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Review, Analyses of azo dyes' synthesis, characterization and biological activity

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Abstract :In this review essay, we discuss how dyes are used to color materials, particularly clothes. These dyes are colored by chromospheres, which are functional groups that absorb light. Azolo, nitro, and carbonyl groups are the most prevalent chromospheres. Another crucial component of dyes is auxochromes, which are functional groups that intensify color. Hydroxyl, amino, sulfate, and carboxylate groups are the most typical chromospheres. Nitrogen to nitrogen double bond serves as the chromosphere in azo dyes. Diazonium salt is combined with a highly active aromatic system to produce these colors.

Keywords: Azo, Dyes Coupling, Auxochrome, chromophoric system, Diazotization.

Introduction

Azo dyes

Azo dyes are organic compounds having the functional group RN=NR′, where R and R′ are commonly aryl. They belong to a family of chemical compounds known as azo compounds, or those bearing the link C-N=N-C. (1) A lot of times, azo dyes are used to color food, leather goods, and clothing. Chemically similar to azo dyes are azo pigments, which are insoluble in water and other solvents. There are various azo dye classification systems and a wide variety of azo dye types. Among the classes are substantial dyes, metal-complex dyes, reactive dyes, and disperse dyes(1). Cotton and other materials made from cellulose are dyed using substance dyes, also referred to as direct dyes. The forces that bind the colors to the fabric are not electrostatic. Another way to classify azo dyes is according to how many azo groups they contain (2). Dyes must have a high level of chemical and photolytic stability in order to be useful.. It is believed that azo dyes do not undergo photolysis degradation because of their stability. The longevity of products dyed with azo dyes depends on ensuring stability against microbial attack, and tests have shown that azo dyes scarcely degrade in aerobic settings over short periods of time. However, in anaerobic environments, biodegradations could lead to visible discoloration.. While the majority of azo pigments are safe to use, some of them, such as ortho-nitroaniline orange and dinitroaniline orange, are mutagenic and carcinogenic. Bladder cancer has historically been associated with exposure to azo dyes manufactured from benzidine because they are carcinogenic. (3).. Some azo dyes break down and release any of a defined group of aromatic amines.. Fewer products were affected since just a few dyes contained an equivalently small amount of amines. More than 60% of known commercial dyes are azo dyes, and they are almost invariably created by diazotizing an aromatic amine and coupling it with an active methylene group or an acidic proton, generally phenol or naphthol, an aromatic amine (typically N-alkylated), or an aromatic amine.. Azo dyes as donor-acceptor chromogens; in truth, every synthetic dye with any commercial significance belongs to this category, with the exception of phthalocyanines and polycyclic quinones. According to earlier sections, some heterocyclic rings have found use in commercial dyes(4), frequently as a result of their enhanced red-shift, brightness, and color strength in comparison to comparable azobenzenesThe bathochromic reaction brought on by the presence of the heterocyclic ring system can be explained by a stronger stabilization of the pertinent canonical dipolar resonance, but it is most likely related to the diene character of the heterocycle. Calculations show that the sulfur atom serves no purpose. The importance of azo dyes is evidenced by the fact that they account for more than 60% of all dye structures that are known to be produced.(5). Although there are many other hues available, blues and greens on hydrophilic fibers don't have strong lightfastness unless they are metallized, and the metallized derivatives have dull colors. These dyes' features vary depending on their chemistry, which ranges from simple monoazo compounds to complicated polyazo complexes with molecular weights of 1800 or more

