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Origin and removal of nitrite in water

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Abstract
Nitrite is widely present in water bodies and has received more and more attention due to its strong biological toxicity. The concentration of nitrite in water is very low, rarely exceeding 3 mg/L. Although the nitrite content of drinking water is low, it may become an important source of nitrite after people drink a lot of water. This article reviews the formation, influencing factors and removal methods of nitrite in water, which is of great significance for understanding and solving nitrite in drinking water.

Keywords: Water, nitrite, denitrifying bacteria, nitrification

Introduction

As a natural component of the nitrogen cycle in the ecosystem, nitrite exists widely in natural waters. The impact of nitrite in water on the environment and organisms has been recognized by people. Nitrite, as a potential hazardous substance, may cause direct or indirect harm to humans, animals and plants. Water is one of the main sources of nitrite ingestion by humans. The high concentration of nitrite from groundwater can cause methemoglobinemia of Infants [1, 2]. The incidence of liver cancer and gastric cancer can be even increase with drinking high concentration of nitrite from groundwater for a long time [3].

The level of nitrite nitrogen should be less than 1 mg/L in the water body from the first edition of the “Guidelines for Drinking Water Quality” of the WHO [4]. The provisional guideline value of nitrite is 3 mg/L in the concluding comments of the 1993 Guidelines [5]. The supplementary to the guidelines published in 1998 believes that the current provisional guideline value is 3mg/L on nitrite for humans supports from JECFA’s comprehensive data [6]. In addition, the supplement also obtained a guideline value of 0.2mg/L for long-term exposure to nitrite, which was derived from the ADI of JECF in 1995. However, this guideline value is only a provisional guideline value due to the uncertainty of observing harmful effects on health and the greater susceptibility of humans than animals. The limit of nitrite is 1mg/L in China from National Drinking Water Hygiene Standard (GB5749-2006) [7].

Nitrite content in natural water is very low, generally rarely over 3 mg/L. The increased use of nitrogen fertilizers in agriculture during the second half of the twentieth century contributed to potential contamination of water supplies. In shallow wells connected to agricultural runoff, nitrite levels may be much higher. The high content of nitrite in drinking water is related to human disease and death. Therefore, the current regulations on nitrite in drinking water in many parts of the world are based on this related to potential negative health effects [8-13].

Source of nitrite in water

Nitrate and nitrite are components of the nitrogen cycle in the ecosystem. Nitrite in water can be formed by chemical or biological means. The main ways of producing nitrite in water are as follows. The first way is that the nitrate in the water is transformed into nitrite by denitrification under anoxic conditions. In this process, denitrifying bacteria reduce nitrate into nitrogen (N_2) through a series of intermediate products (NO^{2-}, NO, N_2O). The second way is that nitrite is produced by the metabolic process of certain microorganisms in the water. Nitrification is the process of converting ammonia to nitrate via nitrite under aerobic conditions. CO_2 is used as carbon source by *nitrosomonas*, which oxidizes ammonia to nitrite and generates energy. In *vitro*, organic matter can inhibit the ammonia oxidation reaction of nitrosating bacteria, while ammonium salt and carbonate can promote the ammonia oxidation of nitrosating bacteria. The nitrifying bacteria involved in the nitrosation process are *Nitrosomonas*, *Nitrosocystis*, *Nitrosococcus*, *Nitrosospira* and *Nitrosogloea*. Many soil microorganisms that can oxidize ammonia to nitrite were isolated by Cutler and Mukerji [14]. Compared with the growth of nitrosomonas under alkaline conditions, the microorganisms from Cutler and Mukerji can generate nitrite at pH 4.8-7.3. In addition, Winogradsky isolates two ammoxidation bacteria from soil and named *Nitrosspirillum* and *Nitrosomonas* (later changed to *Nitrosococcus*) [15]. Krummel and Harms [16] studied the effects of different organics on the activity of ammonia oxidase, then they found that organics inhibited the activity of Nitrosococcus and had no effect on Nitrosomonas. Suzuki [17] proposed the steps of the ammonia oxidation reaction:

