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Dye Degradation Using Microbial Fuel Cells: A Critical Review

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Abstract: ***An MFC or Microbial Fuel Cell is used for treating wastewater and simultaneously helps decolorize azo dyes by using microorganisms as the catalyst. Its primary function is bioelectricity generation, which is very well-established in this field. The degradation of dyes using MFCs has still not been published on a large scale for the bioelectricity generation using the same. This review gives an overview of the whole process and discusses certain factors that might affect the dye degradation process. There are several limitations to this process. The most major one is the high cost of the cathode catalyst. This problem can mainly be solved by making use of a biocathode. The most used microorganisms in this process include Klebsiella, Citrobacter, Enterococcus, and Pseudomonas.***
Keywords: MFC, Azo dye, biodegradation, microorganisms, catalyst

I. INTRODUCTION

The textile industry widely uses dyes. Annually, almost 9 million tons of dyes are produced, and nearly 20-25% of the dyes are lost, mainly during the initial stages of the dyeing process, as most of the dyes do not attach to the binding sites. Such paints are mostly discharged in running water without treatment, which has proven to be a significant environmental hazard. Dye is highly stable in light and during washing; therefore, dye degradation needs to be carried out before we can discharge the dyes in water. Wastewater being released by the textile industry is the primary source of aromatic amides in aquatic systems that have diverse effects on the marine environment. Dye degradation using Microbial Fuel Cell (MFCs) has become popular. These cells make use of certain microorganisms to degrade the dyes that are discharged from the textile industries. The dyes commonly released are azo dyes, an aromatic compound containing the Triple nitrogen bonds and primarily used in synthetic dyes in commercial sectors. Azo dyes, along with some chromatophores, are mainly responsible for coloration. The breakdown intermediates of these azo dyes are known to inhibit the growth of marine life, leading to several unwanted mutagenicity in these organisms. Such synthetic dyes are carcinogenic and toxic, and the residues also pose an environmental threat to global lives. Due to population growth in these recent years, there is an increased demand for fossil fuels which has led to the emission of carbon dioxide and other gases, mainly greenhouse gases, that needs to be eliminated from the environment. Many countries have already started looking for alternatives for this. Microbial Fuel Cells are the most promising alternative, as it uses certain biocatalysts (microorganisms) in their anode chamber. MFC systems can be single-chambered or double-chambered, separated mainly by a proton exchange membrane. As mentioned earlier, microorganisms are primarily placed in the anode chamber and generate electrons from the anerobic oxidation of the substrate. Earlier processes, such as flocculation and coagulation, were used for removing colors from the dye-containing effluents. These processes usually produce a considerable amount of sludge that is harmful to the environment if it is not handled or disposed of properly. Other methods like membrane filtration and adsorption are also inefficient as they produce a considerable number of secondary wastes that must be disposed of properly. Most recently, Enzymatic Decolorization has been used for decolorizing wastewater dye. Still, this process was not very efficient as it faced several problems due to the cost of the enzymes and the stability of the enzyme. Other disadvantages of these physical and chemical processes include high energy costs; therefore, biological methods are preferred. MFCs, as mentioned earlier, are used as they can perform two processes simultaneously. These include the degradation of pollutants and bioelectricity generation. It is proven to produce 50-90% less solid waste than other conventional techniques. MFCs make use of bacteria that are specifically used for carrying out redox degradation of organic matter. MFCS makes full use of the metabolic activities of all the microorganisms for effective electricity generation and adequate removal of pollutants from the wastewater. This technique is also a green technology because it helps bioremediation and energy recycling. This study mainly aims at the bioelectricity production and the degradation of azo dyes as an electrochemically steered module that screens out decolorizers from the natural environment by using the microbial fuel cell. Several parameters affect this process, including the pH, temperature, electrode material, type of membrane, etc. The high cost of the cathodic catalyst can sometimes be the limiting factor.

Until now, metals such as platinum and palladium were used, but now semiconductors such as titanium oxide and copper oxide are replacing them because they are not as costly as metals. Recent studies have also shown the use of silver bromide as a photocatalyst. Copper oxide is the most widely used amongst these as it is a heterogenous catalyst for its properties such as good photocatalysis, easy availability, and non-toxicity. This study reviews the dye degradation by microbial fuel cells and the components associated with the whole system.

A. Microbial Fuel Cells Setup

The Microbial Fuel Cell essentially consists of four main parts which include:(Li 2013)

1) The anodic chamber consists of the microorganisms or the bacteria and the organic matter in an anaerobic environment which is deprived of oxygen.
2) The cathodic chamber, which consists of the saltwater solution, acts as a conductor.
3) The salt bridge or the proton exchange membrane helps in the transport of protons from one chamber to the other, and
4) The external circuit explicitly allows the electrons to enter the cathode and provides or acts as a path for the electrons.

