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Study on the Biotoxicity, Microbial Degradation and Metabolism, and Solidification of Monoaromatic Hydrocarbons (MACHs)

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Abstract

Monoaromatic hydrocarbons (MACHs), also known as aromatic organic compounds, are a general term for benzene and its derivatives. In a broad sense, monoaromatic hydrocarbons include all aromatic compounds. It can be used as an organic solvent in building decoration materials and is also widely used in other industries such as dye manufacturing, rubber manufacturing, pharmaceutical industry, pesticide industry, etc. Therefore, monoaromatic hydrocarbons are common pollutants emitted by human activities and can be widely detected in human living and living environments. With the development of China's urban economy, the improvement of residents' living standards, and the rapid increase in the number of motor vehicles, the pollution of monoaromatic hydrocarbons has become increasingly severe. Monoaromatic hydrocarbons have strong carcinogenic effects and can directly harm human respiratory, hematopoietic, nervous, reproductive and other system organs. Monoaromatic hydrocarbons also have high photochemical reactivity and are closely related to the formation of photochemical smog and aerosols in the atmosphere. Moreover, monoaromatic hydrocarbons have the characteristics of wide pollution sources, long action time, high pollution concentration, and long release cycle. They have been prioritized by the United States Environmental Protection Agency (USEPA) as pollutants for control, and have also been included in China's "blacklist" of environmental priority pollutants.

Keywords

Biotoxicity; Microbial Degradation; Metabolism; Solidification; Monoaromatic Hydrocarbons.

1. Introduction

Phenol (C_6H_5OH), aniline ($C_6H_5NH_2$), and resorcin ($C_6H_6O_2$) are three common monoaromatic hydrocarbons.

Phenol (C_6H_5OH), also known as carbolic acid or hydroxybenzene, has extremely strong corrosiveness and a relatively stable structure. At the same time, phenol is a very important industrial raw material, widely used in industries such as dyes, plastics, spices, pharmaceuticals, pesticides, and coatings. It will be discharged into the environment with industrial wastewater

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and exhaust gas, which will then pollute the water environment and endanger biological safety. Phenol is widely present in various industrial wastewater, and the phenol content in natural water environments often exceeds the environmental self-purification capacity standards, posing a threat to biological health.

Phenol can be used to produce various chemical products and intermediates, such as phenolic resin, caprolactam, adipic acid, bisphenol A, aniline, alkylphenol, epoxy resin, salicylic acid, p-hydroxybenzoic acid, picric acid, pentachlorophenol, etc. [1]. Phenol used to produce phenolic resin and bisphenol A accounts for more than 50% of phenol production, which has also led to significant development of the phenol industry [2]. Phenol is also widely used in industries such as leather manufacturing and papermaking, and is a necessary product for the preparation of leather tanning agents. Phenol is a cytoplasmic toxin that can interfere with normal cell metabolism and ultimately lead to cell death when it enters cells. Therefore, phenol can also be used as a raw material for fungicides and preservatives. Generally, a phenol solution with a concentration of 2% to 5% can be used for disinfection treatment of instruments. Various downstream products of phenol are also very important chemical raw materials, such as the halogenated compound pentachlorophenol, which can be used as a wood preservative.

The preparation method of phenol was relatively simple before World War I and could only be extracted from coal tar. With the advancement of industrial technology and the increase in market demand, various methods for preparing phenol have been developed, such as cumene method, benzene sulfonation method, toluene benzoic acid method, coal tar refining method, sulfonation alkali melting method, benzene direct oxidation method, etc. With the innovation of phenol production technology and process, phenol production has rapidly increased. The total world phenol production has increased from 9.08 million tons in 2008 to 13.213 million tons in 2014, and is expected to reach 15 million tons by 2018; The total consumption of phenol in the world is also showing a gradual growth trend. In 2008, the consumption was 8.359 million tons, increased to 9.6 million tons in 2014, and is expected to reach 12 million tons by 2018 [2]. The total consumption is expected to grow at an average annual rate of 5%. With the development of the domestic economy, the demand and production of phenol have also shown an upward trend: in 2010, the annual production of phenol was 896000 tons, which increased to 1.963 million tons in 2014, an increase of about 54.4% compared to 2010. In recent years, China has built and expanded multiple sets of phenol production plants, greatly increasing the annual production of phenol. It is expected to reach 3.8 million tons by 2018. In recent years, the demand for downstream products of phenol such as phenolic resin and bisphenol A in China has shown an upward trend, and the consumption of phenol will continue to grow.

