



ORIGINAL ARTICLE

Fluoride ions vs removal technologies: A study



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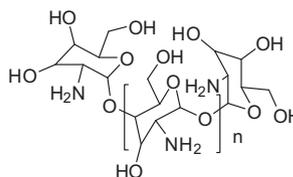
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Membrane technology;
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Natural technology

Abstract Literature reported that drinking water is a precious and scarce resource and it has to be protected and kept free from any kind of contamination. Further, it has to be used carefully without wasting. Literature also reported that fluoride bearing rocks are abundant in India, as a result, fluoride leaches out and contaminates the adjacent water and soil resources. A high concentration of fluoride ions in ground water increases up to more than 30 mg/L. This high concentration of fluoride ions causes many harmful and dangerous effects on our datum. Fluoride ions in larger quantities i.e. 20–80 mg/day taken over a period of 10–20 years result in crippling and skeletal fluorosis, severely damaging the bone. In the present scenario, there is a continuously increasing worldwide concern for the development of fluoride treatment technologies. Possibilities of reducing the high fluorine content in groundwater are by defluorination process/dilution with the surface water which is a very simple technique but the addition of Ca^{2+} ions to a solution in contact with fluorite when experimented in distilled water caused an appreciable decrease in fluoride concentration. In this review article, we emphasized the relationship between high concentrations of fluoride ions and their compounds and their health impact.



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1. Introduction

Literature reported that fluoride ions are present in low to high concentrations in water. It is a vital substance for humans in preventing cavity and in facilitating the mineralization of arduous tissues if taken in different concentrations. Higher levels of fluoride ions in groundwater may be a world-wide downside

that varied from country-to-country and continent-continent-to-continent (Reimann et al., 2003). Excess fluoride ions in drinking water are currently found in all regions of the country (Kloos and Tekle-Haimanot, 1999; Tekle-Haimanot et al., 2006). The limit varies among countries and therefore the age of individuals exposed. World Health Organization (WHO) has set a limit between 0.5 and 1.0 mg/L (WHO, 2006).

Fluoride is a very toxic element and known to cause adverse health effects on humans and animals due to environmental and occupational exposure (Krachler et al., 2001). Fluoride has been classified as a priority pollutant by the United States Environmental Protection Agency and the German Research Council (Cabral et al., 2008). The toxicological and physiological behavior of fluoride is dependent on its oxidation state. Elemental fluoride is more toxic than its salts. Hence, its determination is very important because of its implications in health as well as in pharmaceutical formulations.

In various provinces in developing countries e.g. India, the groundwater is rich in halide and the provisions of different installations are tough. Treatment of contaminated water is the sole choice to offer safe drinking water. India has concerning seventieth rural and quite twenty to half-hour of urban population in several states, depends on spring water for its domestic demand. High concentrations of fluoride ions in water render it unfit for drinking. Fluoride ions are a vital part of drinking water however at a higher concentration i.e. around 1.5 mg/L might cause harmful effects on human health. Its contamination in water has been recognized as a worldwide downside and its concentration in drinking water at several places of the planet exceeds the permissible limits (Swain et al., 2012). Interference of halide with carbohydrates, lipids, proteins, vitamins and mineral metabolism is reported to be attributable to the presence of high concentrations of it in water and intake of higher quantities of fluoride has been reported to result in dental and skeletal pathology (Gong et al., 2012). The Bureau of Indian Standard (BIS) suggested a fascinating limit of one milligram per liter of it in drinking water, which may be extended to 1.5 mg/L as permissible limit, if no totally different supply of drinking water is accessible (BIS, 1991/2003). Various technologies like sorption, natural process, precipitation, electro-dialysis and reverse diffusion are used for the removal of halides mostly fluoride ions from water (Sujana et al., 2009; Kagne et al., 2008; Wu et al., 2009; Biswas et al., 2010; Viswanathan and Meenakshi, 2010; Sundar et al., 2008; Quiroz et al., 2011).

Literature reports a wide variety of methods for the trace level determination of fluoride. Various methods available for the determination of fluoride are, high-performance liquid chromatography with hydride generation-atomic fluorescence spectrometry (HPLC-AFS) Ferreira et al., 2009, non-chromatographic hydride generation-atomic fluorescence spectrometry (Torok and Žemberyova, 2010), electro-thermal atomic absorption spectrometry (AAS) Araujo et al., 2010 high-resolution continuum source graphite furnace atomic absorption spectrometry (Krachler and Emons, 2001), high performance liquid chromatography-inductively coupled plasma-mass (ICP) spectrometry Bosch et al., 2010; Adeloju and Young, 1995 etc. However, these methods are time consuming, costly and laborious.

