Review of literature

2.0 REVIEW OF LITERATURE

Water pollution control is presently one of the major areas of scientific activities. Now a days natural pigments used for colouring textiles have been replaced by “fast colours” which do not fade on exposure to light, heat and water. While coloured organic compounds generally impart only a minor fraction of the organic load to waste water, their colours render them aesthetically unacceptable. Discharge of highly coloured synthetic dye effluent can cause damage to the receiving water bodies (Moosvi *et al.,* 2005).

The new textile effluent contains high concentration of various inorganic chemicals such as sulfides, sulphates, chlorides and carbonate. In particular colour removal has recently become an area of major scientific interest as indicated by the multitude of related research reports (Wagh *et al.,* 2005).

During the past two decades, several decolourization techniques have been reported, few of which has been accepted by some industries. There is a need to find alternative treatments that are effective in removing dyes and colorants from large volume of effluents, which are cost effective like the biological or integrated systems (Anjaneyalu *et al.,* 2005).

In this view, review of literature for the present work entitled “Decolourization of Azo dyes by newly isolated bacterium from the textile effluent” was discussed under the following headings.

2.1. Textile Industry

2.2. Environmental pollution and public health

2.3. Toxic chemicals in the environment

2.4. Dyes

2.5. Impact of azodyes

2.6. Bioremediation and microbial degradation of dyes

2.7. Bacteria in dye decolourization

2.8. Immobilization of cells for degradation of dyes.

2.1. TEXTILE INDUSTRY

Textile industry is one of the oldest industries in the world and there are about 10,000 garment manufactures and 2100 bleaching and dying industries in India (Annual report ministry of textiles, 2004).

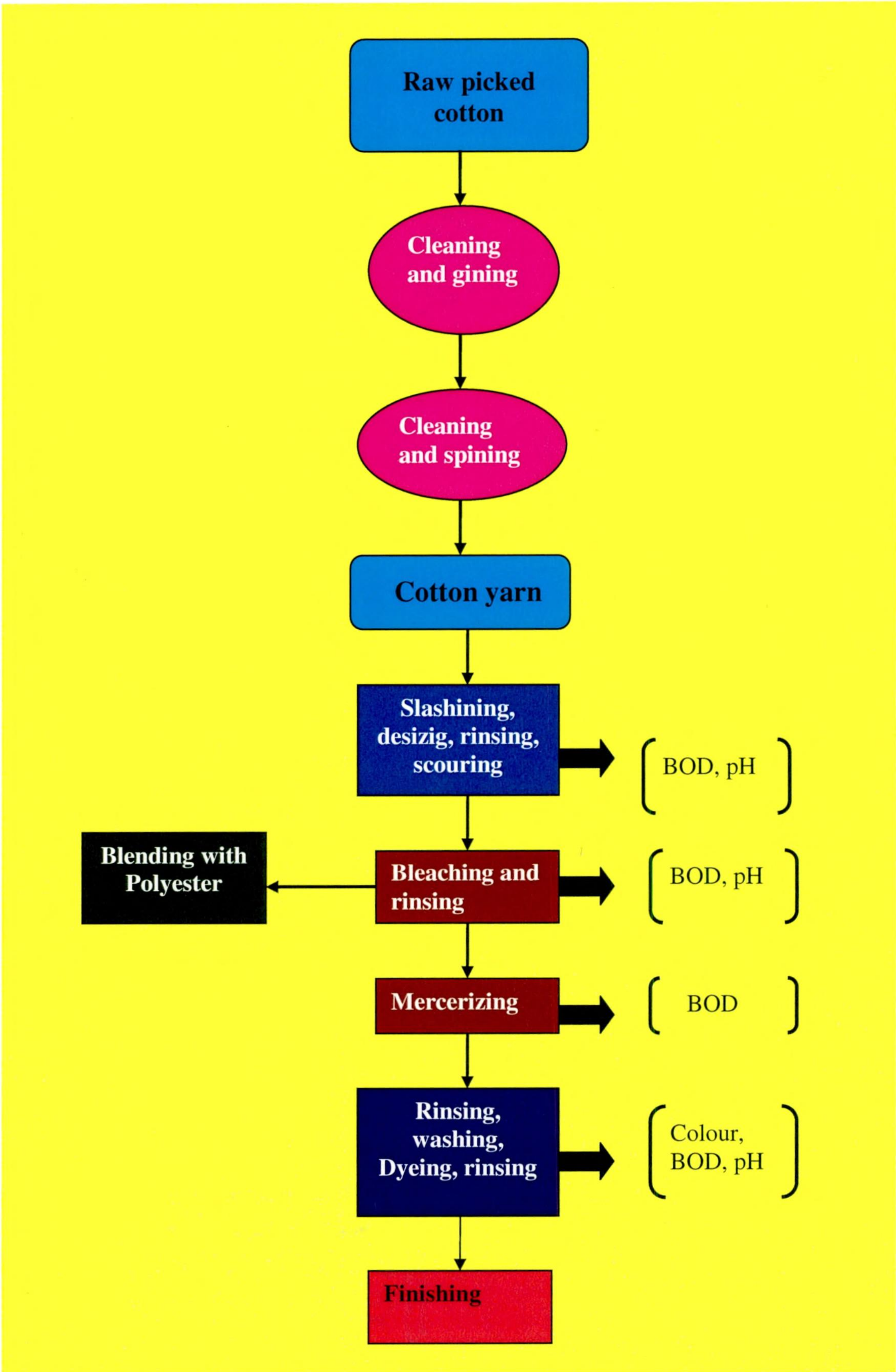
In textile industries bleaching and colouring are the major wet processes with wastewater generation of about 40-120m^3 l^{-1}. Bleaching is employed to oxidize impurities like lignin, pectin and gum to make the yarn / cloth white and also favourite unit for dying of cloths. It is carried out either by using hypochlorite or alkali / hydrogen peroxide. It consumes more water and most of them are discharged as wastewater. In India, limit for Adsorable Organic Halides (AOX) discharge by the textile industries is yet to be fixed whereas in European countries, the limit if AOX in wastewater should not exceed 1mg l^{-1} for discharge into surface water and municipal treatment plants (Ranganathan *et al.*, 2007).

