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Research on treatment of propylene oxide wastewater with high salt concentration

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Abstract. In this paper, experimental study had done in view of the wastewater which discharged from chlorine alkali factory propylene oxide production workshop in Zibo city of Shandong Province. The Pre-oxidation + Biological Contact Oxidation craft has proposed for the epoxy propane production wastewater treatment. In view of the characteristics of this kind of wastewater, the main research contents are three aspects: the discussion of gradually microorganism salinity endurance enhancement, the best test condition of H_2O_2 oxidation for per-oxidation, and the effect verification test of the Pre-oxidation + Biological Contact Oxidation craft.

Keywords: High salinity; Biological Contact Oxidation; Domestication; Pre-oxidation.

1. Introduction

Propylene oxide (PO) is an important organic chemical product, but also an important basic organic chemical raw materials[1]. It widely used in chemical industry, light industry, medicine, food and textile industries. There are several routes to produce propylene oxide in the world such as peroxide method and chlorohydrin method [2, 3]. The propylene oxide production wastewater has the characteristics of high calcium chloride content, high COD and high pH value[4]. It belongs to organic chemical wastewater which is difficult to be biochemical degraded[5]. How to improve the treatment effect about the propylene oxide production wastewater and reduce the impact on the environment is the purpose of this study.

2. Experimental and Theoretical Methods

2.1. Experimental materials

The wastewater which had be used in the experimental study was discharged from chlorine alkali factory propylene oxide production workshop in Zibo city of Shandong Province. The following is the details of the wastewater quality:



Table 1. The details of the propylene oxide production wastewater quality.

Detecting objects	Ca ²⁺ (mg/L)	Cl ⁻ (mg/L)	COD(mg/L)	BOD ₅ (mg/L)	pH
Concentration	16597.13	32082.25	3505.92	771.30	11.47

Table 1 shows the concentration of calcium ion and the concentration of chlorine ion in the wastewater are very high. Even though the concentration of COD in the wastewater is also relatively high, the rate of BOD/COD is only 22% and the pH value reached 11.47. These factors determine that the general microorganisms are difficult to survive in the wastewater.

2.2. Test device

The test device used in the Experiment was made by ourselves. The following is the details of the test system.

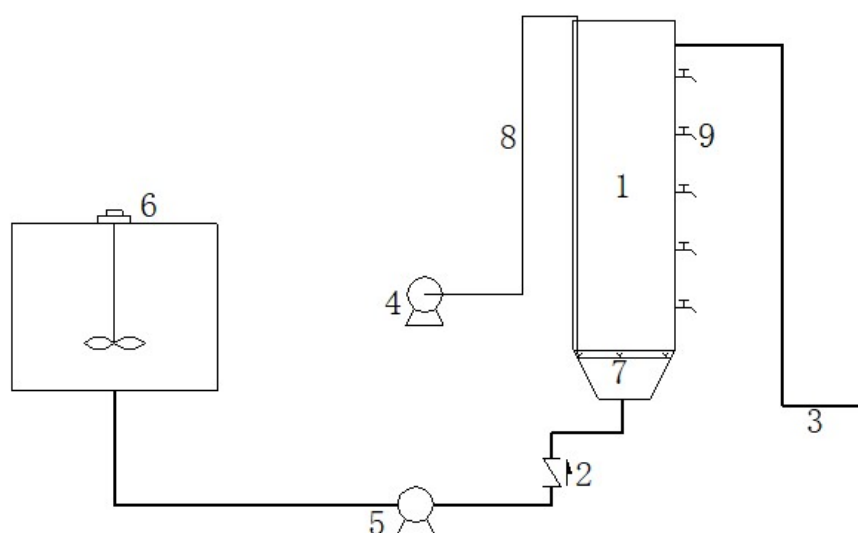


Figure 1. The treatment device of propylene oxide production wastewater. (1. Biological contact oxidation column; 2. Inlet pipe; 3. Outlet pipe; 4. Air compressor; 5. Corrosion resistant pump; 6. Blender; 7. Aeration head; 8. Windpipe; 9. Sampling port)

First of all, we should adjust pH value of the propylene oxide production wastewater which be injected into the pre-oxidation lagoon and add H₂O₂ to wastewater while the wastewater being stirred. Secondly, after being stirred, the wastewater is pumped into biological contact oxidation reactor by creep pump. The wastewater enters from the lower part of the oxidation reactor and flows through the fillers. Finally, the water flows out from the top of biological contact oxidation reactor. The dissolved oxygen used in the experiment is provided by the three pillars of aeration head located in the air diffusion plate in the lower part of biological contact oxidation reactor.

