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Treatment of coal gasification wastewater by a two-phase anaerobic digestion

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ABSTRACT

Coal gasification wastewater (CGW) is a refractory wastewater, whose anaerobic treatment has been a severe problem due to its toxicity and poor biodegradability. Using a two-stage anaerobic digestion as a control, the two-phase anaerobic digestion of real CGW was investigated. After 210 d of operation, the maximum removal efficiencies of COD and total phenols (TP) reached 50–60% and 55–60%, respectively, in the two-phase anaerobic digestion at total hydraulic retention time (HRT) of 48 h; the corresponding efficiencies were at low levels of 40–45% and 42–50%, respectively, in the two-stage anaerobic digestion. COD and TP removal efficiencies increased to 69.7 and 65.9%, when 50% of the effluent was recirculated to the hydrolytic acidogenic reactor. Phenol utilization rate and specific methanogenic activity (SMA) were decreased to 57.6 mg phenol/(gVSS d) and 394.3 mg COD-CH_4/(gVSS d), respectively, as the HRT in the hydrolytic acidogenic reactor was reduced to 18 h. After the two-phase anaerobic digestion, the wastewater concentrations of the aerobic effluent COD could reach below 150 mg/l when compared to 237.2 mg/l if two-stage anaerobic digestion was done and 328.5 mg/l if sole aerobic pretreatment was done. The results suggested that the two-phase anaerobic digestion improved significantly both anaerobic and aerobic biodegradation of real CGW.

Keywords: Phenol; Two-phase anaerobic digestion; Two-stage anaerobic digestion; Coal gasification wastewater

1. Introduction

Due to the present increase in the consumption of natural gas, coal gasification technology is gaining more and more attention. However, wastewater generated during the coal gasification processes contains a large number of toxic and refractory compounds, such as phenolic compounds, cyanide, pyridine, and long-chain alkanes, posing a major challenge to environmental safety [1]. Although the pretreatment processes of ammonia-stripping and solvent extraction are effective for the reduction of ammonia and phenolic compounds, the content of refractory organic compounds in the coal gasification wastewater (CGW) remains high; COD concentration of CGW after physical–chemical pretreatment still reaches 2000–4000 mg/l, of which phenolic compounds was accounted for 40–50% [2].

Biological treatment is by far the most widely applied and cost-effective process for wastewater treatment. However, due to a certain number of refractory and inhibitory pollutants in CGW, COD,

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and total phenols (TP) are poorly removed by the conventional activated sludge process. In China, anoxic–oxic (A–O), anaerobic–anoxic–oxic (A1–A2–O), and sequencing batch reactor processes have been extensively investigated for CGW, but the reduction of effluent COD concentrations to less than 200 mg/l using them is difficult [3–5]. Synthetic CGW for aerobic treatment in granular activated carbon reactors have been documented in recent literatures. However, the requirement for a large volume of granular activated carbon as absorber would be extremely costly on an industrial scale and do not insure their techno-economic feasibility [6].

Recently, much attention has been directed to the anaerobic digestion method due to its capability to improve the biodegradability of coking wastewater [7]. It is reported that the anaerobic digestion system plays important roles in the detoxification of hazardous organic contaminants such as volatile aromatic hydrocarbons, chlorinated solvents, and phenolic aromatics [8]. Due to the toxicity of CGW, however, subjecting it to traditional anaerobic treatment often requires a large volume of clean water as diluent or granular activated carbon as absorber to reduce the inhibitory effect posed on methanogenic bacteria. Consequently, the contribution of anaerobic digestion to COD removal in the biological treatment of actual CGW is less than 30%. Hence, CGW treatment plants are in dire need for an alternative method of enhancing the anaerobic biodegradation of wastewater.

The degradation rate of organic compounds declined because the toxic pollutants seriously inhibited anaerobic bacterial activity. Compared to traditional anaerobic digestion, two-stage or two-phase anaerobic digestion offer several merits, such as increased degradation rate for refractory organics, high methane production rate, improved wastewater biodegradability, and increased detoxification effect of anaerobic bacteria. Many reports on the study and application of two-stage anaerobic digestion or two-phase anaerobic digestion treating wastewater containing toxic and hazardous pollutants have been documented [1,9]. Two-stage anaerobic digestion consists of two identical anaerobic reactors characterized by containing both hydrolytic acidogenic bacteria and methanogenic bacteria, and operated under the same conditions [10]. Using this process, the removal of COD and TP could reach 50–55% and 40–45%, respectively, at an organic loading rate (OLR) of 2.5 kg COD/(m^3 d) and total hydraulic retention time (HRT) of 40 h [11]. At an influent flow distribution ratio of 0.2 in the two-stage UASB system, the effluent COD concentration could be reduced to 900 mg/l, although values of around 1000 and 1100 mg/l are more common, when influent COD concentration of 2000 mg/l [12].

