

Biotechnology in Textile Effluent Treatment (Part 1)

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Abstract

With the increased demand for textile products, the textile industry and its wastewaters have been increasing proportionally, making it one of the main sources of severe pollution problems worldwide. The implementation of increasingly stringent standards for the discharge of wastes into the environment has necessitated the need for the development of alternative waste treatment processes. This paper provides a critical review on the current biotechnological approaches available for textile effluent treatment using different microorganisms. Their advantages and disadvantages and hence their range of applicability are outlined. A review of research directed toward developing enzymatic treatment systems for solid, liquid and hazardous wastes are presented. A large number of enzymes from a variety of different plants and microorganisms have been reported to play an important role in an array of waste treatment applications.

'Save the Earth to save the future'. Right from the inception of urbanisation and industrialisation with advancement in science of technology, it was gradually realised that growth cannot be considered to be a good thing if we ignore the environment in which we live. The textile chemical processing industry has importance of its own, being one of the basic needs of society and currently it is in the midst of a major restructuring and consolidation phase with the emphasis on product innovation, rebuilding and environmental friendliness.

Dyes have been applied to textile and other substrates for thousands of years, and dyers and their suppliers have continually sought to develop new processes and products that lead to better results or lower costs, in turn translating into commercial gain. Over the last few decades, the environmental impact of those products and processes has become an increasingly large part of the dyer's task. Given the growing emphasis on the environment, it is common to have almost any technical advance in the application of dyes, be it dye, auxiliary, or machine, claimed as environmentally beneficial, however spurious such a claim might be.

The terms pollution and contamination are sometimes used interchangeably in environmental matters to describe the introduction of a substance at a concentration sufficient to be offensive or harmful to human, animal or plant life. The word pollution is more strictly used to describe contamination caused or induced by human activities and is typically measured by reference to predetermined permissible or recommended tolerance limits.

The textile industry has a major impact not only on the nation's economy but also on the economic and environmental quality of life in many communities. Textile processing generates various types of waste streams, including water-based effluent as well as air emissions, solid wastes and hazardous wastes. The nature of the waste generated depends on the types of fibres and the chemicals used the type of textile facility, and the

processes and technologies being operated. In quantity, wastewater generation is a major source of pollution from a textile processing factory as the treatments carried out on textile materials are essentially carried out through aqueous medium.

Pollution of communal water bodies by waste dyestuff released from textile plants and dyehouses represents a major environmental concern. Although presently a wide range of physical and chemical methods is available to decolorize dye-contaminated effluents, alternative processes based on biotechnological principles are attracting increasing interest since they often avoid consumption of high quantities of additional chemicals and energy.

Biotechnology in Effluent treatment

Biotechnology is defined as the techniques that use living organisms or parts of organisms to produce a variety of products to improve plants or animals or to develop microorganisms to remove toxics from bodies of water, or act as pesticides.

Biotechnology is a field of applied biology that involves the use of living organisms and bioprocesses in engineering, technology, medicine and other fields requiring bio products. Modern use similar term includes genetic engineering as well as cell- and tissue culture technologies. The concept encompasses a wide range of procedures (and history) for modifying living organisms according to human purposes - going back to domestication of animals, cultivation of plants, and "improvements" to these through breeding programs that employ artificial selection and hybridization. By comparison to biotechnology, bioengineering is generally thought of as a related field with its emphasis more on higher systems approaches for interfacing with and utilizing living things. The United Nations Convention on Biological Diversity defines biotechnology as: "Any technological application that uses biological systems, living organisms, or derivatives thereof, to make or modify products or processes for specific use."

Effluent is an out flowing of water or gas from a natural body of water, or from a human-made structure. Effluent is defined by the United States Environmental Protection Agency as "wastewater - treated or untreated - that flows out of a treatment plant, sewer, or industrial outfall. Generally refers to wastes discharged into surface waters". The Compact Oxford English Dictionary defines effluent as "liquid waste or sewage discharged into a river or the sea". Effluent in the artificial sense is generally considered to be water pollution, such as the outflow from a sewage treatment facility or the wastewater discharge from industrial facilities. An effluent sump pump, for instance, pumps waste from toilets installed below a main sewage line. In the context of waste water treatment plants, effluent that has been treated is sometimes called secondary effluent, or treated effluent. This cleaner effluent is then used to feed the bacteria in bio filters.

