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Enhanced anaerobic biodegradability of real coal gasification wastewater with methanol addition

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Abstract

Coal gasification effluent is a typical refractory industrial wastewater with a very poor anaerobic biodegradability due to its toxicity. Methanol was introduced to improve anaerobic biodegradability of real coal gasification wastewater, and the effect of methanol addition on the performance was investigated in a mesophilic upflow anaerobic sludge bed reactor with a hydraulic retention time of 24 hr. Experimental results indicated that anaerobic treatment of coal gasification wastewater was feasible with the addition of methanol. The corresponding maximum COD and phenol removal rates were 71% and 75%, respectively, with methanol concentration of 500 mg COD/L for a total organic loading rate of 3.5 kg COD/(m^3·day) and a phenol loading rate of 0.6 kg/(m^3·day). The phenol removal rate was not improved with a higher methanol concentration of 1000 mg COD/L. Substrate utilization rate (SUR) tests indicated that the SURs of phenol were 106, 132, and 83 mg phenol/(g VSS·day) at methanol concentrations of 250, 500, and 1000 mg COD/L, respectively, and only 45 mg phenol/(g VSS·day) in the control reactor. The presence of methanol could reduce the toxicity of coal gasification wastewater and increase the biodegradation of phenolic compounds.

Key words: coal gasification wastewater; anaerobic; biodegradability; phenol; methanol

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Introduction

Coal gasification is one of the best methods for acquiring clean coal energy to meet the rising demand in China (Li et al., 2009). However, a coal gasification plant consumes a large amount of water during its manufacturing processes. Coal gasification wastewater is discharged mainly from the gas washing and condensing operations of the coal gasifier. Considering its complex composition and the toxic pollutants contained in it, coal gasification wastewater is regarded as a serious problem in the world (Zhu et al., 2009). Although raw coal gasification wastewater is pretreated through solvent extraction and steam stripping to remove phenols and ammonia, the effluent still contains high concentrations of phenolic compounds as well as refractory and inhibitory compounds (Gai et al., 2008). Conventional anoxic-oxic treatment methods provide cost-effective and efficient techniques for coal gasification wastewater treatment. However, reducing effluent COD to less than 200 mg/L remains difficult (Wang et al., 2002). In recent years, there have been numerous attempts to treat coal gasification wastewater under anaerobic conditions to improve its biodegradability (Ramakrishnan and Gupta, 2006; Kuschk et al., 2010).

Anaerobic process is suitable for the treatment of coal gasification wastewater, but the process is seriously inhibited and has low efficiency. The use of the anaerobic process in COD removal in coal conversion wastewater treatment only contributes 25% to the removal of the anaerobic-anoxic-oxic system (Wang et al., 2002). In this type of wastewater, recalcitrant organics and inhibitory compounds are the most difficult compounds for the anaerobic treatment to break down. For example, phenolic compounds, cyanide, and long chain alkenes are the inhibitors of methanogenic bacteria (Chakraborty and Veeramani, 2006; Hernandez and Edyvean, 2008). This toxicity causes the anaerobic treatment of real coal conversion wastewater to require a large volume of clean water as diluents or granular activated carbon as absorber, which would be very costly on an industrial scale (Kindzierski et al., 1991; Nakhla and Suidan, 1995). Recently, anaerobic co-digestion has been developed for treating refractory wastewater (Youngster et al., 2008; Zhang et al., 2008). Some publications in the field of industrial wastewater treatment described the anaerobic digestion of recalcitrant wastewater with the addition of an easily biodegradable substrate (Perez et al., 2006; Yang et al., 2008). Anaerobic microorganisms can attain a considerable growth rate using co-substrate simultaneously (Brandt et al., 2003). Co-digestion can enhance the biodegradability of the wastewater by increasing the toxic and recalcitrant compounds of degraders, as well as by increasing the absorption capacity of the system (Chen et al., 2008).

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Methanol, as an easily biodegradable substrate, is an available and inexpensive product in the coal gasification industry (Kumabe et al., 2008). Therefore, it may be feasible to improve the anaerobic biodegradability of coal gasification wastewater with the addition of methanol.

