Analysis the Influencing Factors of Toxic Substances Toxicity Threshold on Biological Wastewater Treatment

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Abstract. In the process of biological treatment of wastewater, there are some toxic substances which can inhibit the microorganisms and affect the effect of biological treatment of wastewater. Under different control conditions, the toxicity threshold of toxic substances is very different. The effects of pH, water temperature, dissolved oxygen, treatment process, hydraulic retention time, concentration of organism and acclimation on the toxicity threshold of toxic substances were systematically analyzed. On this basis, the problems that need to be solved in studying toxicity threshold of biological wastewater treatment are put forward.

1. Introduction
All the substances which exist in the wastewater biological treatment engineering and have the function of inhibiting or killing the microorganisms are called toxic substances. Toxic substances commonly found in biological treatment of wastewater can be divided into three categories according to their chemical property: first, heavy metal ions such as lead, cadmium, chromium, arsenic, copper, iron, zinc, mercury, nickel, etc. and second, organic compounds, such as phenol, Formaldehyde, methanol, benzene, chlorobenzene, etc. three is inorganic, such as sulfides. potassium cyanide, sodium chloride, sulfate radical, nitrate, etc. According to the mechanism of toxicity of toxic substances to microorganisms, there are two types: specific type and anesthetic type. Certain types of poisons, such as cyanide, inhibit certain functions; anesthetic types, such as chloroform, cause anesthesia and gradually interfere with microbial functions.

There is a quantitative concept of the toxic effects of toxic substances on microorganisms, and the toxic and inhibitory effects are revealed only when a certain concentration of toxic substances is reached in the environment. Generally, the toxicity threshold of the toxic substance is given by the dead concentration (LC_{50}) of 50% or the active decreasing concentration (IC_{50}) of the tested organism. The smaller the LC_{50} or IC_{50}, the greater the toxicity. The toxicity threshold of toxic substances is usually related to pH, water temperature, dissolved oxygen, and other factors such as treatment process, hydraulic retention time, concentration of organism, domestication and presence of other toxic substances in wastewater.
2. Analysis of influencing factors

2.1. Effect of temperature on toxicity threshold

The influence of temperature on the toxicity threshold of toxic substances in wastewater is mainly manifested in three aspects: First, the increase and decrease of temperature can change the existence of certain toxic substances. The second is that at different temperatures, the activities of the same microorganisms are different and their sensitivity to toxic or inhibitory substances is also different. The third is that temperature changes the toxicity of toxic substances by changing the structure and distribution of aerobic bacteria or the structure of anaerobic granular sludge.

Biological treatment of wastewater containing high concentrations of ammonium ions or ammonium-containing precursors like proteins may have NH\(_3\) toxicity problems. The ionization of NH\(_3\) is related to the pH of the water and also depends on the temperature. At pH=7.0 and T=25°C, free ammonia accounts for 0.6% of total ammonia nitrogen. When the temperature rises to 55°C, the percentage of free ammonia to total ammonia nitrogen will increase by 6 times. Angelidaki and Ahring found that in a high-temperature methane fermentation system containing high concentrations of NH\(_4^+\)-N, when the temperature is increased from 55°C to 65°C, gas production decreases, and at the same time, accumulation of acetic acid can be observed, and methanogens are inhibited; when the temperature changes from 55°C to 65°C When the temperature drops to 40°C, the acetate concentration drops from 2400 mg/L to 900 mg/L, the gas production increases, the process is stable (the effluent VFA is reduced, indicating the release of inhibition caused by NH\(_3\)-N), and the ammonia nitrogen toxicity in the wastewater The threshold is greatly improved. [1] Yang and Speecee observed during the anaerobic methane fermentation process that the same amount of cyanide was added to the anaerobic treatment at 25°C and 35°C, respectively. [2] At a lower temperature of 25°C, cyanide had an effect on gas production. The instantaneous inhibition is greater, and the gas recovery time is significantly longer than that at 35°C. For gas-producing methanogens, the toxicity threshold of cyanide at 35°C is greater than that at 25°C.