Characterization of effluent

Biochemical oxygen demand or BOD: Biochemical oxygen demand or BOD is a chemical procedure for determining the amount of dissolved oxygen needed by aerobic biological organisms in a body of water to break down organic material present in a given water sample at certain J temperature over a specific time period. It is not a

precise quantitative test, although it is widely used as an indication of the organic quality of water. It is most commonly expressed in milligrams of oxygen consumed per litre of sample during 5 days of incubation at 20°C and is often used as a robust surrogate of the degree of organic pollution of water.

Biological Oxygen Demand (BOD) is a measure of the oxygen used by microorganisms to decompose this waste. If there is a large quantity of organic waste in the water supply, there will also be a lot of bacteria present working to decompose this waste. In this case, the demand for oxygen will be high (due to all the bacteria) so the BOD level will be high. As the waste is consumed or dispersed through the water, BOD levels will begin to decline.

Nitrates and phosphates in a body of water can contribute to high BOD levels. Nitrates and phosphates are plant nutrients and can cause plant life and algae to grow quickly. When plants grow quickly, they also die quickly. This contributes to the organic waste in the water, which is then decomposed by bacteria. This results in a high BOD level. The temperature of the water can also contribute to high BOD levels. For example, warmer water usually will have a higher BOD level than colder water. As water temperature increases, the rate of photosynthesis by algae and other plant life in the water also increases. When this happens, plants grow faster and also die faster. When the plants die, they fall to the bottom where they are decomposed by bacteria. The bacteria require oxygen for this process so the BOD is high at this location. Therefore, increased water temperatures will speed up bacterial decomposition and result in higher BOD levels.

When BOD levels are high, dissolved oxygen (DO) levels decrease because the oxygen that is available in the water is being consumed by the bacteria. Since less dissolved oxygen is available in the water, fish and other aquatic organisms may not survive.

Chemical oxygen demand (COD): In environmental chemistry, the chemical oxygen demand (COD) test is commonly used to indirectly measure the amount of organic compounds in water. Most applications of COD determine the amount of organic pollutants found in surface water (e.g. lakes and rivers), making COD a useful measure of water quality. It is expressed in milligrams per liter (mg/L, which indicates the mass of oxygen consumed per liter of solution. Older references may express the units as parts per million (ppm).

Chemical oxygen demand (COD) is a measure of the capacity of water to consume oxygen during the decomposition of organic matter and the oxidation of inorganic chemicals such as ammonia and nitrite. COD measurements are commonly made on samples of waste waters or of natural waters contaminated by domestic or industrial wastes. Chemical oxygen demand is measured as a standardized laboratory assay in which a closed water sample is incubated with a strong chemical oxidant under specific conditions of temperature and for a particular period of time. A commonly used oxidant in COD assays is potassium dichromate ($K_2Cr_2O_7$) which is used in combination with boiling sulfuric acid (H_2SO_4). Because this chemical oxidant is not specific to oxygen-consuming chemicals that are organic or inorganic, both of these sources of oxygen demand are measured in a COD assay.

Total Dissolved Solids (TDS): Total Dissolved Solids (TDS) is a measure of the combined content of all inorganic and organic substances contained in a liquid in molecular, ionized or micro-granular (colloidal sol) suspended form. Generally the operational definition is that the solids must be small enough to survive filtration through a sieve the size of two micrometer. Total dissolved solids are normally discussed only for freshwater systems, as salinity comprises some of the ions constituting the definition of TDS. The principal application of TDS is in the study of water quality for streams, rivers and lakes, although TDS is not generally considered a primary pollutant (e.g. it is not deemed to be associated with health effects) it is used as an indication of aesthetic characteristics of drinking water and as an aggregate indicator of the presence of a broad array of chemical contaminants.