In the present study, anaerobic treatment of real coal gasification wastewater both unsupplemented and supplemented with methanol were investigated in two upflow anaerobic sludge bed (UASB) reactors. The effect of methanol concentration on COD and phenol removal was studied to acquire the optimum dose of methanol. The purpose of the work was to test whether the addition of methanol could enhance anaerobic biodegradability of real coal gasification wastewater and to supply a technically feasible and cost-effective way for anaerobic treatment of recalcitrant wastewater.

1 Materials and methods

1.1 Experimental setup

Two UASB reactors were comprised of plexiglass columns with an internal diameter of 10 cm, a height of 120 mm, and a working volume of 7 L. The reactors were operated at (37 ± 1)°C.

1.2 Inoculum

Anaerobic digested sludge was obtained from full-scale anaerobic reactors which were used for the treatment of coal gasification wastewater of the China Coal Longhua Harbin Coal Chemical Industry Co., Ltd. The sludge was grey-black with good settlement characteristics. Total suspended solid (TSS) was 45.8 g/L and volatile suspended solid (VSS) was 33 g/L in both reactors. Methanogenic activity of the seed sludge was 0.12 g COD-CH_4/(g VSS·day).

1.3 Coal gasification wastewater

Raw coal gasification wastewater was obtained from the lurgi gasifier at China Coal Longhua Harbin Coal Chemical Industry Co., Ltd. Since the raw wastewater was subjected to a series of physico-chemical pretreatments (such as sour gas stripping, extraction with diisopropyl ether and ammonia stripping) to reduce the concentrations of solids, greases, phenols, and ammonium, the wastewater could be treated with the biological process. Table 1 shows the main characteristics of the real coal gasification wastewater. Predominant pollutants in coal gasification wastewater include phenolic compounds, heterocyclic compounds, polycyclic aromatic hydrocarbons, long chain alkenes, amine compounds, ammonia, sulfide, thiocyanate, and cyanide. Phenolic compounds are the main organic pollutants in the wastewater and comprise 40%–50% of the total COD.

Table 1 Main characteristics of the real coal gasification wastewater

Parameter	Value
COD (mg/L)	2500–3500
BOD_5 (mg/L)	700–1100
Total phenols (mg/L)	450–700
Volatile phenols (mg/L)	80–200
Volatile acids (mmol/L)	2–10
NH_3-N (mg/L)	100–150
Bicarbonate alkalinity (mmol/L)	0.5–3
Oil (mg/L)	20–80
Sulfide (mg/L)	20–50
Thiocyanate (mg/L)	20–50
Cyanide (mg/L)	0.2–5
Temperature (°C)	40–50
pH	6.5–8.0

1.4 Start-up (day 1–227) and operation (day 228–359)

The feed nutrients consisted of the following macronutrients (in mg/L): K_2HPO_4 20, KH_2PO_4 10, $CaCl_2·2H_2O$ 20, $FeSO_4·7H_2O$ 15, and $MgSO_4·7H_2O$ 50; micronutrients (in mg/L): $FeCl_3·3H_2O$ 1, $MnCl_2·4H_2O$ 0.5, $ZnCl_2$ 0.5, $CuCl_2$ 0.5, $(NH_4)_2MoO_4·4H_2O$ 0.5, $AlCl_3$ 0.5; $CoCl_2·2H_2O$ 0.5, $NaBO_2·10H_2O$ 0.3, and $NiCl_2·2H_2O$ 0.5. The supplemented methanol used for this study was an analytical reagent. Because the influent pH was in the range of 7.0 to 8.0, no alkalinity was needed to add to the wastewater. During the start-up period, the influent COD (1500 mg/L) and total phenols concentrations (300 mg/L), were controlled by diluting the real wastewater. Methanol was added into the reactor (called the supplemented reactor) to keep the initial methanol concentration at 500 mg COD/L. Although this amount provided 25% of the total influent COD (2000 mg/L), the addition also encouraged the growth of methanogenic bacteria. The coal gasification wastewater concentration and phenol loading rate were gradually increased from 2500 mg COD/L and 0.5 kg/(m^3·day) on day 68 to 3000 mg COD/L and 0.6 kg/(m^3·day) on day 143, respectively. The amount of methanol added was kept at 500 mg COD/L to maintain the stable amount of co-substrate. Meanwhile, another UASB reactor was operated without methanol addition as a control (called the control reactor). When the supplemented reactor reached stable operation, the effect of methanol concentration on the performance was investigated to obtain the optimum amount of methanol. During the entire experimental period, the reactors were operated continuously at constant hydraulic retention time (HRT) of 24 hr with the upflow liquid velocity of 0.375 m/hr. The operational conditions of the supplemented reactor are shown in Table 2.

