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BIO-REMOVAL OF AZO DYES: A REVIEW

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Abstract

Pure aquatic sources are an essential need for a healthy ecosystem and the survival and wellbeing of the diverse species of microbes and macrobes in the enviroment. Synthetic dyes are widely used in textile, paper, food, cosmetics and pharmaceutical industries with the textile industry as the largest consumer. Among all the available synthetic dyes, azo dyes are the largest group of dyes used in textile industry. Textile dyeing and finishing processes generate a large amount of dye containing wastewater which is one of the main sources of water pollution problems worldwide. Several physico-chemical methods have been applied to the treatment of textile wastewater but these methods have many limitations due to high cost, low efficiency and secondary pollution problems. As an alternative to physico-chemical methods, biological methods comprise bacteria, fungi, yeast, algae and plants and their enzymes which received increasing interest due to their cost effectiveness and eco-friendly nature. Biological degradation of azo dyes is considered as an optimum approch for their removal from the environment. It is a green economically viable approach to degrade dyes and effectively reduce their accumulation in the environment.

Keywords: azo dye, microorganism, decolorization, biosorption, enzyme, nanoparticle

Introduction

Dyes are the important industrial coloring chemical compounds. Organic chemicals that own color are known as dyes. Dyes are classified by (i) chromophore 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 [1]. Azo (monoazo, diazo, triazo and polyazo), anthraquinone, triarylmethane and phthalocynine dyes are main groups of dyes. Azo dyes absorb light in the visible region because of their chemical structure, which is characterized by one or more azo bonds (-N=N-) [2]. About 80% of azo dyes are used in the dyeing process of textile industries. They are widely used in the textile, leather, food, paper, cosmetics and pharmaceutical industries. It has been estimated that about 10-15% of the dyes used in dyeing process goes unbound with the textile fibers and are discharged into the environment [3].Release of dye containing effluent derived from various industrial practices into water bodies and surrounding industrial areas is of major concern [4] which have several adverse effects on life including decreased aquatic photosynthesis, ability to exhaust dissolved oxygen and toxic effect on flora, fauna and humans. Presence of dyes in the textile effluent causes an unpleasant appearance by imparting the color and also their breakdown products (colorless amines) are toxic, carcinogenic and mutagenic [5].

TOXICITY OF AZO COMPOUNDS

Azo dyes are compounds with one or more azo groups (-N=N-) linked to an aryl systems which generally has other bonded functional groups as chloro, methyl, hydroxy, nitro, sulphonic acid and its sodium salts etc. These dyes are not basic in aqueous solution due to the limited availability of lone pair of electrons in the -N=N- linked N-atoms of the aromatic azo unit. On reduction aromatic azo dyes give hydrazines and primary amines. Azo dyes are mainly used as colorants and exposure to these compounds may have severe adverse effects and their disposal in the environment results in undesirable ecological changes in the hydro resources, soil and atmosphere. The presence of dyes in the aquatic bodies due to disposal of untreated liquid and solid effluents of textile industries has a negative impact on public health[6]. However the disadvantages of using azo dyes are generally overlooked and they are still extensively used for dyeing fibers because they have good fixative characteristics and are affordable [7].

Considering the health and environment impacts of certain azo dyes their use has been restricted or prohibited by several countries. Many azo dyes induce genotoxic, mutagenic and carcinogenic activity in microorganisms and macroorganisms including mammalian [8-11].

The decay products of azo dyes on prolonged contact with skin or oral cavity are hazardous for human health. Restrictions on the use some azo dyes has been imposed because they release a high concentration of aromatic nitrogenous products such as amines on reductive cleavage of the azo groups.

Some azo dyes have been identified as potential agents for inducing bladder cancer, splenic sarcomas, hepatocellular carcinomas, cell anomalies and chromosome aberrations [12-16]. The toxicity of the azo compounds can be related to the bio-interaction of the dyes or the metabolites formed by the reduction of their azo bond [17] with the cells [18-20].

Azo dyes and substances formed by their disintegration have been tested on living organisms for ascertaining their toxic effects [21-23]. Oral intake of azo dyes by humans may result in the regeneration of aromatic amines by bio or enzyme degradation in the intestinal which may induce carcinogenic reactions [24].

Textile dyes are very extensively used and have diverse impact on the environment and organisms exposed to them. It is important to understand that the toxicological properties of compounds are not structurally related and cannot be attributed to the presence of a similar functional group [25]. Hence the toxicity evaluation of these compounds has to be carefully monitored.

The untreated discharge of azo dyes in water bodies has significant effects on the aquatic environment related to penetration of light and presence of metabolites mainly formed by their degradation under anaerobic conditions [26,27]. Studies investigating the pollution related effects of azo dyes have reported the presence of some azo dyes in certain algae and plants [28] and the adverse effects of effluents containing these dyes on aquatic microbial populations [29]. The release of azo dyes into the environment is dangerous because of the toxic, mutagenic and carcinogenic nature of some of these dyes and of their bio/chemo degradation products [30]. Azo dyes tartrazine and carmoisine which are food colorants have been evaluated and are reported to stimulate oxidative stress [31].

