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Research Progress of Antibiotic Pollution and Adsorption Materials in Aquatic environment

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Abstract: China is the great powers of use and production of antibiotics.The current process of sewage treatment plants can not effectively remove antibiotics in water. Chinese scholars have detected different kinds of antibiotics in major waters of the country, which have potential harm to human body. Among all kinds of antibiotic treatment technologies, adsorption removal technology has the advantages of simple operation, low cost and high removal efficiency. It is a widely concerned antibiotic removal technology. However, at present, few materials have been put into practical application, and more materials with low cost and high efficiency need to be found. Different adsorptive materials have different adsorptivity to different antibiotics. For different antibiotics, different adsorptive materials can be integrated in the future, and the theory can be extended to application.

Key Words: Aquatic environment; Antibiotic; Adsorbent material

1. Introduction

Antibiotics are secondary metabolites of microorganisms that can selectively inhibit the life activities of pathogenic organisms at low concentrations, and their chemical semi-synthetic or completely synthesized derivatives. It can effectively treat bacterial infections or diseases caused by pathogenic microorganisms. Antibiotics are widely used in disease control, agricultural production, animal husbandry and aquaculture[1]. According to statistics, the annual consumption of antibiotics in the world can reach 100-200,000tons[2].

There are many kinds of antibiotics, complex structure and difficult to remove. Because they belong to new pollutants, there is no perfect treatment technology system for antibiotics at present. In this paper, the types, sources and hazards of antibiotics in aquatic environment were reviewed, and the advantages and disadvantages of adsorption technology were analyzed.

2. Classification, source and danger of antibiotics in aquatic environment

2.1 Types and Sources of Antibiotics

Antibiotics in aquatic environment mainly include tetracyclines (TCs), macrolides (MLs), sulfonamides (SAs), quinolones (FQs) and chloramphenicol (CPs). After being absorbed by organisms, about 30%-90% of antibiotics still exist stably in the form of original drugs or metabolites and are discharged with excreta. They can be accumulated in water and soil media through various ways and transmitted along the food chain, thus posing a potential threat to the water environment and even to the drinking water sources, thus causing human long-term exposure to low-concentration antibiotics[3]. Some scholars have detected antibiotics in surface water of some basins in China. Xiaojiao Zhang detected the highest average concentration of macrolides in surface water of Liaohe River basin, 201.88ng · L^{-1}, followed by quinol-ones 124.27ng · L^{-1}, trimethoprim 113.40ng · L^{-1}, sulfonamides 93.93ng · L^{-1} and tetracyclines only 24.37ng · L^{-1}.

China is a large country in using antibiotics. Because of the low prevalence of medical education and the lack of normative guidance and supervision, the antibiotic use rate of outpatient patients is as high as 75%, which is much higher than the requirement of WHO that the average antibiotic use rate should be less than 30%[4]. Only a few of the antibiotics

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entering the human body can be absorbed by the body and metabolized into inactive products. More than 90% of the antibiotics will be directly excreted into the body throug hurine and urine, and eventually enter the environmental[5]. Direct discharge or incomplete treatment of pharmaceutical industrial wastewater will also lead to a large number of antibiotics entering the environmental water body. Pharmaceutical industry iso ne of the main sources of antibiotics in aquatic environment. Animal farming abuses antibiotics to prevent livestock diseases or pro-motethe-irgrowth. The bioaccumulation of antibiotics makes them accumulate in livestock. Most of them are discharged with feces, and some of them remain in the body. The discharge of aquaculture wastew-ater and human consumption have potential toxicity to waterenvironment and human beings. Xiaojiao Zhang and others investigated the source composition of antibiotics in surface water of Liaohe River basin. Among them, 49.1% were human antibiotics and 21.1% were veterinary antibiotics. Antibiot-ics for human and animal workers accounted for 29.8%.

Sewage treatment plant is the last barrier for antibiotics to enter environmental water, but the current sewage treatment process can not effectively remove antibiotics from sewage.Feng Ge et al.[6] analyzed the antibiotic resistance of activated sludge from four sewage treatment plants in Nanjing in 2012. The results showed that the isolates from activated sludge had serious antibiotic resistance, the drug resistance rate was 97.1%, and the multiple drug resistance rate was 80%. This indicated that there were potent-ial ecological and health risks in sludge and effluent of sewage treatment plants.

