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REVIEW ARTICLE

Phytoremediation: Potential flora for synthetic dyestuff metabolism

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Abstract Dumping of dye-laden effluents into different environmental compartments adversely affects equilibrium and integrity of ecological systems. Being genotoxic, mutagenic and carcinogenic these dyes are quite damaging to health of biota (either aquatic or terrestrial). Many of these dyes are resistant to degradation and remediation under natural conditions and through conventional treatment methods. This situation has necessitated the development of effective and efficient wastewater treatment strategies without further stressing the environment and endangering other life forms. To date many biological systems including microorganisms and plants have been assessed for metabolism of dyestuffs. Phytoremediation catalyzed by natural solar driven pumps (green plants) and their associated metabolic processes has emerged as a comparatively new approach and has proven to be one of the most effective environmental friendly strategies for removal, detoxification and decolorization of dyes. Hence, this review quotes the literature of applied aspects of various plant species and their inherent metabolic as well as extractive potentials which enable them to effectively deal with various coloring agents.

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Contents

1. Introduction

Since antiquity humans are interfering and interacting with natural environment for their survival and well-being. The nature and extent of these interactions and interferences in natural processes have a profound impact on the environment and in turn on the human well-being as well. Water, for instance, is one of the essential natural resources for sustenance of life. About 97% of water covers the planet earth as sea water, which is unusable for drinking purposes because of elevated concentrations of salt while remaining 3% is found as freshwater, most of which (79%) is locked up in the form of glaciers and polar ice caps, only 21% of freshwater reserves is available as groundwater (20%) or accessible surface water (1%) for human use. However, with the passage of time, these existing freshwater resources are becoming contaminated and subsequently scarce due to anthropogenic and industrial activities (Research priorities for earth science and public health, 2007; Reddy and Lee, 2012). Moreover, exponentially growing population and progressing industrialization are putting more demands on these dwindling water reserves, thus making it unavailable in various parts of the world, for example, it has been reported that approximately 80% of population is facing water security threats all over the globe (Schwarzenbach et al., 2006; Vörösmarty et al., 2010).

Among anthropogenic and industrial activities, dumping of dye containing effluents originating from various industrial operations (such as dyestuff manufacturing units and dyeing processes) into water pools and surrounding industrial areas is of major concern (Moosvi et al., 2005; Abo-Farah, 2010; Mugdha and Usha, 2012). Application of dyes in a variety of industrial processes including paint and pigment manufacturing, pulp and paper processing, leather tanning, textile dyeing etc. results in the generation of highly colored wastewater (with considerably different volume and effluent composition containing a variety of synthetic dyes) where subsequent dumping of such dye containing effluents into water pools adversely affects ground and surface water resources, and soil properties as well (Sen and Demirer, 2003; Moosvi et al., 2005; Sandhaya et al., 2005; Abo-Farah, 2010). Hence these circumstances have necessitated the development of effective and efficient water treatment strategies for recycling and replenishment of these valuable water resources (Mugdha and Usha, 2012). This article attempts to reconnoiter and evaluate the potential applicability of phytoremediation techniques for decolorization and/or degradation of color rich effluents as an economic, feasible and publically acceptable alternative in comparison to conventional techniques.

2. Dyes and their classification

Complex aromatic compounds that are utilized for coloration of various substrates like fabrics, papers, leather etc. are termed as dyes. Natural dyes, extracted from plant or animal sources, are used in the coloring of food stuff, leather and natural protein fibers such as silk, cotton and wool. However, the provision of narrow or dull range of colors along with exhibition of low color fastness on exposure to washing and sunlight has limited their applicability (Maddhinni et al., 2006; Samanta and Agarwal, 2009; da-Silva et al., 2010). Conversely, aromatic compounds produced via chemical synthesis, termed as synthetic dyes, provide a wide range of colors that are colorfast and bright as well (Kant, 2012). These dyes contain aromatic rings in their chemical structure that in turn hold delocalized electrons along with different functional groups attached to them. The auxochrome groups (as electron donors) are responsible for dyeing capacity while chromogene chromophore (as electron acceptors) imparts color to these dyes. The major chromophoric groups include $-C{=}C-$, $-C{=}O$, $-C{=}N-$, $-NO_2$, $-N{=}N-$ and quinonoid rings while auxochromic groups include $-COOH$, $-OH$, $-SO_3H$, and $-NH_2$ etc. (Carmen and Daniela, 2012; Singh et al., 2012).

Dyes are broadly classified on the basis of (i) chromophoric groups in their chemical structures as azo dyes, anthraquinone dyes and phthalocyanine dyes etc. and (ii) their usage or application method as disperse dyes for polyester and reactive dyes for cotton (Hunger, 2003; Singh et al., 2012), whereas based on their dissociation in aqueous solution dyes can be acidic, basic (cationic), direct reactive (anionic) and disperse/nonionic dyes (Campos et al., 2001). Among all these classes, azo aromatic ones are most pervasive in industry all over the globe (Zille et al., 2005).

3. Origin and disposal of dyestuffs into different substrates

Studies elucidate that majority of industries preferably utilize synthetic dyes for coloring different materials in contrast to natural dyes due to higher efficiency, wide range of colors, bright color imparting properties, stability and resistance against fading as well as washing (You et al., 2010; da-Silva et al., 2010). According to McMullan et al. (2001) and Selvam et al. (2003) commercially available synthetic dyes comprise a fraction of greater than 100,000 of currently known dyes and approximately one million tons of these dyes have been estimated to be produced on annual basis at the international level. Azo dyes are among the most commonly used group of synthetic dyes and account for more than half of annual production. A number of research studies showed utilization of more than 2000 azo dyes by majority of industries for dyeing of food, leather, textiles, pharmaceuticals, cosmetics and plastics etc. (Stolz, 2001; Zille et al., 2004; Adedayo et al., 2004; Kim et al., 2004; Tantak and Chaudhari, 2006; Joshi et al., 2008; Lim et al., 2011). Hence from all these it can be concluded that azo dyes are the major constituents of effluents discharged from various industrial sectors.

During the process of dyeing, large proportions of these dyes remain unbound or unfixed and therefore end up as effluents in sewage water or natural environment (Stolz, 2001; Manu and Chaudhari, 2003). It has been estimated that 10–15% of azo dyes are released as pollutants into the environment during textile dyeing (Stolz, 2001; Chen, 2002) whereas reactive dye losses of up to 50% have been reported by Chen (2002) and Zille et al. (2004) in wash rivulets after application of coloring agents in various dyeing operations.

4. Need for remediation of dyestuffs from contaminated substrates

Hence the dissemination of these dyestuffs has led to severe contamination of water bodies such as rivers, streams, groundwater etc. and surrounding areas especially soils where a cluster of dyeing industries is more concentrated (Stolz, 2001). Dye based effluents and/or wastewater usually have higher concentrations of suspended solids while the presence of dyes in water bodies along with posing turbidity problems also causes an increase in BOD and COD levels. Moreover, chromophoric groups of dyes strongly absorb sunlight thereby inhibit the photosynthetic activity of phytoplanktons including aquatic plants and algal species by preventing light penetration (Abo-Farah, 2010; da-Silva et al., 2010; Kagalkar et al., 2010). Thus, apart from destroying natural quality of water bodies, these dyes also threaten aquatic biota such as flora and fauna by disturbing the ecological balance and posing serious environmental concerns, hence need to be treated or removed prior to their disposal or dispersal into water bodies or surrounding environment (Manu and Chaudhari, 2003; Zille et al., 2004; Kornaros and Lyberatos, 2006; Sudarjanto et al., 2006; Abo-Farha, 2010; Jafari et al., 2012).

Additionally, subjected to fluctuations under environmental conditions especially in aquatic systems, dyes undergo various reactions which in turn change chemical composition or structure of dyestuffs. Such structural alterations and degradation products of dyes (like aromatic amines) may result in the generation of new xenobiotic compounds that vary in their toxicity level (i.e. either become more or less toxic) in contrast to parent compounds (O’Neill et al., 2000; Vijaya and Sandhya, 2003; Franciscon et al., 2012; Shah et al., 2013).

Synthetic dyes have been reported to be carcinogenic and mutagenic in nature especially, through continuous exposure to elevated concentrations of synthetic colorants via multifarious routes. Dyes themselves are severely damaging to various fish and microbiological species as well as causing human ailments especially vital human organs become affected or deceased. So despite exerting minimum organic loads to wastewater, these coloring agents and their metabolites need to be removed not only due to their esthetics but also potential toxicity, mutagenicity and carcinogenicity (Hai et al., 2007; Joshi et al., 2008).