1.5 Analytical methods

COD, BOD, SS, VSS, sulfide, long chain alkenes, thiocyanate, cyanide and NH_3-N were determined according to standard methods. The concentrations of total phenols and volatile phenols were measured by the titration method (Wei et al., 2002). Bicarbonate alkalinity and volatile fatty acids (VFA) were analyzed by the distillation method (Anderson and Yang, 1992). Effluent methanol was measured by gas chromatography as described by Weijma et al. (2000). The biogas production of the reactor was measured by the wet gas flowmeter. Methane content of the biogas was analyzed using a liquid displacement system with a 3 mol/L NaOH solution. In addition, substrate utilization rates (SUR) of phenol and methanol were used to assess

Table 2 Operational conditions employed in the anaerobic treatment of real coal gasification wastewater in the supplemented reactor

Time (day)	CGW_{in} (mg COD/L)	$Methanol_{in}$ (mg COD/L)	Methanol (% of total COD)	TP_{in} (mg/L)	TOLR (kg COD/(m^3·day))	PLR (kg/(m^3·day))	HRT (hr)	VU (m/hr)
1–67	1500	500	25	300	2	0.3	24	0.375
68–142	2500	500	20	500	3	0.5	24	0.375
143–227	3000	500	16.7	600	3.5	0.6	24	0.375
228–292	3000	1000	28.6	600	4	0.6	24	0.375
293–359	3000	250	8.3	600	3.25	0.6	24	0.375

CGW_{in}: influent coal gasification wastewater; $methanol_{in}$: influent methanol concentration; TP_{in}: total phenols; TOLR: total influent organic loading rate; PLR: phenols loading rate; HRT: hydraulic retention time; V_U: upflow velocity.

the biodegradability using the seed sludge and biomass from the UASB reactors. SUR tests were carried out in 140 mL sealed vials with a working volume of 100 mL. The test substrates controlled phenol concentration of 500 mg/L and methanol concentration of 500 mg COD/L. The SUR values of phenol and methanol were expressed as the rates of phenol depletion (mg phenol/(g VSS·day)) and methanol depletion (mg COD/(g VSS·day)), respectively.

2 Results

2.1 Effect of methanol addition on start-up performance (day 1–227)

Influent COD of 1500 mg/L and total phenols concentration of 300 mg/L with influent organic loading rate (OLR) 1.5 kg COD/(m^3·day) and phenol loading rate (PLR) of 0.3 kg/(m^3·day) were applied in the two UASB reactors. In the supplemented reactor, the amount of methanol addition remained at 500 mg COD/L as co-substrate during start-up periods. Figure 1 shows the comparison of anaerobic treatment of the real coal gasification wastewater in the supplemented and control reactors. In the control reactor (Fig. 1d and h), the COD and total phenols removal were around 28% and 25% after 67 days of operation. Although inoculums in the full-scale anaerobic devices had acclimated for the real coal gasification wastewater for over half a year, the treatment efficiency of the organic pollutants was still low because of the toxicity. In the supplemented reactor, COD and phenols removal could reach up to 70% and 60%, respectively, on day 67 (Fig. 1c, g). The addition of methanol altered the metabolic environment and resulted in changes in the effluent. Figure 1 (i and j) illustrates the decrease of effluent volatile phenols. The increase in effluent alkalinity was more prominent in the supplemented reactor than that in the control reactor, which supported that the reactor was operating properly (Fig. 1m, n).