Aniline ($C_6H_5NH_2$), also known as Aniline, Aniline oil, and aminobenzene, is the most representative among aromatic amines. Aniline is widely used in the dye manufacturing industry, it can be used to produce various dyes and organic pigments such as acidic light yellow and golden red; In the rubber manufacturing industry, it can be used to manufacture various antioxidants, accelerators, antioxidants, and stabilizers; The pharmaceutical industry can be used as raw materials for sulfonamide drugs; It is also an important intermediate in the pesticide industry, capable of manufacturing insecticides and herbicides such as sodium chlorpyrifos and alachlor; Aniline also plays an important role in other industries, such as serving as an intermediate in the production of spices, plastics, varnishes, films, etc. With the rise of China's economy and processing manufacturing industry, the demand for aniline has also grown rapidly. From 2005 to 2015, the production of aniline increased by 1.29 million tons. Other downstream products of aniline also have good development prospects and relatively broad market space [3], which has also driven the demand and production of aniline. Currently, China's aniline production has ranked second in the world.

Resorcin ($C_6H_6O_2$), also known as resorcin, 1,3-benzenediol, and m-diphenol, is a very important fine chemical raw material and intermediate. Due to its susceptibility to various

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reactions such as hydrogenation and amination, it is widely used in industries such as rubber, synthetic resins, dyes, pharmaceuticals, and analytical reagents. With the increasing demand for rubber products in the automotive and hose manufacturing industries, the demand for resorcinol in China is also rapidly increasing. According to incomplete statistics, the consumption of resorcinol in China in 2001 was about 4000 tons; In 2003, the consumption of resorcinol in China was approximately 8850 tons; The consumption in 2005 was approximately 13400 tons; Afterwards, the demand for resorcinol in China has been increasing year by year. With the rapid development of the automotive industry in recent years and the significant increase in demand for building materials and home decoration materials, this will inevitably stimulate the consumption of rubber products and wood adhesives, thereby driving the demand for resorcinol.

2. Research on the Biotoxicity and Removal Methods of Monoaromatic Hydrocarbons

2.1. Phenol (C_6H_5OH)

2.1.1. Sub-section Headings

Phenol has high toxicity, which can damage cell structure, affect organ function, damage body health, and even endanger life. When the concentration of phenol exceeds 6.00 mg/L, it can exhibit anesthetic toxicity to zebrafish, swordtail, and peacock [4]. Phenol can affect the activities of various enzymes such as glutathione peroxidase in the liver of young red finned pufferfish [5]. Phenol can affect the respiratory system of juvenile Chinese sturgeon, causing a significant increase in respiratory frequency. With the increase of phenol concentration and exposure time, it can cause suffocation or even death of juvenile fish in severe cases. The three warted swimming crab is more sensitive to the toxicity of phenol. When exposed to an environment with a phenol concentration of 10mg/L for 96 hours, half of the three warted swimming crabs can die. After treating the red snapper with phenol at an initial concentration of 10 mg/L, it was found that after 9 hours of exposure to phenol, the expression of non-specific cytotoxic cell receptors in the head and kidney organs of the experimental group was about 30 times higher than that of the control group [6]; After different treatment times, the expression levels of non-specific cytotoxic cell receptors in other organs and organs were significantly higher than those in the control group; This indicates that phenol treatment induces the activation of cytotoxic reactions in red snapper. Phenol also has toxic effects on fish such as tilapia, silver carp, and wheat carp. According to the "Technical Specifications for Biological Monitoring (Water Environment)", phenol is a highly toxic substance for tilapia, silver carp, and wheat carp.

Phenol is not only toxic to fish, but also to other aquatic organisms, posing a threat to their growth and reproduction. According to reports, phenol mainly inhibits the photosynthesis and respiration of algae, leading to toxic symptoms and even death. When the concentration of phenol in the water environment exceeds a certain value, it kills a large number of bacterial decomposers in the water environment through pathways such as destroying protein structure, leading to the accumulation of organic pollutants in the water and damaging the ecological environment.

2.2. Aniline ($C_6H_5NH_2$)

Aniline, due to its high toxicity and difficulty in degradation, has been included in the list of 129 priority-controlled pollutants by the US EPA, and has also been included in China's "Black List of Priority Controlled Pollutants in Water". The current treatment technologies for aniline containing wastewater include physical, chemical, and biological methods. The physical method uses some adsorption materials or solvents to adsorb and extract aniline in wastewater,

