*Korean J. Chem. Eng.*, **26**(2), 564-568 (2009)

# Removal of COD from coking-plant wastewater in the moving-bed biofilm sequencing batch reactor

**JieYing Jing, Jie Feng, WenYing Li†, and Ying Xu**

Key Laboratory of Coal Science and Technology of Shanxi Province and Ministry of Education,
Taiyuan University of Technology, Shanxi 030024, P.R.China
(*Received 21 July 2008 • accepted 15 October 2008*)

**Abstract**−The objective of this paper is to investigate COD removal efficiency of the coking-plant wastewater by applying the moving-bed biofilm sequencing batch reactor (MBBSBR). The operation is simple and 30% WD-F10-4 BioM$^{TM}$ were packed as carrier materials. It was found that the coking-plant wastewater could be effectively treated with 92.9% of COD removal efficiency at a low organic loading rate (OLR) of 0.449 kgCOD·m$^{-3}$·d$^{-1}$. The removal efficiency decreased gradually down to 70.9% when OLR increased to 2.628 kgCOD·m$^{-3}$·d$^{-1}$. The system has strong tolerance to organic shock loading in this experiment. The COD removal results in the blank experiments of biofilm and sludge showed that the attached biofilm has higher activity than suspended sludge and contributes about 60% to the COD removal.

Key words: COD Removal, Coking-plant Wastewater, Moving-bed Biofilm, Shock Loading, Microorganism Activity

## INTRODUCTION

Coking wastewater contains a wide range of non-biodegradable contaminants, such as hydroxybenzene, phenols, mono-cyclic nitrogen-containing compounds which make the biological treatment results unsatisfied [1,2]. In spite of the fact that conventional activated sludge treatment with anoxic-anaerobic-oxygenous (A-A-O) process can offer an efficient removal of $NH_4^+$-N and COD from the coking wastewater [3,4], being high operating expense, weak tolerance to shock loading and less settle-ability problem at high loading rates still limit the development of the wastewater process [5-7].

A number of investigations [8-12] have reported that the moving-bed biofilm reactor is more advantageous in dealing with industrial wastewater, due to accumulation of high concentration active biomass via microorganism immobilization. Some papers [13-16] have proven that the moving-bed biofilm reactor with A-A-O arrangement possessed good economic feature and the settle-ability problem was improved greatly at high loading rates of COD. But the weak tolerance of shock loading in this system still needs improving [11,17]; also, there are a few about whether the attached biofilm or the suspended sludge should be responsible for the COD removal.

In this paper, MBBSBR was introduced to treat the coking wastewater; the effectiveness and stability of the whole system was evaluated by testing the tolerance of the system to organic shock loading. The COD removal results in the blank experiment of biofilm and sludge were compared to study an individual item's contribution to COD removal at the same organic loading rates.