Electro-analytical methods (Adeloju et al., 1998; Santos et al., 2009; Tanguy et al., 2010; Huiliang et al., 1987; Agrahari et al., 2009), on the other hand, offer the advantages

of low-cost, ease in sample handling, and above all, extremely high sensitivity and are thus the methods of choice for the detection and trace-level determination of fluoride. Chemically modified electrodes (CMEs) have been employed widely in the trace level determination of both metal ions (Khani et al., 2010; Sanghavi and Srivastava, 2011) as well as organic molecules (Ghalkhani and Shahrokhian, 2010; Shahrokhian and Asadian, 2010). CMEs in the form of carbon paste electrodes (CPEs) have been extensively used due to their wide anodic potential range, low residual current, ease of fabrication, easy surface renewal, and low cost. Plain carbon paste electrode (PCPE) has been modified employing various modifiers, viz., nanomaterials (Gadhari et al., 2010; Sanghavi and Srivastava, 2010), surfactants (de Oliveira et al., 2007), copper complexes (Mobin et al., 2010; Vaze and Srivastava, 2007), macrocycles (Kotkar et al., 2007; Shahrokhian et al., 2009), etc. Glassy carbon electrodes (GCEs) are very versatile as electrode materials for trace level determination of organic molecules as they provide high sensitivity, negligible porosity, and good mechanical rigidity. GCEs have been modified by means of various modifiers viz., chitosan, nanomaterials, etc. (Shahrokhian and Ghalkhani, 2010; Zhang et al., 2010; Vaze and Srivastava, 2007).

CPEs are very popular due to their wide anodic potential range, low residual current, ease of fabrication, easy surface renewal and low cost. CMEs are used to lower the detection limits compared to plain carbon paste electrodes (PCPE). Various modifiers, such as macrocyclic compounds (Gaichore and Srivastava, 2010; Mobin et al., 2010), copper complexes (Inês Rosane de Oliveira et al., 2007; Shahrokhian et al., 2009), phthalocyanine (Rivas et al., 2007) and nanomaterials (Yang et al., 2009) have been employed successfully as modifiers for carbon paste electrodes. Carbon nanotubes (CNTs) have triggered a new genre for the development of novel electrode materials due to their amazing structural, mechanical, electrical and physical properties (Dai et al., 2009; Beitollahi et al., 2008; Zhu et al., 2008; Svancara et al., 2008; Gavalas et al., 2004). In addition, surfactants at trace levels have also been employed successfully as modifiers (Jain et al., 2009; Zhang et al., 2002; Li, 2007; Xu et al., 2009; Yang et al., 2009). Carbon nanotubes (CNTs) have started a new era for the development of novel electrode materials due to their amazing structural, mechanical, electrical and physical properties (Kasprzyk-Hordern et al., 2010; Yang et al., 2010).

They have been successfully used as modifiers to obtain very low detection limits. Nafion, a perfluorinated sulfonated cation exchanger with properties of excellent antifouling capacity, chemical inertness and high permeability to cations, has been extensively employed as an electrode modifier for organic molecules (Chou et al., 2009; Cheng et al., 2008; Gadhari et al., 2010). However, these methods have the drawbacks like high cost and laboriousness (time taking) and require pretreatment of the samples. Modern electro-analytical techniques, on the other hand, are extremely sensitive, selective, and do not need pre-treatment or pre-separation. The availability of various chemically modified electrodes at relatively low cost has provided considerable impetus to the use of electro-analytical techniques for analysis of organic molecules as well as metals (Diawara, 2008).

In several cases, the water sources are rendered unsafe not just for human consumption however additionally for different activities like irrigation and industrial wants. Therefore, now

there is a desire to focus attention on the long term impact of water resources and development taking into consideration all the associated problems. In India, halide is the major inorganic waste of natural origin found in groundwater. Herein, the author emphasizes on sources, un-well effects and techniques available for halide removal.

2. Occurrence and sources

Literature reported that fluoride in a minute quantity is an extremely crucial part for normal mineralization of bones and formation of dental enamel. Although, its high intake might lead to slow, progressive crippling scourge referred to as pathology. The square measure quite 20 developed and developing nations that square measure endemic for pathology. The square measure Argentina, U.S.A., Morocco, Algeria, Libya, Egypt, Jordan, Turkey, Iran, Iraq, Kenya, Tanzania, S. Africa, China, Australia, New Zealand, Japan, Thailand, Canada, Saudi Arabia, gulf, Sri Lanka, Syria, India, etc (Gaciri and Davies, 1992).

