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Defluoridation Of Ground Water By Using Different Novel Materials

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Abstract. Fluoride is one of the most abundant mineral present in groundwater. The presence of fluoride is more in groundwater than surface water mainly due to leaching of fluoride-bearing minerals from rocks and sediments. Its inadequate ingestion Causes dental caries and excessive consumption of fluorides in various forms leads to dental problems and skeleton fluorosis. There are several methods available for defluoridation, each of them has certain merits and demerits. Among various methods used for defluoridation of water, adsorption method is relatively simple and economical. In this research article we have discussed different low cost innovative materials which are very efficient and cost effective for defluoridation.

Keywords: fluoride, adsorption, adsorbents

1. Introduction

The most essential component of life on Earth is water, and obtaining drinkable water in the twenty-first century is a serious global concern. Water that is clear and uncontaminated is essential for all living things. Although water covers more than 71% of the earth's surface, due to various contaminations, less than 69% of the water is deemed safe to drink.

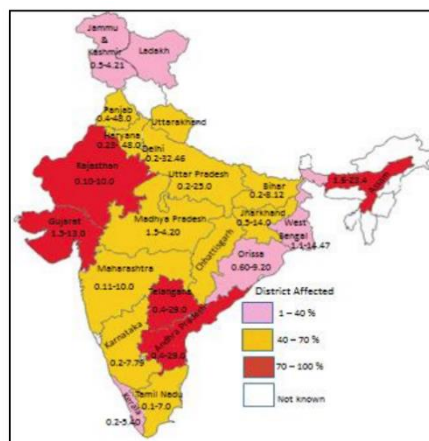
The following factors are the primary contributors of water contamination: industrial waste water discharge, agricultural practices, municipal wastewater, environmental changes, and global warming. Nearly 85% population of India relies on the groundwater for drinking [1] and therefore groundwater quality becomes an important issue to be tackled separately. People of this nation greatly depends on the groundwater and assumed that it is safe, but some researches highlighted pollution of groundwater through various geo-genic and anthropogenic means [2]. The anthropogenic sources include brick kilns, heavy fertilizer use, and industrial wastes. The F-

bearing minerals, such as fluorite, biotite, and amphiboles, are among the geo-genic sources. The presence of these geo-genic minerals, such as fluorite, cryolite, topaz, apatite, amphiboles, micas, sellaite, villiamite, and certain clays, is primarily responsible for F⁻ enrichment in groundwater [3]. As the lightest and most electronegative element in the periodic table, fluorine (F) is a member of the halogen group and Fluoride is the simplest fluorine anion and is abundant in the Earth's crust, approx. 625 mg/kg.

Water sources with significant fluoride levels can be found near the base of high mountains and in regions with sea-derived geological formations. According to WHO estimates, 260 million people worldwide live in areas where drinking water contains excessive amounts of fluoride (>1.5 mg/L) [4]. Numerous regions within the Fluoride Belt around the world have reported cases of fluorosis. Significant fluoride belts can be found on Earth that extend from (i) Syria to Jordan, Egypt, Libya, Algeria, Sudan, and Kenya; (ii) Turkey via Iraq, Iran, Afghanistan, India, northern Thailand, and China; and (iii) Similar belts in America and Japan [1].

India is one of the 23 countries in the world where drinking water is contaminated with fluoride and causes health issues. It has been estimated that drinking of such fluoridated water in 17 of the 32 states in India affects 62 million people, including 6 million children and causes serious diseases called fluorosis [5]. Fluorosis is a disease caused by ingestion / inhalation of Fluoride in excess, which the human body is unable to tolerate. In India, fluorosis has existed for around 85 years. In the British Indian regions of the Madras Presidency [6] and the Nellore district of Andhra Pradesh [7], there was an abundance of fluoride in the groundwater and a high incidence of fluorosis. Numerous States (18 States and 1 UT) in India have reported high fluoride levels, suggesting that endemic fluorosis has become one of the nation's public health issues [8]. Millions of people who live in areas with high fluoride levels are susceptible to fluorosis. There are also reports of industrial fluorosis in several areas of Uttar Pradesh and Gujarat.

The map of India shown below is the compilation of information by UNICEF, India to enable record of the endemicity of Fluorosis disease. It is showing maximum and minimum fluoride detected in each state of India. It is showing the evidence of safe and unsafe water to the community and aware them about contamination.



Source : UNICEF- State of art report on the extent of Fluoride in drinking water and resulting endemicity in India. 1999. New Delhi.

