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Pretreatment of coking wastewater using anaerobic sequencing batch reactor (ASBR)*

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Abstract: A laboratory-scale anaerobic sequencing batch reactor (ASBR) was used to pretreat coking wastewater. Inoculated anaerobic granular biomass was acclimated for 225 d to the coking wastewater, and then the biochemical methane potential (BMP) of the coking wastewater in the acclimated granular biomass was measured. At the same time, some fundamental technological factors, such as the filling time and the reacting time ratio (t_f/t_r), the mixing intensity and the intermittent mixing mode, that affect anaerobic pretreatment of coking wastewater with ASBR, were evaluated through orthogonal tests. The COD removal efficiency reached 38%~50% in the stable operation period with the organic loading rate of 0.37~0.54 kg COD/(m^3·d) at the optimum conditions of t_f/t_r, the mixing intensity and the intermittent mixing mode. In addition, the biodegradability of coking wastewater distinctly increased after the pretreatment using ASBR. At the end of the experiment, the microorganism forms on the granulated sludge in the ASBR were observed using SEM (scanning electron microscope) and fluoroscope. The results showed that the dominant microorganism on the granular sludge was *Methanosaeta* instead of *Methanosarcina* dominated on the inoculated sludge.

Key words: Anaerobic sequencing batch reactor (ASBR), Coking wastewater, Anaerobic pre-treatment
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INTRODUCTION

Coking wastewater is generated in the production of coke, coal gas, tar and other coke by-products. The coking wastewater includes inorganic pollutants such as ammonia, cyanogen, sulfocyan, heterocycle compounds and polycyclic aromatic compounds such as phenol, oils, naphthalene, pyridine, quinoline and anthracites, which are difficult to biodegradation under aerobic conditions (Ganczarczyk, 1972). Discharge of coking wastewater to the environment may cause severe contamination to it and also threaten the normal life of human beings, so it is necessary to treat the coking wastewater in order to reduce its harm to the environment.

The conventional biological treatment of coking wastewater is not efficient enough in providing the required quality criteria (Sotton *et al*., 1999; Yu *et al*., 1997).

Considerable success in wastewater treatment was achieved by addition of special microorganisms and immobilized microorganisms in laboratory-scale treatment of coking wastewater (Huang *et al*., 1995; Wang *et al*., 2002). However, the maintenance of the dominant species' bioactivity and regular supplementation of immobilized microorganisms in practical application is a problem, and their feasibility need to be confirmed.

Pretreatment was often used to make coking wastewater more amenable to biological treatment (Ganczarczyk, 1980) and the common pretreatment approach included equalization and storage, ammonia stripping, chlorination and air flotation. And recently, for treatment of hard to biodegrade wastewater,

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combinations of anaerobic and aerobic treatments were effective and less expensive, in which A/O (anaerobic-aerobic) and A^2/O (anaerobic-anoxic-aerobic) were major methods. In these systems, the anaerobic processes serve as pretreatment for partial degradation of some refractory and inhibitory organic compounds to lighten the load of subsequent anoxic and aerobic processes. So far, A/O and A^2/O are getting popular for treatment of coking wastewater (Zhang *et al*., 1998; Wen *et al*., 1991; Li *et al*., 2001; 2003). Studies showed that the anaerobic treatment could greatly improve the biodegradability of the coking wastewater, and created good condition for subsequent aerobic treatment.

ASBR is a high rate anaerobic process (US Pat. No. 5185079) developed by Dague and co-workers at Lowa State University (Dague *et al*., 1992; Sung and Dague, 1992). The promising feature of the ASBR process is that granular biomass can be achieved, and in this way higher biomass can be maintained in the reactor with efficient biomass setting and a long solids retention time (SRT) (Dague *et al*., 1966; 1970). There are many reports on studies of ASBR (Herum and Dague, 1993; Wirtz and Dague, 1996; Sung and Dague, 1995) but few of them were on the treatment of actual wastewater (Timur and Özturk, 1997; 1999).

The main purpose of this paper was to study the pretreatment of coking wastewater using ASBR, and the optimization of the ASBR process operating parameters such as the ratio of filling time to reacting time (t_f/t_r), the mixing intensity (MI) and the intermittent mixing mode (IMM) by orthogonal test. For elaborating the experiments plan, we use the method of orthogonal test for three factors at three levels in this research.