As per literature available on India, it was 1st detected in Nellore district of Andhra Pradesh in 1937. Since then, research has been exhaustively carried out on different parts of Asian nations to explore halide laden water sources and their impacts on humans in addition to animals (Hiemstra and Van Riemsdijk, 2000; Kundu et al., 2002). At present, it has been calculable that pathology is rife in seventeen states of India (Fig. 1).

3. Urgency to get rid of the higher concentrations of fluoride ions

Fluoride ion concentration in drinking water because of natural and phylogenesis activities has been recognized as the foremost issue worldwide imposing a significant threat to living being's health. Fluorine is an extremely negative aspect and has an extraordinary tendency to induce attraction by charged ions like metallic elements. Therefore the impact of

halide on mineralized tissues like bone and teeth resulting in organic process alternations is of clinical significance as they need the highest quantity of metallic element and can attract the utmost quantity of halide that gets deposited as calcium-fluorapatite crystals. Solid body substance consists chiefly of crystalline hydroxyl apatite. For underneath traditional conditions, once halide is present in water system, most of the eaten halide ions get incorporated into the mineral lattice of metal tissue enamel throughout its formation. The particle gets substituted by halide ion since apatite is more stable than hydroxyl apatite. Thus, an outsized quantity of halide gets certain in these tissues and solely a tiny low quantity is excreted through sweat, piss and stool. The intensity of pathology is not just obsessed with the halide content in water, however conjointly on the halide from different sources, physical activity and dietary habits Fig. 2.

3.1. Dental pathology

Excessive halide intake causes enamel loses its luster but if it will be treated in delicate kind, dental pathology characterized by white, opaque areas on the tooth surface. It is manifested as caramel to black stains and severe indentation of the teeth. This discoloration is also within the sort of spots or horizontal streaks. Normally, the degree of dental pathology depends on the number of times of halide exposure up to the age of 8–10, as halide stains solely the developing teeth whereas square measure are being fashioned within the jawbones and are still underneath the gums. The impact of dental pathology might not be apparent if the teeth square measure already adult before the halide over exposure. Therefore, the actual fact that the associated degree adult shows no signs of dental pathology does not essentially mean that his or her halide intake is among the security limit.

Maximum Limts of Fluorode conc. (mg/L)

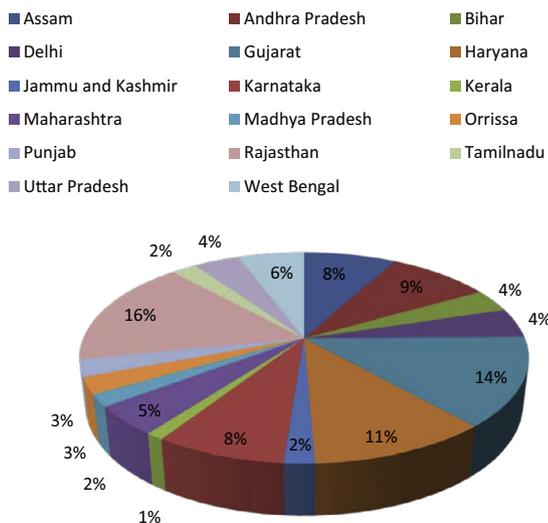


Figure 1 Fluoride concentration in some selected Indian states.

Fluoride concentration (mg/kg) in different food items

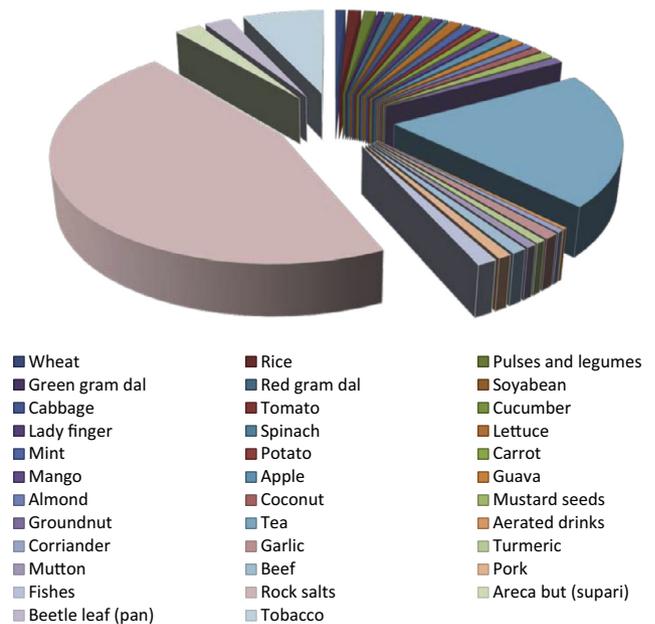


Figure 2 Graph of fluoride's concentration in different food items.

