Simulated Test Studying on CN^- Containing Cassava Starch Industry Wastewater Treated by Anaerobic Process*

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Abstract: The concentration of CN^- ions is usually higher than 32 mg/L in cassava starch industry wastewater, and the quantity of CN^- discharged from this kind of wastewater is up to 1350 kg every day during the season of cassava starch production in Guangxi Province, P.R. China. Hence the aforesaid wastewater has given a great effect to environmental security. Although a lot of organic pollutant and parts of CN^- ions could be removed from this wastewater by anaerobic biological process, yet the cyanogen content in the effluent of the treated wastewater is still much higher than the national drainage standard. It is necessary to use the method of closed management for the final effluent of this wastewater to be treated in a stabilization pond.

Keywords: cassava starch industry wastewater; CN^- ions; anaerobic biological process; security; Guangxi, P.R. China

1. Introduction

Cyanide, including simple cyanide, complex cyanide and organic cyanide (organic nitrite), are highly toxic. The forms of cyanide existed in water are HCN, CN^- or complex ion cyanide. If the wastewater containing cyanide is discharged before treatment, it would pollute the receiving water body, destruct ecological balance of water system, and do harm to the health of people who live around. The harmful characters of cyanide are highly poisonous and fast effective. The poisoning effects of HCN usually appear in symptoms such as red eyes, pain of throat, headache, nausea, spasm etc., and the result indicates that some animals such as cattle and sheep would die of poisoning if they drink the water containing cyanide. The lethal dose of intake cyanide for one time is about (0.39~0.92) g for a cattle and (0.04~0.1) g for a sheep. When the concentration of CN- ions in water body goes up to (0.04~0.1) mg/L, fishes will die. The maximum allowable concentration is 0.01 mg/L for plankton and crustacean. The self-purification micro-organism of water body will be killed when the concentration of cyanide goes up to 0.3 mg/L. When the wastewater containing cyanide inflows and penetrates to farmlands, crop production will bring down.

Cassava is a kind of subtropical plant that can produce cyanide. The wastewater from cassava starch production contains a great deal of CN- ions. Its security or its effect to environment is a lively problem for workers of environmental protection. Anaerobic technology is usually used for treating cassava starch industry wastewater, but whether the security of the effluent can satisfy the requirement of environment or not is worth while for further discussion.

Guangxi is a big province in producing cassava starch. Annual production can reach 150 million tons, which is about 40% of the total output in China. For a long time, there were many events about fishes killed by the leakage of cassava starch industry wastewater. Besides, several reports were issued in the past twenty years about livestock died of this poisonous wastewater Obviously, to study the characteristics of cyanide in cassava starch industry wastewater, and the security of such wastewater is of very important and realistic significance.

2. The Characteristics of Cyanide in Cassava Starch Industry Wastewater

The varieties of cassava starch industry wastewater include cassava cleaning water, first step washing water, second step washing water, modified starch wastewater and mixing production wastewater. The maximum quantity of water is cassava cleaning water, but its pollutant is relatively low. The highest pollutant concentration comes from the first step and the second step washing water which are the main pollutant sources of cassava starch industry wastewater, and the CN- therein does most harm to environment.

In tab.1, the maximum COD concentration of cassava starch industry wastewater can reach 2500 mg/L while the minimum is 200 mg/L. And the COD concentration of the mixing production wastewater can reach (4000~12000) mg/L. It's a kind of high concentration organic industrial

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wastewater. Cassava starch industry wastewater has good biodegradability, so there are many choices of its treatment. According to the quantity of wastewater from cassava starch manufacturer, the discharge of mixing production wastewater in Guangxi was at least 30 million m^3 in 2006, and the discharge of COD was 0.12~0.36 million tons. In other words, an average of 2000 tons COD was discharged everyday. That is equivalent to the quantity of COD in domestic sewage from ten cities of 4 million people. (production period is 120 days every year)

The maximum concentration of CN- in cassava starch industry wastewater is up to 32 mg/L and the minimum is 2.8 mg/L in which the maximum concentration in mixing production wastewater is 5.6 mg/L. Such concentration is solely dangerous to most microorganism. According to the concentration of CN- in mixing production wastewater, the quantity of CN- discharged in Guangxi can be up to 1350 kg everyday. That is enough to kill over 1 million cattle or 10 million sheep. So the cassava starch industry wastewater does serious harm to the environment.

Table 1. Characteristics of Cassava Starch Industry Wastewater

Sorts of Wastewater	COD	BOD	CN^-	SS	Starch	Protein	Amino Acid	Total Sugar
CassavaCleaning Water	200-700	300-100	2.8	1.4-3.7	0	3.6	433.4	0
First Step Washing Water	8000-21000	5000-14000	32.1	1.5-1.9	3.0	5.6	1405.0	1.3
Second Step Washing Water	6000-25000	3000-8500	6.5	1.3-1.5	6.0	3.1	566.9	0
Modified Starch Wastewater	4000-17000	1500-7500	5.6	1.4-2.8	5.5	0.04	510.6	0
Mixing Production Wastewater	4000-12000	2400-7500	5.4	1.0-4.3	7.0	1.5	581.3	1.5

3. Review of Research Status

The toxic mechanism of cyanide is described as follows: The CN- from HCN after coming into animal organism. HCN will be absorbed and conveyed by plasma rapidly. It can combine with Fe, Cu, S and the key compositions of some compounds. Besides, HCN can inhibit cytochrome oxidase from absorbing the dissolved oxygen of plasma. When the enzyme does not work, it will result in asphyxia and death of the cells. The central nervous system of advanced animals needs maximum dissolved oxygen, so they are most strongly influenced.When the oxygen supply is baffled, the main organs of the body will stop and it will result in the death of organism.

