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Environmental Fluoride contamination and Bioremediation through Plant species: A Review

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Abstract

Bioaccumulation of fluoride is resulting from geogenic activities and by anthropogenic actions has become a serious environmental problem. Different parts of the world are facing sensitive issues of fluoride, especially in ground water. The present fluoride contamination scenario and its array of remediation techniques targeting the decontamination of environmental hazards. The use of phytoremediation of fluoride contamination is gaining the scientific attention for sustainable environmental bioremediation. The present review work explains the different aspects of fluoride contamination, bioaccumulation, and bioremediation with implications for effective decontamination of this heavy metal.

Fluoride (F) is a very common environmental pollutant material in groundwater due to natural and anthropogenic activities. In unpolluted freshwaters concentrations of fluoride ion (F–) usually range from 0.01 to 0.3 mg F–/L [6,35]. It is reported that high fluoride concentrations present in India (38.5 mg L_1)[3]. The natural sources of fluoride are weathering and dissolution of minerals, emissions from volcanoes and the rain cycle[4]. Additionally, human activities often lead to increased local fluoride levels. Such as aluminum smelters, phosphate fertilizer plants, plants producing fluoride chemicals (such as hydrogen fluoride, calcium fluoride, sodium fluoride and sulphur hexafluoride), plants manufacturing brick, ceramics and glass, and the use of fluoride containing pesticides can increase the natural background fluoride level of surface waters in more than 100 times. Discharges of fluoridated municipal waters can also cause significant increases (about five times the natural background level) in the fluoride concentration of recipient rivers[12].

Excessive exposure of fluoride in ground water, soil, and air causes ill effects not only to human beings but also to plants

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and animals. As per the World Health Organization guidelines, the upper limit of F in drinking water is 1.5 mg/mL, and mean concentration in ambient air is <0.1 g/m^3. Above 1.5 mg/L of F in drinking water causes mottling of teeth to an objectionable degree. Concentrations between 3 and 6mg/L may cause skeletal fluorosis. Similarly, under natural conditions the content of F in soil is rather low and is between 10 and 1500mg F/kg soil[23]. However, soils that have received large doses of phosphate fertilizers are reported to have elevated levels of F as high as 5300mg F/kg dry weight[19]. Airborne fluorides in the form of HF and SiF4 are most potent environmental pollutants and are between 1 and 3 orders of magnitude more toxic than other common pollutants (*e.g.* O_3, SO_2, Cl_2, or HCl), therefore relatively small releases of fluorides into the atmosphere can result in extensive damage to plant life. In plants, F generally occurs in the range of 1–10mg F/g dry weight in most species. High concentration of F causes various changes in mineral content in plants which are important for physiological and biochemical reactions[33]. Injury to the most sensitive vegetation by HF begins at a concentration <1 ppb, or 0.8 mg/m3, for a 1- to 3-day period, with a long-term threshold concentration of 0.25–0.30 mg/m3. When F enters the plants through soil, it causes toxic effects on them[16]. The general symptoms of F injury such as necrotic lesion, chlorosis, and burning first appear in the leaf tips and margins. Afterwards, physiological parameters, viz. root length, shoot length, dry weight, vigor index, chlorophyll content, catalase activity, tolerance index, germination rate, germination relative index, mean daily germination decreases with increasing F concentration[10]. Besides, fluorides have been found to inhibit or stimulate enzymes involved in glycolysis, respiration, photosynthesis, and metabolite transport across membranes and other processes[13]. Response of F depends upon factors such as dose, duration of exposure, age, and genotypes of plants.

Acute toxic effects :

The acute dose of fluoride may trigger serious systemic toxicity is 5 mg/kg which is known as ‘probably toxic dose’ (PTD)[34]. Such as, sodium fluoride (NaF) is highly soluble and releases large amounts of fluoride compared to calcium fluoride (CaF) which is a less soluble compound. The range of acute toxic dose is 5-8 mg/kg body weight. Symptoms like gastric disturbances, nausea, vomiting with blood, abdominal pain, diarrhoea, weakness, hypotension, severe polyuria and hypocalcaemia are observed in case of acute fluoride toxicity[24].

Chronic toxic effects :

Chronic toxicity of fluoride is more common than acute toxicity. The effects of chronic ingestion of fluoride depend not only on the duration and dose but also on several other factors such as nutritional status, renal function and interactions with other trace elements. After the Absorption of fluorine compounds, first effect is shown in haematological changes than other organs[2]. Blood is easily affected by environmental pollutants and toxicants which may cause various metabolic disorders. The high level of fluoride is a potential pollutant, act as insecticide and rodenticide with high toxicity and directly associated with the haematological damage. Haematological disturbances like microcytic hypochromic anaemia has adverse effects from Sodium Fluoride on lymphatic organs also[1].

Fluoride effects on human physiological processes:

Oxidative Stress: Exposure of fluoride can reduce the glutathione at cellular level, sometimes produce excessive ROS [3,32]. Fluoride inhibits the function of antioxidant enzymes like glutathione peroidase, catalase, GSH reductase, Superoide dismutase etc.[29].

GPCR : The Aluminium tetrafluoride (AlF_4) acts as an analogue of c phosphate moiety of GTP which is present in G protein couple receptor and it is confirmed by F^{19}NMR titration study[11,17]. So this AlF_4 mimicked with PO_4^{3-} in phosphate transfer reactions[7]. AlF_x produce false signal to Gα and effector protein, consequently, Adenyl Cyclase (AC) and Phospholipase C and these generates to cAMP, Inositol 1,4,5 triphosphate, Diacylglycerol, Protein Kinase-A which produce great number of protein. After the formation of protein, some processes are involved by this such as energy transduction, cell metabolism, cytoskeletal protein assembly, growth, aging, apoptosis and so on. These all pathway hampered by the transfer of a phosphoryl group induced by fluoride[17].