## MATERIALS AND METHODS

### 1. Experimental Setup and Operation Condition

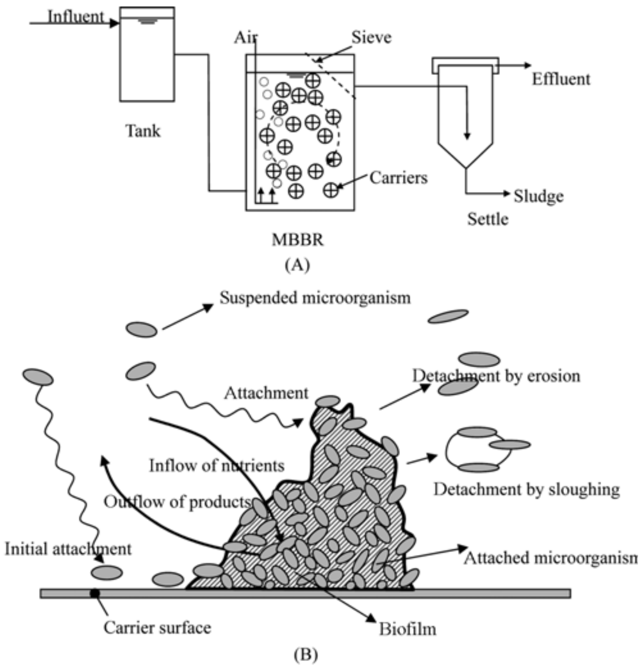


**Fig. 1. (A) Schematic diagram of MBBSBR. (B) Microorganism colonization principle in MBBSBR.**

The schematic diagram of process involved in treating coking wastewater by MBBSBR and the photograph of the microorganism colonization principle are represented, respectively, in Fig. 1(A) and Fig. 1(B). The reactor has 2 L working volume made of a 12 cm (ID) cylinder tube. WD-F10-4 BioM$^{TM}$ carriers were filled into the reactor with 30 vol%. The specification of the used carriers is shown in Table 1. The reactor operated by SBR process without recycling sludge from downstream. The detailed running schedule of the MBBSBR is shown in Table 2. The carriers were perfectly fluidized by air bubbles from an air pump. Temperature and pH value of the system were controlled between the range of 18-22 °C and 7.0-7.5, respec-

†To whom correspondence should be addressed.
E-mail: ying@tyut.edu.cn
‡This work was presented at the 7$^{th}$ China-Korea Workshop on Clean Energy Technology held at Taiyuan, Shanxi, China, June 26-28, 2008.

**Table 1. Specification of the fluidized-biofilm carriers**

| Specification | Feature |
|---|---|
| Material | Composite of polyethylene and inorganics |
| Shape | Tube chip |
| Diameter | 10 mm |
| Length | 10 mm |
| Thickness | 0.4-0.6 mm |
| Specific surface area | 900 $m^2 \cdot m^{-3}$ |
| Density | 0.96-0.98 $g \cdot cm^{-3}$ |

**Table 2. The running schedule of MBBSBR**

| Period setup | Time (h) |
|---|---|
| Filling coking wastewater in anoxic state | 4 |
| Reaction in oxygenous state | 16 |
| Settlement stage | 1 |
| Discharge the effluent | 2 |
| Idling stage | 1 |

Note: 1. SBR is introduced to operate the process of treating coking wastewater, due to the limited conditions, the period is fixed at 24 h; 2. In the experiment, HRT could be changed by changing the amount of effluent; (HRT=(V/Q), where V is the working volume of the reactor; and Q is the flux of the effluent)

tively.

**2. Analytical Methods**

COD and Mixed Liquor Suspended Solid (MLSS) were measured according to $K_2CrO_4$ methods [18]. The amount of biomass attached on the bio-carriers was determined by using 20 carrier elements selected from the MBBSBR randomly. The carrier elements were separated from the wastewater and dried over night at 105 °C. The dried samples were weighed in order to determine the total mass ($M_t$) which included carrier element mass ($M_c$) and the fixed biomass totally. After biomass was washed off, the clean carriers weighed and the amount of biomass attached to the 20 carrier elements ($BS_{20}$) was calculated according to Eq. (1)

$$BS_{20}=M_t-M_c \quad (1)$$

In addition, the amount of biomass in the reactor (BS) could then be determined by Eq. (2). When the filling ratio (FR) is 100%, there will be 585 carriers flowing in unit volume of the reactor, and in this experiment FR value equals to 30%.

$$BS=BS_{20}\times\frac{585L^{-1}}{20}\times FR \quad (2)$$

According to the《Bergey's Manual of Systematic Bacteriology》, depending on the shape characteristics of bacteria, The gram staining [19] and other biochemical reactions are applied to identify the inoculated microorganisms.

## RESULTS AND DISCUSSION

**1. Performance of COD Removal**

Fig. 2 shows the effects of hydraulic retention time (HRT) and influent COD on the COD removal efficiency. The two factors can

