Phytoremediation of fluoride from the environmental matrices: A review on its application strategies

Madara Weerasooriyagedara [a,1], Ahmed Ashiq [a,1], Anushka Upamali Rajapaksha [a,b], Rasika P. Wanigathunge [c], Tripti Agarwal [d], Dhammika Magana-Arachchi [e], Meththika Vithanage [a,b,e,*]

[a] *Ecosphere Resilience Research Center, University of Sri Jayewardenepura, Nugegoda, 10250, Sri Lanka*
[b] *Instrument Center, Faculty of Applied Sciences, University of Sri Jayewardenepura, Sri Lanka*
[c] *Department of Plant and Molecular Biology, University of Kelaniya, Sri Lanka*
[d] *Department of Agriculture and Environmental Sciences, National Institute of Food Technology Entrepreneurship and Management, Haryana, 131028, India*
[e] *Molecular Microbiology and Human Diseases, National Institute of Fundamental Studies, Kandy 20000, Sri Lanka*

A R T I C L E I N F O

Keywords:
Phytoremediation
Bioavailability
Translocation
Uptake
Accumulation
Outline

A B S T R A C T

Fluoride contamination is a global environmental interrogation due to consideration of its long-term persistence in air, soil, and water even at lower levels. Long-term exposure can exert negative impacts on all communities irrespective of the concentrations. Therefore, immediate attention is needed to remediate the negative impacts of fluoride on the environment. Various conventional and modern techniques have been developed to remove fluoride from groundwater mainly due to its high prevalence. Due to limitations such as high cost, labor intensity, regeneration need, and low removal capacity, many existing techniques are not practical for remediating fluoride in water. At the same time, less advertence has been raised for phytoremediation as an effective and environmentally friendly method. This review presents the utilization of potential plants for removing fluoride from environmental matrices, discusses the fluoride translocation mechanisms and its phytotoxicity in plants.

1. Introduction

Fluoride contamination in the environment has been recognized as one of the significant groundwater quality issues for a long time. Being the 13th most abundant elements found in the earth's crust, fluoride is found in different environmental matrices that adversely affect their physiological and biochemical parameters (Singh et al., 2018; Vithanage et al., 2012b; Vithanage et al., 2014). Fluorine is the most reactive and electronegative element in the periodic table and primarily occurs as the negative fluoride ion in the environment. In the Earth's crust, many rocks and minerals contain fluorides and have the ability to leach out by natural weathering and precipitation (Loganathan et al., 2013; Vithanage et al., 2014). It increases the availability of fluoride in the environment, which leads to its entry into the food chain (Fawell et al., 2006). In addition to this, fluoride can enter into the environment from the wastewaters generated from industrial activities such as steel, glass, semiconductors, aluminum, electronics, fertilizer, and insecticide production processes (Kimambo et al., 2019). These industrial effluents and the sewage discharged from the domestic water supplies enhanced with fluoride lead to increase in the fluoride levels in aquatic environment. Volcanic activities and coal combustion contribute to the emission of fluoride rich dust and gasses to the atmosphere as well which are further sources of fluoride leaching into the environment through airborne sources (Fawell et al., 2006).

Although fluoride is considered an essential element for human wellbeing and in regards to the safe limits as stated earlier, excessive doses may cause adverse health effects. Fluorosis has been reported from South Asian, African, Middle East, North, Central, and South American and European regions (Fawell et al., 2006), which has been reported to have detrimental effects on human wellbeing. It was estimated that 56.2 million people were stricken by fluorosis in India, and it was prevalent in 19 States out of 32 (Jagtap et al., 2012; Ranasinghe et al., 2019b, 2019a). Up to date, research emphasis has been addressed more on the hazardous effects of fluoride on the human and animal population;

however, lack of attention has been given on its ecological impact and the cost-effective ways to deliver safe drinking water with optimal fluoride levels is the need of the hour. Hence, there is a critical need to develop sustainable technology or process to remove or detoxify fluoride from the environment.

General defluoridation techniques involve precipitation, ion exchange, adsorption, electrocoagulation, and membrane processes (Chatterjee et al., 2018; Ravulapalli and Kunta, 2017); however, application of these processes are limited to the high cost and high maintenance that they demand (Mohapatra et al., 2009; Premathilaka and Liyanagedera, 2019). Phytoremediation, a green technology, for water quality improvements has been intensively studied during the last few decades due to its cost-effectiveness, environmentally friendly natural clean-up process as well as the ability to detoxify the contaminants significantly. Several plant species have been identified to be utilized for accumulating these contaminants in their tissues especially when it comes to the uptake of trace metals. The understanding of their uptake/translocation through the root and shoot system is limited, and the stress factors it can withstand without compromising the growth of the plant requires detailed attention. Thus, the study of plant and soil interactions in the context of fluoride accumulation is crucial. In this review, an attempt was made to implicate the use of plants for contaminant mitigation of fluoride and elucidate the fluoride uptake and translocation mechanisms of plants, phytotoxicity, and phytoremediation of fluoride as an ecofriendly alternative.

2. Fluoride occurrences and sources

2.1. Global distribution of fluoride

Geographical location is the primary factor that decides the fluoride content in the water (Vithanage and Bhattacharya, 2015). The water and the rock interactions, geothermal springs, tectonic processes, and volcanic activities are the primary routes for fluoride plumes into the groundwater as depicted in Fig. 1 (Chowdhury et al., 2019). In groundwater, high fluoride concentrations varying between 1 and 48 mg L^{-1} are found in many parts of Asia, Africa, China, India, Ghana, Kenya, Sri Lanka along with Rift Valley countries in Africa and USA. When establishing the fluoride intake limits, the two essential factors to be considered are the quantity of water intake and intake from diets. For instance, in arid regions, the fluoride consumption is higher than the temperate regions due to the higher concentrations of fluoride at arid conditions indicating that the fluoride limit for fluorosis should be lower especially for the humid tropics (Escoto et al., 2019; Kumar Yadav et al., 2018; López-Guzmán et al., 2019; Makehelwala et al., 2019; Yadav et al., 2018).

In the Asian region, out of 85 million tons of fluoride deposits on the Earth crust, 12 million tons are found in India (Teotia and Teotia, 1994). Fluoride contamination of groundwater in India has been a severe problem, which is due to the evaporation of groundwater with residual alkalinity (Jacks et al., 2005). According to Kumar et al. (2016) et al., about 50% of the groundwater in Delhi exceeds the maximum permissible level of fluoride in drinking water (Datta et al., 1996; Dehghani et al., 2016; Kumar et al., 2016). Due to the presence of inherent fluoride-rich granite rocks, the groundwater fluoride concentration in Andhra Pradesh, India, is at a high-risk level of exposure. The rocks in Southern India are rich with fluoride which forms the principal reason for fluoride contamination in groundwater (Rao et al., 1993; Singh et al., 2018). In deeper aquifers of Maharashtra, fluoride content is higher than shallow groundwater due to long term residence time along the shallow groundwater levels (Madhnure et al., 2007). Furthermore, the deposition of soil dust paves the way to reported high level of fluoride level in two sites in Uttar Pradesh and Madhya Pradesh in India (Singh et al., 2016).

In Sri Lanka, it was reported that the high fluoride areas are located within the lowland plains due to longer contact time with the geological sites was longer in plains and slow groundwater movement compared to highlands (Premathilaka and Liyanagedera, 2019). Fluoride-bearing minerals such as hornblende, mica, and appetite are in abundance in all of the three major lithotectonic units of the country viz., the Highland, the Wanni and the Vijayan complex. Under humid tropical climate, the weathering of the mineral rocks occurs, and fluoride gets easily leached into the groundwater which is the primary source of drinking water in these arid regions. The seasonal rainfalls, evaporation, and mineralogical compositions of these aquifers significantly control the composition of groundwater, causing an excess or deficiency of

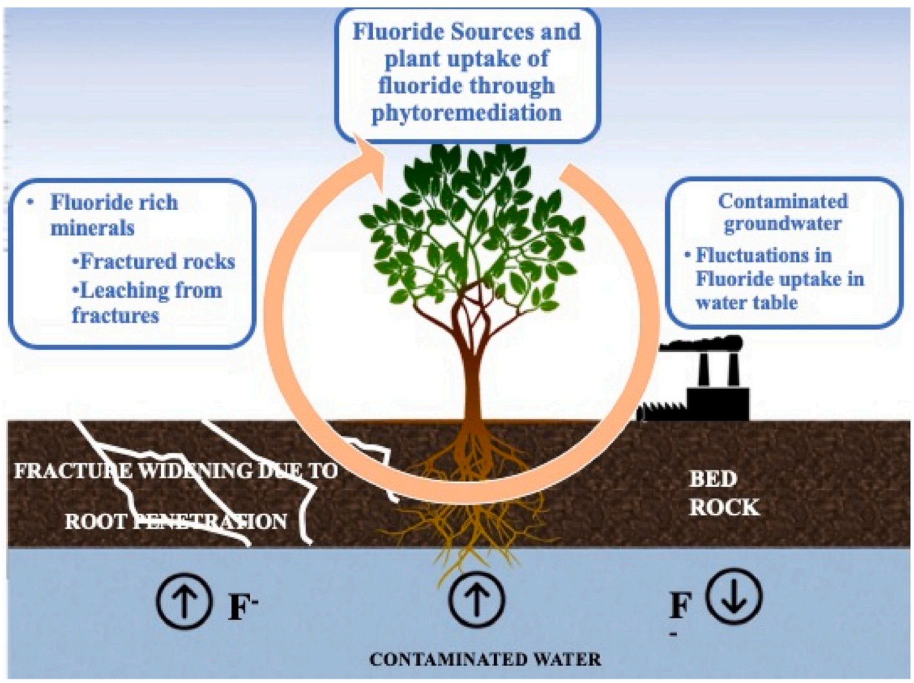

Fig. 1. Fluoride sources and its fate in the environment.

crucial elements in drinking water (Chandrajith et al., 2012; Ranasinghe et al., 2019b, 2019a).

There are several known instances for the link between the geochemistry and climate in these regions and a consistent trend of human diseases in the vicinity. In the dry zone of Sri Lanka, Chronic Kidney Disease of unknown etiology (CKDu) is one of the most common health problems among the farming communities. The disease is geographically constrained to the dry zones of the county and is manifested directly in paddy farmers in the age groups of 30–60 years. The presence of high levels of fluoride and hardness was reported from water in the CKDu prevalent areas (Premathilaka and Liyanagedera, 2019; Lada Sokolova et al., 2019; Wickramarathna et al., 2017). This adds up to the potential toxicology link referred to the intake of fluoride from these drinking water sources.

The fluoride level in groundwater has not changed even after two decades in some areas of north-central part of Sri Lanka, which are higher than 4 mg L^{-1} in groundwater (Young et al., 2011). To add further, around two million people are at risk of being exposed to high fluoride levels in East Punjab, Pakistan, due to fertilizer containing leachable fluoride and coal containing fluoride (Farooqi et al., 2007). This accounts for generations of human settlements being exposed to fluoride consuming drinking water.

Exaggerated fluoride in drinking water has been reported from many parts of China (Gao et al., 2007; Zhu et al., 2007). A salty lake water intrusion has been reported in Yuncheng basin, China, as the source of high concentrations of fluoride in groundwater. Interaction between a recharge area and fluoride-containing minerals was the source of high fluoride in Taiyuan Basin China. High fluoride concentration has resulted in the discharge area of the same basin as well due to evaporation and mixing of karst water (Gao et al., 2007). Oversaturation of fluoride in groundwater of Mizunami, Japan has been reported due to weathering and alteration of granite rocks (Abdelgawad et al., 2009). Ash from the volcanic explosion of Sakurajima volcano, Japan was found to contain average fluoride concentration of 788 mg L^{-1} for 12 years (Nogami et al., 2006).