Synthesis of azo dyes

The subject of today's research is a class of compounds called azo dyes, which are composed of two aromatic fragments connected by an N=N double bond. You may have encountered them in chemical experiments as they are typical pH sensors. Examples include methyl yellow, which has industrial importance and is easy to produce. A two-step process using methyl(orange and red), congo red and alizarine yellow is used to create azo dyes. (6). They have procedure in which an aniline derivative is used to create an aromatic diazonium ion. The diazonium salt is combined with an aromatic component in the following step (shown below is the preparation of methyl yellow) Azo dyes come in a variety of yellow, red, orange, brown, and blue huesAdditionally, azo compounds play a role in a variety of biological processes, including the suppression of DNA, RNA, and protein synthesis, the development of cancer, and biological activity against bacteria and fungi(7). They demonstrate herbicidal, anti-inflammatory, anti-microbial or antiparasitic, anti-ulcer, anti-fungal, antibacterial, antitubercular, antidiabetic, antiseptic, antibiotic, and other chemotherapeutic actions.

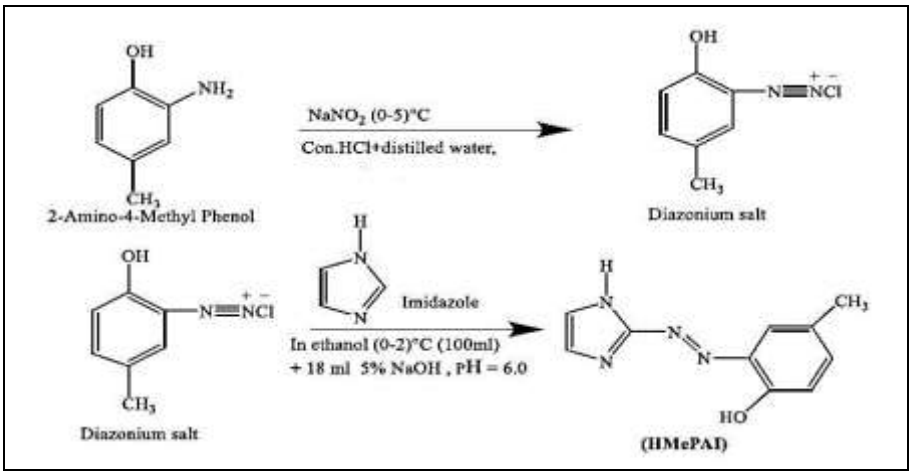

Figure (1)

Diazotization–Diazo Coupling

The protonation of nitrous acid is often used to perform the diazotization and diazo coupling reactions under extremely acidic conditions, while the azo coupling reaction is typically carried out at low temperature in the presence of nucleophilic coupling components. A nucleophilic substrate becomes more reactive as its basicity rises. (8). These traditional acid-base catalyzed processes work well for producing the desired azo-products in nearly quantitative amounts. However, the primary drawback of such synthetic processes is that they are incompatible with the environment. The ecosystem is permanently harmed by the acidic and basic waste products from industry and laboratories, which also upset the ecological balance(9). Solid acids have received a lot of attention in recent years due to their use in organic synthesis since they not only make purification procedures simpler but also help to avoid the environmental release of reaction wastes. Recently, several solid acids have been used to create azo hues. Despite the fact that good product yields are frequently achieved, the diazotization and diazo coupling reactions are difficult due to the presence of numerous competing reactions. (10). For instance, in aqueous media, reaction temperatures above 10 °C typically increase the synthesis of phenol and azophenols are produced when the phenol reacts with unreacted diazonium salts.. The popularity of azo colorants is attributed to how easily they are made by diazotization and azo coupling. By varying the diazo and coupling components, virtually endless possibilities are described. In comparison to other commercial dyes, phenolic azo dyes have a variety of benefits, such as a wide color spectrum, good color fastness, and the capacity to absorb light. These groups are also known as matrix resins or binding resins due to their wide range of uses, accessibility, and extraordinary properties including strong thermal binding stability, great acid resistance, high fire retardancy, etc. Additionally, it has been asserted that naphthols are used as acknowledged intermediates in

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the production of colors. They can also be made at a low cost because the starting materials are readily available, inexpensive chemicals, the majority of the chemistry is performed at or below room temperature, and water is employed as a solvent in every reaction. (11).