The anaerobic digestion process is carried out by two principal groups of micro-organisms: hydrolytic acidogenic bacteria and methanogenic bacteria. Nevertheless, the micro-organisms which take part in the process of anaerobic digestion have different physiological requirements, nutrient requirements, growing kinetics, and levels of sensitivity to the environmental conditions. A separation of phases in the anaerobic digestion process provides good stability to the different groups of micro-organisms and a more specific control of the conditions required for each one. This separation in two-phase allows the enrichment of the different populations of micro-organisms by means of the control of the operational parameters. From process efficiency and stability, it is logical that for the refractory wastewater in the two-phase, anaerobic digestion might perform better when compared to two-stage anaerobic digestion. The toxic and hazardous substances would be converted firstly in the hydrolytic acidogenic reactor, and then effluent pollutants could be biodegradated completely in the methanogenic reactor. Especially, the satisfactory results were confirmed in treating high concentration organic wastewater, such as fermentation wastewater and coking wastewater with the COD removal efficiencies 51 and 47%, respectively [8,13]. To date, however, no study on the biodegradation of real CGW using a two-phase anaerobic digestion has been published.

The purpose of this research was to investigate the effect of two-phase anaerobic digestion on the biodegradation of real CGW at laboratory-scale and to evaluate the process' start-up and efficiency compared with those of two-stage anaerobic digestion. By testing the phenol utilization rate (PUR) and specific methanogenic activity (SMA) of sludge in different reactors, the sludge acclimation process was investigated. In addition, the effects of HRT and effluent recirculation on the performance of two-phase anaerobic digestion were examined. The study also tested whether two-phase anaerobic digestion could enhance the aerobic biodegradability of real CGW and served as a technically feasible and cost-effective treatment process with potential applications.

2. Methods

2.1. Experimental set-up

Four identical UASB reactors, marked R1, R2, R3, and R4, were constructed of cylindrical plexiglass columns, each having an internal dimension of 6 cm, a

total height of 90 mm, and a working volume of 2.0 L. There were five outlets at different heights of 40, 50, 60, 70, and 80 cm on each reactor. Reactors R1 and R2 were connected in a series and served as the two-stage anaerobic digestion reactors. Reactors R3 and R4 were connected by the same way and served as the two-phase anaerobic digestion reactors. All the reactors were operated at temperature of 37 ± 2℃ except reactor R3. To make hydrolytic acidogenic bacteria to become the dominant micro-organisms in the hydrolytic acidogenic reactor, reactor R3 was operated at the room temperature of 15–25℃. Besides, a small amount of $NaHCO_3$ solution was added into the methanogenic reactor (R4) to control pH at 7.0 ± 0.2.

2.2. Inoculum

Initially, seed sludge was collected from the full-scale anaerobic reactors treating real CGW at China Coal Longhua Harbin Coal Chemical Industry Co. Ltd. The reactors had been operating for 12 months, and the sludge was grey-black with good settlement characteristics. After inoculation, the total suspended solids (TSS) and volatile suspended solids (VSS) in the reactors were around 41.2 and 28.7 g/L, respectively. The SMA and PUR of the seed sludge were about 213.4 mg COD-CH_4/(gVSS d) and 30.5 mg phenol/(gVSS d), respectively.

2.3. CGW

Real CGW used in this study was obtained from the full-scale coal gasification plant at China Coal Longhua Harbin Coal Chemical Industry Co. Ltd. The main characteristics of real CGW after phenol extraction with diisopropyl ether and ammonia stripping are shown in Table 1. The wastewater has a complex composition and low biodegradability (BOD_5/COD = 0.25–0.35). Phenolic compounds were the main organic constituents, accounting for about 40–50% of the total COD.

Table 1
Main characteristics of real CGW

Item	Value
COD (mg/l)	2300–2800
BOD_5 (mg/l)	450–600
TP (mg/l)	500–700
Volatile phenols (mg/l)	200–350
Ammonia (mg/l)	100–150
pH	6.2–7.2

The raw wastewater, supplied at a rate of 0.083 L/h, was appropriately diluted with tap water before treatment during start-up period. The feed nutrients added into the influent consisted of following macro-nutrients: K_2HPO_4 20 mg/l, KH_2PO_4 10 mg/l, $CaCl_2{\cdot}2H_2O$ 20 mg/l, $FeSO_4{\cdot}7H_2O$ 15 mg/l, $MgSO_4{\cdot}7H_2O$ 50 mg/l, $FeCl_3{\cdot}3H_2O$ 10 mg/l and micro-nutrients: $MnCl_2{\cdot}4H_2O$ 0.5 mg/l, $ZnCl_2$ 0.5 mg/l, $CuCl_2$ 0.5 mg/l, $(NH_4)_2MoO_4{\cdot}4H_2O$ 0.5 mg/l, $AlCl_3$ 0.5 mg/l, $CoCl_2{\cdot}2H_2O$ 0.5 mg/l, $NaBO_2{\cdot}10H_2O$ 0.3 mg/l, $NiCl_2{\cdot}2H_2O$ 0.5 mg/l [1].

