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Potential process implicated in bioremediation of textile effluents: A review

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ABSTRACT

Today aqua pollution is one of the major global threats. Untreated industrial effluent discharged into ecosystems pose a serious problem to the aqua living organism, plants and human beings. Among pollution causing industries, textile industry accomplish a major attention by environmentalists due to consumption of large volume of water, dyes and chemicals for various processing of textiles. Textile effluents contain carcinogenic aromatic amines, dyes, organic and inorganic materials. Removal of colored compounds from textile industry effluents by physico-chemical and biological methods is currently available. Biological decolorization of dye effluent is receiving much consideration due to cost effective and less regeneration by microorganisms such as bacteria, fungi, actinobacteria, yeast, algae, and plants. Recent promising research on biological decolorization of textile effluent has showed that variety of microorganisms and plants capable of decolorizing wide range of anionic and cationic dyes. This review article deals with the most deliberate part on the effects of various parameters like pH, temperature and dye concentrations and the dye removing efficiency of fungi and bacteria through biodegradation and biosorption mechanism performance. Current status and achievements of biological decolorization and remediation of textile dye effluents, in last few decades is briefly discussed in this article.

Keywords: Textile Dye, Biodegradation, Biosorption, pH, Temperature, Enzymes and bioreactor

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INTRODUCTION

Environmental pollution was caused by release of various chemicals as a consequence of industrial progress which has now become a persistent environmental contaminant. Due to rapid industrialization and urbanization a lot of chemicals including dyes, pigments and aromatic molecular structural compounds were extensively used for several industrial applications such as textiles, printing, pharmaceuticals, food, toys, paper, plastic and cosmetics are manufactured and used in day-to-day life [1].

Textile dyes were classified as azo, diazo, cationic, basic, anthraquione and metal complex based, depending on the nature of their chemical structure [2]. There are more than 100,000 commercially available dyes with over 7 x 10^5 tons of dyestuff produced annually [3,4]. Around 8000 chemical products associated with the dyeing process are listed in the Colour Index (Society of Dyers and Colourists 1976). Chemical structure of the dyes was resistant to fading on exposure to light, water and many chemicals [5].

Discharge of colored effluents from dye manufacturing units and textile processing industries was produced by various textile industry process. The production of high amount of effluents mixes into water leading to pollution of aquatic systems and represent major environmental problems [7]. Color was one of the most obvious indicators of water pollution and discharge of highly colored synthetic dye effluents can damage the receiving water bodies [8]. Colored wastewaters associated with the reactive azo dye constitute approximately 30% of the total dye market.

Amount of dyes in water (less than 1ppm for some dyes) was highly visible and affects the aesthetic merits of water transparency and gas solubility in lakes, rivers and other water bodies. The strong color of textile effluent even at below 1 ppm creates a huge impact on the aquatic environment due to its turbidity, high pollution strength and dye concentrations ranging from 10 -200mg/l. About 10-20% of the dye present in effluent along with organic and inorganic accessory chemicals involved in the dyeing process [2, 9] .

Dyeing industry effluent alters the color and quality of the water bodies has been proved to be hazardous to aquatic ecosystem and it reduces the sunlight penetration which is essential for photosynthesis, it leads to toxicity of fish and mammals. They also inhibit the activity and growth of microorganisms [9,10, 2]. Dyes having higher stability under sunlight and resistance to microbial attack and temperature were identified [11]. The presence of dyes or their degraded products in water will also cause human health disorders such as nausea, hemorrhage, ulceration of skin and mucous membranes. The presence of such toxic compounds also resulted into severe damage to kidney, reproductive system, liver, brain and central nervous system. The environmental and health concern of these potentially carcinogenic pollutants present in textile waste waters has drawn the notice of many workers.

Many dyes were known as carcinogens, such as benzidine and other aromatic components all of which might be reformed as a result of microbial metabolism. It has been already well documented that azo and nitro-compounds were reduced in the sediment and intestinal environment, resulting in the regeneration of the parent toxic amines this compound was not readily removed by typical microbial based waste treatment processes. The highest rates of toxicity were observed for basic, diazo and direct dyes [12]. Some algae and higher plants exposed to effluent rich in disperse dyes at higher concentration have a tendency to bioaccumulate the heavy metal ions from textile effluents. They contaminate not only the environment but also transform the toxicity through the entire food chain, leading to biomagnification. Dye waste water discharged from textile and dye stuff industries containing wide range of chemicals are listed (Table 1). Government legislation was becoming more stringent in most developed countries regarding the removal of dyes from industrial effluents, which in turn is becoming an increasing problem for the textile industries. Most textile industries were developing onsite or implant facilities to treat their own effluent before discharge was fast forthcoming reality [46]. Various techniques have been employed for the treatment of dye metal bearing industrial effluents, which usually come under two broad divisions: abiotic and biotic methods.

Table 1: Various organic and inorganic pollutants and its range in the textile industry raw effluent

S.No	Parameter	Raw effluent
1	Chemical oxygen demand (mg /l)	1,512
2	Biochemical oxygen demand (mg/l)	90.64
3	Surfactants (mg/l)	1.1
4	Color (A559)	1.202
5	pH	10.5
6	Conductivity (mV)	109
7	Hardness (mg/l as $CaCO_3$)	86.5
8	Cyanide (mg/l)	0.2
9	Sodium	70%
10	Phenolyc compounds (mg/l)	0.077
11	Total iron (mg/l)	0.77
12	N-nitrate (mg/l)	2.0
13	Sulfate (mg/l)	345.3
14	Phosphate (mg/l)	12
15	Fluoride (mg/l)	0.64
16	Aluminum (mg/l)	<0.01
17	Arsenic (mg/l)	<0.2
18	Barium (mg/l)	<0.01
19	Boron (mg/l)	<2.0
20	Cadmium (mg/l)	<0.0006
21	Chromium (mg/l)	<0.005
22	Cobalt (mg/l)	<0.007
23	Copper (mg/l)	0.2
24	Lead (mg/l)	<0.02

Conventional Methods

Physical and Chemical methods encompass of flocculation, electrochemistry, ozonation, bleaching, membrane filtration, irradiation and adsorption of activated carbon are commonly used for the treatment of industrial effluents. Classification of physical and chemical treatment methods were highly specific and uneconomical but very effectual. Various types of physical and chemical methods are used in industries.