Diazonium Salts

Given their adaptability and the abundance of the necessary starting ingredients, diazo compounds and dizonium salts are crucial intermediates in organic chemistry. If not properly regulated, these nitrogen-rich substances could leak nitrogen gas(12). In addition to the heat released, thermal runaways are harmful because a significant amount of gas is evolved, which increases pressure. Utilizing flow methods to prepare and consume them in-place is one way to manage this. Only a minimal quantity of these dangerous intermediates are present at any given time, and the temperature is controlled very well as a result(13). Using flow methods, dangerous substances can be produced and consumed in-situ, such. Since safer reaction performance is made possible by this and improved temperature control, numerous reactions involving diazonium salts and diazo compounds are known to occur under continuous flow circumstances. An amine, typically an aromatic aniline, is treated with a nitrite source to produce diazonium salts in most cases. When those are present, they can then carry out a variety of additional reactions in which the diazonium group is substituted either through a nucleophilic substitution, a radical mechanism, or by a nucleophile intermediate(14).

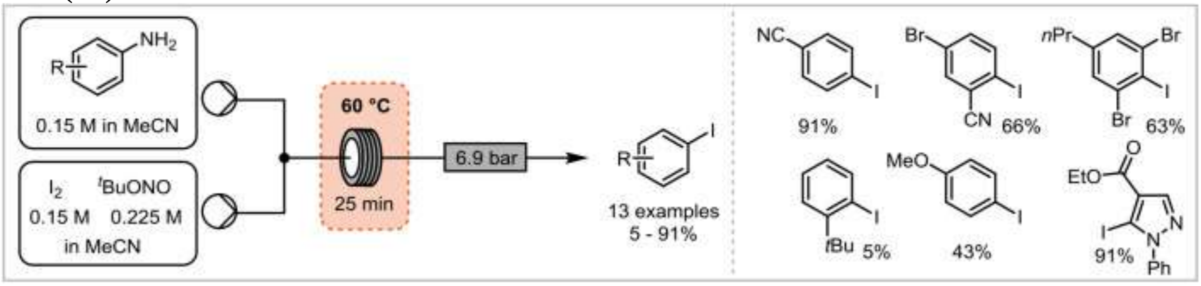

Figure (2)