The intensity of mutagenic activity of an azo dye is also dependent on the products formed after the reduction of their azo group. The reduction results in the formation of aromatic amines which may exhibit higher or lesser carcinogenic and/or mutagenic effects relative to the original compound [18]. It has been observed that in many cases the aromatic amines formed are usually more toxic [32-35] and may induce more intense mutagenic and carcinogenic actions [36]. Besides the reductive products of some azo dyes are reported to generate DNA adducts [37,38] which can be toxic for the microorganisms that are useful for the discolourisation of azo dyes [39-42].

Some examples of the effects of azo dyes or their decomposed products are listed below:

- P-dimethylaminobenzene (p-DAB) is reported to be a potential agent for inducing cytotoxic and genotoxic effects in bone marrow cells and spermatozoids of rats [43].
- The azo dye C.I. Pigment Red 53:1 has been reported to be a potential agent for inducing lung tumours in male rats [44].
- C.I. Disperse Blue 291 dye reported to be a potential agent for inducing genotoxicity and mutagenicity in mammalians [45]

The azo dyes PBTA1 and PBTA2 and their precursors are reported to be potential agents for inducing cytotoxiciy in hamster [46].

- The azo dyes C.I. Disperse Red 1 and C.I. Disperse Orange reported to be potential agents for inducing mutagenicity in mammalians .
- Sudan azo dyes are reported to be a potential agents for inducing genotoxic effects, e.g. Sudan 2 is considered a potential genotoxic for hepatic cells of rats, monoazo Sudan 1 dye is a potential carcinogenic for liver and bladder of mammals, reductive products of Sudan 4 are reported to be potential mutagenic [47].
- Black Dye Commercial Product (BDCP) used for imparting black colour to textile products is very dangerous as it is reported to be a potential for inducing is cytotoxicity, genotoxicity and mutagenicity in Allium cepa. Besides it has also been reported that the toxic effect of the biodegraded products of the dye are more acute than the parent compound [48,49].
- DNA damage and other toxic effects of azo dye Red HE3B (Reactive Red 120) [50], and Direct Red 28 [51] are mainly related to its intermediate metabolites.
- Chlorotriazine reactive Azo Red 120 has been reported to induce mutagenic effects in fishes and mammals [52,53] The nature and position of a substituent relative to the azo or amino group in an azo dye or the amine formed by the degradation of the dye, may influence their toxicity [18,54].
- Azo dyes as Congo Red are reported to induce dysfunction of reproductive organs [55-57].

The conventional detoxification method for azo dyes i.e. chlorination, has been experimentally reassessed [58] and it has been concluded that it is not a fully efficient process as in some cases it may eradicate the toxic effect, in others it may diminish the same but in some cases these effects may be enhanced due to the toxicity of the degradation products

It must however be taken into account that different procedures and methods are employed for the assessment of the toxicity in terms of genotoxicity/ mutagenicity / carcinogenic properties etc. These may be sample or target specific and so it is not essential that the results of an investigation with a specific approach are applicable for other procedures.

METHODS FOR REMOVAL OF AZO POLLUTANTS FROM THE ENVIRONMENT

Pure aquatic sources are an essential need for a healthy ecosystem and the survival and wellbeing of the diverse species of microbes and macrobes in the environment. However the utilization of water for domestic, agricultural and industrial needs has gradually resulted in the pollution of many available hydric sources and this has adversely effected the living organisms depending on such resources for survival. As the need for water grows the possibility of all available water sources being polluted cannot be ruled out [59], Effluents from Industries involved with the production and use of azo dyes are one of the major polluters of the water resources [60]. Installation of efficient effluents treatment plants is essential in these industries.

There are a variety of methods that are being used for the treatment of dye industry effluents. The physical methods for the treatment of dye industry effluents are essentially based on flocculation and filtration using membranes, ion exchange, electro- coagulation etc. and adsorption using activated coal, wood chips, silica gel, etc. [61]. The chemical methods are essentially based on oxidation e.g. ozonization, photochemical or electrochemical degradation etc. Both these approaches have the major setback of being expensive and resulting in secondary pollution. A more employable and efficient process for the treatment of dye industry effluents is based on biological degradation.

Biological degradation of azo dyes is considered as an optimum approach for their removal from the environment. It is a green economically viable approach to degrade dyes and effectively reduce their accumulation in the environment.