Primary sources for TDS in receiving waters are agricultural and residential runoff, leaching of soil contamination and point source water pollution discharge from industrial or sewage treatment plants. The most common chemical constituents are calcium, phosphates, nitrates, sodium, potassium and chloride, which are found in nutrient runoff, general storm water runoff and runoff from snowy climates where road de-icing salts are applied. The chemicals may be cations, an ions, molecules or agglomerations on the order of one thousand or fewer molecules, so long as a soluble micro-granule is formed. More exotic and harmful elements of TDS are pesticides arising from surface runoff. Certain naturally occurring total dissolved solids arise from the weathering and dissolution of rocks and soils.

Total suspended solids (TSS): Total dissolved solids are differentiated from total suspended solids (TSS), in that the latter cannot pass through a sieve of two micrometers and yet are indefinitely suspended in solution. The term "settleable solids" refers to material of any size that will not remain suspended or dissolved in a holding tank not subject to motion, and excludes both TDS and TSS. Settleable solids may include larger particulate matter or insoluble molecules. It is listed as a conventional pollutant in the U.S. Clean Water Act. This parameter was at one time called non-filterable residue (NFR), a term that refers to the identical measurement: the dry-weight of particles trapped by a filter, typically of a specified pore size.

Total organic carbon (TOC): Total organic carbon (TOC) is the amount of carbon bound in an organic compound and is often used as a non-specific indicator of water quality or cleanliness of pharmaceutical manufacturing equipment.

A typical analysis for TOC measures both the total carbon present as well as the so called "inorganic carbon" (IC), the latter representing the content of dissolved carbon dioxide and carbonic acid salts. Subtracting the inorganic carbon from the total carbon yields TOC. Another common variant of TOC analysis involves removing the IC portion first and then measuring the leftover carbon. This method involves purging an acidified sample with carbon-free air or nitrogen prior to measurement, and so is more accurately called non-purgeable organic carbon (NPOC).

Volatile organic compounds (VOCs): Volatile organic compounds (VOCs) refer to organic chemical compounds which have significant vapour pressures and which can affect the environment and human health. VOCs are numerous, varied, and ubiquitous.

Although VOCs include both man-made and naturally occurring chemical compounds, it is the anthropogenic VOCs that are regulated, especially for indoors where concentrations can be highest. VOCs are typically not acutely toxic but have chronic effects. Because the concentrations are usually low and the symptoms slow to develop, analysis of VOCs and their effects is a demanding area.