Different and complicated molecular structures of dyes makes effluent difficult to be treated by conventional physical and chemical process such as coagulation, precipitation, adsorption by activated charcoal, oxidation by

zone, advanced oxidation process, ionizing radiation, ultra filtration and heterologous photocatlytic treatment. These methods are expensive, less efficient and limited application generating wastes which are difficult to dispose. Typical techniques include the classical methods such as adsorption, coagulation, filtration and sedimentation. Although all these techniques were very versatile and useful, they all end up in producing a secondary waste product which needs to be tackled further [13, 147, 148].

Traditional physical and chemical treatments applied for the purification of dyeing wastewater include adsorption with inorganic (mainly, activated carbon materials) and organic supports, coagulation by lime, aluminum or iron salts, filtration and ion exchange. Table 2 depicts the merits and demerits of various physical and chemical methods involved in dye decolourization of industrial effluents. These procedures direct effective decolorization but their application was restricted due to formation of sludge or by the need to regularly regenerate the adsorbent materials. Use of these methods was not completely accepted at present because they are quite expensive and have many operational problems [11]. The main drawback in the implementation of aforementioned techniques was impossible due to high cost, low efficiency and inapplicability to a wide variety of dyes. Other techniques involve chemical oxidation using sodium hypochlorite to remove the color. However, releasing a lot of aromatic amines is carcinogenic otherwise these toxic compounds subsequently aggravate the problem.

Table 2 Various physical chemical treatment methods of textile industry effluent and their merits and demerits

Physical and chemical treatment methods	Merits	Demerits
1. Coagulant/ Flocculants	Simple, economically feasible	High amount sludge production, handling amount and disposal problems, high amount chemicals required for PH adjustment.
2. Membrane separation	All chemical class dye types decolorized	High pressure, expensive, sludge generation incapable for large scale treatment.
3. Ion exchange	Effective with no loss of regeneration.	Regeneration is possible economic constraints, not effective for dispense dye.
4. Oxidation	Rapid and efficient process	High energy cost, chemical required, by products production.
5.Advanced Oxidation process	No sludge production, little consumption of chemicals, efficiency for recalcitrant dyes.	Economically unfeasible.
6. Adsorption on activated carbon	Effective one, high capacity.	Ineffective against disperse and vat dye, regeneration is expensive loss of absorbent.
7. Fenton's reagent	Efficient decolourization for both soluble and insoluble dyes.	Solid waste production, expensive one.
8. Ozonation	No toxic metabolites complete COD, colour removal, applied in gaseous state.	Short half life, stability affected by ancillary chemicals expensive.
9. Photo chemical	No sludge production, foul odours are not produced	Secondary pollutants.
10. Electrochemical destruction	No consumption of chemicals and no sludge production no secondary pollutants.	High amount of electricity required.
11. Irradiation	Efficient in laboratory level and low volumes only.	Sufficient quantities of DO required
12. Electro kinetic coagulation	Excellent removal of direct dyes, economic	Sludge generation, poor result with acid dyes.

Source: Robinson et al. (2001)

Physical and chemical methods of dye removal are effective only if the effluent volume was small, the stability and xenobiotic nature of reactive azo dyes are not totally degraded by conventional wastewater treatment processes that involve light, chemicals or activated sludge. Therefore innovative treatment technologies need to be investigated for textile effluent treatment. On this basis biological remediation of untreated textile effluent is an emerging technology and studied elaborately by environmentalists. Biological treatment of textile effluents may be either aerobic, anaerobic or a combination of both depending on the type of microbe being employed [7]. Microbial decolorization and degradation was an ecofriendly and cost competitive alternative methodology to chemical decomposition processes. Many microorganisms belonging to different taxonomic groups of bacteria, fungi and actinomycetes and algal have been reported for their ability to decolorize the dyes [15].

Bioremediation of Textile Effluent through Biodegradation

Biological treatment methods using bacterial and fungal decolorization, adsorption by bacterial and fungal biomass are represented in Table 3. Bioremediation systems was commonly applied in the treatment of industrial effluents using many microorganisms such as bacteria, yeasts, algae and fungi that have capability to accumulate and degrade different pollutants. The accumulation of chemicals and dyes by microbial mass has been termed biosorption[14]. [15] found that dye biosorption or biodegradation by microorganism was judged by the color of cell mat. Phytoremediation was the use of green plants to detoxify or render harmless environmental pollutants the treatment of textile waste water was sustainable for long term, easy to operate and maintain [16]. There were three principle advantages of biological technologies for the removal of pollutants; first biological processes can be carried out in

situ at the contaminated site; second bioprocess technologies are usually environmentally benign (no secondary pollution) and third ex situ method are cost effective.

Recent fundamental work has revealed the existence of wide variety of microorganisms capable of decolorizing wide range of dyes. The use of microorganisms for the removal of synthetic dyes from industrial effluents offers considerable advantages this process was relatively inexpensive, running costs were low and the end products were completely mineralized with no toxicity. Degradation by mixed culture enhances the process since individual strains attack the dye molecule at different positions or may use decomposed products produced by one strain will be further decomposed by another strain [1,12]. However, it was stressed that the composition of mixed cultures may change during the decomposition process, which interferes with the control of technologies using mixed cultures. Moreover, the efficacy of decomposition considerably depends on the chemical character of the synthetic dye and biodegradation capacity of the microorganism consortium [11].

Decolorization of dyes with pure culture was impractical, as the isolated culture would be dye specific and their application in large scale wastewater treatment plants with a variety of contaminant dyes was not feasible [9,54]. Efficient biodegradation of dyes can be accomplished when catabolic activity of individual strain was complement with each other in a mixed culture community. The other biological treatment method includes bioaccumulation was defined as the accumulation of pollutants by actively growing cells by metabolism and temperature independent and metabolism dependent mechanism steps [3-9].

Textile effluent treatment and decolorization have many difficulties to achieve complete pollutant degradation and dye removal due to wide ranges of pH, salt concentration, temperature, chemical structure and concentration. Based on above mentioned constraints this article reviews the biological remediation of textile effluents research in last few decades reports on progress and highlights the constraints to be research. Biodegradation is a biologically mediated breakdown of chemical compounds when biodegradation was complete the process were called mineralization i.e. the total breakdown of organic molecules into water, carbon dioxide and/or any other inorganic end products[17]. These processes have potential to mineralize dyes to harmless inorganic compounds like carbon-di-oxide, water and the formation of a lesser quantity of relatively insignificant amount of sludge.