Evaporation leads to an incensement in the fluoride level in the natural waters of Kenya, where fluoride concentration was more significantly higher in lake water than groundwater and springs (Gaciri and Davies, 1993). The area surrounding the East African Rift system and Tanzania, volcanic activity, resulted in increasing the fluoride concentration in waters. Many of the lakes in these areas have fluoride concentration reaching up to 1640 and 2800 mg L^{-1} (IPCS Fluorides, 2002). Phosphate industry waste disposal sites in Poland have reported fluoride concentration of about 8 mg L^{-1} (Czarnowski et al., 1996). Due to Silurian-Ordovician aquifer system, in Western Estonia, the fluoride concentration was reported naturally at about 7 mg L^{-1} (Indermitte et al., 2009).

2.2. *Sources of high fluoride in the environment*

Fluoride can enter into the environment through both natural and anthropogenic activities. Naturally, fluoride is an accomplice with many mineral deposits containing fluoride-bearing minerals such as Sellaite, Villianmite. Flourite, Cryolite, Bastnaesite, and Fluoroapatite which occur in most rocks and sediments (Chae et al., 2007, 2006; Saxena and Ahmed, 2003) and can release into the environment through weathering, dissolution and other pedogenic processes. Syenites, granites, quartz monzonites, felsic, and biotite gneisses are considered as the highest fluoride-containing rocks (Kimambo et al., 2019; Kumar et al., 2016; Mukherjee and Halder, 2018; Polonskij and Polonskaya, 2013).

Ideally, when rocks containing these fluoride minerals get exposed through weather agents as in water, alteration of rocks occurs through a series of geochemical reactions whose fluorine gets leached into the water as in depicted in Fig. 1. Hydrothermal vein deposits contain fluorite, fluoro-apatite, fluoride-rich micas, and amphiboles (Ali et al., 2019; Dolejs and Baker, 2007). Wall rock interactions are considered as the leading process on fluoride release into the groundwater (Abdelgawad et al., 2009) (Abdelgawad et al., 2009), and fluorides mainly originate via hydroxy positions in biotite and hornblende, which is concentrated through evaporation resulting residual alkalinity. Therefore, a high level of groundwater concentrations of fluorides is mainly reported in dry parts of the world (Jacks et al., 2005; Mukherjee and Halder, 2018).

Fluoride concentration is positively correlated with HCO_3^- and Na^+ content, as high fluoride groundwater typically has high pH values (Gao et al., 2007). Further alkaline condition, moderate specific conductivity, and their ratios are considered as the significant factors that govern the fluoride dissolution from rocks (Saxena and Ahmed, 2003, 2001). Due to alkaline nature of groundwater (due to the presence of HCO_3^- and Na^+), it has relatively high hydroxyl ions. Accordingly, the OH^- can be replaced by fluoride of the fluoride bearing–minerals, leading to boost the fluoride content in groundwater (Vithanage and Bhattacharya, 2015).

Despite the exceptional situations that have anthropogenic inputs such as phosphate fertilizers, sewage sludge, and industrial pollution, fluoride content in soil ranges from 200 to 300 mg kg^{-1} generally (Edmunds and Smedley, 2005; WHO, 2002). Since fluoride naturally has a strong association with soil, factors influencing the release of fluorides from the soil are chemical speciation, soil chemistry, and climate. The aluminum and iron in soils form complexes with the fluoride at acidic pH, and the adsorption onto soil is significantly high (WHO, 2002). The application of fertilizers makes the soil alkaline and leads to an increased fluoride release from soil to the groundwater. Sources of fluoride in soil and groundwater include volcanic ash, hydrothermal sources, wet and dry deposition of gaseous particulate fluorides, phosphate fertilizers, insecticides, fumigants, rodenticides and herbicides (Datta et al., 2012). Marine aerosols, volcanic gas emissions, and airborne soil dust are considered as natural atmospheric sources of fluoride (Tavener and Clark, 2006). High solubility in volcanic ash may cause to increase the groundwater fluoride content indirectly. Primary anthropogenic sources of fluorides are aerosols from brickwork, phosphate fertilizers, iron and steel production, ceramic industries, and aluminum smelters (Bonvicini et al., 2006; Walna et al., 2007). Further, hydrothermal vein deposits contain fluorite, fluoro-apatite, fluoride-rich micas and amphiboles (Dolejs and Baker, 2007).

2.3. *Problems related to fluoride contamination*

Fluoride abundant drinking water is a boundless problem which can be seen all over the world. As the presence of fluoride in water does not indicate any color, odor, or taste, and it acts as an invisible poison in groundwater. Exaggerated exposure to fluoride paves the way to diseases that can cause calcification of ligament and mottling of teeth skeletal and dental fluorosis (Fawell et al., 2006). Developmental issues in children, decreased cognitive ability, cancer, and crippling bone deformities may demonstrate the long-term ingestion of fluoride-rich drinking water (Dolejš and Baker, 2007). Osteosarcoma (bone cancer) in human males is mainly associated with fluorinated water, which is the third common cancer in children with a death rate of about 50%, and most survivors lose limbs to amputation (Bassin et al., 2006).

As reported earlier, chronic kidney disease has become the most widely spread disease in some parts of the dry zones of Sri Lanka, and fluoride has been proven to be a contributory factor in spreading the etiology of chronic diseases (Ranasinghe et al., 2019b, 2019a). Studies have shown the possible relationship between the fluoride levels in drinking water and the damage it has on the kidney. The detrimental indices for analyzing kidney functions were carefully studied upon viz., the content of creatine in urine and the activities of the lysosomal enzyme, and its co-relation with water fluoride levels (Dissanayake and Chandrajith, 2017; Xiong et al., 2007). This necessitates further, the measures to be taken for safe provision of potable water for the prevention of this particular disease. Among the dry zones of Sri Lanka, the fluoride and the total dissolved solids that contribute to forming complexes with the hard water needs to be pre-treated using reverse osmosis and currently are remediated in these arid areas (Lee et al., 2009; Makehelwala et al., 2019).

To add further, fluoride dosage in drinking water is dependent on the climatic conditions of the region; thus, it is suggested to drop the recommended fluoride level to 0.6–0.8 mg L^{-1} from the existing limit in tropical countries with an average temperature of 31–24 °C (Ranasinghe et al., 2019b, 2019a). The climatic conditions and high intake of water are co-dependent and need to be considered for setting up a standard level for drinking water.

3. Defluoridation

The defluoridation techniques can be broadly divided into four categories, mainly as coagulation & precipitation, adsorption and ion exchange, electrochemical technique, and membrane process. These techniques are being practiced on a commercial scale and yet there exists a gap of identifying an effective, convenient, safe and cheap method to implement widely. Coagulation and adsorption/ion exchange processes are the most widely used fluoride removal techniques. Other sophisticated techniques such as reverse osmosis, electrodialysis, and nanofiltration limit their applications due to high cost and high technical competence, though they assure good quality water (Vithanage and Bhattacharya, 2015). The efficiency of these sorbents differs depending on the surface area, electrostatic nature and other physical parameters that affect the chemistry between the anions and the sorbents. Maximum fluoride adsorption occurs typically at a low range of pH and high temperature. For the most part, Langmuir and Freundlich isotherms fit well and follow first-order kinetics. Co-existing ions in the aqueous solutions do not usually affect the fluoride adsorption because of the strong affinity of electronegative fluoride with the other elements on the sorbents (Yadav et al., 2019, 2018). Phytoremediation has shown keen interest amongst scientists towards an inexpensive and a sounder technique.

Keeping in view the economic aspects of these other defluoridation strategies and the efficiency involved in remediating this pollutant, there is a need to develop more sustainable remediation of fluorine from the environmental matrices. The suitability to different climatic scenes and the mechanisms involved for the uptake of fluoride by pants are yet to further studied.

3.1. *Phytoremediation: the route for defluoridation strategies*

Phytoremediation is an augmenting technology that employs plants to remove contaminants from the environment, which has several advantages over other remediation techniques (del Socorro Santos-Díaz and Zamora-Pedraza, 2010; Karmakar et al., 2018). Phytoremediation is defined as the treatment of environmental pollutants using plants that alleviate the environmental problems without the need to excavate the contaminant material and dispose it off elsewhere. The interest in phytoremediation has increased significantly with the identification of the plants ability to hyper-accumulate the metals (Ghosh and Singh, 2005). Several plant species have been identified, which have tendencies to accumulate higher levels of pollutants in their tissues.

The technique of phytoremediation can be applied for both organic and inorganic pollutants present in the soil, air, and water. In phytoremediation, plants are used to absorb specific contaminants through a plant's root system into the body of the plant from the soil or water, where they are stored and ultimately disposed of (Huang et al., 2004). Phytoremediation associates with phytoextraction (Mondal et al., 2013), rhizofiltration, phytostabilization (Boukhris et al., 2015), and phytotransformation (Chatterjee et al., 2018). Mainly two characteristics are essential for the utilization of plants for phytoremediation, i.e., functional phytoremediation capacity and high production of biomass (Marmiroli and McCutcheon, 2003).

3.2. *Plant as phyto-monitoring agents of fluoride*

Due to the sensitivity of plants to fluoride ions, they can be used as biomonitors for fluoride pollution (Bauthiyal and Ranghar, 2015). The leaves of *Eucalyptus rostrata, Populus hybridus,* and different needle ages of *Pinus radiata* were collected by Rodriguez et al. (2012) at different distances from the Al smelter industry, and the fluoride concentrations were analyzed. Due to the foliar characteristic such as mass and area, as well as the higher capacity of retention on leaf surfaces *E. rostrata* demonstrated the highest values of fluoride accumulation (Rodriguez et al., 2012). Data on the expression of symptoms on fluoride toxicity is correlated with fluoride analysis of *E. rostrata* and *P. hybridus*; it emphasized the importance of the use of these plants as biomonitors for the atmospheric fluorides. This usage will help to determine the source, extent and the rate of the fluoride contamination (Bauthiyal and Ranghar, 2015).

Previous studies demonstrate the ability of plants to remove a variety of pollutants, including antibiotics (Gujarathi et al., 2005), metals (Ghosh and Singh, 2005; Pilon-Smits and Pilon, 2002), pesticides (Henderson et al., 2006) and aromatic compounds. Similarly, constructed wetlands using aquatic plants have been successfully used to accumulate metals such as Cr, Fe, and Pb (Senkondo et al., 2018; Zhang et al., 2010). The appropriateness of using aquatic plants for phytoremediation has been investigated for several metals, including lead, nickel (Axtell et al., 2003) antimony, arsenic, copper, cadmium, and zinc (Ha et al., 2009; Sakakibara et al., 2011).