2.4. Start-up and operation

The start-up was carried out using stepped organic loading to produce most rapid biomass acclimation and development. Organic loadings were enhanced by increasing influent COD concentration upon the attainment of a pseudo-steady state. The start-up period for the two-stage anaerobic digestion and two-phase anaerobic digestion was 210 d. During the start-up period, each reactor was operated continuously without effluent recirculation at a constant HRT of 24 h and an upflow liquid velocity of 0.029 m/h. The COD concentration in the feed was increased step-wise during the three phases of the process, in the following quantities: 1000, 1500, and 2500 mg/l. The corresponding concentrations of TP were around 250, 370, and 600 mg/l, respectively. The removal of COD, TP, and volatile phenols and the running state of the two-phase anaerobic digestion were compared with those of the two-stage anaerobic digestion.

2.5. HRT and effluent recirculation study

2.5.1. Effect of HRT on two-phase anaerobic digestion

The HRT study was initiated after the performance of the two-phase anaerobic digestion reached a steady state at a constant HRT of 24 h. Reactors R3 and R4 were operated at varied HRTs on days 211–303, with an influent COD concentration of 2500 mg/l and a TP concentration of 600 mg/l, in order to determine the optimum HRTs at which COD and TP removals were at a maximum. Details of HRTs in reactors R3 and R4 are as follows: days 211–240, 30 h and 30 h; days 241–271, 18 h and 24 h; days 272–303, 24 h and 18 h. The two-phase anaerobic digestion system was operated without any recirculation during these periods.

2.5.2. Effect of effluent recirculation on two-phase anaerobic digestion

Effluent recirculation is an effective method for treating wastewater containing toxic and hazardous materials. After the HRT study, from days 304 to 319,

the HRT of reactor R4 was gradually restored to 24 h. The effluent recirculation study was performed on days 320–387. Details are as follows: days 320–343, $R = 0.5$; days 344–362, $R^* = 0.5$; days 363–386, $R^* = 1.0$. This part of the study examined the effect of effluent recirculation on the efficiency of two-phase anaerobic digestion in the anaerobic treatment of CGW.

2.6. Biodegradability tests

2.6.1. PUR and SMA tests

PUR was used to assess the biodegradability using the seed sludge and biomass from the UASB reactors. SMA was determined in batch assays with sodium acetate as the substrate. PUR and SMA tests were carried out in 140 ml sealed vials with a working volume of 100 ml. The substrates of phenol and sodium acetate were controlled at a concentration of 300 mg/l and 2,000 mg/l, respectively. PUR and SMA values were expressed as mg phenol/(gVSS d) and mg COD-CH_4/(gVSS d), respectively. The vials were prepared with 3–5 gVSS/L. All tests were performed in triplicate and were incubated at 37˚C and 120 rpm.

2.6.2. Aerobic biodegradability tests

Aerobic biodegradability tests were conducted to evaluate two-phase anaerobic digestion upon increasing the aerobic biodegradability of the CGW; the two-stage anaerobic digestion and aerobic pretreatment were selected as controls. The effluents of two-stage anaerobic digestion and two-phase anaerobic digestion were directly used as two of the objectives of the aerobic tests. Simultaneously, the wastewater with a COD of 2500 mg/l and TP concentration of 600 mg/l underwent aerobic treatment at an HRT of 24 h, and its effluent was the third objective of the tests. The seed sludge was taken from the CGW treatment plant and added to the aerobic reactors in the range of 5000 ± 500 mg MLSS/L. The operation cycle was controlled for 26 h, of which 0.5 h was used for feeding, 24 h for aerobic reaction, 1 h for settlement and 0.5 h for decanting. When these tests achieved a pseudo-steady state, samples of these objectives were measured to evaluate their respective aerobic biodegradability.

2.7. Analytical methods

COD, BOD, TP, volatile phenols, volatile fatty acids (VFA), TSS, VSS and ammonia were determined according to standard methods [14]. pH values were determined daily with a pH meter (pHS-3C, Lei ci, China). Biogas was measured by a gas flow meter and methane content was analyzed using a 3 M NaOH solution.

3. Results and discussion

3.1. Start-up of the two-phase anaerobic digestion and two-stage anaerobic digestion (days 1–210)

During the start-up period, COD concentration in the influent was controlled around 1000, 1500, and 2500 mg/l, respectively. Fig. 1 shows the evolution of COD and TP in the influent and effluent and the removal efficiency obtained with the enhancement of influent pollutant concentration. Initially, COD and TP concentrations in the influent were approximately 1000 mg/l and 250 mg/l, respectively, with the OLR of 1.0 kg COD/(m^3 d) and phenol loading rate (PLR) of 0.25 kg/(m^3 d) in reactors R1 and R3. On day 78, the efficiencies of the two-phase anaerobic digestion in the removal of COD and TP were around 58.2 and 55.6%, respectively, with the influent COD and TP concentrations at 1000 mg/l and 250 mg/l (Fig. 1(a), (c), (e), and (g)). After the influent OLR and phenols loading rate were increased to about 1.5 kg COD/(m^3 d) and 0.37 kg/(m^3 d) on day 93, the two-phase anaerobic digestion was rapidly started up, and the removal of the COD and TP reached 55–60% and 50–55%, respectively, from day 140 onwards (Fig. 1(c) and (g)). On day 152, the influent COD increased to around 2500 mg/l and the corresponding TP concentration increased to around 600 mg/l. After operation of 60 d, the effluent concentrations of COD and TP were below 1,200 and 250 mg/l, respectively, at the end of the start-up period. In the methanogenic reactor, the COD and TP removals were 50–60% and 45–55%, respectively, accounting for about 80% of the total removal efficiencies. On the other hand, in the two-stage anaerobic digestion, the COD and TP removals were both only 40–45% on days 78 and 210 (Fig. 1(d) and (h)). In addition, in the second reactor, the COD and TP removals were both only 10–20%, accounting for about 15% of the total removals. Volatile phenols accounted for 25–35% of the TP, and the removal of volatile phenols by the two-phase anaerobic digestion and two-stage anaerobic digestion reached 70–80% and 65–75%, respectively (Fig. 1(i)–(l)). Fig. 1 (m) and (n) show that the 1.5–2.5 mmol/L molar concentration of volatile fatty acids (VFA) of the two-phase anaerobic digestion effluent was lower than the 2.5–3.5 mmol/L value of those of the two-stage anaerobic digestion effluent.