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in order to remove or reduce the content of aniline in wastewater. Currently, adsorption materials used include activated carbon, resin, 13X zeolite, etc. The method used by Ra mana murthy et al. [7] can extract and recover 99.5% of aniline. The membrane extraction technology, which has emerged in recent years, is also a physical method for treating aniline wastewater. When using silicone rubber membrane as the medium for membrane extraction technology to treat aniline with a concentration of 33081 mg/L, the removal rate can reach 97%. This technology can be applied to treat industrial wastewater with high aniline content. The chemical method for treating aniline wastewater is the catalytic oxidation of aniline through certain media, which can be mainly divided into photocatalytic oxidation, chlorine dioxide oxidation, ultrasonic degradation, biofilm electrode method, supercritical water oxidation method, electrochemical oxidation method, and other methods. KumarA et al. [8] used Ag+loaded TiO2 suspension for photocatalytic treatment of aniline wastewater, which is a type of photocatalytic oxidation method. Kamble SP [9] et al. used concentrated sunlight for photocatalytic degradation of aniline. In addition to using a single traditional physical and chemical method, the two methods can also be combined to remove aniline. For example, the combination of photocatalysis ozone, ultrasonic synergistic electrochemical oxidation, ClO2 oxidation visible light catalysis, etc., the treatment effect using the combination method is better than using a single treatment method. The traditional physicochemical methods for treating aniline wastewater have problems such as high energy consumption, high extraction solvent usage, and susceptibility to secondary pollution. Compared with biological treatment methods, they have advantages such as low energy consumption, green safety, and so on. At present, the biological methods applied to the treatment of aniline containing wastewater mainly include the use of activated sludge, biochar coupling agents, and aniline aerobic degrading bacteria. A variety of efficient aniline degrading bacteria have been screened, including Rhodococcus, Erwinia, Candida tropicalis, Delft's bacteria, Bacillus cereus, Pseudomonas, and Chrysanthemum. The aerobic granular sludge used by Xiang Zhengxin et al. [10] has a more efficient degradation effect on aniline. The aerobic sludge has a degradation rate of up to 99% for aniline with an initial concentration of 6000mg/L within 50 hours, and can be applied to treat industrial wastewater with higher aniline content.

2.3. Resorcin ($C_6H_6O_2$)

Resorcinol wastewater is a typical toxic organic industrial wastewater with high chromaticity and difficulty in treatment.

Physical and chemical methods are mainly used to treat wastewater containing resorcinol, but there is little research on the biodegradation of resorcinol. The physical method can use adsorption materials such as activated carbon and resin to adsorb and treat resorcinol. Ding Junwei et al. [11] used NDA-100 resin to adsorb and treat resorcinol wastewater with a concentration of about 2400 mg/L, which can adsorb and remove about 99% of resorcinol; Resorcinol can also be extracted using solvents such as n-butanol and tributyl phosphate. The chemical principle is to remove resorcinol by oxidizing it. The nano titanium dioxide and Bi-TiO2 prepared by Chen Huajun et al.[12] have good photocatalytic degradation effects on resorcinol. After 60 minutes and 120 minutes of UV and visible light irradiation, the initial concentration of 100 mg/L resorcinol can be degraded by 99.2% and 100%, respectively. Various metals and metal oxides, ultrasound, Bi4O 5Br2, zinc oxide, and other materials can also catalyze the degradation of resorcinol. The physicochemical method for treating resorcinol wastewater also has problems such as high energy consumption, large amount of extraction solvent, and easy secondary pollution. Compared to this, the biological method does not require additional energy supply, avoids significant energy consumption, and improves economic benefits. There are not many screened and discovered biological resources that can be used to degrade resorcinol. Vipul Sharma et al. [13] used an intermittent reactor and Sun et al. [14]

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used an anaerobic sequencing batch reactor to degrade resorcinol, providing a scientific basis and new ideas for the rapid degradation of resorcinol. The microorganisms used for degrading resorcinol include filamentous fungi such as Gliomastix indicus, Acinetobacter genus, and Xanthomonas. Acinetobacter strain JS-4 can degrade resorcinol at an initial concentration of 2000 mg/L by over 97% within 24 hours, while Xanthomonas strain Tl can degrade 98% of resorcinol within 48 hours.

