International Journal of Chemical Engineering Research.
ISSN 0975-6442 Volume 9, Number 1 (2017), pp. 121-136

http://www.ripublication.com

Textile Organic Dyes: Polluting effects and Elimination Methods from Textile Waste Water

Rummi Devi Saini

Chemistry Department
SMDRSD College, Pathankot, 145001,India

Abstract

Colour imparts attraction to the fabric but its use for dying has become a big environmental hazard .Art of applying colour to the fabric is known to mankind since 3500BC. In 1856 W.H. Perkins discovered the use of synthetic dyes which provide a wide range of fast and bright colors. Use of synthetic dyes has an adverse effect on all forms of life. The harmful chemicals present in textile effluents react with many disinfectants especially chlorine and form bi products that are often carcinogens. Colloidal matter presents along with color increases the turbidity, gives bad appearance, foul smell and prevents the penetration of sunlight into water bodies required for the photosynthesis which interfere with the oxygen transfer mechanism and hence marine life. If textile dyes effluents are allowed to flow in drains and rivers it affects the quality of drinking water making unfit for human consumption. So it is important to remove these pollutants from the waste water before its final disposal into water bodies. Here in this paper the textile organic dyes, their polluting effects and various remediation's using physical, chemical and biological methods has been reviewed.

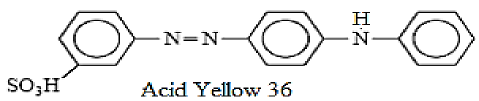
INTRODUCTION:

The residual dyes from different sources such as textile, pulp, paper, pharmaceutical, tannery; industries are wide variety of organic pollutants introduced into our natural water resources or waste water treatment units. One of the main sources with severe polluting problem worldwide is the textile industry and its waste waters containing dyes, 10 – 25%of the textile dyes are lost. During dying process and 2-20% are directly discharged as aqueous effluents in different environmental components (1). The discharge of effluents containing dyes into water is undesirable due to its colour, dyes released and the breakdown products of dyes which are toxic, carcinogenic to life mainly because of the presence of carcinogens present such as naphthalene, benzamine and other aromatic compounds. If not treated these dyes remain in the environment for a long period of time (2,3). Another big issue is, the textile industry consumes large amount of water. So recycling of treated waste water should be done due to the high levels of contamination in dyeing and finishing process. Due to the toxic nature and adverse effect of synthetic dyes on environment the move to natural dyes started worldwide. But due to the use of mordents e.g. chromium to fix color on to the fabric they may be very toxic and render waste water poisonous. Natural dyes also require comparatively large quantity of water. Also about 80% of the dye stuff only stays on the cloth rest drain out even natural dyes high impact on the environment (4).

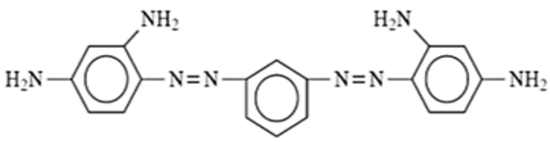
Classification of organic textile dyes

The natural textile dyes were mainly used in textile coloring until 1856 using dyes extracted from vegetable and animal resources. The synthetic dyes were discovered in 1856. These dyes are aromatic compounds having aromatic rings that contain delocalized electrons and also different functional groups. The color of the dye is due to the chromogene-chromophore i.e. acceptor of electrons, in the molecule of dye, and the dyeing capacity of the dye is due to the presence of auxochrome groups i.e. donor of electrons. The chromogene is an aromatic structure which normally contains benzene, naphthalene or anthracene rings carrying binding chromophores that contain double conjugated links with delocalized electrons forming conjugated systems. The groups which mainly act as chromophores are the azo group (-N=N-), methine group (-CH=), ethylene group (=C=C=), carbonyl group (=C=O), carbon-sulphur (=C=S; ≡CS-S-C≡), nitro (-NO2; -NO-OH), nitrozo (-N=O; =N-OH), carbon-nitrogen (=C=NH; -CH=N-), or chinoid groups. The auxochrome groups are ionizable groups, which are responsible for the binding capacity of the dyes molecules onto the textile material. The common auxochrome groups are: -COOH (carboxyl), -NH2 (amino), -SO3H (sulphonate) and -OH (hydroxyl) (5,21).