The ability of the fluoride removal is a factor of plant sensitivity, which is highly variable and depends on species, timing, level of exposure, and duration of exposure (Davison and Weinstein, 1998). Fluoride hyper-accumulation is an essential process for obtaining successful results in phytoremediation. Plant to shoot contaminant uptake ratio also known as translocation factor, plant to root uptake factor also known as bioaccumulation factor, tolerance for maximum uptake of the contaminant that does not affect the biomass growth at the site (Cunningham and Ow, 1996) and ratio of contaminant concentration in plant shoot to soil (enrichment factor) (Lorestani et al., 2011)are the main factors that requires consideration while choosing the right plant. Finding hyper-accumulators is not an easy task that fulfills all the criteria mentioned above. The plants that have a factor more significant than one for either bioconcentration, translocation or enrichment are considered as hyper-accumulators (Lorestani et al., 2011). Detailed knowledge on hyper-accumulator plant species that can accumulate a considerable amount of fluorides is a rapidly growing need. Few of the major plant species capable of fluoride uptake through their root/shoot system are represented in the table below (Table 1).

The underlying pathways for fluoride uptake are depicted in Fig. 2. The mechanism of some plants that have high fluoride resistance is not well understood. Tolerant plants may have a better ability to deactivate fluorides, preferably than the sensitive plants. According to Telesinki et al. (2011), possible mechanisms for fluoride deactivation in plants may include uptake of fluorides through their insensitive metabolic pathways, removal from sites of enzyme inhibition through reaction with organic components, sequestration in vacuoles, reaction with cations and translocation to the leaf surface (Telesinski et al., 2011). Some plants have the capability of exporting internal fluoride in leaves to the exterior leaf surface. For instance, clones of basket willow plant namely 'Bjor' and 'Tora' have the ability of toleration to fluorides at higher levels than 'Jorr' clone, by detoxifying it, at cellular level in the plant or by excluding fluoride at the roots (Bauthiyal and Ranghar, 2015).

According to the study conducted by del Socorro Santos-Díaz and Zamora-Pedraza, 2010), *Camellia japonica, Pittosporum tobira,* and *Saccharum officinarum* were able to remove fluoride up to considerable level (del Socorro Santos-Díaz and Zamora-Pedraza, 2010). Among them, *C. Japonika* seedlings demonstrated a progressive uptake of fluoride

Table 1
Major plant species used for the uptake of fluorides as part of remediation strategies.

Plant species	Accumulation compartments in plants	Media of transport	Characteristic features	References
Atractylis serratuloides	Accumulated in the shoots through phytoextraction	Soil	252 mg kg^{-1} Fluoride concentration	Boukhris et al. (2015)
Olea europaea	Shoot samples taken for analysis accumulates in aerial parts as roots system	Water	• positive interactions between phosphate fertilizer used as competing ions. • 300 µg Fg^{-1} dry weight accumulated	Boukhris et al. (2015)
Triticum aestivum	Shoots and roots studied	water	• chlorophyll studied and found its reason for reduction in shoot and root lengths which further reduced the photosynthetic efficiency. • The uptake influenced by other cationic present in soil (Ca^{2+}) which reduced the fluoride uptake	(Devika and Nagendra, 2011; Mondal, 2017; Mondal et al., 2013)
Lupinus luteus	Shoot and roots biomass studied	soil	• Increased roots and shoot observed due to competing effects coming from N uptake from nitrogen fertilizers input. • Unregulated protein synthesis observed and highly fluorine hyper-accumulative species	Szostek and Ciećko (2017)
Abelmoschus esculentus	roots and shoot	soil and water	• accumulation of fluoride (300 mg L^{-1}) caused decreased in chlorophylls *a* and *b*, thereby, reducing the shoot and roots growth due to lower photosynthetic rates and reduction in N uptake and protein content. • Magnesium and iron translocations decreased further due to fluoride uptake	Iram and TI (2016)
Oryza sativa	seedling stage	soil and water	• reduced germination and growth and low vigor index. Increased lipid oxidation leading to inhibition of growth. • Reduced chlorophylls *a* and *b* pigments leading to low photosynthetic activity and carotenoids degradation observed	Mondal (2017)
Brassica napus	root and shoot biomasses studied	soil studies	• Increased correlation between nitrogen metabolisms and fluorine uptake by plants. • This proves hypersensitivity to fluorine hyperaccumulations and stress on plants.	Szostek and Ciećko (2017)
Raphanus sativus	Shoot studies	soil and water	• Significant decrease in growth • A moderate increase in Nitrogen content and easy uptake to shoot system • Increased activities for super-oxides dismutase, catalase, and peroxidase.	(Mondal et al., 2013; Szostek and Ciećko, 2017)

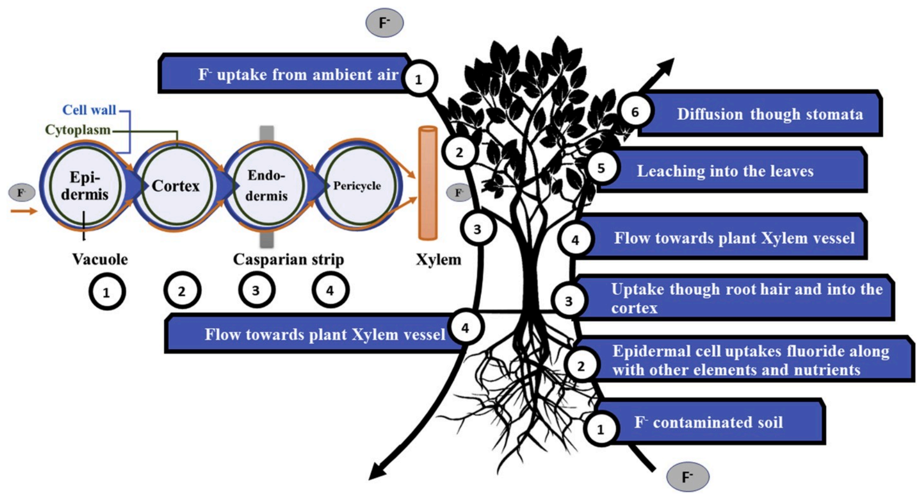

Fig. 2. Brief mechanism scheme for fluoride uptake from both contaminated soil sites and foliar uptake from ambient air.

until seventh day with 0.3 mg L^{-1} of fluoride removal. *P. tobira* culture demonstrated two-fold efficiency than *C. Japonika* while *S. officinarum* showed removal of fluoride up to 1.6 mg L^{-1} until the 21st day without indicating apparent saturation indicating that higher removal could be possible at longer exposure times. *S. officinarum,* which is 20 cm tall was able to remove 40% of the 4 mg L^{-1} fluoride concentration present in the medium. *S. officinarum* is a plant that has one of the highest growth rates. As a stem that can grow up to 4–5 m of height and a growth rate of 20 to 25-fold higher biomass in comparison with the other plants used in this study. The removal of fluorides from the media happens due to activation of the detoxification processes. It has been proposed that tolerant plants may deactivate or sequester fluoride by reaction of fluoride with calcium present in the cell wall, which leads to forming insoluble CaF_2. Fluoride concentration in many areas in the world, including Mexico (Díaz-Barriga et al., 1997), Kenya (Fawell et al., 2006), India (Chatterjee et al., 2018) and Sri Lanka is rarely exceeding the level of 5 mg L^{-1}. Therefore, the use of *S. officinarum* could be a viable plant in these countries to remove fluoride in water (del Socorro Santos-Díaz and Zamora-Pedraza, 2010; Urzúa-Abarca et al., 2018).

Plants with a fibrous root system and higher biomass are known to be ideal for the remediation component of fluoride from water as well as the use of ornamental plants would be an aesthetically pleasant mode of phytoremediation. *Nerium oleander, Portulaca oleracea,* and *Pogonatherum crinitum* were selected to estimate the efficiency of fluoride removal.

Among these three species, *N. oleander* was found to be superior to other plants and showed the highest translocation and bioaccumulation factors which is mandatory for effective phytoremediation (Khandare et al., 2017; Sokolova et al., 2019).

According to Gandhi et al. (2016), anaerobic and laboratory conditions are a favorable and adept way to remove fluoride from aqueous solution by using germinated seeds of *Eleusine coracana, Pennistum glaucum* and *Sorghum bicolor* except *Setaria italica* (Gandhi et al., 2016). The percentage removal is inclined to increase the contact time with all the germinated seeds aside from the sample treated with germinated seeds of *S. italica*. It was found that the percentage removal of fluoride is accelerated with the increase of the amount of germinated seeds at three experimental conditions (laboratory, aerobic, and anaerobic). The maximum removal efficiency was found to be in *P. glaucum* at all three different experimental conditions as 40, 42, 45% at laboratory, anaerobic, and aerobic conditions with 5 mg L^{-1} *P. glaucum* seeds respectively (Boukhris et al., 2015).

Mezghani et al. (2005) found that olive trees could accumulate fluoride up to 300 μg g^{-1} dry weight by their leaves without exhibiting any fluoride toxicity symptoms while leaves of the apricot tree become necrotic with 65,300 μg g^{-1} dry weight (Mezghani et al., 2005). *Synechococcus leopoliensis* cyanobacteria have been isolated in both resistant and tolerant forms and found that the resistant cells demonstrate passive permeation to both fluoride ions and hydrogen fluoride across the membrane (Nichol et al., 1987; Yadav et al., 2018).

The ability of Jebri variety of grapes to balance fluoride accumulation by aligned Ca accumulation was studied by Abdallah et al. (2006) (Abdallah et al., 2006). The study suggested that, when fluoride trapped in the plants in the form of CaF_2, fluoride cannot disturb plant metabolism. This finding affirms the non-translocation of fluoride via phloem towards lower plant organs. In *Chara fragilis* can combine fluoride can chemically combine into insoluble CaF_2 at the deprivation of $CaCO_3$ (Abdallah et al., 2006). This sequestration and solubilization of fluoride play a significant role in detoxification.

Studies conducted using aquatic plants confirmed the ability to use them for fluoride removal. Both *Spirodela polyrrhiza* (Shirke and Chandra, 1991; Singh et al., 2016) and *Hydrilla verticulata* (Sinha et al., 2000) were found to have potential in remediation of fluorides in wastewater. Bioaccumulation of fluorides in submerged plants have been studied using *Myriophyllum spicatum,* and *Ceratophyllum demersum* and demonstrated that elevated fluoride concentrations in water directly affected the fluoride content in the submerged plants (Pińskwar et al., 2006). Submerged polluted water plant parts accumulated 170 times more fluorides than the same plant part in unpolluted reservoir (Jezierska-Madziar and Pinskwar, 2003).

Liming and alum treatment are utilized as a flocculant to precipitate the fluoride present, which thereby increases the alkalinity and the presence of iron complexes thus formed. Implementing phytoremediation and coagulant together could enhance the fluoride uptake and a much higher growth rate in an alkaline environment (Nowack et al., 2006; Wuana and Okieimen, 2011). Kapenja et al. (2017) investigated the combined effect of phytoremediation by *Amaranthus hybridus* in combination with Fe (III) in defluoridation of water. They found that fluoride removal efficiency increased from 3 to 40% at initial concentration of 10 mg L^{-1} with the Fe (III) combination as well as removal efficiency increased with increasing concentration of Fe (III) in fluoride contaminated water (Ally et al., 2017; Kapenja et al., 2017). Similar other studies have been obtained by the use iron (Fe_3O_4) nanoparticle to enhance the fluoride uptake by *Prosopis Julifora* and *Helianthus annus L,;* they investigated the optimal fluoride concentration it can uphold. The uptake (up to 200 mg kg^{-1} of initial fluoride concentration) is in co-relation with the calcium uptake in soil, and the more fluoride in the root and shoot system, the more chlorophyll degradation occurs (Kumari and Khan, 2018a; Martínez-Fernández et al., 2016).