Influent total COD and phenols increased to around 3000 and 500 mg/L, respectively, during day 68–142. On day 72, COD removal was reduced to 31% and 19.7% in the supplemented and control reactors, respectively. On the other hand, phenols concentration in the effluent increased to 324.9 and 451 mg/L in the supplemented and control reactor, respectively (Fig. 1e, f). The control reactor without methanol addition was shown to be ineffective in the biodegradation of phenol compounds, and it restricted COD removal by 20%–35%. However, in the supplemented reactor, COD and phenols removal recovered to 69% and 55% (Fig. 1d, h), respectively on day 84 and reached stable values of 72% and 70% on day 122, respectively. Methane production achieved 3.2 L/day at methanol concentrations of 500 mg COD/L, which far exceeded the value of 0.12 L/day in the control reactor (Table 3). Subsequently, during day 143–227, total influent COD and total phenols increased to around 3500 and 600 mg/L, respectively. Although the acclimation extended over 200 days, the coal gasification wastewater still had a serious effect on anaerobic microorganisms, such that the anaerobic treatment efficiency was lower than 40% in the control reactor (Fig. 1d). With the addition of methanol, COD and phenols removal increased to 71% and 75%, respectively, on day 219 (Fig. 1c, g). Effluent of pH and VFA were 8.0 and 1.5 mmol/L in the reactor (Fig. 1k, o); these values did not vary much during the operation stage.

2.2 Effect of methanol concentrations on the performance (day 228–359)

Figure 2 shows the effect of methanol concentration on COD and total phenols removal in the supplemented reactor. The stimulative effect of the 500 mg COD/L methanol added as external carbon source in the start-up periods was observed. The effects of methanol concentrations of 1000 and 250 mg COD/L on the performance of the supplemented reactor were also investigated. On day 228, the increase in the amount of methanol addition to 1000 mg COD/L resulted in an increase in the influent total COD to 4000 mg/L and TOLR to 4 kg COD/(m^3·day) influent PLR

Table 3 Main parameters of the stable process at different methanol additions

Time (day)	Methanol addition (mg COD/L)	TOLR(kg COD/(m^3·day))	PLR (kg/(m^3·day))	COD removal (g COD/day)	TP removal (g/day)	Residual methanol (mg COD/L)	CH_4 yield (L/day)	SS (g VSS/L)
143–227	0 (blank)	3.03	0.6	6.62	1.36	0	0.12	33.50
143–227	500	3.53	0.6	17.47	3.03	ND	3.20	35.00
228–292	1000	4.01	0.6	15.40	1.89	< 10	3.35	34.70
293–359	250	3.27	0.6	12.06	2.47	ND	2.36	31.90

TP: total phenols; SS: suspension sludge; ND: not detected.