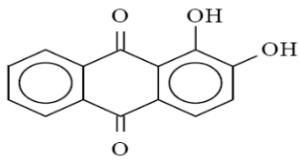
Structure of some of the common dyes



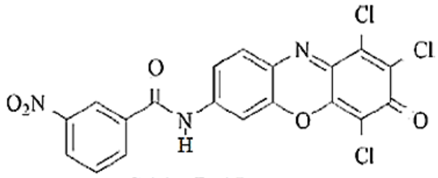
Acid Yellow 36



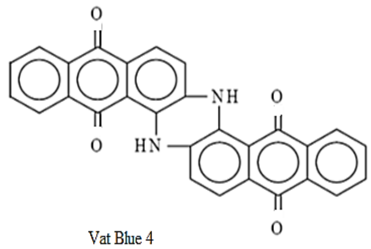
Basic Brown



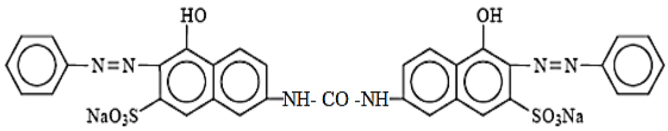
Mordant Red 11



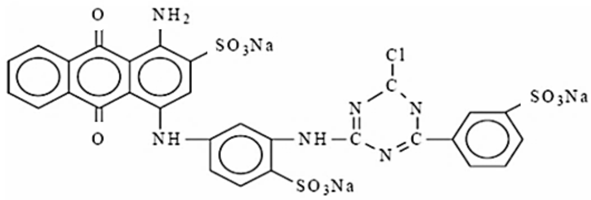
Sulphur Red 7



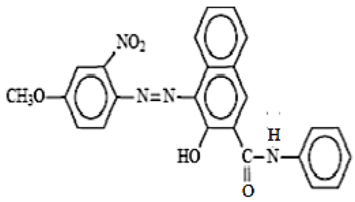
Vat Blue 4



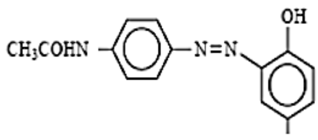
Direct Orange 26



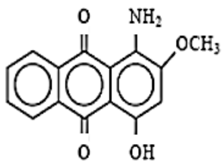
Reactive Blue 5



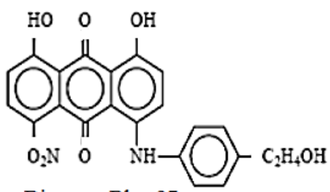
Bluish Red Azoic Dye



Disperse Yellow 3



Disperse Red 4



Disperse Blue 27

The textile dyes are mainly classified in two ways:

(1) based on its application characteristics such as acid, basic, mordant, reactive, direct, disperse, sulphur dye, pigment, vat, azo insoluble.

(2) based on its chemical structure such as nitro, azo, carotenoid, , acridine, quinoline, indamine, diphenyl methane, xanthene sulphur, anthraquinone, indigoid, amino- and hydroxy ketone, phthalocyanine, inorganic pigment, etc.

The textile dyes are also classified as anionic, nonionic and cationic dyes on the basis of the general structure. The major anionic dyes are the direct, acid and reactive dyes (45). The most problematic ones are the brightly coloured, water soluble reactive and acid dyes because they cannot be eliminated from textile industry effluents by conventional treatment systems. The major nonionic dyes (which do not get ionized in the aqueous medium) are disperse dyes, and the major cationic dyes are the azo basic, anthraquinone disperse dyes.

Textile processing technology

The common textile processing technology consists of desizing, scouring, bleaching, mercerizing and dyeing processes (EPA, 1997)(6):

Sizing is the first preparation step, which involves addition of sizing agents such as starch, polyvinyl alcohol (PVA) and carboxymethyl cellulose to provide strength to the fibres so as to minimize breakage.

Desizing is the process used to remove sizing agents prior to weaving.

Scouring is the process in which impurities are removed from the fibres by treating them with alkali solution usually sodium hydroxide to breakdown natural oils, fats, waxes and surfactants.

Bleaching is the step in which unwanted colour is removed from the fibers by treating with chemicals such as sodium hypochlorite and hydrogen peroxide.

Mercerising is a step in which a concentrated alkaline solution is applied to the fabric that is then washed using an acid solution fibres prior to the dyeing step. Mercerising increases the dye-ability, lustre and appearance of the fibre.

Dyeing is the process which involves the addition of colour to the fibres. It usually needs large

volumes of water in the dye bath as well as during the **rinsing step**. Depending on the nature of the fabric, many chemicals like metals, salts, surfactants, organic processing aids, sulphide and formaldehyde, may be added to improve dye adsorption onto the fibres in the dyeing process.

Dye fixation on textile fibres

In general, textile fibres can catch dyes in their structures as a result of physical adsorption which involves van der Waals forces, hydrogen bonds and hydrophobic interactions between the fibre and dye. The binding of the dye in fibres depends on nature and chemical constitution of the dye. The strongest dye-fibre attachment occurs due to chemisorption which involves the formation of a covalent bond along with an additional electrostatic interaction when the dye ion and fibre carry opposite charges.

In alkaline conditions i.e. pH 9-12 , at 30-70ºC temperatures with 40-100 g/L salt concentration, reactive dyes form a reactive vinyl sulfone ($-SO_3-CH{=}CH_2$) group, which forms a bond with the fibres. But, the vinyl sulfone group undergoes hydrolysis in the presence of water and the products formed do not have any affinity with the fibres thus they do not form a covalent bond with the fibres (43). Consequently, a large amount of the dye is washed away in the wastewater. The fixation efficiency varies with the class of azo dye used, and it is about 98% for basic dyes and 50% for reactive dyes (7). Large amounts of salts such as sodium nitrate, sodium sulphate and sodium chloride are used in the dyebath. Sodium hydroxide is extensively applied to increase the pH to the alkaline range.

Fixation degree of different dye classes on textile support (EWA, 2005)(8).

