



A Short Review on Fluoride and Arsenic Constituents in Nigerian Groundwater Networks: Causes, Effects and Suggested Removal Methods

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Article History	Abstract
Received: 06 June 2023 Revised: 05 Sept 2023 Accepted: 12 Nov 2023	<p><i>The quality of water cannot be overlooked as it is an important element required by every being in existence. Water majorly is used as drinking water and if not properly looked after could lead to various health and environmental issues. Fluoride and arsenic are naturally occurring pollutants with their sources being traced to either anthropogenic or geogenic contributions. It is imperative to note that excessive consumption of fluoride and arsenic in water could result to serious health challenges. Elevated constituents of fluoride and arsenic in water have been reported in the northern and southern parts of Nigeria, but their concentrations are more prevalent in the north. The contaminants have been traced to some activities such as mining, improper disposal sites, agricultural practices, industrial effluents among others. Adsorption process has been suggested as the cost effective and environmentally friendly defluoridation, while nanofiltration membranes is the best removal process for arsenic in water.</i></p>
CC License CC-BY-NC-SA 4.0	<p>Keywords: Defluoridation, Arsenic removal processes, Public health, Water treatment and quality, Groundwater pollution</p>

1. Introduction

In this article, the fluoride and arsenic constituents in groundwater of some communities in Nigeria will be reviewed. Fluoride and arsenic are naturally occurring elements that have their benefits, as well as their side effects, when present in water. When fluoride is moderately present in water, it reverses early tooth decay in humans, remineralizes tooth enamel and slows the demineralization process down (Fawell et al. 2006). High intake of fluoride in water could cause tooth discolouration, tooth decay, neurological problems, acne, skeletal weakness, high blood pressure and seizure of breaths (or lead to death). Arsenic can be present in groundwater from mining activities, agricultural activities (such as the usage of wood preservatives, animal feeds and pesticides), metallurgical industries, pharmaceutical industries, semiconductor industries and other human activities. Presence of arsenic in water has also been traced to geogenic pathways (such as volcanic activities and rock-water interactions) (Orosun 2021). In potable water, arsenic poses a deleterious risk to humans, even if it is present at low levels. Over consumption of arsenic constituents could be detrimental to skin, eyes, lungs, kidneys and lymphatic system, which could cause cancer and serious cardiovascular diseases in humans (Moon et al. 2012).

Inaccessibility to potable water with good quality is becoming rampant today (Adagunodo et al. 2018, 2023; Omole et al 2019; Emenike et al. 2017, 2020; Ojoawo and Adagunodo 2023). The World Health Organization (WHO) has notified the concerned bodies that about 884 million people have no access to quality and uncontaminated water (WHO 2011). Lack of clean and quality water can lead to series of water-borne diseases (such as cholera, food poisoning, diarrhea, amoebiasis, shigellogis, leptospirosis, helminthiasis, typhoid, hepatitis A and other infectious diseases) (Ameer 2017). Consumption and usage of unclean water could lead to death. Availability of un-treated water could destroy the marine organisms, which could in-turn lead to increase in water and airborne diseases (Jacobs 2018), thus, affecting all the food chains in an ecosystem. It is evident that water quality does not only control the well-being of man, it is also subjected to the environment and all its inhabitants.

Water quality is an important factor for the health of both humans and the environment. Due to a lack of access to clean water and sanitation, difficulties arise which endanger the lives of millions of people worldwide each year (WHO 2011). Inadequate water quality has been linked to issues such as malnutrition, diarrhea, and infectious diseases, which place a great strain on global health. Moreover, a loss of water quality can also lead to the pollution of environment. Contamination of waterways by pollutants has damaged habitats and reduced the diversity of native species, endangering the health of ecosystems (WHO 2011). Therefore, it is essential that efforts are taken at both local and global level to prioritize the concern of water quality.

According to the World Health Organization (WHO), more than half of the global population lacks access to a safe water source that meets their needs. This statistic reveals there is an alarming public health concern posed by this lack of access to safe water. In addition to increasing instances of serious illness, consumption of poor or low quality water can lead to death due to water-borne diseases (Adagunodo et al. 2023). Poor quality water can cause a number of illnesses and can be a major detriment to human health (Adagunodo 2017a, b; Emenike et al. 2018; Samuel et al. 2018; Adagunodo et al. 2019; Academe et al. 2022; Bayowa et al. 2023).

