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Biological removal of methanol from process condensate for the purpose of reclamation

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Abstract: The biological removal of methanol from condensate of ammonia manufacturing processes for the purpose of reclamation using contact type reactor was studied. Methanol of 60 mg/L was removed completely under an HRT of 1.12 h. Optimal inorganic nutrient dose was determined on evaluating methanol removal performance and dehydrogenase activities (DHA) under different nutrition doses. The optimal inorganic nutrient dose only gave an increase of conductivity of ca. 10 μs/cm^2 in the effluent on treating synthetic condensate containing methanol of 30 mg/L. The results demonstrated that biological removal of methanol was effective for the purpose of recovering the methanol-bearing condensate.

Keywords: reclamation; condensate; methanol removal; biological contact reactor

Introduction

A great amount of condensate is usually produced when carbon monoxide of composite gas is transformed in the ammonia manufacturing process. The condensate contains some methanol (< 30 mg/L) as well as a small amount of inorganic ions (conductivity < 20 μs/cm^2) (Song, 2001; Zhu, 2002), and has been discharged as wastewater. The condensate, however, could be reclaimed as the high quality process water if methanol as well as inorganic ions were removed.

Methanol is highly biodegradable, and could be effectively removed from wastewater with a biological oxidation process. Most of the reports related to methanol removal, however, are limited to wastewater containing high concentration methanol (Wu, 1998; Irene, 1999; Zhao, 1989). Biological activated carbon (BAC) process has been successfully used for the removal of trace organic pollutants like isopropanol, methanol, etc. from used pure water. When the BAC process is applied to the treatment of condensate, however, frequent backwash is required because of the fast growth of bacteria under the relatively high concentration of methanol. In this case, the endurance of activated carbon will become a big challenge (Miller, 1978; Song, 2001).

Biological ceramic contact reactors, on the other hand, have been successfully used to remove low concentration of organic pollutants and ammonia as a pretreatment method in drinking water treatment (Fang, 1995). The ceramic bio-carriers would be much better than activated carbon in terms of endurance. For treating condensate with a biological method, however, addition of inorganic ions is necessary to keep activities of microbes. Inorganic nutrition salts were added (Table 1) to a biological system to remove trace organic compounds from the oligotrophic rinse pure water of semiconductor manufacturing processes (Shibata, 1987). Generally speaking, inorganic ions should be added as little as possible because the condensate will be reused as process water after treatment.

Table 1 Composition of inorganic nutrition solution (for treating TOC of 1 mg/L) (Shibata, 1987) Unit: mg/L

NH_4Cl	0.767	$CaCl_2 \cdot 2H_2O$	0.001
KH_2PO_4	0.305	NaCl	0.001
$MgSO_4 \cdot H_2O$	0.07	$MnSO_4 \cdot 4H_2O$	0.001
$FeSO_4 \cdot 7H_2O$	0.001	$ZnSO_4 \cdot 7H_2O$	0.001
$CuSO_4 \cdot 5H_2O$	0.001	$Al_2(SO_4)_3 \cdot 14H_2O$	0.001

The objective of this study is to establish a biological contact oxidation system for recovering condensate contaminated with methanol. Operational conditions as well as necessary nutrient dose were determined on synthetic condensate wastewater.

1 Materials and methods

1.1 Materials

Fig. 1 shows the schematic diagram of the biological ceramic contact reactor used in this study. A polyacrylate column (132 cm × 5 cm ID) was used as the reactor, and a granular ceramic bio-carrier (Zibo Biocarrier Company, Shandong Province) with a diameter of 2—4 mm was filled in the reactor to give an effective height of 80 cm. The experimental setup was installed in a thermostat room (20 ± 1℃).

Synthetic condensate was prepared by dissolving proper amounts of methanol of reagent grade into deionized water. Seed sludge was taken from an activated sludge plant treating

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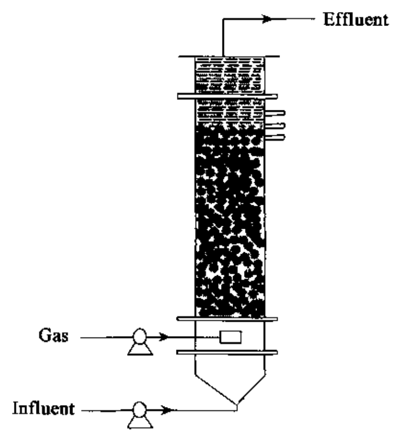


Fig.1 Experimental sketch of biological contact column

methanol-bearing wastewater. Stock inorganic nutrition salt solution was prepared using chemicals of reagent grade.