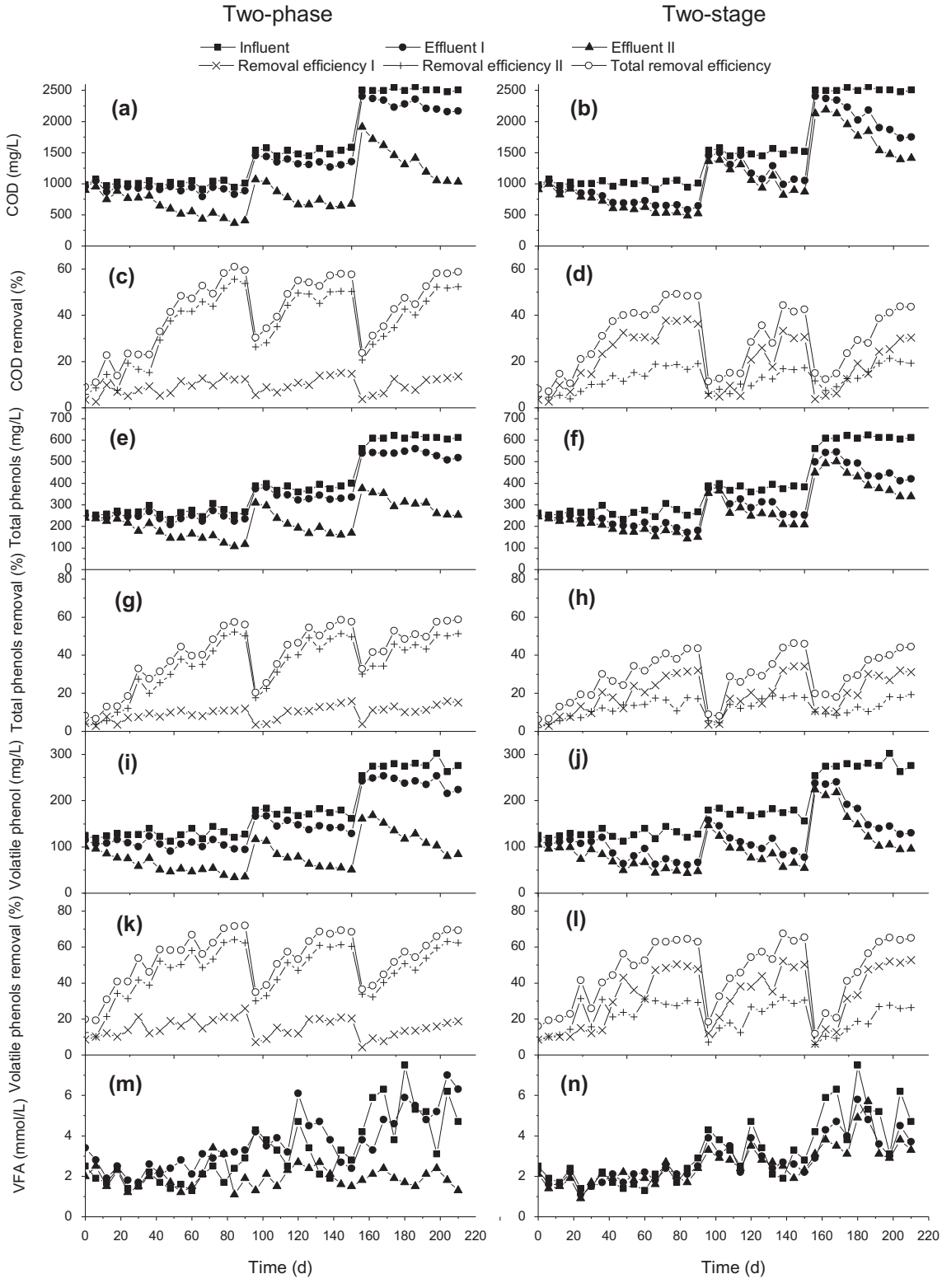

Fig. 1. The start-up of two-phase anaerobic digestion and two-stage anaerobic digestion.
Influent, influent of two-phase or two-stage anaerobic digestion; effluent I, effluent of the first reactor; effluent II, effluent of the second reactor; removal efficiency I, removal efficiency in the first reactor; removal efficiency II, removal efficiency in the second reactor; total removal efficiency, removal efficiency in the whole two-phase or two-stage anaerobic digestion.