Evaluations of fluoride and arsenic loads in groundwater system of some communities in Nigeria have shown an alarming increment in the trend at which these two elements are present in water (Gbadebo 2012; Olusola et al. 2017). The source of fluoride in groundwater is mainly from the rock-water interaction (geogenic source). Consumption of excessive high constituents of fluoride in water for a long period could result to dental fluorosis, skeletal fluorosis and other series of ill-health status in human (Emenike et al. 2018). Meanwhile, arsenic loads in water are known carcinogens. Its overdose in water has been linked to risks such as strokes, coronary heart diseases, peripheral arterial diseases and blackfoot diseases in human (Strom 2004; Moon et al. 2012). Its high levels in water has been linked to endothelial dysfunction and atherogenesis in animals (Jomova and Valko 2011). It is essential that water for human usage should be treated to ensure safety and healthy living status of the consumers. It is advised that governmental bodies (at all cadres) and relevant non-governmental agencies rise to protect the interest of masses by ensuring their well-being and healthy living conditions, through adequate supply of clean and safe water for people, in line with the Sustainable Development Goal's (SDG) agenda (SDG, 2019).

Fluoride Loading

Water fluoridation is a process that is applied to a public water to ensure that the fluoride levels in the water is controlled to minimize tooth decay (Mullen 2005). Fluoride water acts on tooth surfaces, by maintaining low fluoride constituents in saliva. It inhibits the demineralization rates in tooth enamel and catalyses the remineralization rates at the initial stage of cavity. Three main sources of fluoride contamination in water have been identified in Nigeria as: sodium fluoride (NaF), calcium fluoride (CaF₂) and fluorosilicic acid (H₂SiF₆) (FWWASH Nigeria 2019). The fluoride level is altered naturally when either one of these three sources is present in water supply. Apart from these man-made techniques, fluoride contamination can occur occasionally through natural geological processes within the basement complex terrains (Olusola et al. 2017; Oyebola 2017; Emenike et al. 2018; Academe et al. 2022). When there is an adequate control of water quality in place, the level of fluoride constituents in water supply will be monitored and controlled nationally, thereby promoting good dental hygiene and minimizing the overdose effects of fluoride in human.

Fluoride in water is not only peculiar to Nigerian terrain, it occurs naturally in water globally. Various constituents of fluoride have been identified in surface water and groundwater in Nigerian communities. The source of contamination in Nigeria has been either through anthropogenic or geogenic source (Podgorski and Berg 2022). The identified anthropogenic sources in Nigeria are as a result of industrial activities, agricultural activities and water treatment plants, whereas, the identified geogenic sources are through the water-aquifer chemical exchange through varying geological terrains (Morkve and Ballard 2012; Oyebola 2017; Malomo et al. 2018). Despite the benefits of fluoride in water, it is imperative to note that its excessive loads could result to serious health challenges (Morkve and Ballard 2012; Malomo et al. 2018). Elevated constituents of fluoride in water is one of the identified challenges by scientists in Nigeria. The challenges have been categorized into two clusters. Cluster one is the water fluoridation, which adds small amount of fluoride to municipal water supplies. The other cluster is naturally occurring fluoride in rock strata — usually from biotite, fluorite, amphibole, topaz, apatite, cryolite, fluorspar, muscovite and micas have been identified as the potential fluoride contaminants in Nigerian groundwater networks (Oyebola 2017; Onipe et al. 2020).

Fluoride loads in wells and boreholes in Nigerian communities, have repeatedly been shown to pose a significant health risk. In particular, high levels of fluoride may lead to dental problems such as dental fluorosis, skeletal fluorosis, and damage to other parts of the body if consumed on a long-term basis. Furthermore, fluoride works as a cumulative toxin, meaning even small amounts of ingestion over a long period of time can be harmful (Podgorski and Berg 2022). In a review presented by Onipe et al. (2020), levels of fluoride constituents in the Nigerian groundwater networks varied from 0 to 5.6 mg.l⁻¹, with an average of > 4.5 mg.l⁻¹. The range of fluoride constituents obtained in Nigerian groundwater networks could permit health issues such as mild to severe dental fluorosis as well as skeletal fluorosis (Suneetha et al. 2015; Adimalla and Qlan 2019). Other non-fluorosis diseases such as retarded growth, hypocalcemia, polyuria, dyspepsia, polydipsia, osteoporosis, thyroid disorder, hearing difficulty, infertility, cancer, hypothyroidism, loss of mobility, arthritis, intelligence quotient loss and Alzheimer's diseases could also occur (Onipe et al. 2020). Though cases of dental fluorosis have been reported in the northern and southern parts of Nigeria, elevated constituents of fluoride are prevalent in the northern parts than the south.