Mechanism of Azo Coupling

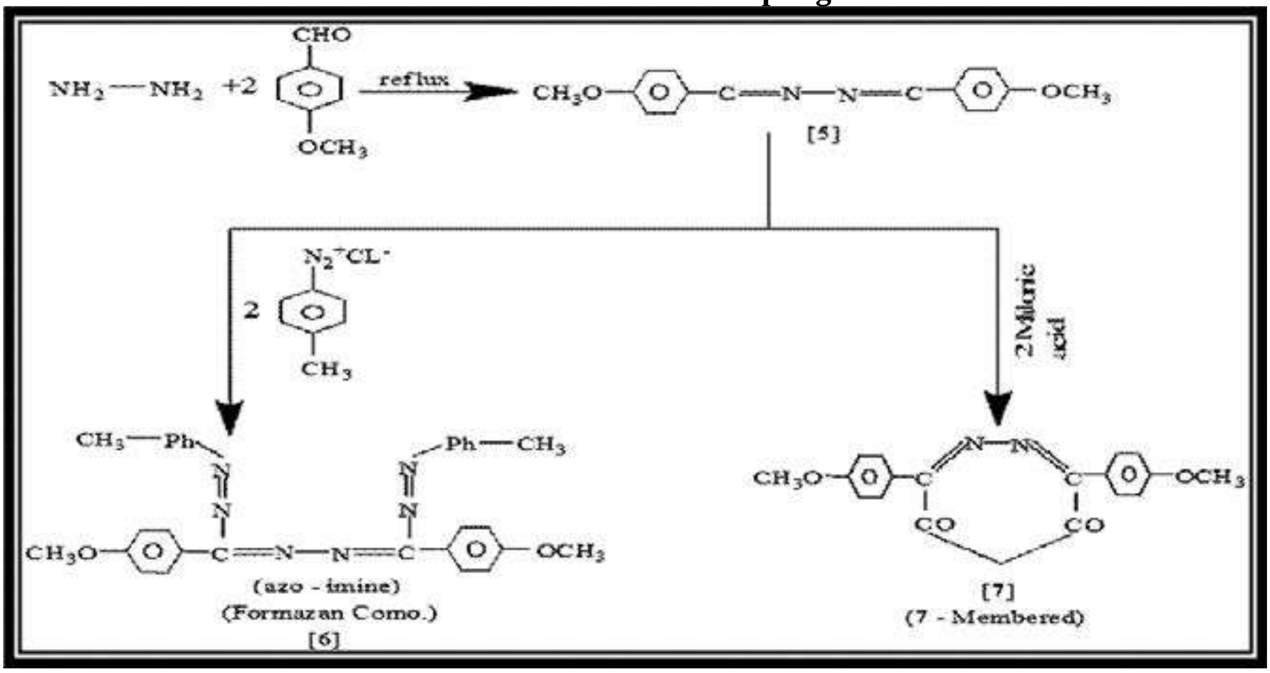

Figure (3)

synthesized various membered rings containing Azo group

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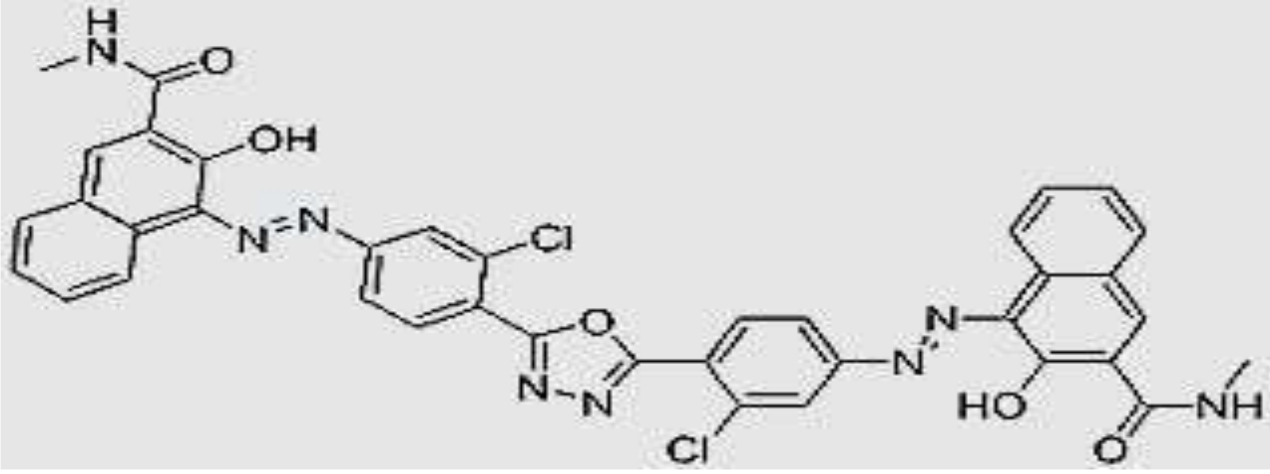

Figure (4)