Phenolic compounds were dominant organic contaminants in CGW and generally comprised around 45% of the total COD. Therefore, the biodegradation of phenolic compounds was directly related to the treatment efficiency of CGW. The severe toxicity usually causes the failure of the two-stage anaerobic digestion treatment of CGW which does not use a large volume of clean water as diluents or granular activated carbon as absorber. In this study, we observed that the two-stage anaerobic digestion degradation of the major organic pollutants in the first reactor and the organic residues in the effluent were difficult to remove in the second reactor. This not only reduced the treatment capacity of the second reactor, but also limited the effect of two-stage anaerobic digestion on the CGW. In the two-stage anaerobic digestion, methane production was observed only in the first reactor, which indicated that a certain concentration of easily biodegradable substrates would be necessary to reduce the toxicity of CGW. However, the degradation rate of easily biodegradable organics was higher than that of refractory organic compounds. When the most easily biodegradable substrates were depleted, the degradation rate of refractory and toxic organic compounds decreased considerably in the second reactor. On the other hand, in the two-phase anaerobic digestion, a separation of phases in the anaerobic digestion process provides good stability to the different groups of micro-organisms and a more specific control of the conditions required for each one. This separation in two-phase allows the enrichment of the different populations of micro-organisms by means of the control of the operational parameters [15]. Toxic and hazardous substances could be converted firstly in the hydrolytic acidogenic reactor. This would alter the metabolic environment and provide more biodegradable substrate for methanogenic reactor, and moreover, the inhibitory effect of CGW posed on the methanogenic bacteria might be weakened [1]. As shown in Fig. 1, the removal efficiencies of the methanogenic reactor were improved hugely in comparison with that of the second reactor of the two-stage anaerobic digestion. Thus, enhancing the biodegradability of refractory organic compounds could be the key to the success of the technology on the anaerobic treatment of real CGW.

3.2. Effect of HRT on the performance of the two-phase anaerobic digestion (days 211–303)

The above investigations illustrated that the two-phase anaerobic digestion was prior to the two-stage anaerobic digestion in the treatment of real CGW in terms of COD and TP removal. After the start-up period of the two-phase anaerobic digestion (days 1–210), the HRT study was carried out to determine the effect of HRT in each reactor on the performance of the two-phase anaerobic digestion. COD and TP in the influent of the two-phase anaerobic digestion were controlled around 2500 and 600 mg/l, respectively. COD and TP evolution in the influent and effluent and removal efficiency obtained with the variation of the HRT are illustrated in Fig. 2. Between days 211 and 240, the HRT of each reactor was kept at 30 h, and the corresponding OLR and PLR of the hydrolytic acidogenic reactor were about 2.0 kg COD/(m^3 d) and 0.48 kg/(m^3 d). The results indicated that the longer HRTs did not cause a significant improvement in the removal of COD and TP. The COD and TP removal efficiencies remained at 55–65%, and their corresponding concentrations in the effluent remained relatively constant at around 1000 and 200 mg/l, respectively, at a pseudo-steady state. From days 241 to 271, average COD and TP removal efficiencies fell notably from 55–65% to 40–50% when HRTs in hydrolytic acidogenic reactor and methanogenic reactor decreased from 30 and 30 h to 24 and 1 h, respectively (Fig. 2(b) and (d)). At the end of the study, HRT in the hydrolytic acidogenic reactor was increased to 24 h, but in methanogenic reactor it was reduced to 18 h. COD and TP removal efficiencies increased gradually and stabilized at 55–65% and 50–60%.

The chemical composition of CGW is very complex and contains a large number of toxic and refractory compounds, such as phenolic compounds, long-chain hydrocarbons, and heterocyclic compounds. These recalcitrant organics might be refractory to the methanogenic micro-organism and should be converted firstly into biodegradable compounds in the hydrolytic acidogenic reactor. It could be found that the HRT in hydrolytic acidogenic reactor is a key factor affecting COD and TP removal in the two-phase anaerobic digestion. When HRT reduced, it led to shorter contact for micro-organisms and more acidogenic bacteria lose, which resulted in low removal efficiency [16,17]. So under the same influent COD and TP concentrations, the decreased HRT of 18 h in hydrolytic acidogenic reactor was insufficient for the complete transformation of recalcitrant compounds. On the other hand, considering its complex composition and the high concentrations of refractory compounds it contained, COD and TP removal efficiencies could hardly be promoted to a higher level only by extending the contact time between the pollutants and the anaerobic micro-organisms. In this study, removal efficiencies ranged between 60 and 65%, except for the