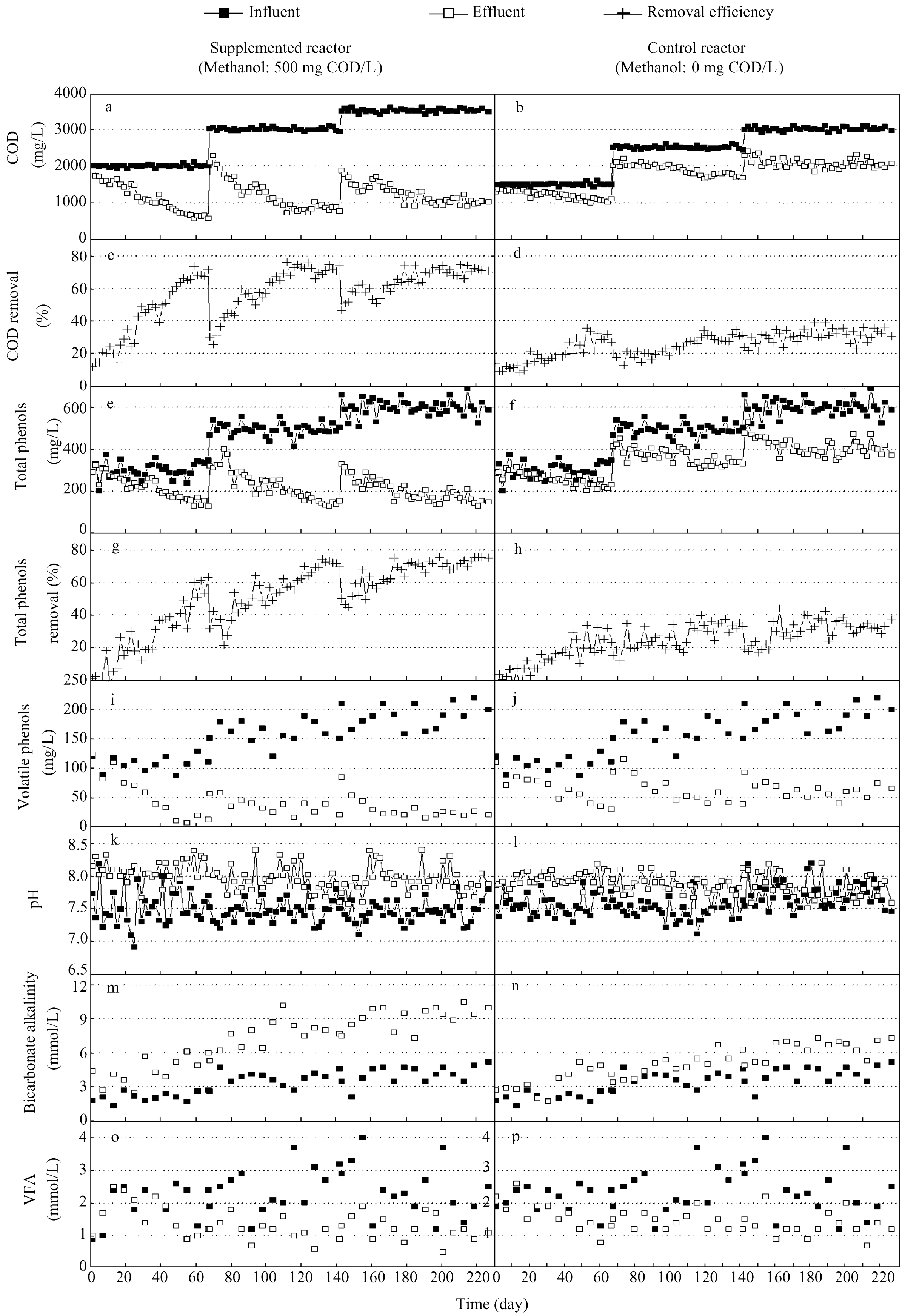

Fig. 1 Comparison on anaerobic treatment of the real coal gasification wastewater in the supplemented reactor and the control reactor.

remained at 0.6 kg/(m^3·day) (Table 2). COD and phenols removal rates decreased to 40%–45% and 30%–35% from 70%–72% and 74%–76%, respectively. Figure 2 clearly shows that increased methanol concentration resulted in a poor performance of the reactor both in terms of COD and phenols removal. From day 260 to 292, effluent COD and phenols concentrations were about 1800 and 320 mg/L along with the removal efficiency in the range of 50%–60% and 40%–50%, respectively. On day 293, the amount of methanol addition was decreased to 250 mg COD/L. Meanwhile, the influent total COD and TOLR decreased to 3250 mg/L and 3.25 kg COD/(m^3·day), respectively, and the influent PLR remained stable. Although there was a significant decline in the amount of methanol added, COD and phenols removal rates still reached 55% and 60%, on day 359 while effluent COD and phenols concentrations were about 1500 and 230 mg/L. The above amounts were lower than the effluent concentrations in the previous period (day 228–292).