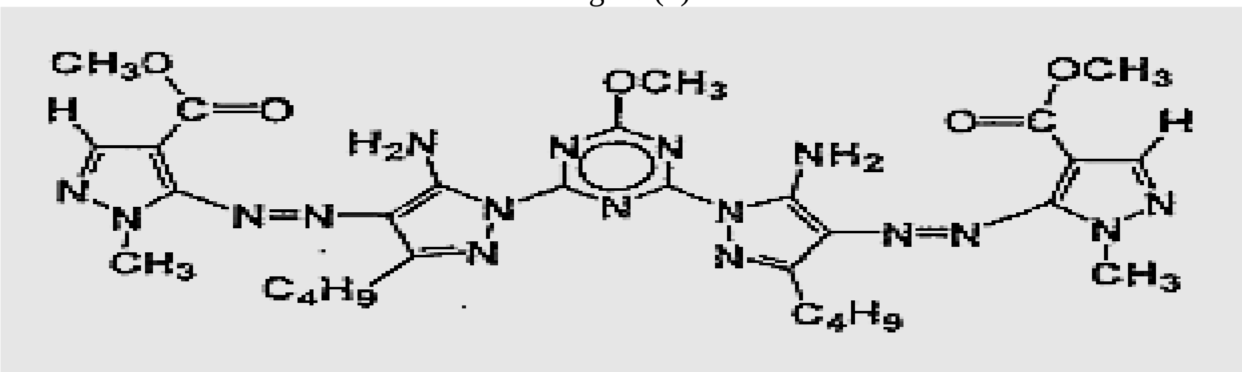

Figure (5)