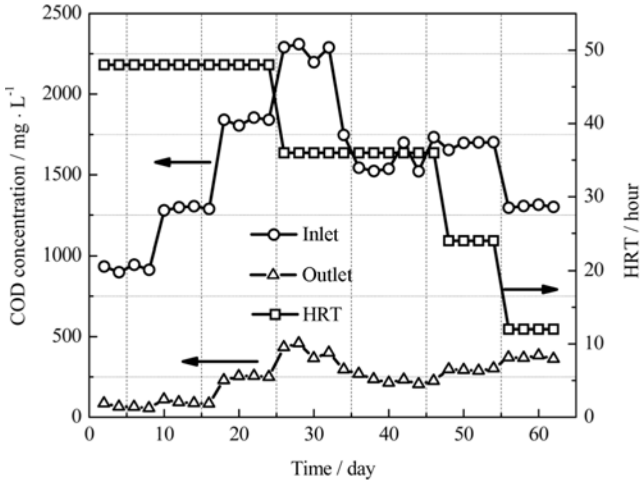


**Fig. 2. COD removal efficiency of MBBSBR with different HRT.**

be synthetically described with the organic loading rate (OLR). In the process of COD removal, the COD removal efficiency was mainly influenced by the activity of the microorganism, which had tight connections with the provided nutritions (e.g., the amounts of organic compounds, which connected with OLR) and the changing exoteric environment (e.g., such as the changing OLR). The OLR worked in two ways to impact the activity of the microorganism, and at the same time the microorganisms were responsible for the COD removal. For one thing, the heteroautotrophic bacteria would reproduce greatly and be dominators with OLR increasing; thus the COD removal would be improved. However, for another thing, an increasing OLR also means the rising concentration of the toxic contaminants, which are harmful to the growth of microorganism.

In this experiment, due to the toxicity of the coking wastewater to the microorganisms, a relatively long HRT, 48 h and a low COD value, 934.9 $mg \cdot L^{-1}$ were used at start stage. While keeping HRT at 48 h constantly, the influent COD value increased from 934.9 $mg \cdot L^{-1}$ to 1,298.4 $mg \cdot L^{-1}$ (correspondingly OLR increased from 0.467 $kgCOD \cdot m^{-3} \cdot d^{-1}$ to 0.649 $kgCOD \cdot m^{-3} \cdot d^{-1}$), the effluent COD was below 100 $mg \cdot L^{-1}$, and the COD removal efficiency was maintained at about 92.9%, which resulted from the growth of the heteroautotrophic bacteria in the MBBSBR. It demonstrated that when the influent COD is less 1,300 $mg \cdot L^{-1}$, with the increasing of influent COD concentration, the microorganisms were offered enough nutrition to grow and accumulate, and therefore, they contributed greatly to the COD removal. It was also obvious that the toxicity of contaminants to the microorganisms could be ignored when the OLR was low.

When the influent COD increased to 1,840.5 $mg \cdot L^{-1}$, as shown in Fig. 2, the effluent COD value became sensitive to the OLR variation; double times increasing in OLR could result in three times effluent COD value changing, This is because most of the contaminants were harmful to the growth of microorganism; the increasing OLR meant the rising concentration of the toxic contaminants, which restrained the growth and activity of the microorganism. As the OLR was higher, the toxicity of the contaminants in the coking wastewater gradually dominated the process of microorganism accumulation, and the microorganisms required an acclimation pro-