Performance and operational parameters with the methanol addition of 0, 250, 500, and 1000 mg COD/L are shown in Table 3. The maximum COD and phenols removal were found to be 17.47 g COD/day and 3.03 g/day, respectively, for total organic loading rate of 3.53 kg COD/(m^3·day) and phenol loading rate of 0.6 kg/(m^3·day) with the methanol addition of 500 mg COD/L. On the other hand, in the control reactor these amounts were only around 6.62 and 1.36 g/day. The methanol concentration of 1000 mg COD/L did not improve the phenols removal efficiency of the system further. While, when methanol concentration decreased to 250 mg COD/L, total phenols removal was 2.47 g/day, which was higher than 1.89 g/day with methanol addition of 1000 mg COD/L. The methanol addition from 0 to 1000 mg COD/L increased methane production from 0.12 to 3.35 L/day. In addition, methanol as an easily biodegradable substrate was utilized as a priority in coal gasification wastewater. It was not difficult to determine that almost all the methanol was degraded and the residual methanol in effluent was less than 10 mg COD/L, even was not detected.

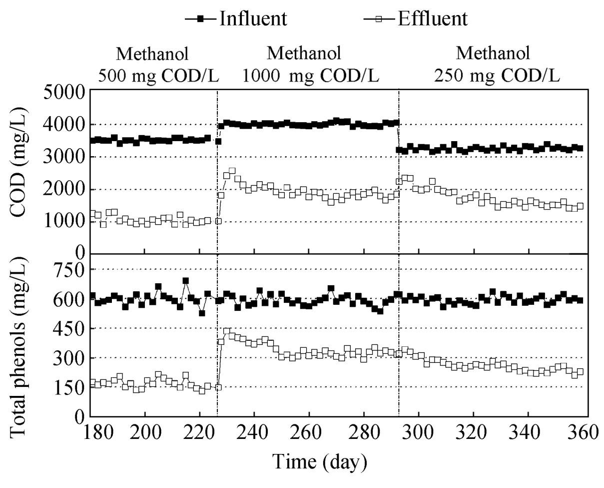

Fig. 2 Effect of methanol concentrations on COD and total phenols removal in the supplemented reactor.

Table 4 Substrate (phenol and methanol) utilization rates for the biomass in the different periods

Time (day)	Methanol addition (mg COD/L)	SUR	
		Phenol (mg phenol/(g VSS·day))	Methanol (mg COD/(gVSS·day))
0	0	27	62
143–227	0 (blank)	45	55
143–227	500	132	124
228–292	1000	83	147
293–359	250	106	140

3 Discussion

Phenolic compounds are dominant organic contaminants in coal gasification wastewater (Yang et al., 2006) and generally comprise 40%–80% of the total COD (Kindzierski et al., 1991). Biodegradation of phenolic compounds represent the treatment efficiency of the real coal gasification wastewater in an anaerobic reactor. According to some studies, wastewaters containing even low concentrations of cyanide, thiocyanate, and pyridine have toxic and inhibitory effects on the anaerobic digestion of phenolic compounds (Gijzen et al., 2000; Chakraborty and Veeramani, 2006). The initial feed of 50% strength (1500 mg COD/L) was intended to reduce the inhibitory effects of these toxic compounds in the control reactor. However, in Fig. 1b and d, the results illustrated that the dilution did not improve the removal efficiencies of COD and phenols. Sludge acclimation in the control reactor did not sequester the strong toxic effect of the wastewater on methanogenic microorganisms. Little methane production and low SUR were observed in the control reactor. This phenomenon had also been reported by Suidan et al. (1983).

Methanol is an easily biodegradable substrate (Sung and Liu, 2003), and its addition to the real coal gasification wastewater could change the organic composition. The addition of methanol clearly caused some improvement on total phenols removal and methane production compared to the control reactor (Fig. 1 and Table 3). Methane production was observed to increase with the increase in the amount of methanol added. In the supplemented reactor, COD and phenol removal reached maximum values with the addition of 500 mg COD/L methanol. Thus, methanol addition did result in increased methane production and phenols degradation in the treatment of real coal gasification wastewater. Co-digestion of real coal gasification wastewater with methanol could significantly improve treatment efficiency; however, this efficiency was not positively correlated with the addition of methanol. Although the phenol SURs were 132 and 106 mg phenol/(g VSS·day) with the methanol addition of 500 and 250 mg COD/L, respectively, the value decreased to 83 mg phenol/(g VSS·day) when methanol concentration was increased to 1000 mg COD/L (Table 4). Anaerobic degradation of methanol was not inhibited by toxic compounds in real coal gasification wastewater. High methanol concentration could influence the original metabolic equilibrium and cause the degradation of phenolic compounds, making these compounds competitively inferior.