3.2. Skeletal pathology

Skeletal pathology affects youngsters additionally as adults. It does not simply manifest till the malady attains a complicated stage. Halide principally gets deposited within the joints of neck, knee, girdle and shoulder bones and makes it troublesome to move or walk. The symptom of skeletal pathology is square measure kind of like rubor or inflammatory disease. Early symptoms embody unpredictable pain, back stiffness, burning like sensation, prick and tingling within the limbs, muscle weakness, chronic fatigue, abnormal metallic element deposits in bones and ligaments. The advanced stage is pathology in long bones and bony outgrowths might occur. Vertebrae might fuse along and eventually the victim is also halting. It is going to even result in a rare bone cancer, sarcoma and eventually spine, major joints, muscles and system get broken.

3.3. Other issues

This side of pathology is commonly unnoticed due to the prevailing notion that halide solely affects bones and teeth. Besides skeletal and dental pathology, excessive consumption of halide might result in muscle fiber degeneration, low hemoglobin levels, deformities in RBCs, excessive thirst, headache, skin rashes, nervousness, medicine manifestations (it affects brain tissue as in the pathological changes found in humans with Alzheimer's disease), depression, channel issues, tract haywire, nausea, abdominal pain, tingling sensation in fingers and toes, reduced immunity, perennial abortions or still births, male sterility, etc. It is conjointly chargeable for alterations within the purposeful mechanisms of the liver, kidney, emission system, central system and genital system, and destruction of regarding sixty enzymes. The consequences of high amount of halide in drinkable for animals square measure analogous to those on kinsfolk. The continual use of water having high halide concentration conjointly adversely affects the crop growth.

4. Technologies of defluoridation

The objective of fluoride removal meant the treatment of contaminated water to bring down fluoride concentration to acceptable limits. The defluoridation techniques will be generally classified into 2 classes, specifically membrane and surface assimilation techniques.

4.1. Membrane process

Although various conventional techniques of water purification described earlier are being used at present to solve the problem of groundwater pollution, none of them is a user-friendly and cost-effective technique due to some or the other limitations and has either no or very long payback period.

4.1.1. Reverse osmosis (RO) membrane process

In the last decade, the RO membrane process has emerged as a preferred alternative to provide safe drinking water without posing the problems associated with other conventional methods [Hu and Dickson \(2006\)](#). RO is a physical process in which the contaminants are removed by applying pressure on the

feed water to direct it through a semi-permeable membrane ([Fig. 3](#)). The process is the reverse of natural osmosis as a result of the applied pressure to the concentrated side of the membrane, which overcomes the natural osmotic pressure. RO membrane rejects ions based on size and electrical charge. The factors influencing the membrane selection are cost, recovery, rejection, raw water characteristics and pretreatment. Efficiency of the process is governed by different factors such as raw water characteristics, pressure, temperature and regular monitoring and maintenance, etc.

There are two types of membranes that can remove fluoride from water: NF and RO. NF is a relatively low pressure process that removes primarily the larger dissolved solids as compared to RO. Conversely, RO operates at higher pressures with a greater rejection of all dissolved solids. Fluoride removal efficiencies up to 98% by membrane processes have been documented by many researchers ([Bason et al. 2006](#); [Szymczyk and Fievet 2005](#); [Lefebvre and Palmeri, 2005](#); [Lefebvre et al. 2004](#); [Cervera et al. 2003](#); [Palmeri et al. 1999](#)).

RO membrane was totally regenerated in every set of experiments. Nano-filtration makes use of a similar overall development as reverse diffusion. For nano-filtration, the membranes have slightly larger pores than those used for reverse diffusion and provide less resistance to passage each of solvent and of solutes. As a consequence, pressures needed are a lot of lower, energy needs are less, removal of solutes is far less complete, and flows are quicker. The property of nano-filtration relative to reverse diffusion may be a specific advantage, and experimental and theoretical analyses are being dedicated to getting a mechanism of substance retention to facilitate production and choice of targeted membranes in addition to optimization of conditions ([Paugam et al. 2004](#); [Tripathy and Raichur 2008](#)).