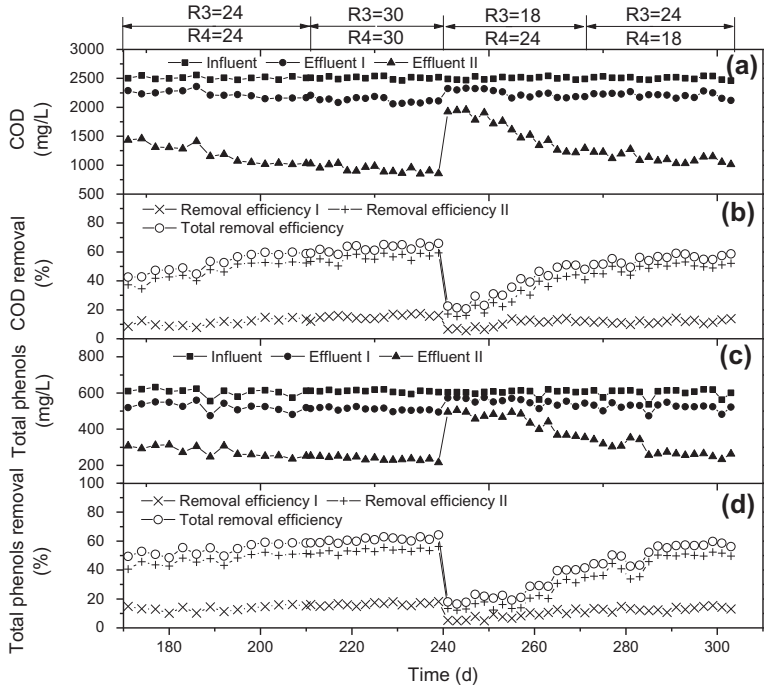

Fig. 2. Effect of HRT on COD and TP removal in the two-phase anaerobic digestion.
Influent, influent of two-phase anaerobic digestion; effluent I, effluent of hydrolytic acidogenic reactor (R3); effluent II, effluent of methanogenic reactor (R4); removal efficiency I, removal efficiency in the hydrolytic acidogenic reactor; removal efficiency II, removal efficiency in the methanogenic reactor; total removal efficiency, total removal efficiency in two-phase anaerobic digestion.

shorter HRT of 18 h employed in the hydrolytic acidogenic reactor, decreasing to 40–50%. Therefore, an HRT of 24 h was adequate to meet the requirements of organic degradation in the hydrolytic acidogenic reactor, and an extended HRT to improve the biodegradation of CGW was unnecessary. After being converted, pollutants in the effluent of hydrolytic acidogenic reactor could be effectively degraded in the methanogenic reactor at an HRT of 18 h.

3.3. Effect of effluent recirculation on performance of the two-phase anaerobic digestion (days 320–386)

The previous running was operated without any recirculation. After the HRT study, from days 304 to 319, the HRTs of the hydrolytic acidogenic reactor and the methanogenic reactor were gradually returned to 24 and 24 h. The effluent recirculation study was performed on days 320–386 to investigate the effect of effluent recirculation on performance of the two-phase anaerobic digestion. Fig. 3 shows the biodegradation of COD and TP in the two-phase anaerobic digestion. From days 320 to 343, 50% of the effluent of two-phase anaerobic digestion was recirculated to the methanogenic reactor. The change in running conditions resulted in a rapid decrease of COD and TP removal. On day 328, the COD and TP concentrations of the effluent increased to 1423 and 330 mg/l, respectively (Fig. 2(a) and (c)). At the end of this phase, the COD and TP removal efficiencies reached 50–55% and 48–53%, respectively. On day 344, 50% of the effluent of the two-phase anaerobic digestion was recirculated to the hydrolytic acidogenic reactor. From days 344 to 355, COD and TP removal efficiencies increased rapidly from 54.3 and 50.2% to 69.7 and 65.9%, respectively; during the same period, the effluent concentrations of COD and TP dropped to 802.8 and 207.3 mg/l, respectively. On day 363, the recycling rate of the effluent was increased to 100%. After operation of 20 d, the COD and TP removal efficiencies increased slightly and stabilized at 68–72% and 66–70%, respectively, on days 383–386.

Effluent recirculation to the hydrolytic acidogenic reactor was not only a dilution method that reduced the toxicity of CGW but was also an effective way to enhance the activity of the biomass in the anaerobic