Dye class	**Fibre type**	**Fixation degree, %**	**Loss in effluent, %**
Basic	Acrilic	95-100	0-5
Acid	Polyamide	80-95	5-20
Disperse	Polyester	90-100	0-10
Direct	Cellulose	70-95	5-30
Reactive	Cellulose	50-90	10-50
Sulphur	Cellulose	60-90	10-40
Metal complex	Wool	90-98	2-10

The problem of large dye-containing effluent has been identified mainly with the dyeing of cellulose fibres particularly with the use of reactive dyes (10-50% loss in effluent), sulphur dyes (10-40% loss in effluent), direct dyes (5-30% loss in effluent), and vat dyes (5-20% loss in effluent). The research is required to focus the attention of the textile coloration industry production techniques that minimise dye wastes, reduce colour loads in the effluent by optimisation of processes, and control automatically the dyeing and printing operation.

Characterisation of Textile Organic Dyes

Colour in wastewater is classified in terms of true or real colour i.e. colour water sample without turbidity, or apparent colour i.e. colour of untreated water sample. The common methods used to measure the colour of dye solution or dispersion or waste water are visual comparison and spectrophotometry. By visual comparison method intensity of the colour is measured or predicted by comparing the colour of sample (textile waste water) with either known concentrations of coloured standard solutions generally a platinum-cobalt solution, or accurately calibrated colour disks. This method is not much applicable for highly coloured industrial wastewaters. Another technique applied is the spectrophotometric method, in which colour-measuring procedures vary between the methods and of the most commonly used are Tristimulus Filter Method, American Dye Manufacturer Institute (ADMI) Tristimulus Filter Method, and Spectra record .

Tristimulus Filter: In tristimulus Filter three tristimulus light filters are placed between the light source such as tungsten lamp and a photoelectric cell inside a filter photometer. The transmittance is converted to trichromatic coefficient and value characteristic of colour.

ADMI Tristimulus: The ADMI colour value offers a true watercolour measure, which can be distinguished in 3 (WL) ADMI, the transmittance is determined at 590, 540 and 438 nm or 31 (WL) ADMI, the transmittance is recorded at each 10 nm in the range of 400-700 nm.

Spectra record: In this method a complete spectrum of the sample textile waste water is recorded and the entire spectrum, or a part of spectrum is compared. In the modified method the areas under an extinction curve gives the colour intensity.

Textile organic dyes environmental hazards:

High concentration of dyes in water bodies stop the oxygenation capacity of the receiving water and cut of sun light thus upsetting the biological activity of aquatic life and photosynthesis process of aquatic plants such as algae, The blue, green or brown colours of water courses is accepted by public but the red and purpide colors in water bodies make people concern. Polluting effects of these dyes is also due to their non-biodegradability, they keep on accumulating in the sediments, in fishes or other aquatic life forms. Decomposition of dyes into pollutants in carcinogenic or mutagenic compounds causing allergies, skin irritation, or different tissue changes (10). Azodyes which are aromatic compounds cause high potential health risk by adsorption of azodyes and their breakdown products like toxic amines through the gastrointestinal tract, skin, and lungs and also formation of hemoglobin adducts. Several Azodyes cause damage of DNA which leads to malignant tumors. Carcinogenic potential of the dye increase when electrodonoting substituents are present in ortho and para position. Toxicity can be reduced with protonation of amino groups. The azodyes such as direct black 38, azodisalecylate and their breakdown derivatives like bezidine, its derivatives, a large number of anilines nitro semis, dimethyl amines etc. are known to induce cancer in human and animals (11). Some azodyeds have been linked to bladder cancer in humans, splenic aromas, hepato carcinomas and nuclear anomalies like chrosomal aberration in mammalian cells (12). The dyes which are made from known carcinogens such as benzidine and other aromatic compounds are reported as the most problematic dyes. Anthroquinone-based dyes because of their fused aromatic ring structure are resistant to degradation. There is evidence that malachite dye has adverse effect on immune and reproductive systems. It is also a geno toxic and carcinogenic agent. CI dispose of blue dye has genotoxic and cytotoxic effects on human cells. It also causes DNA fragmentation.

Separation and elimination procedure to remove textile organic dyes from water:

The organic dyes must be separated and eliminated from water by effective and viable treatments at sewage treatments works or on site by trying to remove, degrade neutralize the harmful pollutants so as to neutralize the harmful effects of industrial effluents. They have detergent, surfactants, weakly biodegradable substances suspended solids along with unused dyes. Due to diverse chemical nature of textile effluents, they are difficult to treat by conventional purification procedures. Treatments like chlorination cannot be used as it release mutagenic products even from less harmful dyes.

Physical methods for removal of organic dye pollutants from waste water:

Adsorption: Adsorption has been found to be one of the most effective and established treatment of wastewater in textile industry as it is an economically achievable process for dyes removal and/or decolourization of textile effluents. The process involves the transfer of soluble organic dyes from wastewater to the surface of the adsorbent which is solid and highly porous material. The adsorbent adsorbs each compound to be removed to its capacity and when it is 'spent' should be replaced by fresh material. The spent adsorbent may be either regenerated or incinerated. The main factors which influence dye adsorption are: interaction between dye & adsorbent, surface area and particle size of adsorbent , pH , temperature and time duration of contact. The most commonly used adsorbent is activated carbon. Activated carbon has been engineered for optimum adsorption of large, negatively charged or polar molecules of dyes. Powdered or granular activated carbon with specific surface area of 500-1500 m2/g; pore volume of 0.3-1 cm3/g; bulk density of 300-550 g/L has been observed to have a practically good colour removal capacity if it is used in a separate filtration step. The cationic mordant and acid dyes are removed with high removal rates (13), whereas dispersed, vat, direct, pigment and reactive dyes are removed with moderate removal rates (1,14).