5. Dyestuffs regarded as recalcitrant in nature

The complex chemical substances which resist degradation, persist or remain intact in environment for longer time durations and are transported extensively over long distances within different geographical locations are referred to as recalcitrant pollutants. Larger molecular sizes due to highly condensed and branched aromatic rings, existence of unusual bonds and substitutions with other compounds (such as Br^- or Cl^-), high stability and toxic nature are some of the attributes that contribute to recalcitrance of a pollutant (Jogdand, 2006; An, 2007).

Dyestuffs, especially synthetic ones, are highly persistent in natural environments and are therefore most difficult to treat due to the presence of complex aromatic structures with delocalized electrons, conjugated double bonds in their molecules and photolytic stability (Zille et al., 2005; Maddhinni et al., 2006). For instance, the reported half-life of hydrolyzed Reactive Blue 19 is 46 years (Hao et al., 2000). Dyes are also amalgamated with heavy metals, which in turn have their own consequences on the surrounding environmental matrices (Maddhinni et al., 2006). Furthermore, synthetic origin to resist fading by induction of different chemical, physical as well as biological agents also render dyes more stable against degradation under natural conditions as well as by conventional treatment processes, hence their removal from effluents is one of the major concerns (Rajaguru et al., 2000; Robinson et al., 2001; Mazmanci and Unyayar, 2005; Pandey et al., 2007; dos-Santos et al., 2007; Murugesan et al., 2007; Bafana et al., 2008).

Azo compounds being xenobiotic in nature, except for 4,4′-dihydroxy azo benzene the only natural azo compound, appear to be recalcitrant and persist in environment for longer durations as natural microflora (biotic) or other decomposition (abiotic) processes going on in nature are unable to mineralize them and reduce their quantities (Gill and Strauch, 1984; Stolz, 2001; Maddhinni et al., 2006; Pahlaviani et al., 2011; Forootanfar et al., 2012).

Azo dyes possess azo linkages (–N═N–), the chromophoric groups that impart color to the substrate, and sulfonic groups ($-SO_3^-$). These azo bonds along with sulfonate moieties due to their strong electron withdrawing nature lead to formation of electron deficient molecules thus reduce the susceptibility of azo dye molecules to oxidative reactions and render them more persistent and recalcitrant, hence most difficult to treat (Field et al., 1993; Coughlin et al., 1999; Chen, 2002; Barragán et al., 2007). Due to their durability, persistence, carcinogenic and mutagenic nature these dyestuffs need to be treated prior to discharge into water bodies or surrounding environment and even if discharged untreated these dyes should be decolorized or degraded in a bid to detoxify them or decontaminate the polluted sites.

6. Conventional technologies for treatment of dyestuffs

Conventionally, numerous physical and chemical methods including adsorption, ultra-filtration, coagulation, flocculation, ozonation, photocatalytic oxidation, advanced oxidation processes, fenton process, chemical and electrochemical coagulation were applied for removal of color from wastewater (Kapdan and Kargi, 2002; Sandhaya et al., 2005; Cañizares et al., 2006; Abo-Farah, 2010, Singh and Arora, 2011; Singh et al., 2012). All these methods are not sufficient to alleviate dye related hazards, additionally, their applications are precluded due to higher energy requirements and costs, processing efficiencies, operational problems, generation of sludge or wastes in huge quantities and its safe disposal, thus can serve as a powerful means of generating secondary pollutants (Kapdan and Kargi, 2002; Sandhaya et al., 2005; Singh et al., 2012). Moreover these methods along with incomplete removal of coloring stuffs from wastewater, except for nonionic dyes, are also inefficient for conversion of these compounds into environmentally acceptable forms (Lee, 2000; Kapdan and Kargi, 2002). Hence alternative methods need to be explored for detoxification of dyestuffs in wastewater streams.

7. Biological treatment methods for dyestuffs

Considering the aforesaid pitfalls related to applications of physicochemical treatment processes for removal of coloring agents from industrial effluents, most of the research focus has been shifted toward exploration and exploitation of more cost effective, sophisticated and efficient methods without further stressing the natural environment and endangering all the life forms. Therefore biological systems i.e. microorganisms as well as plants have been sought out worldwide as most viable, effective and efficient alternatives for treatment and decolorization of dye containing effluents (Khelifi et al., 2008; Reddy and Lee, 2012).

8. Use of microbial cells for treatment of dyestuffs

Remediation or treatment processes accomplished via use of simple biological systems are known as bioremediation, biodegradation and biotransformation etc. Bioremediation utilizes biological agents (microorganisms) for complete removal of contaminants and/or toxic substances from environment whereas transformation and/or conversion of pollutants from highly toxic forms into innocuous ones via chemical modifications brought by living organisms (bacteria and fungi) is referred to as biotransformation (Parales et al., 2002).

Bioremediation has gained much importance due to capability of microorganisms for surviving within hostile environments as they have evolved over thousands of years to flourish under such conditions. Such an adaptable microbial community plays a vital role in reclamation and restoration of contaminated environments because nature through selection pressure has armed these microbial successors with various resistance and catabolic potentials, which are most advantageous in minimizing the extent of pollution (Lalithakumari, 2005) and can be applied for mineralization of complex xenobiotic compounds (Singh and Arora, 2011).

Microbial decolorization and degradation of dye stuffs is considered as environmentally feasible alternative which can lead to detoxification or complete mineralization of color rich effluents. Numerous researches have revealed the existence of a wide variety of microbial systems (bacterial and fungal species either as pure or mixed cultures) regarding efficient decolorization or degradation of colorants (Banat et al., 1996; Chang and Lin, 2001; Asgher et al., 2006; Singh and Arora, 2011; Singh et al., 2012) including *Bacillus subtilis* (Horitsu et al., 1977), *Aeromonas hydrophila* (Idaka and Ogawa, 1978), *Bacillus cereus* (Wuhrmann et al., 1980), *Vibrio logei* (Adedayo et al., 2004), *Rhodopseudomonas palustris* (Wang et al., 2008), *Bacillus megaterium* (Khan, 2011), *Pseudomonas* sp. (Shah et al., 2013), *Sphingomonas* sp. (Ali et al., 2014), *Phanerochaete chrysosporium*, *Penicillium* sp. (Zheng et al., 1999; He et al., 2004), *Polyporus rubidus* (Dayaram and Dasgupta, 2008). However these strategies are effective in the case of certain dyes and have their own drawbacks and limitations as for instance decolorization via fungi is a time-consuming process, moreover, the literature elucidates utilization of fungi for dye degradation as a biocatalyst e.g. extracellular enzymes from *Pleurotus ostreatus* and laccases from *Trametes polyzona* have been used in the decolorization of various synthetic dyes (Banat et al., 1996; Chang et al., 2001; Devi et al., 2012; Chairin et al., 2013).

9. Phytoremediation

Since most of studies concentrated on exploitation of microbial potentials for treatment of dye laden effluents. Recently, scientific community has recognized that plants, growing in vicinities of polluted sites equipped with transport systems (facilitating up take of contaminants within plants from water and soil systems), have inherent metabolic as well as extractive potentials which enable them to effectively deal with accumulated contaminants. Studies have also revealed that plant species are genetically adapting over the passage of time to survive and grow on highly polluted substrates in order to metabolize or detoxify the contaminants to alleviate environmental stresses. Thus suggesting that plants as autotrophic and natural solar-driven bioreactors can effectively be utilized for

Table 1 Summary of various phytotechnological processes and mechanisms involved in the acquisition, removal and detoxification of contaminants.

Phytotechnique	Description	Route of contaminant uptake	Mechanism	Applicability	References
Phytoextraction	Translocates and concentrates contaminants from soil via plant roots into harvestable plant parts e.g. shoots	Uptake by plant roots	Absorption or uptake via dissolution in water or through cation pumps accumulation or sequestration	Inorganic pollutants e.g. metals	McCutcheon and Schnoor (2003) Marmiroli et al. (2006) Ali et al. (2013)
Phytofiltration	Utilizes plants with extensive root systems for removal of pollutants from water	Uptake by plant roots (rhizofiltration), young plant seedlings (blastofiltration) or excised plant shoots (caulifiltration)	Filtration, sorption or precipitation of pollutants surrounding the root zone	Inorganic pollutants e.g. metals	Marmiroli et al. (2006) Macek et al. (2009) Al-Baldawi et al. (2013) Ali et al. (2013)
Phytostabilization	Immobilizes pollutants and reduces their bioavailability	Uptake by plant roots	Sorption Precipitation or complexation in rhizosphere	Inorganic pollutants e.g. metals	Marmiroli et al. (2006) Macek et al. (2009) Ali et al. (2013)
Phytotransformation	Breakdown organic contaminants through plant metabolic activities or plant enzymes	Uptake by plant roots or metabolism within root zone	Absorption by root system resulting in metabolic or enzymatic transformation within or external to plants	Organic pollutants or xenobiotics	Marmiroli et al. (2006) Macek et al. (2009) Al-Baldawi et al. (2013) Ali et al. (2013)
Rhizodegradation	Degrades pollutants by soil dwelling microbes in rhizosphere due to simulation of microbial activity by plant secretions	Transformation within root zone	Secretion of root exudates or enzymes around root zones and subsequent microbial degradation of xenobiotics	Organic pollutants or xenobiotics	Al-Baldawi et al. (2013) Ali et al. (2013)
Phytovolatilization	Transforms pollutants into volatile form or gas phase and their subsequent release in atmosphere through transpiration	Uptake of water soluble pollutants by plant roots	Modification of pollutants during vascular translocation from roots to leaves	Organic pollutants or xenobiotics	Marmiroli et al. (2006) Macek et al. (2009) Ali et al. (2013)

remediation purposes (Campos et al., 2008; Sureshvarr et al., 2010; Kabra et al., 2011).

