Biotransformation of Textile Azo Dyes

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INTRODUCTION

Today we are facing a major environmental problem in the form of increasing pollution. The industrial revolution all over the world has led to increase in the pollution in nature. Wastewater from industries has strong impact on aquatic environment, which is due to the chemical composition of the waste generated from the industries (Mondal, 2008). The pollution problems due to textile industry effluents have increased in many years. The wastewater from the textile industries pose great threat to the environment as large amount of chemically different dyes are used; for various industrial applications significant portion of dyes enter the environment *via* wastewater (Dayaram, 2008). The problems associated with the discharge of wastewater from the industries like textile, paper, food, plastic and cosmetics may cause significant problems such as skin irritation and cancer to humans, etc., also reducing the light penetration that has derogatory effect on photosynthesis phenomenon (Mahmoodi, *et al.,* 2009). The generation of colored wastewaters is a reality for a variety of industrial sectors. Among these residues are effluents arising from textile and printing processes, drycleaners and tanneries, the food industry, manufacture of paints and varnishes, manufacture of plastics and a variety of chemical processes. Commercial dyes have a great variety of colors, and a high stability to light, temperature, detergents and microbial attack (Urra, *et al.*, 2006).From the aesthetical point of view, the presence of the organic matter, particularly carcinogenic compounds in the underground water is not safe for life (Aleboyeh, *et al.*, 2005; Luca, 2006). The available bibliography reports that, approximately 75% of the dyes, discharged from the Western European textile processing industries, belong to the classes of reactive (36%), acid (25%) and direct (15%) (Ollgaard, *et al.*, 1999). The textile finishing has a strong impact on aquatic environment. The consumption of water by the textile finishing industry in Germany was reported as approximately 65 million m^3 for the year 1992 (TVI, 1994). The specific discharge of the wastewater in German textile finishing industry in 1993 amounted to 115 m^3/ ton-textile material, in which the wastewater contained high contents of inorganic and organic substances as dyes, textile additives and basic chemicals (Schonberger and Kaps, 1994).

HISTORY OF DYES

Ever since the beginning of the humankind, people have been using colorants for the painting and dyeing of their surroundings, skins and their cloths. Until the mid of 19th century, all the colors used were of natural origin (Zee, 2002). The first synthetic dye, Mauveine, was discovered by Perkin in 1856. Hence the dyestuffs industry can now rightly be described as mature. However, it remains a vibrant, challenging industry requiring a continuous stream of new products because of the quickly changing world in which we live. The early dyes industry saw the discovery of the principal dye chromogens (the basic arrangement of atoms responsible for the color of a dye). Indeed, apart from

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one or two notable exceptions, all the dye types used today were discovered in the 1800s (Gordon and Gregory, 1983). The discovery of the reactive dyes in 1954 and their commercial launch in 1956 heralded a major break through in dyeing of cotton; intensive research in reactive dyes followed over the next two decades and indeed is still continuing today (Gordon and Gregory, 1983). The concept of research and development was soon followed by the others and new dyes began to appear in the market. In the beginning of 20th century, synthetic dyestuff had most completely supplanted natural dyes (Welham, 2000).

The scale and growth of the textile dyes industry has been inextricably linked to that of the textile industry. World textile production has grown steadily to an estimated 35 X 10^6 tons in 1990 and the estimated world production of the dyes in 1990 was 1 X 10^6 tons (Calder, 1990; Booth, 1988). The most recent and readily available data are from the 1993 SRI report, containing data for 1991 (Ollgaard, *et al*., 1999).

CLASSIFICATION OF DYES

The classification of dyes according to their usage is summarized in the table 1.

Table 1. Usage classification of dyes.

Class	Principal Substrates	Method of Application	Chemical Type
Acid	Nylon, Wool, Silk, Paper, Inks and Leather	Usually from neutral to acidic dyebaths	Azo, Anthraquinone, Triphenylmethane, Azine, Xanthene, Nitro and Nitroso.
Azoic compounds and composition	Cotton, Rayon, cellulose acetate and polyester.	Fiberimpregnated with coupling component and treated with solution of stabilized diazonium salt.	Azo
Basic	Paper, Polyacrylonitrile, modified nylon, Polyester and inks.	Applied from acidic dye baths.	Cyanine, Hemicyanine, Diazahemicyanine, Diphenylmethane, Triarylmethane, azo, azine, Xanthene, Acridine, Oxazine and Anthraquinone.
Direct	Cotton, Rayon, Paper, Leather and Nylon.	Applied from neutral or slightly alkaline baths containing additional electrolyte.	Azo, Phthalocyanine, Styryl, Nitro, benzodifuranone.
Disperse	Polyester, Polyamide, Acetate, Acrylic and Plastic.	Fine aqueous dispersions often applied by high temperature carrier methods; dye may be padded on cloth and baked on thermofixed.	Azo, anthraquinone, Styryl, nitro and benzodifuranone.
Reactive	Cotton, Woll, Silk and nylon.	Reactive site on the dye reacts with the functional group on the fiber to bind the dye covalently to the fabric under the influence of	Azo, anthraquinone, Phthalocynine, formazan, oxazine and basic.

		the heat and pH(alkaline).	
Sulphur	Cotton and Rayon	Aromatic Substrate vatted with sodium sulphide and reoxidized to insoluble sulphur containing product on the fiber.	