Bio sorption has been studied using various less expensive adsorbents of agricultural wastes like rice husk, sugarcane, bagasse, and corncobs etc. or industrial wastes such as coal ashes, peat, clay, bentonite, red soil, bauxite, rice husk, leaf powder, wood chips, ground nut shell powder, rice husks, bagasse pith, wood sawdust, other ligno-cellulosic wastes, etc. which can adsorb and accumulate dyes and other organic compounds from textile effluents with a removal capacity of 40-90% basic dyes and 40% direct dyes (13-22). The advantage of using these materials is mainly due to their widespread availability and low cost, also their regeneration is not required.

The 'spent' material is usually burnt though there is potential to use it for protein enrichment by its solid state fermentation. Though the use of 'low cost' adsorbents for textile dye removal is lucrative but a vast amount of adsorbents are required as these are less efficient than activated carbon.

Irradiation: The irradiation treatment involves the use of radiations usually obtained from a monochromatic UV lamps working under 253.7 nm. It is a simple and effective technique for removing a wide variety of organic contaminants, and disinfecting harmful microorganism. This method needs a constant and adequate supply of oxygen because a large amount of dissolved oxygen is required for effectively breaking down of an organic dye by irradiation. Irradiation treatment of a secondary effluent from sewage treatment plant has been observed to reduce COD, TOC and colour up to 64%, 34% and 88% respectively using a dose of 15 K Gy gamma-rays (23). The efficiency of irradiation treatment can be increased by using catalyst titanium dioxide (24).

Filtration Processes: These are new procedures, which may be used to check organic contaminants and microorganisms present in wastewater. The common membrane filtration types are:

Micro-filtration**:** It is mostly employed for treatment of dye baths containing pigment dyes and for following rinsing baths (25). Suspended solids, colloids from effluents or macromolecules with particle size of 0.1 to 1 micron get removed by microfiltration so microfiltration may be used as a pre-treatment for nano filtration or reverse osmosis (26). MF is effective in removing about 90% of turbidity or silt. Microfiltration membranes are made from polymers such as Poly (Ether Sulfone), Poly Tetrafluoroethylene (PTFE), Poly (Vinylidiene Fluoride), Poly (Vinylidene Difluoride), Poly (Sulfone), Polypropylene,Polycarbonate, etc. When extraordinary chemical resistance or high temperature is required in the operation, ceramic, glass, carbon, zirconia coated carbon, alumina and sintered metal membranes are used. Usually MF and UF operate at 20 to 100 psi transmembrane pressures (Ptm) and velocities of 20 to 100 cm/s (27).

Ultra-filtration: This technique can remove polluting substances such as dyes only 31-76% but can be used to eliminate macromolecules and particles. The treated wastewater cannot be reused for sensitive processes, such as textile dyeing (25) but can be used for rinsing, washing, etc. Ultrafiltration is used as a pre-treatment for reverse osmosis (28) or to remove metal hydroxides (27). UF membranes are made from polymers such as nylon-6, polytetrafluoroethylene (PTFE), polyvinyl chlorides (PVC), polysulfone, polypropylene, acrylic copolymer etc.

Nano-Filtration: It is employed for the treatment of coloured effluents from the textile industry, mostly in a combination of adsorption and Nano-filtration as NF modules are very sensitive to fouling by colloidal material and macromolecules. NF membranes are normally made from cellulose acetate and aromatic polyamides. Inorganic materials, such as carbon based membranes, ceramics, zirconia can also be used in making NF and RO membranes. These can remove low-molecular weight organic compounds, large monovalent ions, divalent ions, hydrolysed reactive dyes, and dyeing auxiliaries. About 70% colour removal has been reported for a NF plant working at 8 bar/18°C, with four polyethersulphonate membranes with molecular weight cut offs of 40, 10, 5 and 3 kda for three different effluents from dyeing cycle of textile industry (29). NF treatment can be reasonably used as an alternative for decolourization of textile effluent.

Reverse Osmosis: This technique is used to eliminate hydrolysed reactive dyes, most types of ionic compounds, chemical auxiliaries in a single step (25). The influent has to be very carefully pre-treated because RO is very sensitive to fouling like NF. RO membranes are usually made from cellulose acetate and aromatic polyamides and of some inorganic materials.

The choice of the membrane process depends upon the nature of the final effluent. The membrane processes in combination with physio-chemical treatment has benefits over the other conventional treatments, such as their ability to recover dye materials along with valued recyclable water, to reduce fresh water consumption and wastewater treatment costs, small disposal volumes as a result minimizes waste disposal costs etc. The main problem with physical method is like excess sludge production. So disposal of solid adsorbent itself becomes a big headache. However physical methods are useful when effluents volume is small.

