Environmental Remediation Technologies, Regulations and Safety

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AN OVERVIEW AND FUTURE PROSPECT

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PREFACE

Phytoremediation which involves the use of plants and rhizospheric organisms for the removal of pollutants is an emerging technology for the clean up of contaminated sites. The removal of textile dyes mediated by plants has been one of the most neglected areas of phytoremediation research. Dyes, which are primary constituents of the wastes from textile industry effluents, constitute a group of recalcitrant compounds, many of which are known to have toxic and carcinogenic effects. Hence, the review focuses on the studies of the mechanisms adopted by plants in the removal of textile dyes and the future scope for research in this area which will help in broadening the horizons of phytoremediation technologies. Plant species many a times referred to as 'green livers', are known to possess a wide range of detoxifying and biotransforming enzymes some of which may also be secreted extracellularly in the rhizosphere and can bring about the transformation of organic pollutants such as textile dyes. The use of *in vitro* plants for phytoremediation studies can help to explore the enzymatic status and the products of metabolism of the dye, thus providing a new dimension to phytoremediation studies. The use of transgenic plants with microbial genes can combine the advantages of both plant and microbial systems for enhanced dye degradation. Biotechnological approaches involving the development of hairy roots and suspension cultures may find good utility in phytoremediation studies. The ultimate aim of phytoremediation involves applying these well studied plant systems at the contaminated sites which may constitute the development of constructed wetlands for on-site treatment of industrial effluents.

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Chapter 1

INTRODUCTION

Since pre historic times innumerable uses of plants as sources of food, shelter, fuel etc., have been known to mankind. But, the newer approach of phytoremediation which involves the use of plant systems and/or rhizospheric organisms to remove content, inactivate or degrade harmful environmental contaminants and to revitalize contaminated sites (Vangronsveld et al, 2009), is an upcoming research area in the field of environmental biotechnology. Conventional techniques for bioremediation that involve the digging up of contaminated soils and disposal of the wastes to a landfill, lead to contamination elsewhere and can create significant risks in excavation, handling and transport of hazardous materials (Vidali, 2001). The chemical treatment methods used have multiple disadvantages such as their high cost, coupled with the formation of a large amount of sludge and the emission of toxic substances (Senan and Abraham, 2004), because of which bioremediation methodologies can be used as alternative technologies for the removal of industrial wastes. Microbial bioremediation processes for the removal of hazardous compounds, have received quite a lot of focus from researchers all over the world because of the high potentiality of prokaryotic systems to perform a variety of functions. But, the use of phytoremediation processes for the removal toxicants (especially textile dyes) is comparatively an unexplored methodology since the fact that plants also possess some inherent metabolic pathways that can breakdown a wide range of toxicants (Chaudhry et al, 2005) was much less realized. Since researchers have now begun to realize the potential of plant systems as effective remediating agents, this new area of phytoremediation has started gaining importance from academicia and industry (Cluis, 2004). Since plants are autotrophic systems of large biomass and require little nutrient input, phytoremediation technologies are easier to manage than microbial bioremediation systems and offer cost effective and aesthetically appealing options for environmental clean up (Cluis, 2004). Afforestation is one of the prescribed ways for minimizing the green house gases in the environment and reducing the effects of global warming since, plants have been known for their consumption of CO_2 and more recently of other gaseous industrial by products. Therefore, the value of plants to counterbalance the hazards of industrialization processes is being appreciated (Cumnningham and Ow, 1996). Phytoremediation can thus serve dual purposes.

The release of large amount of toxic wastes into water bodies is one of the consequences of increasing urbanization and industrialization in the modern world. A variety of organic (pesticides, explosives such as TNT, petrochemicals, chlorinated solvents, etc.) and inorganic (radionuclides, heavy metals such as mercury, lead, etc.) wastes which have toxic effects on the ecosystem have been contaminating our natural resources (Cluis, 2004). Out of the different types of pollutants released, dyes which are released by textile, dyestuff and dyeing industries constitute one recalcitrant group and are known to have carcinogenic and mutagenic effects with a potential toxicity to all life forms (Bafana et al, 2009). Most of the research involving phytoremediation technologies has been focused on the removal of heavy metals and a few organic compounds such as pesticides, polycyclic aromatic hydrocarbons etc. from the environment. The removal of textile dyes mediated by plant systems is still a much unexplored area of phytoremediation research. Hence, the article aims at reviewing the basic research and mechanisms involving the removal of dyes by plants and the application of these technologies at the dye contaminated sites with an insight into the future perspectives of research in this area.