MATERIALS AND METHODS

Coking wastewater

The coking wastewater used in this study was collected from the wastewater treatment plant at Taiyuan Coke Company, China. Wastewater characteristics are summarized in Table 1. Samples were stored at 4 °C in sealed containers with minimum headspace to prevent degradation by reaction with oxygen.

Table 1 Characteristics of the coking wastewater

Parameter	Values
COD (mg/L)	400~1300
Total phenols (mg/L)	170~232
Cyanide (mg/L)	30~35
TKN (mg/L)	253~714
NH_3-N (mg/L)	230~668
Sulfides (mg/L)	65~78
pH	7.2~8.6

Experiment procedure

1. The ASBR experimental system

In this research, tests were conducted using a laboratory-scale ASBR with total volume of 14 L, which provided an effective 12 L liquid volume and 2 L headspace. The cylindrical reactor has inside diameter of 14.8 cm and liquid depth of 69.8 cm. Several 12 mm diameter ports were located along the side of the reactor to enable input and withdrawal of effluent and water samples. The ASBR reactor was installed in an incubator capable of maintaining 35 °C temperature, and had a gas scrubber. A schematic of the ASBR system used in this research is shown in Fig.1. Mixing was accomplished by recirculating biogas through a diffuser at the bottom of the ASBR. The biogas was recirculated from the top of the reactor through a 12 mm diameter tygon tubing with a homemade gas pump. In addition, an 8-L gasbag was attached to the ASBR headspace to ensure that gas was available during decanting. A foam separation bottle on the effluent gas stream to prevent diffuser clogging as a result of solids carried out of the reactors by the gas stream.

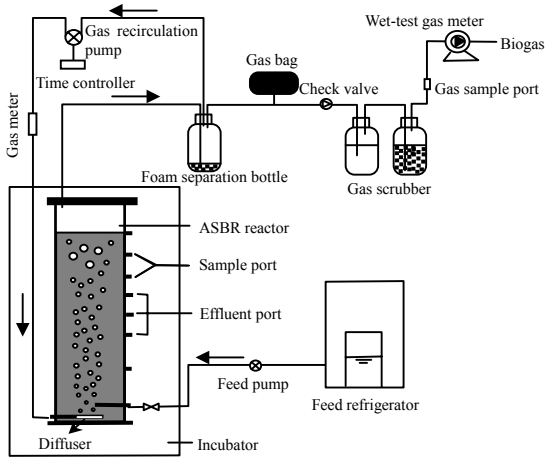


Fig.1 Schematic of ASBR

The ASBR operating principles were relatively simple as described in a previous publication (Sung and Dague, 1992). The reactor sequence included four steps: filling, reacting, settling and decanting. During the filling and reacting steps, the reactor was intermittently mixed through biogas circulation. During the settling step, mixing was shut off to allow biomass solids separation. The decanting step was implemented after sufficient solids separation had occurred. The decant volume was equal to the volume fed during the filling step.

In the initial test, 5 L anaerobic granular biomass was seeded; 7 L sucrose solution at concentration of 7200 mg/L and appropriate quantity of N and P nutrients with the COD: N: P ratio of 300:7:1 introduced into the ASBR reactor, which resulted in biomass concentration of 21.5 g mlvss/L. The system was operated for 20 d under the following conditions: pH of 7.0~8.0, fill influent of 5 L sucrose solution at concentration of 7200 mg/L and cycling period of 24 h (4 h filling period, 19 h reacting period, 0.5 settling period, 0.5 decant period).

2. The acclimation of granular biomass seed

As the anaerobic granular biomass seed was cultivated with high concentration sucrose synthetic wastewater, acclimation was necessary to induce the seeded biomass microorganisms to adapt to the coking wastewater contain not easily degradable compounds. During the acclimation, the ratio of the coking wastewater to the sucrose in the influent was increased correspondingly with the alternative decrease of the total influent concentration, until the influent contained coking wastewater without any sucrose. During this period, the settling effect was so poor that a little small sludge flowed out of the reactor. And the biomass lost by flotation not replaced by new biomass so that in this case, the settling time was extended from 0.5 h to 2.0 h. The acclimation ceased when there was just very little sludge in the effluent while there was still some biomass in the reactor; the sludge had good sedimentation property and the treatment efficiency stabilized. Total acclimation lasted for 225 d.