Techniques of Effluent Treatment

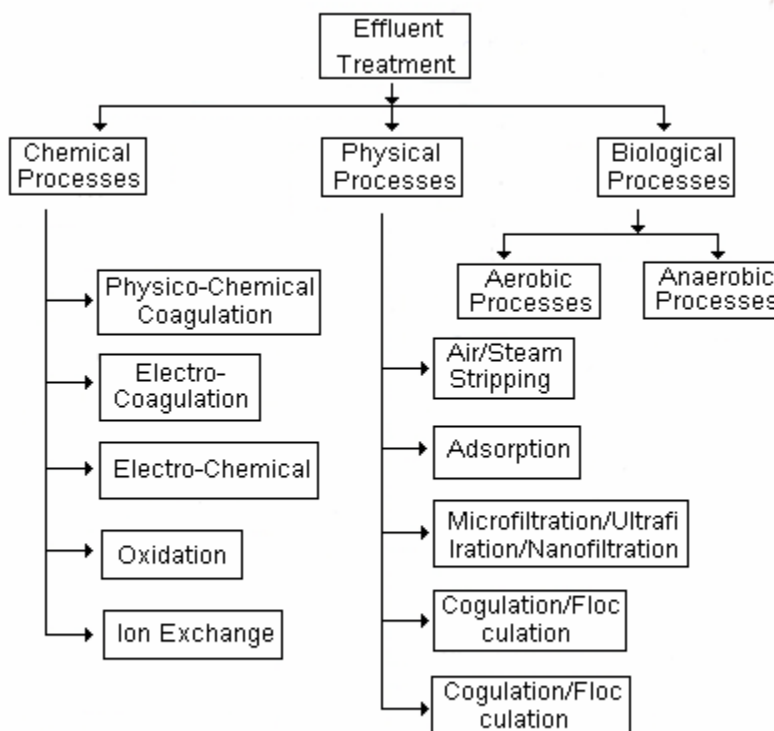


Figure 1: Effluent treatment method

Physical & physico-chemical waste water treatment methods: The main objective of physical treatment is to remove undessolve chemicals particulate matter present in waste water. Although not dye-specific, these methods have been discussed under the sub-heading: adsorption, ion-exchange, flocculation, coagulation and membrane separation.

Adsorption: Adsorption is one of the most effective, economically feasible techniques for the removal of textile dyes. Dyes that are recalcitrant to biological breakdown can often be removed by using adsorbents. The adsorbents most investigated for various types of effluent treatment are dead plants and animal residues, known as biomass, which include charcoals, activated carbons, activated sludge, compost and various plants.

The most widely used adsorbent is activated sludge. Important factors affecting the optimum adsorption of colour with activated sludge are its quality and concentration, the hardness of the water and the duration of the treatment. Although activated sludge

is suitable for removal of various textile dyes, it alone cannot satisfy modern days tight consent limits.

Another adsorbent is activated carbon, but it is very expensive and, for reuse, needs to be treated with solvent. However, the solvent is also expensive. Activated carbon adsorbents are applicable within a wide range of pH, but colour removal is mainly effective for non-ionic and cationic dyes. Unfortunately, most of the dyes used in the textile industry are anionic in their soluble form. One of the main disadvantages of activated carbon is fouling by natural organic matter (NOM). It competes with other organic pollutants for adsorption sites and prevents them from entering the micro-pores by blocking them.

Ion-exchange resins: As activated carbon is expensive and activated sludge alone is not efficient enough for complete colour removal, the search for alternative and cheaper adsorbents continued. Various ion-exchange resins derived from sugar cane bagasse, waste paper, polyamide wastes, chitin, etc., were applied as adsorbents for removal of colour and other organics. Colour-removal efficiency with these ion-exchange resins was comparable with that achieved using activated carbon.

Most of the dyes used in the textile industry are either anionic (such as acid, reactive, direct and metal complex) or cationic (e.g. basic dyes). These dyes form complexes with ion-exchange resin and form large flocs, which can be separated by further filtration. Quaternised sugar cane bagasse is another ion-exchange resin derived from natural products and it has excellent colour removal capacity for hydrolysed reactive dyes. Investigation shows that high salt content in the reactive dye wastewater has a minor influence on colour removal with this resin. Chitosan is also a good adsorbent for the removal of dyes and is most efficient for absorbing dyes of small molecular size. Most ion-exchange resins have poor hydrodynamic properties compared with activated carbon, and it is difficult for them to tolerate the high pressures required to force large volumes of wastewater through the bed at a high flow rate.

McKay carried out a detailed study on colour removal by chitin, which is a by-product of the shellfish industry. Chitin contains -OH and -NH₂ groups and has affinity for dyes. Investigation showed that chitin is only suitable for those dyes that are strongly anionic or weakly anionic in nature, but, even then, the dye separation is too low (only fractions of a milli equivalent per gram of chitin used). It works as a weak-base anion exchanger, but there is a problem of instability at low PH. Although this can be overcome by forming cross-links within the polymeric structure (chitin), this, in turn, results in a lowering of its dye binding capacity. Moreover, mixing of different classes of dyes and addition of surfactants reduces the colour removal efficiency.