Decolorization and degradation of dyes by mixed as well as pure cultures of bacteria and fungi have been studied under aerobic and anaerobic conditions. In most studies, the microbial consortia have been used and found that more effective than pure cultures. In addition to chemical treatment for textile wastes, several environmental and nutritional factors such as pH, temperature, amount of oxygen, and co metabolic carbon sources were influenced by aerobic biodegradation processes [18].

Table 3 Various biological method of textile industry effluent and their merits and demerits

Biological Method	Merits	Demerits
1. Biodegradation	Economical one, biogas production, under anaerobic treatment, metabolic dependent only.	Mixed culture consortium with combined anaerobic and aerobic treatment system only effectively decolorized. Immobilized cells only efficient than free cells, slow process, environmental parameters, maintenance and continuous nutrition requirements.
2. Biosorption	Metabolism independent, live and dead biomass applicable, economically attractive, high selectivity, low operating cost, no toxic effect on micro organisms.	Large scale treatment still not explored, disposal problem of the dye absorbed biomass, required chemical modification of the dye absorbed biomass.
3. Enzymatic	Effective for selective compounds, immobilized enzymes effective one.	Scale up studies and reaction by products analysis needed, cost of enzymes, stability and enzyme inhibition.
4. Phytoremediation	Dyes with metal removal, plant and indigenous micro flora interaction, soil fertility, plant growth promotion, eco friendly, applicable for large volumes.	Secondary pollution need to study, difficult management during monsoon.
5. Conventional biological treatment with aeration.	Efficient in BOD, COD, and TSS reduction with colour removal.	Low amount of TDS content and toxic heavy metal reduction. In effective for non biodegradable dye stuffs reduction.

Source: Robinson et al. (2001)

Dye Degradation by Bacteria

Bacterial biodegradation of textile dyes is an attractive and inexpensive method. Isolation of new strains or adaptation of existing strain for decomposition of dyes will increase the efficiency of bioremediation. Mechanism involved in color removal by bacteria was absorption or adsorption. Effectiveness of biological treatment system was greatly influenced by the operational parameters such as pH, temperature, dye concentration and nutrients. The influence of each parameter on the color removal process must be optimized to increase dye reduction.

Citrobacter sp. decolorizes several recalcitrant triphenylmethane and azo dyes by adsorption mechanism [19]. Reactive orange 16 was effectively degraded by *Enterococcus faecalis YZ* 66 was evaluated by [145]. Biodegradation of acid orange 7 are facilitated by the presence of organism in the surfaces that have convenient pores to permit microbial growth [20]. The majority research focused on studying the biodegradation/decolorization potential of bacteria. An effluent adapted bacterium was found to be more capable in decolorizing the effluent containing reactive black B dye than the effluent non adapted bacteria [21].

Two bacterial strains *Bacillus cereus* (KEB-7) and *Bacillus pumilus* (KEB-10) decolorize indigo dye were reported by [22]. Decolorization and degradation of orange II containing textile effluent with biodigester sludge from a local municipality waste treatment plant using sulphate reducing bacteria was a cheaper alternative way [23]. Decolourization of textile azo dyes by *Staphylococcus arlettae* strain VN -11 by sequential microaerophilic / aerobic process was shown to be very effective in azo dye decolourization .[24].

Effect of pH

The pH plays a major upshot on the efficiency of dye decolorization, and the optimal pH for color removal was 6-10. Adaptation of microorganisms to varying pH enhances the process of effluent treatment. The optimum pH for color removal was neutral to slightly alkaline and the color removal was decreased rapidly at strongly acid or alkaline pH values. Altering the pH within a range of 7-9.5 have a very little effect on dye reduction process [24].

Enterbacter agglomerans decolorizes 90% of methyl red at pH 5-7 under variable period of incubation, whereas maximum decolourization was attained at pH 7 and 9. This result implies methyl red was easily reduced in acid pH only [25]. Degradation of CI reactive red 195 by *Enterobacter* sp. was good at pH 7, however culture at pH 10 resulted in slight and significantly higher decolourization [26]. *Bacillus subtilis* generally exhibited maximum decolorization of acid blue 113 at pH values near to 7-8 [27]. The effect of pH on *Brevibacillus laterosporus* MTCC2298 for decolorization of navy blue 3G at 30^{o}C at broad range of pH (7-11) was studied by [28]. The effect of pH on removal of remazol black B dye decolorization maximum (96%) was found at pH 7 and 8 after 30 hours of incubation period [29].

Effect of Temperature

The rate of color removal increases with increasing initial temperature. The ambient temperature for color removal was 35-45^{o}C. The optimal temperature enhances the production of enzymes in bacteria for decolorization. Color removal was decreased at higher temperatures due to loss of cell viability or denaturation of the enzymes present in the cell. The effect of temperature 20-50^{o}C on anthraquinone decolorization by salt tolerant bacteria was increased with increase in temperature and the final conversion maintained above 95% [30]. The decolorization of dyes acid orange 10 and disperse blue 79 by *Bacillus fusiformis* kmk 5 was optimum at 37^{o}C [31].

Complete degradation of congo red by *Bacillus* sp. ACT 1 and *Bacillus* sp. ACT 2 was found in the temperature 30-45^{o}C. Controversly if the temperature less than 30^{o}C and greater than 45^{o}C growth was insignificant was stated by [32]. *Bacillus laterosporus* decolorize navy blue 3G at 15 and 45^{o}C respectively [28]. However, it has been shown that whole bacterial cell preparation with azo reductase enzyme was relatively thermo stable and remains active at temperatures 60^{o}C for short periods of time.

