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Organic Modification of Natural Clay Minerals and Its Adsorption on Anionic PPCPs

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Chapter 1
Introduction

Abstract The pollution of PPCPs had become a global environmental problem. How to efficiently and deeply control the pollution of PPCPs in the water had become a hot spot and a difficult issue in the global environmental field. Therefore, it was very urgent and necessary to study the efficient PPCPs pollution control and removal technologies. This chapter introduced the concept and pollution status of PPCPs as well as treatment technologies at home and abroad, the research progress of adsorption of PPCPs by clay minerals, and the research progress of organic modified clay minerals on PPCPs. It also introduced the purpose, significance, main content and technical route of this book.

Keywords PPCPs · Natural clay minerals · Organic modified clay minerals

1.1 Current Progress of Antibiotics Contamination and Treatment

1.1.1 The Concept and Classification of Antibiotics

Antibiotics are a class of secondary metabolites, which are produced in the process of life with anti-pathogen or other activities in the microorganisms (including bacteria, fungi, actinomycetes) or higher flora and fauna and can interfere with the development of other living cell functions of chemical substances.

According to the chemical structure, antibiotics can be divided into quinolone antibiotics, β-lactam antibiotics, macrolides, aminoglycoside antibiotics, etc. According to its use, antibiotics can be divided into anti-bacterial antibiotics, anti-fungal antibiotics, anti-tumor antibiotics, antiviral antibiotics, livestock antibiotics, agricultural antibiotics, and other microbial drugs (such as ergotine produced by ergot with pharmacological activity of alkaloids, which has the effect of contracting the uterus), et al. According to the different types, antibiotics have many ways of

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production, such as penicillin by microbial fermentation for biosynthesis. Sulfonamides, quinolones, and other antibiotics can be produced by chemical synthesis. There are semisynthetic antibiotics, whose molecular structures are modified by chemical, biological or biochemical methods.

1.1.2 Current Progress of Antibiotic Contamination

As the population grows, so does the need for animal protein, and so does the need for antibiotics. In 2018, the production of antibiotics in China was 205,000 t. And it grew to 218,000 t in 2019 (Beijing Zhongjing Vision Information Consulting Co., LTD, 2020). China has a problem of an excessive amount of antibiotics for both human and animal use. Humans and animals metabolize antibiotics very slowly, and more than 70% of antibiotics are excreted into the environment same as before (). In addition, China also consumes a lot of antibiotics. Among China's prescription drugs, antibiotics accounted for 70%, while western countries do not half as much as China.

In addition to being used as medicine to treat human diseases, antibiotics are also widely used in animal breeding. One is the application of antibiotics in the prevention and treatment of diseases, and the other is to improve the animal production performance. According to relevant data, about 70% of antibiotics are used in animal husbandry. In animal husbandry, the amount of antibiotic additives in the feed eaten by animals accounts for 45.8%. More than 70% of antibiotics will be eliminated in their original form, and some of them will be disposed into sewage plants along with the domestic wastewater. At present, there is no standard for antibiotic discharge and environmental acceptance criteria. Due to lack of effective treatment, the vast majority of antibiotics will enter surface water, pollute drinking water sources and pollute groundwater through water circulation. Additionally, antibiotics retained by the medical waste in landfills will seep down into groundwater and pollute water supplies. Long-term use of antibiotics in fish pond silt, the presence of antibiotics in animal excrement and sewage sludge, can be used as organic fertilizer for agricultural production. If antibiotics enter the farmland through this route they will pass through the food chain, accumulate in the human body, and be harmful to human health.

1.1.3 Effects of Antibiotics on Environment and Health

Antibiotics are usually characterized by environmental persistence, bioaccumulation, and toxicity. They can migrate freely in the environment, disperse in soil, water and atmosphere, or accumulate in animals and plants, causing different degrees of damage to human health and ecological environment. Since August 2012, when the

Ministry of Health implemented the "Strictest Restriction on Antibiotics" (Administrative Measures on Clinical Application of Antibiotics), antibiotics have been subject to increasingly strict supervision in hospitals and pharmacies. The agricultural sector also constantly issued a list of banned certain antibiotics, However, due to the dispersed farmers, supervision is difficult and ineffective. The situation in the use of antibiotics reflects the difficulties of treatment: there is a lack of comprehensive investigation of the pollution situation, and there are numerous toxic and harmful chemicals; the related scientific research is still relatively weak and the applications of new monitoring methods are less; the cost of "treatment after pollution" is extremely high and there is a lack of effective removal technology.

