

Start-up of a bench-scale UASB reactor treating real substitute natural gas wastewater with glucose addition

Jun Li^{1*}, Tao Xiang¹ and Dongning Chen²

¹School of Municipal and Environmental Engineering, Shenyang JianZhu University, Shenyang 110168, Peoples Republic of China.

²Shenyang Urban Planning Design and Research Institute, Shenyang 110168, Peoples Republic of China.

*Corresponding Author E-mail: junlee@sjzu.edu.cn

Abstract

Investigation on a up-flow anaerobic sludge blanket (UASB) treating real substitute natural gas wastewater (SNGW) with glucose addition was conducted. The UASB was analyzed and addition of glucose remained as co-substrate during the whole start-up period. Excellent treatment performance was achieved when SNGW was treated with 500 mg l⁻¹ glucose. The anaerobic reactor was operated continuously at 35 °C for 125 days. After increasing the organic loading rate, fluctuations in removal efficiencies were observed, which were partly reversible. At the end of the reactor operation, removal of chemical oxygen demand was 60% and 44% respectively. The organic loading rate and hydraulic retention time was 1.2 kg COD/(m³·day) and 72 hrs. Gas chromatography–mass spectrometry (GC/MS) analysis showed that the phenolic compounds decreased to a low level at this condition. The main phenols in the anaerobic effluent were phenol, m-cresol, o-cresol and 2-methyl-Naphthalene. The biodegradation process of microorganisms showed the effect on toxic organic compounds of SNGW with the glucose addition. On the whole, the system exhibited good stability in terms of COD and phenols, and was found to be efficient and convenient method for SNGW.

Key words

Glucose, Phenols, Substitute natural gas wastewater, UASB

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Introduction

In the past decades, with rapid decrease in petroleum resource and increase of crude oil price, application of coal in energy and chemical industries has become more and more important (Gai *et al.*, 2008). Coal conversion processes are promising alternatives for the production of gaseous fuels. But, a coal conversion plant consumes a large amount of water during its manufacturing processes and wastewater is produced. Usually, treatment process consisting of string and extracting is adopted to remove most of the phenols, ammonia, hydrogen sulphide and carbon dioxide prior to biological treatment. Wastewater is discharged mainly from the gas washing and condensing operations of the coal

gasifier. As the wastewater contains high-concentration of complex phenolic compounds which fluctuate in a wide range, the existing treatment processes do not work well enough in many coal-gasification plants (Gai *et al.*, 2008).

In recent years, several attempts have been made to treat with SNGW. Wastewater treatments that effectively remove phenolic compounds include: anoxic, aerobic biological methods (Bajaj *et al.*, 2008; 2010), adsorption and combinations of both (Ganczarzyk and Benedek, 1983, Humenick and Shellenbarger, 1986). Anaerobic treatment has been commonly applied in industries all over the world. Anaerobic biological system offer more potential tool for the treatment of SNGW due to high organic content, as these

systems do not require high energy for aeration and allow recovery of energy in the form of methane in a close system.

Many researchers, including our research group, have done a lot of study in such areas as flow pattern, kinetic, toxicity inhibition, start-up and operation characteristics (Chu LB *et al.*, 2005, Karnchanawong and Kabtum, 2014). Moreover, UASB reactors have been successfully applied for the treatment of brewery wastewater, starch wastewater, molasses alcohol slops, domestics and municipal wastewater (Zhang *et al.*, 2008). But use of UASB reactors in treating SNGW has not been reported earlier.

All over the world, a lot of reactors in the laboratory were fed with synthetic influent, yet not much is known about the SNGW from the real wastewater treatment plant. The real SNGW is more complicated than synthetic water. The anaerobic treatment is generally followed by aerobic treatment and sometimes advanced treatment is necessary in order to meet the discharge standard. If toxicity can be reduced to low level in anaerobic conditions, aerobic treatment may be much simpler and less costly.

Based on the analysis, to reduce the treatment time and land requirement, a rapidly start-up method was investigated in anaerobic reactor. The study was carried out on a bench-scale anaerobic reactor treating the real SNGW with an aim to adapt the microbial flora to start-up the UASB reactor rapidly.

In the present study, the UASB with the current SNGW was analyzed and glucose was added as co-substrate for the whole start-up period. As a comparison, different glucose concentrations were taken into consideration. The effect of glucose concentrations on COD and remove of phenols was studied for optimum addition. Additionally, the aim of this study was also to evaluate the performance (mainly on the removal of COD) of the reactor and to further investigate the removal of phenolic compounds and other toxic organic compounds (by GC/MS analysis) of this real SNGW. Degradability of main organic pollutions has also been discussed. The data obtained in this paper are useful for building a database of hazardous organic diversity in industrial SNGW treatment.

Materials and Methods

Experiment setup : The schematic diagram of bench-scale UASB reactor used in the present study is shown in Fig.1. The UASB reactor was made up of a plexiglass column with an

internal diameter of 10 cm and an overall height of 200 cm. The total volume of the reactor was 15.7 litre, and the working volume was 13.4 litre (excluding head space). The column consisted of three parts: bottom, middle and top with a height of 150 cm and the height-per-diameter ratio of 1:5.

