

Phytoremediation of soil co-contaminated with copper, cadmium and organochlorine pesticides

SUMMARY of THESIS

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Executive Summary

Today, contamination of soil with heavy metal and pesticides is becoming most serious concern. Soils/lands are important target sink for number of contaminants that vary in their composition, concentration and toxicity. Contaminants including metals and pesticide entering the soil system as consequences of various anthropogenic deeds such as faulty waste management practices, improper landfill operations, mining and application of sewage sludge etc. pose a massive threat to human health and natural ecosystem. Contamination of agricultural land not only worsens the soil health but also affects the food quality, production and environmental safety. Due to ubiquitous soil contamination and its associated concerns, finding an innovative and ecofriendly way to clean metal and pesticide pollutant has now become a priority in remediation field.

Phytoremediation has been recognized as an economical technique that explores the potential of plant to accumulate, degrade, immobilize, metabolize or detoxify inorganic and organic contaminants. Till date, there are several promising results indicating that this solar driven botanical remediation might become sustainable alternative to other mechanical chemical approaches for remediation of mildly contaminated soil. Several phytoremediation studies have been conducted by using edible crops such as wheat (*Triticum aestivum* L), tomato (*Solanum lycopersicum*), spinach (*Spinacia oleracea* L), radish (*Raphanus sativus*), potato (*Solanum tuberosum* L) Brassica (*Brassica juncea*) etc. for the removal of various organic and inorganic contaminant, particularly heavy metals. However, the use of edible crops is not safe, because they are consumed by animals and human beings and may cause toxicity on

single or chronic exposure. A good phytoremediator plant should be perennial, unpalatable, have high biomass productivity, and tolerance to biotic & abiotic stresses.

The present work was undertaken to conduct a comparative study of phytoremediation potential of *A. paniculata* with a relatively studied plant *V. zizanioides*. The study was conducted to investigate the physiological and biochemical responses of *A. paniculata* and *V. zizanioides* growing under different concentration of Cu, Cd and organochlorine pesticides. The study was made to investigate the individual and collective phytoremediation potential of *A. paniculata* and *V. zizanioides*, Further, uptake, accumulation and partitioning of Cu, Cd, and organochlorine pesticide in *A. paniculata* and *V. zizanioides* have also been examined. Simultaneously, an effort was made to examine the microbial activity and fertility of rhizospheric soil treated with different concentration of Cu, Cd, and organochlorine pesticides in presence of selected plant species. Moreover, to optimize the associated sustainable and cost-benefit aspect, many researchers have advocated the strategy of combining phytoremediation with energy crops. However, intensive research is still required in this area for better and economically sustainable application. In harmony to this approach, the present study also explored the use of biomass generated after phytoremediation of Cu for the removal of fluoride from contaminated water; a chronic problem in developing countries. Although, low level of fluoride in water is considered as a nutrient because it is essential for bone and teeth development. However, when its concentration exceeds above the permissible level it becomes toxic and leads to fluorosis.

Studies on physiological and biochemical responses of *A. paniculata* and *V. zizanioides* exposed to different concentration of Cu, Cd, and organochlorine pesticides

The objective of this study was to study of physiological and biochemical response of *A. paniculata* and *V. zizanioides* exposed to different concentration of Cu, Cd, and pesticides. During the study, seed germination, biomass production, chlorophyll content, change in level of protein and lipid peroxidation and anti-oxidative enzymes (catalase and peroxidase) has been examined. Seed germination of *A. paniculata* was found to be decreased on increasing the concentration of Cu and Cd. However, at lower concentration of Cu and Cd, the value of seed germination percentage was nearly similar to control. The rate of biomass production of roots and shoots of *A. paniculata* and *V. zizanioides* was decreased significantly on increasing the concentration of contaminants in growing medium. Further, decline in seed germination and biomass production was observed maximum in case of co-contaminated (i.e. Cd+Cu and Cd+Cu+P). It was observed that the chlorophyll content in the leaves of *A. paniculata* and *V. zizanioides* was declined simultaneously on increasing the degree of contamination. However, compared to Cd and Cu, the reduction percentage was high in case of organochlorine pesticides contamination indicating that pesticides are relatively more phytotoxic.

The effect of Cu, Cd and organochlorine pesticides on protein and malondialdehyde (MDA) content in fresh leaves were investigated and it was found that the protein content decreased with increase in Cu, Cd and organochlorine pesticide concentration in soil, whereas, MDA was found to be increased in both the species. The reduction in protein content was observed on increasing the concentration of contaminants which indicates the exposure of high level of Cu, Cd and organochlorine contamination had toxic effect on *A. paniculata* and *V. zizanioides*. However, reduction in protein content in *V. zizanioides* is comparatively lower than the *A. paniculata* indicating its higher tolerance as compare to *A. paniculata*. The degree of negative effect was directly correlated with contamination

level and exposure. The level of MDA content was found higher in *V. zizanioides* than *A. paniculata* which indicates more lipid peroxidation in the leaves of *V. zizanioides* as compared to *A. paniculata*. As the degree of contamination increased the generation of superoxide radical also increased that has caused increased lipid peroxidation (MDA production) and oxidative damages. In order to diminish the oxidative stress the level of anti-oxidative enzymes (peroxidase and catalase) content increased simultaneously. The peroxidase (POD) and catalase (CAT) activity was found to be increased on increasing the level of Cu, Cd and organochlorine pesticides.