Biological technology supplies a new way for degrading cyanide. Compared to other physical and chemical ways, the advantages of biochemical technology are its cost-benefit and reduced secondary pollution at the same time. Under the anaerobic condition, the activity of cyanide degraded by methanogens may be inhibited, but varieties of microorganism can decompose and absorb organic carbon of cyanide by self-adjustment. Accordingly, operating expenses and risk will reduce. Therefore, people become more and more interested in biodegradation of cyanides by microorganism. It has been successfully used in laboratory and practical engineering application. The first commercial scale of biological degradation of cyanide in engineering was carried out by Home-stake[4]. Whereas, to use the usual activated sludge or other biological process on this kind of toxic and hard-degradable compounds, so far the speed of decomposition is too slow, and the effect is not satisfactory . Moreover, when the concentration of CN^- exceeds 20 mg/L, the activated sludge will be poisoned and biochemical treatment effect will be decreased obviously.

The selections of microorganism for degrading cyanide are developed at home and abroad. Good results are obtained when the effective processes are used to treat cyanide wastewater. M.Kowalska et alii studied the process that fixed staphylococcus and pseudomonas which departed from activated sludge on ultra-filtration membrane and used them to treat cyanide wastewater of coke plant. The removal rate of CN- can reach 91%~93%. Researchers of the Institute of Microorganism of the Chinese Academy of Science hang screening bacterium that can decompose acrylonitrile easily on tower filter bed. The effect of treatment of acrylonitrile is obviously improved. The removal rate of acrylonitrile can achieve 99% and the effect is relatively steady in great productive towers.

The cassava starch industry wastewater in China is mainly treated industrially in stabilization ponds, by highly efficient anaerobic, aerobic biological and other ways of treatment. But the prevention and treatment of CN- in this kind of wastewater is seldom reported.

4. The Security of Cassava Starch Industry Wastewater after Treating by Anaerobic Biological Process

Because of the high concentration of organism and the value of B/C is over 0.5, the treatment of cassava starch industry wastewater should first consider anaerobic and aerobic process which can recycle biomass energy from wastewater and decrease the operation costs[8]. In fact, some stabilization ponds possess a long term of operation for treating cassava starch industry wastewater in Guangxi degrading the organic pollutant by anaerobic and aerobic ways.

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Evidently, the security of CN- in cassava starch industry wastewater is worth while discussing. This paper studies on the characteristics of CN- through the simulated experiment of anaerobic biological process. As mentioned above, cyanide in cassava starch industry wastewater may influence metabolism of anaerobic microorganism and even destroy the reaction of anaerobic fermentation. The simulated experiment is according to the system of anaerobic fermentation to speculate the infection of CN- for microorganism. Gas collection with displacement of water has been used for collecting gas from anaerobic fermentation in a SHI fermentation tube. The condition of metabolism is analyzed by the quantity of gas.

4.1 Experimental Device

The experimental wastewater is confected with NaCN, glucose, phosphorus-containing compounds and nitrogen compounds. The value of C:N:P is controlled to 130:5:1 in the experimental wastewater which is similar to the cassava starch wastewater. Both anaerobic micro-organisms and experimental wastewater are put into a 150 ml conical flask. Constant temperature water bath apparatus is used for domestication of anaerobic micro-organisms. All kinds of gases coming from the SHI fermentation tube, which is a kind of special system (Phot.1) for collecting gas, could be easily observed when anaerobic reaction begins. The volume of the SHI fermentation tube for collecting gases is 25 ml. The error of temperature changed in constant temperature water bath apparatus (Phot.2) is normally controlled at positive-negative 1 degree.

Phot.1 SHI fermentation reaction device

Phot.2 Constant temperature water bath apparatus

4.2 Methods of analysis for the experiment

The methods of analysis for the experiment are as follows (tab.2):

Table 2. Methods of analysis for the experiment

Items	Methods of analysis
COD	Rapid determination of COD by microwave sealed digestion method
CN-	Silver nitrate titration
pH value	pHS-3C
Quantity of gas	Gas collection with displacement of water

4.3 Result and Discussion

100 ml anaerobic sludge and 50 ml wastewater are put into every conical flask. The initial concentration of VSS of granular sludge is 32 g/L. According to the results of experiment, the security of cyanide can be appraised properly.