Phytoremediation in recent years has emerged as an energy efficient and ecofriendly remediation technology for decontamination of soil, surface and groundwater, air or other polluted media. A set of techniques emphasizing on the efficient use of plants, their related enzymes and associated microbes for isolation, transportation, sequestration, detoxification and mineralization of toxicants through complex natural biological, physiological and chemical processes and activities of plants and microbes is termed as phytoremediation (Sureshvarr et al., 2010; Khandare et al., 2011a,b; Etim, 2012; Ali et al., 2013). These plants can subsequently be harvested, processed or disposed of safely (Raskin and Salt, 1997; Sigua et al., 2004).

10. Principles and technological aspects of phytoremediation

Plants can uptake contaminants persisting in environment through root system, which by providing a larger surface area, facilitate mobilization, clean up or detoxification of contaminants within plants through various mechanisms i.e. elimination, containment and degradation etc. Such plant properties have been used for effective elimination of wastes including metals, phenolic compounds, azo dyes and colorants, various other organic and inorganic contaminants as well (Sureshvarr et al., 2010; Ali et al., 2013). Hence depending upon the detoxification process, applicability, medium, type and extent of pollution, phytoremediation processes can be classified as phytoextraction, rhizofilteration, phytostabilization (for inorganic contaminants), phytotransformation, rhizodegradation, phytovolatilization (for organic contaminants) as depicted in Table 1 (Raskin and Ensley, 2000; Sureshvarr et al., 2010; Ali et al., 2013). Additionally, phytoremediation efficiencies and uptake mechanisms of pollutants (either organic or inorganic) are greatly influenced by plant species and their characteristics, root zone interactions, properties of medium, chemical properties of contaminants, bioavailability of contaminants, effects of added chelating agents, environmental conditions etc. (Cunningham and Ow, 1996; Tangahu et al., 2011).

A number of green plants including herbs, shrubs and trees (both terrestrial and aquatic) have been reported to be endowed with magnificent abilities for restoration and reclamation of contaminated environments (Sinha et al., 2007). These plant species can act as excluders, accumulators and hyper accumulators. Excluders accumulate pollutants from substrate into their roots but limit their transportation and entry in aerial parts such as shoots. Accumulators concentrate and transform pollutants into inert forms in their aerial tissues whereas hyperaccumlators are capable of accumulating extraordinary higher quantities of pollutants as compared to other plant species (Memon et al., 2001; Sinha et al., 2007; Memon and Schroder, 2009; Sheoran et al., 2011; Malik and Biswas, 2012). Some of the characteristics of phytoremediation as ecofriendly technology have been summarized in Table 2.

11. Decolorization of dyestuffs using phytoremediation

Endeavors associated with revitalization of polluted soils and water bodies with dye-laden wastes revealed that the use of plants as ecologically sound and sustainable remediating agents have gained much of the scientific attention, as it will be aiding in the exploration of degradation potential and enzymatic status of plant species as well as products formed during dye metabolism. All this has added an innovative aspect to phytoremediation studies (Govindwar and Kagalkar, 2010).

Studies have shown that a great deal of plant species like *Brassica juncea*, *Rheum rhabarbarum*, *Tagetes patula*, *Thymus vulgaris*, *Rosmarinus officinalis*, *Phragmites australis*, *Rumex acetosa*, *Typha angustifolia*, *Hydrilla verticillata*, *Nasturtium officinale*, *Petunia grandiflora* Juss., *Glandularia pulchella* and *Armoracia rusticana* (horse radish) etc. possess the ability to absorb, detoxify and metabolize a wide range of synthetic dyes and colorants to curtail the effects of pollution on environmental compartments (Zheng and Shetty, 2000; Aubert and Schwitzguébel, 2002, 2004; Maddhinni et al., 2006; Carias et al., 2007; Nilratnisakorn et al., 2007; Ghodake et al., 2009; Page and Schwitzguebel, 2009; Patil et al., 2009; Govindwar and Kagalkar, 2010; Wathakar et al., 2013; Torbati et al., 2015). As far as screening and exploration of potential plant species for phytoremediation is concerned *Typhonium flagelliforme* was found to have significant dye degradation competency (67%) even in distilled water (free of nutrients) within 4 days, which suggested that applications of such plant species will be helpful in reducing experimental expenses on lab scale (Kagalkar et al., 2010). In another study four plant species were screened and assessed for their potential to treat effluents contaminated with mono- and di-sulphonated anthraquinones. Among these *R. rhabarbarum* (rhubarb) exhibited promising results for the treatment of sulfonated anthraquinones under the provision of hydroponic conditions (Aubert and Schwitzguébel, 2004). Aloe barbadensis extracts were also evaluated for their degradation potential against Congo red and malachite green where the extracts showed decolorization maxima of up to 27.33% for Congo red (Rai et al., 2014).

Table 2 Characteristics of phytoremediation.

Advantages	Limitations
Autotrophic systems	Low biomass and sluggish growth especially in the case of hyperaccumulators
Require little nutrient input, no disposal sites needed	Time consuming
Cost effective	Limited bioavailability of pollutants
Publicly acceptable	Applicable to sites with low to moderate level of contamination
Sustainable and ecofriendly reclamation strategy	Risk of food chain contamination

(Source: Khandare et al., 2011a,b; Telke et al., 2011; Ali et al., 2013).

The degradation potential of *Arabidopsis thaliana* and *Helianthus annuus* was evaluated against several dyes where *A. thaliana* appeared to be more effective in transforming dyes to innocuous byproducts which in turn were entrapped by plant roots (Kamat, 2014). Furthermore, *Chara vulgaris* displayed 95% decolorization of Congo red along with the incorporation of dye within the plant via active involvement of functional groups evident by FTIR analysis (Mahajan and Kaushal, 2013) thus suggesting the phytoextractive potential of these plant species, whereas biotransformation rates of approximately 60% and 40% have been achieved in the case of *Momordica charantia* against Disperse Red 17 and Disperse Brown 1 dyes (Satar and Husain, 2009). All these findings indicate potential applicability of these candidates in the phytoremediation of undesired coloring agents from industrial wastes.

12. Biotransformation pathways utilized by plants for detoxification of dyestuffs

The biotransformation pathways and/or mechanisms plants use to detoxify dyes into innocuous metabolites are still uncertain. However it is likely that the mode of action differs depending upon plant species, the enzymes it produces along with their location and activity. Various mechanisms within plant species for metabolism of synthetic dye stuffs have been proposed hitherto including the following.

12.1. Sorption and speciation of dye stuffs within plant tissues

It has been proposed that some plant species do possess the ability to absorb and decolorize different dyes under the provision of optimum conditions. For instance, Uera et al. (2007) evaluated remediation potentials of selected tropical plant species for ethidium bromide (EtBr) from contaminated soil and found significant differences in absorption potentials of tropical plants including *Brassica alba* (mustard) which showed the highest absorption of EtBr (1.4 $\mu g\ kg^{-1}$) followed by *Solanum lycopersicum* (tomato) and *Vetiveria zizanioides* (vetiver grass) with an average uptake of 1.0 and 0.7 $\mu g\ kg^{-1}$ EtBr, respectively. Similarly, *Eichhornia crassipes* exhibited 99.5% removal efficiency for Black B and 95% for Red RB due to the sorption of dye molecules onto leaves, shoots and roots representing localization as well as speciation of toxic dyes within the plant tissues (Muthunarayanan et al., 2011), additionally this plant species has been reported to cause significant reductions in nitrogenous compounds, BOD, COD and TDS contents of wastewater originating from various dye houses (Shah et al., 2010). The utilization of *E. crassipes* and other wetland plants including *Lemna minor*, *Pistia stratiotes* etc. as potential adsorbents along with their biosorption pathways involved in the removal of dye stuffs and other contaminants from textile effluents have been elucidated in detail by Priya and Selvan (2014) and Rizwana et al. (2014).