The WHO's maximum permissible limit of fluoride in drinking water meets the national standard limit and is confined to 1.5 mg/L in drinking water. The desirable limit of Fluoride in water, as per Bureau of Indian Standards (BIS), is 1 ppm .

There are many Adverse Effects of Fluoride due to Excessive exposure which causes following diseases:

1. Dental Fluorosis 2. Skeletal Fluorosis 3. Thyroid malfunctions 4. Abnormalities in babies born to women with Fluorosis 5. Gastrointestinal disturbances 6. Anemia 7. Allergic manifestation 8. Calcification of ligaments & blood vessels 9. Abnormalities in sperms Excessive exposure to Fluoride increases the risk of: ■ Osteoporosis ■ Hip fractures ■ Teeth damage.

Due to all health problems caused by fluoride pollution, various remediation technologies are given by researchers such as coagulation and precipitation [9,10], membrane processes [11], electrochemical treatments [12], ion-exchange and its modification [13], but the adsorption process is generally accepted as the cheapest and most effective method for removal of fluoride from water [14].

The objective of this article is to review an adsorptive technology of fluoride removal by using various novel materials and investigation is done to focus on a cost-effective adsorptive materials, which is environmentally compatible and at the same time efficient to remove excess fluoride.

2. Defluoridation through Adsorption Using Different Novel Materials

Physical parameters such as adsorption capacity, fluoride ion selectivity, regenerability, compatibility, particle and pore size, initial fluoride concentration, adsorbent dosage, pH of solution, pH zpc of adsorbent, temperature, and contact time all these parameters affect adsorption characteristics. The selection of the adsorbent for the removal of fluoride is the most crucial process because other co-ions in the water reduce the adsorption capacity. The nature of adsorbent plays an important role in mechanism of adsorption.

2.1 Defluoridation using Activated carbon

Activated carbon (AC) has high surface area available for adsorption which makes it suitable for fluoride removal. In a 2007 study, Daifullah et al. examined KMnO₄ modified activated carbons made by one-step steam pyrolysis of rice straw at various temperatures (550, 650, and 750 °C)[15]. They found that lower temperatures promote fluoride adsorption by activated carbon at an ideal pH of 2. Water defluoridation has been accomplished by using carbonaceous material obtained from the pyrolysis of sewage sludge. Using 0.4 g/L, the highest adsorption of 2.84 ± 0.03 mg/g was found, and $82.2 \pm 0.5\%$ of fluoride was removed with 20 g/L of carbonaceous material [16].

Adsorbents for the removal of fluoride have included carbon allotropes with different grades of graphite.

For graphite, the fluoride sorption capacity was reported to be 3.13 mg/g [17]. Lower rank coal with a strong affinity for the fluoride anion is called lignite. Although it stays above 90%, fluoride uptake decreases as fluoride concentration rises. As per Pekar's (2009) findings, a mere 13% of the material remains in the water after leaching [18].

The WHO's recommended health risk level for fluoride is 1.5 mg/L, but even at these low concentrations, the sorption mechanism is still effective, and the lignite also reduced the fluoride concentration below this level.

Sivasankar et al. (2013) created hybrid adsorbents by carbonising ammonium cerium sulfate-impregnated starch in order to create cerium dispersed in carbon (CeDC), a novel and more effective adsorbent[19].

The maximum fluoride sorption that CeDC, a hybrid adsorbent, demonstrated was 29.1 mg/g. Temperature affected CeDC's defluoridation potential, whereas its uptake capacity declined as

fluoride concentrations rose. Waste from the fertiliser industry, carbon slurry can be used as a less expensive adsorbent.

Gupta et al. looked into the adsorption of fluoride on waste carbon slurry (2007). An initial fluoride concentration of 1.0 g/L adsorbent dose resulted in a maximum adsorption capacity of 4.861 mg/g at 15.00 mg/L [20].

Li et al. (2003) created a novel form of carbon material known as ACNT by employing ferrocene as a catalyst in the catalytic breakdown of xylene. Their amorphous carbon, inner cavities, internanotube gaps, and surface defects all contribute to their high defluoridation capacity [21].