CHEMICAL METHODS OF REMOVING DYE FROM WASTE WATER

Oxidative processes

Chemical oxidation is the conversion of pollutants by chemical oxidising agents (such as chlorines, ozone, Fenton reagents, UV/peroxide, UV/ozone etc.) other than oxygen/air or bacteria to similar but less harmful compounds and to easily biodegradable organic compounds.

Oxidation with sodium hypochlorite: In this treatment azo-bond cleavage is initiated and accelerated by the attack of the dye molecule by Cl^{+} at the amino group. The increase in chlorine concentration accelerates the dye removal and decolourization process, and also results in the decrease of pH. The chlorine decolourization is most effective on dyes containing amino or substituted amino groups onthe naphthalene ring i.e. dyes derived from amino-naphtol- and naphtylamino-sulphonic acids (Omura, 1994). This treatment is not suitable for disperse dyes. Due to negative effects of aromatic amines or other toxic molecules on releasing these into water resources, this method is less frequently used.

Oxidation with hydrogen peroxide: The oxidation processes with hydrogen peroxide (H_2O_2) can be used as wastewater treatment in two systems: (1) Homogenous systems based on using visible or ultraviolet light, soluble catalysts such as Fenton reagents(hydrogen peroxide activated by some iron salts without UV irradiation to form hydroxyl radicals (HO**.**) which are strong oxidants than H_2O_2 and other chemical activators such as ozone, peroxidase etc. The Fenton oxidation treatment efficiency depends mainly on effluent characteristics, and operating parameters e.g., colour removal of 31.5 % of has been reported for effluents containing Remazol Arancio 3R, Remazol Rose RB textile dye, by Fenton oxidation at a pH of 4.00, using 0.18-0.35 M H_2O_2 and 1.45 mM Fe2+, after 30 min. of oxidation (22).

(2) Heterogenous systems based on using semiconductors, zeolites, clays with or without ultraviolet light, e.g. TiO2, modified zeolites with iron and aluminium lead to colour removal of 53-83%, COD removal of 68-76% and TOC removal of 32-37% have been reported in the dye-containing effluents by heterogenous catalytic oxidation using 20 mM H_2O_2 and FeY11.5 (1 g/L) of Procion Marine HEXL at pH=3-5, after 10 min. (31).

Advantages of this oxidative treatment comprise reduction of effluent COD, colour and toxicity, and can be used to remove both soluble and insoluble dyes e.g. disperse dyes. Complete decolourization was obtained generally after, the complete Fenton reagent stage i.e. 24 hours. The main difficulty come across is in the separation of the solid photo catalysts at the end of the process (31,32).

Oxidation by Ozonation: Ozone is a powerful oxidising agent and is capable of oxidising aromatic rings causing their cleavage in some textile dyes and decomposition of other organic pollutants in industrial effluents. Ozone causes the cleavage of conjugated double bonds of chromophore in organic dyes resulting in decolorisation but this process is accompanied by the formation of toxic products. Thus ozonisation may be used along with a physical method to prevent this. Even prolonged ozonation can remove these toxic products. Ozone may react directly or indirectly with dye molecules. In the direct method, the ozone molecule acts as the electron acceptor, and hydroxide ion (high pH) catalyse the auto decomposition of ozone to form hydroxyl free radicals (·OH) in aqueous effluents which react with organic and inorganic pollutants. At low pH ozone reacts efficiently with unsaturated chromophoric bonds of a dye molecule by direct reactions (33).

The main advantage of ozone oxidation is that ozone can be applied even in its gaseous state and therefore does not cause increase in the volume of wastewater and sludge. The disadvantages of ozonation are its short halflife i.e. 20 min, its destabilisation by the presence of salts, pH, and temperature,

and the added costs for the installation of ozonisation plant. The efficiency of ozonisation can be improved by using it in combination with irradiation (32) or with a membrane filtration technique (34).

Photochemical oxidation: The UV treatment of dye-containing wastewater in the presence of H_2O_2 can breakdown the dye molecules to smaller organic molecules, or even to ultimate products such as CO_2& H_2O, other inorganic oxides etc. (35). The dye decomposition is initiated by the generation of hydroxyl radicals. This process may be completed in a batch or continuous column unit. The efficiency of this treatment depends on the intensity of the UV radiation, pH, dye structure and the dye bath composition (36). The presence of hydrogen peroxide increases the efficiency of photo oxidation treatment. For example the colour removal of more than 60-90% of Red M5B, H-acid and Blue MR dye-containing effluents, has been observed on working with 400-500 mg/L H_2O_2 at pH 3-7 (37).

Coagulation and precipitation

Coagulation: Coagulation of dyes and other auxiliaries in textile effluents has been successfully done by Aluminum, Iron slats, organic polymer, Flocculants etc. The coloured colloid particles from textile effluents cannot be separated by simple gravitational methods so these are precipitated by some chemicals such as lime, ferrous sulphate, ferric sulphate, ferric chloride, aluminium sulphate, aluminium chloride, cationic organic polymers, etc. which are added to settle down the ruminant dyes and other auxiliaries in textile effluents. These chemicals cause destabilisation of small suspended particles and emulsions mainly by neutralising their charge as a result the particles come together forming cluster of these particles large enough to settle (coagulate) under gravity or become filterable (40). The main disadvantages of this treatment are the process control, impurities such as non-ionic detergents remaining in the effluent, and the sludge produced which has to be separated and dried for later landfilling.