Some of the plants have an inherent molecular mechanism to reduce the toxic effect of fluorides. Saini et al. (2012) investigated the fluoride tolerance potential of *Prosopis juliflora*. This plant has the ability to accumulate available Fluoride in the soil (Saini et al., 2012). The observed bioaccumulation factor and translocation factor values were higher than one, which indicated the high accumulation efficiency and tolerance for fluorides by *P. Juliflora*. Moreno et al. (2003) studied on remediation of Boron and fluoride contaminated sediments using Chinese cabbage. In the laboratory pot tests, the growth rate of Chinese cabbage was not affected by low fluoride concentration (<15 mg L^{-1}) and in the hydroponics tests, fluoride content in both stems, leaves and roots increased 3–10 times higher than the control (Moreno et al., 2003).

The ability of deciduous trees to reduce fluoride contamination was studied by Wang-Cahill and Fields (2007) and suggested that fluorides are mainly aggregated in leaf tissues in tulip poplar trees and emphasized the propensity of use of leaves in fall for fluoride phytoremediation (Kang et al., 2008a,b). The potential of plants to minimize the leachate volume and reduce Cyanide and Fluoride contamination in groundwater had been studied using sycamore (Platanus sp.), green ash (*Fraxinus pennsylvanica*), willow (*Salix nigra*), yellow poplar (*Liriodendron tulipifera*), and bald cypress (*Taxodium distichum*). Based on these results, hybrid willow, sycamore, and black willow are the trees which have a higher potential to be used in reducing the leachate volume. Besides, Cyanide was degraded in the rhizosphere of the plants (particularly bald cypress and hybrid willow), whereas Fluoride accumulated in the soil and plant tissues (Kang et al., 2008a,b).

As a practical aspect of utilizing plants as a phytoremediation strategy for fluoride uptake, constructed wetland found its niche in this regard. For the most part, the North Central Province of Sri Lanka has high fluoride content in the water along with cadmium, hardness, and significantly high ionicity. Athapattu et al. (2017a,b) built a constructed wetland to treat the rejected reverse osmosis water that is typically dumped into the environment. These engineered constructed wetlands contained biochar, tiles, and soil as media along with hyper-accumulative plants (Athapattu et al., 2017a,b). Vetiver grass and *Scirpus grossus* reduced a considerable amount of fluoride (20–85%) and met with the ambient water quality standards. This is also accounted for the biochar contained in the wetland that also adsorbs other competing ions as K^+, Ca^{2+}, Mg^{2+} through chemisorption (Bhatnagar et al., 2011; Mukherjee and Halder, 2018).

Vetiver grass type is highly hyper accumulative and known for remediating trace metals, especially for the uptake of cadmium. The plant is biomass-rich with C4 photosynthetic efficiency, owing to a higher tolerance for extracting pollutants from contaminated sites. They also have subtle, deep, and penetrating root systems, which are ideal for purposes as in a wetland for remediating fluoride flow in the stream (Bandara and Vithanage, 2016; Chen et al., 2004). This bio-geo constructed wetland is considered to be sustainable for effective removal of fluoride especially in the CKDu affected areas whose drinking water utilizes the RO plants (Athapattu et al., 2017a,b).

3.3. Phytotoxicity and concerns for fluoride uptake

Fluorides from the air in the form of HF and SiF_4 are considered as the most potent pollutant and are between 1–3 orders magnitude toxic than other common air pollutants. Hence, release of a small amount of fluoride containing air pollution into the atmosphere leads to extensive damage to plant life (Singh et al., 2018; Weinstein and Davison, 2003). The damages in plants becomes easily visible in its leaf and border-line necrosis. Fornasiero (2001) studied the phytotoxic effects in controlled conditions of *Hypericum perforatum* plants, where the tissues of the leaf becomes reddish-brown and the chloroplast altered and also concluded the reduction in the anthocyanin contents as the major type of cell injury (Baroni Fornasiero, 2003, 2001). Among other studies proven in the literature explained the concentration of HF, more than 1 μg L^{-1} or 0.8 mg m^{-3} for every 1–3 days, with a long-term threshold concentration, can cause injuries to the most sensitive vegetation. Generally, in plants, fluorides occur in the range of 10 μg g^{-1} of dry weight of fluoride. High concentrations of fluorides can cause various alterations in mineral composition in plant which are essential for physiological and biochemical reactions (Weinstein and Davison, 2004). When fluoride enters the plants through soil, it causes various toxic effects on plants. Necrotic lesions, chlorosis, and burning first appearing in the leaf tips and margins are the general symptoms of fluoride injury (Gupta et al., 2009; Gupta and Banerjeea, 2009). Fluoride initially damages the spongy mesophyll and lower epidermis following chloroplasts in the palisade cells, depending on the content in the cell sap (Panda, 2015; Zouari et al., 2017). Jha et al. (2009) studied the fluoride toxicity in *Allium cepa L.* and have found that when there is maximum loaded concentration of 800 mg NaF kg^{-1} to the soil, an adsorption capacity of 55 mg F kg^{-1} soil was obtained with burnt plant tip and finally death of the plant. The study postulated that due to the partitioning of fluoride in the onion, the order of the retention is found in the order roots, shoot and then to the bulb thereby, roots becoming the most accumulated sites for fluoride accumulation (Jha et al., 2009; Yu et al., 2009).

The ability of fluoride to transport across membranes through inhibition or stimulation of enzymes involved during glycolysis, respiration, photosynthesis has been shown by Ram et al. (2014) (Ram et al., 2014). Fluoride interferes with the metabolism of the plant and reduces the rate of cell expansion and cell division which inhabit the early seed development and germination (Karmakar et al., 2016; Ram et al., 2014). At the same time, fluoride intake leads to inappropriate seedling development and unbalanced nutrient uptake (Gadi et al., 2016). Thereafter root length, shoot length, dry weight, vigor index, chlorophyll content, catalase activity, tolerance index, germination rate, germination relative index and mean daily germination like physiological parameters are decreased with increasing fluoride concentration (Datta et al., 2012; Devika and Nagendra, 2011; Gadi et al., 2016).

In a plant system, Ca^{2+} plays a significant role as a crucial secondary messenger that participates in the multiple signaling cascades (Banerjee and Roychoudhury, 2019). Fluoride intake alters the cell permeability by interacting with Ca, which present in the cell wall of the plant (Stevens et al., 1998), which leads to reduce intercellular Ca^{2+} followed by the disrupt the abiotic stress-responsive signaling process (Banerjee and Roychoudhury, 2019). Further, prolonged fluoride stress reduces the underlying physiological processes like reproductive capability and development.

3.3.1. Accumulation of fluorides by plants

Direct uptake via roots and airborne deposition are the major routes of entry of inorganic fluorides into terrestrial plants. In plants, fluoride uptake via stomata is momentous as compared to the adsorption from the soil (Weinstein and Davison, 2003). Plants absorb fluorides through unidirectional distal movements, which eventually accumulated in roots, leaves, and fruits (Devika and Nagendra, 2011).

Fluoride uptake by roots is a passive diffusion process from which most of the fluorides remain exchangeable from roots by mild washing processes. The cell wall acts as the primary barrier to accumulate fluoride. The calcium present in the cell wall acts as a buffer against fluoride accumulation, and a difference intolerance of different plant species towards fluoride accumulation depends on Ca present in the cell wall (Makehelwala et al., 2019; Msagati et al., 2014).

The mechanism of fluoride entering into the cell is not known up to now. However, it has been observed that chloride deficiency accelerates the uptake of fluorides, as being a halide, chloride channels may be mediated by the cellular uptake of fluorides (Miller et al., 1986). Most of the fluorides in roots are in cell walls and intercellular space. Little passes through the cell membrane, plasmalemma or tonoplast promote extrusion of negatively charged fluoride ions, due to low permeability of cell membrane to fluoride ions. Transportation of fluorides towards shoots is limited due to presence of endodermis, which acts as an effective barrier to the vascular tissues. Therefore, fluorides reach the vascular system via non-selective routes that bypass the endodermis (Vithanage et al., 2012a,b).

According to Stevens et al. (1998), uptake of fluoride from the solution by the plant depends on species and ionic strength of the culture media (Stevens et al., 1998). Fluoride concentration in plants increases considerably after a threshold fluoride ion activity in the culture medium is achieved. Initial concentration, the solubility of mineral phases such as Ca and P content, soil type (Fawell et al., 2006; Mohapatra et al., 2009), soil reaction (Conover and Poole, 1972) are considered as main factors that influence uptake and accumulation of fluoride by plants.

The accumulation of fluoride in different parts of the plants comply with the trend of roots > leaves > fruits > shoots. Higher transfer rate is found in leafy vegetation, seed crops than fruiting and tuber vegetables (Gupta et al., 2009). The study conducted by three semi-arid plants, namely *Acacia tottilis, Prospis juliflora,* and *Cassia fistula* showed that an accumulation of fluoride is high in roots followed by leaves and stem. The results indicated that the significant translocation of fluorides from roots into aerial parts of the plant (Baunthiyal and Sharma, 2012). *Helianthemum intricatum*, *Rhanterium suaveolens,* and *Atractylis serratuloids* showed uptake of fluoride in leaves and much higher uptake in *Rosa agrestis* and the leaves of *Oleo europaea* due to the hair-like structures in them with thick epicuticular waxes. This uptake of fluoride is directly linked to the morphological trait in the flora as studies in Tunisia (Boukhris et al., 2015; Mezghani et al., 2005) (Table 1).

Most of the plants are able to uptake a minimum of 10 mg kg^{-1} of fluorides from the soil, while some plants have exceptional properties to accumulate fluorides up to several hundred fluorides mg g^{-1} from the soil. For instance, *Camellia sinensis* accumulate the extensive amount of fluoride in mature leaves from the soil of normal availabilities (Ruan et al., 2003; Singh et al., 2018). However, this mechanism is not well understood. The fluorides in leaves increased linearly with the concentration of the solution or soil, whereas those in roots and stem were mildly affected. The fluorides uptakes by roots are mainly readily transported to the leaves in *Camellia sinensis.* Fluoride accumulation in leaves occurs in the form of free anions or connection with Aluminum, Calcium, and Magnesium (Weinstein and Davison, 2004). Studies have revealed that the presence of fluoride and aluminum together in plant have a strong correlation compared to other elements. Their uptake and translocation are enhanced if both are present in the medium (Weinstein and Alscher-Herman, 1981).

Aquatic plants have a high propensity for accumulating soluble fluorides. Macroscopic species and bacteria, when exposed to high concentrations of fluorides, rarely showed toxic effects. Algae and cyanobacteria differ in their response to fluoride, and cyanobacteria are more sensitive to fluoride toxicity (Bhatnagar and Bhatnagar, 2000). The absence of internal compartmentalization in prokaryotes brings all the constituents under direct attack, once fluoride is inside the cell. Fluoride may interact with most cellular components and thus shows a multipronged effect on cell metabolism being a strong hydrogen bonding agent. The threshold concentration of fluoride is firmly pH dependent at which toxicity manifested varies between algae and cyanobacteria (Bhatnagar and Bhatnagar, 2000).