2.2 Defluoridation using Red Clay Bricks

Defluoridation of groundwater using brick powder as an adsorbent can be used as adsorption of fluoride was found to be 51.0–56.8% in pH range between 6.0 and 8.0 [22]. The removal of fluoride increased from 43.2 to 56.8% for 0.2–2.0 g/100 ml dosage of BP, As contact time was increased, initially, percentage removal also increased, but after some time, it gradually approached an almost constant value. It was reported by researchers that brick powder can be used for adsorption or removal of fluoride [23]. researchers were in a search of easily available, low cost adsorbent and experimented on brick powder which is easily available. They took brick, powdered it for increasing its surface area, washed with water several times, and activated by heating at 105°C for 12 hours. Dried the material then again they crushed it to very fine size and prepared the adsorbent. They studied the adsorption of fluoride on brick powder at different concentration of fluoride, different pH, and also at contact time. They found that at 0.6 gm/100 mL dose of absorbent, at contact time of 120 min, and at pH 6, removal of fluoride is maximum 56%. On increasing the pH, amount of adsorbed fluoride decreases. They found that fluoride removal can be increased by increasing adsorbent dose. The adsorbent can be activated by washing with 0.4 N sodium hydroxide solutions. Eventually they concluded that brick powder adsorbent can be used as nice adsorbent having low cost with efficiency of 56%.

2.3 Defluoridation using Rice Husk

Rice husk is enriched with fiber, protein, and oxygen functionalities (carboxyl, hydroxyl etc.) [24]. Rice husk is a promising adsorbent material for removing different contaminants because it is a low-cost and renewable resource. The typical chemical composition of rice husks is about 32% cellulose, 20% hemicellulose, 21% of lignin, and 20% of other organic matter, such as protein and fat [25,26]. The results showed that if rice husk ash was impregnated with lanthanum for 6 g/L and 240 minutes, respectively. It was discovered that LIRHA brought the fluoride content of naturally occurring water down to a level below what was permitted [27]. Adsorbent performance is dependent on a number of factors, including temperature, pH, stirring time, and concentration. Increased adsorbent concentration, an acidic pH, room temperature, and shorter contact times are all linked to the elimination of fluoride efficacy. Moreover, adsorbent's oxygen functionalities and particle size allow for a higher fluoride ion removal percentage. Depending on the composition of the soil, the adsorbent materials made from agricultural waste include complex organic molecules [28].

2.4 Defluoridation using Building material-based adsorbents

Numerous studies have looked into the ability of different building materials, such as sand, cement, fly ash, brick powder, and concrete, to remove fluoride both with and without treatment or modification [29].

sadia bibi et.al looked into hydrated cement ability to remove fluoride from potable water. The maximum fluoride absorption was found to be 1.72 mg g^{-1} , and the adsorbent demonstrated an 80% efficacy in removing fluoride at pH 7 after a 60-minute contact period and a dosage of 30 g L^{-1} . Since the adsorbent is reasonably priced, regeneration wasn't required.

Kagne et al. investigated the possibility of using hydrated cement to extract fluoride from aqueous solution at various times through batch adsorption tests [30]. They discovered that the hydrated cement removed considerable amounts of fluoride in a broad pH range (3–10). The linear transformed Freundlich and Langmuir isotherms were successfully fitted by the experimental data collected from the batch adsorption studies.

Togarepi et al. conducted a fluoride removal experiment using sand. For use as an adsorbent, it underwent thermal and chemical treatments. Batch experiments were used to investigate a variety of parameters, such as pH, initial fluoride, and adsorbent dose. It was noted that the multilayer sorption and the Freundlich isotherm both fit the experimental data of the activated sand quite well [31].

2.5 Defluoridation using Titanium Di oxide

TiO_2 nanoparticles are used for the removal of fluoride from water sample. TiO_2 adsorption capacity increased after its conversion in nanoparticle since surface area was increased greatly. It was observed that Defluoridation capacity was maximum in pH range 5–6 and temperature 50–60. The study reveals that use of titanium di oxide nanoparticle for defluoridation is very effective and can be applied for removing fluoride from groundwater samples [32].

Conclusion

1. The risk assessment via oral and dermal route exposure reveals that the consumers in majority of the regions are at considerable non-carcinogenic risk and children are at higher risk than adults. The findings are helpful in identifying the affected areas of India and we recommend that the safer options of drinking water should be adopted.
2. This review provides an up-to-date insight into the defluoridation techniques developed and implemented throughout the world and highlights the various types of adsorption technique using different novel materials. The literature survey confirms that despite developing so many novel adsorption techniques for defluoridation over the years, there is still no effective fluoride removal technique that can achieve the desired results in a cost-effective and sustainable manner. Therefore, development of a commercially practical, economical, and sustainable technique is required to prevent people especially the most vulnerable from poor and developing nations (dependent on untreated water) from the hazards of fluoride contamination.

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