Bacteria in the anaerobic environment help create electrons and protons as a part of the oxidation reaction in the digestive process. The negatively charged electrons are then pulled out from the solution in an anode and placed on an electrode usually made of a bare cotton wire glued to nickel epoxy on a carbon cloth. With the help of the external circuit, the electrons are further conducted to the cathodic chamber or, precisely, the cathodic electrode. (Li 2013)

B. Mediator MFCs

In such MFCs, the electron transfer happens from the anode to the cathode and is facilitated by bacterial activities. Mainly chemical mediators are used in MFCs, such as neutral acid, humic red, or anthraquinone 2,6-sulphonate. These chemical mediators are often referred to as "electroactive metabolites." In such MFCs, the presence of oxygen in the anaerobic digestion is of utmost importance as the oxygen helps transfer electrons, which thus interrupts the mediator work as it is less electronegative than oxygen.(Obileke et al. 2021)

C. Mediator less MFCs

In this type of MFCs, electricity is generated with the help of specific microorganisms, and no external mediators are added to the system. The bacteria present in the wastewater help transport the electrons to the electrodes, producing electricity using nanowires. Certain factors need to be taken into consideration while using mediator less MFCs. These include factors like the oxidation of fuel at the anode, and the presence of enzymes, mainly electroactive redox enzymes, that promotes the efficient electron transfer to the negative electrode or the anode and helps in the external resistance of the circuit. These MFCs can also derive energy from plants such as lupines, tomatoes, red sweet rice, and cord grass. "Plant microbial fuel cell" is another name given to this process. (Obileke et al. 2021)

D. Microorganisms and Substrates used in Microbial Fuel Cells

In general, microbes or microorganisms are electrochemically inactive organisms. Most mediators, such as methyl blue, and neutral red, dramatically help the electron transfer from the microbes/microorganisms to the electrodes. Such MFCs are known as mediator MFCs as stated earlier. These mediators are toxic as well as expensive. On the other hand, Mediator less MFCs use electrochemically active microbes, primarily bacteria, to transfer the negatively charged electrons to the electrodes and do not use externally supplied mediators. A particular genus of microorganisms used for the same includes *Geobacter, Enterobacter Shewanella, and Bacillus.* Using single strain also helps in studying the mechanical and physiological details directly. (Solanki, Subramanian, and Basu 2013). Table 1 contains all the microorganisms used in MFCs.

Table 1: Microorganisms used in MFCs

MICROBE FOR MFCs	MODE OF OPERATION	SUBSTRATE USED
Klebsiella pneumoniae	Mediator MFCs	Glucose
Lactobacillus plantarum	Mediator MFCs	Glucose
Geobacter metallireducens	Mediator less MFCs	Acetate
Shewanella putrefacien	Mediator less MFCs	Lactase, glucose, acetate
Shewanella oneidensis MR1	Mediator less MFCs	Lactase
Rhodoferax ferrireducens	Mediator less MFCs	Glucose

The substrate, also known as the anolyte, is the most crucial main factor affecting electricity generation in MFCs. The substrates are rich in organic matter that is present in the wastewater. The performance of the MFC mainly includes the coulombic efficiency, power density, and microbial community in the anode biofilm. Some commonly used substrates are acetate, glucose, lignocellulosic biomass, and brewery wastewater. (Obileke et al. 2021)

Acetate is a straightforward compound that can be degraded easily in MFCs and is extensively used as a substrate for electricity generation. It is also rich in elements like carbon and contains the ions in vinegar or acetic acid and other metabolic pathways for different carbon sources. Other commonly used substrates include glucose, which enhances the MFC's conductivity property. Glucose and acetate are the two most used substrates in electricity generation in MFCs. Other substrates used in MFCs are given in table no 2.(Obileke et al. 2021)

PROPERTIES	ACETIC	GLUCOSE	BUTYRATE	MALATE	CITRATE
Molecular formula	$C_2H_4O_2$	$C_6H_{12}O_6$	$C_4H_8O_2$	$C_6H_8O_5$	$C_6H_8O_7$
Appearance	Colorless liquid or crystal	Colorless solution	Oily and colorless liquid	--	The white, crystalline powder
Boiling point	118º C	100º C	163.5º C	306.4º C	310º C
Solubility in water	Fully miscible	Readily dissolved in water	Insoluble in water	Soluble in water	Soluble in water and insoluble in alcohol
Density	1.049 g/cm^3	1.54 g/cm^3	0.96 g/cm^3	--	1.66 g/cm^3
Acidity pKa	800	500-3000	1000	--	--

Table 2: Types of Substrates used in MFCs

II. DYE DEGRADATION TECHNIQUE IN MICROBIAL FUEL CELLS

Using MFCs for dye degradation before discharging has proven to be a method of energy recovery. The dyes commonly used in industries such as the textile industry include direct dyes, azo dyes, acid dyes, reactive dyes, and dispersed dyes. Among these, the azo dye is aromatic. It consists of a heterocyclic ring linked with the polar and color display groups and is accounted to cause over 70% of the textile effluent. Dye decolorization can be carried at both the anode and the cathode the central reaction in dye degradation in the co-metabolism response. The electrons are usually transferred from the anode with the help of electrochemically active bacteria. The other portion is transferred by reduction cleavage. These two reactions are always found in competition with each other. (Ilamathi and Jayapriya 2018)