$NH^3 + O_2 + AH_2 \rightarrow NH_2OH + H_2O + A$ (1)

$NH_2OH + 2cyt.c(Fe^{3+}) \rightarrow NOH + 2H{+} + 2cyt.c(Fe^{2+})$ (2)

$2cyt.c(Fe^{2+}) + O_2 + 2H^+ \rightarrow 2cyt.c(Fe3+) + H_2O$ (3)

$NOH + A + H_2O \rightarrow NO_2 + AH_2 + H^+$ (4)

The research by Hollocher *et al*. indicated that the O_2 in reaction (1) comes from oxygen molecules, and the O_2 in reaction (4) oxygen comes from H_2O [18]. Cytochrome C participates in the process of energy generation in reactions (2) - (4). Organic compounds only affect reaction (1) and have no effect on subsequent energy generation reactions. Nitrosomonas exists extensively in the soil. It is closely related to domestic sewage, animal manure and soil. For example, Sims and Collins discovered *Nitrosomonas* in desert soils in Australia [19]. *Nitrosophyllum* exists in farmland or grassland soil and the genus is not found in forest soil. This genus is very resistant to drying and storage. More and more evidences showed that *nitrosomonas* and *nitrosomonas* are not the same type of bacteria, and they are the dominant nitrifying bacteria in cultivated soil.

The concentration of nitrite has increased in the water delivery system because of improper use of chloramine for disinfection and control. The chloramine disinfection method will increase the concentration of nitrite in the water supply system, which is prone to excessive nitrite. This is mainly due to incomplete nitrification increasing the concentration of nitrite in drinking water, generally 0.2～1.5 mg/L up to 3 mg/L. Chen Zhonglin *et al*. conducted an investigation on the chloramine disinfection water supply network in a southern city [20]. This study found that the nitrite in the pipe network exceeded the standard severely, however, the concentration of nitrite in raw water after pretreatment will be greatly reduced.

The oxidation reaction of nitrogen is widespread in the air. Under the action of lightning, oxygen and nitrogen combine to form nitrogen oxide compounds in the air. Such compounds are further oxidized to nitrate and nitrite after rain. In general, the rainwater usually contains more ammonia nitrogen, and nitrate nitrogen does not exceed 0.2ppm in rainfall. Davey's research concluded that only 2.5% of total nitrogen in drinking water comes from rainwater and this proportion is increasing with the development of society and economy [21].

Factors affecting the formation of nitrite

The formation of nitrite in water is closely related to denitrification and nitrification process. Therefore, the factors affecting denitrification and nitrification process will be related to the formation of nitrite in water.

1. Factors affecting denitrification

There are many factors that affect denitrification. The temperature has a greater impact on denitrification and 30-60℃ is the optimal reaction temperature. The denitrification reaction can be carried out at 5-40℃, but when the temperature is lower than 15℃, the denitrification rate will obviously decrease. The pH of the denitrification process is controlled at 6.5 ~ 7.5. The pH is higher than 8.0 or lower than 6.0, the denitrification reaction drops rapidly. Dissolved oxygen has an inhibitory effect on denitrification and should be controlled below 0.5mg/L during denitrification. In addition, the denitrification reaction can be carried out smoothly in enough organic carbon source of the water.

2. Factors affecting nitrification

Nitrification is affected by many factors. The optimal temperature is 20-30℃ for nitrification. The reaction rate rapidly decreases below 15℃ and almost completely stops at 5℃. Nitrifying bacteria are very sensitive to changes in pH, and the optimal pH for growth is between 7.0 and 8.0. The nitrification reaction has higher requirements for dissolved oxygen, and the dissolved oxygen should be kept above 2mg/L during the nitrification reaction. Nitrosifying bacteria are autotrophic bacteria, Therefore, the growth is relatively slow, with an average generation time exceeding 10 hours. The too high BOD value (Biochemical Oxygen Demand) in the water will help the rapid reproduction of heterotrophic bacteria, while the proportion of nitrosating bacteria will decrease.