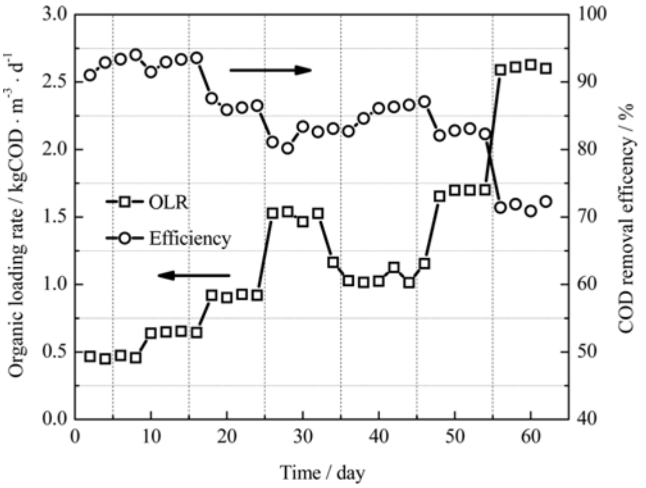


**Fig. 3. Performance of COD removal and organic loading rate in MBBSBR.**

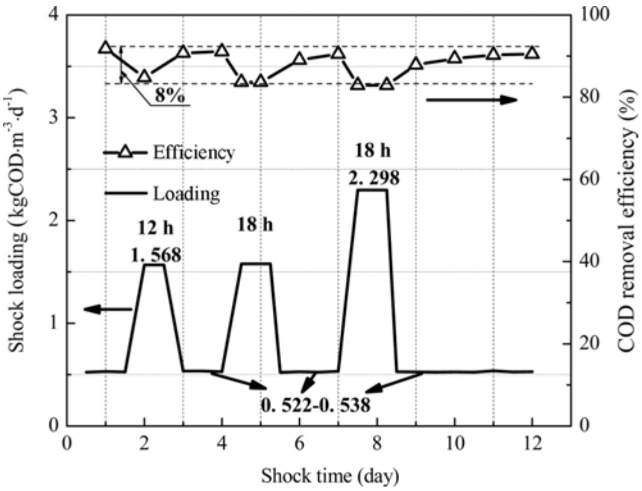


**Fig. 4. Tolerance to loading shock of MBBSBR.**

cessing to the coking wastewater. This trend is more evident with the OLR further rising; for example, when the reactor experienced the highest OLR of 2.628 kgCOD·m$^{-3}$·d$^{-1}$ at the influent COD of 1314.2 mg·L$^{-1}$ and HRT of 12 h, the effluent COD concentration became 382.4 mg·L$^{-1}$.

Fig. 3 shows the variation of OLR and COD removal efficiency during the whole experiment. When OLR was 0.449 kgCOD·m$^{-3}$·d$^{-1}$, the system could obtain 92.9% COD removal efficiency, which was attributed to the organic compounds provided by the influent OLR; this is necessary for the metabolism of microorganism. The COD removal efficiency decreased gradually down to 82.3% with the OLR increasing to 1.701 kgCOD·m$^{-3}$·d$^{-1}$; in this stage, the toxicity of the coking wastewater led to the decline in the COD removal efficiency. A stable operation of the reactor with 70.9% removal efficiency can be still observed even at 2.628 kgCOD·m$^{-3}$·d$^{-1}$ of OLR, which indicates that MBBSBR could tolerate a high OLR. The high concentration of biomass inside the MBBSBR due to immobilization and accumulation of bacteria on the bio-carrier ensures the high treatment efficiency under high loading. It indicates that after a relatively long operation, the microorganisms gradually adapted to the toxic environment, and they could live on the organic compounds existing in the coking wastewater. It demonstrates that the MBBSBR is an effective and feasible process for the removal of COD from coking wastewater.

**2. Influence of Shock Loading**

To investigate the effectiveness and stability of the whole system, experiments were performed at different shock loading rates and shock durations. In this experiment, HRT was kept at 24 h and OLR adjusted by changing the influent COD concentration.

As shown in Fig. 4, when the system operated at a normal loading rate of 0.522-0.538 kgCOD·m$^{-3}$·d$^{-1}$, the COD removal efficiency was over 91.2%. When the OLR increased suddenly to 1.568 kgCOD·m$^{-3}$·d$^{-1}$ and lasted 12 h, the COD removal efficiency of the system would decline to 84.8% and it took 36 h to retrieve COD removal of 91.1%. While the shock loading increased to 2.298 kgCOD·m$^{-3}$·d$^{-1}$ and lasted 18 h, 82.9% COD removal efficiency could be obtained, and the whole system recovered to normal operating conditions in 72 h with a COD removal of 89.4%. During the whole process, the COD removal efficiency declined only 8%, which indicates the whole system was less influenced by the shock loading and MBBSBR can more easily be operated at a high shock loading