Electrocoagulation: Electrocoagulation is an advanced electrochemical treatment for dye and colour removal. It involves processes such as electrolytic reactions at electrodes, coagulation in aqueous effluent and adsorption of soluble pollutants on coagulants, and finally their removal by sedimentation. This treatment is efficient even at high pH for colour and COD removals and the efficiency further depends on the current density and duration of reaction. The colour removal of more than98% has been reported for textile Orange II and Acid red 14 dye-containing effluents in EC treatment(43). In general, decolourisation efficiency in EC treatment has been found to be 90-95%, and COD removal 30-36% under optimum conditions (25).The main drawback of chemical methods is the high cost which prevents it from being extensively used in industry.

BIOLOGICAL METHODS:

It involves microorganisms like fungi and Bacteria and is no cost effective to becoming popular. Biological treatment may involve aerobic and anaerobic degradation by microorganism’s combination.

Aerobic biological treatment: Biological treatment of activated sludge was the most used in large scale textile effluent treatment. The main microorganisms responsible for biodegradation of organic compounds are bacteria such as *Aeromonas Hydrophilia*, *Acetobacter liquefaciens*, *Bacillus cetreus*, *Bacillus subtilis*, *Klebsiella pneunomoniae*, *Pseudomonas* species, *Sphingomonas*, etc.; fungi such as white-rot fungi: *Hirschioporus larincinus*, *Inonotus hispidus*, *Phanerochaete chrysosporium*, *Phlebia tremellosa*, *Coriolus versicolor*, etc.; algae such as *Chlorella* and *oscillotoria* species etc. Furthermore, some bacteria, white-rot fungi, mixed microbial cultures have been found to be able to degrade dyes using enzymes, such as manganese dependent peroxidases (MnP), lignin peroxidases (LiP), H_2O_2-producing enzime such as glucose-1-oxidase and glucose-2-oxidase, along with laccase, and a phenoloxidase. In biological aerated filters the organisms are grown on inert media that are held stationary during normal operation and exposed to aeration. In case of azo dyes, their nitro and sulfonic groups are quite intractable to aerobic bacterial degradation (44). However, in the presence of azo reductases (oxygen-catalysed enzymes), some aerobic bacteria reduce azo compounds to aromatic amines (46). About 80% colour removal by degradation of azo dyes (i.e. Acid Red 151; Basic Blue 41; Basic Red 46, 16; Basic Yellow 28, 19) in an aerobic biofilm system has been indicated , which can be improved to more than 90% by adding activated carbon (PAC) or bentonite in aeration tank. (37).

Anaerobic Biological Treatment: Anaerobic biodegradation of water-soluble dyes including azo dyes is mainly reported to take place by a redox reaction with hydrogen leading to the formation of methane, carbon dioxide, hydrogen sulphide, other gaseous compounds and releasing electrons. These electrons reduce the azo bonds in azo dye, causing decolourization of the effluent with the formation of toxic amines (47). An additional carbon organic source such as glucose is necessary. A major advantage of anaerobic system in addition to decolourization of textile effluent is the production of biogas, usable for heat and power generation which will reduce energy costs. The main advantage of biological treatment as compared to certain physico-chemical treatments is that over 70% of organic matter expressed by COD may be converted to biosolids (37). The disadvantage is that the biological treatment process require long time period, hence the effluents has to be stored in large tanks for the process.

A combination of physical and biological processes has been proposed by Robinsons et. al (2001)(45) which involves adsorption of dye on agricultural waste in a continuous process followed by dye degradation using solid state fermentation by micro-organisms like white ret fungi. Here the solid waste left is non-toxic and can be used as fertilizer.

CONCLUSION

The natural and synthetic dyes which make our life colorful also cause a lot of pollution of our water bodies. Effluents from dying industry contain very harmful chemicals. The easiest way to access their impact is to study toxicity of water on aquatic plants and animals. The organic dyes should be discharged up to only certain strict limits in final effluents discharged untreated in natural water resources. Removal of Dye from textile effluents is an environmental issue which can be solved by use of adequate mechano-physic-chemical and biological treatment of textile effluents.

REFERENCES

1. Cooper P. (1995). *Color in dyehouse effluent*, Society of Dyers and Colourists, ISBN 0 901956694, West Yorkshire BDI 2JB, England
2. Forgacs, E Crestile, T., Oros, G., (2004), Removal of synthetic dyes from waste water. A review environmental international, 30, pp. 953-971