The water consumption and wastewater generation from a textile industry depends upon the processing operations employed during the conversation of fibre to textile fabric.

On the basis of waste and wastewater generation, the textile mills can be classified into two main groups viz., dry processing mill and woven fabric finishing mills. In the dry processing mill, mainly solid waste is generated due to the rejects of cotton. In the other group, desizing, scouring, bleaching, mercerizing, dying, printing and packing are the main processing stages (Figure 1).

The textile industry can also distinguish based on the raw materials used and they are raw cotton, raw wool and synthetic materials. The nature of the processing exerts a strong influence on the potential impacts associated with textile manufacturing operations due to the different characteristics associated with these effluents (Table 1) (Yusuff and Sonibare, 2004).

FIGURE 1



Cotton fabric production and associated water pollutants

Textile industry is one of the high pollution causing industries in India and plays a role creating water pollution problems of considerable magnitude by discharging partially treated or untreated wastewater (Verma *et al.,* 2005).

TABLE 1

Effluent Characteristics from Textile Industry

Process	**Effluent composition**	**Nature**
Sizing	Starch,waxes,carboxymethyl cellulose (CMC), polyvinyl alcohol(PVA), wetting agents.	High BOD and COD
Desizing	Starch, CMC, PVA, fats, waxes, pectins.	High BOD, COD, dissolved solids
Bleaching	Sodium hypochlorite, Cl2, NAOH, H2O, acids, surfactants, NaSiO3, sodium phosphate, short cotton fibre.	High alkalinity
Mercerizing	Sodium hydroxide, cotton wax	High pH, low BOD.
Dyeing	Dye stuffs, urea, reducing agents,oxidizing agents, acetic acid, detergents, wetting agents.	Strongly coloured, high BOD, heavy metals
Printing	Pastees,urea,starches, gums, oils, binders, acids, thickeners, cross-linkers, reducing agents, alkali.	Higly coloured, high BOD, oily appearance, Slightly alkaline.