There are however some limitations which restrict the utility of the biological degradation process. Considering that azo dyes are synthetic compounds with complex chemical structure having relatively higher photo and chemo stability [21,62-65] they are generally not mineralized by aerobic biodegradable process [66,67]. Biodegradation under aerobic conditions may result in the formation of intermediate products, mainly amines [67,68] which may enhance the toxicity. Complete biodegradation of many dyes has been observed under anaerobic conditions as this is effective in the total mineralization of the intermediate products i.e. amines [69,70]. Complete biodegradation of azo dyes under anaerobic conditions involves the reductive cleavage of the azo bonds followed by the degradation of the aromatic amines.

In the past few decades several investigations have been conducted to explore the potential use of microorganisms as bacteria [71-74] and macro organisms as yeast [75-78] fungi, algae [79-81] and even plants [82-83] for the removal of azo dyes from the environment. The results of some studies are encouraging and certain microorganisms have been identified which can mineralize certain azo dyes in controlled environmental conditions [84]. The use of the process has limitations and is applicable only for some azo dyes [85-87].

The use of bacteria for the removal of azo dyes is recognized as the most useful and many species of bacteria e.g. Mycobacterium avium; Klebsiella sp., Proteus mirabilis; Rhodococcus sp., Aeromonas sp., Pseudomonas luteola and Bacillus sp., Pseudomonas sp., and Shigella sp., [71-74] are reported to be useful for biodegradation of azo dyes. The main processes by which bacterial anaerobic biodegradation of azo dyes may take place include, enzyme catalytic cleavage [60] and reduction which can be undefined involving unknown electron carriers [88-90] or defined involving ferrous ions or sulphil radicals.

Some yeasts species exhibit the ability to degrade azo dyes. The extent of degradation however may be limited to the azo bond cleave and formation of aromatic amines [75-78] or be complete [91]. In either case it is important to observe that the dyes or their metabolites have no adverse effect on the yeast involved and the products formed by degradation do not enhance the toxicity. The variety of yeasts that are promising for biodegradation of azo dyes are limited. Different species of yeast that have been investigated and Saccharomyces cerevisae has been identified as an important organism for the mineralization of certain azo dyes [92].

The degradation of azo dyes by fungi has been investigated and a large variety of fungi have been identified for their biodegradation. The degradation process by white-rot fungi is suggested to take place via an oxidative mechanism [93]. Some other fungi that are reported to be effective as biodegrading agents include Coriolus versicolor [94-95] Pleurotus ostreatus [63]; Cunninghamella elegans [96-97], Bjerkandera adusta [98-99] and several basiciomycete fungi [100]. It is important to note that degradation of azo dyes by some fungi as Neurospora crassa may result in the formation of aromatic amines resulting in higher ecotoxicity.

Some algae species are reported to have the ability to biodegrade azo dyes involving a reduction mechanisms [101] e.g. Oscillatoria [80] Spirogyra [81] and Chlorella [79-80]. Similarly the use of plants for the removal of azo dyes has also been explored and some plants have been identified as being potent for their removal e.g. Rheum rabarbarum [83] Blumea malcommi [102] Brassica juncea, Sorghum vulgare and Phaseolus mungo [103] Paulownia tomentosa [104], etc. However their utility appears limited as the tolerance level of plants is generally low and their use for industrial needs demands field cultivation.

CONCLUSIONS:

Azo dyes account for the majority of all dyestuffs produced and employed in the textile industries. They are considered as electron – deficient xenobiotic compounds containing the aromatic functionality with one or more azo (-N=N-) groups. Textile industries are largest generator of dye containing wastewater The release of dye containing effluent into the environment is of great concern due to its aesthetic value, toxicity, mutagenicity and carcinogenicity. Therefore, effluents from textile industries have serious environmental concern and the removal of dyes from effluent is necessary prior to their disposal. Biological processes including microorganisms such as bacteria,fungi, yeast, algae and plants overcome the limitations of physico-chemical techniques and provide an alternative approach to existing technologies for removal of azo dyes. These methods are inexpensive, environment friendly and applicable to different structural varieties of dyes.

This review emphasizes the potential of biological systems and their possible mechanisms for decolorization and degradation of azo dyes. Bacteria is the most frequently applied microorganisms for the removal of dyes from textile effluents because they are easy to cultivate, adapted to survive in extreme environmental conditions and

decolorize the azo dyes at a faster rate as compared to other available microorganisms. The effectiveness of microbial processes for removal of azo dyes depends on the adaptability and the activity of selected microorganisms. For mineralization of azo dyes, treatment systems having mixed microbial populations or consortium are more effective due to concerted metabolic activities of the microbial community. The role of oxidative and reductive enzymes and their possible mechanisms to understand the biochemical basis of decolorization and degradation of azo dyes are also addressed in this review.

Moreover, the development of innovative nanotechnologies is the future solution to the problem of colored wastewater of textile dyeing industries. Nanotechnology coupled with conventional biological processes will play a critical role in increasing.

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