3. BMP (biochemical methane potential) measurement

At the end of coking wastewater acclimation, the biochemical methane potential (BMP) was measured. BMP reflects the amount of organic contaminant in the wastewater that can potentially be converted into methane by anaerobic process. Therefore, BMP can be used to evaluate the efficiency of anaerobic treatment process.

BMP was determined at 35 °C. Seeded culture of 100 ml acclimated anaerobic granular biomass and 350 ml coking wastewater (with the COD of 800 mg/L) were introduced into a 500 ml serum bottle anaerobically purged with carbon dioxide and nitrogen gases. Some background inorganic nutrients were introduced into airproofed (with rubber cap) serum bottles (Speece and McCarty, 1964) (Table 2). To eliminate error introduced by the gasses generated by the self-decomposition of anaerobic biomass, control test was needed to correct the error. The control test was prepared according to the same procedure prescribed above, but it was done without any addition of coking wastewater and acclimated anaerobic granular biomass.

The gas produced in the anaerobic reactions includes CO_2 and CH_4. Because CO_2 production does not represent COD reduction under anaerobic conditions, it is necessary to eliminate CO_2. In this study, 0.1

Table 2 Background inorganic nutrients added in BMP test

Fractions	Values in reactor (mg/L)
NH_4Cl	400
$MgSO_4·7H_2O$	400
KCl	400
$Na_2S·9H_2O$	300
$CaCl_2·2H_2O$	50
$(NH_4)_2HPO_4$	80
$FeCl_2·4H_2O$	40
$CoCl_2·6H_2O$	10
KI	10
$(NaPO_3)_6$	10
$MnCl_2·4H_2O$	0.5
NH_4VO_3	0.5
$CuCl_2·2H_2O$	0.5
$ZnCl_2$	0.5
$AlCl_3·6H_2O$	0.5
$NaMoO_4·2H_2O$	0.5
H_3BO_3	0.5
$NiCl_2·6H_2O$	0.5
$NaWO_4·2H_2O$	0.5
Na_2SeO_3	0.5
Cysteine	10
$NaHCO_3$	6000

mol/L sodium hydroxide solution was used as a CO_2 absorbent, so the gas produced in the anaerobic reactions contains CH_4 only. Gas production from all bottles was measured periodically at incubation temperature (35 °C) by the liquid displacement method.

4. Orthogonal test

Empirical data obtained during the acclimation procedure revealed that three key factors affect COD removal efficiency were: the ratio of filling time to reacting time (t_f/t_r), the mixing intensity (MI) and the intermittent mixing mode (IMM). In order to select the optimal ASBR operating parameters, orthogonal test was conducted after the acclimation. In the orthogonal test, the operating cycle period, settling period and decant period were 24, 2.0, and 0.5 h respectively, and influent pH was adjusted to 7.0~8.0.

The typical operation of ASBR with fast filling time (Dague *et al*., 1992; Sung and Dague, 1992) leads to a low ratio of fill time to reaction time (t_f/t_r). But this operating strategy may cause the acid formation problem observed by Suthaker *et al*.(1991). Considering the toxicity of the coking wastewater and the accumulation of acid resulting from the fast filling, the filling time was extended properly and three levels of the t_f/t_r was selected as 0.3, 0.5 and 1.0 in this study. As to the mixing intensity, sufficient intensity should be selected to ensure uniform conditions throughout the reactor and effective contact of the wastewater with the granulated biomass to improve the mass transfer flux. While excessive intensity of mixing may shear the anaerobic granular biomass and result in poor solids separation. Usually the mixing was supplied by biogas recirculation or mechanical agitation (when biogas cannot insufficiently provide suitable mixing) (Sung and Dague, 1995; Zaiat *et al*., 2001; Rodrigues *et al*., 2003). It was reported that intermittent mixing rather than continuous mixing resulted in superior performance (Dague *et al*., 1970). Therefore, intermittent mixing supplied by biogas was applied in this study.

In the experiments plan we use the method of orthogonal test for three factors at three levels. By levels we mean the values taken by the factors. Table 3 lists the factors to be studied and the assignment of the corresponding levels. The orthogonal array $L_9(3^4)$ shown in Table 4 was chosen with 9 rows corresponding to the number of tests and 4 columns at three levels.

