Application status and prospects of biological deodorization in China

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Abstract. With the development of urbanization, industry, agriculture and aquaculture, malodorous pollution has become increasingly serious. Odour pollutants can be produced by non-biological or biological pathways, which not only have a great negative impact on the regional ecological environment, but also cause great harm to the health of local people and animals. Compared with physical method, chemical method and adsorption method, biological deodorization method has the characteristics of high odour removal rate, environmental friendliness and low cost. Biological method is gradually becoming the preferred technique for odour removal in some odour producing areas. In this paper, the mechanism, the patent application status and the application prospect of biological deodorization are summarized and analysed, so that we can have a deeper understanding of biological deodorization.

1. Malodorous pollution and biological deodorization method

The definition of malodorous pollutant in "malodorous pollution discharge standards" (GB14554-93) is all the stimulation of the olfactory organs caused by people not as fast and damage to the living environment of the gas substances. Malodorous pollution is a kind of gas pollution caused by various odorous gases emitted by malodorous pollutants which can not only cause olfactory discomfort, but also damage respiratory system, circulatory system, nervous system and endocrine system, and even lead to organism intoxication.

Malodorous pollution mainly comes from pollutant centralized treatment facilities in industrial production, involving many industries such as petrochemical industry, biological fermentation, metallurgy, pharmaceutical, sewage treatment and municipal waste treatment. As breeding industry has gradually become an important economic source of suburban and rural residents, the manure of livestock and poultry cannot be degraded in time, which leads to increasingly serious malodorous pollution. Common malodorous pollutants are classified into sulfur-containing compounds, such as SO2, H2S, etc.; nitrogen-containing compounds, such as NH3, amines, indoles; halogens and derivatives, such as chlorine gas, halogenated hydrocarbons; aliphatic hydrocarbons and aromatic hydrocarbons; and oxygen-containing compounds, such as phenol, aldehydes [1]. How to remove these malodorous pollutants and reduce the air pollution in urban suburbs and rural areas has become a hot issue of environmental protection.
At present, there are physical method, chemical method, adsorption method and biological method to discharge malodorous pollution [2]. The physical method is mainly to carry out olfactory perception of the malodorous odor through masking or dilution diffusion, but not to remove the malodorous pollutants. The chemical method is mainly to convert malodorous pollutants into other substances through chemical reactions. If the conditions are not properly controlled, secondary pollution will occur. The adsorption method uses porous materials to adsorb malodorous gas, but the adsorbent is replaced frequently and the cost is high. Biological methods include activated sludge method, biological filtration membrane method, biological trickling filter tower method and biological filter method. Biological deodorization method mainly uses the metabolism of microorganism to decompose malodorous pollutants and remove malodorous pollution completely. Compared to other methods, it has the characteristics of higher removal rate, less of secondary pollution, and lower equipment maintenance cost. As biological deodorization method has great economic advantage, it has become the fastest growing deodorization technology in recent years.

2. Principle of biological deodorization method

Biological deodorant is used in biological deodorization which is to fix the selected deodorant microorganisms on the carrier and oxidize and degrade the malodorous pollutant through a certain biochemical pathway. The deodorization process of biological deodorant is a comprehensive process of gas diffusion and biochemical reaction. The deodorization mechanism can be divided into three stages. First, the malodorous pollutants contact with water and dissolve in water or adhere to the surface of water. Second, the malodorous pollutants dissolved in water were absorbed into microorganism cells. The malodorous pollutants which are insoluble in water are first attached to the surface of the microbial body, decomposed into soluble substances by secreting extracellular enzymes by the microbial, and then absorbed into the cell. Finally, microorganisms decompose and utilize the malodorous pollutants as nutrients for metabolism to eliminate the odor [2].

2.1. Removal of odorous sulfur-containing gases

H2S is the main component in odorous sulfur-containing gases. Beggiaota and Thiobacillus aerobic bacteria, as well as Chlorobium and Chromatium photosynthetic bacteria are used to remove H2S. These species of bacteria, through vulcanization, can oxidize H2S to substances such as elemental sulfur or sulfate, thus achieving the removal of H2S [3].

Aerobic bacteria can oxidize H2S to sulfate and obtain energy. Photosynthetic bacteria are anaerobic bacteria utilizing H2S as a hydrogen donor for CO2 reduce through cyclic photophosphorylation under anaerobic light conditions to realize the H2S oxidation to sulfur element or further oxidation to sulfate.

2.2. Removal of odorous nitrogen-containing gases

NH3 is the main target for the removal of odorous nitrogen-containing gases. The traditional biological denitrification process includes nitrification and denitrification. First, ammonia nitrogen is oxidized to nitrite by chemotrophic bacteria such as Nitrosobacteria. Nitrite can be oxidized to nitric acid by self-healing bacteria, such as Nitrobacter. Then, nitrite was converted into gaseous nitrates N2 and N2O by anaerobic denitrifying bacteria such as Bacillus Licheniformis, Paracoccus Denitrifican and Pseudomonas [4].

Recently, the discovery of Pseudomonas, Alcaligenes Faecalis, Bacillus subtilis and Pseudomonas Putida has made it possible for the aerobic denitrifying bacteria which have two types of living style to live efficiently in one reaction system. Meanwhile, many heterotrophic nitrifying bacteria also have aerobic denitrification, such as Paracoccus denitrificans GB17 and Pseudomonas SP. The discovery of these new functional strains provides a theoretical basis for the research and development of new denitrification technologies.
2.3. Removal of hydrocarbon odorous gases

Hydrocarbon odorous gases mainly come from petrochemical industry. It can be successfully degraded by *Pseudomonas*, *Achromobacter*, *Corynebacterium* and *Candida*. Hydrophobic surfaces outside the microbes are formed through the pili or the outer capsule of lipids or proteins, which are randomly attached by oil droplets in water. Some microorganisms can also secret glycolipids, lipoproteins and glycoproteins to emulsify oil droplets into many tiny particles, thus expanding the surface area of insoluble hydrocarbons in water and facilitating the adhesion of microorganisms. Notably, some emulsifiers can promote the degradation of some hydrocarbons as well. Hydrocarbon odorous gases include aliphatic and aromatic hydrocarbons. Both aliphatic and aromatic hydrocarbon degradation pathways are rapidly catalyzed by dehydrogenase or oxygenase in microorganisms [5].

