[23,24]. The level of fluoride in clay soil is 1000 mg/kg.[25] The contamination of soil with fluoride is a result of using phosphorus fertilisers which have 1–1.5% fluorine.[25] The toxicity of fluoride-contaminated soil comes after the inhalation of soil contaminants which have vaporised or through contaminated groundwater after the leaching of fluoride from adjacent fluoride-contaminated soil.[21] A concentration above 2.6 mg/L F is considered to be highly contaminated.[26] It was found that the level of fluoride in groundwater is higher than that in surface water due to percolation of fluoride from the soil to groundwater through a leaching process.[21] Some studies have also found grasses and forage that have higher levels of fluoride than those in industrialised areas.[21,23] Volcanic ash contains a high level of fluoride and contamination of the geochemical cycle with fluoride occurs frequently.[21,27] Fluoride from a volcanic eruption may cover a wide area and remain for many years. After decaying and leaching, fluoride wreaks havoc on domestic and wild animals.[21]

Anthropogenic sources

Human activities that bring about anthropogenic fluoride contamination include the development of industries, the introduction of motor vehicles, the use of fluoride-containing pesticides, and the deliberate addition of fluoride to drinking water supplies, toothpaste and mouthwashes, refrigerants, and fire extinguishers. The average concentration of fluoride in normal areas (unpolluted/non-industrialised) is generally less than 0.1 $\mu g/m^3$.[21]

Fluoride levels at global scale

Around the world, 23 nations, including South Africa, are situated in the condemnatory region with regard to their fluoride levels.[21] A global indication of maximum fluoride levels in drinking water is shown in Supplementary table 1.

Human exposure

Water scarcity, rapid population growth, and unfavourable climate changes have led to more communities relying on drinking water that has excessive fluoride content.[28] Water, food and oral hygiene products are the main sources of fluoride exposure for human beings.[29,30]

Toxicity of fluoride

The World Health Organization (WHO) guidelines indicate 1.5 mg/L as the highest fluoride content that is permissible in drinking water.[31] Consumption of fluoride above the permitted limit of 1.5 mg/L is considered harmful to health and could result in dental fluorosis among other effects.[32-34] As stated by WHO[32], consumption of water containing higher fluoride levels, in the range of 3 mg/L to 6 mg/L, could account for skeletal fluorosis.[32,35,36]

Defluoridation techniques

This section focuses on various techniques and materials employed globally for water defluoridation. Defluoridating methods may loosely be classified into two categories: 1) additive methods and 2) adsorptive methods.[37] Various methods and materials, as listed in Table 1, have been used to defluoridate drinking water.

Adsorption

This technique involves the adsorption of fluoride ions onto the surface of an active agent. In the adsorption method, a bed of greater surface activity is chosen, and water is passed through the bed. Due to surface activity, fluoride ions get preferentially adsorbed onto the bed surface, thereby causing a reduction in fluoride ions in the exit stream.[39]

Ion exchange

This technique utilises synthetic chemicals. Anion and cation exchange resins are used to remove fluoride. These resins are commercially produced and hence they are expensive and not cost-effective in most circumstances.[37,42]

Precipitation and coagulation

Precipitation methods rely on the addition of a chemical precipitant or coagulant to transform dissolved, moderately soluble fluoride salts into insoluble fluorapatite. Sedimentation or filtration is then required for separation of the solids from the liquid, thereby removing the fluoride.[38]

Reverse osmosis

Reverse osmosis has emerged as the ideal method for water defluoridation, thus providing safe drinking water without presenting the challenges that are normally associated with other methods such as ion exchange resins, addition of chemicals to achieve coagulation and total reliance on electricity to sustain electrocoagulation.[43] Reverse osmosis uses a semi-permeable membrane that traps a significant array of contaminants but allows water molecules to pass through when water is pushed under pressure through the membrane.[39]

Nanofiltration membrane

Nanofiltration is reported to be the most recent improvement among all the membrane processes that are used for defluoridation of drinking water and wastewater. Properties of nanofiltration membrane cut across reverse osmosis and ultrafiltration.[44,45]

Electrocoagulation

Electrocoagulation is a process that uses an electrical charge to destabilise and aggregate contaminant particles, ions, and colloids to hold them in solution. Instead of expensive chemical reagents, the process removes heavy metals, suspended solids, emulsified organics and many other contaminants from water using electricity. It is a complex process that takes place through serial steps.[46-49]

The fluoride removal performance of these different defluoridation techniques is compared in Supplementary table 2.