Neurotoxicity : Fluoride-induced neurotoxicity interest has grown significantly since the 2016 report of the National Toxicology Program (NTP) on Fluoride Toxicity that recommended the USEPA. It has been set a new drinking water standard that is approximately 0.03–1.5 ppm [30].

Thyroid gland : TSH is secreted from pituitary and the receptor of TSH belongs to the GPCR category. So, AlF4 mimicked to the TSH by switching its association with G protein. In the exposure of Fluoride, over production of cAMP is occurred, it leads to a feedback mechanism resulting desensitization of TSH receptor and reduce the activity of thyroid gland[25].

Liver : Being a very active site of metabolism, the liver is too much sensitive by fluoride toxicity. Fluoride make degenerative and inflammatory changes in the liver such as dilatations of sinusoids, hepatic hyperplasia, accumulation of amorphous and crystalline bodies in the hepatocytes around the hepatic vein. Fluoride-linked occurrence of a rare form of liver cancer (hepatocholangio-carcinoma) in mice has been reported[26].

Kidney : Kidney is the key route of excreting fluoride from the body. Fluoride activates the NFjB signalling pathway, increasing nitric oxide (NO) through inducible nitric oxide synthase (iNOS) and increasing prostaglandin E2 (PGE2) and enhancing the expression of mRNA of many inflammatory cytokines. Examples include cyclooxygenase-2 (COX-2), tumour necrosis factor-a (TNF-a), interleukin- 1b (IL-1b), interleukin-6 (IL-6), and interleukin- 8 (IL-8). Fluoride able to change the cellular entry, potential intracellular interactions, and conceivable mechanisms of causing fluoride toxicity in renal tubular epithelial cells[22].

Bones : Fluoride have been associated

with a weakening of bones and an increase in hip and wrist fractures. Consumption of fluoride at levels beyond those used in fluoridated water for a long period of time causes skeletal fluorosis. In some areas, particularly the Asian subcontinent, skeletal fluorosis is endemic. It is known to cause irritable-bowel symptoms and joint pain. Early stages are not clinically obvious, and may be misdiagnosed as (seronegative) rheumatoid arthritis or ankylosing spondylitis[15].

Phytoremediation :

Phytoremediation involves the use of green plants to decontaminate both organic and inorganic pollutants from soil, water and air[14]. A search for F hyper-accumulators is an important process for phytoremediation in F-endemic areas. Four important characteristics used in defining a plant as a hyperaccumulator are (i) translocation factor that is the ratio of contaminant concentration in plant shootto root, (ii) bioconcentration factor or bioaccumulation factor, that is the ratio of contaminant concentration in plant roots to soil, (iii) tolerance which is manifested by insignificant or no reduction in the shoot biomass of plants grown in contaminated sites[36], and (iv) enrichment factor meaning ratio of contaminant concentrationin plant shoot to soil[21]. *Camellia japonica*, *Pittosporum tobira*, and *Saccharum officinarum* are able to remove F from water efficiently. *S. officinarum* showed maximum capability of removing F which suggests an activation of the detoxification processes in its metabolism[9].

Phytoremediation is an augmenting technology that utilize plants to remove contaminants from the environment, it has several advantages than other remediation techniques[18]. The interest in phytoremediation has increased significantly with the identification of the plants which have ability to hyper-accumulate the metals in their tissues. Plants tolerant and resistant to F are good candidate for remediating F from water and soil as they have inherent molecular mechanism in their cellular machinery to reduce or retard toxic effects of F. In this regard, Saini *et al*.[27] investigated the F tolerance potential of *Prosopis juliflora*. Organ-wise accumulation of F, bioaccumulation factor, translocation factor, growth ratio and F tolerance index were examined for *P. juliflora* plants grown in F enriched soil. Plant accumulated high amounts of F in roots. The bioaccumulationand translocation factor values were found to be >1 which showedhigh accumulation efficiency and tolerance of *P. juliflora* towards F. Another study was done comparing two varieties of mulberry towards F sensitivity[20]. Mulberry variety, Kanva (M4) showed lesser inhibition in all of photosynthetic parameters like leaf area, chlorophyll-a and chlorophyll-b as compared to Mulberry variety (S54), reflecting tolerance nature of M4 variety.

Concentration of fluoride in many areas of the world, including Mexico, Kenya, India and Sri Lanka is rarely exceeding the level of 5 mg /L [8]. *S. officinarum* is a viable plant in these countries to remove fluoride in water[31].

Spirodela polyrrhiza is a potential aquatic plant which can able to intake fluoride from waste wate[27]. *Scirpus grossus* can reduce a considerable amount of fluoride (20–85%). It is also known for the biochar contained in the wetland that also adsorbs other competing ions as K+, Ca^2+, Mg^2+ by chemisorption[8].

In view of the present-day context of these heavy metal pollutants is increased day by day. It's very urgent to solve this problem but it is not so easy work, it need to think that selection and subsequent use of the fluoride resistant plants from the contaminated ecological niche which have the possible transform of the scenario of plant-assisted fluoride decontamination. Applying the knowledge of current research from interdisciplinary sciences, plant fluoride bioremediation will probably become more effective, profitable, socially acceptable and eco-friendly. By virtue of identifying the diverse groups of terrestrial and aquatic plants which have the ability to accumulate fluoride thousands of times more uptake than their origin, can be employed successfully for fluoride remediation. Phytoremediation of fluoride would be a safe, secure, and cost-effective method towards removing fluorides from soil and water.

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