4.3.1 Results at Different Temperatures

For two months domestication of anaerobic granular sludge from beer plant, the sludge has obvious ability of tolerance to cyanide. On the condition that the COD of the influent is 1800 mg/L and CN- is 30 mg/L, the results at different temperatures (34℃，36℃，38℃) are shown in fig.1. As the temperature rises, the quantity of gas and the removal rate of COD will increase. This phenomenon is the same as the rule of anaerobic biological reaction. In other words, the ability of metabolism is strengthening with the increasing of temperature at medium temperature stage. The concentration of CN^- achieves 30 mg/L, but the removal rate of COD is relatively high, which is from 28% to 69%. The anaerobic microorganism after domestication can metabolize normally in cassava starch industry wastewater which contains high concentration of CN-.

According to the results of repeating experiments, the instances of cyanide removal rate in the wastewater of different CN^- concentrations and different temperatures is statistically calculated. The effect on them is noted in tab.3. The removal rate of CN^- concentration decreased from 36 degrees to 30 degrees. It shows that increasing temperature is favorable to cyanide removal. There are two reasons to explain this result. On the one hand, the high temperature is beneficial to metabolism of anaerobic

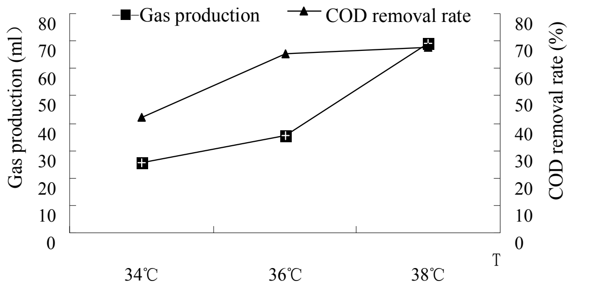

Figure 1 The effect on treatment of CN- wastewater at different temperatures

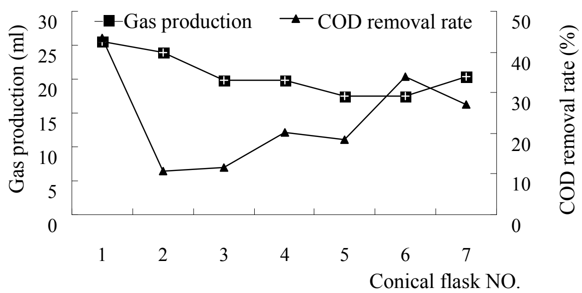

Figure 2 The effect on anaerobic biological reaction with different concentrations of CN-

microorganism, on the other hand, with the increase of temperature, the stabilization of HCN will decrease and it will be decomposed because of volatilization. But on such conditions, high concentration of CN^- will still remain in the wastewater. And it is far from the standard of allowable security.

4.3.2 Results from different concentration of CN^-

When the temperature of the system is 38 degrees and COD in the influent is 1800 mg/L, different concentrations of CN^- are put into different conical flasks. The concentrations of CN^- are respectively 0, 12, 30, 48, 66, 84, 96 mg/L. After several experiments, the arithmetic average quantity of gases and the removal rate of COD are shown in fig.2.

Fig.2 shows the decrease of gases in quantities with the increase of CN- in the influent, and the changes are in a stable pattern. The highest removal rate of COD is over 40% when there is no cyanide in the conical flask. Whereas, with the increase of CN^- ions, the removal rate of COD is rising obviously. When the concentration of CN^- is up to 84 mg/L, the removal rate of COD has decreased a little. The results show that the existence of cyanide will certainly inhibit methanogens, but it has little influence on metabolism of the whole domestic anaerobic microorganism. It is even considered that organic carbon of cyanide takes part in biochemical reaction. When the concentration of CN- is up to 84 mg/L, the removal rate of CN- is over 30%.

Table 3. The removal rate of CN- at different temperatures

Temperature of system (℃)	36	34	32	30	remark
CN^- 41.8(mg/L)	85.12	83.35	80.54	64.91	
CN^- 60.6(mg/L)	86.95	80.89	62.21	42.81	
CN^- remain (mg/L)	6.2~7.9	6.9~11.6	8.1~22.9	14.6~34.7	Standard: 05
Removal rate in average	91	88	78	54	

5. Recognitions and Conclusions

1) The concentration of CN^- in cassava starch industry wastewater is exceedingly high and the CN^- in mixing production wastewater exceeds 5 mg/L, in which many kinds of microorganism can be killed. Therefore, the discharge of cassava starch industry wastewater must be strictly managed in order to prevent unexpected poisoning.

2) Recently, cassava starch industry wastewater is mainly treated by high efficiency anaerobic biological technology and by other ways in a stabilization pond. These treatments can degrade a great deal of organic pollutant in the wastewater and it can also remove parts of CN^-, but the removal rate is very limited. In the stabilization pond, because of its low temperature, and the removal rate of CN^- in the wastewater is also very low, so the cyanogen content in the effluent still shows high danger.

3) If the cassava starch industry wastewater is not treated by other special de-cyanation process, the effect of de-cyanation by biological treatment would be very limited, especially the wastewater has just been treated in a stabilization pond. Therefore, closed management of the effluent is still needed to prevent the wastewater from doing harm to the environment. The effluent after biological treatment can be used for irrigation. This is a way out for the relative safety of water resources.

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