2.3. Detecting objects and instrument

According to the experimental content of this subject, detecting COD, BOD₅, Cl⁻, DO, Ca²⁺ and pH value in water are necessary. In this study, we have used Portable pH meter, 78-1 magnetic heating stirrer, Peristaltic Pump BTO1-100, JJ-6 digital display DC constant speed mixer, Air compressor ACD-012, Oven, Muffle furnace, Incubator.

3. The domestication of microorganisms and research of effect on COD removing rate

Since the seed sludge used in this experiment is conventional activated sludge which be taken from the urban sewage treatment plant, and therefore we need to gradually enhance microorganism salinity endurance. The whole process of domestication begins in the Cl^- concentration about 6000mg/L, and gradually increase the Cl^- concentration to get the microorganism which can survive in high salt concentration water. During the course of experiment, the dissolved oxygen concentration of water taken from the upper water intake of the biological contact oxidation reactor need to be maintained between 4—8mg/L. The initial pH value of water should be kept about 9 at each stage of domestication. In this study, we need to take a water sample once in a while and detect the COD of all samples. When the COD of samples gradually remains stable, we can begin the next stage of domestication.

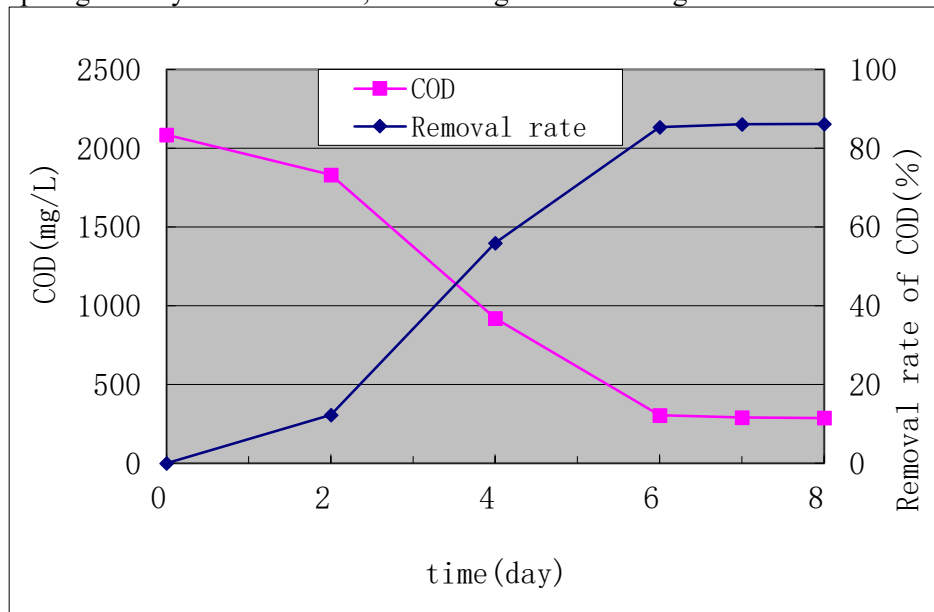


Figure 2. The degradation rule of COD when Cl^- is 10000mg/L

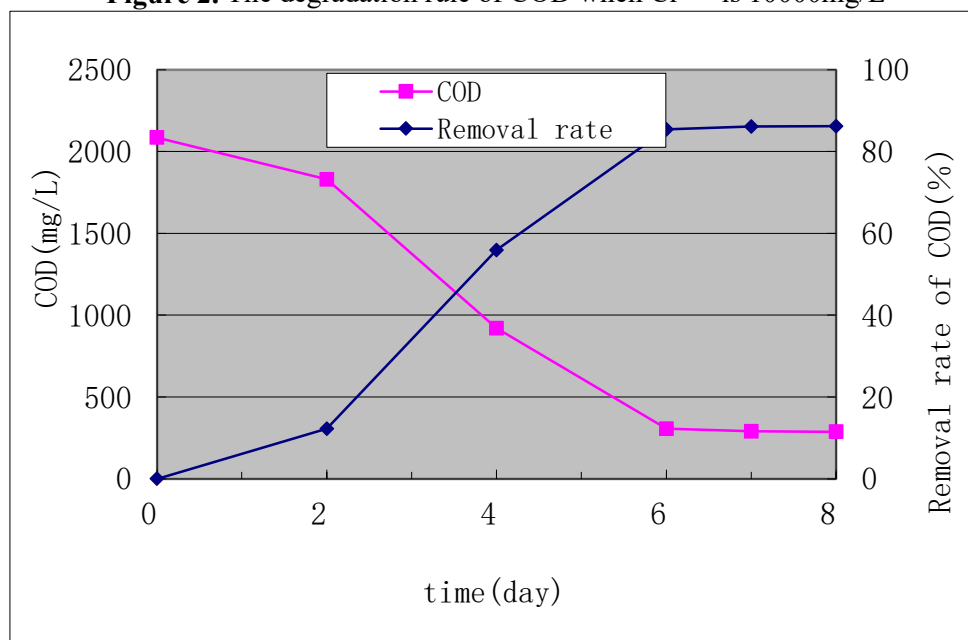


Figure 3. The degradation rule of COD when Cl^- is 12500mg/L

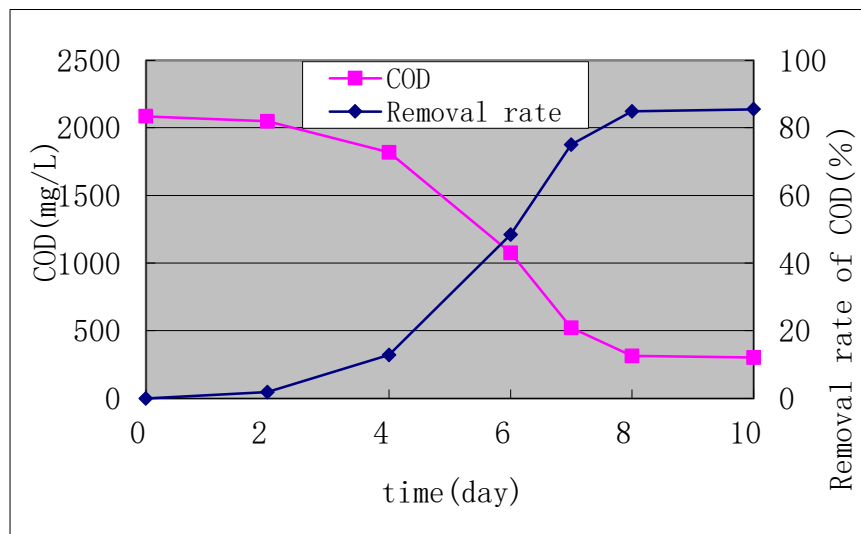


Figure 4. The degradation rule of COD when Cl^- is 14500mg/

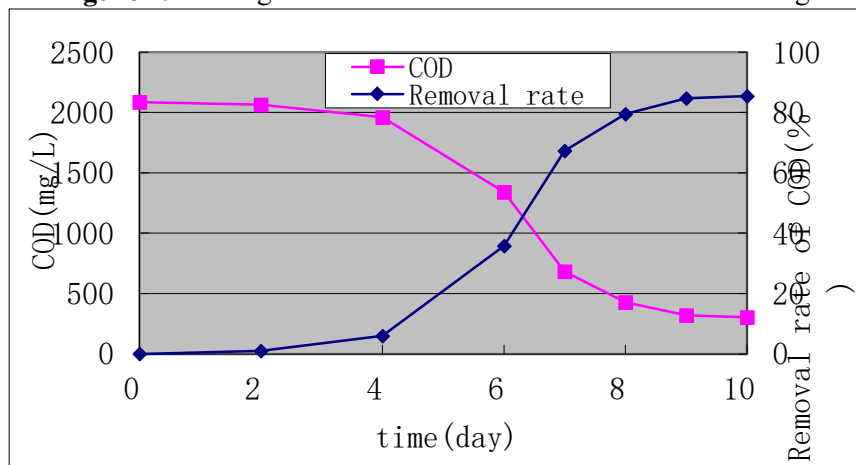


Figure 5. The degradation rule of COD when Cl^- is 16500mg/L

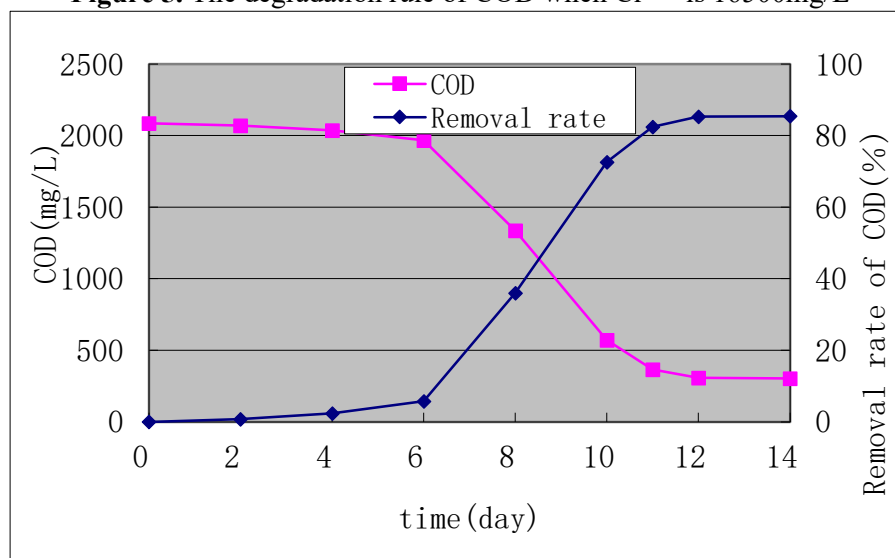


Figure 6. The degradation rule of COD when Cl^- is 18500mg/L

From the figures, we can get a large of information. During the course of domestication, the microorganism will be in an adaptation period for some time at the beginning of each stage of domestication because of a sudden increase of water salinity, and the COD removing rate is very low in the adaptation period. The substance of domestication for enhancement microorganism salinity endurance is the directive breeding about microorganisms which can survive in high salt concentration water^[7]. The microorganisms can produce certain amino acids with the increase of water salinity. These amino acids play an important role in the mediation of the solute concentration in cells. They can be quickly synthesized and degraded to constitute osmotic adjustment substances in cells to make microorganisms produce a large number of solute or keep the solute got from the outside staying in cells. And help microorganisms get water from the high salt environment so as to be able to maintain normal life activities.

4. The jar test of pre-oxidization

The main purpose of adding H_2O_2 to wastewater in the experiment is because it can improve the biodegradability by changing molecular structure of organic compounds in propylene oxide wastewater. So the hydrogen peroxide direct oxidation is taken for the pretreatment of biological treatment^[8]. In the jar test, through adjusting the H_2O_2 dosage, pH and reaction time in succession, we can draw a conclusion of their influence on the COD treatment effect of wastewater to determine the optimal operating condition.