The UASB reactor was operated under mesophilic condition (35°C) and its temperature was maintained by circulating hot water through the reactor jacket.

The aerobic reactor was not core, but it played important role in eliminating COD produced in UASB. The aerobic reactor was also made up of a plexiglass column, with an internal diameter of 15 cm and an overall height of 132 cm, the total volume was 23.3 litre and the working volume was 17.8 litre. A PVC (polyvinyl chloride) flexible filler was used as a support medium. The temperature in the aerobic reactor was kept constant at 25°C.

Inoculums (seed sludge) : Anaerobic digested sludge was obtained from the Wastewater Treatment Plant. It was black in color with good settlement. The digested sewage sludge, which contained SS and VSS concentration of the sludge was 65 g l⁻¹ and 24.7 g l⁻¹, respectively and the value of VSS/SS was 0.38. The amount of inoculated sludge was approximately 55% volume of the reaction part.

Substitute natural gas wastewater (SNGW) : The real SNGW was obtained from Coal Industry Group. The samples were preserved in PVC containers. A detailed description of

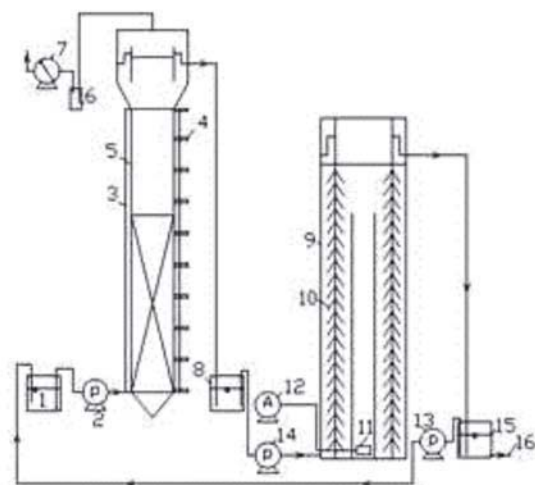


Fig. 1 : Schematic diagram of UASB and aerobic reactor treating SNGW. 1: Feed tank; 2: Anaerobic influent pump; 3: Water seal; 4: Sampling ports; 5: UASB; 6: Gas seal; 7: Gas meter; 8: Storage vessel; 9: Aerobic reactor; 10: Filler; 11: Aeration joint; 12: Aeration pump; 13: Reflux pump; 14: Aerobic influent pump; 15: Outlet tank; 16: Outlet pipe

Table 1 : Characteristics and composition of raw SNGW

Parameter	Value
COD (mg l ⁻¹)	3500-4000
BOD (mg l ⁻¹)	500-700
pH	8.5-9
Total phenols (mg l ⁻¹)	850-950
Volatile phenols (mg l ⁻¹)	450-530
NH ₄ ⁺ -N (mg l ⁻¹)	150-180
VFA (mg l ⁻¹)	80-120

the composition and features of SNGW is summarized in Table 1.

Analytical methods : Effluent was collected and filtered for further analysis. Before analysis, the liquid sample was filtrated first with filter paper. As per standard protocol of APHA (2012), the following parameters were analyzed: COD, BOD, total phenols, volatile phenols. Net COD was calculated following the formula :

$$\text{Net COD} = \frac{\text{COD}_{\text{in}} - \text{COD}_{\text{out}} - C_g}{\text{COD}_{\text{in}} - C_g} * 100\%$$

where, COD_{in}, influent concentration (mg l⁻¹); COD_{out}, effluent concentration (mg l⁻¹); C_g, glucose concentration (mg l⁻¹).

The concentration of VFA was determined by gas chromatography (Shimadzu, Japan) by flame ionization detector (FID). For GD/MS analysis, 100 ml waste water samples were first extracted with dichloromethane, then dehydrated with dry sodium sulphate, condensed into 1 ml and finally analyzed with Autosystem XL GC/ TurboMass MS (Perkin Elmer, US). Photomicrographs were taken by scanning electron microscope (SEM) (HITACHI-S3000N, Hitachi Ltd., Tokyo, Japan).

Start-up : The feed nutrients consisted of the following macro-nutrients: K₂HPO₄ (20 mg l⁻¹), KH₂PO₄ (10 mg l⁻¹), CaCl₂·2H₂O (20 mg l⁻¹), FeSO₄·7H₂O (15 mg l⁻¹) and MgSO₄·7H₂O (50 mg l⁻¹) And micro-nutrients: MnCl₂·4H₂O (0.5 mg l⁻¹), ZnCl₂ (0.5 mg l⁻¹), CuCl₂ (0.5 mg l⁻¹), (NH₄)₂

MoO₄·4H₂O (0.5 mg l⁻¹), AlCl₃ (0.5 mg l⁻¹); CoCl₂·2H₂O (0.5 mg l⁻¹), NaBO₂·10H₂O (0.3 mg l⁻¹) and NiCl₂·2H₂O (0.5 mg l⁻¹). The influent pH of raw SNGW ranged from 8.5 to 9 and no additional alkali was needed. During the start-up period, reactor pH was adjusted to 7.0 using hydrochloride and glucose was added in the reactor to keep the initial concentration at 500 or 1000 mg l⁻¹. The operational conditions are shown in Table 2.