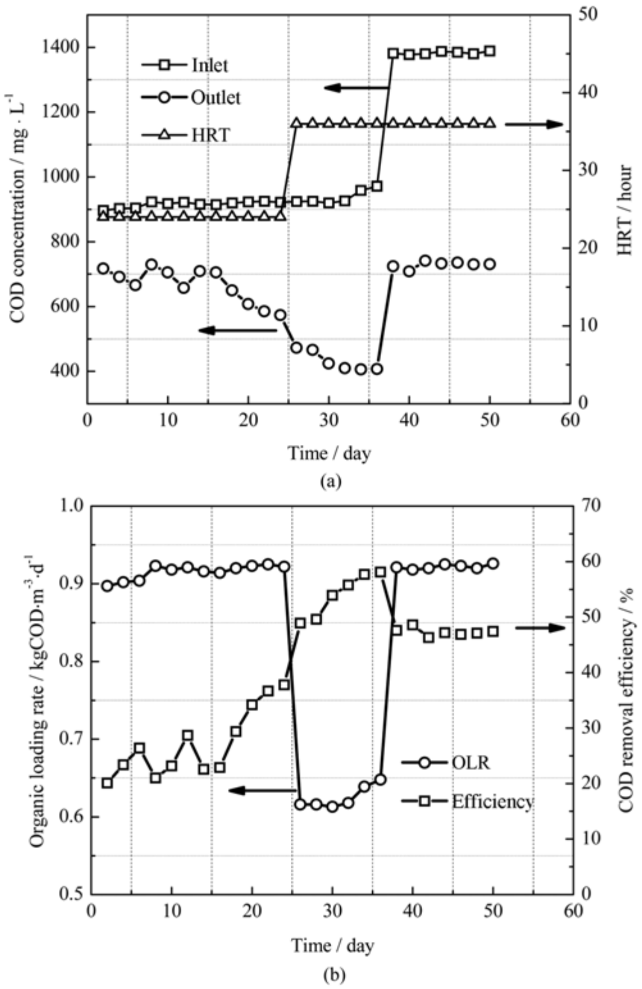


**Fig. 5. Performance of biofilm phase for COD removal.**

compared with an activated sludge process. A high organic loading rate and strong tolerance to shock loading were the excellent advantages of the biofilm reactor. It is suggested that the high accumulation of biomass in MBBSBR contributes considerably to the strong tolerance of this system to shock loading.

**3. Effectiveness and Contribution of Biofilm**

To study the biofilm accumulated on the bio-carrier used in this system and its function in COD removal, all the suspended sludge was taken out of the reactor to run a blank experiment of biofilm. The performance of the biofilm for removing COD is shown in Fig. 5.

When the influent COD concentration was controlled at about 920 mg·$L^{-1}$ with 24 h of HRT, the system presented instability at the beginning period (from day 1 to day 20), and the reasons of the instability were suggested as a high organic loading rate and a new environment exerted in the biofilm, indicating the biofilm attached on the bio-carriers required an acclimation process to the coking wastewater after it was in a new environment. The COD removal efficiency tended to increase gradually after the 20th day, when the microorganisms in the biofilm had adapted to the coking wastewater and they lived on the organic compounds in the coking wastewater. The COD removal efficiency of 34.2-58.1% at OLRs of 0.61-0.93 kgCOD·$m^{-3}$·$d^{-1}$ in the biofilm process correspond to about 40-60% of the overall COD removal efficiency obtained at the same OLRs in the biofilm plus sludge process in Fig. 3. It is obvious that the attached biofilm contributes more to COD removal. Furthermore, the biomass concentration was measured at the end of the experiment in Fig. 3, and it was found that 1,301 mg·$L^{-1}$ of biomass attached on the bio-carriers and 3,721 mg·$L^{-1}$ for the suspended biomass at the bottom of the reactor, indicating that the biofilm has higher activity than sludge. We identified the microorganisms in biofilm, and the characteristics of inoculated microorganisms are shown in Table 3. By comparing with the manual, the bacteria marked 1, 2 and 4 are pseudomonas bacteria, 3 is micrococcus bacterium, and 5 belongs to nitrobacterium. The high activity of these biomass in the biofilm process ensures the high treatment capacity and operational stability, which makes the MBBSBR process attractive and promising to application in the treatment of highly concentrated wastewater. Therefore, the self-floating bio-carrier was effective to form active biofilm in this system.

## CONCLUSIONS

MBBSBR can eliminate 92.9% of COD from coking-plant wastewater at OLR of 0.449 kgCOD·$m^{-3}$·$d^{-1}$. And 70.9% removal efficiency can be achieved even if OLR is increased to 2.628 kgCOD·$m^{-3}$·$d^{-1}$. The results indicate that MBBSBR is a good alternative of SBR to treat the coking wastewater. The shock loading test showed that MBBSBR has a strong tolerance to high OLR concentration. The blank COD removal experiment of biofilm and sludge indicated that the attached biofilm has higher activity than suspended sludge and contributes about 40-60% to the COD removal.