3. Hao, O.J., H. Kim, O.J, Chiag P.C. (2000), decolourisation of waste water critical review in environmental Science and Technology 30,pp 449-505
4. Biosorption Processes From Wastewater Treatment (chapter 7). In: Lignin: Properties and Applications in Biotechnology and Bioenergy, Ryan J. Paterson (Ed.), Nova Science Publishers, 27 pp., ISBN 978-1-61122-907-3, New York, U.S.A.
5. Welham, A. (2000). The theory of dyeing (and the secret of life). Journal of the Society of Dyers and Colourists, Vol.116, pp.140-143 Suteu, D.; Zaharia, C. & Malutan, T. (2011a). Biosorbents Based On Lignin Used In
6. EPA. (1997). *Profile of the textile industry*. Environmental Protection Agency, Washington, USA
7. Bertea, A. & Bertea, A.P. (2008). Decolorisation and recycling of textile wastewater (in Romanian), Performantica Ed, ISBN 978-973-730-465-0, Iasi, Romania
8. EWA. (2005). *Efficient use of water in the textile finishing industry*, Official Publication of the European Water Association (EWA), Brussels, Belgium
9. Bisschops, I.A.E. & Spanjers, H. (2003). Literature review on textile wastewater characterisation. Environmental Technology, Vol.24, pp. 1399-1411
10. F.M.D Chequer, D.J. Dorta, D. Palma de Oliveira (2011). Azo Dyes and Their Metabolites: Does the Discharge of the Azo Dye into Water Bodies Represent Human and Ecological Risks? Advances in Treating Textile Effluent, Prof. Peter Hauser (Ed.), ISBN: 978-953-307-704-8, InTech.
11. Puvaneswari, N., et al. (2006) Toxicity assessment and microbial degradation of azo dyes. Indian journal of experimental biology 44(8): 618.
12. Lima et al. (2007) Mutagenic and carcinogenic potential of a textile azo dye processing plant effluent that impacts a drinking water source. Gen Tox and Environ Mutagenesis. Vol 626:1–2
13. Anjaneyulu, Y.; Sreedhara Chary, N. & Suman Raj, D.S. (2005). Decolourization of industrial effluents – available methods and emerging technologies – a review. *Reviews in Environmental Science and Bio/Technology*, Vol.4, pp. 245-273, DOI 10.1007/s11157-005-1246-z
14. Nigam, P.; Armou, G.; Banat, I.M.; Singh, D. & Marchant, R. (2000). Physical removal of textile dyes and solid-state fermentation of dye-adsorbed agricultural residues. Biores. Technol., Vol.72, pp.219-226
15. Bhattacharya, K.G & Sarma, A. (2003) Adsorption characteristic of the dye. Dyes pigments, Vol.52, PP 211-222
16. Gupta, G.S.; Singh, A.K.; Tayagi, B.S.; Prasad, G. & Singh, V.N. (1992). Treatment of carpet and metallic effluent by China clay. J.Chem.Technol.Biotechnol., Vol.55, pp. 227-283
17. Ozcan, A.S.; Erdem, B. & Ozcan, A. (2004). Adsorption of Acid Blue 193 from aqueous solutions onto Na-bentonite and DTMA-bentonite. J.Coll.Interf.Sci., Vol.280, No.1, pp.44-54

18. Robinson, T.; McMullan, G.; Marchant, R. & Nigam, P. (2001). Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. Bioresource Technology, vol.77, pp.247-255
19. Suteu, D. & Zaharia, C. (2008). Removal of textile reactive dye Brilliant Red HE-3B onto materials based on lime and coal ash, *ITC&DC, Book of Proceedings of 4th International Textile, Clothing & Design Conference – Magic World of Textiles*, pp.1118-1123, ISBN 978-953-7105-26-6, Dubrovnik, Croatia, October 5-8, 2008
20. Suteu, D.; Zaharia, C.; Bilba, D.; Muresan, A.; Muresan, R. & Popescu, A. (2009a). Decolorization wastewaters from the textile industry – physical methods, chemical methods. Industria Textila, Vol.60, No.5, pp.254-263
21. Suteu, D.; Zaharia, C. & Malutan, T. (2011a). Biosorbents Based On Lignin Used In Biosorption Processes From Wastewater Treatment (chapter 7). In: *Lignin: Properties and Applications in Biotechnology and Bioenergy*, Ryan J. Paterson (Ed.), Nova Science Publishers, 27 pp., ISBN 978-1-61122-907-3, New York, U.S.A. www.intechopen.
22. Zaharia, C.; Suteu, C. & Muresan, A. (2011). Options and solutions of textile effluent decolourization using some specific physico-chemical treatment steps. *Proceedings of 6th International Conference on Environmental Engineering and Management ICEEM'06*, pp. 121-122, Balaton Lake, Hungary, September 1-4, 2011
23. Borrely, S.I.; Cruz, A.C.; Del Mastro, N.L.; Sampa, M.H.O. & Somssari, E.S. (1998). Radiation process of sewage and sludge – A review. Prog.Nucl.Energy, Vol.33, No.1/2, pp. 3-21
24. Krapfenbauer, K.F.; Robinson, M.R. & Getoff, N. (1999). Development of and testing of TiO2- Catalysts for EDTA-radiolysis using γ-rays (1st part). *J.Adv.Oxid.Technol.*, Vol.4,No.2, pp.213-217
25. Ramesh Babu, B.; Parande, A.K.; Raghu, S. & Prem Kumar, T. (2007). Textile technology. Cotton Textile Processing: Waste Generation and Effluent Treatment. The Journal of Cotton Science, Vol.11, pp.141-153
26. Ghayeni, S.B.; Beatson, P.J.; Schneider, R.P. & Fane, A.G. (1998). Water reclamation from municipal wastewater using combined microfiltration-reverse osmosis (ME-RO): Preliminaryperformance data and microbiological aspects of system operation. Desalination, Vol.116, pp. 65-80
27. Naveed, S.; Bhatti, I. & Ali, K. (2006). Membrane technology and its suitability for treatment of textile waste water in Pakistan. *Journal of Research (Science)*, Bahauddin Zakariya University, Multan, Pakistan, Vol. 17, No. 3, pp.155-164
28. Ciardelli, G. & & Ranieri, N. (2001). The treatment and reuse of wastewater in the textile industry by means of ozonation and electroflocculation. Water Res., Vol.35, pp. 567-572
29. Alves, B.M.A. & Pinho, D.N.M. (2000). Ultrafiltration for colour removal of tannery dyeing wastewaters., *Desalination*, Vol.1303, pp. 147-154

