ISSN: 1813-4890

Dye degradation product studies

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Abstract

In order to further understand how ligninase achieves the degradation of dye molecules and its process pathway, researchers have taken various effective methods to analyze and identify the intermediate and final products of enzymatic degradation of dye, and speculate the degradation path of dye molecules. Commonly used analytical instruments include ultraviolet-visible spectroscopy full-wavelength scanning analysis (UV-vis), Fourier infrared spectroscopy (FTIR), gas chromatography-mass spectrometry (GC-MS), liquid chromatography-mass spectrometry (LC-MS) and so on. UV-vis analysis mainly determines whether dye molecules are effectively decolorized by comparing the changes of the maximum absorption peak before and after degradation of dye molecules. FTIR analysis mainly compares the changes of characteristic functional groups before and after degradation of dye molecules to determine whether dye molecules are effectively degraded. Gas chromatography-mass spectrometry (GC-MS) and liquid chromatography-mass spectrometry (LC-MS) were used to identify degradation products and intermediates in the degradation process of dye molecules, and further speculate the degradation path of dye molecules.

Keywords

Dye; Degradation Pathways; Pollution.

1. Status of degradation product analysis

According to relevant research reports, lignerase degradation dye Congo red may form toxic intermediates, azo dye enzymatic degradation intermediate analysis as shown in Table 1-3, toxic intermediate products are mainly amine-containing compounds, therefore, the identification and toxicity assessment of degradation products is a particularly important part of dye degradation. Lignin-degrading enzymes secreted by Aspergillus niger have a lower molecular weight and less benzene ring structure, such as sodium naphthalene sulfonate and cycloheptadienoide, and significantly reduced toxicity [1]. Daiane Iark et al. reported similar results, with laccase degradation of the azo dye Congo Red resulting in a degradation product with an m/z value of 255.23 ($C_8H_3N_2O_8$-), an oxidized compound with a significantly open ring and significantly reduced toxicity [2]. Similar studies have shown similar metabolites in the degradation of Congo red by Ganoderma lucidum laccase [3]. These results show that most azo dyes produce amines during degradation, but in turn are degraded into fully oxidized small molecules .

ISSN: 1813-4890

Table 1 Analysis of Congo red degradation products

Fungus	Enzyme	Dye	Degradation products	Reference
Oudemansiella canarii	Lac	Congo red	naphthalene derivatives	[39]
Aspergillus niger	Lip, Mnp	Congo red	Sodium naphthalene sulfonate, cycloheptadienylium	[61]
Ganoderma lucidum	Lac	Congo red	Amines, the desulfonation of metabolites	[62]
Ceriporia lacerata	Mnp	Congo red	naphthylamine and benzidine	[63]

2. Speculation of degradation pathways

Based on the analysis and identification of degradation products, researchers have focused on understanding and speculating about the mechanism of how these chromophores decompose. Taking the laccase degradation of the azo dye Congo red as an example, 1) the asymmetric degradation of the azo bond will first occur, and then it will be further oxidized; 2) asymmetric degradation of C-N bonds of intermediate products and their deamination; 3) The degradation product is further dehydrogenated by opening the ring, and the benzene ring is opened; 4) The final formation of complete oxidized compounds. [4] The degradation of the azo dye Congo red by Aspergillus niger secreted by Aspergillus niger by Nedra Asses et al. has a similar degradation mechanism, but also differs [5]. Possible degradation pathways: 1) complete deamination at the same time, and accompanied by the loss of two sodium atoms; 2) The deamination of some dyes and the asymmetric cleavage of C-N bonds between intermediate products, benzene rings and azo groups may be interrupted. 3) After the asymmetric C-N bond is broken, the ring opening and dehydrogenation reaction of benzene forms low molecular weight and stable degradation products, such as sodium naphthalene sulfonate and cycloheptadienylamium. According to the research progress of degradation pathway, more and more decomposition mechanisms have been explored. There are also some differences in the degradation process of lignerase from different sources to the same type of dye molecule, which may be related to the performance of the enzyme molecule itself.

3. Toxicity studies of degradation products

According to the identification of degradation products, it has been proved that the degradation process may be accompanied by the production of toxic products, so the toxicity assessment of degradation products is a very important part of supporting whether the dye molecules are effective in degradation. Researchers usually use phytotoxicity experiments and microbial toxicity experiments to detect whether the toxicity of dyes after degradation is weakened, and further measure whether the degradation of dyes is meaningful. Phytotoxicity experiments usually use plant seeds or seedlings to assess the toxicity differences before and after dye degradation. For example, Nedra Asses et al. reported that the germination and growth of Zea mais and Solanum lycopersicum seeds were used to assess the difference in toxicity before and after degradation of Congo red dye, and it was shown that Congo red toxicity was significantly reduced after degradation [6]. Microbial toxicity experiments are based on the growth of strains to reflect the toxicity differences before and after dye degradation. Related studies have used strain B. Céreus and E. Coli evaluates both untreated and treated dye solutions for toxicity assessment at recorded 600 nm OD[7].

ISSN: 1813-4890

Acknowledgements

The project was supported by the projects of Land Engineering Construction Group of Shaanxi Provincial (DJNY2022-18).

References

[1] Asses N, Ayed L, Hkiri N, Hamdi M. Congo Red Decolorization and Detoxification by *Aspergillus niger*: Removal Mechanisms and Dye Degradation Pathway [J]. BioMed Research International, 2018:1-9.

[2] Mota T R, Kato C G, Peralta R A, Bracht A, Morais G R, Baesso M L, Peralta R M. Decolourization of Congo Red by Ganoderma lucidum Laccase: Evaluation of Degradation Products and Toxicity [J]. Water Air & Soil Pollution, 2015, 226(10):1-11.

[3] Wang N, Chu Y, Wu F, et al. Decolorization and Degradation of Congo red by a newly isolated white rot fungus Ceriporia lacerate from decayed mulberry branches[J]. International Biodeterioration & Biodegradation, 2017, 117:236-244.

[4] Zheng F, Cui B K, Wu X J, et al. Immobilization of laccase onto chitosan beads to enhance its capability to degrade synthetic dyes [J]. International Biodeterioration & Biodegradation, 2016, 110:69-78.

[5] Kumar M, Mishra A, Singh SS, et al. Expression and characterization of novel laccase gene from Pandoraea sp. ISTKB and its application [J]. International Journal of Biological Macromolecules, 2018.

[6] Wang T N, Zhao M. A simple strategy for extracellular production of CotA laccase in Escherichia coli and decolorization of simulated textile effluent by recombinant laccase [J]. Applied Microbiology and Biotechnology, 2017, 101(2):685-696.

[7] Hildén K, Mäkelä M R, Lundell T, Kuuskeri J, Chernykh A, Golovleva L, Archer, D B, Hatakka A. Heterologous expression and structural characterization of two low pH laccases from a biopulping white-rot fungus Physisporinus rivulosus [J]. Applied Microbiology & Biotechnology, 2013, 97(4):1589-1599.