2.2. Effect of pH value on toxicity threshold

The pH value has a great influence on the toxicity threshold of certain toxic substances in wastewater. Regarding the toxicity of metals in water, the acidity and alkalinity of the solution simultaneously affects the active sites on the cell surface and the existence of metal ions. When the pH rises, the precipitation or complexes of insoluble substances such as hydroxides or carbonates will be produced, which reduces the concentration of free metal ions in the water and reduces toxicity. Conversely, when the pH value decreases, the concentration of free heavy metal ions in the water increases and the toxicity increases. In conventional anaerobic treatment, the 50% toxicity threshold of Cu\(^{2+}\) in wastewater is 15 mg/L. By neutralizing the acidic copper-containing wastewater and alkaline wastewater according to a certain ratio and then entering the biochemical tank, in the experiment, the copper ion concentration in the wastewater reached a maximum of 140 mg/L, and the treatment effect was still good, and the removal rate of copper ions was as high as 99.2%. The COD removal rate is 85%, and the activity of activated sludge is not inhibited. Therefore, after pH adjustment, the copper ion toxicity threshold in wastewater biological treatment is significantly increased.

The pH value can also change the existence form of certain inorganic or organic substances in wastewater, thereby changing its toxicity threshold. For example, the toxicity of ammonia nitrogen is caused by free ammonia, and pH has a great influence on the proportion of free ammonia in ammonia nitrogen. Parkin and Owen reported that at T=35°C and pH=6.5, free ammonia only accounted for 0.4% of total ammonia nitrogen, and when the pH rose to 8, free ammonia accounted for 9.9% of total ammonia nitrogen. [3] Free ammonia nitrogen has an IC\(_{50}\) value of 50 mg/L for the methanogenic activity of undomesticated granular sludge. Therefore, for wastewater containing high-concentration ammonia nitrogen, after adjusting its pH from 8 to 6.5, the ammonia nitrogen toxicity threshold in wastewater biological treatment will increase nearly 25 times. Some scholars have studied the methanogenic toxicity of capric acid to the anaerobic granular sludge of UASB reactor. The research results show that capric
acid has a strong inhibitory effect on the methanogenic activity of anaerobic granular sludge, and the pH will affect the existence form of capric acid in the liquid phase. The lower the ratio, the greater the ratio of free capric acid, the more severe the inhibition of anaerobic granular sludge and the lower the IC\textsubscript{50} value.

2.3. Effect of dissolved oxygen on toxicity threshold
Dissolved oxygen is a very important parameter that affects the action of microorganisms. Both hypoxia and oxygen-rich environments are not conducive to the adsorption and removal of toxic substances by microorganisms. In the process of using fusion bacteria-activated sludge aeration adsorption to remove nickel, it was found that when the dissolved oxygen is 2.5 mg/L~4.5 mg/L, the toxicity of nickel to activated sludge is the least, and the removal rate can reach 81.43%. When the solution DO is 0.5 mg/L, the activity of the bacteria is inhibited by hypoxia, and the mutagenic effect of nickel damages the cell membrane and DNA. The toxicity is obvious, and the removal rate of nickel is reduced by 15.99%. When the dissolved oxygen is 8 mg/L, due to prolonged exposure to a highly oxygen-enriched environment, the rate of microbial anabolism increases, which causes nutrient deficiency and increases the toxicity of nickel, which causes the microbial activity to continue to decline, and the removal rate A decrease of 10.78%. Komori et al. reported that under aerobic conditions, Cr\textsuperscript{6+} decreases with the increase of the initial dissolved oxygen concentration. When the DO in the solution is higher than 4.5 mg/L, the reduction of Cr\textsuperscript{6+} by Enterobacter cloacae is inhibited, and Cr\textsuperscript{6+} Shows strong toxicity. [4]

2.4. Effect of treatment process on toxicity threshold
The toxic substances in the wastewater show a great difference in toxicity to aerobic bacteria and anaerobic bacteria. Sulfate basically does not show toxicity in the aerobic treatment system, but it is reduced to H\textsubscript{2}S in the anaerobic reactor and increased Toxicity. It is generally believed that methane bacteria are more sensitive to toxic substances than aerobic microorganisms. This statement is inaccurate. According to the IC\textsubscript{50} concentration values of different organic substances against undomesticated methanogens and activated sludge measured by Blum and Speece, we can see that for organic substances such as benzene, toluene, phenol, m-toluene, 2-aminophenol, aerobic bacteria Groups are much more sensitive than methanogens. [5] Among them, 2-aminophenol is 155 times more toxic to aerobic bacteria than to methanogens. Table 1 lists the IC\textsubscript{50} concentration values of some of the organic substances against methanogens and aerobic heterotrophic bacteria.