Effect of Dye Concentration

The effect of dye concentration strongly influences the rate of dye removal and also impacts the toxicity of dye molecule. Percentage of dye removal increased with increase in time irrespective of initial dye concentration. Decline in the decolorization rate due to toxicity of the dye to bacteria it mainly inhibit the metabolic activities or inadequate biomass concentration for the uptake of higher concentration of dye. Decolorization activity of *Bacillus subtilis* was studied for acid blue 113 at different dye concentrations varying from 50-300 mg/l. The rate of decolorization increased with increase in dye concentration up to 200mg/l [27]. Azo dye navy blue 3G decolorization by *Brevibacillus laterosporus* MTCC2298 showed 80% dye removal within 48 hour under static condition at the dye concentration of 50mg/l [28].

Bacterial consortium obtained from tanning and textile waste water was reported to bioaccumulate 80% of reactive black B dye with concentration 59.3mg/l in presence of Cr (VI) in 7 days [33].

Effects of Nutrients

Nutrients plays an important role in dye decolorization process, higher amount of nutrients significantly influences the growth of micro organism and enhance the degradation of dyes in aqueous solution. *Pseudomonas* sp. BSP-4 isolated from azo dye contaminated soil capable to decolorize azo dye black E by utilizing it as nitrogen source up to 300 ppm in 36 hours [34]. *Enterobacter agglomerans* decolorize methyl red in the presence of 1, 2 and 4% of

glucose where as in absence of glucose the rate of decolourization of methyl red by *Enterobacter agglomerans* was less only [35]. Similarly *Pseudomonas aeruginosa* and *Brevibacillus choshinensis* isolated from effluent decolorize textile effluent in the presence of 10% glucose very effectively within 7 days was reported by [149].

Sodium nitrate present in the media act as nitrogen source and enhance the decolourization of malachite green and methyl orange was observed by [36]. *Citrobacter* sp. strain KCTC 18061 showed 70% decolorization of textile effluent within 5 days along with 1% glucose. On the other hand there is no significant effect on color removal of dye effluent in the presence of 1% nitrogen source yeast extract, tryptone and peptone [37].

Dye Degradation by Fungus

Fungus was capable for oxidizing different chemical compounds and degrading several dyes, including azo dyes and mineralizing persistent aromatic pollutants. The ability of fungus to degrade diverse group of compounds depends upon the nonspecific ligninolytic enzymatic system containing lignin peroxidase, manganese peroxidase and laccase. The degradation and mineralization of dyes by white rot fungi was widely studied. The fungus *Geotrichum* sp. CCMI 1019 has ability to decolorize large amounts of dyes like reactive black 5, reactive red 158 and reactive yellow 27 [18, 38, 39].

In the case of *Phanaerochaete chrysoporium* a ligninolytic fungus preadapted to the medium and degrade the azo benzene constitute of azo dye for aromatic ring cleavage [40]. Textile industry waste water has been decolorized by production of manganese dependent peroxidase (MnP), lignin peroxidase (Lip) and laccase which are the enzymes of white rot fungus *Irpex lacteus* in stationary cultures without adding any chemicals [41].

Effect of pH

pH of dye affects the growth of fungus and dye decolorization process. Majority of the fungi grow only in acidic pH. Almost all fungal dye decolorization studies showed that higher dye removal rate take place in acidic pH range. Acidic pH range has considered as optimum pH for fungal dye decolorization process.

The decolorization of textile dye by *Aspergillus fumigatus* XC6 and it shows decolorization over a pH range of 3-8 using dyes as sole carbon and nitrogen source was examined by [42]. Remazol brilliant blue R (RBBR) dye decolorization was maximum in pH 7, above which it slightly decreased was reported by [43]. The concept of fungal growth and dye decolorization usually occurs at low pH values, and it was clearly supported by *Aspergillus niger* and *Pencillium* sp. decolorization of both reactive and direct dye solution, at pH 4.5 and 4 [44]. The pH increased from high acidic conditions pH 3 to pH 4 decolorization of orange II dye increased and maximum removal of color (86-34%) was observed at pH 5 was stated by [45].

Effect of Temperature

Temperature mainly influences the fungal dye degradation system and fungal growth pattern. Based on the growth temperature, higher dye degradation rate present up to 35-40^{o}C latter dye decolorization process decreased due to decline phase of fungal growth occur. *Aspergillus niger* dye decolorization studies showed reduction of direct dye both at 28^{o}C and 35^{o}C respectively, also with *Penicillium* sp. the maximum color removal at temperature 35^{o}C [44]. The effect of temperature on growth by incubating the cultures at various temperatures (25-40^{o}C), for crystal violet and malachite green attained maximum decolourization at 30^{o}C [47]. The results in this report agree with [48] who showed the optimum temperature for decolorization of crystal violet by *shewanella* sp. NT0Vl at 30-40^{o}C. Similar results were obtained by [49] reported that 28^{o}C was the optimum temperature for RBBR decolorization by nonlignolytic fungus *Myrothecium* sp. IMER1. Orange II dye decolorization activity of *Phanaerochaete chrysosporium* was found to increase with increase in incubation temperature from 24-30^{o}C [45].

Effect of Dye Concentration

Growth of fungi was affected by the presence of high concentration of dye. [50] reported the maximum dye stuff (turquoise blue G, phthalocyanin dye) concentration tolerated by *C.versicolor* was 1200mg/l. Decolorization efficiency was high if dyestuff concentrations were 100-250mg/l (in 3-5 days) and nearly 700-1200mg/l (9 days). It indicates decolorization of dye decreases with increasing dye concentration. [51] observed decolorization of reactive blue 25 by *Aspergillus ochraceus* NCIM-1146 take more time to decolourize at increased dye concentration. The effect of dye concentration on decolorization of orange II by *Phanerochaete chrysosporium*, keeping other operational parameters constant (temp 30^{o}C and pH5), for 50 and 100mg/l concentration of dye removal was almost same but as concentration increased, removal of dye started to decrease [45].

Effect of Nutrients

Nutrient constituent in the medium have marked effect on color removal along with natural supplements had a positive impact on dye decolorizaiton. *Aspergillus fumigatus* XC6 supplemented with the various carbon and

nitrogen sources particularly ammonium sulphate had significant effect on effluent color reduction [42]. The effect of carbon and nitrogen sources in amaranth dye decolorization, by *Ganoderma* sp. WR-1 was studied. Starch and yeast extract was the best nutrients for amarnath dye decolorization in 8 hour [46]. Similarly [47] showed starch was the best carbon source for crystal violet decolorization by *Fusarium solani*. In case of malachite green, glucose and sodium nitrite favored the dye decolorization. The decolorization of vat dyes by *Coriolus versicolor* maximum decolorization of cibacron blue only by starch. In addition they proved that all the nitrogen sources were found to inhibit the laccase activity and dye decolorization [52].