Results and Discussion

Performance of startup stage : The UASB reactor data during the start-up is shown in Fig. 2-9.

At the initial stage of reactor operation between 1-41 days, HRT of the reactor remained for 96 hrs. The reactor was once fed with dilute tap water and added glucose of concentration 1000 mg l⁻¹. At first, the influent total COD and phenols were about 2500 mg l⁻¹ and 450 mg l⁻¹, the COD and phenols loading rate was 0.6 kg COD/(m³·day) and 0.11 kg/(m³·day) respectively. Only 28% COD was removal on the first day. The COD removal reached >44% within one week of operation. Then, the OLR was lightly increased to about 0.8 kg COD/(m³·day). There was a temporary decrease in removal which improved as soon as the microbial flora was acclimatized to new concentration and the phenol removal was 29%. Accumulation of non-degraded phenols in the reactor totally prevented COD removal. As the nature of wastewater varied on the 28th day, the OLR decreased to 0.7 kg COD/(m³·day), the COD and phenol removal reached to 72% and 65% respectively.

The mass distribution between total dissolved COD, VFA and phenols in the effluent indicated that there was an accumulation of intermediate products of anaerobic phenol metabolism in UASB. But this was temporary and at the end of this stage, the COD and net COD removal reached to 67% and 49%. The phenols and volatile phenols removal reached to 75% and 64%, respectively, on the 41st day.

Table 2 : Operational conditions in the anaerobic treatment of SNGW

Stage	Times (days)	COD _{in} (mg l ⁻¹)	TPh _{in} (mg l ⁻¹)	Glucose (mg l ⁻¹)	Dilute water	Avg. OLR (kg COD/(m ³ ·day))	Avg. PLR (kg/(m ³ ·day))	HRT (hour)
1	1-41	2449-3033	388-466	1000	Tap water	0.7	0.12	96
2	42-64	2374-2885	449-496	500	Tap water	0.6	0.12	96
3	65-112	2374-2952	452-493	500	Aerobic water	0.9	0.17	72
4	113-125	3102-3618	457-512	1000	Aerobic water	1.2	0.17	72

TPh_{in}: the influent of the total phenol, PLR: phenol loading rate, Avg.: average

The glucose concentration decreased from 1000 to 500 mg l⁻¹ on day 42nd. Between 42nd-64nd days, HRT of the reactor was kept for 96 hrs, the reactor was fed once with dilute tap water and glucose concentration was decreased from 1000 mg l⁻¹ to 500 mg l⁻¹. The total COD and phenol content in the influent was about 2374 mg l⁻¹ and 470 mg l⁻¹, the COD and phenols loading rate was 0.6 kg COD/(m³·day) and 0.11 kg/(m³·day) respectively. When OLR was decreased to 0.6 kg COD/(m³·day), the performance was stable and on average 60% COD removal and COD removal was kept at >50%. It was observed that presence of sludge in the UASB reactor reduced exposure of microorganisms to phenol toxicity. The decreased OLR did not have any negative effect on COD removal. At the end of 2nd stage, COD removal was 65% with 40% net COD removal. The phenol and volatile phenol removal reached 59% and 68%, respectively on 64th day. The present study showed that phenol concentration at 470 mg l⁻¹ was degraded by anaerobic system with external carbon source.

The reactor was in a steady state except for some short term fluctuations in removal efficiencies during 2nd stage. It was observed that the fed water with decreased glucose addition, the COD and phenol removal reached its maximum values when 500 mg l⁻¹ glucose was added. So, it can be inferred that addition of glucose resulted in increased methane production and phenol degradation in the treatment of SNGW.

Dissolved oxygen in aerobic reactor was 4.8-5.5 mg l⁻¹ and this effluent was kept in a vessel and later on it was added to SNGW artificially. The vessel was maintained as a closed barrel with a narrow mouth, without any external air supply. On adding to SNGW, low dissolved oxygen was observed, as DO concentration was approximately nil in UASB reactor.

Between days 65th to 112nd, HRT of the reactor decreased to 72 hrs; the reactor was once fed with aerobic water with glucose concentration of 500 mg l⁻¹. Total COD and phenols in the influent was around 2700 mg l⁻¹ and 470 mg l⁻¹, the COD and phenol loading rate were 1kg COD/(m³·day) and 0.15 kg/(m³·day). In UASB reactor, dilution with aerobic water had a negative effect on COD and phenol removal efficiency and resulted in steep decline. The COD and phenol removal efficiency decreased to 32% and 14% on the 74th day. The result indicate that the reactor biomass was not able to adapt the feeding of water. The inhibition effect of phenol diluted with

aerobic water was more profound on methanogenic bacteria than dilution with tap water. The aerobic water consisted of toxic substances. With the reactor in a working state, the COD and net COD removal reached upto 65% and 47%. The phenol and volatile phenol removal reached 25% and 52% respectively on day 112nd.