Coagulation: Coagulation has also been widely used for color removal textile waste waters. Although this process removes color only partially, it also reduces COD to varying extent depending upon the coagulant used. Coagulation result from lowering of the Zeta potential at the surface of the particles and the association of these particles and the association of this particles to form flocculated agglomerates. A number of cationic, anionic, or non -ionic polymer are used for coagulant for color removal. At least four major difficulties present themselves in coagulation process. The first is that

expensive chemicals which eventually are to be thrown away are used. Secondly, High water soluble dyes resist coagulation or necessitate the use of high amount of coagulants, both these parameters increase cost tremendously. Thirdly, the color coagulate solid waste is generated which also requires ways and means of legislative disposal. The fourth or perhaps the most serious disadvantage is the toxicity of the sludge produced and increase in total dissolved solids in the treated waste water. In spite of all of these limitations, color removal from the waste waters and research input in this area is continued unabated.

Electro-coagulation is another economically feasible method for removal of organic matter from textile waste water and is prized for the production of less quantity of sludge as excess use of chemicals at the chemical coagulation process could be avoided in electro coagulation process. Additionally, the coagulants are generated by electro-oxidation of sacrificial soluble anode, thus the addition of chemical is either not necessary or is at least minimized.

Membrane Technology: Various separation techniques including microfiltration, ultrafiltration, nanofiltration and reverse osmosis have been applied in the textile industry for the recovery of sizing agent from effluent and some of these methods are effective treatments for removal of color from waste water regardless of the type of dyestuff used. Microfiltration is of no use for waste water treatment because of its large pore size. Membrane can act as a physical barrier to specific components waste water without degradation of these compounds. Membrane potentially allows the removal and reuse of dyes, chemicals & process water. Ultrafiltration has been successfully applied for recycling high molecular weight & insoluble dyes (e.g. indigo & disperse dyes), auxiliary chemicals & water. The separation technique offers a viable alternative to biological treatment. Hydrolysed reactive dyes, the most problematic to remove by conventional methods of color removal have been successfully removed from textile effluent using nanofiltration and reverse osmosis method. The major disadvantages of these processes are high capital cost combined with higher energy cost & short membrane life. The membranes are prone to clogging & need to be regenerated frequently.

Chemical methods for waste water treatment: A variety of approaches have been used to remove dyes from textile waste effluent streams. The key chemical methods of decolorisation of textile waste waters are neutralization, oxidation and reduction are presented here.

Neutralization: In general, waste water discharge from the textile chemical processing industries is alkaline and requires neutralization using mineral acid with the help of pH control system prior to secondary treatment. The principal reagents for neutralizing acid waste are sodium hydroxide, sodium carbonate and hydrated calcium hydroxide.

Oxidation: The most widely studied chemical decoloration method is oxidation because of the simplicity of the process. In this process, as the dye molecules are oxidized, they are broken down into small, colorless molecules like carbon dioxide, water, nitrogen, aldehydes, acid sulphate etc depending upon the dye structure and on the strength of the oxidant[9]. Conventional chemical oxidation of dye typically involves the use of

oxidizing agents such as chlorine & chlorine dioxide, ozone (O₃), hydrogen peroxide and permanganate.

Electrochemical oxidation is another dependable technology which is relatively new has been used for removal of color, BOD, COD, TOC, solids & heavy metal such as calcium, copper and zinc from textile waste waters. The efficiency of the process depends on several parameter e.g. potential difference and currents intensity, nature & number of electrodes & distance between them, pH, and salt concentration of the solution etc. Electrochemical treatment is effective for removing disperse reactive and acid dyes along with textile auxiliary such as leaving agent.

Biological method of color removal: Although presently a wide range of physical and chemical methods are available to decolorize dye-contaminated effluents, alternative processes based on biotechnological principles are attracting increasing interest since they often avoid consumption of high quantities of additional chemicals and energy, ability to produce less sludge, cost effectiveness & environmental benignity. Biological treatment either aerobic or anaerobic, is generally consider to be the most effective means of removing wastes from wastewater enriched in organic constituents. Microorganism plays a crucial role in the minimization of complex organic molecules and xenobiotic compounds. An advantage of the biological treatment over certain physic-chemical treatment methods is that over is that over 70% of the organic materials, determined by COD analysis may be converted to biosolids.