3.3.2. Effect of fluoride uptake on plants

3.3.2.1. a. Chlorophyll, carbohydrate, and protein in plants. The presence of fluoride in soil, water, or air exhibited the inhibitory effect on the pigments of leaves. The pigment contents were found to be declined with the increasing initial concentration of fluoride. Fluoride accumulation in plants leads to retard the chlorophyll level of the plant leaves, thereby reducing the carbohydrate synthesis (Khandare et al., 2017). Chlorophyll breakdown in leaves during the stress that caused due to fluoride accumulation or incorporation of δ-aminolevulinic acid into pathways of chlorophyll synthesis pave the way to reduce the chlorophyll content (Saini et al., 2013). The metabolism of amino acids and nitrogen significantly affects the plant when fluoride present as contaminants. In the same study, there was a correlation between nitrogen metabolism and fluoride stress among these hypersensitive plants. *Lupinus luteus* accumulated high amounts of total nitrogen in their shoots, and thus they indulge in higher fluoride uptake by increasing protein synthesis (Banerjee and Roychoudhury, 2019; Szostek and Ciećko, 2017).

Fluorides are also known as potent enzyme inhibitors, which conclusively affect physiological processes such as carbohydrate metabolism (Miller, 1993). Therefore, fluoride accumulation was able to reduce the conversion of sugars into carbohydrates (Asthir and Singh, 1995). According to Khandare et al. (2017)the chlorophyll level in *N. oleander, Portulaca oleracea* and *Pogonatherum crinitum* were found to be reduced from 30.2, 24.6 and 26.8 up to 28.3, 10.6 and 16.2 μg mL^{-1} respectively after15 days exposure (Khandare et al., 2017). Similarly, the carbohydrate levels *Nerium oleander, Portulaca oleracea,* and *Pogonatherum crinitum* were declined by 16, 50, and 44%, respectively. The total protein in *N. oleander, P. oleracea,* and *P. crinitum* were reduced by 15, 53, and 38% however, protein level reduction was not significant after15 days in *N. oleander* leaves. However, after fluoride accumulation, protein level reduction was noted in *P. oleracea* and *P. crinitum* (Reddy and Kaur, 2008).

In another study, significant chlorophyll reduction of leaves of *Pistum sativum*, *Oryza sativa,* and *Triticum aestivum*, was observed (Bhargava and Bhardwaj, 2010; Gupta and Banerjeea, 2009). In accordance with the study conducted by Shirke and Chandra (1991) there was no effect of fluoride up to 25 mg L^{-1} on total chlorophyll in *Spirodela polyrhiza*. However, the total chlorophyll degradation was observed by Karmakar et al. (2016) in *Eichhornia crassipes*, *Pistia stratiotes* and *Spirodela polyrhiza* at the 20 mg L^{-1} fluoride concentration. This may be due to temperature difference of the two studies conducted and granulation of chloroplast, enzymatic inhibition, and loss of subcellular organization may be the referencing factors for pigment loss due to accumulation of fluoride in *E. crassipes, P. stratiotes* and *S. polyrhiza* (Karmakar et al., 2016). Reduction of the chlorophyll content in the leaves of *H. perforatum* and *C. sinensis* could be seen with the fluoride accumulation (Huang et al., 2011). Prolonged contact with this fluoride anion (fluoride concentration of 2.5 mg L^{-1}) was able to reduce the chlorophyll content up to 40–60% as it can directly involve in photosynthesis (Camarena-Rangel et al., 2015).

The total protein content in the plants was found to be declined with the increasing initial fluoride concentrations (Karmakar et al., 2016). Proline and cysteine like amino acids conserve the plant tissues from the damage caused by due to heavy metal or contaminant stress conditions. Generally, they are generated from protein degradation (Bauddh and Singh, 2012). The stress caused due to intrusion of high fluoride levels induce the synthesis of free amino acids in higher plants, and the amount of free amino acids in tissue depends on the storage protein degradation (Yang and Miller, 1963). The highest reduction was observed at 20 mg L^{-1} initial concentration in the leaves of *E. crassipes*, *P. stratiotes,* and *S. polyrhiza* (Karmakar et al., 2016). After 10 mM fluoride solution exposure, sugar and starch content of *Amygdalis communis* leaves were also found to be reduced by 75 and 85%, respectively (Elloumi et al., 2005). Correspondingly paddy seedlings that were exposed to 10 mL^{-1} NaF solution were found to demonstrate 30% reduction in sugar content after 15 days (Gupta et al., 2009; Gupta and Banerjeea, 2009).

There are two known channels to which fluoride uptake takes place in plants: anion channel and the apoplastic transport channel. In anion channel, the fluoride gets accumulated in leaf from the ambient air through the stomata that further undergoes a pressure within the cell wall (Baunthiyal and Ranghar, 2015). Since these fluoride ions cannot commute easily through the lipid membranes and due to its polarization of proteins, which now makes it viable for easy transport of ions in and out of the cell. This creates a temporary depolarization of the membrane, thereby blocking the fluoride ion outflow (Zhang et al., 2016). A brief schematic diagram of the mechanism of uptake of fluoride from root to shoot system of plant from contaminated soil is depicted in Fig. 2. The apoplastic transport system is mostly more prevalent in the root system mainly due to the presence of positive charges on the cell wall. The apolplastic transport system in stomata is also exemplified in Fig. 2. The entry of fluoride ions directly into the xylem/phloem through the epidermis of the secondary roots and further bypasses the casparian strip (Singh et al., 2018; Zhang et al., 2016).

3.3.2.2. b. Plant responses to biotic and abiotic stress. In addition to the adverse effect of fluoride on chlorophyll and total protein, the mechanism of fluoride uptake needs to be further investigated to understand the factors contributing to plant stress. The interaction pathways through which plants respond from biotic and abiotic stressors, needs to be well established (Gassmann et al., 2016; Hendry et al., 1987). Chlorophyll, as discussed earlier, gets continuously synthesized and degraded at once and with the stressors, metabolisms tend to shift from anabolism to catabolism and chlorophyll get degraded to a great extent (Chang et al., 2019; Gutbrod et al., 2019; Hendry et al., 1987).

The oxidative stress is an impending phenomenon after plant exposes to various abiotic stresses as well as antioxidant enzymes play a significant role in scavenging oxidative stress in plants (Kumar et al., 2009). To examine the marker enzymes of the oxidative stress, the roots and leaves of the plants are tested generally before and after fluoride removal (Karmakar et al., 2016). The activities of catalase (CAT), superoxide dismutase (SOD), and glutathione peroxidase (GPX) in the roots of the *Portulaca oleracea* and *Pogonatherum crinitum* were observed to be at a high level. However, on the other hand, *N. oleander* roots showed lowered expression in the activities of CAT, SOD, and GPX of 77, 153 and 71% respectively after inductions (Karmakar et al., 2016; Loganathan et al., 2013). However, *N. oleander* revealed that SOD, CAT, and GPX to be induced by 280, 242 and 243% consequently. This might be due to superior translocation of fluoride exhibited by *N. oleander*.

C. sinensis and mulberry cultivars were also demonstrated significant inflated levels in SOD and CAT on fluoride exposure (Kumar et al., 2009). According to Saini et al., 2013), CAT and peroxidase activities in *P. Juliflora* were found to be increased by 3.2 and 2.7 folds, respectively. In Karmakar et al. (2015), GPX and CAT activities were studied and the maximum were achieved at 20 mg L^{-1} initial concentration of fluoride in the leaves of *Eichhornia crassipes*, *Pistia stratiotes* and *S. polyrhiza* (Karmakar et al., 2016; Saini et al., 2013).

4. Merits and demerits of phytoremediation

Phytoremediation is a technique that is relatively easy to implement as it does not require expensive equipment or highly specialized personnel (Gandhi et al., 2016). The cost of other conventional remediation method for fluoride remediation from water may vary between the US $ 10- US$ 1000 m^{-3}, whereas the cost for the use of phytoremediation may cost as low as US $ 0.05 m^{-3} (Marmiroli and McCutcheon, 2003). A variety of organic and inorganic compounds can be successfully removed from phytoremediation technique. It can be used either as an in-situ or ex-situ application (Safari Sinegani and Dastjerdi, 2008). The use of in-situ application is widespread and reliable because it minimizes the disturbance of the soil and the surrounding environment leading to reduction in the spread of contamination through air or waterborne wastes (Gandhi et al., 2016).

Disposal sites are not required in the case of phytoremediation, and public acceptance is high as it is more aesthetically pleasing and avoids excavation and transport of polluted media, hence reducing the risk of spreading the contamination. It has the potential to treat sites that are polluted not only with fluoride but also with more than one type of pollutant. The distribution of contaminants to air and water is decreased by preventing leaching and soil erosion that may result from water activity and wind (Ghosh and Singh, 2005). When properly implemented, it is considered as a green technology, which is applicable for different organic and inorganic pollutants. Thus, attempts on remediation of fluoride contaminated water by phytoremediation method requires stringent policy strengthening and advocating the need for such a holistic approach with the vital notion of safe disposal mechanism for the so contaminated biomasses are soundly addressed. This could otherwise accomplish a whole sets of national policy of eco-friendly development and create scientific, social-economic improvements among scientists, environmentalists, and agriculturists who gets involved in the application of phytoremediation technique and strengthens the applicability for fluoride uptake by such hyperaccumulators (Gandhi et al., 2016; Kumari and Khan, 2018b).

Plant tolerance to fluoride uptake is the essential requisite for phytoremediation and most of the time; it is the invasive species that are great in phytoremediation. If the invasive plants are utilized viably, it can profusely control their abundance. Most of the water hyacinth attracts special attention to taking up fluoride which is otherwise treated as a non-destructible weed. *Eichornia crassipes* (water hyacinth), have the ability to uptake both inorganic and organic pollutants and very resilient to drastic climatic conditions.

However, time is the most severe limitation of phytoremediation; it is a lengthy process, which may take several years or longer to clean up hazardous waste sites (Rajakaruna et al., 2006). In most situations, phytoremediation is confined to the rooting depth of the plants used for the studies (Gandhi et al., 2016). Vegetation conservation in intensively contaminated areas is convoluted and human health can be impacted by the entry of pollutants into the food chain through animal feeding on the contaminated plants (Vidali, 2001). It can affect biodiversity if invasive and non-native species are used for the process. Harvested plant biomass produced from the phytoextraction may be classified as a hazardous waste under the Resource Conservation and Recovery Act (RCRA), which leads to raising a problem in consumption of contaminated plants by wildlife and subject to proper handling and disposal (Gandhi et al., 2016). Unfavorable climate may limit the growth of plants and mass production thus reducing the efficiency of process (Safari Sinegani and Dastjerdi, 2008).

5. Conclusive remarks and future perspectives

Being one of the most abundant elements with about 0.3 g kg^{-1} of the earth's crust fluoride has the ability to enter into the environment through natural processes which has accelerated due to anthropogenic activities at present while attaining a detrimental impact to living, non-living environment and their interactions (Fig. 1). Many defluoridation techniques have been explored since 1930's. Applications of these techniques in the developing nations will have their limitations and thus necessitates a low-cost measure. Among the other existing membrane processes, reverse osmosis or adsorptive measures, defluoridation requires high cost and skilled operations and consistent maintenance. However, a detailed understanding of the plants that can perform in phytoremediation for fluoride uptake in significant amounts from the environment and yet perform at the least toxicity, safe and much cheaper, is an approach to be considered for a long-term strategy.

Within the last few decades, the need for the phytoremediation has increased, and minimal studies have been conducted on bioremediation of fluorides. Water and soil have become an intense area of study as plant-based phytoremediation comes into the research arena to improve quality. Biotechnological improvements of plants to increase phytoremediation will be an option which may need future attention. A detailed study on the hyper-accumulators of fluoride would be a safe, secure, and cost-effective method towards removing fluorides from soil and water. By virtue of identifying the diverse groups of terrestrial and aquatic plants so far, which have the ability to accumulate fluoride thousands of times more uptake than their origin, can be employed successfully for fluoride remediation.