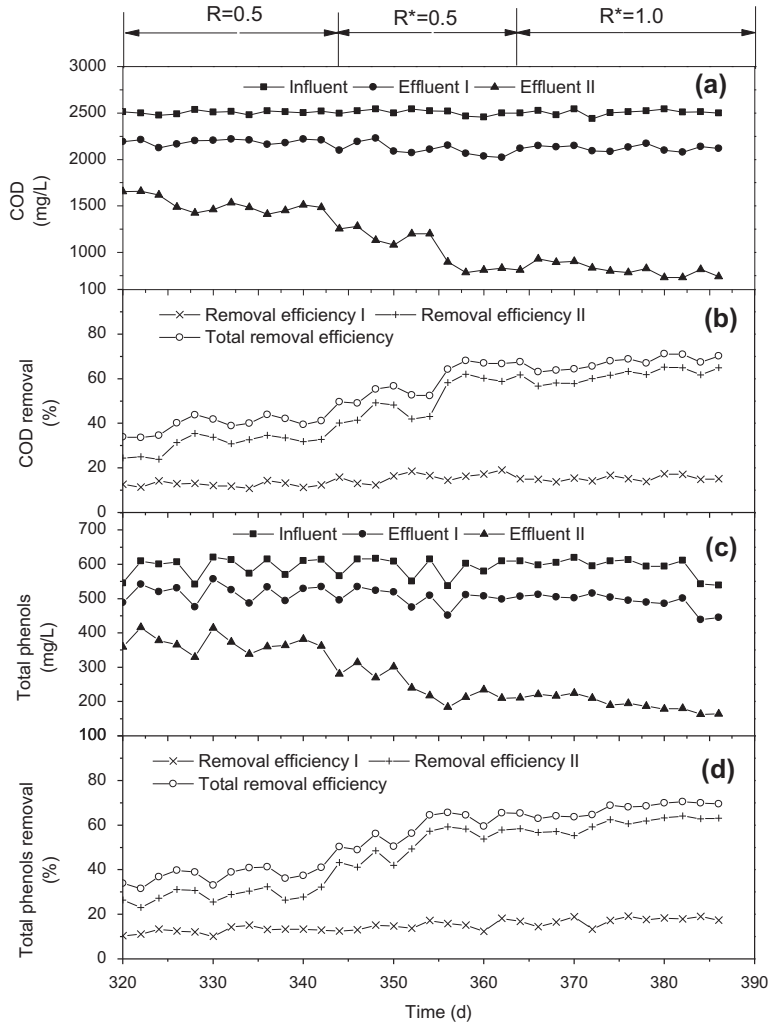

Fig. 3. Effect of effluent recirculation on COD and TP removal in the two-phase anaerobic digestion.
Influent, influent of two-phase anaerobic digestion; effluent I, effluent of hydrolytic acidogenic reactor (R3); effluent II, effluent of methanogenic reactor (R4); removal efficiency I, removal efficiency in the hydrolytic acidogenic reactor; removal efficiency II, removal efficiency in the methanogenic reactor; total removal efficiency, total removal efficiency in two-phase anaerobic digestion; $R = 0.5$, 50% of the effluent of two-phase anaerobic digestion was recirculated to the methanogenic reactor; $R^* = 0.5$ (1.0), 50% (100%) of the effluent of two-phase anaerobic digestion was recirculated to the hydrolytic acidogenic reactor.

reactors [18]. However, the effluent recirculation led to a rapid decline in treatment efficiency, especially in terms of TP removal when 50% of the effluent was recirculated to the methanogenic reactor. As previously mentioned, the anaerobic metabolites of phenolic or other compounds might possibly inhibit the activity of methanogenic bacteria. On the one hand, effluent recirculation to the methanogenic reactor might induce an accumulation of refractory inhibitors, disturb the original metabolic environment in the methanogenic reactor, and cause inhibition of phenols degradation and methanogenesis. On the other hand, the dilution of recycle liquid also might cause difficulty in the uptake of ready biodegradable substrates by methanogenic bacteria.

3.4. Biodegradability tests

3.4.1. PUR and SMA tests

PUR tests using phenol as the sole substrate and SMA tests using sodium acetate as the substrate

were carried out for the biomass during the different periods, as shown in Table 2. At the end of the start-up period, on day 206, the PUR tests and SMA tests displayed a variant increase of PUR and SMA for the biomass in different reactors. In the two-stage anaerobic digestion, higher PUR and SMA values were obtained in reactor R1 in comparison with those in the reactor R2. The primary reason was that the CGW contained several easily biodegradable components such as volatile fatty acids, low molecular PAH, and phenol. These components allowed anaerobic sludge in reactor R1 to maintain a higher metabolic activity. However, when the most easily biodegradable substrates were depleted in reactor R1, residual compounds in the effluent would inhibit the activity of micro-organisms in reactor R2. The results also indicated that the highest PUR and SMA were observed in the methanogenic reactor with values of 74.3 mg phenol/(gVSS d) and 539.2 mg COD-CH_4/(gVSS d), respectively. One reasonable explanation was that the toxic and refractory compounds might have been transformed into easily biodegradable components in the hydrolytic acidogenic reactor and utilized as an extra substrate by bacteria in the methanogenic reactor. During the periods of HRT study, on day 269, PUR and SMA values for the biomass in methanogenic reactor dropped sharply from 79.1 mg phenol/(gVSS d) and 562.1 mg COD-CH_4/(gVSS d) to 57.6 mg phenol /(gVSS d) and 394.3 mg COD-CH_4/(gVSS d), respectively, since the HRT in the hydrolytic acidogenic reactor reduced from 24 to 18 h. On day 362, the values increased to 87.9 mg phenol/(gVSS d) and 619.5 mg COD-CH_4/(gVSS d), respectively, when 100% of the effluent was recirculated to the hydrolytic acidogenic reactor. In general, the two-phase anaerobic digestion significantly enhanced the PUR and SMA for the biomass in the methanogenic reactor. This could be the main reason for the improvement of treatment efficiency in the system.