Water defluoridation using bone char

Mechanism of defluoridation

Bone char is one of the most promising methods for the treatment of drinking water with excess fluoride concentration in developing countries.[25] This is mainly because it is rather inexpensive as it is produced from animal bones, can be synthesised in adequate amounts and to the desired quality[50], and can also be regenerated by simply reheating[51]. The ability of bone to defluoridate water was reported by Smith and Smith in 1937.[52] Several scholars and organisations have investigated defluoridation by bone char and the outcomes show

Table 1: Different defluoridation techniques and the materials employed[37-41]

Adsorption	Ion exchange	Precipitation and coagulation	Membrane	Electrocoagulation
Activated alumina	Anion exchange resins: NCL poly anion resin, Tulsion A27, Lewatit–MIH–59, Amberlite IRA–400, Deacedodite	Contact precipitation	Reverse osmosis	Electrolysis: aluminium electrode
Bone char	Cations	IISc Method	Electrodialysis	
Calcined clay		Nalgonda technique: lime, alum, lime and alum	Direct contact membrane distillation (DCMD)	
Mud pots				
Bio-adsorbents: tea ash, eggshell powder				

impressive efficiency.[53-55] Bone char consists largely of hydroxyapatite and a significant amount of calcium carbonate while carbon accounts only for 10% (w/w).[56] Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are used to assess, respectively, the outside and internal morphology of the prepared bone char, whereas the chemical composition is often determined by the application of energy dispersive X-ray spectroscopy (EDX).[57]

There are two basic ways to char bones for the production of bone char: (1) calcination, in which atmospheric air provides oxygen during the heating process, and (2) pyrolysis, in which the heating process takes place in an oxygen-deprived environment. According to previous investigations, bone char that is produced by calcination at temperatures higher than 600 °C inhibits the adsorption process[58,59], whereas bone char produced at temperatures below 400 °C may influence the taste and odour of the treated water.[60]

Water defluoridation by charred bone is achieved through ion exchange and adsorption that result in the replacement of the carbonate of the apatite in the bone char with the fluoride in the water.[38,58] This defluoridation technique involves more than one reaction, as shown in Equations 1 and 2, and the efficiency of bone char to remove fluoride from water depends on the level of fluoride in the raw water, pH, contact time and amount of char used (available surface area).[61]

$$\mathrm{Ca_{10}(PO_4)_6(OH)_2 + 2\,F^- \leftrightarrow Ca_{10}(PO_4)_6F_2 + 2\,OH^-} \qquad \text{Equation 1}$$

$$\mathrm{\left(Ca_3(PO_4)_2\right)_n CaCO_3 + 2\,F^- \rightarrow \left(Ca_3(PO_4)_2\right)_n CaF_2 + CaCO_3^{2-}} \qquad \text{Equation 2}$$

There is no universal water defluoridation method that perfectly meets all social, financial, economic, environmental and technical requirements. However, using charred bone as a medium for water defluoridation has a few advantages.[62] With this defluoridation approach, there is no daily addition of chemicals, working load and continuous power supply. High removal efficiency can be achieved. There is no demand for skilled operation as the defluoridation set-up is simple to construct. Construction materials are cheap and widely available. The method comes at a controlled risk of declination of the inherent quality of water, and it is a highly profitable technique that could remove a maximum of 66% of fluoride.[38,63]