Typical character of a relatively slow growth in UASB was observed, which might be an adaptive response for increasing the carbon concentration. Organic carbon was also utilized for the growth of biomass. Between day 113th to 125th, HRT of the reactor was kept for 72 hrs the reactor was fed once with dilute aerobic water and 1000 mg l⁻¹ glucose. The influent total COD and phenol was around 3600 mg l⁻¹ and 480 mg l⁻¹, the COD and phenol loading rate were 1.2 kg COD/(m³·day) and 0.15 kg/(m³·day). In the UASB reactor, the COD and net COD removal reached to 60% and 49%, respectively. The phenol and volatile phenol removal reached upto 28% and 58% respectively, on the 125th day. At this stage, the glucose concentration in the influent feed was increased from 500 mg l⁻¹ to 1000 mg l⁻¹. The phenol removal efficiency was 34%, but when the reactor was run longer under given operational conditions these efficiency decreased to 28%, which might be due to slow growth of phenol adapted microorganisms, as well as due to phenol toxicity to glucose and phenol consuming microorganisms in the reactor that resulted in low utilization of available substrate. Glucose utilization enhanced degradation of toxic compounds and strengthened the digestion activity of refractory compounds. Under unfavorable conditions, more adverse effect on phenol removal than COD removal was observed because easily degradable glucose was the major carbon source in the feed. The UASB reactor removal of the remaining COD and phenol may be complementary under such condition.

In the present study with complex phenols of SNGW, simultaneous degradation of COD and phenols were observed. The results suggest the capability of microorganisms to degrade COD and phenols and the pathways during the degradation of complex phenols mixture under anaerobic conditions. The pH and VFA concentration remained in the favorable working range for anaerobic conditions as 6.5-8.2 and 73-330 mg l⁻¹ respectively.

Performance of the reactors showed that pH of the effluent decreased from 7 to 8.4. The reactor operation was terminated on 125th day, as the sludge started to accumulate. At the end of operation, the removal of COD and net COD