| Inhibitor          | Undomesticated methanogens(mg/L) | Aerobic heterotrophic bacteria (mg/L) |
|--------------------|----------------------------------|--------------------------------------|
| Benzene            | 1200                             | 520                                  |
| Toluene            | 580                              | 110                                  |
| Phenol             | 2100                             | 1100                                 |
| M-toluene          | 890                              | 440                                  |
| 2-Aminophenol      | 6.2                              | 0.04                                 |
| Xylene             | 250                              | 1000                                 |
| Nitrobenzene       | 13                               | 370                                  |
| P-cresol           | 91                               | 260                                  |
| 4-Nitrophenol      | 4                                | 160                                  |
| 1, 2, 4 trichlorotoluene | 120                           | 7700                                 |
2.5. Effect of hydraulic residence time on toxicity threshold
In the toxicity test, prolong the hydraulic retention time, so that the unit biomass metabolism rate is far lower than its maximum metabolism rate. Under this condition, because the organism has sufficient storage and metabolism capacity to offset the toxicity, the administration of poison has almost no effect on the organism. The toxicity threshold measured at this time is often greater than the toxicity threshold in the case of short hydraulic retention time or high system load rate. Some scholars put a certain concentration of aniline into a three-phase fluidized bed reactor, and observed the inhibitory effect of aniline on nitrifying bacteria by changing the hydraulic residence time. In the experiment, when the HRT was 4 h, the digestive activity of nitrifying bacteria was completely inhibited, and the nitrification rate was zero. With the prolongation of HRT, the nitrification rate rapidly increased from 37.63% at HRT=6 h to 84.95% at HRT=10 h. With the further extension of HRT, the growth of nitrification rate slowed down. When HRT was 16 hours, the nitrification rate reached 98.02%. This shows that in the process of nitrification and denitrification, by controlling HRT, the toxic effect of aniline on nitrifying bacteria can be reduced and the IC\textsubscript{50} concentration of aniline can be increased.

2.6. The effect of organism concentration on toxicity threshold
The same poison concentration is added to the reactor with different biological concentrations. Due to the high biological concentration, the ratio of the poison to the biomass is reduced, that is, the poison allocated to the unit weight of the organism is reduced. If toxic substances are absorbed or degraded, the toxicity threshold of the toxic substances will be different under different organism concentrations. However, if the organism does not absorb or degrade the poison, regardless of the concentration of the organism, the environmental concentration of the poison will remain unchanged. In this case, the high organism concentration simply compensates for the decrease in specific activity and the toxicity of the toxic substance. The threshold will not change.

Yang and Speece put 2.5 mg/L of cyanide into three reactors with different concentrations of organisms, and the recovery time of gas production from high to low concentrations of organisms was 30 d, 40 d, and 50 d, respectively. [2] The toxicity of the same amount of cyanide to high-concentration organisms is less than that of low-concentration organisms. Ohtake et al. observed that in industrial wastewater containing 182 mg/L of Cr\textsuperscript{6+}, when the initial cell density of Enterobacter cloacae decreased from 7×10\textsuperscript{8} to 4×10\textsuperscript{8} cell/ml, the reduction rate of Cr\textsuperscript{6+} dropped sharply, and at 2×10\textsuperscript{8} cell/ml, almost no Cr\textsuperscript{6+} reduction reaction occurred. Some scholars have found that when the COD is 8 000 mg/L, the ammonia nitrogen is 2 000 mg/L, and other conditions remain unchanged, only the sludge concentration in the IC reactor is changed. The cumulative gas production per unit weight of concentrated sludge is about 3 times and 1.6 times that of low-concentration sludge. Therefore, appropriately increasing the sludge concentration is beneficial to improve the tolerance of the system to ammonia nitrogen.