[53] found that urea as nitrogen source resulted in decolorization of textile dye by *Aspergillus niger*. Congo red dye decolorization studies showed that glucose and starch provided the highest decolorized zones in diameter. In nitrogen sources urea and yeast extract showed higher decolorization activity [22].

Bioremediation of Textile Effluent through Biosorption

The uptake or accumulation of chemicals by microbial mass has been termed as biosorption. It was mainly taking place in the cell wall, where as the mechanism includes adsorption and absorption will differ according to the biomass type [53, 55]. Both bacterial and fungal cells were reported for their capability for partial or complete removal of dyes by using adsorption. Not all dyes adsorb to a particular type of biomass. Eventhough, some fungi decolourize dye by but in white-rot fungi both adsorption and degradation can occur simultaneously or sequentially [50]. Biosorption was not a practical approach for treating industrial effluents because of the problems associated with disposal of the large volumes of biomass after biosorption [18].

Bacterial Biosorption

Since the bacteria were widely used in different food and pharmaceutical industries they were generated as waste, which can be attained free or at low cost from these industries. Due to the cell wall constituents of bacteria such as peptidoglycan and the role of functional groups, such as carboxyl, amine and phosphonate, many bacteria have been found to bind with variety of dye classes. The binding mechanisms as well as the parameters influencing the passive uptake of dyes from textile effluents were pH, temperature and dye concentrations [53].

Effect of pH

pH of dye solution plays a major role in biosorption and affects the interaction of dyes with biomass. Different dye classes require different pH ranges, basic dyes require conditions, where as reactive dyes demand strong acidic conditions for their optimum biosorption. [57]. Influence of pH on the biosorption of the reactive dye using the simulated remazol effluent at pH 5 was identified by [58]. *Corneybacterium glutamicum* was a potent biosorbent and extremely dependent on the pH of the dye solution. Effective pH for biosorption of reactive red 4 at pH 1. The decarboxylated *C.glutamicum* performed well in the decolorization of the effluent within the pH range of 2-5 with maximum decolorization was observed in pH less than 5 [54, 57]. Reactive dye adsorption decreases with increases in the pH above 5 require pretreatment of raw biomass to make effective biosorption [60-62]. The pH was found to affect the biosorption capacity and it shows acidic condition exhibit higher dye uptake rate [63].

The waste biomass of *C.glutamicum* evaluated as a potential biosorbent for the treatment of reactive orange 16 was extremely dependent on the pH variation [64].

Effect of Temperature

Temperature was found to affect biosorption only to a lesser extent within the range of 20-35^{o}C [65]. Higher temperature usually enhances sorption due to the increased surface activity and kinetic energy of the solute [66]. However the exothermic nature of some adsorption processes, increase in temperature has been found to reduce the biosorption capacity of the biomass [67]. Temperature was well known to play an important role in both uptake of metal ions and dye ions by microorganisms. Effect of temperature on the adsorption of dye has been studied over a range of 25-45^{o}C by thermophilic Cyanobacteria *Phormidium* sp. and decline in sorption capacity with increase in temperature above 45^{o}C [68].

Effect of Dye Concentration

The initial dye concentration seems to have impact on biosorption if increased concentration results in high solute uptake. However at higher concentration the sites available for sorption become fewer compared to the moles of solute present, hence the removal of solute was strongly dependent upon the initial solute concentration [66].

Acid anthraquinone TB4R dye decolorized by three strains of bacteria such as *Bacillus gordonale*, *Bacillus benzeovorans* and *Pseudomonas putida* biosorbe the dye up to 200-1000mg/l. The total color removed during calculation of the initial reaction rate than recalculated for michaelis-menten kinetics indicates that the enzyme does not bind to the substrate firmly and reaction strongly dependent on the dye concentration within each system [69].

Fungal Biosorption

Fungal biosorption was identified by binding of solute to the biomass by processes which do not involve metabolic energy or transport, although such processes may occur simultaneously where live biomasses were used. Therefore, it can occur in either living or dead biomass [70]. Dead cells remove dyes through the mechanism of biosorption which involve physico-chemical interactions such as adsorption, deposition and ion exchange. In case of *Aspergillus niger* different functional groups in the fungal biomass play different roles in biosorption of different dyes [71]. Consortium containing *Aspergillus flavus, Aspergillus wentti, Basidiomycetes and Acremonium* kiliense act as biosorbent and effectively decolorize wide range of dyes was reported by [146]. Use of certain low cost adsorbents for dye removal has been extensively reviewed [72]. Waste fungal biomass which was a byproduct of industrial fermentation can be used as a cheap source of biosorbent [73]. Amino, carboxyl, thiol and phosphate groups present in the fungal cell wall were responsible for binding of dye molecules [74]. Dye molecule biosorption onto cell surface appears to be a quick process and often completes in a matter of hours [75].

Effect of pH

The pH of the effluent influences the chemistry of dye molecule and fungal biomass. Biosorption capacity of fungal biomass for acidic dye increases with decreases in pH and for basic dyes increases with increase in pH [76]. The fungal cell wall was composed of polysaccharides, proteins, lipids, melanin along with several functional groups capable of binding to dye molecules [76,77]. It was expected that amino groups of the fungal cell wall compounds will also be protonated at acidic pH values. Higher dye uptake obtained at lower pH values may be due to the electrostatic attraction between negatively charged dye anions and positively charged cell surface [78-80]. It was supported by [71] that biosorption of basic blue 9, acid blue 29, congo red and disperse red 1 by *Aspergillus niger* biomass could decreased at final pH 6.