We hypothesized that the degradation of methanol could enhance the bacterial detoxification of toxic compounds and strengthen the digestion activity of recalcitrant compounds. Adding the appropriate amount of methanol might change the predominant species of methanogens or shift the methanogenic population to encourage initial methane production and sequester toxicity. The methanol addition of 500 mg COD/L represented the optimum condition for maximum COD and phenol removal in the real coal gasification wastewater in this study. Moreover, the synergistic effect did not always require a fixed ratio of methanol addition to the objective wastewater. Once adapted, the anaerobic bacteria could retain viability and activity at concentrations that far exceed the initial inhibitory concentrations. The effective removal of COD and total phenols could be completed with the decreased ratio of methanol COD to total influent COD from 25% to 8.3%. The initial co-substrate concentration played an important role in improving the activity of methanogenic and acetogenic bacteria and in enhancing the removal of toxic and recalcitrant substances during acclimation periods. The addition of excessive or insufficient amounts of methanol might make it difficult to obtain satisfactory results within a short period.

Methanol can be easily obtained from the coal gasification industry (Kumabe et al., 2008), making the co-digestion of coal gasification wastewater with methanol substrate or its manufacturing wastewater a feasible option. In fact, the co-substrate is not unique and other easily biodegradable substrates have been observed in laboratory scale studies (Cheng et al., 1998; Ramakrishnan and Gupta, 2006). Thus, co-digestion is a promising method to enhance the anaerobic biodegradability of coal gasification wastewater. Our findings also suggest the potential application of the method specifically for phenols removal in real wastewater. Further research is required to establish the optimum conditions for co-digestion treatment of coal gasification wastewater under anaerobic conditions.

4 Conclusions

To improve the biodegradability of coal gasification wastewater, anaerobic treatment with the addition of methanol was performed in UASB reactors. Results indicated that anaerobic biodegradability of the coal gasification wastewater studied improved greatly upon the addition of 500 mg COD/L methanol with the influent total COD 3500 mg/L and phenol concentration 600 mg/L. The requirement of methanol addition ratio to the coal gasification wastewater was not fixed and the addition of excessive or insufficient amounts of methanol might make it difficult to obtain satisfactory results within a short period. Anaerobic treatment of coal gasification wastewater with other co-substrates, such as volatile acids and phenol, also offers a viable option in terms of cost and efficiency.

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References

Anderson G K, Yang G, 1992. Determination of bicarbonate and total volatile acid concentration in anaerobic digesters using a simple titration. *Water Environment Research*, 64(1): 53–59.

Brandt B W, van Leeuwen I M M, Kooijman S A L M, 2003. A general model for multiple substrate biodegradation: Application to co-metabolism of structurally non-analogous compounds. *Water Research*, 37(20): 4843–4854.

Chakraborty S, Veeramani H, 2006. Effect of HRT and recycle ratio on removal of cyanide, phenol, thiocyanate and ammonia in an anaerobic-anoxic-aerobic continuous system. *Process Biochemistry*, 41(1): 96–105.

Chen Y, Cheng J J, Creamer K S, 2008. Inhibition of anaerobic digestion process: A review. *Bioresource Technology*, 99(10): 4044–4064.

Cheng J, Suidan M T, Venosa A D, 1998. Anaerobic biotransformation of 2,4-dinitrotoluene with ethanol, methanol, acetic acid and hydrogen as primary substrates. *Water Research*, 32(10): 2921–2930.

Gai H J, Jiang Y B, Qian Y, Kraslawski A, 2008. Conceptual design and retrofitting of the coal-gasification wastewater treatment process. *Chemical Engineering Journal*, 138(1-3): 84–94.