1.2 Analytical methods

Methanol analysis was conducted on a gas chromatograph (9A, Shimadzu Co., Japan) with a flame ionisation detector (FID) and a chromosorb 101 column(60—80, 2 m × Φ3 mm). The carrier gas(N_2) flow was 80 ml/min, and the injection temperature was 250℃. The TOC was measured using a TOC-500 analyzer(Shimadzu Co., Japan). Microbes on bio-carriers were examined by SEM (Model S-570, Hitachi, Japan). The dehydrogenation activities (DHA) of microbes were measured on a spectrophotometer (722S, Shanghai Analytical Instrument Co., China) at 490 nm according to a reference (Chung, 1989). All of the other analysis was conducted according to the Standard Methods of Water and Wastewater Monitoring of China (1998).

1.3 Experimental methods

The contact bioreactor was aerated for 1 d without inflows of wastewater following addition of 6.75 g seed sludge. Then, the synthetic condensate was introduced into the system at a flow rate of 30 L/d, which was equivalent to an HRT of 1.12 h. The methanol concentration in the influent was about 32 mg/L during the first 33 d, and then increased to 60 mg/L. The inorganic nutrition solution was added to the influent in a dose to TOC ratio equivalent to the same of that used by Shibata (Shibata, 1987). Samples periodically taken from the effluent were centrifuged immediately to remove the biomass, and then refrigerated at 4℃ for methanol and TOC analysis.

Inorganic nutrition solution was prepared according to previous studies(Table 1; Shibata, 1987), and the optimal dosage of the nutrition solution was determined using the previous dosage as the base (N_0) at an influent methanol concentration of 32 mg/L. The performance of the reactor was evaluated for 5—7 d under each nutrition dose. In the same time, proper amount of bio-carriers was taken out from the contact reactor for the determination of DHA and SS.

Bio-carriers were taken from the reactor at 20 cm levels from the bottom on the twenty-fifth day and were examined by SEM. A reference blank of carrier was also taken before the microorganisms were inoculumed.

2 Results and discussion

2.1 Performance of the contact reactor

The reactor was operated under 2 methanol concentrations for 50 d following startup, and variations of methanol and TOC are shown in Fig. 2. Steady removal of methanol was achieved shortly after the startup of the reactor because inoculation of seed sludge acclimated to methanol. Residual methanol began to be detected when the influent concentration was increased to 60 mg/L. Methanol disappeared again from the effluent 3 d later, indicating that the bio-system was very stable for methanol removal.

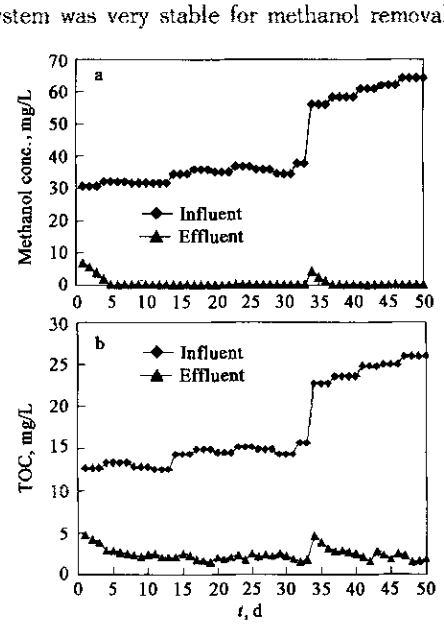


Fig.2 Variations of (a) methanol; (b) TOC

As shown in Fig. 2b, a residual TOC between 2.0 and 2.5 mg/L was successively detected under steady conditions. No other organic components except methanol were used for preparation of synthetic condensate. So, the TOC in the effluent was the products of microbial metabolic activities, and refractory to biodegradation. However, it seems that the effluent TOC was not in proportional to the influent methanol concentration as shown in Fig. 2b.