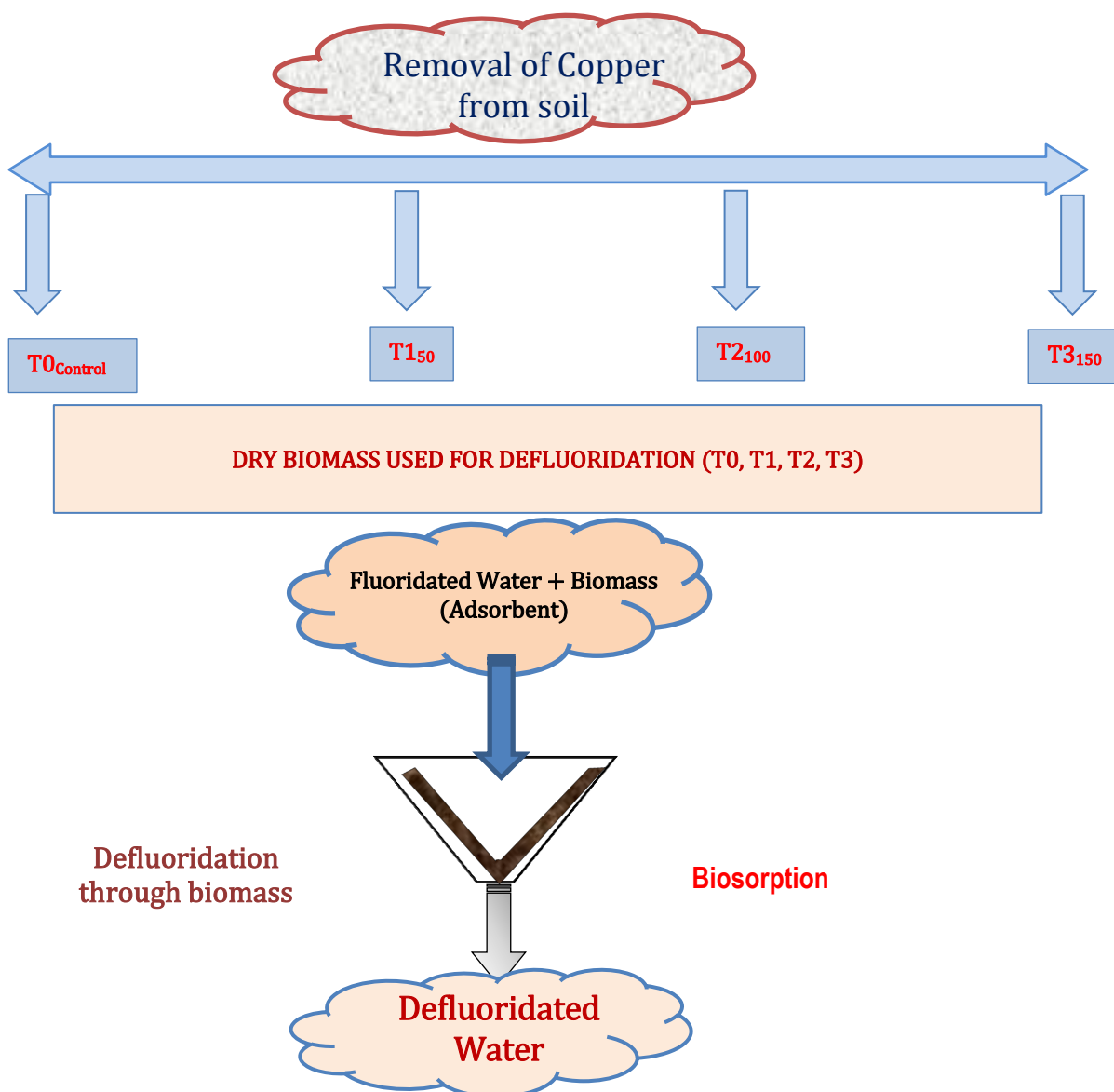
Studies on individual and collective phytoremediation potential of *A. paniculata* and *V. zizanioides* to remediate Cu, Cd, and organochlorine pesticides