Chapter 2

DYES-TOXICITY AND NEED FOR PHYTOREMEDIATION

Dyes are known to have complex structures that are difficult to degrade (Nilratnisakorn et al, 2007). With the advancement of technologies, enhancement has been made in dye properties so that they provide resistance to fading, provide improved delivery to fabrics and have increased variety of shades. These additional properties make them highly resistant to environmental degradation, thus increasing pollution (Togo et al, 2008). Sulfonated anthraquinones are generally the parent compounds for a vast array of dyes and thus the waste waters of textile industries are likely to contain these compounds which are recalcitrant and toxic (Page and Schwitzguébel, 2009). The difference in the chromophoric groups of dyes facilitates their classification into different types such as azo, triphenylmethane, anthraquinone, indophenol, diazonium, quinone dyes etc. Moreover, the nature of substituents attached to the basic aromatic ring structure also differs because of which they are not uniformly susceptible to bioremediation (Aubert and Schwitzguébel, 2004). In case of sulfonated dyes, the organosulfonate group plays an important role in altering the solubility and dispersion properties of the xenobiotic molecule and increases its recalcitrance to environmental breakdown, because of the thermodynamically stable carbon-sulfur bond (Duc et al, 1999). The mechanisms for the carcinogenicity of azo dyes that have been identified include metabolic activation to reactive electrophilic intermediates that covalently bind to DNA. Triphenylmethane dyes are known to cause reproductive abnormalities in rabbits and fish (Chen et al, 2010). Sometimes the products formed after the processing of these dyes themselves are toxic. In the environment, azo bonds of these dyes are reduced to liberate benzidine and other aromatic amines, which may cause adverse systemic health effects or cancer. Urinary bladder cancer is the most common form of cancer caused by exposure to benzidine. Stomach, kidneys, brain, mouth, esophagus, liver, and gall bladder might also be targets (Bafana et al, 2009). Toxicity of reactive dyes has been reported at concentrations as low as 5.2 mg/l (Nilratnisakorn et al, 2007). Hence, it is extremely important to implement technologies that completely remove such recalcitrant compounds from the environment or biotransform them into products that have reduced toxicity. Hence, for the targeted removal of such hazardous wastes from industrial effluents, plants can be used as efficient systems.