4.1.2. Dialysis and electro-dialysis

Dialysis separates solutes by transport of the solutes through a membrane rather than using a membrane to retain the solutes while water passes through it as in reverse osmosis and nano-filtration. The membrane pores are much less restrictive than those for nano-filtration, and the solute can be driven through by either the Donnan effect ([Bosch et al., 2010](#)) or an applied

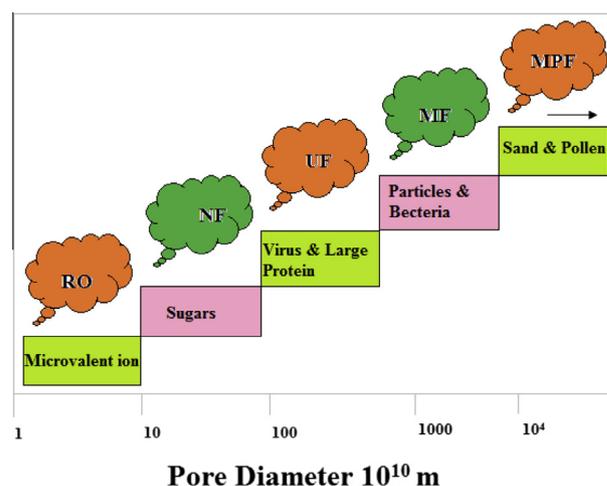


Figure 3 Range of nominal pore diameters for commercially available membranes.

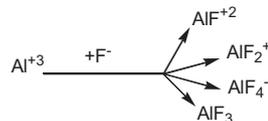
electric field (Adeloju and Young, 1995; Adeloju et al., 1998; Santos et al., 2009; Szymczyk et al. 2006; Tanguy et al., 2010). Literature revealed that the Donnan dialysis process in a counter current flow system where the anion-exchange membrane was loaded with sodium chloride and the feed was 0.001 M NaF together with other sodium salts. Fluoride migrated into the receiver as other ions migrated into the feed. This technique was later used to defluoridate solutions made to simulate high fluoride African ground waters (> 30 mg/L fluoride) and whatever other ions were present the fluoride in the feed could be brought below 1.5 mg/L (Huiliang et al., 1987).

Later, combining dialysis with adsorption, the group added aluminum oxide and zirconium oxide to the receiver to force the Donnan equilibrium in the direction of fluoride flow-out of the feed. In this way it was possible to maintain a flow of feed while leaving the receiving solution in place or renewing only in batches. The cation composition remained unchanged, whereas anions, except chloride, were partially eliminated and substituted by chloride ions, giving a fluoride concentration of 1.5 mg/L (Agrahari et al., 2009; Khani et al., 2010).

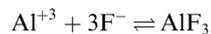
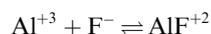
4.2. Adsorption techniques

4.2.1. Alumina and aluminum based adsorbents

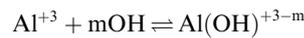
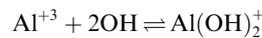
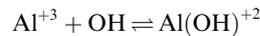
4.2.1.1. Alumina. Activated alumina contains aluminum oxide (Al_2O_3) grains prepared to have a sorptive surface. When the water passes through a packed column of activated alumina, pollutants and other components in the water were adsorbed onto the surface of the grains. The activated alumina process was carried out in sorption filters (Maliyekkal et al. 2006; Camacho et al. 2010; Tang et al. 2009). In order to avoid the monitoring of water quality, the unit was supplied with a water meter allowing for direct indication of the cumulative water flow. After treatment of, for example, 2000 L equivalent to 250 BV of water containing about 5 mg/kg^{-1} , the unit was opened for renewal of the 8 kg of medium. Alternatively, the unit was dismantled for regeneration by the dealer. Therefore, the formation of various fluoride complexes is an important factor on the adsorption of fluoride by activated alumina from aqueous solution shown as below:



An aqueous solution of fluoride ions containing activated alumina may not be clearly soluble and form various aluminum species, including several fluoride and hydroxyl-aluminum complexes. A series of generalized stepwise equilibrium equation for Al-F complex formation can be expressed as follows:



The complex formation of aluminum ions with hydroxyl ions in aqueous solution can be written as:



The adsorption of fluoride by activated alumina was varying over the solution pH possibly because of the electrostatic interaction between the surface of alumina and dominant fluoride species in solution. A column made of polyethylene (35 mm diameter and 200 mm height) was used for evaluating the performance of aluminum hydroxide coated RHA adsorbent for the removal of fluoride from water (Sanghavi and Srivastava, 2011). The column consisted of several layers of different materials as shown in Fig. 4. About 20 g of washed and dried AH coated RHA is placed in between the bottom and top layers of sand.