Sureshvarr et al. (2010) using GC–MS analysis ascertained that *Eucalyptus* species play an effective role in the absorption of azo dyes from soil contaminated with effluents of paper and pulp industry. Furthermore, *T. angustifolia*, *T. flagelliforme* and roots of *Blumea malcolmii* have been reported to assimilate, degrade and remove relatively significant quantities of Reactive Red 141 (up to 60%) from a mixture of synthetic dyes, Brilliant Blue R (up to 80%) and malachite green (up to 45%), respectively (Nilratnisakorn et al., 2007; Kagalkar et al., 2009, 2010). Similarly plant biomass, dye concentration, pH and temperature highly influences the dye absorption process as observed in the case of *Hydrocotyle vulgaris* roots, *N. officinale* and *Azolla filiculoides* against C.I. Acid Blue 92. These plants exhibited constantly the same removal efficiency against the dye during four repeated runs (Vafaei et al., 2013b; Khataee et al., 2013; Torbati et al., 2015). The hairy roots of *G. pulchella* also showed effective absorption of different textile dyes provided (Kabra et al., 2011). Hence it is evident from the above mentioned facts that biosorption phenomenon within different plant species is vital in sequestration, accumulation and subsequent metabolism of toxic dyes.

12.2. Bioremoval of dye stuffs by enzymatic activities of plants

Additionally, it has been speculated that dye decolorization using plants (possessing multitude of enzymatic constituents governing decolorization) is stringently dependent upon the presence and induction of certain enzymes upon exposure to dye stresses (Kagalkar et al., 2010). Therefore commemorating the enzymatic dependency various cell cultured and intact plants have been investigated for bioremoval of toxic dyes. Wild and tissue cultured plants of *Portulaca grandiflora* have been reported to display effective decolorization (up to 98%) of sulfonated diazo dye (Navy Blue HE2R), which was accredited to significantly enhanced activities of lignin peroxidase, DCIP (2,6-dichlorophenol-indophenol) reductase and tyrosinase (Khandare et al., 2011b). Moreover, tissue cultured *B. malcomii* (shrub) decolorized Direct Red 5B along with the induction of lignin peroxidase, tyrosinase, DCIP reductase, azoreductase and riboflavin reductase indicating their crucial role in dye metabolism (Kagalkar et al., 2009).

Studies evaluating the potential of wild plants for degradation of Remazol Red (sulfonated azo dye) and Brilliant Blue R, respectively concluded that veratryl alcohol oxidases in *Aster amellus* while laccases in the case of *T. flagelliforme* along with above mentioned enzymes played a significant role in the metabolism of respective dyes (Kagalkar et al., 2010; Khandare et al., 2011a). All these plant species also exhibited the capability of decolorizing different dyes and mixture of dyes along with a significant reduction in BOD and COD content especially in the case of treatment with *A. amellus* and *T. flagelliforme*. Involvement of laccases, tyrosinases, azoreductases and 2,6-dichlorophenol indophenol reductases from *Nopalea cochenillifera* cell cultures and intact plants has also been reported to play an essential role in the transformation of Red HE7B into nonhazardous metabolites (Adki et al., 2012). Similarly, *Cucurbita pepo* seems to be more effective in the degradation of azo dyes (Direct Yellow), where high rates of decolorization were observed by peroxidases (Boucherit et al., 2013). Peroxidases from crude extracts of *P. australis* were found to degrade Acid Orange 7 and its aromatic amine derivatives up to 70% within 120 h in the presence of H_2O_2. Likewise, C.I. Basic Red 46 and C.I. Acid Blue 92 dyes were degraded magnificently under increased activities of superoxide dismutases and peroxidases in *L. minor* and *N. officinale*. Moreover, these plant species can be successfully used for almost four consecutive decolorization cycles (Movafeghi et al., 2013; Torbati et al., 2015), whereas polyphenol oxidases from banana pulp have significantly decolorized Direct Red 5B (up to 90%) and Direct Blue GLL (80%) just within 48 and 90 h, respectively (Jadhav et al., 2011). Therefore, all these studies confirm the crucial roles of enzymes in the tolerance of plants against dyes molecules and subsequent detoxification of these contaminants. Moreover the effects of different environmental parameters on the activities of peroxidase enzymes among *T. angustifolia*, *Arundo donax* and *P. australis* (macrophytic species) for degradation of Amaranth and Amido Black (azo) dyes were also assessed by Haddajia et al. (2014). Results revealed the highest peroxidase activity in the leaf extracts of *P. australis*, with a dye decolorization efficiency of 93% (Amarnath) and 87% (Amido Black) within 120 h, showing their dependency on dye and enzyme concentration, time, temperature and pH (Haddajia et al., 2014).

Plant roots also facilitate transformation and degradation of dyestuffs by involving intracellular enzymes like tyrosinases, laccases, NADH-DCIP reductases and lignin peroxidases etc. (Ghodake et al., 2009; Patil et al., 2009; Kagalkar et al., 2009, 2010). For example, hairy roots of *B. juncea* showed Methyl Orange decolorization up to 92% within 4 days which was found to be mediated by intracellular laccases (Telke et al., 2011), while, degradation of Direct Yellow 12 was reported to be very efficient in the presence of horse radish peroxidase extracted from horse radish roots. The enzyme was even more efficient in dye removal when immobilized with acrylamide gel and removed 78% of the dye (Maddhinni et al., 2006). Similarly in another study among the hairy root cultures of different plants, roots of *T. patula* were selected for testing the decolorization of Reactive red 198. Results showed dye removal capacities of up to 110 $\mathrm{mg\,L^{-1}}$ by hairy roots of *T. patula* through a significant induction of biotransformation enzymatic activities. These roots have been reported to exhibit same removal efficiencies for at least five repetitive runs (Patil et al., 2009). Moreover, increased activities of laccases, lignin peroxidases, tyrosinases and NADH-2,6-dichorophenol-indo phenol reductases were observed in the roots of *Petunia grandiflora* (wild and tissue cultured plants) during decolorization of disulfonated triphenylmethane dye (Brilliant Blue G), color removal efficiencies of up to 86% by wild as well as tissue cultured plants have been reported (Watharkar et al., 2013). Likewise, *H. vulgaris* root system efficiently removed up to 95% of C.I. Basic Red 46 and ROS under increased activity of superoxide dismutase, peroxidase and catalase enzymes (Vafaei et al., 2013a). Telke et al. (2011) also ascertained significant bioremoval of textile dyes by purified (intracellular) laccases from root hairs of *B. juncea* in association with ABTS as redox mediator indicating effective detoxification of dyes via laccase–ABTS systems. All these findings suggested that hairy roots can be considered as a good source of enzymatic detoxification of dyes. Moreover the metabolic pathways and enzyme-based detoxification mechanisms operating in plant root hairs have been elucidated by Agostini et al. (2013). Taken together all these results support the fact that enzymes do play an important role in the bioremoval of dyes so their mechanisms need to be determined individually.

12.3. Stress avoidance and tolerance mechanisms within plants

Nilratnisakorn et al. (2008) studied mechanisms of stress avoidance and dye removal in plants using *T. angustifolia*. Precipitation of dye molecules with calcium complexes and silicon within plant tissues as dye–metal complexes observed via X-ray diffractions suggested avoidance mechanism involving metal ions (facilitating precipitation of dyes in root and leaf areas), where plant may breakdown dye molecules into smaller ones (due to induction of proteins, increased enzymatic activities and release of protons by plant cell wall and cell membrane) so that they can easily be translocated across the semipermeable membranes of plants without hampering the photosynthetic activity by dye. Plants might release these molecules into surrounding soil (rhizosphere) in order to maintain soil pH, gaseous composition through phytochemical reactions and lead to fixation of these altered compounds in soil, thus relieving the plant from toxic effects of dyes (Bassindale et al., 2003; Nilratnisakorn et al., 2008). FTIR studies showed involvement of amides and siloxane groups in the removal of dye by the plants, where NH bending of amide and C–OH or C–O–C bending of cellulosic groups was shifted due to replacement of these groups by aromatic rings and sulfonate groups of dye molecules indicating their transportation and translocation within the plant. The plants utilize dye molecules (accumulated within intracellular spaces) for growth thus resulting in the decolorization of dye that was evident by higher growth rates of plants, suggesting facilitation of dye removal by proteins and amide groups of plants (Nilratnisakorn et al., 2007, 2008). Additionally, TEM-EDX analysis of plants indicated involvement of Fe, Si and Ca in the absorption of dye molecules by root and leaf cells (Nilratnisakorn et al., 2008). Moreover, the involvement of ascorbate–glutathione pathway in the detoxification of azo dyes (Acid Orange 7) in *P. australis* along with various enzymatic activities has also been proposed by Carias et al. (2008), where increased glutathione S-transferase activity leads to the conjugation of dye molecules due to the scavenging action of enzymes, thus protecting the plant against chemical stress.

