



Fluoride Contamination for Water and Soil: Its Effective Treatment Approach

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Water shortage is identified as a chief crisis of the 21st century. It is calculated that in 2015 roughly 663 million public lack access to safe drinking water globally. Fluoride (F) is a foremost reason for the world water shortage, affecting nearly 200 million people on planet. It is observed that approximately 24 countries are severely affected by elevated F content in drinking water. High F concentration in different countries was reported due to the geographical belt of high F which extends from the Syrian Arab Republic through Egypt, Algeria and the Rift Valley. Another F belt stretches from Turkey through Iraq, Afghanistan, India, Thailand and China. Elevated F concentrations in soil were identified in Pakistan, China, Sri Lanka and India. Around 85 million tons of F deposits are found in the earth crust and out of it 12 million were reported in India. According to the available literature, 17 states of India were reported with high F concentration in water. The most critically affected states are Punjab, Haryana, Rajasthan, Gujarat and Uttar Pradesh.

After water, tea infusions are the most popular beverages consumed worldwide by communities. It is well-known that tea plants can accumulate F, for example, in 1930 it is reported that *Camellia sinensis* (tea plant) is a hyperaccumulator plant of F. F concentrations above permissible limit were reported in tea drinks of India.

F rich rocks are the main natural source of F contamination in water and soil. The common minerals which are rich in F are Fluorspar—CaF₂ (lime stones and sandstones), Cryolite—Na₃AlF₆ (granites) and Fluoro-apatite—Ca₃(PO₄)₂Ca (FCl₂). F is considered as beneficial to health up to a certain limit (0.5 to 1.5 mg L⁻¹) as it avoid the tooth decay and considered necessary for growth of the formation of dental enamels. After a certain level it (>1.5 mg L⁻¹) becomes a threat to human health, and can cause severe health problems. The rural population is more prone to F contamination as in some places, the available techniques are neither acquainted nor affordable. The fluorosis is reported more prevalent in rural population due to excess F contaminated water inevitably consumed by the rural population. F is known to cause mottled enamel, osteoporosis, crippling skeletal fluorosis, thyroid imbalance, growth retardation, kidney imbalance, types of morbidity and in severe cases leading to mortality. F also affects plants such as necrotic lesion, chlorosis, decrement in chlorophyll content, catalase activity and germination rate.

Several conventional methods have been reported for the removal of F from the soil such as electrokinetic systems, phytoremediation, excavation and landfill. In recent years, phytoremediation has been considered as effective and low cost technology for F removal from soil. Phytoremediation is the process of utilizing green plants for the remediation of diverse pollutants from soil. Several plants are considered suitable for phytoremediation which belong to families like Brassicaceae, Poaceae, Euphorbiaceae and Caryophyllaceae. To

conquer the problem, different F accumulating plants have been identified such as *Acacia tortilis*, *Cassia fistula*, *Diapensia lapponica*, *Shortia galacifolia* etc. But, *Prosopis juliflora* is considered most suitable as it can survive in wide range of soils such as sandy, saline, rocky and alkaline and its roots can penetrate to great depths as approximately 40 cm in 8 weeks. *P. juliflora* has higher biomass, long root system and also have higher ability to grow fast in nutrient poor soil as other hyperaccumulators. Thus, *P. juliflora* is a proved suitable hyperaccumulator plant for F remediation.

However, phytoremediation process has certain limitations: time consuming and lower biomass. For increasing the efficiency of hyperaccumulator plants various amendments has been used such as chelating agents and microbes (Plant Growth Promoting Rhizobacteria, PGPR). But further amendments are required in the phytoremediation process. However, the question arises is that how the F accumulation efficiency of the plant can be enhanced for the remediation of agricultural soils? Currently, the application of nanoparticles (NPs) in agriculture and pollutant remediation has increased, revealing the effective and greener approach. Moreover, NPs have also been used for remediation of several pollutants such as polychlorinated biphenyls (PCBs), chromium (Cr) and trichloroethylene (TCE) from soil. Recently, Fe₃O₄ NPs were also identified as potential iron fertilizers for *Arachis hypogaea* plant and showed increased root and shoot length. Thus, nanomaterials application can be explored for enhancing the phytoremediation efficiency of plants for F remediation. Both positive and negative effects of nanomaterials on different plants have been reported. Such as TiO₂ NPs increases the root and shoot length with the treatment of 60 mg Kg⁻¹ and decreases the root and shoot length above 60 mg Kg⁻¹ concentration in *Triticum aestivum*.

Several methods have been developed to efficiently remove F from water, including nanofiltration (NF), forward osmosis (FO), reverse osmosis (RO), coagulation, electrocoagulation, electrochemical oxidation, ion exchange and adsorption. Among the reported techniques, adsorption is considered more advantageous for the rural population as it is inexpensive, rapid, easy to operate and highly efficient. Different conventional adsorbents were identified but nanomaterials proved extremely capable for F remediation due to their high surface-to-volume ratio.

Nanoparticles (NPs) are mentioned as particles of 1 nm to 100 nm size. Nanotechnology offer information about development of nanomaterials and their exceptional properties with utilization in different sectors such as environmental, pharmacology and medicine. For the synthesis of nanomaterials, green chemistry route proved beneficial as compared to the chemical methods in term of its cost-effectiveness, environment-friendly and scalable properties. The main advantage of using plants for the synthesis of NPs is that they are easily available and non toxic, have a broad variety of metabolites that are used for reduction of metal ions. The mechanism for the metal NPs synthesis is plant-assisted reduction due to phytochemicals. The various phytochemicals responsible for reduction are terpenoids, amides, flavones, aldehydes, ketones and carboxylic acids.

However, one more challenge the scientists are facing is the separation of NPs from solution after adsorption as NPs suspension form fine colloids in aqueous solution. For solving the reported problem, researchers have utilized nanomaterials impregnated on support matrices. Various experiments have been conducted using nanomaterials support matrices such as poly (acrylic acid) (PAA), polyurethane (PU) and poly (vinyl alcohol) (PVA). Recently, polyurethane foams (PUF) has been widely utilized and found promising in various water filtration systems because of its outstanding features of high-temperature resistance, UV resistance, enhanced mechanical property, abrasion resistance, easy availability and low cost. The impregnation of nanomaterials on the matrices can be accomplished through a variety of methods, such as surface nucleation, blending and dip coating. Dip coating method is proved to be more applicable for impregnation because of the cost-effective and easy

handling. However, the adsorption capacity of material available is relatively low, expensive, uneasy and unsuitable for rural areas.

High F content in water and soil is directly responsible for enhanced F concentrations in plants which affect its growth and productivity; it also acts as a secondary source for F to humans. Therefore, F concentration in plants depends on the water and soil content, thus its detection is an essential requirement. Initial analytical methods developed for F ions detection such as ion selective electrodes, ion monitoring probes, confocal microscopy and ion chromatography are all expensive, time consuming, requires large sample size, skilled labor and are non-portable. Thus, it is required to develop cost-effective, sensitive, user-friendly, and portable colorimetric naked eye detector for F ions detection in soil and plant samples. With the advancement in nanotechnology, the solution may be clearer thanks to the colorimetric technique that utilizes the unique carbon quantum dots (CQDs) for the F sensing. CQDs are carbon NPs with sizes below 10 nm which have outstanding properties such as size and wavelength dependent photoluminescence, resistance to photobleaching and ease of bioconjugation. The researchers have used CQDs and developed an optical probe for assay of biothiols using the prepared NPs. Thus, CQDs can be utilized for the development of colorimetric detector for F sensing.