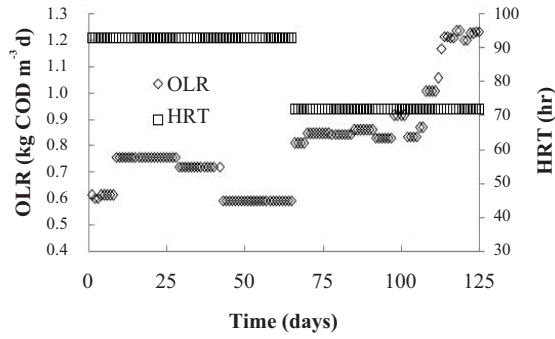


Fig. 2 : OLR and HRT from day 0 to 125

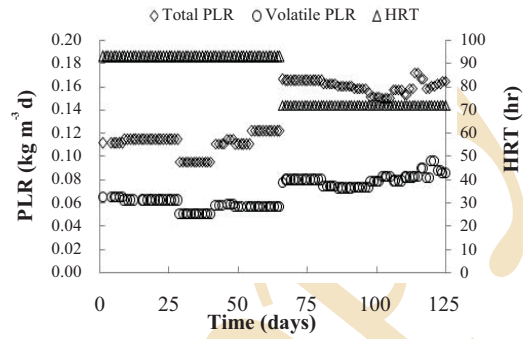


Fig. 6 : Total PLR, Volatile PLR and HRT from day 0 to 125

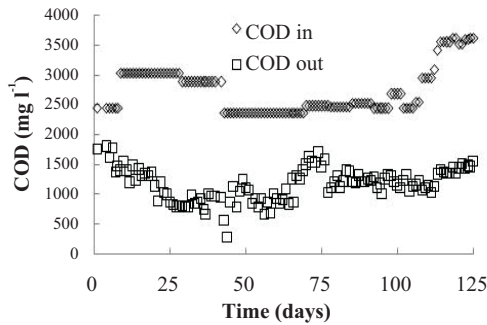


Fig. 3 : CODin and CODout from day 0 to 125

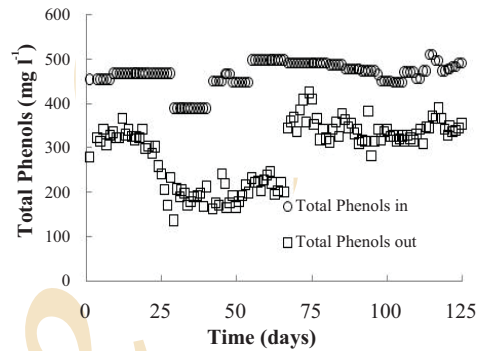


Fig. 7 : Total Phenols in and Phenols out from day 0 to 125

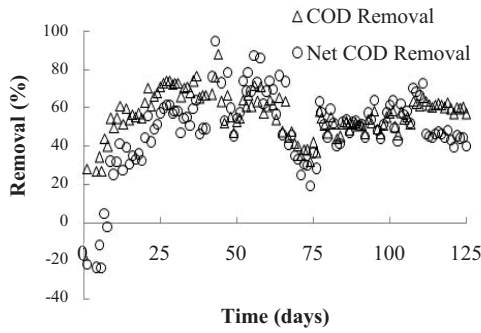


Fig. 4 : COD and Net COD from day 0 to 125

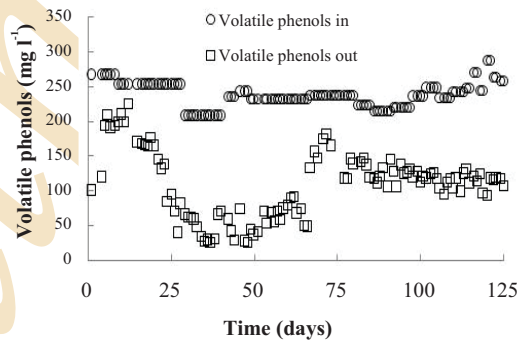


Fig. 8 : Volatile Phenols in and Phenols out from day 0 to 125

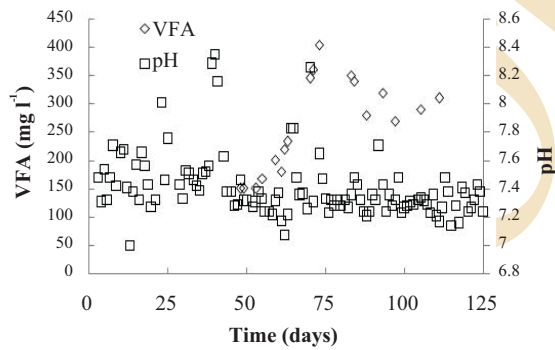


Fig. 5 : VFA and pH from day 0 to 125

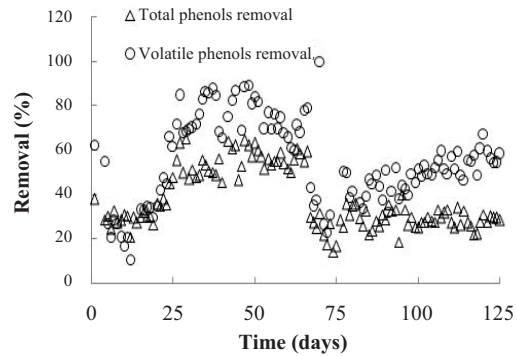


Fig. 9 : Total phenols and volatile phenols removal from day 0 to 125

were 60% and 44% respectively. The OLR was 1.2 kg COD/(m³·day) and the HRT was kept for 72 hrs. The PLR in the UASB was 0.17 kg / (m³·day), with a removal rate of 28%. During the whole operation, anaerobic system was operated in a water seal.

GC/MS analysis : After 125 days of operation, in order to further investigate the removal of different organic compounds, raw SNGW and anaerobic effluent were taken from the top of the reactor and were analyzed with GC-MS. Their main components (percentages greater than 0.6%) are listed in Table 2. The main components of raw wastewater were phenol compounds that include phenols, M-Cresol, O-Cresol, and, 2-Cyclopenten-1-one, 2-methyl-. From Table 2, it is evident that the components in raw and anaerobic effluent were similar. In anaerobic effluent, a part of the components was related to raw material. Most of them were phenolic compounds, such as phenols and M-Cresol, which are frequently found in the biological treatment effluent. The anaerobic effluent also contained Azulene and Dibenzofuran, although they were of different types. These components were mostly derived from anaerobic bacterial metabolism and were not directly related to raw pollutants. They were frequently found in anaerobic effluent of other types of wastewater also. It was 71.35% of the total organic components in the raw wastewater. Twelve kinds of organic compounds were detected in the SNGW, and 5 kinds of organic compounds were completely removed during biodegradation process. The average COD and phenol degradation efficiency was 60% and 28% respectively. It indicates that the biodegradation process of microorganisms possesses the effect to toxic organic compounds of SNGW.

Characteristics of granular : In anaerobic reactor, the microorganisms at bottom are of great importance in the anaerobic degradation of SNGW. After 125 days of operation, the OLR was 1.2 kg COD/(m³·day) and HRT was 72 hrs and PLR was 0.17 kg / (m³·day). To investigate the effect of UASB reactor, the sludge from the bottom of the reactor was studied with scanning electron microscope. The SEM photographs of the sludge are shown in Fig.10. According to the low OLR, it did not form the bio-granule sludge. Fig.10 a and 10 b show the surface of the sludge. Rod-shape bacteria resembling *Methanothrix* were dispersed over the sludge. It shows that feeding the reactor with phenol and glucose was effective to enhance the development of methanogenic sludge.

The SEM plate-micrographs ($\times 20000$ times) of domesticated bacteria are presented in Figs. 10 c and 10 d. They show long filamentous rods having a typical morphology of *Methanothrix*, which produce methane as a byproduct in anoxic conditions (Zinder *et al.*, 1984). In addition, morphologically similar forms comparable to *Methanospirillum* were also observed. The bacteria were also intertwined with filamentous rods. They were scanty in number. It could be attributed to the toxicity of raw SNGW. It also indicates that the degrading bacteria was acclimatized to raw wastewater after 125 days of domestication. Once adapted, the anaerobic bacteria could retain viability and activity at SNGW.