The bottom and top sand layers provide support to AH coated RHA. Tap water spiked with a known fluoride concentration is prepared and stored in the reservoir and then passed through a column containing aluminum hydroxide coated RHA. The filtered water drawn from the bottom of the column is collected in a storage vessel at regular intervals (Fig. 4). The water flow rate flowing through the column is regulated by a stop cock. AH coated RHA has shown good adsorption capacity for fluoride removal; for example the adsorption

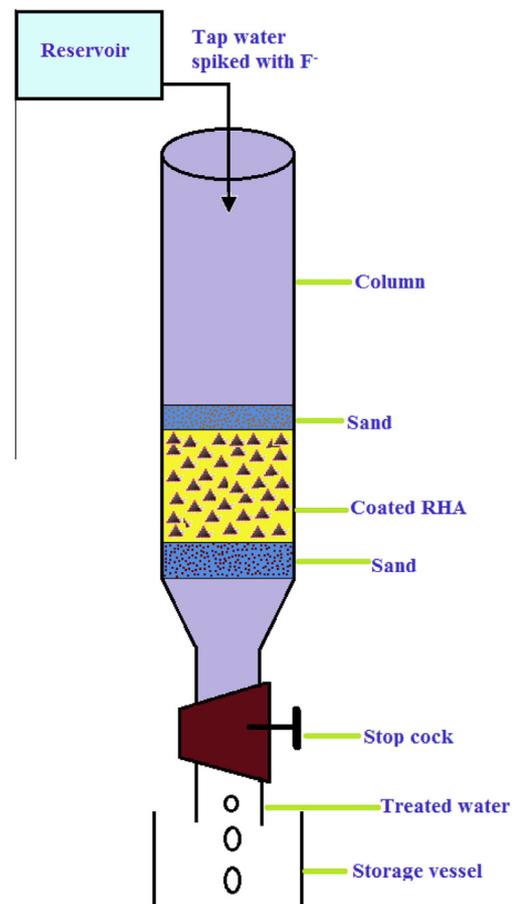


Figure 4 Schematic of column experiments for fluoride removal rice husk ash (RHA).

studies indicate 15.08 mg/g of adsorption capacity while column studies show 9.5 mg/g capacity. The fluoride removal of coated RHA is linearly proportional to the amount of coated RHA used; hence the coated RHA can be easily scaled up to a filtration unit/device for practical use. The fluoride adsorption capacity of coated RHA used in the filter was found to be 9 mg/g. A filter made of 750 g coated RHA has treated 1250 L of 5 mg/L of fluoride spiked tap water to below the WHO limit of 1.5 mg/L of fluoride in treated water (Ghalkhani and Shahrokhian, 2010; Shahrokhian and Asadian, 2010). The flow rate of 5 L/h was maintained through the experiment. The adsorption data followed the Freundlich isotherm confirming multilayer adsorption.

4.2.1.2. Alumina plus manganese dioxide. Manganese dioxide is an efficient sorbent which is insoluble and not hazardous. It is not used directly because it may be required in higher quantities compared to the present work with dispersion over disposed earthen-ware (DEW). Several studies have shown interest in the use of manganese oxide in fluoride removal: MnO₂ coated alumina (Gadhari et al., 2010; Sanghavi and Srivastava, 2010; de Oliveira et al., 2007; Mobin et al., 2010; Vaze and Srivastava, 2007), bentonite clay with incorporated MnO₂ (Kotkar et al., 2007), MnO₂ coated activated carbon (Shahrokhian et al., 2009; Ma et al., 2009), KMnO₄ modified activated carbon (Shahrokhian and Ghalkhani, 2010) and hydrated oxides of manganese ores. The fluoride removal of DEW with 0.025% MnO₂ was effective at a pH of 7.15. The regeneration of the spent sorbent was found to be efficient by washing it with 1.5 M NaOH which reveals the reversibility of the reaction used during the fluoride removal (Sivasankar et al., 2011; Mohapatra et al., 2004).

4.2.2. Bauxite

In recent years, to find out a cost effective alternative for removing high fluoride content from waters, many naturally occurring geomaterials have been tested (Zhang et al., 2010; Vaze and Srivastava, 2007; Gaichore and Srivastava, 2010). Bauxite is one of the abundantly available minerals, mainly consisting of oxides of alumina, iron, silica and titania. In some earlier studies, adsorption ability of heat activated bauxite for the removal of anionic pollutants like Cr (VI) and As (III) has been reported (Mobin et al., 2010; Inês Rosane de Oliveira et al., 2007). Thermally activated titania rich bauxite was studied for F removal from aqueous solutions (Shahrokhian et al., 2009). However, no literature is available on fluoride adsorption efficiency of untreated bauxite. In our previous work, untreated geomaterials like chromite overburden, low and high grade nickel ores have demonstrated considerable adsorption efficiency for fluoride from water (Rivas et al., 2007).