2.2 Perniciousnes of antibiotics

Long-term exposure to low-concentration antibiotic residues in aquatic environment can make bacteria resistant and endanger the survival of aquatic animals and plants. Hongyan Shen et al.[7] found that streptomycin-containing wastewater, penicillin-containing wastewater and oxytetracycline-containing wastewater had chronic toxic effects on zebrafish and brocade carp. Based on the role of antibiotics, the strains with insufficient resistance in water and soil will be killed by antibiotics, while the predominant strains will multiply in large numbers. Therefore, long-term antibiotic pollution will change the community of aquatic microorganisms and soil microorganisms[8].

The main purpose of antibiotics is to kill some pathogenic bacteria. When a large number of antibiotics remain in the organism or environment, they will inevitably do harm to some lower organisms with the same or similar target organs, tissues or cells. When the concentration of antibiotics in human body is too high, it may cause chronic toxicity, allergic reactions and “three-in-one“ effect, causing human bacteria. Population disorders are easy to cause infection and threaten human physiological function and health[9]. Resistance to antibiotics and antibiotics has now become a major concern for public health institutions and leaders worldwide. The World Health Organization has released a recent report describing the crisis of antibiotic resistance and the lack of clinical demand for new antibiotics in the face of increasing demand. Due to the limitation of science and technology and abuse of existing antibiotics, the speed of research and development of new antibiotics is far behind that of antibiotics that are resistant to human body[10].

3. Adsorbent material

Studies at home and abroad show that the removal rate of antibiotics in existing sewage treatment processes, such as conventional treatment technology, membrane treatment, oxidation and adsorption, is not very high. Adsorption refers to the accumulation of substances from gas or liquid phase to the surface of adsorbents, which may involve physical or chemical adsorption. In the past decades, although adsorption technology is well-known technology, there is no extensive exploration on the removal of antibiotics. Compared with other removal technologies, adsorption technology has the advantages of simple operation, low cost and high removal efficiency. Different adsorbents have different adsorption effects on different antibiotics. The most widely used antibiotic adsorbents include activated carbon (ACs), carbon nanotubes (CNTs), bentonite, ion exchange resin and biochar (BC). Studies have shown that for sulfamethoxazole, different adsorbents show the following trends: biomass carbon > multi-walled carbon nanotubes > graphite = clay minerals. For tetracycline adsorbents, the trend is:single-walled carbon nanotubes > graphite > multi-walled carbon nanotubes = activated carbon > bentonite = humus = clay minerals. The preparation cost of different adsorbents was also calculated. The order of preparation cost was: bioc-har < activated carbon < ion exchange resin < carbon nanotubes[11].

Activated carbon has been widely used in the removal of organic matter from sewage. Activated carbon, whether granular or powdered, has a large number of microporous, modified surface and high adsorption capacity. Recent studies have found that the adsorption efficiency of antibiotics by activated carbon or modified activated carbon varies from 74% to 100%. After surface chemical modification, the specific surface area and pore structure of activated carbon will be significantly improved, and the adsorptioncapacity of specific low concentration organic pollutants will also be significantly improved, so the modified activated carbon with high adsorption performance has become the focus of the research field of activated carbon. At present, the surface modification of activated carbon often uses oxidation modification, reduction modification and loading metal modification, etc[12]. In Sun Rui jie's experiments, $Fe(NO3)_3$ solution was used to modify activated carbon, and the adsorption capacity of activated carbon to Cefradine was improved. At the same time, activated carbon and iron salts are widely sourced, cheap, simple and easy to operate, so modified activated carbon as an economic, efficient and safe adsorbent for the treatment of cefradine wastewater has great market prospects. Of course, the main drawbacks of activat-ed carbon are high production cost and high regeneration cost.