Bones from wild animals

While extensive research has been done on defluoridation using bone char from bones obtained from domestic bovines, porcines, ovines, caprines, chickens, fish, camels, and other undeclared sources (Supplementary table 3), there is no mention of the use of bones of animals in the wild. The bones of wild animals, including birds, even those in captivity, are believed to have higher calcium content than the bones of domestic animals because their main diet is based on natural materials. Studies have found a relationship between meat protein and elevated levels of growth hormone, which in turn is connected to increased laying down of calcium and phosphorus, as well as other minerals, on the matrix of bone, thus minimising bone fractures.[64] Therefore, the use of such bones is envisaged to enhance defluoridation of water. On the other hand, the use of antibiotics in domestic and semi-wild animals to fight and prevent infections that lead to diseases and to promote growth in animals is likely to have some impact on bone composition, thus establishing yet another difference in the composition of bones from wild, semi-wild and production animals.[65] Rosol et al.[66] found that mithramycin, an antibiotic that has anti-tumour properties, inhibited the stimulation of bone resorption in dogs. Phenylbutazone, a non-steroidal compound that is commonly used for temporary treatment of pain, fever and stiffness in animals, was found to reduce the rate at which some minerals align in order to respond to defects in cortical bone in horses.[67]

Defluoridation in Africa

There is a relationship between volcanic activities, hot springs (particularly those that have higher pH), gases that are released from earth's crust, and igneous and metamorphic rocks.[68-71] The world map in Amini et al.[72] illustrates the likelihood of fluoride concentrations that surpass 1.5 mg/L in groundwater. Figure 1 shows the African countries with elevated fluoride concentrations in water.

Various studies have demonstrated a relationship between most cases of dental fluorosis that occur in South Africa and the concentration of fluoride in groundwater that is intended for drinking[74-76], therefore rural communities are those mainly affected by dental fluorosis. Fluoride concentrations that exceed the WHO threshold of 1.5 mg/L have been reported in many areas and provinces in South Africa, such as the Free State, Limpopo, North-West and KwaZulu-Natal Provinces.[15,31,71]

Column and batch studies for defluoridation

Removal of fluoride from the solution is normally managed through a column[77,78] or batch set-up. In a column set-up, a vertical column that contains the prepared adsorbent is used, and the solution is run from the top through the adsorbent as pulled and guided by gravity. The treated solution is collected at the bottom of a column. In a batch set-up, both the prepared adsorbent and the solution are mixed and adsorption is allowed to take place over a controlled period of time with continuous stirring throughout the process. As a result of simultaneous mixing of the adsorbent and the solution, and the subsequent agitation of the mixture, the resultant solution requires separation that could be achieved by filtration, centrifugation or decantation.[79]

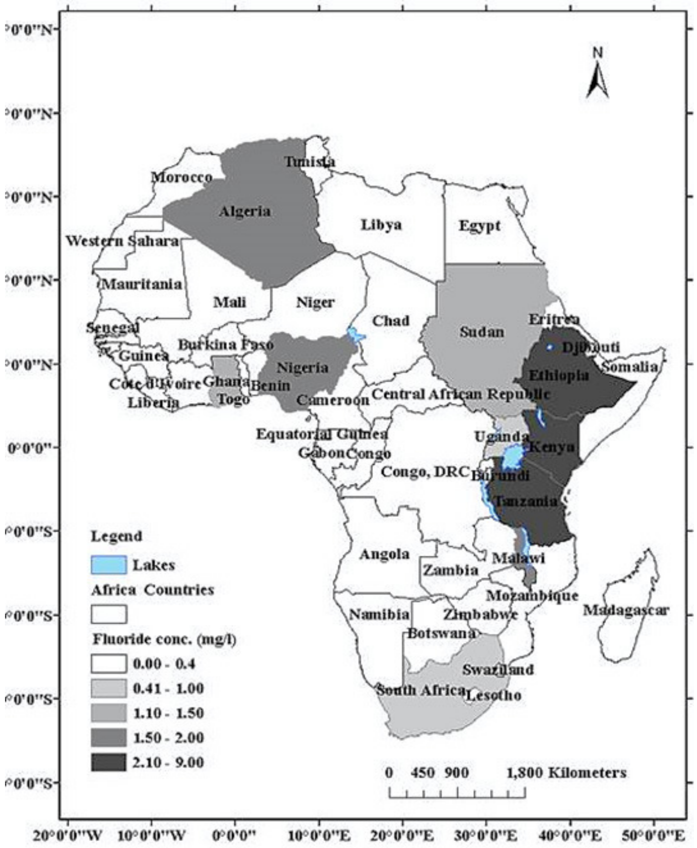
Adsorption isotherms are needed to better describe the interaction of solutes with the adsorbents. In line with the optimised use of the adsorbent, it is just as important to measure the rate of adsorption at constant concentration. Adsorption kinetics are important to assess the dispersal of the adsorbate at the pore level of the adsorbent. Batch adsorption experiments are required to carry out adsorption isotherms and kinetics tests.[25] The maximum capacity of the adsorbent under the set operating conditions is indicated by the quantity of fluoride ions adsorbed at the equilibrium time. Adsorption isotherm and kinetics experiments are key in optimising the use of adsorbents.[80] Ion chromatography is used to analyse the total fluoride in water.