The degradation of dyes can be a specific or non-specific process. A relationship between molecular weight and the decolorization rate implies it is non-specific, as the reduction reaction for the same is non-specific. On the other hand, if the reduction is intracellular and requires the presence of azo-reductase enzymes, it is said to be specific. For improved performance of MFCs, the stabilization and complete acclimation of the entire system are very important.(Ilamathi and Jayapriya 2018)

Azo dyes contain triple nitrogen bonds, and the reaction at the cathode has been illustrated below:

$$-N{=}N- + 2e + 2H^+ \rightarrow -NH{-}NH- \quad (1)$$

$$-N{=}N- + 4e + 4H^+ \rightarrow -NH_2{-}NH_2- \quad (2)$$

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The temperature is maintained at 303 K, so the bacteria are incubated at the lab scale. For a methyl orange-fed cathode, the potential is maintained at 0.7V at 0.05 mM concentration. The following formula can calculate the maximum electromotive force of the MFC:

$E^{o'} = E_o - RT/nF \ln(\phi)$

Where ϕ is typically the ratio of the products formed to the reaction raised to the power of stoichiometric coefficients.(Ilamathi and Jayapriya 2018).

Certain dyes, such as acid orange 7, make the mineralization of azo dyes possible under anoxic conditions. But there are possibilities of degrading sulfonated aromatic amines under anaerobic conditions. This eventually needs to be further degraded under aerobic conditions. One of the most critical problems in MFC biotreatment is the toxicity caused by the resulting aromatic amines. The whole process of dye degradation requires a proper sequential anaerobic-aerobic environment.(Ilamathi and Jayapriya 2018)

The azo dyes used for decolorization and electricity generation include Sunset Yellow FCF(coloring food), Allura Red, and Taurine. (Texas et al. 2021). Certain synthetic dyes are also used, including Hot spring soil and pond water. (Tacas et al. 2021)

A. Electrodes for Dye Water Treatment

The main factors on which the transfer of negatively charged electrons in a microbial fuel cell depends are the compatibility of redox potential, the character of the surface and the conductivity of the material being used. The cost of the electrode used plays a vital role in deciding how the whole MFC system would work at a large scale, making it the most important among all the MFC components. The material used as the anode must be made up of a conductive surface that is non-corrosive and has high conductive biofilm formation.

Materials such as non-corrosive stainless steel are widely used as anodes in different forms and shapes. Other carbons, such as carbon paper, thick graphite rods, foams, sheets, etc., have also been used as anodes. Nowadays, the three-dimensional electrode has gained much popularity among the masses due to its large surface areas, which increase not only the volumetric power density but also the attachment of the bacteria. Their performance can also be improved by improving the electrochemical behavior and enhancing the electrodes' surface area chemistry. (Ilamathi and Jayapriya 2018)

For the process of dye decolorization, carbon sources are used mainly in the form of paper or cloth. The anode is made up of porous carbon cloth, and the cathode is made up of an identical size which mainly comprises polytetrafluoroethylene and acts as the diffusion layer at the facing side for decolorizing the red color. It has also been found that azo dyes fight for the electrons from the co-substrates, not from the anode. According to Sun et al., 2012, the anode surface doubled and simultaneously increased its net power by almost 150%, and the time required for decolorization was also decreased from 168 hours to 72 hours. If the size of the anode was quadrupled, there was complete decolorization of Congo red within 26 hours. (Ilamathi and Jayapriya 2018)

For dye decolorization, graphite-based electrodes are more commonly used in MFCs. This is due to its chemical stability and high electrical conductivity.

The low porosity in graphite rods limits the power density as the microbes have adhered less to the anode. The cathode is not given utmost importance for the dye decolorization MFCs as oxygen is utilized as the primary negatively charged electron acceptor in this chamber, which can be improved by using mediators.(Ilamathi and Jayapriya 2018) Other cathodes used for dye degradation using MFCs include rutile-coated cathodes. Recent studies have also shown the use of bio-catalyzed cathodic compartments (Clauwaert et al., 2007). The high cost of platinum catalyst and Nafion membrane can be replaced by using granular activated carbon as an anode or biocathode. Granular activated carbon (GAC) used in single-chambered MFC also includes other additional advantages, such as there is no need for further adjustments to the pH values and a need for pre-treatment like autoclaving. It also dramatically minimizes the issues that can be caused due to use of expensive materials in dye wastewater treatment. (Ilamathi and Jayapriya 2018)

The most commonly used electrodes that help in dye decolorization are carbon or graphite electrodes. Still, most of the color removal can be best achieved by using carbon-based electrodes, with the positive cathode being made up of platinum. But since platinum is expensive, they were replaced with carbon nanotubes (CNTs) which have proven to be a potential electrode application in recent times.