Source: (Yusuff and Sonibare, 2004).

Textile wastewater contain numerous chemicals such as dyes pigments, axillaries, surfactants, solvants, organic and inorganic salts which causes severe pollution problem for the receiving fresh waters (Lancioti *et al.*, 2004). Dyeing effluent is one of the large contributors to textile effluent and such coloured wastewater has a seriously destructive impact on the environment (Blackburn, 2004).

In textile industry, colour is applied to finished products through dyeing. Dyes used are designed to resist exposure to sweat, light, water, oxidizing agents and microbial attack (Tavares *et al.,* 2006).

A significant proportion of synthetic organic dye stuffs are lost annually to wastewater streams which eventually enter the environment. Of the dyes currently on the market and used in the textile industry, approximately 50% are azo-diazo compounds and because their environmental fate remains largely unknown, they are considered to represent an appreciable hazard (Bustard *et al.*, 2003).

2.2. ENVIRONMENTAL POLLUTION AND PUBLIC HEALTH

Environment is broadly defined as the total planetary inheritance of all resources. These days due to development, forest and grasslands are converted into farms, houses and commercial spaces, raw materials are extracted for energy and commerce, waterways are dammed and diverted, degradation of environment by the release of substances that cause a health hazard or contaminate the soil, water or air is said to be polluting the environment (Yassi and Kjellstrom, 2004).

Environmental pollution is becoming the global problem, over a last few decades a large scale usage of chemicals in various human activities has grown very fast, particularly in countries like india that has to go for rapid industrialization in areas like health and sanitation (Naik *et al .,* 2007).

Pollution in general can be seen as something harmful to the wellbeing of the particular environment. Pollution prevention is an aspect of sustainable development as it saves money, reduces liability and promotes working environment. Pollution is the waste which is disposed in the air, water and a land (Sundar, 2005).

The development of industries and services, intensification of agriculture, the enlargement of urbanized area, the development of information technology and the huge increase of transports has favoured human needs. On the other hand, this development has also caused a considerable increase of pollution with consequent damage to the ecosystem (Giordani *et al.,* 2005).

The presence of heavy metals in industrial and urban waste water is one of the main causes of water and soil pollution. Accumulation of these elements in wastewater depends on a number local factor such as type of industries in the region and people's way of life and awareness of the impacts to the environment by careless disposal of water (Wang *et al.*, 2005).

The discharge of toxic effluents from various industries adversely affects water resources, soil fertility, aquatic organisms and ecosystem integrity (Puvaneswari *et al.,* 2006). Many reports indicate that textile dyes and effluent have toxic effects on the germination rates and biomass concentration of several plant species which play many important ecological functions such as providing the habitat for wildlife, protecting soil from erosion and providing bulk of organic matter that is significant to soil fertility (Dastida and Sreekrishnan, 2009).

Dye may significantly affect photosynthetic activity in aquatic life because of reduced light penetration and may also be toxic to some aquatic life due to the presence of aromatics as metals and chlorides etc (Aksu, 2005). In addition, the coloured industrial effluents significantly reduce oxygen solubility in receiving waters and are thus an important environmental hazard (Guijaro *et al.,* 2009).

The textile effluent contains organic and inorganic chemical species which has adverse effect on the growth of all plants and animals, because textile effluent used for irrigation contains heave metals (Ni, Cd, Cr, Pb and Hg) which accumulates in various parts of plants that result in various clinical problems in animals as well as in human beings including hepatic and renal system damages, mental retardation and degradation of basal ganglia of brain and liver (Rehman *et al.*, 2009).

The measurement of cellular and subcellular responses to chemical contaminants in sentinel organisms used as bioindicators from aquatic environments allow early detection of biological effects as well as assessment of the extent of concentration and/or effectiveness of industrial effluents (Grinevicious *et al.,* 2009).

Number of epidemiologic studies was performed to evaluate possible health risks in textile industry workers. Contact dermatitis, asthma, irritation of eyes and skin, chronic bronchitis, tuberculosis has been reported among textile workers. Genotoxic risks like sister chromatid exchanges (CEs) and chromosomal aberrations were investigated. The frequency of chromosomal aberration was significantly higher in workers (Donbak *et al.*, 2006).