Biosorption of methyl violet, basic fuchsin and their mixture using dead fungal biomass of *Aspergillus niger*, while maximum sorption for basic fuchsin was seen at pH 6 and for dye mixture, maximum sorption was seen at pH 5 and it confirmed sorption was independent of pH [81]. Reactive blue 4 dyes were maximum biosorped by *Phanerocheate chrysoporium* was observed at pH 3 [73]. The optimum pH for dye biosorption by loofa sponge immobilized fungal biomass (LSIFB) and free fungal biomass (FFB) on the removal of remazol brilliant blue R (RBBR) dye. The maximum uptake of RBBR was found at pH 2 for FFB and LSIFB respectively and then declined sharply with further increase in pH [82-84]. Higher biosorption of acid violet dye at pH 5.7 using native biomass of *Penicillium* sp was showed by [85]. Dried *Neurospora crassa* showed higher biosorption capacity on burazol blue ED dye, the optimum pH was determined as 1 [86]. This result was coordinated by [87].

Effect of Temperature

Versatile textile dye effluent was produced at relatively high temperature therefore temperature was an important factor for the real application of the fungal biosorption. Fungal biomass has capable of removing dye at higher temperature due to increased surface activity sites and increased kinetic energy of dye molecules. *Rhizopus nigricans* exhibited very high adsorption of selected dyes, (50mg/l) concentration at 20^{o}C and it shows increasing the temperature from 30 to 40^{o}C have different effectswas reported by [88]. Temperature significantly affected rate of dye adsorption based on the different dyes present in dye solution. *Aspergillus foetidus* biomass was very efficient in decolorizing solution containing RB5 dye or mixture of dyes, composite and industrial effluent. The sorption capacity was strongly dependent on the temperature and increase significantly with increase in temperature from 30-50^{o}C [89]. Biosorption capacity of acid violet dye by *Penicillium* sp. at temperature was 35^{o}C were examined by [85]. Biosorption capacity of *Aspergillus bisporus* increased from 31.31 to 33.07 g/l of acid red 44 dye when the temperature was increased from 20-40^{o}C [90]. Majority of these reports indicate that biosorption capacity of the fungal biomass increases with increase in temperature.

Effect of Dye Concentration

Dye concentration of dye solution also influences the removal of dye from aqueous solution by fungal biomass. Sorption capacity increased in higher initial dye concentration and provides an important driving force to overcome all mass transfer resistance of the dye between the aqueous and solid phases; thus increase the uptake of dye. Depending on the chemistry of the different dyes and the binding capacity of the biomass, the adsorption percentage varied for fungal biosorption. This might be due to the saturation of the available binding sites on the biosorbent [87]. Adsorption of dyes to the mycelium did not contribute to microbial decolorization since a maximum of 1.5% of indigoid, azo and anthraquinonic dyes added was bound to the mycelium except for basic red 9, for which 7% of the dye had bound to the mycelium after incubation of 6 days [91]. Adsorption of remazol blue, remazol orange and cibacron red using *Rhizopus arrhizus* biomass and increase the uptake capacity of the microbial biomass was 190 and 150 mg/g of dye biomass was investigated by [79].

It should be noted that molecular weight of dye molecules has an important influence on the removal efficiency and biosorption capacity of the biomass [47]. Dye removal were diminished with increasing dye concentration due to nearly complete converge of the binding sites of sorbents at high dye concentration [83]. These results are contrast with [92] that studied the decolorization of dye waste water through fungi by biosorption and bioaccumulation discussed the effect of various dye concentration on the dye removing efficiency of different fungi. The increase in dye concentration increases the rate of decolorization of dye waste waters. [87] reported that the adsorption capacity of non viable *A.niger* was significantly affected by higher dye concentrations of CI direct blue 199, adsorption capacity increased linearly with increasing initial dye concentration from 200 to 400mg/l.

Other Microbial Cultures

The effectiveness of dye decolorization depends on the adaptability and activity of particular microorganisms. Last few decades many microorganisms have been found to be capable of degrading dyes, these include bacteria, filamentous fungi, Yeast, algae, and actinomycetes also have advantages to treat textile waste water. To the present, the use of yeast, actinomycetes and algae in treating textile waste water has been very limited. They not only grow rapidly similar to bacteria, but comparable to filamentous fungi they also have the ability to resist unfavorable environments. Only a few reports on the degradation of textile waste water by these organisms have appeared.

Algae

Several species of *Chlorella* and *Oscillatoria* were capable of degrading azo dyes to their aromatic amines and to further metabolize the aromatic amines to simpler organic compounds. Some were even capable of utilizing azo dyes as their sole carbon and nitrogen source [93]. The biodegradation of azo dyes by the algae (*Chlorella pyrenoidosa*, *C.vulgaris* and *Oscillatoria tenuis*) has also been assessed. According to the data, the azo reductase of the algae was responsible for [94]. In addition, the algae can play a direct role in degradation of azo dyes. *Chlorella vulgaris* have biosorption capacity for several reactive dyes were reported by [95]. Dried *Spirogyra rhizopus* have ability to decolorize acid red 274 dye by both biosorption and biocoagulation process and the removal amounts decreased while the removed concentration of AR 274 dye increased with increasing *S.rhizopus* concentration [77]. The potential of *Cosmarium* sp. belonging to green algae was investigated as a viable biomaterial for biological treatment of triphenylmethane dye and malachite green [96]. Immobilized thermophilic cyanobacterial strain *Phormidium* sp. has good decolorization activity under thermophilic condition [97]. Agitated batch sorption performed on algae *Spirogyra* 102 revealed the ability of test biosorbent to remove azo dye from the aqueous phase at acidic pH 2 at optimized temperature 30^{o}C and dye concentration 5mg/l [98].

Actinomycetes

Actinomycete strains have been reported to decolorize reactive dyes, including anthraquinone, phthalocyanine and azo through adsorption of dyes to the cellular biomass without any degradation. Other Cu based azo dyes, such as formazan-copper complex dyes, were completely decolorized through degradation by the same actinomycete strains [99]. *Streptomyces ipomoea* decolorized azo dyes orange II by production of salt resistant laccase under versatile pH [100].

Yeasts

Yeasts, such as *Klyveronyces marxianus* have capacity to decolorize dyes [101]. Actively growing *Kluyveromyces marxianus* IMB3 yeast cells under aerobic conditions almost completely decolorize remazol black B within 24 hours at various acidic pH values. Maximum colour removal was achieved [102]. [103] Ttwo novel dye decolorizing yeast strains of *Pseudozyma rugulosa* Y-48 and *Candida krusei* G-1, exhibited excellent color removal of reactive azo dye. *Saccharomyces cerevisiae* MTCC463 effectively decolorize methyl red due to biodegradation and it shows different rate of metabolism at different pH with involvement of azo reductase [104]. Biosorption capacity of reactive orange 16 on the dead cells of brewery yeast biomass increased with decreasing initial pH and temperature and pH was found by [105].