Using unpolished graphite over carbon electrodes is cost-effective, mainly during large-scale production. The changes in the characteristic of dyes, such as the concentration, structure, or charge, may affect the decolorization process, and the output power might also vary greatly. (Ilamathi and Jayapriya 2018)

Table no; three consists of information about various electrodes used in the dye decolorization process. (Ilamathi and Jayapriya 2018)

Name of the dye degraded using the MFC	Classification of dye	Proposed dye intermediates	Power/voltage generation	References
Congo Red	Azo dye	Destructed aromatic rings	400 mW/m^2	Li et al. (2010)
Reactive Blue 160	Azo dye	Phenyl methadiamine and 5-sulphonthranilic acid	80 ± five mV	Chen et al. (2010)
Malachite green	Basic dye	--	6738 ± 1.87 mW/m^2	Chen et al. (2014)
Alizarin yellow R	Azo dye	p-Phenylenediamine (PPD) and 5-aminosalicylic acid (5-ASA)	--	Cui et al. (2014)

Table 3 :intermediates that are proposed for specific dye degradation processes

B. Proton Exchange Membrane for Dye Wastewater Treatment

This proton exchange membrane separates the anode and the cathode compartments in a Microbial Fuel Cell. This membrane must help separate and stop the transfer of specific substrates or oxygen. It must only allow the positively charged protons to move across the two compartments in MFCs. Nafion is mainly used, but it is the high cost of this. The absence of a proton exchange membrane leads to the possible accumulation of protons near the anode, which ultimately lowers the pH and affects the kinetics of microbial (bacterial) growth. The surface area of the Proton exchange membrane plays a vital role in MFCs. By increasing the surface area of the proton exchange membrane, internal resistance can be limited inside the cell. Another factor that determines the performance of the Proton Exchange Membrane is membrane fouling. This problem can be solved by using Cation Exchange Membrane (CEM). The CMI-700 has proven to be the newest breakthrough in the azo dye feeding cathode, but even Cation Exchange Membrane experiences membrane fouling due to a ferric ion catholyte. The effective permeability of the microfiltration membrane is also an essential factor in degrading cleavage in the azo dye. In a single-chambered MFC, there is a possibility of employing membranes that provides faster decolorization, according to HOU et al. (2011). The Ultrafiltration Membrane, such as UFM-5kD, provides the quickest decolorization of the azo dyes. Researchers are slowly moving to use membrane-less MFCs for dye decolorization. (Ilamathi and Jayapriya 2018)

C. Construction of Fuel Cells for Dye Degradation

MFC is widely used for electricity generation. Apart from that, it is extensively used in dye degradation. The main challenge is setting up a good MFC at affordable costs. The main factor that needs to be considered while setting up a MFC is the determination of the power expressed in volumetric efficiency regarding the decolorization of dyes. The primary loss in such systems includes the Ohmic failures, which must be overcome to attain the maximum use of the architecture. Both anode and cathode production is involved in electricity generation and dye decolorization. According to research, 90% of dye decolorization can be achieved by using a power density of about 274 mW/m^2 when glucose is used as the substrate. (Ilamathi and Jayapriya 2018). The decolorization of certain dyes, such as orange I, orange II, and methyl orange, were conducted in the cathode chamber using a phosphate buffer. Liu et al. (2009). The bottle reactors are extensively used in single-chambered and double-chambered MFCs for dye decolorization. This is also because bottle reactors are easily autoclaved. Dye decolorization can be conducted in anaerobic and aerobic mediums, as mentioned before. In conditions where oxygen is not required, like anaerobic conditions, the triple nitrogen bonds of azo dyes are converted to aromatic amines. In aerobic conditions, it is mineralized to the aromatic amines.

Recent studies have shown the use of up-flow membrane-less MFC and floating MFC for the betterment of scaling up procedure in dye degradation of aromatic amines and for simultaneous electricity generation.

D. Mechanism of Dye degradation

The mechanism involved with dye degradation involves specific steps such as the enzymes, chemical reduction by certain biological reductants such as sulfide, and low molecular weight mediators (if used). In most of the MFCs, the mechanism of dye degradation remains the same, especially in anaerobic anodic degradation. An extra step involves the negatively charged electron and positively charged proton transfer through the membrane and the external circuit. The biosorption of the living cells primarily removes the color. The proton exchange membrane helps transfer the protons and electrons produced at the anode and is oxidized by the bacteria. (Solanki, Subramanian, and Basu 2013). The azo dyes are broken down at the cathode producing confident toxic intermediates. Therefore, it can be said that dye degradation occurs at the anode and occurs in anaerobic conditions. (Li et al., 2010). The toxic intermediates that are formed from aromatic amines are removed by aerobic treatment. This dye decolorization mainly occurs due to the adsorption of the color by the biomass.

