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Biodegradation of Phenolic Contaminants: Current Status and Perspectives

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Abstract. Phenolic compounds, a class of toxic pollutants in water, come mainly from a variety of industrial processes. The industrial application for biodegradation has become an important topic in recent years. In this review, we discuss the present situation, properties, and pollution characteristics of phenolic contaminants, factors affecting the degradation of phenols, microbial species and biodegradation methods. The challenges and opportunities in developing biodegradation processes of phenolic contaminants are also discussed.

1. Introduction

In soil and water pollution, phenolic substances are the most representative environmental endocrine disruptors, and it has toxic effects on almost all organisms. Phenolic contaminants mainly include bisphenol compounds, phenols, alkyl phenols and natural steroid hormones, which are widely, used in industry, such as pesticides, pharmaceuticals, preservatives, fungicides and so on. The annual production of phenol pollutant is very large, for example, the annual output of biphenyl A is up to 4.69 million tons [1]. Thus, the treatment of phenol pollutant is urgent.

Phenol is a kind of compound substituted that hydrogen on aromatic hydrocarbons are replaced by OH radicals. The unique properties of phenolic compounds determine its wide application in industry and great difficulty to degrade naturally. Phenolic-wasted water mainly comes from coking, gas, oil refining and other chemical and pharmaceutical processes [2]. Phenolic compounds, a kind of archetypal poison, can be inhaled into the organism through the mouth or contact with the skin and mucous membranes, resulting in the formation of insoluble proteins and the loss of cell activity, especially in the nervous system. Phenol-containing wastewater has serious effects on water supply and aquatic life. In addition, the toxicity of phenol can inhibit the growth rate of microorganisms in water and affect the ecological balance. The low concentration of phenol-containing wastewater in irrigated farmland will also make the crops contain phenols and affect edible. The high concentration of phenol-containing wastewater directly leads to crop death [3]. Therefore, the harmful effects of phenolic pollutants on the environment are enormous, and how to effectively degrade the phenol pollutants in water has become a problem that needs to be solved in the world.

2. Biodegradation

2.1. Microbial species

2.1.1. Bacteria. The bacteria degrading phenols are divided into two types: the first type has the ability to use phenols as the sole source of carbon. These bacteria contain enzyme systems degrading phenols, which often live in a bad environment with phenol contamination. This type of bacteria mainly include: staphylococcus, micrococcus, corynebacterium, arthrobacter, acinetobacter and alcaligenes. The second type must rely on other carbon sources to degrade phenols. This type of bacteria mainly decomposes phenols through co-metabolism pattern, which usually needs two or more bacteria working together [4].

The phenol-degrading bacteria generally have their unique properties, inducement of phenol degradation ability, diversity of the matrix degradation and synergistic of phenol degradation. The inducement of phenol degradation ability suggests that the degradation ability of phenol can be improved greatly after adaptive mutation in bacteria. There are two ways to mutate phenol-degrading bacteria: increasing the concentration of phenol and increasing the dosage one time. The results show that the strains which are screened by gradually increasing the concentration of phenol had the strongest degradation ability of phenol. Adaptive mutation of phenol-degrading bacteria is a result of inducing and selecting. In the process of adaptive mutation, the phenol-resistant strains are screened out by increasing the concentration of phenols, which greatly shortens the adaptation period of the bacteria and improves the degradation efficiency [5]. The diversity of matrix degradation means that isolation and screening of phenol-degrading bacteria with a single phenolic substance as carbon source can degrade other phenolic substances and refractory organics. For example, Bacillus coagulans, separated from single carbon source, can also grow with diphenyl dichloride and naphthalene as carbon source. The synergistic of phenol degradation indicates that the degradation ability of mixed strains is significantly higher than that of single strain. The mixed strains even have strong degradation ability when the phenol concentration is high [6].

2.1.2. Fungi. The main fungus of phenolic pollutants degradation are filamentous fungi, including fusarium, white-rot fungi, penicillium and so on. In the case of white-rot fungi, it can degrade chlorophenol contaminants through a series of enzymatic reactions. The degradation and mineralization of the chlorophenol contaminants by white rot fungi depend mainly on the system of their extracellular enzyme and lignin-degrading enzyme. Lignin-degrading enzymes include peroxidase and laccase, and the most important peroxidase is lignin peroxidase and manganese peroxidase. Even if the molecular structure change, the white-rot fungi also has the detoxification effect to the chlorophenol and little harm to the sensitive substance. [7]

Yeast mainly includes candida albicans, candida maltosa, trichosporon cutaneum, and oidium and so on. The research shows that the yeasts have a strong ability to degrade phenols and tolerate phenols with high initial concentration. Furthermore, large volume and good sedimentation performance are favorable for recycling and utilization. [8].

2.1.3. Algae. Some algae can also be involved in the degradation of phenolic contaminants. The study found that tolypothrix can degrade alkylphenol and the degradation rate is determined by the growth rate of algae and the initial concentration of Phenolic substances [9].