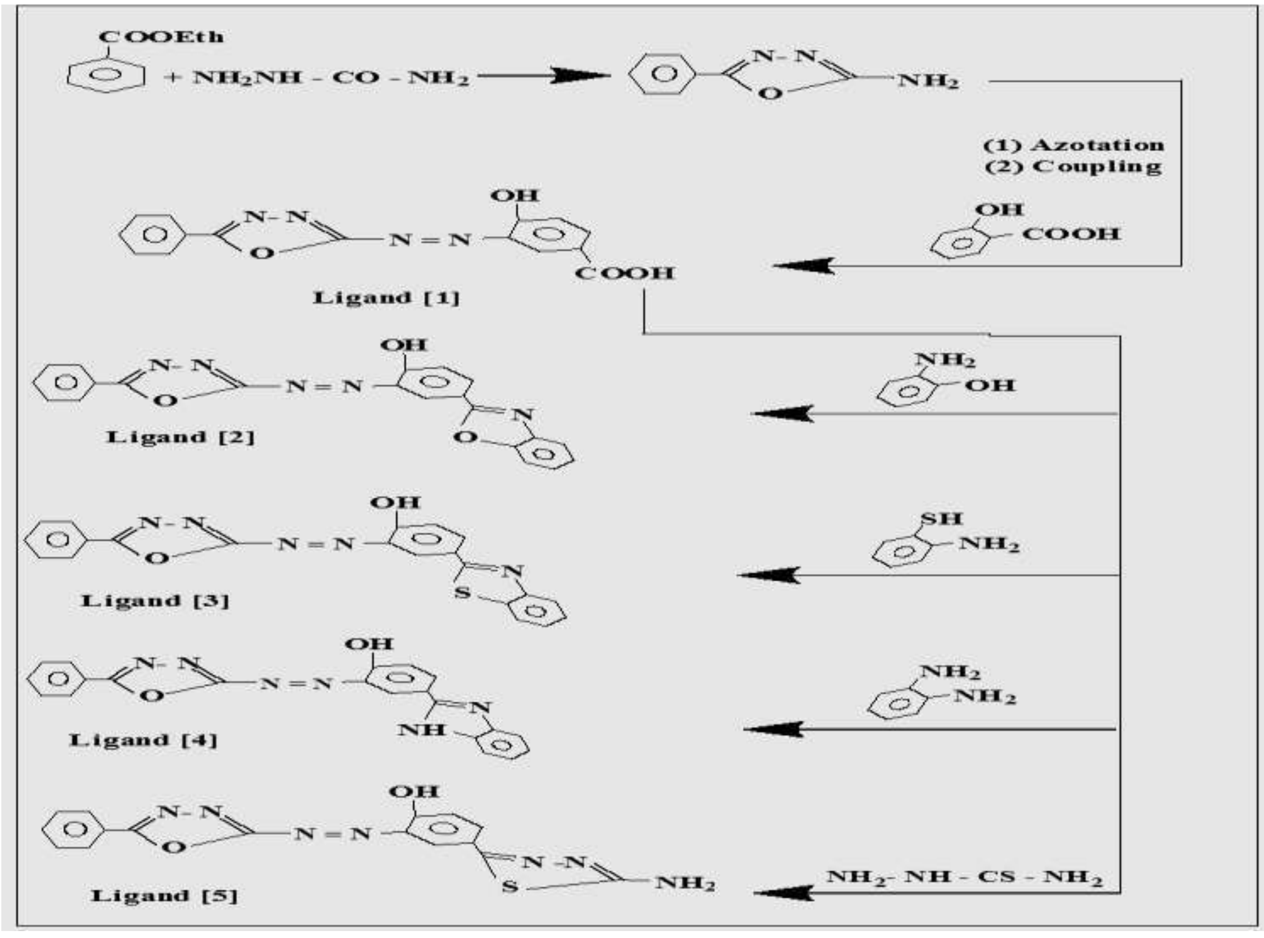

Figure (6)

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Application of azo dye

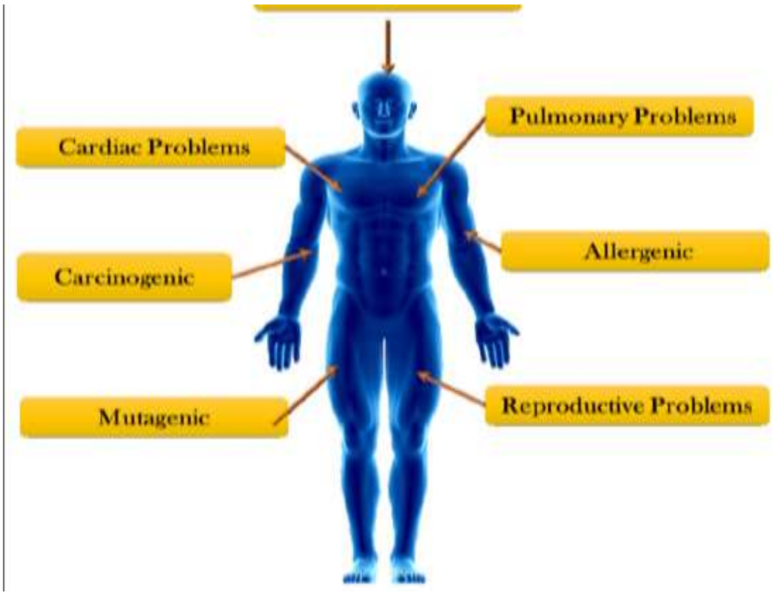

Figure (7)

Azo dye biodegradation

The environment is filled with filamentous fungus that live in ecological niches like soil, active plants, and organic waste. An crucial part of fungi's survival is their ability to quickly change their metabolism to different carbon and nitrogen sources. This metabolic activity is made possible by the development of a vast number of intracellular and extracellular enzymes that can break down complex organic contaminants of various types(15).. In addition to producing and secreting a large variety of primary and secondary metabolites, filamentous fungi are also capable of performing a wide range of complex conversions, such as the hydroxylation of complex polyaromatic hydrocarbons, organic waste, dye effluents, and steroid compounds. . The most effective methods for treating colorful and metallic effluents seem to be fungi. Due to the largely non-specific character of their ligninolytic enzymes, including as lignin peroxidase (LiP), manganese peroxidase (MnP), and laccase, these fungi are able to break down a wide variety of organic substances. A secondary metabolic process known as fungal degradation of aromatic compounds begins when resources (C, N, and S) become scarce(16).. As a result, even though the enzymes are best produced in starvation-like circumstances, the cultures must be maintained with additional energy substrates and nutrients.