Chapter 3

SELECTION OF PLANT SYSTEMS FOR REMEDIATION OF TEXTILE DYES

For the removal of textile dyes from the environment, the selection of an appropriate plant with certain desirable characteristics is one of the most important preliminary steps in phytoremediation research. Though several plants have shown the ability to remediate contaminated soils; non edible plants are generally selected to be applied onto dye contaminated sites. Most of the studies on phytoremediation of textile dyes demonstrate their removal through either degradation of the dye or the adsorption and/or accumulation of the dye. Accumulation of organic compounds such as sulfonoaromatics has been shown in Rhubarb species (Duc et al, 1999). Compounds accumulated in the plant roots could be further translocated to shoots and leaves. To prevent the accumulated dye compounds or their metabolites from entering the food chain, the use of non edible plants is always preferred. Different types of grasses, ferns, weeds or agricultural wastes have been suggested and tested for the removal of dyes. *Phragmites* species have shown immense potential to remediate textile waste waters. *Phragmites australis,* a reed which is a component of the wetland community has been extensively studied for remediation of textile effluents and mainly with respect to the removal of the dye, Acid Orange 7 (Carias et al, 2007). Many native populations of *Phragmites autralis* are benign in that they pose little or no threat to other species. Among 10 different species of macrophytes screened, *Phragmites karka* was found to have broad amplitude of pH tolerance and was found to be growing well in alkaline, neutral and acidic textile wastewaters resulting in considerable shoot density and biomass to achieve maximum translocation of water and assimilation of nutrients. This makes the plants highly suitable for the treatment of textile waste waters that may be contaminated with different types of acidic as well as basic dyes. The good growth of underground organs in these species thereby provides maximum surface area to assimilate pollutants (Sharma et al, 2005). In addition, the plant should be fast growing and should have a deep rooted system that enables it to reach the pollutants easily. Larger biomass and surface area of the plant system can facilitate more efficient removal of the dye. Kagalkar et al have demonstrated that increase in plant biomass in terms of increasing number of plants used, gave higher % decolorization values. Reports have shown the efficient degradation of the dye Direct Red 5B (DR5B) with *Blumea malcolmii,* a deep rooted and fast growing plant system that forms sufficiently large biomass and can grow in soils with little nutrient availabilities (Kagalkar et al, 2009). Thus, a plant that has the ability to remove dye molecules from the environment and also have a good biomass can prove to be potent for phytoremediation. The plant *Typhonium flagelliforme* which has recently been reported for degradation of the dye Brilliant Blue R, exhibits dye degradation capacity when used even in distilled water, devoid of any other nutrients. The use of such plants can help to reduce the overall cost of the experiments (Kagalkar et al, 2010). Not all plants will be able to demonstrate similar responses or have similar removal rate for all dyes. In addition, for the phytotreatment of textile dyes, additional perspectives that should be kept in mind while selecting the plant species include high uptake rate of the pollutant, high translocation factor (TF) in case of phytoextraction, presenting the ability to translocate contaminants to the shoot and high tolerance level towards the dye (Zabłudowska et al, 2009). Hence, extensive screening of different plant species can help us to understand the selective abilities of a particular plant to remove a dye or a group of dyes. Moreover, textile effluents are generally mixtures of different dyes because of which plants that can be potent phytoremediators of textile industry wastes will be the ones that will be able to demonstrate the capacity to remove a large number and a diverse group of textile dyes eg., the species *B. malcolmii* showed the capacity to decolorize five different dyes, namely Direct Red 5B, Reactive Red 2, Methyl Orange, Malachite Green and Golden Yellow HER to varying extents (Kagalkar et al, 2009). *Typhonium* plantlets that have been studied for their phytoremediation potentialities, showed the additional advantage of remediating textile effluents and synthetic mixture of dyes along with 8 individual dyes, out of which maximum decolorization was obtained for the dye Brilliant Blue R (BBR) which was about 80%. To quantitate the % removal of color from dye effluents or synthetic dye mixtures, American Dye Manufacturers' Institute (ADMI 3WL) tristimulus filter method is used. The % removal of ADMI in case of mixture of dyes was 47% while in case of textile effluents was found to be 28% (Kagalkar et al, 2010). Many edible plants have been known to possess dye decolorizing abilities because of the rich enzymatic status of these plants. Though such plants are unsuitable for field applications, their enzymes can be extracted and used for degradation of various textile dyes. The species of *Sorghum vulgare*, *Phaseolous mungo* and *Brassica juncea* have shown the potential to decolorize the dye Reactive Red 2 and have also demonstrated to possess abilities to decolorize and detoxify textile effluents (Ghodake et al, 2009). Even though different plants are capable of degrading the same dye molecule, the products formed after degradation are likely to be different indicating that the pattern of transformation of the xenobiotic molecule is dependent upon the plant species (Page and Schwitzguébel, 2009). Plants that degrade the dye molecules into non toxic products are preferable for phytoremediation. Hence, the selection of the plant will depend upon the genetic make up of the plant that manifests in terms of varied enzyme activities in the plant and differential absorptive capacities resulting into variable patterns for the removal of dyes. Moreover, all the plants selected should be in the same stage of growth and should have almost equivalent dry weights and should have almost similar root and shoot lengths (Kagalkar et al, 2009) that can help to achieve reproducibility of results. Further, the plants selected should preferably be from the same area since factors such as age of the plant, soil conditions, nutrient status, light availability etc are factors that can affect the removal of the dye. In addition, the use of flowering plants for the removal of textile dyes would offer aesthetically appealing systems and will serve dual purposes of bioremediation and will also allow the flowers to be used for decorative purposes, thus serving economic benefits.