Table 3 Assignment of the levels to the factors[a]

Levels	Factors		
	t_f/t_r	*MI*	*IMM*
1	0.3	0.017	30 s/20 min
2	0.5	0.025	30 s/30 min
3	1.0	0.033	100 s/45 min

[a] t_f/t_r: The fill time to reaction time ratio; IMM: Intermittent mixing mode; MI: Mixing intensity (L biogas/(L reactor volume·min))

Table 4 Orthogonal array $L_9(3^4)$ in this test[a]

$L_9(3^4)$ test	t_f/t_r	*MI*	*IMM*	Blank
1	0.3	0.017	30 s/20 min	1
2	0.3	0.025	30 s/30 min	2
3	0.3	0.033	100 s/45 min	3
4	0.5	0.017	30 s/30 min	3
5	0.5	0.025	100 s/45 min	1
6	0.5	0.033	30 s/20 min	2
7	1.0	0.017	100 s/45 min	2
8	1.0	0.025	30 s/20 min	3
9	1.0	0.033	30 s/30 min	1

[a] t_f/t_r: The fill time to reaction time ratio; IMM: Intermittent mixing mode; MI: Mixing intensity (L biogas/(L reactor volume·min))

5. Stable operation of ASBR

The optimal conditions selected through the orthogonal test were applied for stable ASBR operation. And the biomass in the ASBR reactor, the BOD_5/COD ratio of the influent and the effluent were determined during the stable operation.

Analytical methods

Soluble COD, BOD_5 were analyzed following the procedures in the standard methods (American Public Health Association, 1992), and samples contained no SS (suspended solid). The biomass in ASBR was measured by weighing method.

Size classification was achieved by wet sieving in perspex cylinders (Ø 65 mm×100 mm) equipped with a sieve plate. After filling the sieve column with mineral medium and placing the sample on top, it was flushed with nitrogen gas. During gentle intermittent swirling the granules settle throng the sieve plates according to their size.

RESULTS AND DISCUSSION

BMP assay

When there was no biogas generated in both

bottles of the sample test and the control test, the BMP test ended. The results of the BMP study are given in Fig.2 showing that the net gas production of 46.3 ml was equal to the sample test gas production volume minus the control test gas production volume.

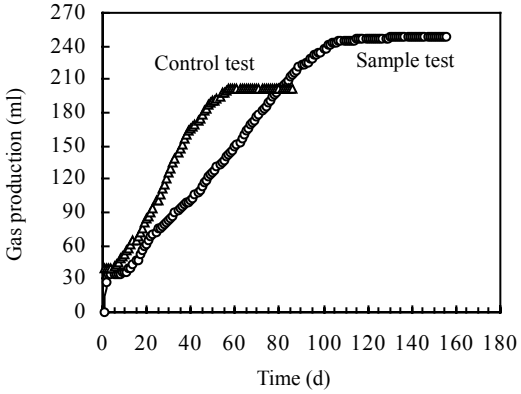


Fig.2 BMP determination gas production curve

BMP was referenced either to sample volume (m^3 CH_4/m^3 sample), sample mass (m^3 CH_4/kg sample) or sample organic content (m^3 CH_4/kg COD) (Oven *et al*., 1979). The latter method permits direct transfer of results into percent organic matter converted to methane. Since 395 ml methane at 35 °C is equivalent to 1 g of COD removed from the wastewater during the anaerobic process, there is a stoichiometric relationship which allows calculation of the COD reduction in the liquid phase. In the sample test of the BMP assay, 350 ml coking wastewater was assayed with 100 ml of anaerobic granular biomass inoculums. After 130 d of incubation, 248.6 ml CH_4 was produced in all. As to the control test, there were 100 ml anaerobic granular biomass inoculums without the addition of coking wastewater. After only 58 d of incubation, the gas production stopped, and 202.3 ml CH_4 was produced in all. Therefore, the net CH_4 production was 46.3 ml, and the BMP result was 0.165 m^3 CH_4/kg COD.

In theory, 350 ml coking wastewater with COD of 800 mg/L used in the BMP assay should produce 110.6 ml CH_4 at 35 °C under anaerobic conditions based on the stoichiometric relationship mentioned above. Therefore, the percent coking wastewater converted to methane was 41.9%.