## ACKNOWLEDGMENTS

This work was financially supported by the Biochemical Engineering Program of 211 Project in Taiyuan University and Technology, Shanxi Nature Science Foundation (No. 20051017), Shanxi Returned Scholar Research Project (No. 2005-21) and Program for Changjiang Scholars and Innovative Research Team at University in MOE (IRT0517), China.

## NOMENCLATURE

BS : the total amount of biomass in the reactor [mg·$L^{-1}$]
$BS_{20}$ : the amount of biomass attached to the sampled carrier elements [mg]
FR : the filling ratio of the carriers in the reactor [%]
HRT : hydraulic retention time [h]
MBBSBR : the moving-bed biofilm sequencing batch reactor process
MLSS : mixed liquor suspended solid [mg·$L^{-1}$]
Mc : the mass of sampled carrier elements [mg]
Mt : the total mass composed of the sampled carrier element mass and the fixed biomass [mg]
OLR : organic loading rate [kgCOD·$m^{-3}$·$d^{-1}$]

## REFERENCES

1. R.Qi and Z. X.Yu, *Modern Chemical Industry*, **25**, 57 (2005).
2. T. Z. Liu and S. Y. Tian, *China Water and Wastewater*, **21**, 79 (2005).
3. H. Y. Wang, F. Yang and J. N. Wu, *Coal Scientific Technology*, **35**, 62 (2007).
4. P. M. Sutton, J. Hurvid and M. Hoeksema, *Water Environ Res.*, **71**, 5 (1999).
5. S. C. Liu, G. H. Wang and G. F. Xue, *WISCO Technology*, **46**, 56 (2008).
6. P. Yang, B. Wang and Y. F. Shi, *Journal of Chemical Industry and Engineering*, **53**, 1085 (2002).
7. K. H. Lee, J. H. Lee and T. J. Park, *Korean J. Chem. Eng.*, **15**, 9 (1998).
8. S. Chen, D. Z. Sun and J.-S. Chung, *Waste Management*, **28**, 339 (2008).
9. S. J. Kim, J. S. Kim and Y. Suzuki, *Korean J. Chem. Eng.*, **24**, 1042 (2007).

**Table 3. Characteristic of inoculated microorganisms**

| Strain assay | Colony characteristic | Gram reaction | Morphology | Catalase assay |
|---|---|---|---|---|
| 1 | Maize rotundity, lubricous wettish surface | Negative | Short rod | Positive |
| 2 | Maple rotundity, lubricous wettish surface, glossy | Negative | Oviform | Positive |
| 3 | Yellow rotundity, lubricous wettish surface, glossy | Positive | Sphericity | Positive |
| 4 | Bright yellow rotundity, lubricous wettish surface | Negative | Short rod | Positive |
| 5 | Radial cream, lubricous wettish surface | Negative | Ellipse | Positive |

10. Y. Choi, D. Hayes and K. Johnson, *Korean J. Chem. Eng.*, **24**, 633 (2007).
11. Y.-S. Jeong and J. S. Chung, *Process Biochemistry*, **41**, 1141 (2006).
12. S. Luostarinen, S. Luste and L. Valentin, *Water Research*, **40**, 1607 (2006).
13. P. M. Sutton and A. P. Togna, *Water Environment and Technology*, **18**, 44 (2006).
14. H. U. Nam, T. H. Lee and S. H. Park, *Korean J. Chem. Eng.*, **21**, 635 (2004).
15. I. A. Comett, S. M. Gonzalez and P. Wilderer, *Wat. Sci. Tech.*, **47**, 155 (2003).
16. J. H. Lee, H. U. Nam and T. J. Park, *Korean J. Chem. Eng.*, **16**, 303 (1999).
17. M. S. Kumar, A. N. Vaidya and N. Shivaraman, *Environmental Engineering Science*, **17**, 221 (2000).
18. American Public Health Association, *Standard methods for the examination of water and wastewater 19th ed.* APHA, Washington (1995).
19. Q. Y. Zhou and T. Y. Gao, *Microbiology of environmental engineering*, HEP, Beijing (2000).