E. Coulombic Efficiency and Treatment Efficiency

Acceptance or Coulombic Efficiency is defined as the measure of the amount of energy that is present during the emitting of the energy used during the charging of the cell. Usually, if the dye concentration increases, the coulombic efficiency also increases. The same goes for the power density.

F. Factors affecting Microbial Decolorization

1) Effect of pH

pH plays an integral role in the process of dye decolorization process. The optimal pH that needs to be maintained for dye degradation ranges between 6 and 10. The tolerance to high pH is the main aim for such industrial dye decolorization processes, which involve using reactive azo dyes and need to be carried out under alkaline conditions—organisms such as fungi and yeast show degradation at neutral or acidic pH. The dye decolorization process takes place at optimal pH and keeps decreasing rapidly with solid alkaline and strong acidic pH. The dye molecule's transport can be affected by the increase or decrease in the pH. The movement of a dye molecule across the membrane is also considered the rate-limiting step in this process.(Khan, Bhawana, and Fulekar 2013). There are certain exceptions in the case of decolorization using Brilliant blue G utilizing a combination of *Galactomyces geotrichum* and *Bacillus sp,* which showed no dependence on pH, and the decolorization of dye was also observed at pH 5 to 9 (Jadhav et al., 2008). The pH tolerance during decolorization plays a significant role and makes the dyes fit for other biological treatments of other dyeing mill effluents.

2) Effect of Temperature

Another critical factor in the process involved with microbial vitality is temperature. Studies have been carried out to study the activation energy for dye decolorization, mostly of azo dyes. A narrow range of temperatures has been determined for the decolorization of dyes, particularly azo dye, which is carried out by complex microorganisms that inhabit the active sludge. Temperature also affects the biomass yield, growth rate, and reaction mechanism. At optimum temperature, decolorization takes place at a normal rate. With the increasing temperature, there is a decrease in the degradation of the azo dyes. This is specifically credited to the loss of cell vitality and denaturalization of azo reductase enzyme. This proves that the decolorization rate decreases with the temperature above the optimum range. (Khan, Bhawana, and Fulekar 2013)

3) Effect of Dye Concentrations

Earlier studies showed that dye concentration and decolorization rate are inversely proportional to each other, which means with the increase in dye concentration, there is a gradual decrease in the decolorization rate. This is probably due to the hazardous effect of the dyes. This effect of shades is regarding biomass concentration. The growth of microorganisms is also inhibited by the reaction of azo dyes with sulfonic acid. This affects the aromatic rings and the development of microorganisms when there is a high dye concentration. The type of dye used is also essential, even though toxicity is significantly associated with dye concentrations.(Khan, Bhawana, and Fulekar 2013)

4) Effect Of Nitrogen And Carbon Sources Supplements

Carbon and nitrogen supplements are essential in the biodegradation of dyes. Azo dyes lack such sources, which makes their degradation a little tricky. A complicated organic source, for example, peptone or yeast extract, is required for dye decolorization, mostly azo dyes. The most commonly available organic source is glucose. Several research has been conducted on decolorizing azo dyes in the presence of various origins, primarily carbon and nitrogen. This research has also proven that carbon sources are less effective in contributing to decolorization. This is so because of the carbon sources assimilating in the cell. Adding specific nitrogen sources such as peptone, yeast extract, beef extract, or urea has a contrasting effect as they can generate NADH, which plays a role as an electron donor and helps decrease the number of azo dyes by using microbes. This helps in successful dye degradation. The carbon sources such as fatty acids, tapioca, starch, yeast extract, or glucose under anaerobic conditions can help reduce azo bonds. (Khan, Bhawana, and Fulekar 2013)

5) Effect of Agitation and Oxygen

Environmental conditions such as oxygen can influence the process of dye degradation as well as decolorization. The habitat's oxidative or reductive status indirectly affects the microbes' metabolism, affecting dye decolorization. Under strict anaerobic conditions, the decolorization of azo dyes was the most effective. In particular static and shaking conditions, oxygen was a decolorization effect. Mostly in shaking conditions, the inefficiency in the decolorization of dyes was observed, which demanded better oxygenation.(Khan, Bhawana, and Fulekar 2013)

6) Effect of Structure of the Dye

It has been noticed that the dyes with more superficial structures, which means low molecular weight, have more rates of colour elimination and the rate of removal are generally lower in case of dyes with an electron-withdrawing group. Color removal is also faster in the case of monoazo dye compounds concerning the diazo or triazo ones. A substituent present at the para position in an azo dye is more capable of decolorization than those at ortho or meta positions in a phenyl ring. Azo compounds comprising methyl, sulpho, nitro, or methoxy groups are found to be less biodegraded than amino or hydroxyl groups. (Khan, Bhawana, and Fulekar 2013)