Phytoremediation of Textile Effluent

Phytoremediation was the use of vegetation for insitu treatment of contaminated soil, sediments and water. Plants have ability to withstand higher concentration of organic chemicals without toxic effects, and they can absorb and convert chemicals to less toxic metabolites by releasing root exudates, enzymes. The use of engineered metal accumulating plants for environmental cleanup was an emerging biotechnology [2]. The expression of oxidases from higher plants augmented the catabolic potential of microbes [106]. In turn microbial genes straightened the tolerance of higher plant to poly R-487 [107]. Polymeric dye tolerant plants may be useful in phytoremediation because they could provide a rhizosphere suitable for colonization of microbes with efficient degrading potential. The plant derived compounds can induce production of fungal redox enzymes [108]. Initial screening of *M.pulegium* clonal lines MPH-4 indicated that this plant species was a potential candidate for phytoremediation due to its high level of phenolics and its ability to sequester the aromatic pollutant, anthraquinone polymeric dye R-478 [106].

Ten aquatic macrophytes, were screened for tolerance towards textile dye waste waters to raise constructed wetlands for their phytoremediation. Among the 10 species of macrophytes, only *Phragmites* had broad capacity for pH tolerance, growing well in the alkaline, neutral and acidic waster with multiplying rapidly in dye waste water both in the lab as well as field studies [109]. Treatment of synthetic reactive dye waste water by narrow leaved cattails *Typha angustifolia linn* and the maximum color removal at day 14 under the pH condition decreased from 9-8 with various concentration of dye [110]. *P.australis* effectively uses the ascorbate glutathione pathway for the detoxification of AO7 was examined by [111]. Supplementary aeration in up flow constructed wetland reactor facilitate the decolorization, degradation and mineralization of aromatic amines from the reduction of azo dye acid orange 7 (A07) containing waste water [112]. Wild plants of *B.malcolmii* could decolorize the malachite green, red HE4B, methyl orange and reactive red 5B within three days. Decolorization of direct red B induced by lignin peroxidase, azo reductase and riboflavin reductase in the roots and to produce secondary metabolites of dye after phytotransformation [113].

Bioremediation of Textile Effluent using Enzymes

A large number of enzymes from different plants and microorganisms have been reported to play an important role in array of waste treatment applications. The enzymatic decolorization of industrial dyes was a big challenge due to large diversity of chemical structures [114, 115]. Enzymes can act on specific recalcitrant pollutants to remove them by precipitation or transformation to other products [116]. Enzymes offered several advantages such as greater specificity, better standardization, easy handle and store and no dependence on bacterial growth rates [117]. White-rot fungi were able to degrade dyes using lignin peroxidase (LiP) and manganese dependent peroxidase (MnP) [124]. Other enzymes used for this purpose include H_2O_2 producing enzymes, such as glucose-2-oxidase along with laccase and phenoloxidase enzyme [118].

Laccase (benzendiol: oxygen oxido reductases Ec. No.1.10.3.2) was an enzyme that oxidizes a large variety of organic substrates and this enzyme contains multicopper phenolic compounds thereby avoiding the formation of toxic aromatic amines [119]. It was secreted by great number of white rot fungi, such as *Trametes versicolor, Phlebia radiata, polyporus pinisitus* and *Penicillium chrysogenum* over 60 fungal strains from various classes [17]. Various textile dyes have been decolorized by *Trametes hirsuta* laccase to an extent of 80% and showed no general rule in detoxification tendencies [91]. Purified laccase from *Pycnoporus cinnabarinus* has been previously used for the degradation of diazo dye Chicago sky blue [120]. The enzyme was widely distributed in fungi; however its biological function were still not totally clarified [121].

[122] suggested that higher laccase degradation rate correlates with the accessibility of the amine groups, reactive black 5 was hardly decolorized. The marine derived culture NIOCC # 2a with laccase proved to be more efficient in the decolorization of textile effluents and synthetic dyes brilliant green and congo red than the culture NIOCC # 312 having MnP and lip activity. Whereas remazol brilliant blue R and poly R-478 were better decolorized by NIOCC # 312 than NIOCC # 2a [123]. Decolorization of azo dyes by using purified laccase enzyme from *Trametes trogii* exhibit good result was reported by [125]. Regarding bacterial laccase little information was available concerning their substrate specificities towards dye decolorization. Laccase has been reported as an inducible enzyme during degradation of azo dyes by various bacteria [126]. Researches on the function of purified laccase were insufficient and its role in decolorization remains poorly understood.

Peroxidase (E.C.1.11.1.7) was heme-containing enzymes that were widely distributed in plants, microorganisms and animals [127]. [128] stated that decolorization of dye by manganese peroxidase. (Ec.11.1.13) from fungi of different species namely *Debaryomyces polymorphus, Candida tropicalis* and *Umbelopsis isabellin* were tested against the degradation of reactive blue 5 dye it showed effective decolorization. The significance of the manganese peroxidase was proved by *Lentinula edodes* showing decreased activity in the absence of manganese ions and hydrogen peroxide The decreased invitro activity of the dye decolorization confirm the necessity of manganese peroxidase [129]. The manganese peroxidase produced by *Phanerochaete sordida* showed higher range of 90% decolorization of azo and anthraquinone dye [130]. [131] compared the fungal isolates and enzymatic treatment in the degradation of reactive blue 5 dyes. The degrading capacity of the enzyme manganese peroxidase was 1.5 times greater than the fungal isolates.

LiP (Ec.1.11.1.14) also known as ligninase or dirayl propane oxygenase and this enzyme were first reported in 1983. Lignin peroxidase obtained from *Phanerochaete chrysosporium* was effective against methylene blue and azure B dyes [132]. [133] reported the degradation of xyelene cyanol, fuchsine and rhodamine B dye by using lignin peroxidase obtained from *pseudomonas desmolyticum* NC1M2112 coupled with glucose oxidase. The coupling action was effective in the presence of hydrogen peroxide and also improved the efficacy of degradation along with lignin peroxidase. [134] showed that lignin peroxidase obtained from *Acinetobacter calcoaceticus* NCIM 2890 was treated against reactive brilliant red K-2BP showed 85% effective and the dye concentration was about 60 mg/l.