2.7. Effect of sludge acclimation on toxicity threshold
Organisms have a rare domestication ability for certain poisons. Toxic substances at the same concentration may be inhibitory to non-domesticated organisms and can completely lose the activity. But to properly domesticated organisms, it will not cause a decrease in activity. After full domestication, the toxicity threshold of certain poisons may increase by 10 times. According to reports, the tolerance concentrations of general bacteria to phenol and cyanogen are 50 mg/L and 1 mg/L~2 mg/L, however, it can be increased to 300 mg/L~500 mg/L and 20 mg/L~30mg/L after acclimation.

Yang et al. placed methanogenic bacteria in an environment of 2.5 mg/L of chloroform. The gas production almost stopped at first, and it took about a week to recover. After regular exposure to the same dose of chloroform, there is no longer any reduction in activity. [7] Li and Speece used acetic acid as the primary substrate to domesticate anaerobic organisms in wastewater containing high Na\textsuperscript{+} concentration. The first input of acetic acid and 15 000 mg/L Na\textsuperscript{+}, it took more than 50 days for anaerobic organisms to produce methane. However, after 40 days of no feed phase, on the 90th day, when acetic acid was added for the second time, gas production was quickly restored. [8] Compared with the control group (Na\textsuperscript{+} concentration is 0), it has almost the same maximum gas production rate. Bhattacharya and
Parkin reported that the toxicity threshold of Ni to microorganisms increased by 5 times after domestication. [9]

3. The influence of the interaction between toxic substances on the toxicity threshold

Wastewater often contains a variety of toxic and harmful substances to microorganisms. Generally speaking, when these toxic substances work together, they will have the following three behaviors: synergy; antagonism; and non-relevance.

After adding Zn\(^{2+}\) or Cu\(^{2+}\) to the sewage treatment system, the toxicity of its toxicity on biological phosphorus removal far exceeds the effect of Zn\(^{2+}\) or Cu\(^{2+}\) alone, which greatly affects the biological phosphorus removal effect, showing a synergistic effect. Some scholars have determined through experiments that the inhibition rate of 0.99mg/L of 2,4-dichlorophenol on the nitrifying bacteria in the industrial wastewater activated sludge treatment system is 46.8%. The inhibition rate of 20 mg/L phenol is 50%. The sum of the two inhibition rates is 96.8%, which is basically the same as the 95.1% inhibition rate actually measured when phenol and 2,4-dichlorophenol coexist. When phenol and 2,4-dichlorophenol work together, it also shows a synergistic effect. Daoming and Forster proposed that K\(^+\) may be an inhibitor in coffee wastewater, and Ca\(^{2+}\) may be an antagonist of this inhibition. When Ca\(^{2+}\) is added, the system operation can be improved, and the COD removal rate can reach 70%. When Ca\(^{2+}\) is added for the second time, a higher COD removal rate can be reached again. [10] These results indicate that Ca\(^{2+}\) can antagonize the effect of high concentrations of K\(^+\), which is beneficial to the operation of the system.

4. Conclusion

First, the toxicity ranges of some toxicants in wastewater biological treatment systems are often reported in the literature, but they are often different from each other. Therefore, data on toxicity must be interpreted in accordance with the conditions for verification and a toxicity database of common toxic substances must be established on that basis.

Second, acclimation can greatly improve the tolerance of microorganisms to some toxic substances, and even enable microorganisms to take toxic organic substances as nutrients, its degradation. Therefore, domestication is an effective way to increase the toxicity threshold of toxic substances.

Third, when the wastewater biological treatment system is impacted by toxic substances, the quality of the influent water is first analyzed to determine whether the influent contains toxic substances and their concentrations. If toxic substances are present, their sources should be identified to prevent their continued release into the water. At the same time, according to the influence of Ph, temperature, dissolved oxygen and hydraulic retention time on the toxicity of the toxic substances, the technological parameters can be adjusted, and the corresponding antagonists can be added to the biological treatment system to reduce the toxicity of the toxic substances to the microorganisms.

Acknowledgments

This work was financially supported by the Project of Ministry of water resources of China (2019)

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