12.4. Plant–microbe synergism in the metabolism of dye stuffs

In addition to this, plants also possess great potential to degrade contaminants by forming symbiotic associations with rhizospheric microbes (Glick, 2010). In such associations the fibrous root system supports pollutant degrading species by provision of favorable environmental conditions and nutritious compounds, thus enhancing microbial activities and pollutant metabolism in the root zone (Nie et al., 2011). Such interactions with respect to the metabolism of various dye stuffs have been investigated for many plant species e.g. *P. grandiflora* (Khandare et al., 2013), *P. grandiflora* (Watharkar et al., 2013) etc.

All these studies to some extent are helpful in understanding the basic mechanisms which plants utilize in decolorization and detoxification of synthetic dyes. However, molecular aspects regulating these processes largely remain elusive. For instance genes responsible for the metabolism of dye stuffs within the plant body still need to be sequenced and identified for their potential exploitation even outside plant cells in order to facilitate remediation of these contaminants in an environment friendly manner. Similarly exact locations of the enzymes operating within the plants for decolorization of the dyes still need to be traced in order to elucidate the functional roles that enzymes play in the detoxification of these colorants. In short an understanding of all these aspects will be opening new portals for application of aquatic, ornamental as well as terrestrial plant species in the phytoremediation of dye-laden effluents (Kamat, 2014; Khataee et al., 2013).

13. Conclusions

Phytoremediation using green plants has been explored and studied extensively regarding the absorption or decolorization of dyestuffs originating from various sources throughout the world. However the technique is still in early stages of development as little data is available regarding the mechanisms of action of these plants during metabolism of dyestuffs. Hence a lot of research is needed for exploration of dye degrading plant species, their operating remediation mechanisms, applications of various additives and influence of associated microbial activities for improvement of phytoremediation processes. Moreover the applied molecular techniques and creation of transgenic plants will decipher the specific metabolic pathways involved in dye metabolism, which will further boost the applicability of phytoremediation technologies for alleviating the impacts of dye laden wastes on various environmental compartments.

References

Abo-Farha, S.A., 2010. Comparative study of oxidation of some azo dyes by different advanced oxidation processes: fenton, fenton-like, photo-fenton and photo-fenton-like. J. American Sci. 6 (10), 128–142.

Adedayo, O., Javadpour, S., Taylor, C., Anderson, W.A., Moo-Young, M., 2004. Decolourization and detoxification of methyl red by aerobic bacteria from a wastewater treatment plant. World J. Microbiol. Biotechnol. 20, 545–550.

Adki, V.S., Jadhav, J.P., Bapat, V.A., 2012. Exploring the phytoremediation potential of cactus (*Nopalea cochenillifera* Salm. Dyck.) cell cultures for textile dye degradation. Int. J. Phytorem. 14 (6), 554–569.

Agostini, E., Talano, M.A., González, P.S., Oller, A.L.W., Medina, M.I., 2013. Application of hairy roots for phytoremediation: what makes them an interesting tool for this purpose? Appl. Microbiol. Biotechnol. 97, 1017–1030.

Al-Baldawi, I.A.W., Abdullah, S.R.S., Suja, F., Anuar, N., Mushrifah, I., 2013. Comparative performance of free surface and sub-surface flow systems in the phytoremediation of hydrocarbons using *Scirpus grossus*. J. Environ. Manag. 130, 324–330.

Ali, H., Khan, E., Sajad, M.A., 2013. Phytoremediation of heavy metals: concepts and applications. Chemosphere 91, 869–881.

Ali, L., Alhassani, H., Karuvantevida, N., Rauf, M.A., Ashraf, S.S., 2014. Efficient aerobic degradation of various azo dyes by a *Sphingomonas* sp. isolated from petroleum sludge. J. Bioremed. Biodegrad. 5, 3–13.

An, T., 2007. Persistent organic pollutants in water and wastewater and their treatment by advanced oxidation processes. Res. J. chem. Environ. 11 (4), 1–2.

Asgher, M., Shah, S.A.H., Ali, M., Legge, R.L., 2006. Decolorization of some reactive textile dyes by white rot fungi isolated in Pakistan. World J. Microbiol. Biotechnol. 22, 89–93.

Aubert, S., Schwitzguébel, J.P., 2002. Capillary electrophoretic separation of sulphonated anthroquinones in a variety of matrices. Chromatographia 56, 693–697.

Aubert, S., Schwitzguébel, J.P., 2004. Screening of plant species for the phytotreatment of wastewater containing sulphonated anthraquinones. Water Res. 38 (16), 3569–3575.

Bafana, A., Chakrabarti, T., Krishnamurthi, K., Devi, S.S., 2008. Biodiversity and dye decolorization ability of an acclimatized textile sludge. Bioresour. Technol. 99, 5094–5098.

Banat, I.M., Nigam, P., Singh, D., Marchant, R., 1996. Microbial decolorization of textile dye containing effluents, a review. Bioresour. Technol. 58, 217–227.

Barragán, B.E., Costa, C.M., Márquez, C., 2007. Biodegradation of azo dyes by bacteria inoculated on solid media. Dyes Pigments 75, 73–81.

Bassindale, A.R., Brandstadt, K.F., Lane, T.H., Taylor, P.G., 2003. Enzyme catalyzed siloxane bond formation. J. Inorg. Biochem. 96, 401–406.

Boucherit, N., Abouseoud, M., Adour, L., 2013. Degradation of direct azo dye by *Cucurbita pepo* free and immobilized peroxidase. J. Environ. Sci. 25 (6), 1235–1244.

Campos, R., Kandelbauer, A., Robra, K.H., Artur, C.P., Gubitz, G.M., 2001. A rapid and sensitive method for the quantification of protein using the principle of protein-dye binding. Anal. Biochem. 72, 248–254.

Campos, V.M., Merino, I., Casado, R., Pacios, L.F., Gomez, L., 2008. Review: phytoremediation of organic pollutants. Span. J. Agric. Res. 6, 38–47.

Cañizares, P., Martínez, F., Jiménez, C., Lobato, J., Rodrigo, M., 2006. Coagulation and electrocoagulation of wastes polluted with dyes. Environ. Sci. Technol. 40 (20), 6418–6424.

Carias, C.C., Novais, J.M., Martins-Dias, S., 2008. Are *Phragmites australis* enzymes involved in the degradation of the textile azo dye acid orange 7? Bioresour. Technol. 99 (2), 243–251.

Carias, C.C., Novais, J.M., Martins-Dias, S., 2007. *Phragmites australis* peroxidases role in the degradation of an azo dye. Water Sci. Technol. 56 (3), 263–269.

Carmen, Z., Daniela, S., 2012. Textile organic dyes-characteristics, polluting effects and separation/elimination procedures from industrial effluents-a critical overview. In: Puzyn, T. (Ed.), Organic Pollutants Ten Years After the Stockholm Convention: Environmental and Analytical Update. Pub. InTech, Europe, pp. 55–86.

Chairin, T., Nitheranont, T., Watanabe, A., Asada, Y., Khanongnuch, C., Lumyong, S., 2013. Biodegradation of bisphenol A and decolorization of synthetic dyes by laccase from white-rot fungus *Trametes polyzona*. Appl. Biochem. Biotechnol. 169 (2), 539–545.

Chang, J., Chou, C., Lin, Y., Lin, P., Ho, J., Hu, T.L., 2001. Kinetic characteristics of bacterial azo-dye decolorization by *Pseudomonas luteola*. Wat. Res. 35 (12), 2841–2850.

Chang, J., Lin, C., 2001. Decolorization kinetics of a recombinant *Escherichia coli* strain harboring azo-dye-decolorizing determinants from *Rhodococcus* sp. Biotechnol. Lett. 23, 631–636.

Chen, B., 2002. Understanding decolorization characteristics of reactive azo dyes by *Pseudomonas luteola*: toxicity and kinetics. Process Biochem. 38, 437–446.

Coughlin, M.F., Kinkle, B.K., Bishop, P.L., 1999. Degradation of azo dyes containing aminonaphthol by *Sphingomonas* sp strain 1CX. J. Ind. Microbiol. Biotechnol. 23, 341–346.