7) Effect of Electron Donor

The organic compounds of the textile industry and the azo dyes act as a substrate. This is generally for the growth of anaerobic bacteria. This also helps in complete decolorization. It is therefore required for the presence of an external substrate that is an electron donor that helps in enhancing the decolorization performance. For good colour removal quality, it is essential to get the best type and electron donor availability.(Khan, Bhawana, and Fulekar 2013)

8) Effect of Redox Mediator

Redox mediators also play an essential factor in azo dye degradation by enhancing the reductive processes in anaerobic conditions. These compounds are also enzymatically reduced to hydroquinone which reduces the azo dyes in a chemical reaction.(Khan, Bhawana, and Fulekar 2013)

G. Enzymes involved in Microbial Decolorization and Degradation of Azo Dyes

1) Azo Reductases

According to Chang et al., 2010, azo reductases help in catalyzing the reductive cleavage (that is, the triple nitrogen bonds of azo dyes) to produce the colorless aromatic amine products. Several research has been carried out on azo reductases. It has been proved that this class of enzymes has proven to be effective or helpful for environmental biotechnology. The azo enzyme reductases can be further classified as flavin-independent azo reductases and flavin-dependent azo reductases enzymes. The flavin-dependent can be further classified based on the co-factors, such as NADH, NADPH, or both. The azo reductase derived from the bacteria represents the novel families of the enzyme and shows little similarity to other reductases. (Khan, Bhawana, and Fulekar 2013)

2) Lignin Peroxides

Lignin peroxides are referred to as LiP and was first reported in 1983. This enzyme helps in catalyzing the oxidation of non-phenolic aromatic lignin and other similar compounds. This enzyme also helps in catalyzing the oxidation reaction of the side chains in lignin and other similar compounds. This enzyme also mineralizes various combinations ranging from polychlorinated biphenyls

recalcitrant aromatic compounds and dyes. Lignin peroxide derived from *Bjerkandera adusta* helps transform the six industrial azo dyes and phthalocyanine dyes. Lignin peroxide plays vital in catalyzing the reduction of dyes such as Procion Brilliant Blue HGR, Acid Red 119, Ranocoid Fast Blue, and Navidol Fast Black. This lignin peroxide was derived from *Phanerochaete chrysosporium* grown on the neem hull waste. (Khan, Bhawana, and Fulekar 2013)

3) Laccases

These are enzymes that contain copper and those which helps in catalyzing the oxidation of several inorganic and aromatic substance. This enzyme is known to have a wide range of substrates that can help in bioremediation as well as industrial purposes. There are straightforward requirements for laccase catalysis, including the presence of a substrate and oxygen gas. The two main qualities of this enzyme are the evident stability and the lack of inhibition which makes this enzyme acceptable and attractive for the biotechnological industries. The enzyme laccase is monomeric, dimeric, or tetrameric glycoproteins. It is attached to four copper atoms per monomer. This is altogether connected to the catalytic site. The oxidation of the substrate is carried out by Type I copper, which also helps impart the blue color to the enzyme. Laccase helps decolorize the azo dyes without direct cleavage of the azo bonds. This helps in avoiding the development of toxic aromatic amines. (Khan, Bhawana, and Fulekar 2013)

4) Tyrosinases

This enzyme helps in catalyzing the oxidation of phenols. It is also used in the taking away phenol in which either the molecular hydrogen peroxide or oxygen(molecular) is the oxidant. This reaction, catalyzed in the presence of catalysts, is carried out in two steps. The first step, hydroxylation of monophenols, leads to the formation of ortho-diphenols, and the resulting product is generally known as mycophenolate. In the second oxidation step, the ortho-diphenols are converted to ortho-quinone, which helps in inactivating the tyrosinase activity. This is also referred as the ortho-diphenols step. Therefore, it is said that tyrosinase acts as cresolase and catecholase activity. Tyrosinase also functions as a marker in the oxidative enzymes, which are usually involved in the azo dye degradation. Tyrosinase is involved in the degradation of Direct Blue-6 by *Pseudomonas desmolyticum* NCIM 2112 (Kalme et al, 2012) and helps in dispersing dye brown color by a consortium of microbes which includes *Galactomyces geotrichum* and other *Bacillus sp.*(Khan, Bhawana, and Fulekar 2013)

5) Manganese Peroxides

This enzyme helps oxidize hydrogen peroxide to intermediary compounds, which helps promote the oxidation of Mn^{2+} to $Mn^{3+.}$ This Mn^{3+} formed is later stabilized by oxalic acid, an organic acid that leads to the formation of the Mn3+ organic acid complex. Hence, it is evident that manganese peroxides help oxidize the natural substrate, lignin, in the textile dyes. Manganese peroxides also help decolorize azo dyes and phthalocyanine complexes in an Mn^{2+} unconventional manner. This treatment, in the presence of enzymes, helps in the catastrophic destruction of the chromophoric groups and the chemical nature and structure of the dye. The dye degradation using the microbe, *Phanerochaete chrysosporium*, was mainly carried out by manganese peroxide. This enzyme decolorized two chemically different dyes, namely, Ranocid Fast Blue and Procion Brilliant H-GR produced by the novel bacterium, Serratia marcescens. The two dyes belonged to the azo(Ranocid Fast Blue) and the anthraquinone groups(Procion Brilliant H-GR). (Khan, Bhawana, and Fulekar 2013)