Method of removing nitrite from water

European and American countries paid attention to the problem of nitrite pollution earlier and developed a series of treatment processes. Some practical drinking water denitrification plants were established in Europe in the early 1980s, while the United States shut down some seriously polluted groundwater wells. With the increasing shortage of water resources, the research of nitrite pollution has attracted more and more attention about drinking water. The treatment process of nitrite includes chemical method, biological method and physical method [22-24].

1. Oxidation or reduction method

NO_2^- ions has the characteristic of being oxidizing and being reduced under acidic conditions. The oxidation or reduction process for treating nitrite in water has the advantages of simple equipment and low processing cost, is currently a commonly used method in the world. The nitrogen in nitrite is an intermediate valence, which can be oxidized and reduced under certain conditions. Eventually, NO_2^- ions will be transformed into less toxic or non-toxic substances. The oxidants used in this method include some strong oxidants, such as ozone, hydrogen peroxide, sodium hypochlorite, etc.

2. Membrane separation method

Membrane separation methods include reverse osmosis and electrodialysis. The reverse osmosis membrane has no selectivity for nitrite, but the removal rate of various ions is proportional to their valence states. The reverse osmosis membranes used mainly include composite membranes such as acetate membranes and polyurethane membranes. Reverse osmosis removes nitrite and other inorganic salts at the same time, so reverse osmosis method will reduce the salinity of effluent. Electrodialysis and reverse osmosis have similar denitration efficiency, but Electrodialysis method is only applicable to soft water. Membrane separation method is suitable for small water supply facilities. Its disadvantage is that it is expensive, produces concentrated waste brine, and has secondary pollution problems.

3. Ion exchange method

The ion exchange method is to remove harmful ions from water by exchanging ions on an ion exchanger with ions in the water. The ion exchange method plays an extremely important role in the treatment of industrial water and the production of soft water or pure water. The ion exchange method in industrial wastewater treatment is mainly used to recover precious metal ions, as well as to treat radioactive wastewater and organic wastewater. This method has the advantages of high removal rate, high recovery rate, and convenient operation and control, etc.

4. Biochemical treatment method

Biochemical treatment methods are mainly divided into aerobic biological treatment and anaerobic biological treatment. They have been widely used and are currently one of the most effective treatment methods at home and abroad. Especially in wastewater treatment, they play an increasingly important role. Anaerobic organism treatment uses facultative anaerobic organism to degrade pollutants under anaerobic conditions. Under anaerobic conditions, NO_3^- or NO_2^- is used as the electron acceptor to convert ammonia into N_2. NO_2^- is a key electron acceptor. Compared with aerobic methods, anaerobic treatment methods have disadvantages such as long treatment time and poor effluent quality, which limit their application and slow development. Aerobic biological treatment methods include mainly include activated sludge and biofilm method. The activated sludge method relies on the aggregation, adsorption, oxidation and decomposition of suspended and flowing microbial populations in the aeration tank to remove organic matter from wastewater. The biofilm method allows microbial communities to adhere to the surface of certain carriers and purify water by metabolizing organic substances in the water. In recent years, some new water treatment processes have been developed and shared, such as the biological activated carbon method. These methods have many advantages and are also valued by people.

Conclusion

Nitrite, as the intermediate product of nitrogen cycle in ecosystem, widely exists in water. It is of great practical significance to study the range, degree and depth of nitrite pollution in water, the source of pollutants, the causes, modes and mechanisms of pollution, especially the treatment methods and prevention measures of nitrite pollution in water. (1) Protect drinking water sources and prevent various diseases caused by nitrite pollution, such as Methemoglobin disease, cancer, etc. (2) Protect water sources for agriculture and animal husbandry, prevent nitrite poisoning of livestock, improve crop resistance and insect resistance, improve the quality and grade of crops, vegetables and fruits, and ensure people's food safety.

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Consent for publication

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