Acknowledgements

Grant ICRP/NSF-NSFC/2019/BS/01 by the National Science Foundation, Sri Lanka is acknowledged.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.gsd.2020.100349.

Conflicts of interest

No conflict of interest among authors is declared.

References

Abdallah, F. Ben, Elloumi, N., Mezghani, I., Garrec, J., Boukhris, M., 2006. Industrial fluoride pollution of jerbi grape leaves and the distribution of F, Ca, Mg, and P in them. Fluoride 39–43.
Abdelgawad, A.M., Watanabe, K., Takeuchi, S., Mizuno, T., 2009. The origin of fluoride-rich groundwater in Mizunami area, Japan—mineralogy and geochemistry implications. Eng. Geol. 108, 76–85.
Ali, S., Fakhri, Y., Golbini, M., Thakur, S.K., Alinejad, A., Parseh, I., Shekhar, S., Bhattacharya, P., 2019. Concentration of fluoride in groundwater of India: a systematic review, meta-analysis and risk assessment. Groundw. Sustain. Dev.
Ally, J.K., Lenus, C.M., Hezron, T.M., 2017. The effect of Amaranthus hybridus on fluoride removal by iron (III) salts as fluoride coagulants. Afr. J. Environ. Sci. Technol. 11, 207–212.
Asthir, B., Singh, R., 1995. Fluoride-induced changes in the activities of sucrose metabolizing enzymes in relation to starch accumulation in sorghum caryopsis, raised through liquid culture. Plant Physiol. Biochem.
Athapattu, B.C.L., Thalgaspitiya, T.W.L.R., Yasaratne, U.L.S., Vithanage, M., 2017a. Biochar-based constructed wetlands to treat reverse osmosis rejected concentrates in chronic kidney disease endemic areas in Sri Lanka. Environ. Geochem. Health 39, 1397–1407.
Athapattu, B.C.L., Thalgaspitiya, T.W.L.R., Yasaratne, U.L.S., Vithanage, M., 2017b. Biochar-based constructed wetlands to treat reverse osmosis rejected concentrates in chronic kidney disease endemic areas in Sri Lanka. Environ. Geochem. Health.
Axtell, N.R., Sternberg, S.P.K., Claussen, K., 2003. Lead and nickel removal using Microspora and Lemna minor. Bioresour. Technol. 89, 41–48.
Bandara, T., Vithanage, M., 2016. Phytoremediation of shooting range soils. Phytoremediation: Manag. Environ. Contam. Volume 3.
Banerjee, A., Roychoudhury, A., 2019. Fluorine: a biohazardous agent for plants and phytoremediation strategies for its removal from the environment. Biol. Plant. (Prague) 63, 104–112.
Baroni Fornasiero, R., 2001. Phytotoxic effects of fluorides. Plant Sci. 161, 979–985.
Baroni Fornasiero, R., 2003. Fluorides effects on Hypericum perforatum plants: first field observations. Plant Sci. 165, 507–513.
Bassin, E.B., Wypij, D., Davis, R.B., Mittleman, M.A., 2006. Age-specific fluoride exposure in drinking water and osteosarcoma (United States). Cancer Causes Control 17, 421–428.
Bauddh, K., Singh, R.P., 2012. Cadmium tolerance and its phytoremediation by two oil yielding plants Ricinus communis (L.) and Brassica juncea (L.) from the contaminated soil. Int. J. Phytoremediation 14, 772–785.
Baunthiyal, M., Ranghar, S., 2015. Accumulation of fluoride by plants: potential for phytoremediation. Clean 43, 127–132.
Baunthiyal, M., Sharma, V., 2012. Phytoremediation of fluoride contaminated water and soil: a search for fluoride hyperaccumulators. J. Agric. Technol. 8, 1965–1978.
Bhargava, D., Bhardwaj, N., 2010. Effect of sodium fluoride on seed germination and seedlings growth of Triticum aestivum var. raj. 4083. J. Phytol. 2, 41–43.
Bhatnagar, A., Kumar, E., Sillanpää, M., 2011. Fluoride removal from water by adsorption—a review. Chem. Eng. J. 171, 811–840.
Bhatnagar, M., Bhatnagar, A., 2000. Algal and cyanobacterial responses to fluoride. Fluoride 33, 55–65.
Bonvicini, G., Fregni, A., Palmonari, C., 2006. Fluorine compounds in gaseous emissions from industrial sources: the case of ceramic industries. Adv. Fluor. Sci. 1, 225–249.
Boukhris, A., Laffont-Schwob, I., Mezghani, I., Kadri, L. El, Prudent, P., Pricop, A., Tatoni, T., Chaieb, M., 2015. Screening biological traits and fluoride contents of native vegetations in arid environments to select efficiently fluoride-tolerant native plant species for in-situ phytoremediation. Chemosphere 119, 217–223.
Camarena-Rangel, N., Velázquez, A.N.R., del Socorro Santos-Díaz, M., 2015. Fluoride bioaccumulation by hydroponic cultures of camellia (Camellia japonica spp.) and sugar cane (Saccharum officinarum spp.). Chemosphere 136, 56–62.
Chae, G.-T., Yun, S.-T., Kim, K., Mayer, B., 2006. Hydrogeochemistry of sodium-bicarbonate type bedrock groundwater in the Pocheon spa area, South Korea: water–rock interaction and hydrologic mixing. J. Hydrol. 321, 326–343.
Chae, G.-T., Yun, S.-T., Mayer, B., Kim, K.-H., Kim, S.-Y., Kwon, J.-S., Kim, K., Koh, Y.-K., 2007. Fluorine geochemistry in bedrock groundwater of South Korea. Sci. Total Environ. 385, 272–283.
Chandrajith, R., Padmasiri, J.P., Dissanayake, C.B., Prematilaka, K.M., 2012. Spatial distribution of fluoride in groundwater of Sri Lanka. J. Natl. Sci. Found. Sri Lanka 40.
Chang, G., Yue, B., Gao, T., Yan, W., Pan, G., 2019. Phytoremediation of phenol by Hydrilla verticillata (L.f.) Royle and associated effects on physiological parameters. J. Hazard Mater., 121569

Chatterjee, S., Mukherjee, M., De, S., 2018. Defluoridation using novel chemically treated carbonized bone meal: batch and dynamic performance with scale-up studies. Environ. Sci. Pollut. Res. 25, 18161–18178.

Chen, Y., Shen, Z., Li, X., 2004. The use of vetiver grass (Vetiveria zizanioides) in the phytoremediation of soils contaminated with heavy metals, 19, 1553–1565.

Chowdhury, A., Adak, M.K., Mukherjee, A., Dhak, P., Khatun, J., Dhak, D., 2019. A critical review on geochemical and geological aspects of fluoride belts, fluorosis and natural materials and other sources for alternatives to fluoride exposure. J. Hydrol. 574, 333–359.

Conover, C.A., Poole, R.T., 1972. Influence of fluoride on foliar necrosis of Cordyline terminalis cv Baby Doll during propagation. Fla State Hort. Soc. Proc.

Cunningham, S.D., Ow, D.W., 1996. Promises and prospects of phytoremediation. Plant Physiol. 110, 715.

Czarnowski, W., Wrześniowska, K., Krechniak, J., 1996. Fluoride in drinking water and human urine in Northern and Central Poland. Sci. Total Environ. 191, 177–184.

Datta, J.K., Maitra, A., Mondal, N.K., Banerjee, A., 2012. Studies on the impact of fluoride toxicity on germination and seedling growth of gram seed (Cicer arietinum L. cv. Anuradha). J. Stress Physiol. Biochem. 8.

Datta, P.S., Deb, D.L., Tyagi, S.K., 1996. Stable isotope (18O) investigations on the processes controlling fluoride contamination of groundwater. J. Contam. Hydrol. 24, 85–96.

Davison, A., Weinstein, L., 1998. Effects of fluorides on plants. Earth I. J. 13, 12–13.

Dehghani, M.H., Haghighat, G.A., Yetilmezsoy, K., McKay, G., Heibati, B., Tyagi, I., Agarwal, S., Gupta, V.K., 2016. Adsorptive removal of fluoride from aqueous solution using single- and multi-walled carbon nanotubes. J. Mol. Liq. 216, 401–410.

del Socorro Santos-Díaz, M., Zamora-Pedraza, C., 2010. Fluoride removal from water by plant species that are tolerant and highly tolerant to hydrogen fluoride. Fluoride 43, 150–156.

Devika, B., Nagendra, B., 2011. Phytotoxicity of fluoride on a wheat variety (Triticum aestivum var. Raj. 4083) and its bioaccumulation at the reproductive phase. Asian J. Exp. Sci. 25, 37–40.

Díaz-Barriga, F., Navarro-Quezada, A., Grijalva, M.I., Grimaldo, M., Loyola-Rodríguez, J. P., Deogracias Ortiz, M., 1997. Endemic fluorosis in Mexico. Fluoride 30, 233–239.

Dissanayake, C.B., Chandrajith, R., 2017. Groundwater fluoride as a geochemical marker in the etiology of chronic kidney disease of unknown origin in Sri Lanka. Ceylon J. Sci. 46.

Dolejs, D., Baker, D.R., 2007. Liquidus equilibria in the system K2O–Na2O–Al2O3–SiO2–F2O– 1–H2O to 100 MPa: I. Silicate–fluoride liquid immiscibility in anhydrous systems. J. Petrol. 48, 785–806.

Edmunds, W.M., Smedley, P.L., 2005. In: Fluoride in Natural Waters Essentials of Medical Geology. BJ Alloway and O Selinus.

Elloumi, N., Abdallah, F. Ben, Mezghani, I., Rhouma, A., Boukhris, M., Tunisia, S., 2005. Effect of fluoride on almond seedlings in culture solution. Fluoride 38, 193.

Escoto, D.F., Gayer, M.C., Bianchini, M.C., da Cruz Pereira, G., Roehrs, R., Denardin, E.L. G., 2019. Use of Pistia stratiotes for phytoremediation of water resources contaminated by clomazone. Chemosphere 227, 299–304.

Farooqi, A., Masuda, H., Firdous, N., 2007. Toxic fluoride and arsenic contaminated groundwater in the Lahore and Kasur districts, Punjab, Pakistan and possible contaminant sources. Environ. Pollut. 145, 839–849.

Fawell, J., Bailey, K., Chilton, J., Dahi, E., Magara, Y., 2006. Fluoride in Drinking-Water. IWA publishing.

Fornasiero, R.B., 2001. Phytotoxic effects of fluorides. Plant Sci. 161, 979–985.

Gaciri, S.J., Davies, T.C., 1993. The occurrence and geochemistry of fluoride in some natural waters of Kenya. J. Hydrol. 143, 395–412.

Gadi, B.R., Bhati, K., Goswami, B., Rankawat, R., Kumar, S., Kumar, R., Ram, A., Pooja, V., Laxmi, V., Singariya, P., 2016. Sources and phytotoxicity of fluorides in the environment. Env. Impact Biodivers 251–266.

Gandhi, N., Sirisha, D., Asthana, S., 2016. Phytoremediation of fluoride (f-) from water using germinated seeds. Int. J. Adv. Res. Eng. Appl. Sci. 5, 16–28.