In the present study we tried to explore the fluoride removal efficiency of untreated bauxite. The bauxite sample collected from the eastern-ghats (Orissa) of India was used for defluorination of synthetic as well as fluoride bearing ground water collected from fluoride endemic villages near by Tarabalu, Atri and Taptapani hot water springs of Orissa, India. The geochemical and geoelectrical investigations were carried out around Tarabalu hot spring area to delineate the extent of fluoride concentration in ground water found by other researchers (Yang et al., 2009). In this area of the Orissa state,

fluoride levels in groundwater ranges between 2 and 6 mg L⁻¹ and many residents of nearby villages suffer from fluorosis. Therefore, a locally available and cost effective F adsorbent for this region is thus highly desirable (Erdem et al. 2004; Bhakat et al. 2007; Das et al. 2005).

4.2.3. Red mud

Red mud (RM) is a solid waste residue formed after the caustic digestion of bauxite ores during the production of alumina. Red mud is a highly alkaline waste material with pH 10–12.5. Red mud is mainly composed of fine particles containing aluminum, iron, silicon, titanium oxides and hydroxides. Due to the alkaline nature and the chemical and mineralogical species present in red mud, this solid waste causes a significant impact on the environment and proper disposal of waste red mud presents a huge challenge where alumina industries are installed.

In last decades, development in using red mud as adsorbents for gas cleaning and waste-water treatment as well as catalysts for waste gas and liquid cleaning has also been widely reported. Utilization of industrial wastes for another waste treatment produces many benefits in terms of economy and environment. Utilization of red mud will produce significant benefits in terms of environment and economics by reducing landfill volume, contamination of soil and ground water, and release of land for alternative uses Sujana et al. (2009). Moreover, it can be used to produce valued materials for other applications thus saving natural resources. In the past decades, much effort has been expended to utilize the components of red mud for bulk applications, especially in water treatment. However, it should be noted that red mud contains many metal ions and organics, which will be released under certain conditions.

4.2.4. Clays and soils

4.2.4.1. Clay. The terms clays and clay minerals are often used interchangeably yet have slightly different meanings, particularly when used across scientific disciplines (Dai et al., 2009). For example, “clay” is used by engineering geologists and sedimentologists to describe geological materials $> 4 \mu\text{m}$ in size, by soil scientists to denote the soil fraction containing particles $2 \mu\text{m}$ size, and colloidal scientist’s $1 \mu\text{m}$. Mineralogists define ‘clay’ as a naturally occurring material composed of fine-grained minerals, which is generally plastic at appropriate water contents and will harden when dried or fired. Clays may therefore be mixtures of fine-grained clay minerals and clay-sized crystals of other minerals such as quartz, carbonate, and metal oxides. The term ‘clay minerals’ however is not restricted by particle size but refers to phyllosilicate minerals and to minerals which impart plasticity to clay and which harden upon drying. Phyllosilicates are a large family of minerals that commonly show layered structures and include kaolin, smectite, chlorite, mica and serpentine groups (Kamble et al. 2009; Bergaya et al. 2006; Kiurski et al. 2012; Wang et al. 2002; Agarwal et al. 2003).

4.2.4.2. Fired clays. Various techniques and processes were used to remove the pollutants from contaminated printing wastewaters. Among all proposed approaches, adsorption is one of the most popular methods and is currently considered as an effective, efficient and economic process for printing

wastewater purification. Also, this process is found to be superior to other techniques for printing developer treatment because of its easy operation and removal intensity of toxic substances. Adsorption with inexpensive and easily available adsorbents makes the removal of zinc ions from printing wastewater to be an economically viable alternative [Moges et al. \(1996\)](#). Some natural adsorbents such as clays matched these requirements. Clay minerals are effective natural adsorbents due to their small particle sizes, lamellar structures, and negatively charged surfaces. These characteristics make them good cation adsorbents with large specific surface areas. The use of fired clays as adsorbents is inexpensive, since these materials can be easily prepared (firing temperature below 1000 °C) and regenerated. Thus, clay and clay minerals can be promising adsorbents for environmental purification purposes ([Beitollahi et al., 2008](#) ; [Wang and Reardon 2001](#)).

