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Biodegradation and Decolorization of Dye Wastewater: A Review

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Abstract. The total production of all kinds of dyes in China has reached 900,000 tons. Dyes are used in various industries, such as textiles, foods, paper-making and plastic industries. In these industries, a large quantity of dye wastewater is produced and dye contamination changes the water color, enhances the eutrophication, depletes oxygen and ultimately disturbs aquatic organisms to great extent. Dye wastewater has become one of the key pollution sources. In recent years, dye biodegradation has been extensively explored. The paper reviews biodegradation of dyes under aerobic, anaerobic, anaerobic-aerobic conditions and the degradation of dyes by microorganisms. Moreover, we summarized the possible degradation mechanisms of dyes to provide the basis for biological treatment of dye wastewater.

1. Introduction

In recent years, the production of dye wastewater is increasing rapidly. It is estimated that more than 100,000 tons of dyes are produced each year and about 10% of the dyes are discharged into the environment, thus causing serious harm to aquatic organisms and human health [1]-[3]. In the dye production process, benzene, naphthalene, anthraquinone and other compounds are used as raw materials and usually chelate with metals or salts to generate dye wastewater containing acids, alkali, salts, halogen, hydrocarbons, nitro, amine, dyes, corresponding intermediates and other substances. Moreover, some dyes may be decomposed to produce carcinogenic aromatic amines or dyes containing pyridine, cyanide, phenol and heavy metals such as mercury, cadmium, and chromium. The wastewater components are complex and toxic [4]-[6]. It is necessary to develop effective ways to degrade dyes and other organic contaminants from wastewater. Many researchers at home and abroad are exploring new methods for the treatment of dyestuff wastewater. China has initially developed some treatment methods through experimental studies, including physical, chemical, biochemical and several combined treatment methods. Physical and chemical methods have some limitations including high operating cost, interferences from other components in the wastewater and large amounts of sludge, whereas biological methods have low operation costs and stable effects. Therefore, biological methods have been widely used [7]-[10]. Biological treatment methods of azo dye have some degradation effects and the biodegradation mechanisms and ways of the dyes have been explored. The isolation and identification of dye intermediates is important in the exploration of the biodegradation mechanism and degradation pathway of dyes [11]. Different dye structures involve different biodegradation pathways. The biodegradation pathways of dyes mainly depend on the molecular structures of dyes, microorganisms, related enzymes and other factors. However, in general, the biodegradation process of dyes is generally divided into two phases. In the first phase, under anaerobic conditions, decolorization is realized through reduction and pyrolysis of dyes, but harmful aromatic amines are generally produced. In the second phase, under aerobic conditions, the intermediate aromatic amines are further utilized by aerobic bacteria in aerobic reactors and decomposed into small inorganic molecules such as CO_2 and NH_3, which are utilized by microorganisms to synthesize protoplasms and ultimately realize dye degradation [12], [13]. Reductive degradation of dyes may be ascribed to azo-reductases, redox mediators, and chemical reducing agents such as sulfides or compositions. Another degradation mechanism of dyes may involve cytosolic flavin-dependent reductions, transfer the electrons to the azo dye via soluble flavin, and finally decolorize dyes. Therefore, the biodegradation of dyes has gradually become one of the hotspots in the environmental field. The dye biodegradation methods include aerobic treatment, anaerobic treatment, combined aerobic-anaerobic treatment, and microbial treatment. The four methods of decolorization and degradation of dyes are discussed below.

2. Decolorization and Degradation of Dye Under Aerobic Conditions

Dye degradation under aerobic conditions is mainly catalyzed by specific enzymes and most of them are azo reductase. Some aerobic microorganisms in the presence of azo reductase and other factors can reduce azo dyes and produce intermediate metabolites such as aromatic amines, which can be further degraded by microorganisms under aerobic conditions so as to achieve the complete mineralization of azo dyes. Liang et al. [14] studied the degradation of azo dye alizarin yellow R (AY) in a combined process of iron-carbon micro-electrolysis and aerobic bio-contact oxidation. Under the optimum conditions (the hydraulic retention time of 6 h and the reflux ratios of 1 and 2), AY degradation efficiency in the final effluent was more than 96.5% and the total organic carbon (TOC) removal rates were 69.86% and 79.44%, respectively. Iron carbon micro-electrolysis significantly increased the removal rate of AY and the generated small-molecule acids and aldehydes could be further degraded in aerobic reactors. The biological method combined with physical and chemical methods provides a new method and choice for the treatment of dye wastewater.

3. Decolorization and Degradation of Dye under Anaerobic Conditions

Anaerobic digestion of dye wastewater is a promising technology. The decolorization and degradation of azo dyes under anaerobic conditions is a relatively simple and nonspecific reduction process involving the azo reduction mechanism relying on redox intermediates. In direct enzymatic catalysis, non-specific azo reductase in microorganisms directly catalyzes the reduction of azo dye. However, the existence of this enzyme has not been directly verified. The reduction reaction relying on cofactors and redox mediators may be the main mechanism for the degradation of azo dyes under anaerobic conditions. At present, the main redox intermediates are FAD and NAD(P)H, etc. and they can receive electrons from an azo-reductase and then transfer the electrons to the azo dye. Then azo-bonds (-N=N-) are destroyed to produce aromatic amines, which decolorize the azo dye. The spontaneous non-specific reduction reaction between the azo dye and redox intermediates mainly depends on the redox potential. According to related reports, under the anaerobic conditions, the redox potential of 50 mV can lead to effective decolorization of azo dyes. However, the cleavage of the chromophore groups of dyes results in a colorless, odorless, and toxic intermediate metabolites of aromatic amines, which are commonly mineralized under aerobic conditions. Furthermore, it has been reported that the presence of oxygen usually suppresses the reduction activity of the azo bond because aerobic respiration may dominate the utilization of NADH and impede the transfer of electrons from NADH to the azo bond. It has also been reported that aromatic amines containing functional hydroxyls and carboxyl groups can be mineralized under anaerobic conditions. Some aromatic amines which are prone to undergo self-oxidation can be degraded under anaerobic conditions.