2.2 Effects of inorganic nutrition dosage

Microbes could not live without the existence of proper amount of inorganic nutrition, and so the inorganic nutrition solution was prepared and added to the synthetic condensate. From the viewpoint of pure water production, however, inorganic salts are not favorable. So, the minimum dose of the inorganic solution was determined by gradually decreasing the dose of nutrition solution from the value(N_0) proposed by Shibata(Shibata, 1987) in several steps, and variations of methanol and DHA are shown in Fig. 3.

When nutrition dose was changed from N_0 to $N_0/3$, the

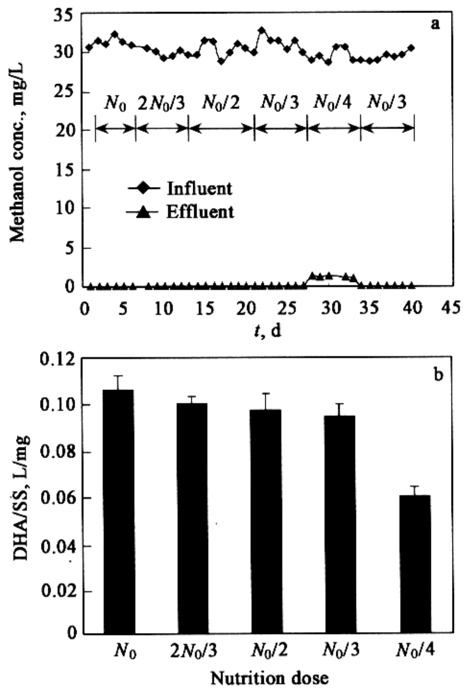


Fig.3 Effect of (a) nutrition ratio on methanol removal; (b) dose on specific DHA

methanol concentration in effluent was under the detection limit. However, if the nutrition dose was decreased further to $N_0/4$, residual methanol began to be detected in the effluent. The residual methanol, however, disappeared again the nutrition dose was increased from $N_0/4$ to $N_0/3$.

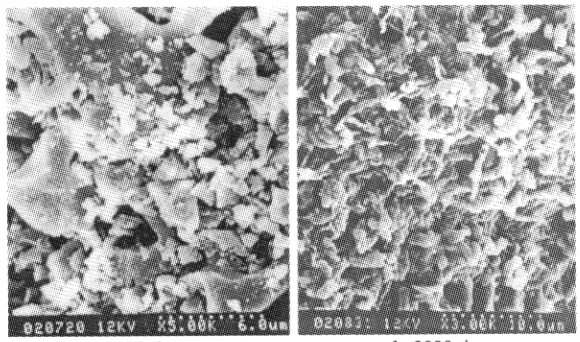
DHA indicates the metabolic activities of microbes to some extent. As shown in Fig. 3b, the specific DHA (the ratio of DHA to SS) only decreased slightly with the decrease of nutrition dose from N_0 to $N_0/3$, indicating that the microbial activities were not affected markedly under the conditions. However, the specific DHA decreased sharply when the nutrition ratio was decreased from $N_0/3$ to $N_0/4$, which was in accordance with the above methanol removal result. It is clear that a nutrition ratio of $N_0/3$ was necessary for maintaining the stable performance of the biological system, which resulted in an increase of conductivity of ca. 10 μs/cm in the effluent.

2.3 SEM images of biofilm

Fig. 4 shows the SEM images of bio-carrier section and biofilm on bio-carrier surface. It is clear that the bio-carrier has a very coarse surface, which is proper for biofilm formation. Round-shape bacteria together with some rod-shape bacteria constituted the dominating microbes on bio-carrier surface, indicating the diversity of the microbial community.

3 Conclusions

Synthetic condensate containing methanol of 60 mg/L was treated with a biological ceramic contact reactor under an HRT of 1.12 h and methanol load of 1.15 kg/(d · m^3).



a. 5000 times b. 3000 times

Fig.4 SEM images of bio-carrier section and biofilm on bio-carrier surface (a) 5000 times; (b) 3000 times

Methanol in the effluent was under detection limit, and TOC in the effluent was less than 2.5 mg/L under steady operation condition, demonstrating a stable methanol removal performance of the biological ceramic contact reactor.

The minimum inorganic salt dose for stable methanol removal was determined, giving an increase of conductivity of 10 μs/cm^2 in the effluent.

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