Dyes are usually stable organic molecules & thus more difficult to biodegrade. Other factors that influence biodegradation of the dye include high water solubility and high molecular weight, which inhibits permission through biological cell membranes. Biological removal of dyes from textile and dye industrial waste water can be broadly classified into three categories: aerobic treatment, anaerobic treatment and combined anaerobic-aerobic treatment.

Aerobic treatment involves the use of free oxygen dissolve in waste water to degrade organic constituents in the presence of microorganisms. Dye themselves are generally resistance to oxidative degradation, since one of the most important requirement of commercial dyes is resistance in fading caused by chemical & photo oxidation. The conventional aerobic treatment systems are stabilizing ponds, aerated lagoons, trickling filter (packed bed reactor) and active sludge.

The anaerobic treatment takes place in absence of free oxygen and converts organic compounds to methane and carbon dioxide. In case of biological treatment alone is insufficient to decolorised the dye wastewater or the colored textile effluent, a combination of chemical pre-treatment and aerobic or anaerobic degradation of textile dye waste could be employed.

The biodegradability of the dyes may significantly be influenced by the substituents & their placement in the chromophore. It has been observed that ionic azo dyes with hydroxyl & amino groups are more likely to undergo repid degradation compared to the dye appended with methyl, amino, acetamidoor nitrogroups, compared to unsubstituted chromophores. Adsorption of microbes to the substrate is another important feature for successful aerobic & anaerobic decoloration.

Aerobic treatment:

Activated Sludge: The most generally employed aerobic treatment system for dye waste water is activated sludge system wherein, microorganism are suspended in aerated waste water. [4] A large microbial pollution thus created a significant amount of biological sludge, but its disposal increases the overall cost of treatment process. In aerobic treatment, micro-organisms in the activated sludge utilize dissolved oxygen to convert the wastes into more biomass and carbon dioxide. Organic matter is partially oxidized and some of the energy produced is used for generating new living cells under the formation of flocks. The flocks are allowed to settle and are then removed as sludge. A proportion of the sludge removed is recycled back to the aeration tank to maintain the micro-organism population. The remainder of the sludge can be fed back in a subsequent anaerobic treatment. Combinations of anaerobic/aerobic pilot plant for the treatment of coloured textile effluents are very powerful, especially for the elimination of azo dyes.

Aerobic bacteria have been described that oxidatively decolorize many dyes from several classes, among which azo dyes always turned out to be the most recalcitrant compounds. The absorption of dyes on activated sludge is mainly dependent on dye properties such as molecular structure, the number & the position of the substituent in the dye molecule & its solubility. Adsorption increase if the chromophore bears hydroxyl & nitro groups but diminishes with the presence of sulphonate groups, owing to the increase aqueous solubility of the dyes. The more sulfonic acid groups are present in the dye structure, the more soluble and, therefore, the less responsive to treatment is the dye to the activated sludge process. Basic and direct dyes respond well to treatment in the activated sludge process. However, reactive dyes and some acid dyes seem to cause more of a problem. It is generally considered that the activated sludge process removes only low levels of these dyes.

In certain study it is describe that, all reactive reactive dyes of chlorotriazine group exhibited zero bioelimination. A CI Reactive Black 5- a sulphatoethyl sulphone dyes ($R=SO_3 Na^+$) resists bioelimination by active sludge, however, its hydrolysed form ($R=H$) exhibited 35% bioelimination.

Dyes are generally very resistant to degradation under aerobic conditions. Dyestuff removal currently occurs in the primary settling tank of a WWTP for the water insoluble dye classes (disperse, vat, sulphur, azoic dyes), while the main removal mechanism for the water soluble basic and direct dyes in conventional aerobic systems is adsorption to the biological sludge. Reactive dyes, however, adsorb very poorly to sludge and are thus major troublemakers in relation to residual colour in discharged effluents.