To ensure that the fluoride in water supply are within the permissible limit varying from 0.6 to 1.5 mg.l⁻¹ as prescribed by the WHO standard, defluoridation of public water is recommended. Defluoridation occurs when the concentrations of fluoride in water is controlled to an ideal permissible level (Suneetha et al. 2015). Some of the methods to be considered in the removal of fluoride in water include precipitation, ion-exchange, reverse osmosis, nano filtration, electro dialysis, Donnan dialysis, electro coagulation, adsorption and membrane based methods. The method(s) of defluoridation to use will depend on some factors such as economic status, community's knowledge on the challenge, local conditions, availability of materials and re-use status of exhausted materials, adoption of the recommended method(s) by the community among others. Based on the strength and weaknesses of each method of defluoridation listed, Suneetha et al. (2015) suggested that the best method to adopt is the adsorption process. The adsorption process of removing fluoride constituents from water can be from physical or chemical process. Adsorbents can remove fluoride from water at 2.0 mg.l⁻¹ or when the pH of water ≤ 3. Various activated carbon adsorbents have been prepared from eco-friendly and affordable materials (such as agricultural wastes, domestic materials and readily available plants), their fluoride removal strength is a top-notch.

Arsenic Loading

Arsenic is an organic metalloid, it is naturally present in food and water. More than 100 million people are actively exposed to arsenic constituents > 50 µg.l⁻¹ (Moon et al. 2012). Arsenic can be leached into the groundwater networks by using highly rich arsenic pesticides for agricultural practices. Groundwater can also be contaminated from industrial activities, mining works, localized mineral deposits overlying the aquiferous stratum and high rainwater with elevated constituents of arsenic. Countries such as Iran, Latin America, Pakistan, Taiwan, Chile, Mexico, Turkey, Bangladesh, United States of America, Spain, Argentina, India and China have been of great concern to the WHO due to their excessive levels of arsenic contamination in their groundwater networks (Orosun 2021; Woodard 2022; Pezeshki et al. 2023).

The recent study by Orosun (2021) revealed that most surface water, hand-dug wells (from shallow aquifers) and boreholes (from deep aquifers) across the northern and southern parts of Nigeria contained elevated arsenic constituents > 0.01 ppm, 10 µg.l⁻¹ or 10 ppb, being the arsenic limit in water as set by the WHO. The increasing trend in levels of arsenic in the Nigerian groundwater networks has been attributed to solid waste disposal methods, agricultural works and mining of various embedded natural resources in the near-surface without "the enforcement" of policies to monitor and control the public health and protect the Nigerian environment (Olafisoye et al. 2012; Ayantobo et al. 2014). The geochemical assessment of 797 groundwater samples in the north-central part of Nigeria revealed varying arsenic levels ranging from 0.05 to 1.73 mg.l⁻¹ (Udogbo 2016). The range of arsenic constituents in the north-central exceeded the WHO limit of 0.01 mg.l⁻¹ for drinking water. In Orosun (2021) study, the estimated non-cancerous effect of arsenic in water was exceedingly high. In addition, the groundwater quality assessment by Kolawole et al. (2020) showed some colouration in the hand-dug well water samples, which indicates a slightly acidic condition in comparison to the borehole samples without any colouration in the north-central, Nigeria. Acidic water are classified to be mixed with calcium magnesium chloride (CaMgCl), while alkaline water in nature are classified to be mixed with calcium magnesium bicarbonate (CaMgHCO₃). The study of Izah and Srivastav (2016) indicated that arsenic constituents in Ogun State groundwater networks are higher than the permissible standards set by the governing bodies such as the Standards Organisation of Nigeria (SON), the World Health

Organization (WHO) and the United States Environmental Protection Agency (USEPA) (Emenike et al. 2017; Adejumo et al. 2018).

