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Treatment Effect On Coking Wastewater Using Three-phase Biological Fluid-bed With New Ultrastructure Biological Carriers

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***Abstract*—The degradation of COD and ammonia nitrogen (NH_3-N) in coking wastewater was researched using the new ultrastructure biological carriers in three-phase aerobic biological fluid-bed. The results show that the optimum conditions of the new biological carriers are as follows: HRT of 20 h, neutrality skew alkaline pH (about 7.5) and dissolved oxygen (DO) of 2~5mg/L. Under the optimum conditions, the removal efficiency of COD and NH_3-N can reach 82% and 87%, respectively, when the influent concentration of COD and NH_3-N is about 3000 mg/L and 60mg/L. At the same time, comparison with the activated sludge process and common biological ceramisite carriers, it is found that the most excellent treatment effect and the strongest resistance to impact are obtained under the condition of the shortest HRT in this new ultrastructure biological carriers reactor, and the effluent of two-stage reactors in series can reach the first national discharge standard, which will has a wide application prospect.**

Keywords- Biological Carrier; Three-phase Biological Fluid-bed; Coking Wastewater; COD; Ammonia nitrogen

I. INTRODUCTION

With the rapid development of industry, water pollution is more severe. Coking wastewater is one of the serious pollution sources。Because of the complex water quality and the high content of refractory organic compods in coking wastewater, the effluent using the existent treatment technology couldn't meet the state discharge standard completely. Nowadays, although the effluent quality has been improved by new treatment technology, there are many technical defects, such as the long hydraulic retention time, the increase of treatment cost using powder active carbon, coagulate or carbon source.

Because fluidized state of biological fluid-bed is beneficial to the mass transfer of gas-liquid-solid, its treatment efficiency is about ten times higher than this of activated sludge, and there isn't significiant increase of energy consumption and operation cost. Therefore, the three-phase aerobic biological fluid-bed technology has become one of the research hotsports [1-3]. And the choice of biological carriers, which is one of the cores of biofilm technology, is the key process. Because of the significant influence on the efficiency, energy consumption, stability and reliability of biological fluid-bed, biological carriers have been universally regarded [4-6]. But the great mass of biological carriers has certain deficiency on the start speed and quantity of biofilm, the tightness between biofilm and carrier, the cell viability of microorganism, the oxygen utilization coefficient, etc.

In this paper, the degradation of COD and ammonia nitrogen (NH_3-N) in coking wastewater was researched using the new ultrastructure biological carriers in three-phase aerobic biological fluid-bed. And the capability of this new carrier was compared with that of activated sludge and common biological ceramic.

II. MATERIALS AND METHODS

A. Wastewater and Seed sludge

In this test, coking wastewater was taken from coking workshop of a certain chemicial plant in Heilongjiang province. Becouse of its high COD concentration, it was used after dilution and adding inorganic salts which were needed by the growth of microorganism. And its water quality was listed in Table 1.

TABLE I. WATER QUALITY OF COKING WASTEWATER IN THIS TEST

Index	Concentration
COD/ $mg.L^{-1}$	20000~30000
BOD_5 / $mg.L^{-1}$	1500~3000
NH_3-N / $mg.L^{-1}$	600
TP / $mg.L^{-1}$	0
pH	8~9.5
Tatol Phenol/ $mg.L^{-1}$	1000~1400

Volatile Phenol/ mg.L^{-1}	800~1200

The seed sludge with 2.9 g MLSS/L concentration was taken from the activated sludge tank in Harbin gasification plant. And it was mixed with biological carrier in the equal ratio. The volum of mixture was about 30% of the biological fluid-bed reactor.

B. *Experimental Equipment*

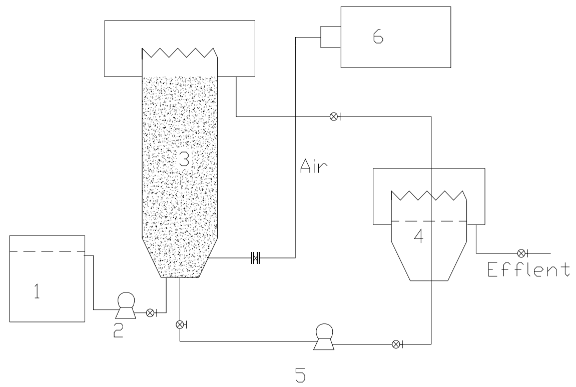
The continuous flow three-phase aerobic biological fluid-bed was used as experimental reactor, which was plotted in Fig. 1. This cylindric reactor with the radial-flow sedimentation tank was made of organic glass. The influent flow was controled by the peristaltic pump. The temprature of reactor was 18-25 ℃. The sludge and carriers in the reactor were fluid. The volum of carriers was 30% of reactor. And the equipmental specification of this reactor system was listed in Table 2.