Cunningham, S.D., Ow, D.W., 1996. Promises and prospect of phytoremediation. Plant Physiol. 110, 715–719.

da-Silva, M.R., de-Sa, L.R.V., Russo, C., Scio, E., Ferreira-Leitao, V.S., 2010. The use of HRP in decolorization of reactive dyes and toxicological evaluation of their products. Enzyme Res. 2010, 703824–703831.

Dayaram, P., Dasgupta, D., 2008. Decolorization of synthetic dyes and textile wastewater using *Polyporus rubidus*. J. Environ. Biol. 29 (6), 831–836.

Devi, V.M., Inbathamizh, L., Ponnu, T.M., Premalatha, S., Divya, M., 2012. Dye decolorization using fungal laccase. Bull. Environ. Pharmacol. Life Sci. 1 (3), 67–71.

dos-Santos, A.B., Cervantes, F.J., van-Lier, J.B., 2007. Review paper on current technologies for decolorization of textile wastewaters: perspectives for anaerobic biotechnology. Bioresour. Technol. 98, 2369–2385.

Etim, E.E., 2012. Phytoremediation and its mechanisms: a review. Int. J. Environ. Bioenergy 2 (3), 120–136.

He, F., Hu, W., Li, Y., 2004. Biodegradation mechanisms and kinetics of azo dye 4BS by a microbial consortium. Chemosphere 57, 293–301.

Field, J.M., Stans, A.J.M., Kato, M., Schrea, G., 1993. Enhanced biodegradation of aromatic pollutants in cocultures of anaerobic and aerobic bacterial consortia. Anton van Leeuwenhoek Int. 67, 47–77.

Forootanfar, H., Moezzi, A., Aghaie-Khozani, M., Mahmoudjanlou, Y., Ameri, A., Niknejad, F., Faramarzi, M.A., 2012. Synthetic dye decolorization by three sources of fungal laccase. Iran. J. Environ. Health Sci. Eng. 9, 27–35.

Franciscon, E., Grossman, M.J., Paschoal, J.A.R., Reyes, F.G.R., Durrant, L.R., 2012. Decolorization and biodegradation of reactive sulfonated azo dyes by a newly isolated *Brevibacterium* sp. strain VN-15. SpringerPlus 1, 37–47.

Ghodake, G.S., Telke, A.A., Jadhav, J.P., Govindwar, S.P., 2009. Potential of *Brassica juncea* in order to treat textile effluent contaminated sites. Int. J. Phytoremediation 11, 297–312.

Gill, M., Strauch, R.J., 1984. Constituents of *Agaricus xanthodermus* Genevier: the first naturally endogenous azo compound and toxic phenolic metabolites. Zeitschrift Fur Naturforschung C. J. Biosci. 39, 1027–1029.

Glick, B.R., 2010. Using soil bacteria to facilitate phytoremediation. Biotechnol. Adv. 28, 367–374.

Govindwar, S.P., Kagalkar, A.N., 2010. Phytoremediation technologies for removal of textile dyes: an over view and future prospectus. Nova Science Publishers Inc., New York, USA.

Haddajia, D., Bousselmia, L., Saadanib, O., Nouairib, I., Ghrabi-Gamma, Z., 2014. Enzymatic degradation of azo dyes using three macrophyte species: *Arundo donax*, *Typha angustifolia* and *Phragmites australis*. Desalination Water Treat. 1, 1–10.

Hai, F.I., Yamamoto, K., Fukushi, K., 2007. Hybrid treatment systems for dye wastewater. Cri. Rev. Environ. Sci. Technol. 37, 315–377.

Hao, O.J., Kim, H., Chang, P.C., 2000. Decolorization of wastewater. Crit. Rev. Environ. Sci. Technol. 30, 449–505.

Horitsu, H., Takada, M., Idaka, E., Tomoyeda, M., Ogawa, T., 1977. Degradation of p-aminoazobenzene. Eur. J. Appl. Microbiol. 4, 217–224.

Hunger, K., 2003. In: Industrial Dyes: Chemistry, Properties. Applications. Pub. Druckhaus Darmstadt GmbH, Darmstadt, Germany, pp. 1–2.

Idaka, E., Ogawa, Y., 1978. Degradation of azo compounds by *Aeromonas hydrophila* var. 2413. J. Soc. Dyers Color. 94, 91–94.

Jadhav, U.U., Dawkar, V.V., Jadhav, M.U., Govindwar, S.P., 2011. Decolorization of the textile dyes using purified banana pulp polyphenol oxidase. Int. J. Phytoremediation 13, 357–372.

Jafari, N., Kasra-Kermanshahi, R., Soudi, M.R., Mahvi, A.H., Gharavi, S., 2012. Degradation of a textile reactive azo dye by a combined biological-photocatalytic process: *Candida tropicalis* Jks2-TiO2/Uv. Iran. J. Environ. Health Sci. Eng. 9, 33–39.

Jogdand, S.N., 2006. Environmental Biotechnology: Industrial Pollution Management, third ed. Himalaya Publishing House, Mumbai, India.

Joshi, T., Iyengar, L., Singh, K., Garg, S., 2008. Isolation, identification and application of novel bacterial consortium TJ-1 for decolorization of structurally different azo dyes. Bioresour. Technol. 99, 7115–7121.

Kabra, A.N., Khandare, R.V., Kurade, M.B., Govindar, S.P., 2011. Phytoremediation of a sulphonated azo dye green HE4B by *Glandularia pulchella* (Sweet) Tronc. (Moss Verbena). Environ. Sci. Pollut. Res. 18, 1360–1373.

Kagalkar, A.N., Jagtap, U.B., Jadhav, J.P., Bapat, V.A., Govindwar, S.P., 2009. Biotechnological strategies for phytoremediation of the sulphonated azo dye Direct Red 5B using *Blumea malcolmii* Hook. Bioresour. Technol. 100, 4104–4110.

Kagalkar, A.N., Jagtap, U.B., Jadhav, J.P., Govindwar, S.P., Bapat, S.A., 2010. Studies on phytoremediation potentiality of *Typhonium flagelliforme* for the degradation of Brilliant Blue R. Planta 232 (1), 271–285.

Kamat, R.B., 2014. Phytoremediation for dye decolorization (Ph.D. thesis). Kansas State University, Manhattan, Kansas.

Kant, R., 2012. Textile dyeing industry an environmental hazard. Nat. Sci. 4 (1), 22–26.

Kapdan, I.K., Kargi, F., 2002. Biological decolorization of textile dyestuff containing wastewater by *Coriolus versicolor* in a rotating biological contractor. Enzyme Microb. Technol. 30, 195–199.

Khan, J.A., 2011. Azo dye biodegradation by azoreductase from *Bacillus megaterium*. Adv. Biotechnol. 10 (7), 21–27.

Khandare, R.V., Kabra, A.N., Awate, A.V., Govindvar, S.P., 2013. Synergistic degradation of diazo dye Direct Red 5B by *Portulaca grandiflora* and *Pseudomonas putida*. Int. J. Environ. Sci. Technol. 10, 1039–1050.

Khandare, R.V., Kabra, A.N., Kurade, M.B., Govindwar, S.P., 2011a. Phytoremediation potential of *Portulaca grandiflora* Hook. (Moss-Rose) in degrading a sulfonated diazo reactive dye Navy Blue HE2R (Reactive Blue 172). Bioresour. Technol. 102, 6774–6777.

Khandare, R.V., Kabra, A.N., Tamboli, D.P., Govindwar, S.P., 2011b. The role of *Aster amellus* Linn in the degradation of a sulfonated azo dye Ramazol Red: a phytoremediation strategy. Chemosphere 82, 1147–1154.

Khataee, A.R., Movafeghi, A., Vafaei, F., Lisar, S.S.Y., Zarei, M., 2013. Potential of the aquatic fern *Azolla filiculoides* in biodegradation of an azo dye: modeling of experimental results by artificial neural networks. Int. J. Phytoremediation 15, 729–742.

Khelifi, E., Gannoun, H., Touhami, Y., Bouallagui, H., Hamdi, M., 2008. Aerobic decolourization of the indigo dye-containing textile wastewater using continuous combined bioreactors. J. Hazard. Mat. 152, 683–689.

Kim, T.H., Lee, Y., Yang, J., Lee, B., Park, C., Kim, S., 2004. Decolorization of dye solutions by a membrane bioreactor (MBR) using white-rot fungi. Desalination 168, 287–293.

Kornaros, M., Lyberatos, G., 2006. Biological treatment of wastewaters from a dye manufacturing company using a trickling filter. J. Hazard. Mater. 136, 95–102.