At present, antibiotic residues are commonly detected in soil, water, animal, plant samples, and in surface water and even in groundwater several hundred meters below the surface. Haihe River and Zhujiang River basin are the two most seriously polluted rivers with average concentrations dozens of times higher than those in western basins such as Brahmaputra River. About 46% of the antibiotics that were seen going into the water, and 54% went into the soil. Sacher et al. (2001) collected 108 underground water samples from Germany and found that there were 60 kinds of antibiotics in the water samples at the level of μg/L. Tong et al. (2009) found that groundwater and surface water in Hubei Province contained a variety of typical quinolone antibiotics, and the content of quinolone antibiotics in surface water (0.01 μg/L) was significantly higher than that in groundwater (0.001 μg/L). Sun's study (2009) on surface water quality analysis in Xiamen also showed that surface water was polluted by antibiotics. In addition to detecting antibiotics in surface water in areas with high human activity, antibiotic contamination has also been detected in surface water in some scenic areas. Golet et al. (2001) detected ng/L quinolone antibiotics in the streams of the watershed in the valley of Grat, Switzerland. Tang et al. (2018) tested 12 kinds of sulfonamides from 14 sampling points in the water in the Nanjing section of the Yangtze River, and the results showed that 8 kinds of sulfonamides were detected in the surface water of the southern section of the Yangtze River, with a concentration range of 13.2–21.0 ng/L, with an average value of 16.2 ng/L. Liu et al. (2020) found that the concentration of antibiotics in Qingshan Lake, Taihu Lake in China, ranged from 0.05 to 940 ng/L, and the concentration of antibiotics in groundwater ranged from 0.57 to 503 ng/L. Li (2020) found that the average concentration of antibiotics in the sediments of Jiaxing and Shangyuna sewage areas was 48,180.7 ng/L, and the average concentration of antibiotics in the sediments was 34.8 ng/g and 74.67 ng/g, respectively.

Half of China's antibiotics go to the farming industry. And a large amount of sewage treatment equipment for antibiotic treatment is inadequate. Untreated sewage from many cultivation enterprises is discharged directly into rivers or used to irrigate fields. China has yet to establish a clear standard for antibiotics in sewage. The overuse of antibiotics in humans and animals is believed to be a major cause of the development of drug-resistant bacteria. During the breeding cycle of animals in China, farmers and farmers have been feeding them a small number of drugs., these drugs are not used to cure the sick animals, but to promote growth, and suppress from close contact with each other's waste caused by disease, animals eat antibiotics, after only a few is absorbed, most with faeces. The resistant bacteria can spread to humans through the environment, eating the meat of the animals, or in some cases becoming "superbugs" making it difficult even impossible to treat the infection with conventional antibiotics without the development of new drugs. The threat has been exposed in humans. The abuse and resistance of antibiotics in animals has become one of the major public health problems worldwide. Doctors are faced with fewer choices and less time to make decisions. They are often troubled by the agonizing choice of how to save a patient's life. Antibiotics can save lives, but the threat of abuse is even direr. Zhang (2005) also detected a high content of antibiotics (1.57–6.29 mg/kg) in chicken, cow, and pig manure. After the usage of antibiotic-containing sludge or livestock manure, the soil was seriously polluted by antibiotics, and the pollution was persistent. Ma (2007) found that the total concentration of antibiotics in pig manure was up to 10.83 mg/kg. Zhou et al. (2007) surveyed antibiotics in northern farmland soil, showing that the antibiotic content in common soil was at μg/kg level, while the antibiotic content in the soil-applied organic fertilizer was relatively high and varied widely, fluctuating between μg/kg level and mg/kg level, among which the content of sulfamethazine in the soil was as high as 900 mg/kg. Chu et al. (2021) established an estimation model of the carrying capacity of livestock and poultry manure polluted farmland based on the ecological risk value of antibiotics in farmland soil and studied aquaculture and planting production system in Heilongjiang Province and Xinjiang Production and Construction Corps. The results showed that high ecological risk antibiotics such as sulfadiazine and enoxacin should be the main measures to prevent the ecological risk of antibiotics in farmland soil of Heilongjiang Province and Xinjiang Production and Construction Corps.

Antibiotics can also enter the farmland soil system through the agronomy of sludge, the application of organic fertilizer and irrigation water, causing the pollution of antibiotics in the soil, leading to the absorption and accumulation of antibiotics in vegetables, and thereby threatening human health through the food chain. Different plant varieties had different effects on the accumulation of antibiotics in soil, and the accumulation of antibiotics in plants increased with the increase of soil antibiotic content. The soil of a vegetable base in the south where organic fertilizers were used contained antibiotics. Li et al. (2008) found that the content of antibiotics in the soil of vegetable base reached the level of several hundred micrograms per kilogram. The study of antibiotics in the soil in the pearl river delta led by Tai et al. (2010) showed that quinolone, tetracycline and sulfa antibiotics were widely detected in the pearl river delta and even high-grade vegetable base soil (such as pollution-free vegetable production base, green vegetable production base, and organic vegetable production base), levels in dozens to hundreds of micrograms per kilogram. Lillenberg et al. (2010) found that cucumber, barley, and lettuce could all absorb and accumulate antibiotics, ciprofloxacin, and enrofloxacin. Wu (2011) in Guangzhou and Dongguan vegetable quinolones, according to a study by 4 kinds of quinolones compounds (ciprofloxacin, norfloxacin and maintain, and grace of sand) the detection rate of not less than 90%, melon kind of antibiotic content in different kinds of vegetable averages (including 91.29 g/kg, in all kinds of vegetable products the first place, and the average content of antibiotics in leaf vegetables was 52.30 μg/kg, which was