All aromatic compounds absorb the electromagnetic energy but only those that absorb light with the wavelengths in visible range (approx. 350 – 750 nm) are coloured. Dyes contain chromophore groups like –C=C-, -C=N-, -C=O-, -N=N-, -NO_2 and quinoid rings etc. Based on the chromophore groups, the dyes can be classified into 20-30 groups like, Azo, Anthriquinone, Phthalocynine and triarylmethane are the most important groups.

1. Acid Dyes – This is the largest class of the dyes. Acid dyes are anionic compounds mainly used for dyeing the nitrogen containing fabrics like cotton, wool, polyamide, silk and modified acryl. Most acid dyes are azo, anthraquinones or triarylmethane compounds the adjective ‘acid’ refers to the pH in the dye baths rather than presence of acid groups.
2. Reactive Dyes – These dyes are with the reactive group that forms the covalent bonds with the OH-, NH-, or SH-, groups in the fiber. The use of reactive dyes has been increased since their introduction in 1956. These dyes do not get fixed easily to the fabric even after the addition of the high quantities of salt and ureum (upto 60 to 200 g/l). These dyes are usually small azo compounds, anthraquinones, or metal complex azo compounds.
3. Direct dyes – These are relatively large molecules with high affinity for cellulose fibers. Direct dyes are mostly azo dyes with more than one azo or Phthalocynine bond, stilbene or oxazine compounds.
4. Basic Dyes – Basic Dyes are cationic compounds that are used for dyeing acid group containing fibers like polyacryl. Most basic dyes are diarylmethane, triarylmethane, anthraquinone, or azo compounds.
5. Mordent dyes – These dyes are fixed to the fabric by the use of a mordent, a chemical that combines the dyes and the fabric. These dyes are used with wool, leather, silk, paper and modified cellulose fibers. Mostly these dyes are azo, oxazine or triarylmethane compounds. The mordents used are dichromates or chromium complexes.
6. Disperse Dyes – These dyes are poorly soluble, that penetrate the synthetic fibers. The dyes in the dye baths are the fine disperse solutions. These dyes are the third largest group of dyes in the colour index. They are usually small azo or nitro compounds, anthraquinone, or metal complex azo compounds.
7. Vat Dyes – These are water insoluble dyes that are particularly used to dye the cellulose fibers. These dyes are reduced to their leuco form to dissolve and impregnate the fabric. All vat dyes are anthraquinone or indigoids. ‘Vat’ refers to the vats that were used for the reduction of the indigo plants through fermentation process.
8. Sulphur Dyes – These dyes are complex polymeric aromatics with heterocyclic S-containing rings. Dyeing with sulphur dyes involves reduction and oxidation comparable to vat dyeing. They are mainly used for dyeing cellulose fibers.

DYES AND ENVIRONMENTAL CONCERNS

Dyes are visible in the water in very low concentrations as low as 1 mg/l^{-1}. The textile wastewater typically contains the dyes in the range of 10-200 mg/l^{-1}(O’Neil, *et al.*, 1999) and therefore usually highly coloured. As these dyes are so designed that they sustain in natural environments in very harsh conditions. The release of these dyes in the environment present an ecotoxic hazard and introduces potential danger of bioaccumulation that may eventually affect man by their magnification in food chain. Generally the effluent is highly colored with high biological oxygen demand (BOD) and chemical oxygen demand (COD), has high conductivity and alkalinity.

BIOACCUMULATION

The bioaccumulation of the dyes in fish has been investigated in the research promoted by ETAD (Ecological and Toxicological Association of Dyes and Organic Pigments Manufactures). The bioconcentration factors of dyes were determined, and it was observed that the water soluble dyes were not bioaccumulated whereas the water insoluble dyes bioaccumulated (Anlikar, 1979). Also these dyes being recalcitrant in nature, they are potentially toxic to humans and other life (Yoo, 2000), and if these compounds magnify in the environment and enter the food chain they may endanger sustainability of life on earth.