Lalithakumari, P.D., 2005. Microbes: a tribute to clean environment. <http://www.envismadrasuniv.org/newsletter1.htm> (accessed on 21st January, 2014).

Lee, R., 2000. Coagulation and flocculation in wastewater treatment. Water Wastewater 141, 29–32.

Lim, C.K., Bay, H.H., Kee, T.C., Majid, Z.A., Zaharah, I., 2011. Decolorization of reactive black 5 using *Paenibacillus* sp. immobilized on to macrocomposite. J. Bioremed. Biodegrad. S1, 004.

Macek, T., Uhlik, O., Jecna, K., Novakova, M., Lovecka, P., Rezek, J., Dudkova, V., Stursa, P., Vrchotova, B., Pavlikova, D., Demnerova, K., Mackova, M., 2009. Advances in phytoremediation and rhizoremediation. In: Singh, A., Kuhad, R.C., Ward, O.P. (Eds.), Soil Biology: Advances in Applied Bioremediation. Springer-Verlag, Berlin Heidelberg, pp. 257–277.

Maddhinni, V.L., Vurimindi, H.B., Yerramilli, A., 2006. Degradation of azo dye with horse radish peroxidase (HRP). J. Indian Inst. Sci. 86, 507–514.

Mahajan, P., Kaushal, J., 2013. Degradation of Congo red dye in aqueous solution by using phytoremediation potential of *Chara vulgaris*. Chitkara Chem. Rev. 1, 67–75.

Malik, N., Biswas, A.K., 2012. Role of higher plants in remediation of metal contaminated soils. Sci. Rev. Chem. Commun. 2, 141–146.

Manu, B., Chaudhari, S., 2003. Decolorization of indigo and azo dyes in semi-continuous reactors with long hydraulic retention time. Process Biochem. 38, 1213–1221.

Marmiroli, N., Marmiroli, M., Maestri, E., 2006. Phytoremediation and phytotechnologies: a review for the present and the future. In: Twardowska, I., Allen, H.E., Haggblom, M.M., Stefaniak, S. (Eds.), Soil and Water Pollution Monitoring, Protection and Remediation. Springer, Dordrecht, The Netherlands, pp. 403–416.

Mazmanci, M.A., Unyayar, A., 2005. Decolourisation of reactive black 5 by *Funalia trogii* immobilised on luffa cylindrical sponge. Process Biochem. 40 (1), 337–342.

McCutcheon, S.C., Schnoor, J.L., 2003. Phytoremediation: Transformation and control of Contaminants. John Wiley & Sons Inc., Hoboken, New Jersey, pp. 3–16.

McMullan, G., Meehan, C., Conneely, A., Kirby, N., Robinson, T., Nigam, P., Banat, I.M., Marchant, R., Smyth, W.F., 2001. Microbial decolourization and degradation of textile dyes. Appl. Microbiol. Biotechnol. 56, 81–87.

Memon, A.R., Aktoprakligil, D., Ozdemir, A., Vertii, A., 2001. Heavy metal accumulation and detoxification mechanisms in plants. Turk. J. Bot. 25, 111–121.

Memon, A.R., Schroder, P., 2009. Implication of metal accumulation mechanisms to phytoremediation. Environ. Sci. Pollut. Res. 16, 162–175.

Moosvi, S., Keharia, H., Madamwar, D., 2005. Decolourization of textile dye reactive violet 5 by a newly isolated bacterial consortium RVM 11.1. World J. Microbiol. Biotechnol. 21, 667–672.

Movafeghi, A., Khataee, A.R., Torbati, S., Zarei, M., Lisar, S.S.Y., 2013. Bioremoval of C.I. Basic Red 46 as an azo dye from contaminated water by *Lemna minor* L.: modeling of key factor by neural network. Environ. Prog. Sustain. Energy 32 (4), 1082–1089.

Mugdha, A., Usha, M., 2012. Enzymatic treatment of waste containing dyestuffs using different delivery systems. Sci. Rev. Chem. Commun. 2 (1), 31–40.

Murugesan, K., Nam, I.H., Kim, Y.M., Chang, Y.S., 2007. Decolorization of reactive dyes by a thermostable laccase produced by *Ganoderma lucidum* in solid state culture. Enzyme Microb. Technol. 40 (7), 1662–1672.

Muthunarayanan, V., Santhiya, M., Swabna, V., Geetha, A., 2011. Phytodegradation of textile dyes by Water Hyacinth (*Eichhornia crassipes*) from aqueous dye solutions. Int. J. Environ. Sci. 1 (7), 1702–1717.

Nie, M., Wang, Y., Yu, J., Xiao, M., Jiang, L., Yang, J., Fang, C., Chen, J., Li, B., 2011. Understanding plant-microbe interactions for phytoremediation of petroleum polluted soil. PLoS one 6 (3), 1–8.

Nilratnisakorn, S., Thiravetyan, P., Nakbanpote, W., 2007. Synthetic reactive dye wastewater treatment by narrow-leaved cattails (*Typha angustifolia* Linn.): effects of dye, salinity and metals. Sci. Total Environ. 384, 67–76.

Nilratnisakorn, S., Thiravetyan, P., Nakbanpote, W., 2008. Synthetic reactive dye wastewater treatment by narrow-leaved cattail: Studied by XRD and FTIR. Asian J. Energy Environ. 9, 231–252.

O'Neill, C., Lopez, A., Esteves, S., Hawkes, F.R., Hawkes, D.L., Wilcox, S., 2000. Azo-dye degradation in an anaerobic-aerobic treatment system operating on simulated textile effluent. Appl. Microbiol. Biotechnol. 53, 249–254.

Page, V., Schwitzguebel, J., 2009. The role of cytochromes P450 and peroxidases in the detoxification of sulfonated anthroquinones by rhubarb and common sorrel plants cultivated under hydroponic conditions. Environ. Sci. Pollut. Res. Int. 16, 805–816.

Pahlaviani, M.R.M.K., Massiha, A., Issazadeh, K., 2011. An innovative approach to biodegradation of textile azo dyes by native bacterial strains in Iran. Int. Conf. Biotechnol. Environ. Manag. 18 (2011), 72–75.

Pandey, A., Singh, P., Iyengar, L., 2007. Review bacterial decolorization and degradation of azo dyes. Int. Biodeterior. Biodegrad. 59, 73–84.

Parales, R.E., Bruce, N.C., Schmid, A., Wackett, L.P., 2002. Biodegradation, biotransformation and biocatalysis. Appl. Environ. Microbiol. 68 (10), 4699–4709.

Patil, P., Desai, N., Govindwar, S., Jadhav, J.P., Bapat, V., 2009. Degradation analysis of Reactive Red 198 by hairy roots of *Tagetes patula* L. (Marigold). Planta 230 (4), 725–735.

Priya, E.S., Selvan, S.P., 2014. Water hyacinth (*Eichhornia crassipes*) – an efficient and economic adsorbent for textile effluent treatment – a review. Arab. J. Chem. http://dx.doi.org/10.1016/j.arabjc.2014.03.002.

Rai, M.S., Bhat, P.R., Prajna, P.S., Jayadev, K., Rao, P.S.V., 2014. Degradation of malachite green and congo red using *Aloe barabadensis* mill extract. Int. J. Curr. Microbiol. Appl. Sci. 3 (4), 330–340.

Rajaguru, P., Kalaiselvi, K., Palanivel, M., Subburam, V., 2000. Biodegradation of azo dyes in a sequential anaerobic-aerobic system. Appl. Microbiol. Biotechnol. 54, 268–273.

Raskin, I., Ensley, B.D., 2000. Recent developments for in situ treatment of metal contaminated soils. In: Phytoremediation of Toxic Metals: Using Plants to Clean Up the Environment. John Wiley and Sons Inc., New York.

Raskin, R.D., Salt, D.E., 1997. Phytoremediation of metals: using plants to remove pollutants from the environment. Curr. Opin. Biotechnol. 8 (2), 2–6.

Reddy, D.H.K., Lee, S.M., 2012. Water pollution and treatment technologies. J. Environ. Anal. Toxicol. 2 (5), 103–104.

Research priorities for earth science and public health, 2007. Exposure pathways. In: Earth Materials and Health: Research Priorities for Earth Science and Public Health, The National Academies Press, Washington D.C., USA, pp. 63.

Rizwana, M., Darshan, M., Nilesh, D., 2014. Phytoremediation of textile waste water using potential wetland plant: ecosustainable approach. Int. J. Interdiscip. Multidiscip. Stud. 1 (4), 130–138.