Textile industries generate millions of liters of untreated effluents per day which are directly discharged into drinking water resources, such as rivers and lakes. This alters pH, increases biochemical oxygen demand (BOD) and chemical oxygen demand (COD) and gives intense colouration (Telke *et al.*, 2009).

The presence of carcinogens has been reported in the combined wastewater of dyeing and printing units. They pose problems because they may be mutagenic and carcinogenic and cause severe damage to human beings such as dysfunction of the kidneys, reproductive systems, liver, brain and central nervous system (Raghuvanshi *et al* .,2005).

Textile effluents has been ranked second in toxicity among the eight industrial sectors represented using a series of bioassays assessing the acute, sublethal and chronic toxicity at various trophic levels and has been associated with the occurrence of occupational tumors of the urinary bladder (Bakshi *et al* ., 2006).

2.3. TOXIC CHEMICALS IN THE ENVIRONMENT

Colour in wastewater has now been considered as a pollutant that needs to be treated before discharge. Different colouring agents like dyes, inorganic pigments, tannins and lignins usually impart colour. More than 8000 chemically different types of dyes are currently manufactured and the biggest consumers of these dyes are the textile industries, dye and dye intermediate industries, tannery and kraft bleaching industries which are probably the most potential contributors as far as colour pollution is considered (Anjaneyulu *et al.*, 2005).

Textile dyes are one of the most prevalent types of chemicals use today. Around 10,000 different dyes with an annual production of more than $7x10^5$ metric tonnes are commercially available worldwide. Some of the azodyes, xanthane dyes and anthroquinone dyes are known to be very toxic and mutagenic to living organism (McMullan *et al.*, 2001).

2.4. DYES

All molecules absorb electromagnetic radiation but differ in the specific wavelengths absorbed. Some molecules have the ability to absorb light in the visible spectrum (400-800nm) and as a result, they are themselves coloured. The dyes are molecules with delocalized electron systems with conjugated double bonds that contain two groups: the chromopore is a group of atoms, which controls the colour of the dye and it is usually an electron-withdrawing group. The most important chromophores are –C=C-, -C=N-, -C=O, -N=N-, $-NO_2$ and –NO groups.

The auxochrome is an electron donating substituent that can intensify the colour of the chromophore by altering the overall energy of the electron system and provides solubility and adherence of the dye to the fiber. The most important auxochrome are NH_2, $-NR_2$, -NHR, -COOH, -SO_3H, -OH and $-OCH_3$ groups. Based on the chemical structure or chromophore, 20-30 different dye groups can be identified.

Azo (monoazo, diazo, triazo, polyazo), anthroquinone, phthalocyanine and triarylmethane dyes are quantitatively the most important chromopores.

Mineral colours like copper sulphate ($CuSo_4$) and tin chloride ($SnCl_2$) or vegetable and animal dyes were widely used at 18^{th} century. Such natural dyes have now been almost completely replaced by slow and expensive process of traditional dyeing and the fact that synthetic dyes have relatively stronger colours (Mathur *et al.*, 2003).

Textile processing industries largely employ azo dyes. They are aromatic hydrocarbons, derivatives of benzene, toluene, naphthalene, phenol and anline. Azodyes are the most important group of synthetic colourants that are extensively used in textile, pharmaceutical and printing industries. A wide variety of azodyes with anthraquinone, polycyclic and triphenylmethane groups are being increasingly used in textile dyeing and printing process. They are important groups of xenobiotic compounds and are recalcitrant in biodegradation process.

Azodyes may be direct, acid or basic. Direct dyes are relatively large molecules with high affinity especially for fibers. Acid dyes are anionic compounds that are mainly used for dyeing nitrogen containing fabrics like wool, polyamide, silk and modified aryl. Basic dyes are cationic compounds that are used for dyeing acid group containg fibers usually synthetic fibers like modified poly aryl (Vander zee 2002).Dye composition might be a important factor causing unstable decolourization because the textile effluent contaning a wide range of structurally diverse dyes. The degree of decolourization depends on the type of the dye, molecular weight and substitution groups of the dye molecules. Azo compounds with an hydroxyl or amino group being more likely to be degraded than those with methyl, methoxy, sulfo or nitro groups (Supaka *et al.*, 2004).