Biodegradation of bacteria

Diesel's hydrocarbon structure has been shown to be susceptible to breakdown by several microbes. Bacteria isolated from polluted settings, such as Pseudomonas sp., Bacillus sp., and Acinetobacter sp., are thought to degrade pollutants more effectively in terms of adaptability, resistance, tolerance, and survival. Their unique metabolism has already been Utilizing a variety of microorganisms will help to biodegrade the hydrocarbons in diesel fuel(17).. It is well known that bacteria may biodegrade diesel. It is known that some bacterial species can use diesel as the only source of carbon. While some single bacterial species can carry out a whole biodegradation by themselves, others require a group of them. Numerous elements, which are enumerated in, have an impact on the processes of diesel degradation. The biodegradation method's main benefit is that it is environmentally beneficial. After treatment, there are almost no safe compounds left in the environment. After application, the bacteria that are involved in the degradation process will naturally decay and stop polluting the environment(18).

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Via fungus, biodegradation of plastic polymers

Solid, non-biodegradable plastic polymers pose a serious hazard to the entire world and require many years to disintegrate. The biodegradation process is the most effective and best way for decomposing plastic when compared to other degradation processes due to its non-polluting mechanism, environmental friendliness, and cost-effectivenessThe biodegradation of synthetic plastics is a very slow process that also involves the environment and the activities of microbial species that have not been domesticated(19). Fungi are important players in the biodegradation of plastics; they work on plastics by secreting enzymes that break down the material, including cutinase, lipase, and proteases as well as lignocellulolytic enzymes.. Effective breakdown can also happen when pro-oxidant ions are present. The high molecular weight polymer disintegrates into a low molecular weight polymer due to the oxidation or hydrolysis of the enzyme, which creates functional groups that increase the hydrophilicity of polymers. This leads to the degradation of polymers within a few days... Some well-known species that efficiently breakdown materials are Aspergillus nidulans, Aspergillus flavus, Aspergillus glaucus, Aspergillus oryzae, Aspergillus nomius, Penicillium griseofulvum, Bjerkandera adusta, Phanerochaete chrysosporium, Cladosporium cladosporioides, etc. Studies have shown that when photodegradation and thermo-oxidative mechanisms are combined with biodegradation, plastics disintegrate more fast and easily. In order to break down different kinds of plastic polymers, numerous fungal species are involved in various enzymatic pathways in this review, which provides up-to-date information on them(20).

Using algae and enzymes, biodegradation

Algae and cyanobacteria have the ability to break down and solubilize various hues, with the reduction appearing to be correlated with the chemical composition of the colors and the type of algae used. Azole reductases, peroxidases, lactases, and other significant enzymes have demonstrated a potent ability to remove fabric colors from objects for the AD breakdown of organic contaminants.. (21). The aromatic amine coupling processes brought on by the decolonization of the dyes were accelerated by a lactase in Myceliophthora thermophile. The first stage of a two-part procedure called appropriate AD mineralization is typically anaerobic color removal. The oxidation phase that follows the initial stage of the procedure subsequently destroys the dangerous byproducts that were created. (22). Oxidative enzymes, the bulk of which are lactases, broad-specific peroxidases, and tyrosines, carry out the subsequent phase. Algae do not require additional nutrients to remove colors, in contrast to bacteria and fungi that do, which require the addition of carbon and other components.