Performance of the UASB system is discussed in the present section. Each modification in operational/feed parameter was observed. Glucose was the source of carbon and electron donor in the SNGW feed improved proliferation

Table 2: Organic compounds in the raw SNGW and effluent

Organic compounds	Formula	MolWt	Raw wastewater		Effluent	
			Area	Area%	Area	Area%
Acetic acid,chloro-,2-phenylethyl ester	C ₁₀ H ₁₁ ClO ₂	198	2681291	3.21	-	-
Pentanoic acid	C ₅ H ₁₀ O ₂	102	5627164	6.73	-	-
2-Methyl-2-cyclopenten-1-one	C ₆ H ₈ O	96	4695461	5.62	2281374	4.41
Phenol	C ₆ H ₆ O	94	39010979	46.71	33511116	64.83
1-Methoxy-1,4-cyclohexadiene	C ₇ H ₁₀ O	110	1035248	1.24	-	-
M-Cresol	C ₇ H ₈ O	108	5572130	6.67	5995052	11.6
O-Cresol	C ₇ H ₈ O	108	10320046	12.35	1816196	3.51
Heptanoic acid	C ₇ H ₁₄ O ₂	130	5540267	6.63	-	-
1-methyl-Naphthalene	C ₁₁ H ₁₀	142	941341	1.13	1690220	3.27
2-methyl-Naphthalene	C ₁₁ H ₁₀	142	546772	0.65	1774284	3.43
1,4-Methanonaphthalene,1,4-dihydro	C ₁₁ H ₁₀	142	1155742	1.38	978733	1.89
1H-Indene,1-ethylidene-	C ₁₁ H ₁₀	142	1265400	1.51	-	-
Azulene	C ₁₀ H ₈	128	-	-	673200	1.3
Dibenzofuran	C ₁₂ H ₈ O	168	-	-	683020	1.32

Note : Symbol “-” means the compounds was not detected. Area%, mass percentage, was calculated according to the total area

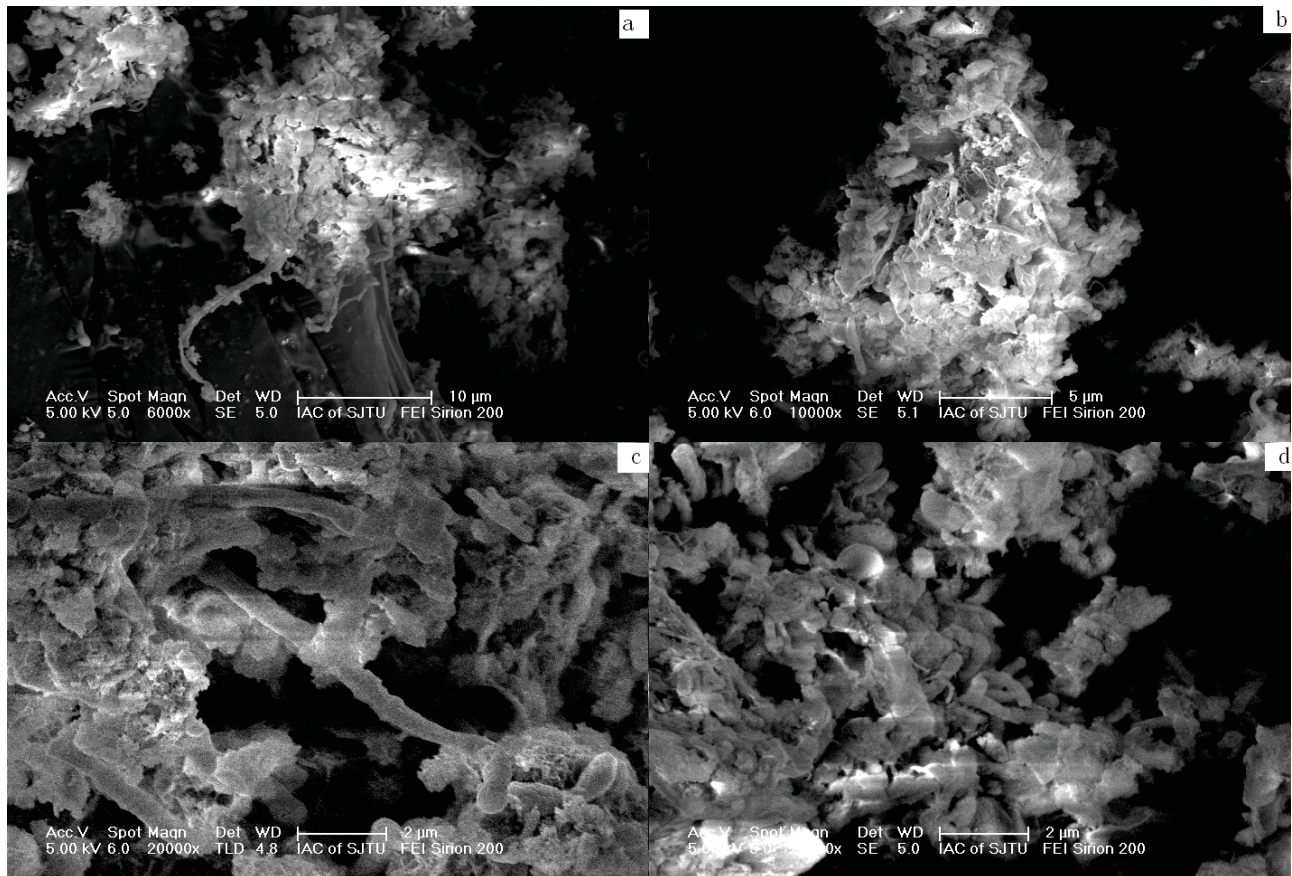


Fig. 10 : Scanning electron microscopic photographs of sludge degrading complex phenolic mixture and glucose. (a) The surface of sludge (6000 \times) (b) The surface of sludge (10000 \times) (c) *Methanothrix*-like bacteria (20000 \times) (d) *Methanothrix*-like bacteria (20000 \times)

of phenol-degrading bacteria and their response to changes in OLR were observed.