Gijzen H J, Bernal E, Ferrer H, 2000. Cyanide toxicity and cyanide degradation in anaerobic wastewater treatment. *Water Research*, 34(9): 2447–2454.

Hernandez J E, Edyvean R G J, 2008. Inhibition of biogas production and biodegradability by substituted phenolic compounds in anaerobic sludge. *Journal of Hazardous Materials*, 160(1): 20–28.

Kindzierski W B, Fedorak P M, Hrudey S E, 1991. Anaerobic treatability of a phenolic coal conversion wastewater after diisopropyl ether extraction. *Water Research*, 25(4): 479–484.

Kumabe K, Fujimoto S, Yanagida T, Ogata M, Fukuda T, 2008. Environmental and economic analysis of methanol production process via biomass gasification. *Fuel*, 87(7): 1422–1427.

Li K Z, Zhang R, Bi J C, 2009. Experimental study on syngas production by co-gasification of coal and biomass in a fluidized bed. *International Journal of Hydrogen Energy*, 35(7): 2722–2726.

Kuschk P, Stottmeister U, Liu Y J, Wiessner A, Kästner M, Müller R A, 2010. Batch methanogenic fermentation experiments of wastewater from a brown coal low-temperature coke plant. *Journal of Environmental Sciences*, 22(2): 192–197.

Nakhla G F, Suidan M T, 1995. Anaerobic toxic wastes treatment: dilution effects. *Journal of Hazardous Materials*, 42(1): 71–86.

Perez M, Rodriguez-Cano R, Romero L I, Sales D, 2006. Anaerobic thermophilic digestion of cutting oil wastewater: Effect of co-substrate. *Biochemical Engineering Journal*, 29(3): 250–257.

Ramakrishnan A, Gupta S K, 2006. Anaerobic biogranulation in a hybrid reactor treating phenolic waste. *Journal of Hazardous Materials B*, 137(3): 1488–1495.

Suidan M T, Siekerka G L, Kao S W, Pfeffer J T, 1983. Anaerobic filters for the treatment of coal gasification wastewater. *Biotechnology and Bioengineering*, 25(6): 1581–1596.

Sung S W, Liu T, 2003. Ammonia inhibition on thermophilic anaerobic digestion. *Chemosphere*, 53(1): 43–52.

Wang J L , Quan X C, Wu L B, Qian Y, Hegemann W, 2002. Bioaugmentation as a tool to enhance the removal of refractory compound in coke plant wastewater. *Process Biochemistry*, 38(5): 777–781.

Wei F S, Qi W Q, Sun Z G, Huang Y R, Shen Y W, 2002. Water and Wastewater Monitoring and Analysis Method (4th ed.). China Environmental Science Press, Beijing.

Weijma J, Stams A J M, Hulshoff Pol L W, Lettinga G, 2000. Thermophilic sulfate reduction and methanogenesis with methanol in a high rate anaerobic reactor. *Biotechnology and Bioengineering*, 67(3): 354–363.

Yang C F, Qian Y, Zhang L J, Feng J Z, 2006. Solvent extraction process development and on-site trial-plant for phenol removal from industrial coal-gasification wastewater. *Chemical Engineering Journal*, 117(2): 179–185.

Yang Q, Shang H, Li H, Xi H, Wang J L, 2008. Biodegradation of tetrachlorothylene using methanol as co-metabolic substrate. *Biomedical and Environmental Sciences*, 21(2): 98–102.

Youngster L K G, Somsamak P, Häggblom M M, 2008. Effects of co-substrates and inhibitors on the anaerobic O-demethylation of methyl tert-butyl ether (MTBE). *Applied Microbiology and Biotechnology*, 80(6): 1113–1120.

Zhang B, He P J, Lü F, Shao L M, 2008. Enhancement of anaerobic biodegradability of flower stem wastes with vegetable wastes by co-hydrolysis. *Journal of Environmental Sciences*, 20(3): 297–303.

Zhu X P, Ni J R, Lai P, 2009. Advanced treatment of biologically pretreated coking wastewater by electrochemical oxidation using boron-doped diamond electrodes. *Water Research*, 43(17): 4347–4355.