Regular consumption of contaminated water containing arsenic may lead to skin, lung and bladder cancers, as well as heart diseases, high blood pressure and diabetes (Strom 2004; Jha et al. 2023). It is therefore essential that national, regional and local regulations are enforced to tackle the problem of arsenic loading in wells and boreholes. Water is not only ingested but can be used in cooking, washing and bathing. The most common way to get health issues is via ingestion, as the chemical levels of unchecked water could cause issues to internal organs over a long period of time. It is essential that environmental monitoring and checking of the water quality in our communities is taken with utmost seriousness in order to ensure the well-being of people and create a healthier community in line with the SDG agenda.

Arsenic exist in various forms in water, so also its toxicity relies on the form at which is present. Inorganic arsenic occurs in two oxidation levels, arsenic III(As₃) and arsenic V(As₅). The toxicity of As₃ is exceedingly higher than As₅, because of its solubility in water. If As₃ exist in water, it is advisable to pretreat the As₃ and convert to As₅ via oxidation by chlorine processes. When As₃ has been converted to As₅, more arsenic complexes can be removed in water at the final treatment stage using any of these methods: ion exchange, reverse osmosis and distillation (Nicomel et al. 2016; Hering et al. 2017; Woodard 2022).

Ion exchange is a process used to soften and deionize water in order to get rid of its contaminants. It is used to eliminate inorganic arsenic from water. Ion exchange systems are more efficient at removing As₅ than As₃. Due to the high alkalinity of hand-dug wells, ion exchange is not an effective option for groundwater, except an adequate pretreatment is put in place. In case of a valve failure, some of the captured As₅ may be released into the treated water. Ion exchange with anion resin reduces the water pH, thereby increasing its corrosivity. A water network that passes through metal plumbing requires neutralizer for final water treatment adopting the ion exchange process.

Reverse osmosis pushes water under pressure through a semi-permeable membrane. It removes, arsenic, lead, copper, chloride, sodium and other contaminants. Reverse osmosis is capable to eliminate As₅ at higher rate than As₃, thereby enhancing its pretreatment results. If a well is contaminated with arsenic, it is preferred to treat the well using a point-of entry reverse osmosis system. The system allows filter to be used at every outlets. Reverse osmosis, though is costly, can efficiently remove As₃ from water prior to its usage. Despite its efficiency in water treatment and removal of metalloids, such as arsenic in water, it divests mineral constituents from water, which results to a flat and bland taste of the treated water.

Distillation process works by heating of water, collecting the steam, and cooling the steam to the liquid state. When water is heated-up, all contaminants are get rid of, except contaminants with higher boiling point than that of water. This process is efficient to eliminate soluble minerals and heavy metals such as mercury, arsenic and lead. Distillers are countertop systems that must be filled manually. It is costly and less environmental friendly. It required regular monitoring to ensure its efficiency and effectiveness. It cannot be connected directly to the source, thereby resulting to production of small quantities of water per time. Removal of contaminants having similar or higher boiling points in comparison to water require accurate pressure and temperature for its operation. When the minerals are removed, the oxygen in water becomes lowered, thereby producing a flat taste like that of the reverse osmosis treatment.

The available processes of removing arsenic in contaminated water were documented by Pezeshki et al. (2023). Some of the highlighted arsenic removal processes include ZnO nano-photocatalyst, zero-valent iron nanoparticles, electrocoagulation, dissolved air flotation, chemical precipitation, oxidation, ion exchange, lime lightning, surface adsorption, electrolysis, coagulation and flocculation, and membrane processes – which are divided into nanofiltration and reverse osmosis. Nanofiltration membranes was considered as the best, because it was able to remove noticeable constituents of heavy metals, such as arsenic, at low pressures, while the quality of water produced is high, which validates its low costs of production (Siddique et al. 2020; Pezeshki et al. 2023).

4. Conclusion

It The water supplied across different regions in Nigeria has shown divers levels of fluoride and arsenic constituents. The fluoride and arsenic constituents in the north is higher than that of the south. The arsenic concentrations in the Northern parts of Nigeria are high due to the mining and the increase in industrial activities, which is safe to assume, has disrupted the geogenic nature of the subsurface strata. Since ingestion is the major pathway of transfer of these constituents to human, regular groundwater

quality check in Nigeria (in accordance with the standards of the SON, WHO and USEPA) is essential to avoid various waterborne crises that could arise from consumption of contaminated water. To reduce further groundwater contamination, it is best advised not to have any industrial activities in and around the residential areas, since most households in Nigeria today solely rely on groundwater supply for their activities.

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