Direct dyes lack fastness during washing and so they are popularly used in items that are less likely to require fastness during washing like paper. A direct diazo dye commonly used in the paper industry is congored, which is intended primarily for the colouration of paper products. It is a recalcitrant and a known carcinogen. Congored is the sodium salt of benzidinediazo-bis-1-naphthylamine-4-sulfonic acid (Buan *et al.*, 2009).

The majority of these dyes are recalcitrant so that they can confer colour on various raw materials moreover certain dyes and dye precursors and some aromatic amines produced through biotransformation of dye compounds have been shown to be carcinogenic (Plumb *et al.*, 2001).

2.5. IMPACT OF AZODYES

The impact of azodyes in food industry and their degraded products on human health has caused concern over a number of year's inspite of legislation controlling their use in several countries. Over 3,000 tones of azodyes were certified in the year (1991) by Food and Drug Administration (FDA) for use in foods, drugs and cosmetics.

Some azodyes have been linked to human bladder cancer, splenic surcomas, hepatocarcinomas and nuclear anomalies in experimental animals and chromosomal aberrations in mammalian cells. Some azodyes induce liver nodules in experimental animals and there is a higher incidence of bladder cancer in dye workers exposed to large quantities of azodyes.

In human, malachite green (MG) causes irritation to the gastrointestinal tract upon ingestion. Contact of MG with skin causes irritation, redness and pain. Upon contact with eye will lead to permanent injury of human eyes and laboratory animals (Kumar *et al.*, 2005).

Textile effluents were also found to be responsible for the decrease in the RBC count and the Hb content in male wister rats. And also fish mortality has been recorded in a pond receiving textile effluents due to the presence of H_2S, NH_3 and Cl_2 (Mathur *et al.*, 2003).

Sensitization to azo dyes has been seen in textile industry, 20% of the workers dyeing cotton with red azoic dyes, developed occupation eczema (Giusti *et al.*, 2004).

Malachite green (MG) is a triphenyl methane dye, which is most widely used for colouring purpose, amongst all other dyes of its category (Gupta *et al.*, 2004). MG has properties that make it difficult to remove from aqueous solutions. If the solution containing MG discharged into receiving streams, it will affect the aquatic life and cause detrimental effects in liver, gill, kidney, intestine and gonads (Daneshvar *et al.*, 2006).

2.6. MICROBIAL DEGRADATION OF DYES

The textile industry is a major user of water, starting from washing raw wool or manmade fiber production up to garment manufacturing, with diminishing water resources due to rapid population growth and industrial development, reuse of municipal and industrial waste water after treatment and elimination of potential pollutants become more critical.

Conventional treatment processes have long been established in removing many chemical and microbial contaminants of concern to public health and the environment. Methods like chemical precipitation, coagulation, adsorption and flocculation have their own disadvantages. Huge amount of sludge is formed during effluent treatment process by chemical precipitation method.

This sludge is toxic and highly problematic to safe disposal. The detoxification and disposal of the sludge is a problem to the textile dye units. Environmental lesigislation is also being imposed to control the release of dyes, in particular agro-based compounds through waste water from dyeing factor and textile industry into the environment (McMullan *et al.*, 2001).

However treatment with biological agents remains the best solution of the problem. Ability of microorganisms to decolourize and metabolize dyes has been known and the use of bioremediation based technologies for treating textile waste water has attracted interest. A large number of microorganisms belonging to different taxonomic groups of bacteria, algae, fungi and yeast have been reported for their ability to decolourize azodye (Vitor and Corso, 2008).

BIOREMEDIATION

Bioremediation is an in expensive mean to remove hazardous substances from the contaminated effluent. Bioremediation constitutes the use of natural biota and their processes for pollution reduction. It is a cost effective process and the end products are non hazardous (Ahmedna *et al.*, 2004).