3.4.2. Aerobic biodegradability tests

Aerobic biodegradability tests were conducted to compare the aerobic biodegradation of CGW via pretreatment with two-stage anaerobic digestion and two-phase anaerobic digestion and with sole aerobic pretreatment. The results of the aerobic biodegradability tests are shown in Table 3. The anaerobic effluents of the two-phase anaerobic digestion and the two-stage anaerobic digestion were treated using the oxic process at an HRT of 26 h. At the end of the start-up period, on day 206, the COD and TP concentrations of the effluent in the two-phase anaerobic digestion–oxic process were 122.9 and 41.8 mg/l, respectively, which were obviously lower than the concentrations of 237.2 and 73.5 mg/l yielded by the two-stage anaerobic digestion–oxic process. In the oxic–oxic process, although the effluent COD and TP concentrations could quickly reach 459.1 and 176.3 mg/l, respectively, in the first oxic stage at an HRT of 24 h, the COD and TP concentrations of the effluent from the second oxic stage still contained 328.5 and 122.4 mg/l.

The recalcitrant organic compounds in the CGW were the most difficult for the anaerobic digestion to break down; and they can greatly inhibit the activity of micro-organisms in the aerobic reactors. The effect of anaerobic digestion on refractory wastewater was not only the organics removal but also the improvement of aerobic biodegradability for post-treatment [19]. Anaerobic digestion, especially the two-phase anaerobic digestion, significantly enhanced the decomposition of refractory organics, which could then be eliminated using the aerobic process. The refractory

Table 2
Results of PUR and SMA tests

Time (days)	PUR mg phenol/(gVSS d)				SMA mg COD-CH_4/(gVSS d)			
	R1	R2	R3	R4	R1	R2	R3	R4
0	30.5	30.5	30.5	30.5	213.4	213.4	213.4	213.4
206	51.4	40.7	39.5	74.3	406.7	379.2	275.3	539.2
238			44.7	79.1			287.9	562.1
269			41.5	57.6			253.9	394.3
302			43.5	72.8			264.5	512.9
340			44.2	58.3			259.2	408.7
362			49.8	85.2			301.2	604.8
385			48.4	87.9			312.6	619.5

R1, the first reactor of the two-stage anaerobic digestion; R2, the second reactor of two-stage anaerobic digestion; R3, the hydrolytic acidogenic reactor; and R4, the methanogenic reactor.

Table 3
Results of the aerobic biodegradability tests

Process	COD_{in} (mg/l)	COD_{eff} (I) (mg/l)	COD_{eff} (II) (mg/l)	TP_{in} (mg/l)	TP_{eff} (I) (mg/l)	TP_{eff} (II) (mg/l)
TSA(I)-oxic(II)	2522.8	1427.5	237.2	601.5	320.4	73.5
TPA(I)-oxic(II)	2522.8	1012.8	122.9	601.5	227.6	41.8
Oxic(I)-oxic(II)	2522.8	459.1	328.5	601.5	176.3	122.4

TSA: two-stage anaerobic digestion; TPA: two-phase anaerobic digestion; oxic: aerobic process; I, pretreatment stage; II, aerobic treatment stage; COD_{in}, influent COD; COD_{eff} (I), effluent COD in the pretreatment stage; COD_{eff} (II), effluent COD in the aerobic treatment stage; TP_{in}, influent total phenols; TP_{eff} (I), effluent total phenols in the pretreatment stage; TP_{eff} (II), effluent total phenols in the aerobic treatment stage.

and inhibitory compounds could be converted and detoxicated by micro-organisms in the hydrolytic acidogenic reactor. Therefore, the two-phase anaerobic digestion facilitated the eventual elimination of certain refractory organics under aerobic conditions. By GC/MS analysis, the two-phase anaerobic digestion–oxic effluent showed a significant decline in the kinds and amounts of phenolic compounds and other ingredients it contained compared with the other two effluents. Furthermore, the degradation capability of the two-phase anaerobic digestion for phenolic compounds was shown to be better than that of the two-stage anaerobic digestion.

4. Conclusion

Poor biodegradability is a typical characteristic of real CGW. Results indicated that the two-phase anaerobic digestion yielded higher treatment efficiency for CGW than did two-stage anaerobic digestion. An HRT of 24 h was adequate to meet the requirements of organic degradation in the hydrolytic acidogenic reactor, and the longer HRTs did not significantly improve the COD and TP removal efficiencies in the two-phase anaerobic digestion. The removal efficiencies of COD and TP increased by approximately 8–13% and 5–10%, respectively, since 50% of the effluent was recirculated to the hydrolytic acidogenic reactor. After two-phase anaerobic digestion, the wastewater concentrations of the aerobic effluent COD could reach below 150 mg/l compared with 237.2 mg/l if two-stage anaerobic digestion was done and 328.5 mg/l if sole aerobic pretreatment was done. The study demonstrated the two-phase anaerobic digestion could serve as a technically feasible and cost-effective method with potential applications for anaerobic treatment of CGW.

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