30. Omura, T. (1994). Design of chlorine – fast reactive dyes – part 4; degradation of amino containing azo dyes by sodium hydrochlorite. Dyes Pigments, Vol.26, pp.33-38
31. Neamtu, M.; Zaharia, C.; Catrinescu, C.; Yediler, A.; Kettrup, A. & Macoveanu, M. (2004). Fe-exchanged Y zeolite as catalyst for wet peroxide oxidation of reactive azo dye Procion Marine H-EXL. Applied Catalysis B: Environmental, Vol.78, No.2, pp.287-294
32. Zaharia, C.; Suteu, D.; Muresan, A.; Muresan, R. & Popescu, A. (2009). Textile wastewater treatment by homogenous oxidation with hydrogen peroxide. Environmental Engineering and Management Journal, Vol.8, No.6, pp.1359-1369
33. Adams, C.D. & Gorg, S. (2002). Effect of pH and gas-phase ozone concentration on the decolourization of common textile dyes. J.Environ.Eng., Vol.128, No.3, pp. 293-298
34. Lopez, A.; Ricco, G.; Ciannarella, R.; Rozzi, A., Di Pinto, A.C. & Possino, R. (1999). Textile wastewater reuse: ozonation of membrane concentrated secondary effluent. Water Sci. Technol., Vol.40, pp. 99-105
35. Yang, Y.; Wyatt II, D.T & Bahorsky, M. (1998). Decolorisation of dyes using UV/H2O2 photochemical oxidation. *Text.Chem.Color*., Vol.30, pp.27-35
36. Slokar, Y.M. & Le Marechal, A.M. (1997). Methods of decoloration of textile wastewaters. Dyes Pigments, Vol.37, pp.335-356
37. Anjaneyulu, Y.; Sreedhara Chary, N. & Suman Raj, D.S. (2005). Decolourization of industrial effluents – available methods and emerging technologies – a review. Reviews in Environmental Science and Bio/Technology, Vol.4, pp. 245-273, DOI 10.1007/s11157-005-1246-z
38. Kim, T.H.; Park, C.; Lee, J.; Shin, E.B. & Kim, S. (2002). Pilot scale treatment of textile wastewater by combined processes (fluidized biofilm process– chemical coagulation – electrochemical oxidation). J.Hazar.Mat. B, Vol.112, pp.95-103
39. Vlyssides, A.G.; Papaioannou, D.; Loizidoy, M.; Karlis, P.K. & Zorpas, A.A. (2000). Testing an electrochemical method fortreatment of textile dye wastewater. Waste Manag.,Vol.20, pp.569-574
40. Zaharia, C.; Diaconescu, R. & Surpăţeanu, M. (2007). Study of flocculation with Ponilit GT-2anionic polyelectrolyte applied into a chemical wastewater treatment. Central European Journal of Chemistry, Vol.5, No.1, pp.239-256
41. Lin, S.H. & Chen, L.M. (1997). Treatment of textile waste waters by chemical methods for reuse. Water Res., Vol.31, No.4, pp.868-876
42. Venkat Mohan, s.; Srimurli, M.; Sailaja, P. & Karthikeyan, J. (1999). A study of acid dye colour removal using adsorption and coagulation. Environ.Eng.Poly., vol.1, pp.149-154
43. Daneshvar, N.; Sorkhabi, H.A. & Tizpar, A. (2003). Decolorization of orange II by electrocoagulation method. Sep.Purifi.Technol., Vol.31, pp.153-162
44. Dos Santos, A.B.; Cervantes, F.J. & Van Lier, J.B. (2004). Azo dye reduction by thermophilic anaerobic granular sludge, and the impact of the redox

mediator AQDS on the reductive biochemical transformation. Applied Microbiology and Biotechnology, Vol.64, pp.62-69

45. Robinson, T.; McMullan, G.; Marchant, R. & Nigam, P. (2001). Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. Bioresource Technology, vol.77, pp.247-255
46. Stolz, A. (2001). Basic and applied aspects in the microbial degradation of azo dyes. Appl.Microbiol.Biotechnol., Vol.56, pp.69-80
47. Banat, M.E.; Nigam, P.; Singh, D. & Marchant, R. (1996) Microbial decolourization of textile dye containing effluents, a review. *Biores. Technol.*, Vol.58, pp. 217-227