Gao, X., Wang, Y., Li, Y., Guo, Q., 2007. Enrichment of fluoride in groundwater under the impact of saline water intrusion at the salt lake area of Yuncheng basin, northern China. Environ. Geol. 53, 795–803.

Gassmann, W., Appel, H.M., Oliver, M.J., 2016. The interface between abiotic and biotic stress responses. J. Exp. Bot. 67, 2023–2024.

Ghosh, M., Singh, S.P., 2005. A review on phytoremediation of heavy metals and utilization of it's by products. Asian J. Energy Environ. 6, 18.

Gujarathi, N.P., Haney, B.J., Linden, J.C., 2005. Phytoremediation potential of Myriophyllum aquaticum and Pistia stratiotes to modify antibiotic growth promoters, tetracycline, and oxytetracycline, in aqueous wastewater systems. Int. J. Phytoremediation 7, 99–112.

Gupta, S., Banerjee, S., Mondal, S., 2009. Phytotoxicity of fluoride in the germination of paddy (Oryza sativa) and its effect on the physiology and biochemistry of germinated seedlings. Fluoride 42, 142.

Gupta, S., Banerjeea, S., 2009. Fluoride accumulation in paddy (Oryza sativa) irrigated with fluoride-contaminated groundwater in an endemic area of the Birbhum District, West Bengal. Fluoride 42, 224–227.

Gutbrod, K., Romer, J., Dörmann, P., 2019. Phytol metabolism in plants. Prog. Lipid Res.

Ha, N.T.H., Sakakibara, M., Sano, S., 2009. Phytoremediation of Sb, As, Cu, and Zn from contaminated water by the aquatic macrophyte Eleocharis acicularis. Clean 37, 720–725.

Henderson, K.L.D., Belden, J.B., Zhao, S., Coats, J.R., 2006. Phytoremediation of pesticide wastes in soil. Z. Naturforsch. C Biosci. 61, 213–221.

Hendry, G.A.F., Houghton, J.D., Brown, S.B., 1987. Tansley review No. 11. The degradation of chlorophyll-a biological enigma. New Phytol. 255–302.

Huang, J.W., Poynton, C.Y., Kochian, L.V., Elless, M.P., 2004. Phytofiltration of arsenic from drinking water using arsenic-hyperaccumulating ferns. Environ. Sci. Technol. 38, 3412–3417.

Huang, P.M., Li, Y., Sumner, M.E., 2011. Handbook of Soil Sciences: Properties and Processes. CRC Press.

Indermitte, E., Saava, A., Karro, E., 2009. Exposure to high fluoride drinking water and risk of dental fluorosis in Estonia. Int. J. Environ. Res. Publ. Health 6, 710–721.

IPCS Fluorides, E.H.C. 227, 2002. UNEP ILO WHO.

Iram, A., Ti, K., 2016. Effect of sodium fluoride on seed germination, seedling growth and biochemistry of abelmoschus esculentus. J. Plant Biochem. Physiol. 4–6, 04.

Jacks, G., Bhattacharya, P., Chaudhary, V., Singh, K.P., 2005. Controls on the genesis of some high-fluoride groundwaters in India. Appl. Geochem. 20, 221–228.

Jagtap, S., Yenkie, M.K., Labhsetwar, N., Rayalu, S., 2012. Fluoride in drinking water and defluoridation of water. Chem. Rev. 112, 2454–2466.

Jezierska-Madziar, M., Pinskwar, P., 2003. Fluoride in common reeds (Phragmites Australis) sampled from the old Warta reservoirs near Lubon and Radzewice, Poland. Fluoride 36, 21–24.

Jha, S.K., Nayak, A.K., Sharma, Y.K., 2009. Fluoride toxicity effects in onion (Allium cepa L.) grown in contaminated soils. Chemosphere 76, 353–356.

Kang, D.H., Tsao, D., Wang-Cahill, F., Rock, S., Schwab, A.P., Banks, M.K., 2008a. Assessment of landfill leachate volume and concentrations of cyanide and fluoride during phytoremediation. Bioremediat. J. 12, 32–45.

Kang, S., Mauter, M.S., Elimelech, M., 2008b. Physicochemical determinants of multiwalled carbon nanotube bacterial cytotoxicity. Environ. Sci. Technol. 42, 7528–7534.

Kapenja, A.J., Msigala, L.C., Mwakabona, H.T., 2017. The effect of Amaranthus hybridus on fluoride removal by iron (III) salts as fluoride coagulants. Afr. J. Environ. Sci. Technol. 11, 207–212.

Karmakar, S., Mukherjee, J., Mukherjee, S., 2016. Removal of fluoride contamination in water by three aquatic plants. Int. J. Phytoremediation 18, 222–227.

Karmakar, S., Mukherjee, J., Mukherjee, S., 2018. Biosorption of fluoride by water lettuce (Pistia stratiotes) from contaminated water. Int. J. Environ. Sci. Technol. 15, 801–810.

Khandare, R.V., Desai, S.B., Bhujbal, S.S., Watharkar, A.D., Biradar, S.P., Pawar, P.K., Govindwar, S.P., 2017. Phytoremediation of fluoride with garden ornamentals Nerium oleander, Portulaca oleracea, and Pogonatherum crinitum. Environ. Sci. Pollut. Res. 24, 6833–6839.

Kimambo, V., Bhattacharya, P., Mtalo, F., Mtamba, J., Ahmad, A., 2019. Fluoride occurrence in groundwater systems at global scale and status of defluoridation – state of the art. Groundw. Sustain. Dev. 9, 100223.

Kumar, K.A., Varaprasad, P., Rao, A.V.B., 2009. Effect of fluoride on catalase, guiacol peroxidase and ascorbate oxidase activities in two verities of mulberry leaves (Morus alba L.). Res. J. Earth Sci. 1, 69–73.

Kumar, M., Das, A., Das, N., Goswami, R., Singh, U.K., 2016. Co-occurrence perspective of arsenic and fluoride in the groundwater of Diphu, Assam, Northeastern India. Chemosphere 150, 227–238.

Kumar Yadav, K., Gupta, N., Kumar, A., Reece, L.M., Singh, N., Rezania, S., Ahmad Khan, S., 2018. Mechanistic understanding and holistic approach of phytoremediation: a review on application and future prospects. Ecol. Eng.

Kumari, S., Khan, S., 2018a. Effect of Fe3O4 NPs application on fluoride (F) accumulation efficiency of Prosopis juliflora. Ecotoxicol. Environ. Saf. 166, 419–426.

Kumari, S., Khan, S., 2018b. Effect of Fe3O4 NPs application on fluoride (F) accumulation efficiency of Prosopis juliflora. Ecotoxicol. Environ. Saf. 166, 419–426.

Lee, S., Choi, J.-S., Lee, C.-H., 2009. Behaviors of dissolved organic matter in membrane desalination. Desalination 238, 109–116.

Loganathan, P., Vigneswaran, S., Kandasamy, J., Naidu, R., 2013. Defluoridation of drinking water using adsorption processes. J. Hazard Mater. 248, 1–19.

López-Guzmán, M., Alarcón-Herrera, M.T., Irigoyen-Campuzano, J.R., Torres-Castañón, L.A., Reynoso-Cuevas, L., 2019. Simultaneous removal of fluoride and arsenic from well water by electrocoagulation. Sci. Total Environ. 678, 181–187.

Lorestani, B., Cheraghi, M., Yousefi, N., 2011. Phytoremediation potential of native plants growing on a heavy metals contaminated soil of copper mine in Iran. World Acad. Sci. Eng. Technol. 77, 377–382.

Madhnure, P., Sirsikar, D.Y., Tiwari, A.N., Ranjan, B., Malpe, D.B., 2007. Occurrence of fluoride in the groundwaters of Pandharkawada area, Yavatmal district, Maharashtra, India. Curr. Sci. 675–679.

Makehelwala, M., Wei, Y., Weragoda, S.K., Weerasooriya, R., Zheng, L., 2019. Characterization of dissolved organic carbon in shallow groundwater of chronic kidney disease affected regions in Sri Lanka. Sci. Total Environ. 660, 865–875.

Marmiroli, N., McCutcheon, S.C., 2003. Making phytoremediation a successful technology. Phytoremediation Trans. Contr. Contam. 85–119.

Martínez-Fernández, D., Barroso, D., Komárek, M., 2016. Root water transport of Helianthus annuus L. under iron oxide nanoparticle exposure. Environ. Sci. Pollut. Res. 23, 1732–1741.

Mezghani, I., Elloumi, N., Abdallah, F. Ben, Chaieb, M., Boukhris, M., 2005. Fluoride accumulation by vegetation in the vicinity of a phosphate fertilizer plant in Tunisia. Fluoride 38, 69–75.

Miller, G.W., 1993. The effect of fluoride on higher plants. Fluoride 26, 3–22.

Miller, G.W., Pushnik, J.C., Giannini, J., 1986. A model for subcellular distribution of fluoride in higher plants: relation to in vitro concentrations required for enzyme inhibition. Studies in Environmental Science. Elsevier, pp. 241–251.

Mohapatra, M., Anand, S., Mishra, B.K., Giles, D.E., Singh, P., 2009. Review of fluoride removal from drinking water. J. Environ. Manag. 91, 67–77.

Mondal, N.K., 2017. Effect of fluoride on photosynthesis, growth and accumulation of four widely cultivated rice (Oryza sativa L.) varieties in India. Ecotoxicol. Environ. Saf. 144, 36–44.