4.2.5. Carbon

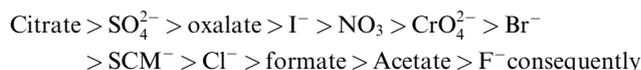
Few carbon based sorbents have also been explored for fluoride removal by various researchers. Bhargava and Killedar conducted fluoride adsorption onto fishbone charcoal in a moving media adsorption system. The ratio of attained equilibrium sorbate concentration to the initial sorbate concentration and the fluoride removal capacity of the sorbent were found to vary inversely with the sorbent mass input rate, and varied directly with the sorbate flow rate and initial sorbate concentration. The ratio of attained equilibrium sorbate concentration to the initial sorbate concentration was found to be a function of the sorbent-sorbate mass input rate ratio ([Daifullah et al., 2007](#)). In a study conducted by Kaseva, optimization and application of the regenerated bone char media for the defluoridation of drinking water in Tanzania was carried out. The regeneration temperature of 500 °C for 2 h was found optimum and the smallest grain size particle of bone char (0.5–1.0 mm) yielded the best fluoride removal. Results indicated that the highest fluoride removal and adsorption capacity were 70.64% and 0.75 mg/g, respectively. Continuous down flow adsorption mode at room temperature was also adapted to defluoridate drinking water using zirconium impregnated activated charcoals by [Zhu et al. \(2008\)](#). Fluoride adsorption capacity of impregnated activated charcoals was 3–5 times higher to that of plain activated charcoal. Zirconium ion impregnated coconut fiber charcoal (ZICFC) showed maximum fluoride uptake followed by ground nut shell and coconut shell charcoals due to its large surface area. ZICFC was found effective for 21 L (8.0 mg F⁻/L) test solution and 6 L (2.47 mg F⁻/L) tap water. Regeneration of ZICFC was conducted by elution with 0.02 M NaOH solution.

4.2.5.1. Alumina-impregnated graphitic carbon. Ramos et al. studied adsorption of fluoride from an aqueous solution on plain and alumina-impregnated activated carbons, prepared by stirring with an aluminum nitrate solution at a fixed pH, followed by calcinations under nitrogen at a temperature of 300 °C ([Svancara et al., 2008](#)). The adsorption of fluoride on impregnated carbon was shown to be dependent upon both the pH of the impregnating solution and the temperature of calcination. Impregnated carbon was shown to have a fluoride adsorption capacity of 3–5 times that of plain activated carbon. With the increase in calcination temperature from 300 to 1000 °C, uptake of fluoride decreased.

4.2.5.2. Carbon nanotubes. Exploring the application of carbon nanotubes to adsorbing fluoride, a team led by Yan-Hui Li prepared aligned carbon nanotubes (ACNT), by the decomposition of xylene catalyzed by ferrocene. The authors found this material to adsorb 4.5 mg/g fluoride from 15 mg/L fluoride at pH 7, and the adsorption capacity to increase with increasing acidity owing to the increasing positive charge on the surface. The adsorption isotherms generated under identical conditions for activated carbon, g-Al₂O₃, a typical soil and carbon nanotubes showed that the order of adsorption was: carbon nanotubes > soil > g-Al₂O₃ > activated carbon.

4.3. Synthetic resins

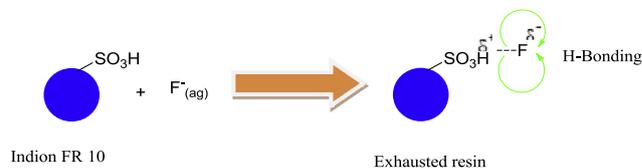
Fluoride removal by means of ion exchange technology using anion-exchange resins is difficult, since the order of selectivity for anionic species by anion-exchanger resins is as follows:



The cation/chelating type resins were equally employed for sorption of fluoride. Research work on fluoride removal ([Zhang et al., 2002](#)) has been carried out using metal loaded cation exchangers such as silica gel and alumina gel or chelating resins where high valence metal such as irons (III), Lanthanum (III), Cerium (IV) and Zirconium (IV) have been loaded as metals. From the above studies, it is clear that the mechanism of fluoride removal by CER mainly governed by ion exchange:



The fluoride removal capacity of the resin IND may be controlled by an adsorption mechanism. The equilibrium data agree with both Freundlich and Langmuir isotherms. The low values of chi-squared analysis, negative values up to -20 KJ/mol of free energy change (delta G°), positive values of entropy change (delta S°), and the values of sticking probability between 0 and 1 clearly indicate the dominance of physio-sorption. The absorption of fluoride by IND may be represented as follows:



The pH_{zps} at 3.5 supports the fact that the process of fluoride removal over a wide range of pH studied is governed by physio-sorption. Since the adsorption is due to H-bonding, the more electronegative F⁻ ion gets adsorbed first and then the other anions ([Gavalas et al., 2004](#)). The preference of adsorption of anions may be in the following order: F⁻ > Cl⁻ > NO₃⁻ > SO₄²⁻ etc.

waste materials (e.g. red mud, slag, sludge) which possess metal oxides, have been used to lower the fluoride concentrations and could be possible alternatives as low-cost adsorbents. Common techniques used for defluoridation are coagulation-precipitation, membrane process and ion exchange. The problem with these three techniques is that they are either too expensive or they further pollute the water. Researchers from the Indian Institutes have discovered an effective method to remove fluoride from drinking water that is less expensive than conventional filtration processes and is safe to use.

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