C. *Biological Carriers*

In this experiment, the biological carrier was a new biosynthesis material with ultrastructure framework, which was made of various active sludges with the curing on ultrahigh temprature. The basic performance parameters of this biological carrier were listed in Table 3. It was found that the particle size and density of this carrier were both smaller, so it could have good fluidization state under the condition of little energy consumption. And according to the observation in the scan electron microscope, it was also found that this carrier had rough surface, good layer structure and abundant tunnel pore structure, which all was favorable to the attachment of microorganism and the adsorption and mass transfer of contamination in wastewater.

TABLE II. SPECIFICATION AND TYPE OF REACTOR SYSTEM

Equipment	Specification and type
Aerobic biological fluid-bed	V_e=20.3L（Φ180×h800mm）
sedimentation tank	V_e=2 L, H_e=120mm
Gas flow meter	LZB-3WB
Gas pump	YB-W300
Peristaltic pump	BT100-2J



1-Wastewater tank；2- peristaltic pump；3- aerobic biological fluid-bed；4- sedimentation tank；5- Sludge pump；6- Gas pump

Figure 1. Sketch map of experimental equipment

TABLE III. BASIC PERFORMANCE PARAMETERS OF THIS BIOLOGICAL CARRIER

Particale Size / mm	Specific Surface area / m^2.m^{-3}	Porosity / %	Bulk Density g.cm^{-3}
0.6-1	8700	67	0.18

D. *Analysis Method*

The national standard method was used to measure the concentration of COD and ammonia nitrogen. The concentration of total organic carbon was deternined by Shimadzu TOC-V CPN analyzer. The date of pH was determined by pHS-25 pH meter, and the concentration of dissolved oxygen was determined by model JPB-607 dissolved oxygen analyzer. The characteristic of microorganism was observed by XSP-16A microscope everyday.

III. RESULT AND DISCUSSION

A. *Domestication of sludge on ultrastructure biological carrier*

1) *Result of running*

At first, the seed sludge was domesticated in 4 stages. In the first period, the seed sludge was actived in culture solution for 24 hours of aerating time, which used dextrose as carbon score with COD concenration of 1500 mg/L, pH of 7.0, DO of 2 mg/L. In the second period, the seed sludge was cultured under the continuous influent, which used dextrose and little coking wastewater as carbon score, and the concentration of COD was about 1500 mg/L, DO was between 2 and 7 mg/L, HRT was 22 hours. In the third period of 11 days, the quantity of dextrose was decreased, and the wastewater quantity was increased, the concentration of COD was between 1500 and 2000 mg/L, ammonia nitrogen was about 40 mg/L, other conditions remained invariant. In the forth period, after the wastewater replaced dextrose, the loading of COD was gradually improved from 2.18 to 3.27 kg/（m^3・d）, the COD concentration was 3000 mg/L, ammonia nitrogen was about 45 mg/L, other conditions remained invariant.

The inffluent concentration and removal efficiency of COD and ammonia nitrogen in the third and forth domestication period was plotted in Fig. 2 and 3.

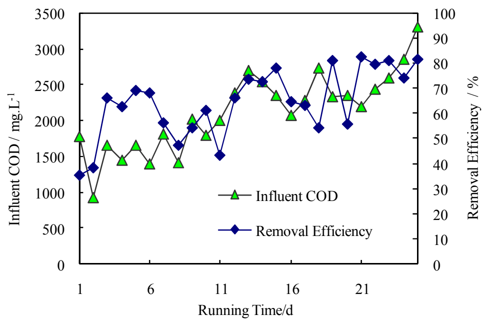


Figure 2. Inffluent concentration and removal efficiency of COD in the third and forth domestication period

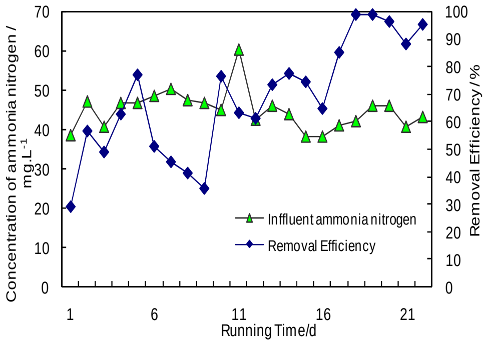


Figure 3. Inffluent concentration and removal efficiency of ammonia nitrogen in the third and forth domestication period