Research gaps on carbonised bone in Africa

Sorbent prepared from charred bone is an affordable method of removing fluoride from groundwater, and bones from production animals are most extensively used in this regard. However, the issue of optimum particle size required for maximum fluoride removal has not been given adequate attention, particularly for bones from wild animals, including birds. It is generally accepted that the finer the particles the higher the uptake, because of the increase in surface area. However, very fine particles also have the problem of aggregation, which impedes adsorption. Therefore, determination of the optimum particle size to achieve maximum removal is essential.

It is also generally believed that the removal of fluoride is the direct reaction of calcium compound(s) in the bone with fluoride in the water to form calcium fluoride compounds as indicated in the equations above. However, it is still not clear whether the driving mechanism is that of mesoporosity or microporosity. It is important to know the driving mechanism as this will assist when considering the recovery of fluoride from the adsorbent. A detailed morphology of bone char will heighten our understanding of the structural arrangement of the bone(s) under study, and hence of the driving process(es). Furthermore, information on the defluoridation of water using various types of bone char prepared from the bones of wild animals is still scarce. The use of antibiotics to treat and control clinical diseases in domestic and semi-wild animals and to enhance growth in production animals is likely to have an impact on bone composition, thus establishing yet another difference in the composition of bones from wild, semi-wild and production animals.

Studies on defluoridation of water using bone char have so far used batch and column models. These models have been tested and are reliable. However, the scaling down of the use of bone char to a domestic level requires a cheaper and less elaborate process and packaging. Packaging of bone char in the form of a tea bag can be very useful at domestic levels, particularly for low-resourced rural communities that are commonly found in Africa and some parts of Asia and South America.



Source: Malago et al.[73] *(under CC-BY-4.0 licence)*

Figure 1: Map of Africa illustrating the countries with high fluoride concentrations in their water.

Conclusions

This review highlights the scarcity of water, the subsequent reliance on groundwater as an alternative source of potable water in some nations and communities, the contamination of groundwater with fluoride, fluoride toxicity, and different water defluoridation techniques. When all methods are compared, there is no universal water defluoridation method that perfectly meets all social, financial, economic, environmental, and technical requirements. However, using bone char as an adsorbent in fluoride removal has a few advantages. With this defluoridation approach, there is no daily addition of chemicals, working load and continuous power supply. There is no demand for skilled operation as the defluoridation set-up requires minimal effort to construct. The materials required for construction are affordable and abundantly available. There is a low risk of the original water declining with this method. Adsorption using bone char is a useful technique that has the capacity to remove up to 66% of fluoride. Ingestion of fluoride affects human health in various significant ways, and can negatively impact quality of life. Whilst fluorosis is not deadly, moderate fluorosis causes the deterioration of dental aesthetics and severe fluorosis can lead to disorders of the skeletal system. In the absence of any practical cure, prevention of fluorosis remains the only solution. The key and immediate preventive measure is to consume water that has an acceptable fluoride level. This can be achieved by treating drinking water that is contaminated with fluoride to significantly lower the fluoride level. That being the case, water purification techniques should be further investigated, and new ones developed to ultimately achieve a method that is both safe and inexpensive.

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Competing interests

We have no competing interests to declare.

Authors' contributions

S.P.M.: Writing – initial draft; project management; data collection. J.O.O.: Conceptualisation; student supervision; writing – revisions. R.J.: Student supervision.

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