[135] obtained lignin peroxidase from *Acinetobacter calcoecitus* NCIM 2890 and its showed a maximum of decolorizing activity against astrazon red FBL, along with 0.05 % (w/v) of tween 80 was added to the effluent showed 42% removal of COD and 87% of decolorizing activity.

Several microorganisms produce soluble cytosolic enzymes with low substrate specificity which reductively cleaves the azo bond at the expense of a reducing agent, typically NAD(P)H, serving as electron donors for reaction. The occurrences of these enzymes are called as azo reductases. Under anaerobic conditions, such as anoxic sediments many bacteria gratuitously reduce azo dyes by unspecific, soluble, cytoplasmic reductases known as azo reductases. These enzymes were reported to result in the production of colorless aromatic amines which may be toxic, mutagenic and possibly carcinogenic to animals.

Anaerobic degradation of textile dyes yields only azo reduction and mineralization does not occur. Furthermore, azo reductases have been shown to be very specific enzyme thus cleaving only azo bonds of selected dyes [136]. [137] confirmed the decolorization of azo dyes with azo reductases can be enhanced by electron withdrawing groups at the aromatic ring, especially ortho substitutions shows good effect. Azo reductase from thermoalkalophilic *Bacillus* sp. were able to reduce a large structural variety of systematically substituted azo dyes was confirmed by [138]. New DyP (dye decolorizing peroxidase) from *Trametes cucumeris* Dec 1, which decolorized more than 30 types of synthetic dyes. DyP was a main enzyme that degrades azo and anthraquinone dyes [139, 140]. Further DyP from *Trametes cucumeris* Dec 1 was able to decolorize anthraquinone dye reactive blue 5 to light red-brown compounds [137].
VP (Versatile peroxidase) (Ec.1.11.1.16) has been recently described as new family of ligninolytic peroxidases, together with lignin peroxidase and manganese peroxidase obtained from *Phanerochaete chrysosporium* [40]. These enzymes exhibited both lignolytic peroxidase and manganese peroxidase activity and therefore these enzymes were called as hybrid manganese peroxidase-lignin peroxidase or versatile peroxidase. Versatile peroxidase from various sources *Pleurotus pulmonarius* was previously reported [141]. A new versatile peroxidase was identified and purified from an extracellular fluid of novel strain *Bjerkandera* sp. and this enzyme catalyzes the decolorization of RBBR [142]. Recalcitrant dyes could be successfully decolorized by peroxidases in the presence of some suitable redox mediators. Treatment of recalcitrant pollutants by using enzyme-redox mediator system will be significantly useful procedure for targeting number of dyes with diversified structures.

Bioremediation of Textile Effluent using Bioreactor
Bioreactors were the only exsitu bioremediation process, numerous different reactor configurations used in textile wastes treatment. It was classified into aerobic and anaerobic reactor. They are widely used for decolorization and degradation of textile effluent by using biological sources. Several research papers have been published on combined, sequential or integradated anaerobic–aerobic bioreactor treatment of azo dye containing waste water [143]. Various reactor systems used for production of lignin peroxidase or manganese peroxidase by white rot fungi and biological dye decolorization process have been reported. These reactor systems include stirred tank reactors, packed bed bioreactor, airlift reactors or bubble columns, rotating disk reactor, silicone membrane reactor, fixed film reactors, rotating biological contactors, immersion and tray reactor.

Three different reactor configurations (Continuous Packed bed bioreactor, fed batch fluidized-bed bioreactor and continuous fluidized-bed bioreactor) were designed and tested for decolorization of azo dye orange II by white rot fungus. All the bioreactors showed high stable decolorization activity in long-term operation [49]. Anaerobic decolorization of azo dye acid orange 7 (AO7) was studied in continuous up flow stirred packed-bed reactor (USPBR) filled with biological activated carbon (BAC) [144]. The majority of the reactors were designed to retain high biomass in the reactor.

CONCLUSION

The above mentioned methods contain both merits and demerits and the dye degradation depends on the dye character, pH and other ancillary additives. Rapid dye decolorizing microbes need to be isolate (with total colour removal) usage of single cultures in the large scale application and their inability to degrade all different dyes present in the actual effluent was the drawbacks for their commercial application. Therefore the use of mixed culture seems to have more potential for large scale application at field level. The main area to concentrate was not only for color removal instead of that complete degradation and conversion of textile effluent into completely mineralized waste to use as a biofertilizer for the growth of the crops. It is essential to estimate the toxicity with respect to decolorization, because decolorized materials may remain toxic unless the product retains in the cells. Efficient post treatment method such as aerobic treatment methods after decolorization is essential to degrade the aromatic amines which are formed in the anaerobic step/ microaerophilic condition/ anoxic condition. The main goal to achieve complete mineralization of dyes depends upon maintaining the process in which initial decolorization takes place

under microaerophilic/ anaerobic conditions followed by oxidation of the aromatic amines/ secondary pollutants using an aeration step. Anaerobic/ microaerophilic systems could reduce the color intensity more satisfactory than the aerobic processes, however the intermediate products are carcinogenic aromatic amines which need to be further decomposed by an aerobic treatment. The sequential processes of aerobic treatment followed by anaerobic treatment are potential, effective and not have been studied till now. It is very necessary to find out the elaborate enzymatic system responsible for the complete decolorization and degradation of dyes is in urge. Genetic engineering may be useful in bioremediation, genetic engineering of toxic chemical degrading micro organisms is to develop "super bug'' capable of detoxifying or degrading a large number of pollutants they are designing of potential pathway for degradation, development of enzyme system, manipulation of the genes for degradation and putting them in microorganism make them very powerful with bioaugmentation technology. Liquid state fermentation is incapable to remove dyes so in future research mainly concentrates only on adsorption techniques by means of solid state fermentation.Research on degradation of dye by using bacterial biosorption need to be concentrate in future. Degradation of dye is a complex process works to detoxify, decolorize, and degrade the dyes are done in lab scale only. Hence the need of effective complete conversion of textile effluent into useful liquid waste by using microbes is required.

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