In the third domestication period, although the coking wastewater was increased continuously, the removal efficiency of COD improved rapidly from 30% to 60% and kept relative stable after 2 day, and the removal efficiency of ammonia nitrogen was fluctuated between 40% and 70%. In the forth period, the concentration of influent COD was increased slowly, but the activity of sludge wasn't influenced significantly, the removal efficiency of COD was increased remarkably, the date was over 70%, when the loading of COD was 2.72kg/（m^3 · d）on 14-16 day. Because the concentration of ammonia nitrogen always was low, its removal efficiency was increased with COD. After domestication of 21 day, when influent COD was about 3000 mg/L, the removal efficiency of COD and ammonia nitrogen were about 80% and 100%, respectively. It showed that the sludge was mature and had the good activity and the strong resistance to impact load. According to the result of influent and effluent TOC, the TOC removal efficiency of the fluid-bed reactor was above 85%. It indicated that the coking wastewater was mineralized and the organic pollutants were degradated more thoughly in this fluid-bed reactor with new ultrastructure biological carriers.

2) Characteristic of Biological Phase

After the start-up of reactor, because of the good adsorption capability of this new biological carrier, the sludge attached on its surface and grew fastly. Ater 7 days, the biofilm was observed and the color of sludge was changed from black to grey. And after 28 days, the color of biofilm was snuff color and the concentration of sludge was 4396mg MLSS/L. According to tne microscope, a mass of zoogloea was observed aboud the carrier, the microorganism had high activity, and protozoa and metazoa, such as the rotifer and infusorian, was also observed. It showed that the sludge was mature.

B. Compare of activated sludge, common biological ceramic and new ultrastructure biological carrier

Three group experiments were done using activated sludge no any carrier, common biological ceramic and new ultrastructure biolocial carrier, respectively. The conditions of three group experiments were that COD was 3140～4107mg/L, BOD was 814～1257mg/L, temprature was 20℃～27℃, pH was 6.9～7.6 and the highest influent flow was 0.5m3/h. At first, the experiments were running for 7 days under 0.1 m3/h of influent flow, then the hydraulic retention time was changed though the change of influent flow. Three group experiments were done for about 70 days. The results were listed in Table 4.

TABLE IV. COMPARER OF TREATMENT EFFECT ON COKING WASTEWATER USING THREE DIFFERENT METHODS

Treatment Method	**HRT / h**	**Runtime / d**	**Removal Efficiency of COD / %**	**Removal Efficiency of ammonia nitrogen / %**
Activated sludge	39	8	92.96	79.32
	26	14	86.32	68.67
	16	4	65.40	66.28
Common biological ceramic carrier	54	8	92.33	83.13
	36	14	90.57	76.93
	23	40	84.75	67.22
New ultrastructure biological carrier	36	8	99.98	85.40
	25	14	90.82	83.57
	16	40	85.77	75.21

From Table 4, it showed that when the hydraulic retention time of activated sludge was less than 26 hours, the removal efficiency of COD and ammonia nitrogen were all decreased obviously. When the hydraulic retention time was less than 16 hours, this treatment system came to nothing, the detection index was low, and the sludge was no activity.

The treatment effect using common biological ceramic was better than that using activated sludge. It had the resistance to impact load. But with the increase of influent flow, the removal efficiency of COD and ammonia nitrogen were all decrease. The effluent couldn't reach the standard under the condition of the longer hydraulic retention time.

The good treatment effect was obtained in the fluid-bed reactor using the new ultrature biological carrier. Under the shortest hydraulic retention time, the removal efficiency of COD and ammonia nitrogen were the best, especially the removal efficiency of COD was about 100%. And this treatment system had the good effluent quality and the strongh resistance to impact load.

IV. CONCLUSION

The better treatment effect on coking wastewater in Three-phase biological fluid-bed with new ultrastructure biological carriers was obtained. Under the good condition (20 hours of HRT, 7.5 of pH, 2~5mg/L of DO), when the influent concentration of COD and ammnia nitrogen was about 3000mg/L and 60mg/L, respectively, the removal efficiency of COD and ammnia nitrogen was about 82% and 87%, respectively. According to the comparer with common biological cerimic and activated sludge, the reactor using new ultrastructure biological carrier had the best treatment effect and the strongest resistance to impact load.

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