The BMP gas production curve in Fig.2 showed that in the first 58 d, the gas production rate of the control test was higher than that in the coking wastewater sample test. This showed that the coking wastewater inhibiting effect on anaerobic biomass inoculums, but that the anaerobic microorganisms adapted to coking wastewater gradually after long time acclimation. Acclimation of 225 d was conducted before the BMP assay, which showed that the gas production rate was still low. The gas production lasted for 130 d, which was far more than the 30~60 d suggested for BMP assay. From the result of the BMP assay it could be concluded that the biodegradability of the coking wastewater was rather low. Therefore, long time acclimation of the inoculated anaerobic granular biomass to the coking wastewater is essential for satisfactory treatment.

Orthogonal test

The test results of the 9 tests arranged by orthogonal array L_9 (3^4) are given in Table 5 presenting the effect of the various factor levels on the COD removal efficiency. The tests under each testing condition were conducted for 15 d. The average of the last ten days' COD removal efficiency is given in the last row of Table 5. In the orthogonal test, the error in the response variable (COD removal efficiency) resulted from the fluctuating influent coking wastewater concentration. There are three levels of each factor in Table 5. With every level occurring three times, so the total number of the test was 9.

Table 5 can be used to analyze the optimal level for every factor. For the factor t_f/t_r, $K_{12}>K_{13}>K_{11}$. It shows that level 2 (t_f/t_r was 0.5) was the optimal level for the factor of t_f/t_r. For the factor MI, $K_{22}>K_{23}>K_{21}$. It indicates that level 2 (mixing intensity was 0.025 L biogas/(L reactor volume·min)) was the optimal level for the factor of mixing intensity. For the factor IMM, $K_{33}>K_{32}>K_{31}$. It shows that level 3 (intermittent mixing mode was 100 s/45 min) was the optimal level for the factor intermittent mixing mode.

In Table 5, S_j is the quadratic sum of dispersion factor j. From S_j we can determine the importance of different factor. Therefore, the relation $S_1>S_3>S_2$ indicates that the factor t_f/t_r is the most important parameter affecting treatment efficiency.

In addition, R_j the range of K_{jl}, and the value of R_j reflect the importance of the factor j. Here $R_1>R_3>R_2$, which indicates that the factor of t_f/t_r was the most important parameter affecting treatment efficiency.

Table 5 The orthogonal array for COD removal efficiency

Test	1	2	3	4	Y_j (Mean value)
	t_f/t_r	*MI*	*IMM*	Blank	COD removal efficiency
1	0.3	0.017	30 s/20 min	1	16.6
2	0.3	0.025	30 s/30 min	2	15.7
3	0.3	0.033	100 s/45 min	3	15.9
4	0.5	0.017	30 s/30 min	3	25.2
5	0.5	0.025	100 s/45 min	1	35.5
6	0.5	0.033	30 s/20 min	2	27.0
7	1.0	0.017	100 s/45 min	2	20.4
8	1.0	0.025	30 s/20 min	3	19.3
9	1.0	0.033	30 s/30 min	1	25.0
K_{j1}	48.2	62.2	62.9	77.1	K=200.6
K_{j2}	87.7	70.5	65.9	63.1	P=4471.2
K_{j3}	64.7	67.9	71.8	60.4	
R_j	39.5	8.3	8.9	16.7	
Q_j	4733.5	4483.3	4484.8	4524.7	Q=4812.7
S_j	262.3	12.1	13.6	53.5	S_T=341.5

t_f/t_r: The fill time to reaction time ratio; MI: Mixing intensity (L biogas/(L reactor volume·min)); IMM: Intermittent mixing mode; K_{jl}: The sum of the three results according to the specific level in the row j, here l represents the level, j represents the row. In this paper, for example, $K_{11}=Y_1+Y_2+Y_3$, $K_{23}=Y_3+Y_6+Y_9$, and so on; $K=\sum_{l=1}^{3}K_{jl}$, $P=\frac{1}{9}K^2$, $Q_j=\frac{1}{3}\sum_{i=1}^{3}K_{jl}^2$, $S_j=Q_j-P$, $Q=\sum_{i=1}^{9}Y_j^2$, $S_T=Q-P$, $R_j=\max\{K_{jl}, l=1,2,3\}-\min\{K_{jl}, l=1, 2, 3\}$

The same result of analysis was obtained by using S_j (the quadratic sum of dispersion), so the result from this orthogonal test was credible. As for the intermittent mixing mode, the best value of 100 s/45 min was the biggest of three values (30 s/20 min, 30 s/30 min and 100 s/45 min). So higher IMM values were used for conducting further study which revealing poor effect of sedimentation on biomass in the reactor. Therefore, t_f/t_r of 0.5, mixing intensity of 0.025 L biogas/(L reactor volume·min) and intermittent mixing mode of 100 s/45 min, were the optimal conditions for the orthogonal test.