It was observed that the accumulation of Cu and Cd increased significantly on increasing the level of contamination and exposure time ($p > 0.005$). Both the plants have accumulated significant amount of metal in their root and shoots. While accumulation of organochlorine was observed only in root and shoot of *V. zizanioides* as *A. paniculata* plants were not survived in organochlorine pesticide contaminated soil (except in combination with *V. zizanioides* at lowest concentration i.e. P1). Further, the accumulation of Cd and Cu was higher in roots of both the plants than shoots. The level of accumulation of Cu in shoot of *A. paniculata* was higher than the shoot of *V. zizanioides*. However, the accumulation of Cd and Cu in root of *V. zizanioides* was many folds higher than that of *A. paniculata* roots. In case of collective phytoremediation i.e. when both the plants were grown in same pot, the accumulation of metal in their individual roots and shoots were lower than the plants grown individually. However, if we collectively sum-up the metal accumulation by *A. paniculata* and *V. zizanioides* growing in same pot was found to be higher than the individual accumulation in *A. paniculata* or *V. zizanioides* grown in separate pots.



(a) *A. paniculata*

(b) *V. zizanioides*



Graphical abstract for the study

Studies on uptake, accumulation and partitioning of Cu, Cd, and organochlorine pesticides in selected plant species

Uptake and accumulation of Cu, Cd in both the plants and Organochlorine pesticides (OCPs) in *V. zizanioides* varied significantly at different level of treatments and exposure time. As the level of contaminants in growing medium increases the level of accumulation also increased significantly. Although, *A. paniculata* had accumulated significant amount of Cd and Cu in their tissues however, uptake of Cd and Cu in *V. zizanioides* was many fold higher than *A. paniculata*. Translocation factors (TF) of metal for both the plants were lower than 1 indicating the accumulation of metal in shoots (per gram of dry weight) was lower than root. TF for metal in *V. zizanioides* was very low, which indicates that the metals were mainly concentrated in root tissue. The total metal accumulation in shoot and root may vary because of the higher biomass of shoots compared to roots. TF for Cu in *A. paniculata* and *V. zizanioides* was higher than Cd indicating that the translocation of Cu in shoot was higher than Cd. However, TF for OCPs in *V. zizanioides* was observed higher than metals indicating that the translocation of OCPs in above ground parts was higher than the Cd and Cu.

Studies on microbial activities and fertility of rhizospheric soil treated with different concentration of Cu, Cd, and pesticides in presence of selected plant species

Microbiological load/ Colony forming unit (cfu) and dehydrogenase activity were found to be decreased significantly on increasing the concentration of metal and OCPs. However, at high level of contamination the values are approximately same because only resistant bacteria can survive at high level of contamination. High concentration of metals in soil caused reduction of microbial activity that affects the

microbial population and diversity as well. Microbiological population and dehydrogenase activity of soil of both the plants are correlated with each other and reduced simultaneously with the treatment after 30, 60 and 90 days.

Fertility of soil treated with different concentration of Cu, Cd and OCPs were analyzed by measuring the NPK and organic carbon content. The balance level and ratio of NPK in soil is considered as beneficial for plant growth and development. It was observed that the level of organic carbon (%) and available NPK in soil were decreased significantly on increasing the concentration of Cu, Cd and OCPs. However, the decline of NPK and OC content was higher in case of Cd contamination than Cu. Further, the *V. zizanioides* planted soil have higher NPK and OC content than the *A. paniculata* planted soil probably because *V. zizanioides* have well developed massive root system and higher microbial root activity which helps to maintain the NPK and OC level in soil. At high concentration of contaminant, the microbial activity was declined and simultaneously the level of NPK and OC was also reduced. Thus the presence of microbial activity could be a possible reason for the soil fertility.

Application of copper phyto remediated plant biomass for the defluoridation of water

Several batch experiments were executed to study the feasibility of defluoridation of water using *A. paniculata* and *V. zizanioides* leaves as biosorbent under different conditions and found that the adsorption capacities of both biosorbent found to be influenced by contact time, pH, initial fluoride concentration and adsorbent dose. It was found that the removal efficiency of fluoride was increased on increasing the contact time, initial F concentration, adsorbent dose and decreasing pH. The fluoride removal efficiency of *A. paniculata* was found to be higher than the *V.*

zizanioides. Further the Q_{\max} (maximum adsorption capacity) obtained from langmuir isotherm model for *A. paniculata* ($Q_{\max}= 3.8\text{mg/g}$) was higher than *V. zizanioides* ($Q_{\max}= 2.32 \text{ mg/g}$) incating that the adsorption capacity of *A. paniculata* was higher than *V. zizanioides*. Furthermore, the R_L value and Freundlich constant (n) is greater than 1 which confirms the favorable adsorption process.

From the above study, we can conclude that the *V. zizanioides* have high tolerance and potential for the remediation of Cu, Cd and OCPs and can be considered as a suitable candidate for phytoextraction. Likewise, *A. paniculata* can be considered as a moderate phytoremediator of Cu and Cd. However, its high adsorption capacity for fluoride makes it a good biosorbent for defluoridation of water.