2.2. Degradation factors

The chemical composition and structure of phenolic compounds have an important role on the biodegradation performance. Taking Chlorophenol as an example, those with more halogen substituents are more susceptible to biodegradation [10]. At the same time, the position of substituent has a great effect on biodegradation, such as the degradation sequence of chlorophenol is as follows: Adjacent position > Separated position > Opposing positions. Natural microorganisms often have poor degradation ability of phenolic compounds, but the microbial degradation ability of phenolic compounds can be greatly improved by mutagenesis. The changes of environmental conditions such as temperature, pH value, dissolved oxygen, nutrients and toxic substances, affect the metabolic activity of microorganisms and the physicochemical properties of phenols, thus affecting the biodegradation performance of phenolic compounds.

3. Method

The degradation of phenol pollutant is finally going into the sewage treatment stage, thus the selection of sewage treatment method is very important for the degradation of phenol pollutant. At present, the main biodegradation methods include activated Sludge, biofilm reactor, biological contact oxidation, biological fluidized bed and immobilization technology (Table 3-1).

Table.3-1. Principe and properties of five main biodegradation methods

Method	Principle	Properties
Activated Sludge	Adsorption and oxidative decomposition of phenols by aerobic bacteria and other protozoan in activated sludge	Simple equipment, Good treatment effect, High preprocessing requirements, Unsuitable for large-scale sewage treatment
Biofilm reactor	Using biofilm to stabilize and clarify waste water	Stable water quality, Simple operation, Degradation of Refractory Organic, Finite reaction unit volume, Difficult to control microbial biomass
Biological contact oxidation	Microorganisms attach to the surface of the filler in the form of a fixed biofilm and are in contact with the required purified sewage	Combination of biofilm and activated sludge
Biological fluidized bed	Fluidization state of the carrier for attaching microorganism	Combination of membrane separation technology and bioreactor
Immobilization	To locate Microorganisms or enzymes in limited-space area by chemical or physical means	High microbial density, Fast reaction speed, Low microbial loss, Easy separation of products, Miniaturization of processing equipment

3.1.1. Immobilization. The application of immobilized technology in wastewater treatment is the most extensive, and it also has obvious effect in the degradation of phenol pollutant. Immobilization techniques include immobilized enzyme technology and immobilized microorganism technology.

3.1.2. Immobilized enzyme. Laccase is a metal-containing oxidase, which plays an important role in biodegradation of phenolic contaminants. However, the catalytic reaction of laccase is not stable enough under certain operating conditions, the laccase cannot be reused because it is water-soluble molecule and cannot be separated from the substrate and product in the water [11]. The best solution is the immobilization of laccase. The stability of laccase could be improved, and the continuous reaction could be achieved after immobilization [12].

3.1.3. Immobilized microorganism. Immobilized microorganism technology is developed from immobilized enzyme technology. Immobilized microorganism technology can increase microbial biomass and keep it high bioactivity. The main advantages of this method as follows: the activity of enzymes will not be reduced without extracting enzymes from cells; microbial density is high; the reaction speed is fast; toxicity tolerance is strong; the product is easy to separate; the equipment is miniaturized. The effect of immobilization is only determined by the nature of the microorganism and carrier and the environmental characteristics [13].

3.1.4. Immobilization method. The commonly immobilization methods can be divided into three categories: adsorption, embedding and covalent bonding method (Table.3-2). The embedding method has good comprehensive performance and is the most widely used.

Table.3-2. Principe and properties of three main immobilization method

Method	Principle	Properties
Adsorption	Enzymes or microorganisms adsorbed on the surface of the carrier or electrode by the physical action of hydrophobic interaction and salt bonding	Simple process, More types of carriers, Combination instability
Embedding	Enzymes or microorganisms are wrapped in the carrier, substrates and products can enter and leave the carrier	Mild reaction conditions High immobilization efficiency Mass transfer resistance.
Covalent binding	Covalent reaction of the groups on the carrier with the enzyme molecule or microbial surface groups	Combination stability, Complex operation, Activity inhibition.

4. Conclusions and perspectives

Over the past decades, owing to the economic pressure and public concern about environmental pollution, it would be a great chance for researchers to explore new applications and technologies in biodegradation. Current trend based on the focused-directed evolution will continue and even accelerate. As outlined above, the application of Immobilization Technology in wastewater treatment has been more and more extensive, and has also achieved remarkable results in the aspect of phenolic contaminants degradation particularly. However, because of the huge annual production of phenolic contaminants, many phenol-degrading microorganisms have not been able to expand the scale of phenolic wastewater treatment. The problem is that the removal rate of phenol in actual production cannot all reach the national standard, so that may cause secondary pollution. Therefore, we must continually pay attention to the degradation of phenol contaminants, and develop more solutions for industrial applications.

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