4.1. The influence of the initial pH value

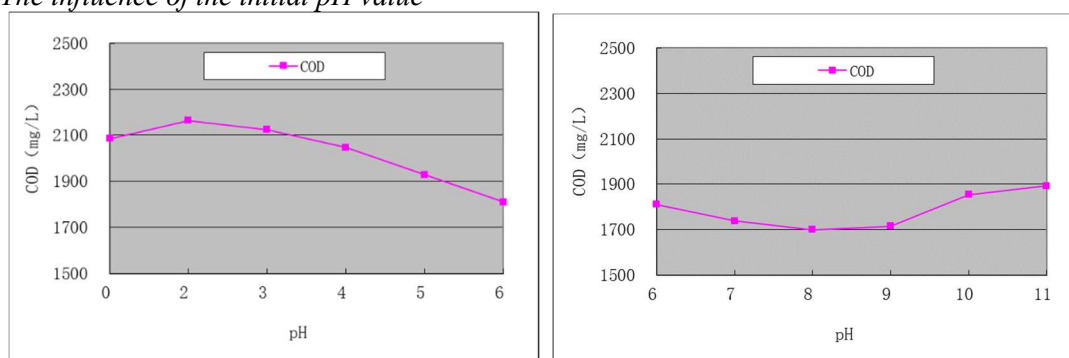


Figure 7. The COD degeneration effect is best **Figure 8.** The COD removing rate can achieve

As shown in Figure 7 and Figure 8, the COD degeneration effect is best and the COD removing rate can achieve 18.52% when the initial pH value is about 8. With the continued rise of pH, the COD removing rate does not rise but decreased. That's because in the case of high pH value, even though H_2O_2 can decompose completely, the oxidation ability of H_2O_2 is weaker than in low pH value and most of decomposition is invalid, so the COD removing rate can't reach the maximum. The COD removing rate begin to rise when the pH value began to decline from 8. Especially when the pH value to 2, the COD is even bigger than the initial COD. That's because the decomposition of H_2O_2 is slow and part of H_2O_2 doesn't decompose completely under acidic conditions^[9], that leading to some impact on the determination result of COD.

Detecting the BOD_5 of water samples after reaction in the case of the initial pH value is about 8, the results are as follows:

Table 2. Biochemical comparison of the pre-oxidization before and after.

	COD(mg/L)	BOD_5 (mg/L)	B/C
Before	2085.92	455.30	0.22
After	1699.64	494.08	0.29

As shown in Table 2, B/C has elevated from about 0.22 to about 0.29, and the biodegradability of the wastewater has enhanced.

4.2. The influence of the dosage of H_2O_2

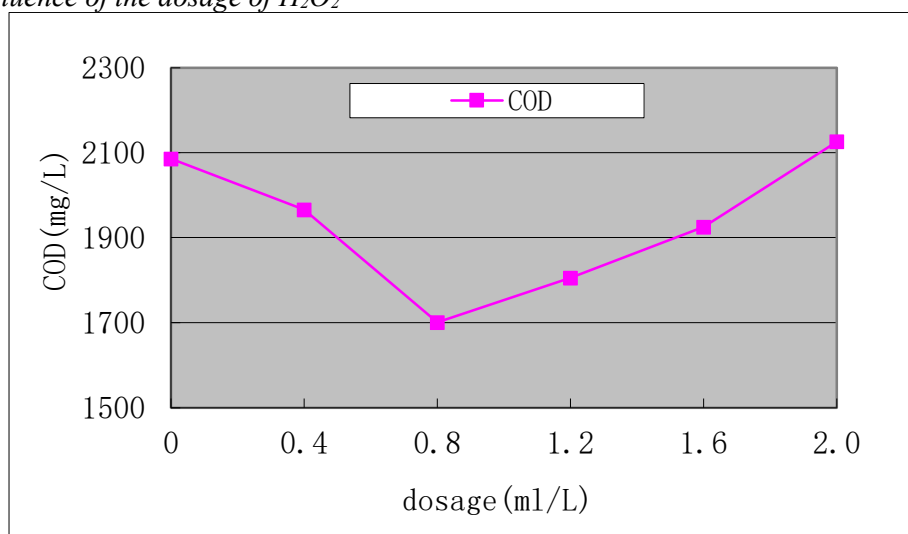


Figure 9. The reaction results under different dosages of H_2O_2

As shown in Figure 9, the COD degeneration effect is best and the COD removing rate can achieve 18.46% when 30% H_2O_2 dosage is about 0.8ml/L. When the dosage of H_2O_2 is less than 0.8ml/L, with the dosage increased, the removing rate of organic compounds in water is also increased. When the dosage of H_2O_2 is greater than 0.8ml/L, with the dosage increased, the COD does not decrease but increased. That's because part of H_2O_2 doesn't react completely, that leading to some impact on the determination result of COD.