H. Microorganisms And Their Application For Treatment Of Dye Containing Wastewaters

It is usually seen that in a standard aerobic sewage treatment plant, the degradation of azo dyes is not performed by the microorganisms such as bacteria. Still, some of it is physically adsorbed in the sewage sludge. This situation is quite like the difficulties faced when the isolation of microbes, mostly bacteria with "aerobic azoreductase" activity, is carried out. This is the prime reason conventional sewage treatment plants are not acceptable for the degradation of azo dyes and are soon replaced by various chemo-physical techniques. The chemo-physical treatment plants are required for the proper treatment of textile wastewater. The effluents discharged from several textile industries are produced in varying compositions and are structurally quite diverse. This can be seen in the same industry in a brief period. Several problems arise if the wastewater is present in large volumes or due to the nature of synthetic dyes and the control of biomass. This problem can be overcome using immobilized enzyme such as laccase, which has been extensively applied in this field. (Khan, Bhawana, and Fulekar 2013)

Laccase has the unique capability to catalyze the oxidation of a vast spectrum of pollutants. The degradation of azo dyes in wastewater treatment systems can be achieved by anaerobic reduction. The main problem in the anaerobic or oxygen-deprived treatment of azo dyes by bacteria is the formation of amines that anaerobic conditions cannot metabolize.

If these amines are presumed carcinogens, then the accumulation of these azo dyes is relevant, for example, naphthylamine or benzidine derivatives.(Khan, Bhawana, and Fulekar 2013)

The most reasonable action plan for dye degradation is using both anaerobic and aerobic systems. The biodegradation of these aromatic amines is an aerobic process.

The feasibility of this aerobic process was applied on a sulfonated azo dye, Mordant Yellow 3. Many different reactor configurations have been used since then, including an anaerobic sludge blanket, fixed film, rotating biological contractors, and anaerobic baffled reactors used for anaerobic processes and activated sludge and turning physical contractors for the aerobic processes. The decolorization process usually occurs in the anaerobic or oxygen-deprived zones, and the percentage of color removed ranges from 70 to 95%.

In the end, it proves that the aerobic or anaerobic systems are filled with different substrate mixtures with high chemical and biological oxygen demand (COD and BOD). This Biological Oxygen Demand and Chemical Oxygen Demand can mainly be pulled off in the anaerobic stage of wastewater treatment.

The azo dyes are hesitant to degrade under aerobic conditions, but they can be easily degraded under anaerobic conditions. (Khan, Bhawana, and Fulekar 2013)

Therefore, an ideal condition for degrading dyes is an anaerobic treatment followed by aerobic treatment of the wastewater. It is the perfect condition for wastewater treatment, especially in the textile industry.(Khan, Bhawana, and Fulekar 2013)

I. Scalability and Cost

To date, the potential of MFC has long been exploited. The main things associated with the proper functioning of MFCs include the electrode and membrane characteristics, the system architecture, and the microorganisms used in the system. Earlier, it was reported that simultaneous power generation and dye degradation using an MFC could be profitably exploited. MFC demands high cost if the dye degradation is carried out on a large scale, but at a pilot scale, it was found to be entirely feasible. (Ilamathi and Jayapriya 2018)

J. Future Perspectives

This process of biodegradation of several synthetic like azo dyes using microorganisms such as bacteria, fungi, yeasts, and algae has gained a lot of interest in these years. It is the most promising approach for treating wastewater, primarily synthetic dyes discharged from different textile industries. The ability of these microorganisms to degrade the dyes can be slowly enhanced by increasing the concentration of synthetic organic dyes. The decolorization rate can be improved by the adaption of the microbial community toward the toxic compounds. The microorganisms that are usually exposed to a higher level of pollutants show various mechanisms for degrading different dyes. This happens mainly due to the expression of genes that encode enzymes that help in the degradation of the dyes. Genetic engineering and acclimatization are two very useful technologies that can be applied to this process. These can be useful in designing super degraders. The process acclimatization is better and natural as the built-in setup of the microorganisms is not disturbed in this process. This is due to the incorporation of new genes. This is why many scientists are still skeptical about the use of genetically modified organisms. Not being sure and the fear of these genetically modified organisms changing the environment hinders the use of genetically modified organisms. (Khan, Bhawana, and Fulekar 2013)