Chapter 4

PLANT MECHANISMS FOR THE REMOVAL OF DYES

A) MECHANISMS INVOLVING ADSORPTION AND/OR ACCUMULATION OF TEXTILE DYES

Plant mechanisms behind the removal of textile dyes, which are a group of organic pollutants, may be diverse. Though phytodegradation or phytotransformation are the most predominantly observed mechanisms adopted by plants for the degradation of organic compounds, the removal of textile dyes by plants also utilizes the mechanisms of adsorption and accumulation on plant surfaces. It has been established that the binding of xenobiotics to roots occurs by adsorption followed by its absorption into the plants (Davies at al, 2005). *Posidonia oceanica* leaf sheaths have shown effective adsorptive removal of the textile dye, Reactive Red 228. Moreover, the authors also demonstrated changes in the adsorptive capacities with changes in factors such as temperature and pH. Increase in temperature favored the better adsorptive removal of the dye which was probably because of the greater movement of the adsorbent material. Besides, the highest dye removal efficiency was found at pH 5 which might correspond to the rate of dissociation of the studied dye with maximum ionization of the molecule. The use of orange peels, banana peels, neem leafs, peanut hulls and agricultural wastes have also been suggested for the removal of various dyes (Ncibi et al, 2007). Untreated pulverized plant leaves of *Salsola vermiculata* revealed interesting adsorptive properties for Methylene Blue and iodine from aqueous solutions. Further, the activation of these plant leaves by treatment with zinc chloride gave better adsorptive properties. In this plant too, the effect of pH on the adsorption capacity of the chemically activated plant was investigated which showed a decrease in the adsorption capacity at lower pH values which may be because of the competition of protons with the dye molecules for available adsorption sites. The iodine number value which determines the capacity of the adsorbent to remove color from the solution, evaluated in terms of adsorption of iodine from the adsorbent pointed out that significant additional surface area can be achieved through zinc chloride activation and that microporosity contributes considerably to the total surface area of the prepared material making it a very good adsorbent for small compounds (Bestani et al, 2008). Thus, the inherent adsorptive capacity of the plant material can be enhanced through such activation techniques. The significant adsorption of Methylene Blue by this plant shows its potentiality in the remediation of textile dyes and effluents. Adsorptive removal of the dye Malachite Green by the roots of *Blumea malcolmii* was also reported where the % adsorption of the dye by the plant was approximately 45% (Kagalkar et al, 2009). The adsorption of a number of dyes was reported on the roots of *Typhonium flagelliforme* plantlets that were used for dye degradation experiments (Kagalkar et al, 2010). Phytoremediation processes not only involve the adsorption of the dye on the root or shoot systems of the plant but also involve the accumulation of dyes into plant tissues. Narrow-leaved Cattails (*Typha angustifolia* Linn.) that has the capacity to absorb a large amount of nutrients, has been demonstrated for the removal of the commercial diazo reactive dye, Reactive Red 141. The plant demonstrates the ability of 60% removal of the dye. After 28 days of exposure of the plant to synthetic reactive waste water containing the dye, the intercellular space of the plant showed the presence of the dye which was confirmed with transmission electron microscopy connected with electron dispersive X ray spectroscopy (TEM-EDX). Moreover, the plant also shows the precipitation of metal complexes with the dye which according to the authors are probably mechanisms to avoid damage to the plant (Nilratnisakorn et al, 2007). Rhubarb (*Rheum rabarbarum*) species have shown to accumulate synthetic anthraquinones which are starting materials for the production of a large number of synthetic dyes. The transpiration stream concentration factor (TSCF) was determined to detect the concentration of the accumulated compound in the xylem sap of these plants (Aubert and Schwitzguébel, 2004). When this value exceeds unity, the movement of the compound is faster than water. Among the different sulfonated anthraquinones the TSCF value obtained for anthraquinone-1-sulfonic acid was 2.5 which helped the authors to conclude that the movement of the pollutant was faster than water.