Table 3. Biochemical comparison of the pre-oxidization before and after.

	COD(mg/L)	BOD ₅ (mg/L)	B/C
Before	2085.92	455.30	0.22
After	1700.82	504.06	0.30

As shown in Table 3, B/C has elevated from about 0.22 to about 0.30, and the biodegradability of the wastewater has enhanced. So the best 30% H_2O_2 dosage is about 0.8ml/L.

4.3. The influence of reaction time

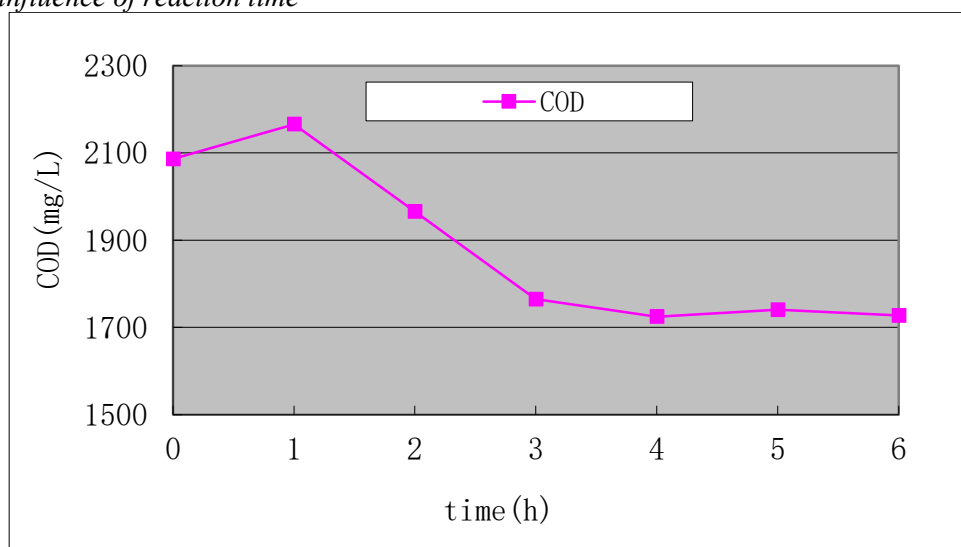


Figure 10. The results under different reaction time

As shown in Figures 10, in the first hour after adding H_2O_2 to wastewater, the COD doesn't decrease but rise because the H_2O_2 added to water doesn't react completely. During the second to third hours, the COD removing rate increases with the extension of time and basically maintains a linear relationship with reaction time. When the stirring reaction time more than 4 hours, the COD is basically unchanged. That demonstrate that H_2O_2 react completely.

Table 4. Biochemical comparison of the pre-oxidation before and after.

	COD(mg/L)	BOD ₅ (mg/L)	B/C
Before	2085.92	455.30	0.22
After	1724.90	502.28	0.29

As shown in Table 4, B/C has elevated from about 0.22 to about 0.29, and the biodegradability of the wastewater has enhanced. So the best stirring reaction time is 4 hours.

According to the results of the tests, the optimal operating condition of H_2O_2 direct oxidation is that: the pH value is about 8, 30% H_2O_2 dosage is about 0.8ml/L, and the stirring reaction time is 4 hours. After pre-oxidation with H_2O_2 , the biodegradability of the wastewater has enhanced.

5. The research of the Pre-oxidation + Biological Contact Oxidation craft

5.1. The Biological Contact Oxidation craft

Taking a certain amount of propylene oxide wastewater and adjusting pH value to about 9, then make the wastewater is pumped into biological contact oxidation reactor by creep pump. During the course of test, the aeration quantity remains in 36L/h from beginning to end. The water samples are taken once every 12 hours and the COD of all samples are detected.