Dye removal by yeast occurs through the physical biosorption of the dye in a nonspecific manner to the periphery of the cell, followed by specific accumulation in the wall and interior of the cell. Yeast biomass is an inexpensive, readily available source of biomass that has potential for dye accumulation at lower pH values. (Vitor and Corso, 2008).

Various fungal strains have proved more efficient in decolouriztion of textile dyes mostly belonged to the group of whiterot fungi. Dyes are removed by fungi by the biosorption method.

The *Aspergillus niger* SA1, isolated from sludge have the ability to decolourize four different textile dyes (Ali *et al.*, 2008).and the whiterot fungi *Phanerochaete chrysosporium* were studied for the decolourization of indigo dyes (Cing *et al.*, 2003).

The biomass of *Aspergillus* strain is feasible to apply in biosorption process to remove dyes from textile effluents. The conversion of fungi biomass as biosorbants of xenobiotics might generate profit and at the same time, reduce the disposal cost of biomass from industrial fermentation processes (Corso and Almeida, 2009).

Whiterot fungi biodegrades textile dye stuffs by their extracellular enzyme system. However, it is difficult to keep them in functional form in conventional wastewater treatment system, because of their nutritional requirement and environmental conditions (Rahim *et al.*, 2008).

Whiterot fungi that produce lignolytic enzymes, such as lignin peroxidise, manganese peroxidise and laccase have been studied extensively because of their ability to degrade various organic compounds (Wesenberg *et al.*, 2003).

Microbiological treatment of sludge is the best way for detoxification. The whiterot edible mushroom grows efficiently on sludge and produces high level of laccase and reduced the toxicity of the sludge (Murugasan, 2002).

2.7. BACTERIA IN DYE DECOLOURIZATION.

Environmental biotechnology relies upon the pollutant degrading capacities of naturally occurring microbial consortium in which bacteria play a central role (Senan and Abraham, 2004).

The ability of biological treatment process for decolourization of industrial effluent is ambiguous, different and divergent. Observations indicate that dyes themselves are not biologically degradable since microorganism's donot utilize the colour constituents as a source of food (Ong *et al.*, 2005).

Microbial degradation of azodye generally needs two steps involving

a) Decolourization of azodye by the reduction of azobonds

b) Degradation of azodye metabolites or aromatic amines (Pandey *et al.*, 2007).

The most generally accepted hypothesis for the azodye reduction is that many bacterial strains possess rather unspecific cytoplasmic enzymes which act as "azoreductase". An azo reductase was purified from *E.faecalis* by hydrophobic anion exchange and affinity chromatography (Punj and John 2008). Maier *et al.*, (2004) have shown that, an azoreductase is responsible foe azodye reduction by *Bacillus strain SF.* A sequential anaerobic and aerobic treatment process based on mixed culture of bacteria isolated from textile dye effulent contaminated soil has been used to degrade sulfonated azodyes orange-G, amido black, direct red.

An anaerobic step followed by an aerobic step may represent a significant advancement in biological treatment and decolourization in the future. Because under anaerobic or microphilic conditions, azodyes are degraded to aromatic amines by the enzyme azoreductase secreted by microorganisms. These aromatic amines are toxic, mutagenic, carcinogenic and are a potential source of concern in the environment. Under aerobic conditions, the aromatic amines are metabolized further, therefore completing the detoxification of aromatic amines (Jones and Falkinham, 2003).

In last few years, several microorganisms have been found to decolourize and transform to completely mineralize azodyes. The bacterial metabolism of azodye is initiated by a reductive cleavage of azobond in most cases, which results in the formation of amines. These reductive processes have been studied in some aerobic bacteria, which grow on azo compounds. The sulfonated amines that are formed in the course of these reactions may be degraded aerobically (Stolz, 2001).

There are several reports on the aerobic reduction of azodyes by bacteria in the presence of another carbon sources. Certain aromatic amines and sulfonated amino aromatics are degraded by aerobic bacteria. It has been suggested to combine the anaerobic cleavage of the azodyes with an aerobic treatment system for the degradation of amines formed.