III. CONCLUSION

The synthetic dyes discharged from the textile industries pose serious health hazards. It is also one of the main reasons for medical and aesthetic problems. The need for cost-effective and technically feasible processes is becoming very important due to the increasing use of such toxic substances by various industries. The regulations have also become tough day by day. There are different physical and chemical that are employed for the use of wastewater that contains synthetic dyes. There are various severe limitations with all these processes, such as low cost, limited versatility, low efficiency, and the production of sludge, which is the secondary waste. The bioremediation process is a cost-effective, biofriendly and environment benign method for removing hazardous material from industrial wastewater. As mentioned earlier, the reductive cleavage of azo dyes produces aromatic amines that are toxic so it is necessary to assess the extent of mineralization by making use of amine bacterial degrader. The anaerobic and aerobic biological methods are the most appropriate method for degradation of azo dyes. The optimization of these processes is of utmost importance as many physicochemical parameters influence the decolorization performance. The azo dye-containing wastewater can be enhanced further by using techniques from molecular biology and biochemistry and may be coupled with advances in genomics and proteomics.

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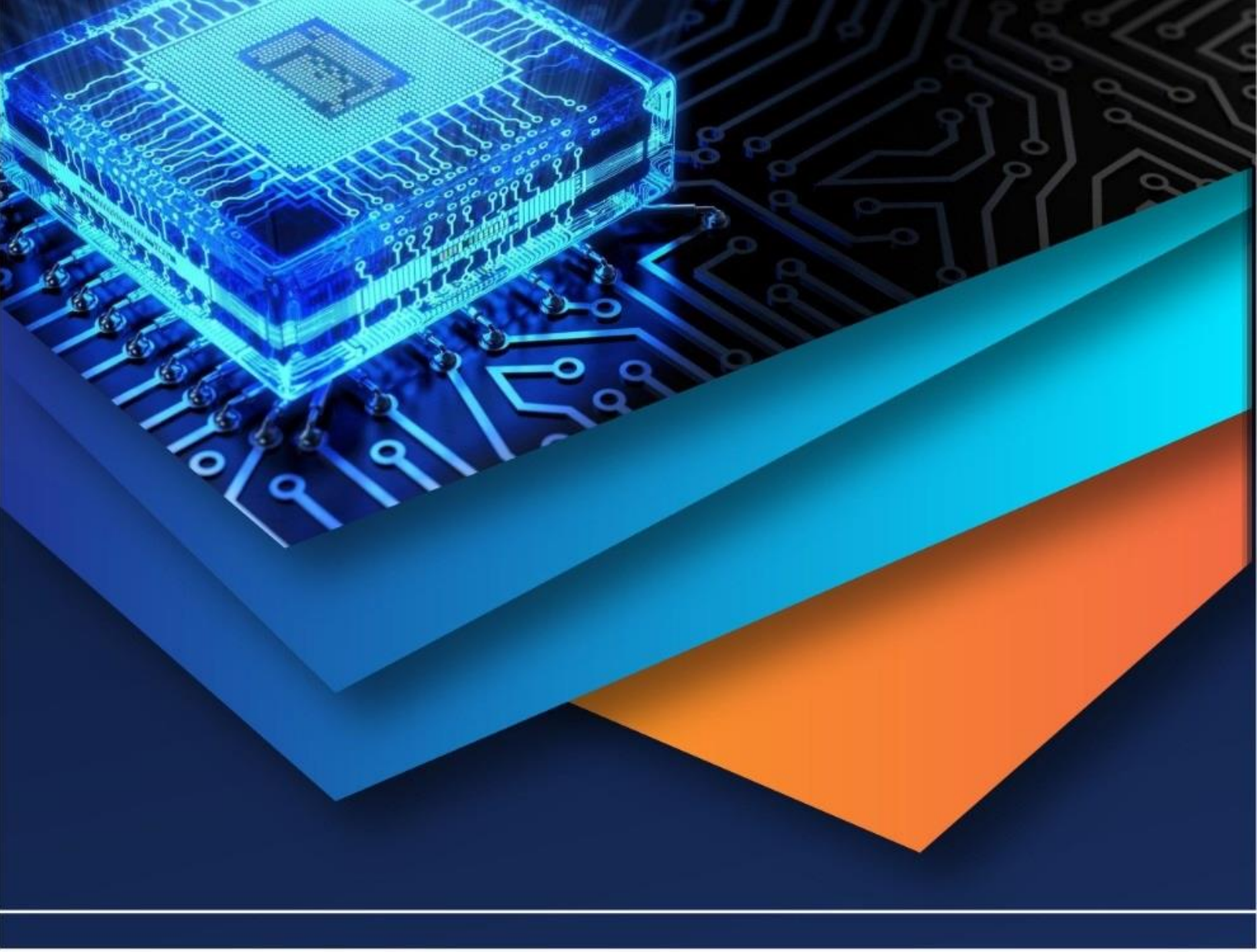

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