References

1. Valery M. Dembitsky&Tatyana A. Gloriozova (2017) Pharmacological and Predicted Activities of Natural Azo Compounds, Natural Products and Bioprospecting volume, 7, 151–169.
2. Sykes P (1974) Agide Book to Mechanism in Organic Chemistry. (5thedn), Longman, UK.
3. Brewster RE, McEwen WE (1971) Organic Chemistry (30thedn).
4. Marry BA (2005) Organic Reaction Mechanism. Jon Willey sons, USA.
5. Fieser LF, Eilliamson KL (1983) Organic Experiment. (5thedn), DC Heath and company Toronto, Canada.
6. Carey FA, Sundberg RJ (1983) Advanced Organic Chemistry, part A: strures and Mechanisms. (2ndedn), Plenum Press, New York, USA.
7. Aljamali NM (2014) Synthesis of seven-memberd hetero cyclic compounds via pericyclic reaction As J Rech 7: 810-838.
8. Wilson CO, Givold O (1966) Text book of Organic Medicinal and pharmaceutical Chemistry. (5thedn), Pitman Medical Publishing Co. ltd, London, UK.
9. Aljamali NM (2015) Review in (NMR and UV-VIS) spectra As J Rech 7: 11.
10. Aljamali NM, Survey In Aromatic Compounds Int J Curr Res Chem Pharma Sci 1: 121-51.
11. Aljamali NM, Review In Cyclic Compounds With Heteroatom Int J Curr Res Chem Pharma Sci 1: 88-120.

ISSN NO: 2770-0003
Date of Publication: 17-09-2022

12. Ju Y, Kumar D, Varma RS (2006) Revisiting Nucleophilic Substitution Reactions: Microwave-Assisted Synthesis of Azides, Thiocyanates, and Sulfones in an Aqueous Medium J Org Chem 71: 6697-6700.
13. Iranpoor N, Firouzabadi H, Akhlaghinia B, Azadi R (2004) Conversion of Alcohols, Thiols, Carboxylic Acids, Trimethylsilyl Ethers, and Carboxylates to Thiocyanates with Triphenylphosphine/Diethylazodicarboxylate/NH4SCN Synthesis,1: 92-96.
14. Iinuma M, Moriyama K, Togo H (2012) Simple and Practical Method for Preparation of [(Diacetoxy)iodo]arenes with Iodoarenes and m-Chloroperoxybenzoic Acid Synlett, 18: 2663-2666.
15. Bhalerao DS, Agamanchi KG (2007) Efficient and Novel Method for Thiocyanation of Aromatic and Hetero-aromatic Compounds Using Bromodimethylsulfonium Bromide and Ammonium Thiocyanate Singlet 19: 2952-2956.
16. Valery M. Dembitsky, Tatyana A. Gloriozova & Vladimir V. Poroikov (2017) Pharmacological and Predicted Activities of Natural Azo Compounds, Natural product and Bioprospecting, 7, 151–169.
17. Abed Al Aziz Al Quntar, Tatyana A. Gloriozova, Nick Savidov & Valery M (2019) , Oxetane-containing metabolites: origin, structures, and biological activities, Applied Microbiology and Biotechnology, 103, 2449-2467.
18. Vladimir V. Poroikov, Alexander O. Terent'ev& Nick Savidov (2018) Peroxy steroids derived from plant and fungi and their biological activities, Applied Microbiology and Biotechnology, 102, 7657–7667
19. Vladimir V. Poroikov, Tatyana A. Gloriozova & Andrew B. Imbs (2018) Naturally occurring aromatic steroids and their biological activities, Applied Microbiology and Biotechnology, 102, 4663–4674.
20. A.Z.El-SonbatiaM.A.DiabaA.A.El-BindaryaSh.M.MorganbA.M.Barakat (2016) Spectroscopic, geometrical structures, DNA and biological activity studies of azo rhodanine complexes, Journal of Molecular Liquids, 224, 105-124.
21. Ewelina Węglarz-Tomczak & Łukasz Górecki (2012) Azo dyes–biological activity and synthetic Strategy, Chemik Science-Technique-Market, 66(12):1298-1307.
22. Ahamed W. Naser*, Hassan T. Ghanem**, and Abid Allah M. Ali (2010) Synthesis and Characterization of New Azo-Schiff Bases and Study Biological Activity of Some These Compounds, J. of university of anbar for pure science, : Vol.4:NO.3. :