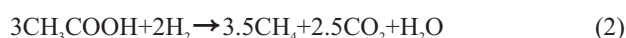
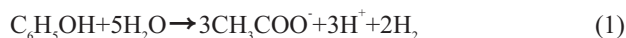
Phenolic compounds are dominant organic contaminants in coal gasification wastewater (Yang *et al.*, 2006). They are generally comprised of 40-80% of total COD (Kindzierski *et al.*, 1991). The SNGW contains cyanide, thiocyanate and pyridine though in a low concentration and have toxic effects on the anaerobic digestion of phenolic compounds. Phenol is one of the recalcitrant compound which is a growth inhibitor to bacteria at 0.5 mmol l⁻¹ concentration and is bactericidal at 21 mmol l⁻¹ concentration to the population which are not adapted to phenols (Heipieper *et al.*, 1991). Glucose is an easily biodegradable substrate and its addition can change the structure of organic components in the SNGW. Kar *et al.* (1996) reported that phenol and glucose utilization starts simultaneously by the microbial population which was acclimatized to a mixture of both carbon sources. Most of the previous studies (Fang *et al.*,

2006; Gali *et al.*, 2006; Tawfiki *et al.*, 1999; Zhou and Fang, 1997; Goeddertz *et al.*, 1990; Zhou *et al.*, 2010) on phenol degradation under different conditions, utilizing mixed or pure cultures have indicated that mixed cultures permit faster phenol degradation than pure culture. The co-substrate is not unique and other easily biodegradable substrates have been observed in the laboratory-scale study (Ramakrishnan and Gupta, 2006).

At the start of the reactor, the main source of COD in the influent were phenol and glucose. Utilization degree of phenolic compounds in anaerobic reactor represents the anaerobic treatment efficiency of SNGW. When glucose concentration was increased from 500 mg l⁻¹ to 1000 mg l⁻¹, there was an improvement in total phenol removal. Bioactivity of anaerobic system caused a drop in COD, as well as phenol removal. This indicates that aerobic water had a toxic and inhibitory effect on these bacteria which could degrade COD and phenol from day 65th.

Uygur and Kargir (2004) reported a decrease in COD removal from 95% to 79% (initial concentration: 1200 mg l⁻¹ COD), when phenol concentration was increased from 400 mg l⁻¹ to 600 mg l⁻¹ in a four step (anaerobic/oxic/anoxic/oxic) sequencing batch reactor. Similar trend was observed during degradation of phenol wastewater (Fang *et al.*, 2006). In a similar study, Nakhla and Suidan (1995) employed a fluidized bed reactor for treatment of coal gasification wastewater and reported 99.5% phenol removal at HRT for 4-8 hrs at a PLR of 0.3 kg/(m³·day). The literature survey reveals that the COD and phenol removal are functional type of carbon source, characteristics of sludge and type of reactor. Whenever changes in COD or phenol concentrations were made, the reactor did not run in a stable manner and revealed fluctuations in removal efficiencies, which were partially or fully recoverable. In the present study, COD and phenol removal generated an effluent containing intermediate acids in the UASB reactor.

By comparing the GC/MS of water, it can be deduced that the phenolic compounds were degraded considerably in the anaerobic reactor. Theoretically, under anaerobic condition phenol conversion is given below (according to Fedorak *et al.*, 1986):



In the present study, glucose was provided along with phenol as carbon source. Ninety-five percent conversions of phenol-COD to methane from influent phenol of 1290 mg l⁻¹ of UASB reactor has been reported (Fang *et al.*, 1996). During the treatment, although majority of organic pollutants were removed through anaerobic treatment process, there were still a significant amount of toxic contaminants present in the effluent.

Therefore, it can be concluded that glucose utilization enhanced bacterial detoxification of toxic compounds and strengthened the digestion activity of recalcitrant compounds. An appropriate glucose addition might change the predominant species of methanogens. The performance of the reactor on addition of 1000 mg l⁻¹ represented optimum condition for stable COD and phenol removal in real SNGW.

Operational problems and countermeasures: Some of the operational problems inherent in the laboratory scale experiment and countermeasures are listed here. Sludge flotation occurred twice. Some sludge floated on the surface when HRT was decreased. Pipelines were blocked by sludge

or sedimentation of inorganic blockage compound. Regular cleaning of sediments from the pipelines was required to avoid blockage.

Anaerobic digestion of SNGW was carried out in an UASB reactor. The reactor exhibited high efficiency in treating SNGW. The reactor was operated at 35 °C for 125 days. The removal of COD and net COD were 60% and 44% respectively. The OLR was 1.2 kg COD/(m³·day) and the HRT was 72 hours. The PLR in the UASB was 0.17 kg/(m³ d), with a removal rate of 28%. The mixed microbial flora obtained from the sewage sludge could be adapted to degradation of SNGW with glucose as co-substrate without any pretreatment. Twelve kinds of organic compounds were detected in the SNGW and five kinds of organic compounds were completely removed during the biodegradation process. It indicated that biodegradation process of microorganisms had toxic effect on organic compounds of SNGW. SEM examination of sludge showed diverse group of microorganisms. Rod-shape bacteria, long filamentous rods and *Methanothrix*-like bacteria were observed on the surface.