Stable operation of ASBR

According to the orthogonal test, the COD removal efficiency increased as intermittent mixing time increased from 30 s/30 min to 100 s/45 min. So it was estimated that the COD removal efficiency would increase as the intermittent mixing time because larger than 100 s/45 min. However, a 20 d's experiment operated under condition of larger intermittent mixing time (120 s/45 min) showed that there was a decline of biomass in the ASBR and that the increase in suspended sludge in the effluent was due to the long mixing time. So 100 s/45 min was selected as the optimal intermittent mixing mode.

A stable operation of three months was carried out under the optimal conditions stated above. In ASBR, when the influent coking wastewater COD concentration was 796~1304 mg/L, influent ammonia nitrogen concentration was 230~668 mg/L, and influent pH was 7.2~8.6, COD removal rate can steadily reach 38%~50%, which agrees with the BMP determination result. Furthermore, the BOD_5 and COD of the effluent and influent of the coking wastewater to the ASBR were measured, and the sample measured for BOD_5 and COD contained no SS. The ratio of BOD_5/COD, COD removal efficiency and biomass in the stable operation are given in Table 6. The results indicated that the average ratio of BOD_5/COD to the influent was 0.27, while the average ratio of BOD_5/COD to the effluent was up to 0.58, which showed that the biodegradability of the coking wastewater increased greatly after the pretreatment using ASBR. During the stable operation, there was higher biomass to be maintained in the reactor and solids retention time (SRT) was more than 150 d, so there was very little biomass overflowing out of the reactor (Table 6).

During the stable ASBR operation, there was a steady-going run and the COD removal efficiency was as high as 38%~50% even with the fluctuating in-

Table 6 The result in the stable ASBR operation

Time (d)	COD removal efficiency (%)	BOD_5/COD (Influent)	BOD_5/COD (Effluent)	Biomass (g/L)	Effluent SS (mg/L)	*SRT* (d)
7	41.3	0.28	0.54	23.5	152	154.6
14	42.5	0.29	0.60	23.8	145	164.1
21	39.6	0.32	0.54	23.2	136	169.1
28	41.0	0.31	0.59	23.4	143	163.6
35	44.6	0.31	0.61	23.8	139	171.2
42	50.3	0.29	0.61	23.6	143	165.0
49	45.7	0.23	0.57	23.7	147	161.2
56	44.6	0.23	0.58	24.0	151	158.9
63	45.1	0.26	0.62	24.1	160	150.6
70	43.5	0.27	0.60	23.9	144	166.0
77	38.6	0.29	0.55	23.7	145	163.4
84	42.9	0.28	0.56	23.6	138	171.0
91	45.8	0.27	0.57	23.8	143	166.4

fluent of coking wastewater. According to Table 6, the BOD_5/COD ratio increased greatly. All these results were due to the higher granular biomass maintained in the ASBR, and the granular biomass had good sedimentation property which resulted in the long SRT inductive to treatment efficiency. The different bacteria on the granular biomass are spaced farther a part than the bacteria of the suspended biomass, and can slightly metabolize the intermediate products of the reaction.

Granular biomass microorganism

The seeded anaerobic granular biomass used in the ASBR had relatively larger particle size, most of which were 1.0~3.0 mm, among which 9.6% were larger than 3 mm. After the granular biomass had acclimated to coking wastewater, the shape of the granular biomass became approximately spheroid, the particle size decreased mostly to about 0.5~2.0 mm, with no particle being larger than 3 mm. Some large particles were bonded together by several small particles. The granular biomass was characterized by softness, tenacity, and viscosity.