ECOTOXICITY OF DYES

Due to the fact that dyes are synthesized chemically and photolytically stable, they are highly visible in very low concentrations also and persist in natural environments for longer period of time (Nigam, *et al*., 2000; Rieger, *et al*., 2002). Consequently the release of these potentially toxic dyes can be ecotoxic and can affect man through the food chain (Van der Zee, 2002). Acute toxicity of dyes is generally low. Algal growth and fish mortality are not affected by dye concentration below 1 mg/l. Most toxic dyes for algae and fishes are basic and acidic dyes (Greene and Baughman, 1996; Little and Chillingworth, 1974). The sulphonated azo dyes appear to decrease the toxicity by enhancing urinary excretion of the dye and its metabolites (Brown and DeVito, 1993). Sensitization to azo dyes is seen since 1930 in the workers of textile industry (Giusti, *et al*., 2004). Many studies have been conducted on the toxicity of the aromatic amines from the azo dyes (Weisburger, 2002). An investigation of several hundred commercial textile samples reveled that, nearly 10 percent were mutagenic in AMES test (McCarthy, 1997). Many textile effluents contain heavy metals that are complexed in azo dyes (Wallace, 2001). Azo dyes in their pure form are seldom mutagenic and carcinogenic (Brown and DeVito, 1993). But when these azo dyes are reduced, they form the aromatic amines which are very toxic, mutagenic and carcinogenic in nature. In humans, various organs like liver and kidneys can reduce the azo dyes to form the aromatic amines. The literature studies reveled that the sulphonated aromatic amines, in contract to some unsulphonated analogues, have generally no or very low genotoxicity and tumorigenic potential (Jung, *et al*., 1992).

DYE REMOVAL TECHNIQUES

Majority of physical, chemical and biological color removal techniques work either accumulation of the dyes in the sludge, solid supports or by complete destruction of dye molecule. During the decolorization processes, it is expected that the system will prevent the transfer of the pollution from one part of environment to the other (Vandevivere, *et al*., 1998; Hao, *et al.,* 2000; Robinson,*et al.,* 2001). Currently, the major methods of textile wastewater treatment involve physical and/or chemical processes such as membrane filtration, coagulation/flocculation, precipitation, flotation, adsorption, ion exchange, ion pair extraction, ultrasonic mineralization, electrolysis, chemical reduction and advanced chemical oxidation (Gogate and Pandit, 2004). The advanced oxidation process includes chlorination, bleaching, ozonation, feton oxidation, photocatalytic oxidation and wet air oxidation (Slokar and Le Marshal, 1998; Robinson, *et al*., 2001; Pizzolato *et al*., 2002; Alton and Ferry, 2003; Kusvuran, *et al*., 2004). Such methods are costly and accumulation of concentrated sludge creates a disposal problem (Robinson, *et al*., 2001). There is also the possibility of secondary pollution problem due to excessive chemical use. So the biological processes can be used for effective and efficient treatment of the dye containing wastewater.

The biological techniques include biosorption and biotransformation in aerobic, anaerobic, combined aerobic/anaerobic conditions by using bacteria, fungi, actinomycetes, yeasts, algae and enzymes (Heinfling, *et al.,* 1998; Rafiie and Coleman, 1999; Semple, *et al.,* 1999; Nyanhongo, *et al.,* 2002; Blumel and Stolz, 2003; Shrivastava, *et al.,* 2005). Microorganisms play an important role in mineralization of the biopolymers and xenobiotic compounds, like azo dyes (Lie, *et al.,* 1998).

ANAEROBIC BIODEGRADATION

Under aerobic conditions, the dyes are not readily metabolized (Stolz, 2001), but on the other hand in anaerobic treatment, the dyes get reduced by the microorganisms by forming the aromatic amines as the degradation product. The reductive cleavage of the dyes occur in anaerobic conditions (Nigam, *et al.,* 1996; Beydilli, *et al.,* 2000; Stolz, 2001; Van der Zee, *et al.,* 2001; Van der Zee, *et al.,* 2003; McMullan, *et al.,* 2001). These aromatic amines are toxic, mutagenic and carcinogenic to mammalians (Blumel, 2002; Pinheiro, *et al*., 2004). The anaerobic consortia do not degrade the aromatic amines but they are readily degraded in aerobic conditions (Baird, *et al.,* 1977). The anaerobic systems can decrease the color intensity more satisfactorily than aerobic process (Hao, *et al.,* 2000; Beydilli, *et al.,* 2000; Robinson, *et al.,* 2001; Naim and Abd, 2002). Biodegradation of the dyes is generally only feasible if it is reduced first. Some specialized strains of bacteria have developed the ability to reduce these dyes by special oxygen tolerant reductases (Kulla, 1981). However, these reductases have a narrow substrate range (Zimmerman, *et al.,* 1982). On the other hand, the reduction of these dyes is ubiquitous capacity of many microorganisms under anaerobic conditions (Carliell, *et al.,* 1995; Donlon, *et al.,* 1997; Razo-Flores, *et al.,* 1997; Walker, 1970). Therefore anaerobic conditions are preferable for azo dye reduction.