Robinson, T., McMullan, G., Marchant, R., Nigam, P., 2001. Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. Bioresour. Technol. 77 (3), 247–255.

Samanta, A.K., Agarwal, P., 2009. Application of natural dyes on textiles. Indian J. Fiber Textile Res. 34, 384–399.

Sandhaya, S., Padmavathy, S., Swaminathan, K., Subrahmanyam, Y.V., Kaul, S.N., 2005. Microaerophilic–aerobic sequential batch reactor for treatment of azo dyes containing simulated wastewater. Process Biochem. 40, 885–890.

Satar, R., Husain, Q., 2009. Phenol-mediated decolorization and removal of disperse dyes by bitter gourd (*Momordica charantia*) peroxidase. Environ. Technol. 30 (14), 1519–1527. http://dx.doi.org/10.1080/09593330903246432.

Schwarzenbach, R.P., Escher, B.I., Fenner, K., Hofstetter, T.B., Johnson, C.A., von-Gunten, U., Wehrli, B., 2006. The challenge of micropollutants in aquatic systems. Science 313, 1072–1077.

Selvam, K., Swaminathan, K., Keo-Sang, C., 2003. Microbial decolourization of azo dyes and dye industry effluent by *Fomes lividus*. World J. Microbiol. Biotechnol. 19, 591–593.

Sen, S., Demirer, G.N., 2003. Anaerobic treatment of real textile wastewater with a fluidized bed reactor. Water Res. 37, 1868–1878.

Shah, M.P., Patel, K.A., Nasir, S.S., Darji, A.M., 2013. Isolation, identification and screening of dye decolorizing bacteria. American J. Microbiol. Res. 1 (4), 62–70.

Shah, R.A., Kumawat, D.M., Singh, N., Wani, K.A., 2010. Water hyacinth (*Eichhornia crassipes*) as a remediation tool for dye-effluent pollution. IJSN 1 (2), 172–178.

Sheoran, V., Sheoran, A., Poonia, P., 2011. Role of hyperaccumulators in phytoextraction of metals from contaminated mining sites: a review. Crit. Rev. Environ. Sci. Technol. 41, 168–214.

Sigua, G.C., Holtkamp, M.L., Coleman, S.W., 2004. Assessing the efficacy of dredged materials from Lake Panasoffkee, Florida: implication to environment and agriculture. Part 2: pasture establishment and forage quality. Environ. Sci. Pollut. Res. 11 (6), 394–399.

Singh, K., Arora, S., 2011. Removal of synthetic textile dyes from wastewaters: a critical review on present treatment technologies. Cri. Rev. Environ. Sci. Technol. 41, 807–878.

Singh, P., Iyengar, L., Pandey, A., 2012. Bacterial decolorization and degradation of azo dyes. In: Singh, S.N. (Ed.), Microbial Degradation of Xenobiotics. Springer, Heidelberg Dordrecht London New York, pp. 101–131.

Sinha, R.K., Herat, S., Tandon, P.K., 2007. Phytoremediation: role of plants in contaminated site management. In: Singh, S.N., Tripathi, R.D. (Eds.), Environmental Bioremediation Technologies. Springer-Verlag, Berlin Heidelberg, pp. 315–330.

Stolz, A., 2001. Basic and applied aspects in the microbial degradation of azo dyes. Appl. Microbiol. Biotechnol. 56, 69–80.

Sudarjanto, G., Lehmann, B.K., Keller, J., 2006. Optimization of integrated chemical–biological degradation of a reactive azo dye using response surface methodology. J. Hazard. Mater. 138, 160–168.

Sureshvarr, K., Bharathiraja, B., Jayakumar, M., Jayamuthunagai, J., Balaji, L., 2010. Removal of azo dye compounds from paper industries wastes using phytoremediation methodology. Int. J. Chem. Sci. 8 (1), 687–700.

Tangahu, B.V., Abdullah, S.R.S., Basri, H., Idris, M., Anuar, N., Mukhlisin, M., 2011. A review on heav ymetals (As, Pb and Hg) uptake by plants through phytoremediation. Int. J. Chem. Eng. 201, 1–31.

Tantak, N.P., Chaudhari, S., 2006. Degradation of azo dyes by sequential Fenton's oxidation and aerobic biological treatment. J. Hazard. Mater. 136, 698–705.

Telke, A.A., Kagalkar, A.N., Jagtap, U.B., Desai, N.S., Bapat, V.A., Govidwar, S.P., 2011. Biochemical chracterization of laccase from hairy root culture of *Brassica juncea* L. and role of redox mediators to enhance its potential for the decolorization of textile dyes. Planta 234, 1137–1149.

Torbati, S., Movafeghi, A., Khataee, A.R., 2015. Biodegradation of C.I. Acid Blue 92 by *Nasturtium officinale*: study of some physiological responses and metabolic fate of dye. Int. J. Phytoremediation 17, 322–329.

Uera, R.B., Paz-Alberto, A.M., Sigua, G.C., 2007. Phytoremediation potentials of selected tropical plants for ethidium bromide. Environ. Sci. Pollut. Res. 14 (7), 505–509.

Vafaei, F., Movafeghi, A., Khataee, A.R., Zarei, M., Lisar, S.S.Y., 2013a. Potential of *Hydrocotyle vulgaris* for phytoremediation of a textile dye: inducing antioxidant response in roots and leaves. Ecotoxicol. Environ. Safety 93, 128–134.

Vafaei, F., Movafeghi, A., Khataee, A., 2013b. Evaluation of antioxidant enzymes activities and identification of intermediate products during phytoremediation of an anionic dye (C.I. Acid Blue 92) by pennywort (*Hydrocotyle vulgaris*). J. Environ. Sci. 25. http://dx.doi.org/10.1016/S1001-0742(12)60306-4.

Vijaya, P.P., Sandhya, S., 2003. Decolorization and complete degradation of methyl red by a mixed culture. Environmentalist 23, 145–149.

Vörösmarty, C.J., McIntyre, P.B., Gessner, M.O., Dudgeon, D., Prusevich, A., Green, P., Glidden, S., Bunn, S.E., Sullivan, C.A., Liermann, C.R., Davies, P.M., 2010. Global threats to human water security and river biodiversity. Nature 467, 555–561.

Wathakar, A.D., Khandare, R.V., Kamble, A.A., Mulla, A.Y., Govindwar, S.P., Jadhav, J.P., 2013. Phytoremediation potential of *Petunia grandiflora* Juss., an ornamental plant to degrade a disperse, disulfonated triphenylmetnae textile dye Brilliant Blue G. Environ. Sci. Pollut. Res. 20, 939–949.

Watharkar, A.D., Rane, N.J., Patil, S.W., Khandare, R.V., Jadhav, J.P., 2013. Enhanced phytoremediation of Navy Blue RX dye by *Petunia grandiflora* Juss, with augmentation of rhizospheric *Bacillus pumilus* strain Pgj and subsequent toxicity analysis. Biosour. Technol. 142, 246–254.

Wuhrmann, K., Mechsner, K.L., Kappeler, T., 1980. Investigation on rate determining factors in the microbial reduction of azo dyes. Eur. J. Appl. Microbiol. 9, 325–338.

Wang, X., Cheng, X., Sun, D., Qi, H., 2008. Biodecolorization and partial mineralization of Reactive Black 5 by a strain of *Rhodopseudomonas palustris*. J. Environ. Sci. 20, 1218–1225.

You, S., Damodara, R.A., Hou, S., 2010. Degradation of Reactive Black 5 dye using anaerobic/aerobic membrane bioreactor (MBR) and photochemical membrane reactor. J. Hazard. Mater. 177, 1112–1118.

Zheng, Z., Levin, R.E., Pinkham, J.L., Shetty, K., 1999. Decolorization of polymeric dyes by a novel *Penicillium* isolate. Process Biochem. 34, 31–37.

Zheng, Z., Shetty, K., 2000. Azo dye-mediated regulation of total phenolics and peroxidase activity in thyme (*Thymus vulgaris* L.) and rosemary (*Rosmarinus officinalis* L.) clonal lines. J. Agric. Food Chem. 48 (3), 932–937.

Zille, A., Górnacka, B., Rehorek, A., Cavaco-Paulo, A., 2005. Degradation of azo dyes by *Trametes villosa* laccase over long periods of oxidative conditions. Appl. Environ. Microbiol. 71 (11), 6711–6718.

Zille, A., Ramalho, P., Tzanov, T., Millward, R., Aires, V., Cardoso, M.H., Ramalho, M.T., Gübitz, G.M., Cavaco-Paulo, A., 2004. Predicting dye biodegradation from redox potentials. Biotechnol. Prog. 20, 1588–1592.