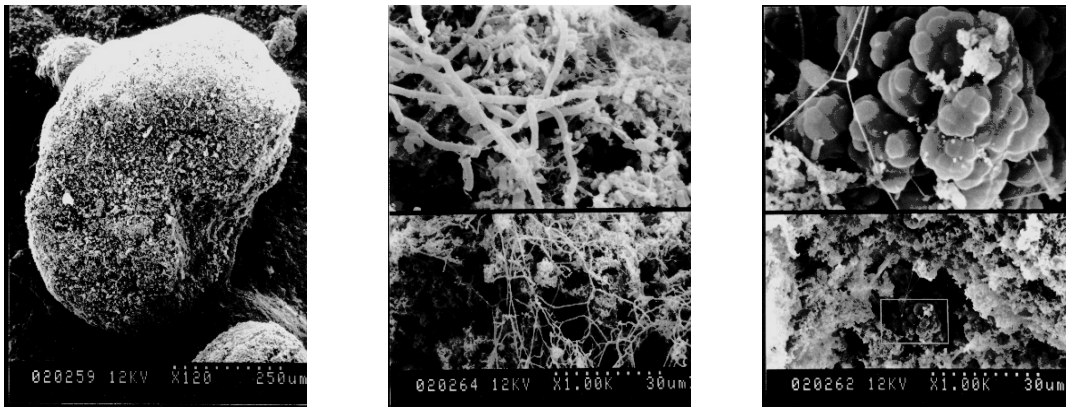
The predominant bacteria attached to the seeded granular biomass were *Methanosarcina* both on the surface of the particle and in the middle of the sludge (Tian, 2001). After ASBR anaerobic pretreatment of coking wastewater, the microorganisms on the granular biomass in the ASBR was observed using SEM (scanning electron microscope) and fluoroscope. The surface of the granular biomass in the ASBR was densely occupied by many small cavities (Fig.3a), which were the passages formed due to the release of gas generated by internal bacteria and to inlet's substrate entering into the biomass. The observed result showed that the main body of granular biomass was *Methanosaeta* in the middle part of the granular sludge (Fig.3b). A small mass of *Methanosarcina* was found in the outer hole of the granular biomass (Fig.3c). The top parts of Fig.3b and Fig.3c are amplification of the bottom parts of the pictures. *Methanosaeta* and *Methanosarcina* have different metabolization characteristics (μ_{max} and k_s), and *Methanosaeta* has lower substrate affinity than *Methanosarcina* as mentioned elsewhere (Sekiguchi *et al*., 1999; Wu *et al*., 1996). Many substances in coking wastewater in the influent of the ASBR resist biodegradation and the concentration of influent was low, which were favorable for *Methanosaeta* instead of *Methanosarcina* to be the dominant bacteria in the ASBR as observed in this study.

CONCLUSION

The following conclusions were derived from the results of the tests described above:

In this study, the acclimation lasted for 225 d. The long time acclimation of the inoculated anaerobic granular biomass was essential for inducing the microorganisms to adapt to the coking wastewater without disrupting granular biomass activity.

The BMP assay indicated that 0.165 m^3 CH_4/kg COD had been converted into methane in coking



(a) (b) (c)

Fig.3 SEM images of granular biomass in ASBR (a) Surface of the granular biomass; (b) *Methanosaeta* in the middle part of the granular sludge, the up part is magnification (×6) of the lower part; (c) *Methanosarcina* in the outer hole of the granular biomass, the up part is magnification (×6) of the lower part

wastewater under anaerobic condition. The result of the BMP assay showed that the maximum mechanization of the coking wastewater under anaerobic condition was 41.9%.

Analysis of the orthogonal test results showed that when the coking wastewater was pretreated using ASBR, the optimal t_f/t_r, the mixing intensity and the intermittent mixing mode were 0.5, 0.025 L biogas/(L reactor volume·min) and 100 s/45 min respectively. The cycle of ASBR operation was 24 h, of which the filling time was 7.17 h, the reacting time was 14.33 h, the settling time was 2.0 h and the decant time was 0.5 h. When the OLR ranged from 0.37 to 0.54 g COD/(L·d), the removal efficiency of COD reached 38~50%. The SRT was more than 150 d.

There was a great increase of the biodegradability of coking wastewater after its pretreatment with ASBR, and the ratio of BOD_5/COD also increased from 0.27 in influent to 0.58 in effluent.

At the end of treatment of coking wastewater using ASBR, the predominant bacteria on the granular biomass was *Methanosaeta* instead of *Methanosarcina* that dominated in the seeded granular biomass.

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