This study would be useful for estimating the response of reactor biomass to process change or influent composition during operation. It was feasible for glucose as co-substrate in the SNGW treatment. It is a potential anaerobic treatment using co-digestion method for the removal of COD and phenols in the SNGW.

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References

- APHA : Standard Methods for the Examination of Water and Wastewater. 20th Edn., Washington DC: APHA, AWWA (2012).
- Bajaj, M., C. Gallert and J. Winter : Biodegradation of high phenol containing synthetic wastewater by an aerobic fixed bed reactor. *Bioresour. Technol.*, **99**, 8376-8381(2008).
- Bajaj, M., C. Gallert and J. Winter: Effect of phenol addition on COD and nitrate removal in an anoxic suspension reactor. *Biores. Technol.*,

- 101, 5159-5167 (2010).
- Chu, L.B., X.W. Zhang and F.L. Yang: Characterization of granulation process during UASB start-up. *Environ. Sci. Technol.*, **28**, 22-23 (2005).
- Fedorak, P.M., D.J. Roberts and S.E. Hurdey : The effect of CN- on methanogenic degradation of phenolic compounds. *Water Res.*, **20**, 1315-1320 (1986).
- Fang, H.H.P., T. Chen, Y.Y. Li and H.K. Chui : Degradation of phenol in wastewater in an upflow sludge blanket reactor. *Water Res.*, **30**, 1353-60 (1996).
- Fang, H.H.P., D.W. liang, T. Zhang and Y. Liu : Anaerobic degradation of phenol wastewater under thermophilic condition. *Water Res.*, **40**, 427-434 (2006).
- Ganczarczyk, J.J. and A. Benedek : State-of-the-art in coke plant effluent. *Crit. Rev. Env. Sci. Technol.*, **13**, 103-115 (1983).
- Goeddertz, J.G., A.S. Weber, W.C. and Ying : Startup and operation of an anaerobic biological activated carbon (AnBAC) process for treatment of a high strength multicomponent inhibitory wastewater. *Environ. Prog.*, **9**, 110-117 (1990).
- Gai, H.J., Y.B. Jiang, Y. Qian and A. Kraslawski : Conceptual design and retrofitting of the coal-gasification waster treatment process. *Chem. Eng. J.*, **138**, 84-94 (2008).
- Humenick, M.J. and K. Shellenbarger : Treatment of UCG condensate by gas stripping, solvent extraction, activated carbon and sludge. *In Situ*, **10**, 93-108 (1986).
- Heipieper, H.J., H. Keweloh and H. Rehm: Influence of phenols on growth and membrane permeability of free and immobilized *Escherichia coli*. *Appl. Environ. Microbiol.*, **57**, 1213-1217 (1991).
- Kindzierski, W.B., P.M. Fedorak and S.E. Hrudey : Anaerobic treatability of a phenolic coal conversion wastewater after diisopropyl ether extraction. *Water Res.*, **25**, 479-484 (1991).
- Kar, S., T. Swaminathan and A. Baradarajan : Studies on biodegradation of a mixture of toxic and nontoxic pollutant using *Arthrobacter* species. *Bioprocess Biosyst. Eng.*, **15**, 195-199 (1996).
- Karnchanawong, S. and K. Kabtum : Toxicity of sodium and potassium ions on performance of UASB System. *Advan. Mat. Res.*, 953-954, 1105-1108 (2014).
- Nakhla, G.F. and M.T. Suidan : Anaerobic toxic wastes treatment: dilution effects. *J. Hazard. Mater.*, **42**, 71-86 (1995).
- Ramakrishnan, A. and S.K. Gupta : Anaerobic biogranulation in a hybrid reactor treating phenolic waste. *J. Hazard. Mate. B.*, **137**, 1488-1459 (2006).
- Uygur, A. and F. Kargir : Phenol inhibition of biological nutrient removal in a four step sequencing batch reactor. *Process Biochem.*, **39**, 2123-2128 (2004).
- Yang, C.F., Y. Qian, L.J. Zhang and J.Z. Feng : Solvent extraction process development and on-site strial-plant for phenol removal from industrial coal-gasification wastewater. *Chem. Eng. J.*, **117**, 179-185 (2006).
- Zhou, G.M. and H.H.P. Fang : Co-degradation of phenol and m-cresol in an UASB reactor. *Biores. Technol.*, **61**, 47-52 (1997).
- Zhang, Y.J., L. Yan. L.N. Ci, X.H. Long, Z.J. Mei and Z.J. Zhang : Start-up and operation of anaerobic EGSB reactor treating palm oil mill effluent. *J. Environ. Sci.*, **20**, 658-663 (2008).
- Zhou, J.Y. X.J. Yu, C. Ding, Z.P. Wang, Q.Q. Zhou, H. Pao and W.M. Cai: Optimization of phenol degradation by *Candida tropicalis* Z-04 using Plackett-Burman design and response surface methodology. *J. Environ. Sci.*, **23**, 22-30 (2010).