Recently an aerobic bacterial consortium consisting of two isolated strains BF1, BF2 of *Pseudomonas* and *P.putida MTCC1194* have been developed for aerobic degradation of a mixture of seven commercial textile azodyes in India. This bacterial consortium was able to decolourize the textile azodyes at alkaline pH of 9-10.5 and salinity of 0.9-3.68g/l in mineral media and stimulated textile effluent. The analysis of degradation products shows that dyes are converted to low molecular weight compounds (Senan and Abraham 2004).

Similarly, a mixture of bacterial isolates from domestic sevage treatment plant has been reported to be effective in decolourization of reactive azodyes, red RB, blue M2B and yellow. The mixed cultures could decolourize 95% of red RB and blue M2B. Decolourization remarkable enhances when peptone is used in the medium for growing the mixed culture (Vijaya *et al.,* 2003).

Kodam *et al*., (2005) reported a 100% decolourization of the sulfonated azodyes Reactive Red 2, Reactive Red 141, Reactive Orange 4, Reactive Orange 7 and Reactive Violet 5 by a aerobic bacterium KMK48, within 36h of incubation at room temperature and neutral pH.

The bacterial strain *Shewanella putrefaciens* are the most efficient azodye degrading bacteria because treatment time required by this strain was as short as 4h for complete decolourizarion of 100mg/l of ARS8 and DR-81 dyes under static conditions (Khalid *et al*., 2008).

The *Bacillus subtilis* was used to decolourize the Acidblue 113. It exhibited 90% decolourization ability within 50h when it is supplemented with starch and peptone and the decolourization is due to the dye degradation which was confirmed by HPLC (Gurulakshmi *et al* ., 2008).

The bacterial consortia C15 showed best colour removal in static culture with 80-100% colour removed in less than 72 hours. The performance of C15 exceeds the performance of individual bacterial isolates (Khadijah *et al*., 2009).

The strain *Kocuria rosea MTCC1532* degrade malachite green into non-toxic compounds due to their DCIP reductase enzyme (Parshetti *et al.*, 2006).

Bacillus sp isolated from textile effluent decolourize the methyl orange without the need for any exogenous carbon source (Pourbabaee *et al.*, 2005). Bacillus sp isolated from the effluent has the ability to degrade the textile azodye Navy blue 2GL in static condition at 48hr (Dawkar *et al.*, 2009).

Not only the organisms isolated from the effluent, and also the microorganism from food, like lactic acid bacteria have the ability to modify azodyes (Diaz and Mc Feeters 2009).

Similarly *Pseudomonas aeruginosa* isolated from the soil near the tannery degrade the Navitan Fast Blue S5R which is very important commercial diazodye in the tannery and textile industries (Nachiyar and Suseela , 2003).

2.8. IMMOBILIZATION OF CELLS FOR DEGRADATION OF DYES.

Whole bacterial cells are widely applied for reduction of azodyes present in textile dyeing waste water (Pearce *et al.*, 2003). Bacteria can degrade and detoxify a wide range of compounds. A promisining method of exploiting this ability is the application of immobilized cell technology. Immobilization prevents cell washouts and allows a high cell density to be maintained in a continuous reactor. Since the catalytic stability is often improved by immobilization. Microorganisms may degrade higher concentrations of toxic compounds than their free cell counterparts. It has been suggested that immobilization results in enhanced substrate uptake because of increased nutrient availability at solid-liquid interface or the damage to the cell wall facilitating entry of substrate (Kuhad *et al.*, 2004).

A microbial consortium having a high capacity for rapid decolourization of azodye was immobilized by a phosphorylated polyvinyl alcohol (PVA) gel. The immobilized cell beads exhibited a colour removal capability of 75% even at a high concentration of 500mg/l within 12h using flask culture (Chen *et al.*, 2003).

Immobilization method using biomass support particles has several advantages over other methods. Numerous carriers have been studied for immobilization method with good results obtained in many cases with carriers such as sintered glass, nylon web, polyurethane foam, porus polystyrene and silicon tubing observed that immobilized white rot fungus ,*Irpex lacteus* on polyurethane foam and pine wood have been found to decolourize the dyes and effluents effectively then pre mycelium.