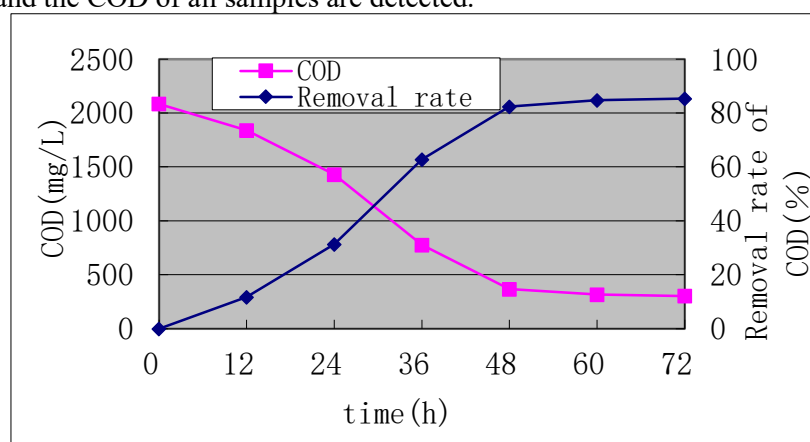


Figure 11. The COD of water with Biological Contact Oxidation craft

As shown in figure 11, the COD degrades rapidly and almost basically maintains a linear relationship with time in the first 48 hours of the test. After reaction for 60 hours, the COD is basically unchanged. After reaction for 72 hours, the COD is stable at around 304mg/L. The COD removing rate can achieve 85%

5.2. The test of the Pre-oxidation + Biological Contact Oxidation craft

Taking a certain amount of propylene oxide wastewater injects into the pre-oxidation lagoon and adjust pH value to about 8, then add 30% H_2O_2 0.8mg/L to wastewater while the wastewater being stirred. After stirring for 4 hours, taking a water sample to detect the COD. Adjust pH value to about 9 and make the wastewater is pumped into biological contact oxidation reactor by creep pump. During the course of test, the aeration quantity remains in 36L/h from beginning to end. The water samples are taken once every 12 hours and the COD of all samples are detected.

The COD of water sample which have been added with H_2O_2 is 1705.83mg/L, the COD removing rate achieve 18.22%

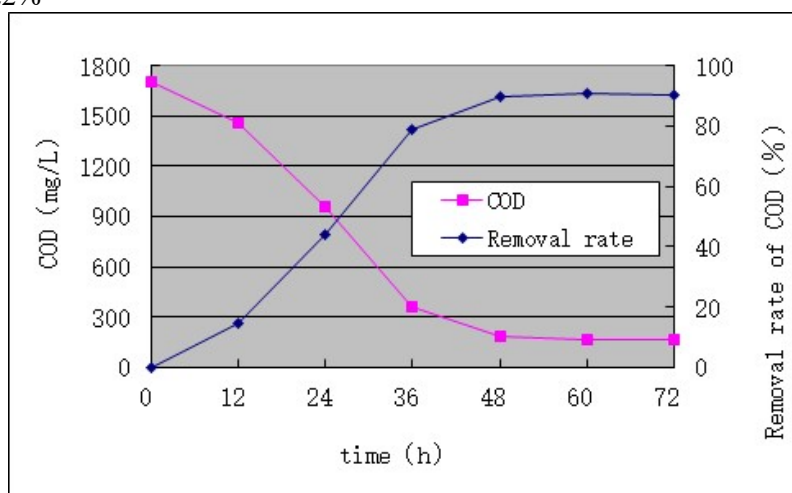


Figure 12. The COD of water with the Pre-oxidation + Biological Contact Oxidation craft

After pre-oxidization, the degradation curve of COD is similar to that of wastewater have not been added with H_2O_2 . After reaction for 48 hours, the COD is basically unchanged. After reaction for 72 hours, the COD is stable at around 170mg/L. The total removal rate of COD can achieve 92% with pretreatment.

6. Conclusion

During the course of domestication, with the increase of water salinity, the adaptation period of the microorganism will take more time. According to the results of the jar tests, the optimal operating condition of H_2O_2 direct oxidation is that: the pH value is about 8, 30% H_2O_2 dosage is about 0.8ml/L, and the stirring reaction time is 4 hours. Compare the pre-oxidization before and after, the biodegradability of the wastewater obtains a certain enhancement after pre-oxidization. Compare the two crafts, the pre-oxidization enhanced the biodegradability of wastewater, that makes the residence time decreases in the biological contact oxidation reactor, and the total removal rate of COD can achieve 92%.

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