2.4. Removal of odorous oxygen-containing gases

Odorous oxygen-containing organic gases, such as aldehydes and phenols, are easily soluble in water, and the removal principle of such odorous gases by microorganisms is similar to that of hydrocarbon odorous gases, which is mainly through the efficient catalytic degradation by enzymes[6].

The common phenolic pollutants, such as phenol, bisphenol A, nonylphenol and pentachlorophenol, can be degraded by *Rhizobium*, *Fusarium* and *Candida*. The decomposition is catalyzed by Oxygenases or dehydrogenases in microorganisms to reduce phenolic pollutants into CH₄, CO₂ and other harmless end products. Formaldehyde can be degraded by *Pseudomonas Putida* and *P. Aeruginosa*. The key enzyme to catalyze formaldehyde degradation is formaldehyde dehydrogenase. In the presence of glutathione and NAD⁺, formaldehyde is oxidized into formic acid which is then converted into CO₂ by formic acid dehydrogenase.

3. The status of Patent application for biological deodorant

Data have been collected from China Patent Full-Text Database (CNKI Version) which contains three suture database -- invention patent, utility model and appearance design patent in China. A total of 3,543 biological deodorization-related patents published from 1987 till now were retrieved from the 10,991,078 patents, including 2,226 invention patents, 1,312 utility model patents and 5 appearance design patents. At present, 1388 patents are authorized, 1263 cases are under verification, and 892 cases are invalidated. A total of 794 biological patents published from 1987 to 2020 were retrieved with the keywords “biological deodorant”, including 728 invention patents and 66 utility model patents. In these cases, 125 are authorized, 509 are under verification, and 160 are invalidated.

The trends in patent application for biological deodorization and biological deodorant in China were shown in Fig.1. The number of patents filed from 1987 to 2002 was in the single digits, and the number of patents grew very slowly. Since 2003, the growth rate of patent applications for biological deodorization and biological deodorant began to speed up, especially in latest 5 years. From 2014 to 2019, the number of patents for biological deodorization is accounting for over 75% of the total while for biological deodorant, it is over 85% of the total. In recent years, China has made great progress in scientific research on microbial products with the rapid development of leading industrial enterprises. China has formulated many policies and technical standards for microbial products to ensure the healthy development of microbiologica industry. With the popularization and application of various new technologies, microbial products have been widely used in agriculture, aquaculture, water pollution and other aspects. These favorable industries and policies have laid a good foundation for the development of biological deodorant and deodorant. Therefore, since 2010, biological deodorization technology has entered the growth period of the technical system. In this period, the technical performance parameters are rapidly improved, the output is rapidly increased, and the cost is reduced. With the increase of the rate of return, the investment to the industry is greatly increased, and specific resources are introduced into the market to make the system more efficient. At present, Market awareness of biological deodorization has greatly improved. It is beneficial for biological deodorants to enter the environmental protection market.
Figure 1. Trends in patent application for biological deodorization and biological deodorant in China

4. Application of biological deodorization

4.1. Odorous solid waste treatment
With the acceleration of urbanization, more and more solid wastes are produced in cities. Because of the strong odor generated by the traditional landfill method, microbial deodorant applying during the process of municipal solid waste storage and processing has become one of the most potential applications for biological deodorization in the future. It was reported that strains isolated from landfill sludge and landfill leachate showed better environmental adaptability and were more effective in eliminating NH$_3$ than EM bacteria [7].

4.2. Odorous livestock and poultry manure treatment
Breeding industry is an important part of agriculture, but the increasing harmless and intensive treatment of livestock and poultry waste has become a problem that troubles us, including the odorless treatment of livestock and poultry manure. The data show that, compared with the sewage discharge of human beings, the excrement and sewage discharge of livestock and poultry breeding is 10 times to dozens of times that of human beings on average. Therefore, it is one of the key directions for the development of new microbial deodorant to realize efficient deodorization of livestock and poultry wastes. The data show that, compared with the sewage discharge of human beings, the excrement and sewage discharge of livestock and poultry breeding is 10 times to dozens of times that of human beings on average. Therefore, it is one of the key directions for the development of new microbial deodorant to realize efficient deodorization of livestock and poultry wastes [8].

4.3. Centralized sewage treatment
Waste and sewage are constantly produced in urban life, agriculture, breeding and industry. Deodorization is a necessary step in modern sewage treatment. In order to solve the malodorous pollution problems caused by the degradation of organic compounds by microorganisms or volatilization of malodorous substances in sewage, the sewage treatment plants often modify the original sewage treatment plant or add corresponding air purification equipment to collect odorous gases into the aeration tank. Odorous gases are degraded, oxidized or adsorbed by microbial community on the activated sludge together with the original pollutants in sewage to realize deodorization while purifying
the sewage. At present, biological deodorization methods used in sewage treatment plants include activated sludge method, biofilter method, biological mixer and biofilm method.

5. Conclusion
In this paper, the mechanism, the patent application status and the application prospect of biological deodorization are summarized and analyzed, so that we can have a deeper understanding of biological deodorization. Although biological deodorization has a broad application prospect for its advantages and security comparing with the traditional methods, there are still many problems to be solved in biological deodorization technology.

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