At present, experts are increasingly interested in replacing activated carbon as adsorbent, aiming at finding new low-cost and effective adsorbents from by-products or wastes of industrial or agricultural production. Biochar is not ordinary charcoal, but a kind of charcoal with abundant carbon content. It carbonizes wood, grass, corn stalk or other crop wastes by pyrolysis under hypoxic conditions. The charcoal, which is formed by plants and aims at fixing carbon elements, is called "biochar" by scientists. BC can be used as the main adsorbent for the removal of antibiotics, because it shows a high removal efficiency(up to 100%), depending on the type of antibiotics. The cheap preparation method and high removal rate of biochar indicate that it will become a potential substitute for activated carbon as an antibiotic adsorbent. Wenze He et al[14]. prepared biochar materials by pyrolysis of Astragalus residue under anaerobic atmospheres of 200, 400, 500, 600 and 700℃ respectively. It was found that the equilibrium adsorption capacity of BC (700℃) to sulfamethazine increased by nearly 181 times compared with the original Astragalus residue. Zhang Hanyu et al.[15] prepared reed-based and sludge-based biochar from reed straw andsludge of municipal sewage treatment plant at 500℃. The saturated adsorption capacity of norfloxacin could reach 2.13 mg·g-1 and 2.09mg·g-1. Both studies have achieved the goal of "waste from scrap".

Ion exchange is a process in which cations or anions in liquid medium are exchanged with cations or anions on solid adsorbents and remain electrically neutral in two phases. Ion exchange resin is a kindof macromolecule compound with functional group (active group of exchange ion), network structure and in solubility, usually spherical particles. The results show that ion exchange resin can effectively remove antibiotics from water and wastewater, and the removal rate is as high as 90%. The adsorption removal rates of tetracycline and sulfonamide on ion exchanger were 80% and 90%, respectively. Therefore, ion exchange equipment can significantly remove some antibiotics from wastewater. However, the problems associated with this material are backwashing and regeneration, as well as the emergence of fouling and potential irreversible accumulation[11].

Clay minerals (clay minerals) are water-bearing aluminosilicate minerals with layered structure, which are the main mineral components of clay rocks and soils. Bentonite is a kind of aluminium silicate adsorbent with high specific surface area and pore volume. Bentonite can be used as an adsorbent for antibiotics in water and wastewater. So far, however, the removal of antibiotics by bentonite has not been extensively studied, and only a few literatures have reported it. Some studies have found that the adsorption rate of ciprofloxacin on bentonite is higher, the removal rate is 99%. Yanhong Zhang [16] and other experiments found that the removal rates of ciprofloxacin hydrochloride and norfloxacin reached 95% by diatomite and montmorillonite. Zeolite and pumice have good adsorption effect on antibiotics in water.

The cost of preparation and regeneration of adsorbents are important factors for the practical application of adsorbents in removing pollutants from the environment. The preparation cost of adsorption includes raw material cost, production cost, regeneration cost and process loss cost. The raw materials of some adsorption materials can be neglected, depending on their precursors. Taking biochar as an example, itscost depends on local raw material supply, processing demand, reactor availability, pyrolysis parameters, production of value-added accessories and material vulnerability. Carbon nanotubes (CNTs) in wastewater treatment plants are cheaper and more adaptable than activated carbon. But its preparation cost is too high. Regeneration of adsorption materials refers to the physical, chemical or biological method of separating or decomposing adsorbates on the surface of adsorption materials to restore their adsorption properties.In chemical regeneration, oxidation regeneration, solvent regeneration, photocatalytic regeneration, electrochemical regeneration and pyrolysis regeneration are commonly used. Physical regeneration includes heating desorption regeneration, microwave radiation regeneration, ultrasonic regeneration and supercritical fluid regeneration. The regeneration of adsorbent depends on the type of adsorbent after it reaches the saturation of pollutants[17].

4. Summary and Prospect

(1) The abuse of antibiotics seriously endangers the health of aquatic animals, plants and human beings. It is necessary to popularize medical education and reduce the use of antibiotics. Regulate supervision and market regulation, and use antibiotics scientifically.

(2) The existing sewage treatment plants can not effectively remove antibiotics in the water, so the effluent from the primary sedimentation tank should be treated in depth.

(3) Develop new adsorbents with low cost and high efficiency, and put theory into practice. Finally enter the market.

(4) There are many kinds of antibiotics, and the adsorption efficiency of different adsorbents is different. Because one treatment technology can not completely remove all pollutants in wastewater, it is necessary to combine more than one treatment method into a complete system and integrate various antibiotic adsorption technologies. Antibiotics in water should be treated in a targeted and systematic manner.

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