Cao et al. [15] used the electro-assisted microbial system to degrade Reactive Brilliant Red X-3B (RBRX-3B) dye under anaerobic conditions and compared the degradation of RBRX-3B by an electro-assisted microbial system (EAMS), a microbial system (MS) and an electrochemical system (ECS). The comparison results showed that the degradation efficiency of RBRX-3B in EAMS was 10% higher than the total degradation efficiency of MS (61.9%) and ECS (27.1%). The EAMS in which the anaerobic microbial system was combined with the electrochemical system could accelerate RBRX-3B degradation. RBRX-3B was transformed to nontoxic hydrocarbons and toxic compounds in

EAMS so as to achieve the complete mineralization of the dye. This technology provided a new option for the treatment of dye wastewater.

4. Decolorization and Degradation of Dyes under Anaerobic-Aerobic Conditions

In general, some azo dyes with simple structures can be completely biodegraded, but the aromatic amines of azo dyes under anaerobic conditions often cannot be further degraded under anaerobic conditions, thus resulting in the accumulation of toxic substances. These aromatic amines are biodegradable under aerobic conditions, so the combined aerobic-anaerobic process for treating azo dye wastewater is a good way to completely degrade the dye.

Melgoza R M and Cruz A [16] studied the degradation of dyes in textile wastewater by anaerobic/aerobic reactors and observed that the colorant disperse blue 79 (DB79) was converted into aromatic amines in the anaerobic phase to decolorize wastewater by microbes. The generated aromatic amines were subsequently mineralized in the aerobic section, thus eliminating the dye toxicity. Mohan S V and Babu P S [17] found that the degradation efficiency of dyes under anaerobic conditions was higher than that under aerobic and anaerobic conditions, so they believed that anaerobic conditions had the dual advantages of aerobic and anaerobic degradation of dyes. Ong et al. [18] compared the biodegradability of four heavy azo dyes in anaerobic/aerobic (SBR1) reactors and aerobic (SBR2) reactors and found that anaerobic/aerobic (SBR1) and aerobic (SBR2) reactors realized 95% COD removal, whereas the anaerobic/aerobic (SBR1) and aerobic (SBR2) reactors realized the decolorization rates of 93% and 50%. The decolorization rate of anaerobic/aerobic (SBR1) reactor was higher than that of aerobic (SBR2) reactor.

5. Microbial Decolorization and Degradation of Dyes

In recent years, the previous studies on the microbial degradation of wastewater were mainly focused on the breeding of a variety of excellent decolorization strains for degradation and adsorption of dyes in wastewater, efficient engineering bacteria and other enhanced technologies. The azo dyes can be decolorized by a wide variety of microorganisms, including bacteria, fungi, actinomycetes, algae and so on. Differences in the growth environment and metabolism mechanisms among different microorganisms affect the decolorization efficiency of azo dyes. Therefore, it is of great significance to understand the mechanisms of decolorization and degradation of different microorganisms for creating a suitable living environment for microorganisms, which contributes to the decolorization and degradation of azo dyes. Li et al. [19] studied the decolorization effect of the electroactive bacterium *Shewanella oneidensis MR-1* on the azo dye cationic red X-GRL. Under optimal anaerobic conditions (pH 5.5-8.0, 30-40 ℃, and reaction time of 12 h), *Shewanella oneidensis MR-1* showed a higher decolorizing capacity for X-GRL. Liu et al. [20] studied the decolorization of methyl orange by *Bacillus circulans BWL1061*, a newly isolated salt tolerant strain. The results showed that the newly isolated salt tolerant strain azo reductase, NADH-DCIP reductase and laccase were involved in the degradation of methyl orange by *BWL1061*. In addition, the strain *BWL1061* could also degrade aromatic amines, thereby reducing the toxicity of the dye. Song et al. [21] isolated a salt-tolerant yeast, G1, which could decolorize various azo dyes, and studied the decolorization performance of the strain against acid red B (ARB). Under optimal conditions, the decolorization rate of 50 mg/L of ARB within 16 h was up to 98% and the intermediate aromatic amines could be further mineralized. NADH-DCIP reductase was identified as key decolorization reductase. Peroxidase, manganese peroxidase, and laccases were important oxidoreductases for further degradation of decolorization intermediates. Therefore, it is necessary to screen the dominant strains of efficient degradation of dyes for the decolorization of dye wastewater.

6. Conclusion

Among the treatment methods of dye wastewater, the dye biodegradation is important. The physical and chemical treatment processes of dye wastewater are inefficient and costly and produce refractory pollutants, thus resulting in secondary pollution. The biological methods are eco-friendly and efficient with low cost and widely concerned. However, to date, the mechanisms of biological decolorization of dyes are still not clear, and it is difficult to screen efficient decolorizing bacteria. In the future, it is necessary to explore the biological decolorization and degradation of dyes, screen efficient decolorization bacteria, and provide the theoretical basis for the studies on the decolorization of dye wastewater. However, laboratory studies of dye wastewater treatment are far from treatment practices.

Therefore, the future studies should focus on the treatment practices of dye wastewater so as to provide a feasible process for the treatment of dye wastewater.

7. References

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