3. Research on Microbial Degradation and Solidification Pathways of Monoaromatic Hydrocarbons

3.1. Degradation Metabolic Pathways

Microbial degradation of phenol has two pathways: anaerobic and aerobic. The anaerobic pathway of microbial degradation of phenol is carried out by first carboxyl ting phenol to 4-hydroxybenzoic acid. 4-hydroxybenzoic acid is converted into acetyl CoA through the benzoic acid pathway through the action of related enzymes, and finally converted into acetic acid, which is then degraded and utilized by the acetic acid related degradation pathway. The aerobic pathway for microbial degradation of phenol first involves the conversion of phenol to catechol by phenol hydroxylase on the cell membrane and cytoplasm. The catechol is then catalyzed by catechol 1,2-dioxygenase to form acetyl CoA and succinyl CoA through ortho pathway ring opening cleavage, or by catechol 2,3-dioxyase to form pyruvate and acetaldehyde through meta pathway ring opening cleavage, Finally, the intermediate of the tricarboxylic acid cycle is formed and enters the tricarboxylic acid cycle to complete the degradation of phenol [15]. Currently, most of the phenol degrading bacteria screened belong to aerobic bacteria, which degrade phenol through aerobic pathways. The specific degradation pathways through aerobic pathways vary among different strains: some strains are catalyzed by catechol 1,2-dioxygenase through the ortho ring opening pathway; Some strains are catalyzed by catechol 2,3-dioxygenase through the meta ring opening pathway; Some strains have both open-loop pathways.

Under different conditions, the pathways of microbial degradation of aniline vary [16]. Under anaerobic conditions, Aniline Desulfurization Bacteria [17] first carboxylate aniline to form p-aminobenzoic acid, and then undergo reductive deamination. The aerobic pathway of microbial degradation of aniline also requires the involvement of catechol dioxygenase. The AN3 strain of Acidophilic Pleuromonas aeruginosa degrades aniline through an aerobic pathway. Firstly, aniline is deoxygenated and deaminated to form catechol under the catalysis of aniline dioxygenase. Subsequently, caftechol is converted to 2-hydroxyhexenehemic acid through meta ring opening catalyzed by catechol 2,3-dioxygenase. Then, under the catalysis of 2-hydroxyhexenehemic acid dehydrogenase and NAD+, a dehydrogenation reaction is carried out to form 4-oxalylcrotonate, Afterwards, 2-keto-4-envaleric acid is catalyzed by 4-oxalylcrotonate decarboxylase to form 2-keto-4-envaleric acid, which can be synthesized into 4-hydroxy-2-envaleric acid in water. Then, with the assistance of NADH, 4-hydroxy-2-envaleric acid aldolase catalyzes the cleavage to form acetaldehyde and pyruvate, and finally enters the tricarboxylic acid cycle to synthesize cellular matter and metabolic energy.

3.2. Microbial Solidification Research

Immobilized microbial technology is a biotechnology that immobilizes microorganisms on carriers to make them highly dense and maintain their bioactive functions. Under suitable conditions, it can also add value to meet application needs. The use of immobilized microbial technology to treat industrial wastewater has advantages such as easy control of the reaction process, increased microbial concentration, improved microbial stability, easy solid-liquid separation after reaction, easy recycling, and reduced operating costs [18]. There are many

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methods for immobilizing microorganisms. To improve the immobilization effect, increase the activity of immobilized microorganisms, and enhance their environmental resistance, two or more immobilization methods can be combined.

Sodium alginate (SA) is a linear block copolymer formed by glycosidic bonds. The application of sodium alginate in the field of sewage treatment can be divided into two main modes: one is to directly use sodium alginate to adsorb metal ions. The principle is that after sodium alginate dissolves in water, it releases a large amount of -COO-, which can combine with heavy metal ions such as copper, lead, and mercury in the water to generate insoluble precipitation of alginate heavy metal salts. By utilizing this principle, sodium alginate can be directly used as an adsorbent or prepared into a membrane for the treatment of heavy metal contaminated water environments. In addition, sodium alginate can be directly applied to adsorb heavy metal ions after modification, such as sodium alginate modified with epichlorohydrin for adsorbing cadmium ions, sodium alginate modified with chloroacetic acid carboxylation for adsorbing copper ions, and modified sodium alginate for adsorbing thorium (IV) [19]. The adsorption effect of modified sodium alginate on heavy metal ions has been improved to varying degrees. The second is to use sodium alginate as an embedding agent to immobilize certain microorganisms with special effects and then use it for sewage treatment. This type of method is often used to treat oily wastewater, wastewater containing organic pollutants, etc.

Polyvinyl alcohol (PVA) is a white flake or powder solid, with good viscosity and film-forming properties in its aqueous solution. It is non-toxic, odorless, and has good biocompatibility, providing a good living and breeding space for microorganisms. Therefore, it is also a commonly used material for immobilization. Polyvinyl alcohol can be prepared as a membrane or used as an embedding agent to immobilize certain microorganisms, and is applied to adsorb or degrade heavy metal ions or certain organic pollutants in wastewater. Yun Zhang et al. [20] used large network polyvinyl alcohol (MR-PVA) microspheres for adsorbing Pb2+, with a maximum adsorption capacity of 213.98 mg/g, which can effectively adsorb and treat wastewater containing Pb^{2+}.

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