Mondal, N.K., Kundu, M., Das, K., Bhaumik, R., Datta, J.K., 2013. Biosorption of fluoride from aqueous phase onto aspergillus and its calcium-impregnated biomass and evaluation of adsorption kinetics. Fluoride 46, 239–245.
Moreno, D.A., Víllora, G., Ruiz, J.M., Romero, L., 2003. Growth conditions, elemental accumulation and induced physiological changes in Chinese cabbage. Chemosphere 52, 1031–1040.
Msagati, T.A.M., Mamba, B.B., Sivasankar, V., Omine, K., 2014. Surface restructuring of lignite by bio-char of Cuminum cyminum – exploring the prospects in defluoridation followed by fuel applications. Appl. Surf. Sci. 301, 235–243.
Mukherjee, S., Halder, G., 2018. A review on the sorptive elimination of fluoride from contaminated wastewater. J. Environ. Chem. Eng. 6, 1257–1270.
Nichol, B.E., Budd, K., Palmer, G.R., MacArthur, J.D., 1987. The mechanisms OF fluoride toxicity and fluoride resistance IN synechococcus leopoliensis (cyanophyceae) 1. J. Phycol. 23, 535–541.
Nogami, K., Iguchi, M., Ishihara, K., Hirabayashi, J., Miki, D., 2006. Behavior of fluorine and chlorine in volcanic ash of Sakurajima volcano, Japan in the sequence of its eruptive activity. Earth, planets Sp. 58, 595–600.
Nowack, B., Schulin, R., Robinson, B.H., 2006. Critical assessment of chelant-enhanced metal phytoextraction. Environ. Sci. Technol. 40, 5225–5232.
Panda, D., 2015. Fluoride toxicity stress: physiological and biochemical consequences on plants. Int. J. Bioresour. Environ. Agric. Sci. 1, 70–84.
Pilon-Smits, E., Pilon, M., 2002. Phytoremediation of metals using transgenic plants. CRC Crit. Rev. Plant Sci. 21, 439–456.
Pińskwar, P., Jezierska-Madziar, M., Godyn, H., Arczyńska-Chudy, E., Golski, J., 2006. Fluorine content of two submerged plant species in four warta river oxbow lake reservoirs near poznań, Poland. Fluoride 39, 310–312.
Polonskij, V.I., Polonskaya, D.E., 2013. Fluoride contamination of soil and phytoremediation. Agric. Biol. Plant Biol. Sect.
Premathilaka, R.W., Liyanagedera, N.D., 2019. Fluoride in drinking water and nanotechnological approaches for eliminating excess fluoride. J. Nanotechnol.
Rajakaruna, N., Tompkins, K.M., Pavicevic, P.G., 2006. Phytoremediation: an affordable green technology for the clean-up of metal contaminated sites in Sri Lanka. Ceylon J. Sci. 35, 25–39.
Ram, A., Verma, P., Gadi, B.R., 2014. Effect of fluoride and salicylic acid on seedling growth and biochemical parameters of watermelon (Citrullus lanatus). Fluoride 47, 49–55.
Ranasinghe, N., Kruger, E., Chandrajith, R., Tennant, M., 2019a. The heterogeneous nature of water well fluoride levels in Sri Lanka: an opportunity to mitigate the dental fluorosis. Community Dent. Oral Epidemiol. 47, 236–242.
Ranasinghe, N., Kruger, E., Tennant, M., 2019b. Spatial distribution of groundwater fluoride levels and population at risk for dental caries and dental fluorosis in Sri Lanka. Int. Dent. J. 1–8.
Rao, N.V.R., Rao, N., Rao, K.S.P., Schuiling, R.D., 1993. Fluorine distribution in waters of Nalgonda district, Andhra Pradesh, India. Environ. Geol. 21, 84–89.
Ravulapalli, S., Kunta, R., 2017. Defluoridation studies using active carbon derived from the barks of Ficus racemosa plant. J. Fluor. Chem. 193, 58–66.
Reddy, M.P., Kaur, M., 2008. Sodium fluoride induced growth and metabolic changes in Salicornia brachiata Roxb. Water Air Soil Pollut. 188, 171–179.
Rodriguez, J.H., Wannaz, E.D., Pignata, M.L., Fangmeier, A., Franzaring, J., 2012. Fluoride biomonitoring around a large aluminium smelter using foliage from different tree species. Clean 40, 1315–1319.
Ruan, J., Ma, L., Shi, Y., Han, W., 2003. Uptake of fluoride by tea plant (Camellia sinensis L) and the impact of aluminium. J. Sci. Food Agric. 83, 1342–1348.
Safari Sinegani, A.A., Dastjerdi, F.S., 2008. The potential of Irankoh indigenous plant species for the phytoremediation of cadmium and lead contaminated land. Soil Sediment Contam. 17, 181–188.
Saini, P., Khan, S., Baunthiyal, M., Sharma, V., 2012. Organ-wise accumulation of fluoride in Prosopis juliflora and its potential for phytoremediation of fluoride contaminated soil. Chemosphere 89, 633–635.
Saini, P., Khan, S., Baunthiyal, M., Sharma, V., 2013. Effects of fluoride on germination, early growth and antioxidant enzyme activities of legume plant species Prosopis juliflora. J. Environ. Biol. 34, 205–209.
Sakakibara, M., Ohmori, Y., Ha, N.T.H., Sano, S., Sera, K., 2011. Phytoremediation of heavy metal-contaminated water and sediment by Eleocharis acicularis. Clean 39, 735–741.
Saxena, V., Ahmed, S., 2001. Dissolution of fluoride in groundwater: a water-rock interaction study. Environ. Geol. 40, 1084–1087.
Saxena, V., Ahmed, S., 2003. Inferring the chemical parameters for the dissolution of fluoride in groundwater. Environ. Geol. 43, 731–736.
Senkondo, Y.H., Mkumbo, S., Sospeter, P., 2018. Fluorine and copper accumulation in lettuce grown on fluoride and copper contaminated soils. Commun. Soil Sci. Plant Anal. 49, 2638–2652.
Shirke, P.A., Chandra, P., 1991. Fluoride uptake BY duck-weed spirodela-polyrrhiza. Fluoride 24, 109–112.
Singh, G., Kumari, B., Sinam, G., Kumar, N., Mallick, S., 2018. Fluoride distribution and contamination in the water, soil and plants continuum and its remedial technologies, an Indian perspective– a review. Environ. Pollut 239, 95–108.
Singh, J., Singh, P., Singh, A., 2016. Fluoride ions vs removal technologies: a study. Arab. J. Chem. 9, 815–824.
Sinha, S., Saxena, R., Singh, S., 2000. Fluoride removal from water by Hydrilla verticillata (lf) Royle and its toxic effects. Bull. Environ. Contam. Toxicol. 65, 683–690.
Sokolova, L.G., Zorina, S.Y., Belousova, E.N., 2019. Zonal cultivars of field crops as a reserve for the phytoremediation of fluorides polluted soils. Int. J. Phytoremediation 21, 577–582.
Stevens, D.P., McLaughlin, M.J., Alston, A.M., 1998. Phytotoxicity of the fluoride ion and its uptake from solution culture by Avena sativa and Lycopersicon esculentum. Plant Soil 200, 119–129.
Szostek, R., Ciećko, Z., 2017. Effect of soil contamination with fluorine on the yield and content of nitrogen forms in the biomass of crops. Environ. Sci. Pollut. Res. 24, 8588–8601.
Tavener, S.J., Clark, J.H., 2006. Fluorine: friend or foe? A green chemist's perspective. Adv. Fluor. Sci. 2, 177–202.
Telesinski, A., Snioszek, M., Smolik, B., Malinowska, K., Mikiciuk, M., Cichocka, J., Zakrzewska, H., 2011. Fluoride uptake in hydroponic culture by different clones of basket willow, Salix viminalis L. Fluoride 44, 255.
Teotia, S.P.S., Teotia, M., 1994. Dental caries: a disorder of high fluoride and low dietary calcium interactions (30 years of personal research). Fluoride 27, 59.
Urzúa-Abarca, D.A., Fuentes-Aceituno, J.C., Uribe-Salas, A., Lee, J. chun, 2018. An electrochemical study of silver recovery in thiosulfate solutions. A window towards the development of a simultaneous electroleaching-electrodeposition process. Hydrometallurgy 176, 104–117.
Vidali, M., 2001. Bioremediation. an overview. Pure Appl. Chem. 73, 1163–1172.
Vithanage, M., Bhattacharya, P., 2015. Fluoride in the environment: sources, distribution and defluoridation. Environ. Chem. Lett.
Vithanage, M., Dabrowska, B.B., Mukherjee, A.B., Sandhi, A., Bhattacharya, P., 2012a. Arsenic uptake by plants and possible phytoremediation applications: a brief overview. Environ. Chem. Lett.
Vithanage, Meththika, Jayarathna, L., Rajapaksha, A.U., Dissanayake, C.B., Bootharaju, M.S., Pradeep, T., 2012b. Modeling sorption of fluoride on to iron rich laterite. Colloids Surfaces A Physicochem. Eng. Asp. 398, 69–75.
Vithanage, M., Rajapaksha, A.U., Bootharaju, M.S., Pradeep, T., 2014. Surface complexation of fluoride at the activated nano-gibbsite water interface. Colloids Surfaces A Physicochem. Eng. Asp. 462, 124–130.
Walna, B., Kurzyca, I., Siepak, J., 2007. Variations in the fluoride level in precipitation in a region of human impact. Acid Rain-Deposition to Recovery. Springer, pp. 33–40.
Wang-Cahill, F., Fields, K., 2007. Investigation of fluoride distribution in deciduous trees at a hazardous waste landfill. In: The Annual International Conference on Soils, Sediments and Water. University of Massachusetts.
Weinstein, L.H., Alscher-Herman, R., 1981. Physiological responses of plants to fluorine. Proceedings-Easter Sch. Agric. Sci. Univ. Nottingham.
Weinstein, L.H., Davison, A., 2004. Fluorides in the Environment: Effects on Plants and Animals. Cabi.
Weinstein, L.H., Davison, A.W., 2003. Native plant species suitable as bioindicators and biomonitors for airborne fluoride. Environmental Pollution.
WHO, 2002. Fluorides, environmental health criteria number.
Wickramarathna, S., Balasooriya, S., Diyabalanage, S., Chandrajith, R., 2017. Tracing environmental aetiological factors of chronic kidney diseases in the dry zone of Sri Lanka—a hydrogeochemical and isotope approach. J. Trace Elem. Med. Biol. 44, 298–306.
Wuana, R.A., Okieimen, F.E., 2011. Heavy metals in contaminated soils: a review of sources, chemistry, risks and best available strategies for remediation. Isrn Ecol.
Xiong, X.Z., Liu, J.L., He, W.H., Xia, T., He, P., Chen, X.M., Yang, K., Di Wang, A.G., 2007. Dose-effect relationship between drinking water fluoride levels and damage to liver and kidney functions in children. Environ. Res. 103, 112–116.
Yadav, K.K., Gupta, N., Kumar, V., Khan, S.A., Kumar, A., 2018. A review of emerging adsorbents and current demand for defluoridation of water: bright future in water sustainability. Environ. Int. 111, 80–108.
Yadav, K.K., Kumar, S., Pham, Q.B., Gupta, N., Rezania, S., Kamyab, H., Yadav, S., Vymazal, J., Kumar, V., Tri, D.Q., Talaiekhozani, A., Prasad, S., Reece, L.M., Singh, N., Maurya, P.K., Cho, J., 2019. Fluoride contamination, health problems and remediation methods in Asian groundwater: a comprehensive review. Ecotoxicol. Environ. Saf.
Yang, S.F., Miller, G.W., 1963. Biochemical studies on the effect of fluoride on higher plants. 1. Metabolism of carbohydrates, organic acids and amino acids. Biochem. J. 88, 505.
Young, S.M., Pitawala, A., Ishiga, H., 2011. Factors controlling fluoride contents of groundwater in north-central and northwestern Sri Lanka. Environ. Earth Sci. 63, 1333–1342.
Yu, X.Y., Ying, G.G., Kookana, R.S., 2009. Reduced plant uptake of pesticides with biochar additions to soil. Chemosphere 76, 665–671.
Zhang, B.Y., Zheng, J.S., Sharp, R.G., 2010. Phytoremediation in engineered wetlands: mechanisms and applications. Procedia Environ. Sci. 2, 1315–1325.
Zhang, X.-C., Gao, H.-J., Yang, T.-Y., Wu, H.-H., Wang, Y.-M., Zhang, Z.-Z., Wan, X.-C., 2016. Anion channel inhibitor NPPB-inhibited fluoride accumulation in tea plant (Camellia sinensis) is related to the regulation of $Ca2+$, CaM and depolarization of plasma membrane potential. Int. J. Mol. Sci. 17, 57.
Zhu, J., Zhao, H., Ni, J., 2007. Fluoride distribution in electrocoagulation defluoridation process. Separ. Purif. Technol. 56, 184–191.
Zouari, M., Elloumi, N., Bellassoued, K., Ben Ahmed, C., Krayem, M., Delmail, D., Elfeki, A., Ben Rouina, B., Ben Abdallah, F., Labrousse, P., 2017. Enzymatic antioxidant responses and mineral status in roots and leaves of olive plants subjected to fluoride stress. South Afr. J. Bot. 111, 44–49.