Pilot-scale Study of Biological Synergist Effect on High Salinity Pesticide Wastewater Biological Treatment

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Abstract. Pesticide wastewater belongs to typical hardly-degradable industrial wastewater. Biochemical system pollutants removal efficiency was in low level because of high salt content and high biological toxicity. Adding biological synergist into biological system to improve the biological system activity, the pilot-scale study results show that: The COD Cr and NH3-N removal rate has increased significantly after adding the biological synergist into the biological system. The COD Cr average removal rate of experimental group was 91.2%, and the control group was 84.5%; The experimental group of NH3-N removal rate up to 93.2% on average, higher than 51.4% of control group, and the nitrification efficiency was improved significantly. The specific oxygen uptake rate (SOUR) of the synergistic sludge was higher than that of the control group, indicating that the microbial metabolism rate was improved, the sludge structure of the experimental group was tight, and the metazoa appeared. The biological activity was better than that of the control group.

1. Introduction
A large amount of high salinity pesticide organic wastewater will be produced in the pesticide companies, which contains a large number of inorganic salts, organic solvents and pesticide intermediates, etc., and it has the characteristics of high concentration, high salinity and difficult to degrade[1,2]. At present, it still lacks economical and effective treatment technologies for such wastewater. The wastewater in this pilot-scale study was taken from a pesticide company in Binzhou, Shandong. This wastewater has high COD Cr, high toxicity, high salinity, which contains bio-refractory and toxic organic pollutants such as prometon, propazine, acetochlor, metolachlor and bentazone, and these pollutants have higher biological toxicity[3,4], which lead to the low efficiency of the existing wastewater treatment system. It is difficult to meet the requirements of the design process that the influent COD Cr is 500 mg/L and the influent NH3-N is 45 mg/L in the Sewage treatment plant.

Based on the principle of microbiology and nutrition, this study aims at the poor biochemical ability of the biochemical treatment system of pesticide wastewater in Shandong province. The biological synergistic technology of SAES Environmental Science and Technology Co., Ltd was used to carry out bio-augmentation pilot study on biochemical system.

Without changing technological process of the original biochemical system, by adding biological synergist in A pool and O pool, the activity of sludge in biological treatment process was improved, the removal of COD Cr and NH3-N was improved, and achieved the purpose of biological efficiency.
2. Materials and methods

2.1 Experimental water and inoculation sludge
The experimental wastewater was taken from the regulation tank of a pesticide enterprise in Binzhou, Shandong. The inoculated activated sludge was taken from the biochemical aeration tank of the wastewater treatment system. The water-quality index and the activated sludge index are shown in Table 1.

| Pollutant index | pH   | COD Cr / (mg/L) | BOD5 / (mg/L) | NH3-N / (mg/L) | TDS / (g/L) | SOUR (mg/(g.h)) |
|----------------|------|-----------------|---------------|----------------|-------------|----------------|
| Value          | 7.40-7.62 | 2850-3420       | 540-650       | 83-102         | 24.5-26.2   | 24.2-30.5      |

2.2 Experimental material
The SAES efficient biological synergist was provided by the SAES Environmental Science and Technology Co., Ltd. The synergist is mainly composed of microbial agents and highly dispersed carbon based carriers and the microorganism is immobilized on a carbon-based carrier. The synergist can improve the living environment of microorganism, the population and quantity of the functional microorganism in the biochemical system, and improve the degradation rate of the refractory pollutants in the wastewater.

2.3 Experimental process
The pilot-scale process was consistent with on-site wastewater treatment process, and the process flow is shown in the figure 1. (ozonation tank after regulation tank)

2.4 Experimental methods
In this experiment, two A/O systems were synchronized for three months. After a month of stable operation, the biological synergist was added to the A1 pool and the O1 pool of the experimental group. The dosage was 10 g/L, and the control group did not add.

After the system operation was stable, the effluent data was recorded and the specific oxygen uptake rate (SOUR) was measured. SOUR is the amount of oxygen consumed per unit time of activated sludge measured under the condition of no nutrients, which can reflect the metabolic activity of microorganisms[5]. Observe the active sludge microscopy regularly. The control group of the whole experiment period was the same as the test group except that no bio-additive was added.
2.5 Experimental method
The changes of dissolved oxygen were determined by portable dissolved oxygen meter. CODCr, NH3-N and other water-quality indexes were determined by national standards[6].

3. Results and discussion

3.1. Comparison of effluent CODcr in the pilot-scale
The effluent of the system was stable after a week of adding biological synergist. And then determined the effluent of CODCr. The results were shown in the figure 2.

It can be seen from the figure 2: When the influent CODCr was the same, after adding biological synergist, the average CODCr of the test group was 276 mg/L, which was obviously lower than the 486 mg/L/L in the control group. The average CODCr removal rate of the test group was 91.2%, which was higher than that of the control group, and the effluent standard rate also increased from 81.3% to 100%.

Figure 2 The CODCr removal efficiency of two systems

3.2. Comparison of effluent NH3-N in the pilot-scale

Figure 3 The NH3-N removal efficiency of two systems
It can be seen from the figure 3: When the average value of the influent NH3-N is 91.6 mg /L, the average effluent NH3-N of the test group is 6.2 mg /L, which is obviously lower than the 44.5 mg /L in the control group. The average NH3-N removal rate of the test group is up to 93.2%, which is higher than that of the control group, and the rate of the effluent reaches the standard rate from 46.3% to 100%.

3.3. Changes in SOUR of activated sludge in the pilot-scale
According to the figure 4, the endogenous respiration rate of the experimental group adding biological synergist was higher than that of the control group, indicating that adding biological synergism enhanced the endogenous respiration intensity and increased the use of organic matter, which corresponded to the removal rate of CODCr and NH3-N in the experimental group was higher than that in the control group.

3.4. The structural changes of activated sludge in the pilot-scale
From the above figure 5, because of the biological toxicity of pesticide wastewater, the microorganism activity of the control group was low, the zoogloea was loose without protozoa and the biochemical system was fragile. In the experimental group, the carbon-based carrier and zoogloea combined closely, and flocculant zoogloea was obviously larger than the control group because of adding the biological synergist.
In the experimental group, the metazoan, such as the watchworm, phosphorus could be seen, and the biological activities were higher than the control group.

4. Conclusions
During the operation of high salinity pesticide wastewater, the effluent CODCr and NH3-N are unstable due to the high toxicity and high salinity. Using biological synergistic technology in the wastewater treatment process, the biological activity of high salt pesticide wastewater biochemical system was improved, the effluent CODCr and NH3-N value was relatively stable, and the qualified rate of total discharge water was 100% without changing the technological process and facilities of the original biochemical system.

(1) Biological Synergistic Technology could improve the CODCr removal rate of biochemical system in the pesticide wastewater significantly, and the average removal rate of CODCr in the biochemical system could reach 91.2%, which reached the requirements of the design value.

(2) Biological Synergistic Technology could improve the nitrification efficiency of the biochemical system in pesticide wastewater significantly. The average removal rate of NH3-N in the experimental group adding biological synergist was 93.2%, while the control group was only 51.4%.

(3) Biological Synergistic Technology could improve the SOUR of activated sludge and the removal rate of CODCr, which indicated that the addition of biological synergist could promote the metabolic activity of microorganism and improve the effect of wastewater treatment.

(4) The sludge activity of the system was obviously improved, the flocculant zoogloea became dense, and the metazoan began to appear after adding biological synergist.

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