Although aerobic treatment removes 60-70% of the organic matter from textile waste waters, the toxicity level is hardly reduced due to the presence of organic matter which cannot be degraded and requires tertiary treatment to remove toxicity. Another major problem with aerobic biological treatments of the dye waste water is the difficulties in acclimatizing the microorganisms to the substrate due to the constant change in the waste influx due to the changes in the batch dyeing operations. Thus, conventional aerobic systems fail to degrade many dyestuffs and may experience mechanical

breakdown, expensive capital and running costs, susceptibility to shock loadings, occupation of large area of the land.

Anaerobic treatment: Anaerobic treatment occurs in sealed tanks and converts the waste into methane and carbon dioxide. Where nitrogenous and sulfide-containing pollutants are present, ammoniacal substances and hydrogen sulfide are produced. At some municipal sewage treatment plants, the sludge formed by the aerobic treatment process passes into tanks for anaerobic treatment. Considerable heat is produced from anaerobic treatment. By using heat exchangers to extract the heat, the bioenergy can be utilized to heat buildings. The methane produced is collected, compressed and then used in generators to produce electricity. The electricity produced can power site processes and the surplus is sold to the national grid. The production of this power not only reduces the running costs of the treatment plant but also provides a welcome income, thus reducing the costs further.

Primary degradation and decolourisation of dyes with azo-based chromophores can be achieved by the reduction of the azo bond (-N=N-). This can be done by using strong reducing agents such as sodium hydrosulphite, thiourea dioxide, sodium formaldehyde sulphonylate and sodium borohydride. The rate of decoloration is however dependable on dye structure as well as additional organic carbon source. The reduction of azo bond is overall a 4e⁻ process, (figure), 2e⁻ in reducing azo bonds to hydrazine link followed by another 2e⁻ reduction process to the constituting amines.

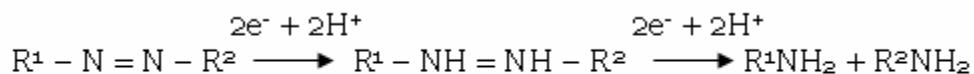


Figure 2: Reduction of azo bond

The amines produced by the reduction of the azo dyes are colourless but they are very resistant to further degradation under anaerobic conditions. Under aerobic conditions the mineralisation of these amines can be accomplished. Complete treatment can thus be obtained by a sequenced anaerobic/aerobic treatment. Recently, however, the complete anaerobic mineralisation to methane of an azo dye decolourisation product (S-aminosalicylate) by a sludge ' adapted to the degradation of 2-nitro-phenol was reported.

It has been shown that azo and nitro compounds are reduced in the sediments and are the intestinal environmental resulting in the generation of toxic amines. The amines produced are colorless and are resistance to further degradation under anaerobic conditions. The intentional generation of aromatic toxic amines that are generally more toxic than the dye itself, is not appealing from an environmental or regulatory perspective. Thus, the breakdowns of azo dyes to their corresponding amines necessitate a subsequent aerobic treatment for complete mineralization. The major advantage of anaerobic system apart from decoloration is production of biogas (if complete mineralization of organic contaminant to methane and oxygen occurs) that can be used to generate heat & power to meet the energy requirements. The anaerobic process generally occupy less space, treat waste waters more efficiently with lower running costs and produce less sludge.

Scouring and desizing effluents are major contributors to the organic load in textile effluents. Traditional sizes such as starches and their derivatives are readily biodegradable under aerobic and anaerobic conditions. However, bulking of activated sludge occurs frequently if a large proportion of the waste stream consists of desizing waste water. The use of recyclable sizes such as polyvinyl alcohol (PVA) is a viable option for integrated companies and can give organic load reductions of up to 90% in the wastewater from desizing operations. Anaerobic treatment produces a much smaller volume of sludge when compared with aerobic treatment and no aeration is needed, a factor which represents a major cost in aerobic treatment, given the high BOD levels involved. This gives the anaerobic digestion process a potential economic advantage.

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