The aromatic amines generally resist any further biodegradation in anaerobic environments (Field, *et al.,* 1995). The anaerobic treatment was first investigated using the intestinal anaerobic bacteria (Allan and Roxon, 1974; Brown, 1981; Chung, *et al.,* 1992; Walker and Rayn, 1971). Recently Razo-Flores, *et al.,* (1997) investigated the fate of Mordent Orange I (MO-I) and Azodisalicylate (ADS) under methanogenic conditions using continuous upflow-anaerobic-sludge-blanket (UASB) reactors and concluded that, the dyes were degraded by anaerobic microorganisms.

Chinwetkitvanich, *et al.,* (2000) concluded that higher initial colour concentration might be dangerous to acid forming bacteria, which results into less dye removal. The reduction of the dyes proceeds better in anaerobic thermophilic conditions than under mesophilic conditions, although the thermophilic process seems to be less stable as compared to the mesophilic process (Willetts, *et al.,* 2000). The studies carried out by Ganesh, (1992) and Loyd, (1992) showed that, the dyes Reactive Black 5 and Navy 106, from the textile effluent were completely decolorized by treating them in an anaerobic reactor by using minimal medium. Hang, *et al.,* (1991) reported that, the metabolites resulting from the reduction of the azo dye Mordant Yellow 3 (6-aminonaphthalene-2-sulphonate and 5-aminosalicylate) were not degraded in the anaerobic system which gave rise to decolorization. Kremer, (1989) reported, the anaerobic degradation of the dye Acid red 88 resulted in the formation of the naphthionic acid and 1-amino-2-napthol.

AEROBIC BIOTRANSFORMATION

For a long period of time, it was assumed that, the dyes remained recalcitrant when treated in aerobic conditions. The enzymes present in the bacteria were used for this process of decolorization, but these enzymes too had very narrow substrate range (Kulla, *et al.,* 1983; Zimmerman, *et al.,* 1984). A few bacterial species have shown decolorization of the dyes in the wastewater aerobically, either in activated sludge or in fixed film systems (Jiang and Bishop, 1994; Hao, *et al.,* 2000). Recently occurrence of conversion of the sulphonated dyes was reported by Heiss, *et al.,* (1992) and Shaul, *et al.,* (1991).

In some studies it was observed that, under aerobic conditions, the colour was completely removed but it required an additional energy and carbon source. Similarly the degradation of the dyes was observed in the aerobic biofilm reactor (Costerton, *et al.,* 1994; Harmer and Bishop, 1992; Jiang and Bishop, 1994). Quezada, *et al.,* (2000) reported that, 73% of the dye Acid Red 151 was transformed to carbon dioxide by using an aerobic sequenced biofilm reactor. Also Kale and Thorat, (2010) reported, the use of acclimatized aerobic bacteria for the degradation of the dye Reactive Red M5B, which showed complete decolorization and degradation of the dye containing solution. This degradation was confirmed by GCMS analysis. In anaerobic treatment, the dye reduction leads to formation of aromatic amines, these aromatic amines are generally do not degrade in nature and get accumulated (Brown and Hamburger, 1987; Field, *et al*., 1995), with the exception of few aromatic amines characterized by the presence of hydroxyl/carboxyl groups (Heider and Fuchs, 1997; Khun and Suflita, 1989). Mineralization of the aromatic amines by aerobic bacteria and aerobic sludge in treatment plants is more common and therefore aerobic conditions are preferable to degrade the accumulated aromatic amines (Brown and Laboureur, 1983; Manalney, 1986).

The integration of the aerobic and anaerobic conditions in a single biofilm has been proposed and proven to be the good strategy for mineralization of dyes (Hung, *et al.,* 1991; Kudlich, *et al.,* 1996). Inside the biofilm, anaerobic conditions will result in the dye reduction yielding aromatic amines. These aromatic amines are susceptible for mineralization in periphery of the biofilm. There are some reports in which, addition of oxygen to the granular sludge under integrated aerobic/anaerobic conditions was seen beneficial for the biomass and the COD removal. However the oxygen was not required for certain specific biodegradation such as aerobic degradation of aromatic amines in the integrated aerobic/anaerobic process for mineralization of dyes (Kato, *et al.,* 1993; Shen and Guiot, 1995; Zitomer, 1998; Zitomer and Shrout, 1998).

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