

Original Research

The Effect of Anaerobic Co-Substrate on Removal of COD, Phenol and Methane Production in Coal Gasification Wastewater Treatment

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Abstract

In this paper, potato starch wastewater (PSW) was adopted as anaerobic co-substrate added in influent of coal gasification wastewater (CGW). The control anaerobic biofilters (AF) and supplemented AF were investigated in our research. Without co-digestion, both of the COD and total phenol removal rates were only 30%, respectively. However, adding PSW (COD = 1000 mg/L) as co-substrate meanwhile increasing concentration of CGW in influent step by step from phase 1 to phase 3. In phase 1 and 2, the effluent COD and total phenol reached 1000 mg/L and 50 mg/L, respectively. Further increasing COD of PSW to 1500 mg/L in phase 4, the removal rates of COD and total phenol almost reached 50%, respectively. The methane production rate was increased to 260 mLCH₄/gCOD/d. In order to further improve the treatment efficiency in co-digestion, the two-stage AFs were adopted in our next study, the result indicated that with adding PSW (COD = 1500 mg/L) in the first stage AF (R1) and extending the HRT of R1 to 48 h, both of the total removal rates of COD and total phenol almost reached 75%, respectively, meanwhile methane production rate of the second AF (R2) rising to 300 mLCH₄/gCOD/d in phase 4.

Keywords: coal gasification wastewater, co-digestion, anaerobic biofilters, two-stage anaerobic biofilters

Introduction

Coal chemical industry is a very promising industry in China and coal gasification is known as the leading

technology in the new coal chemical industry. However the increasing control of pollutant emission by the state is undoubtedly a challenge for the coal chemical industry, which has huge consumption and huge wastewater output [1]. The coal gasification wastewater (CGW) contains many complex, toxic and refractory pollutants such as phenolics, heterocyclics, ammonia

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and sulfide [2-4]. Although through solvent extraction and steam stripping pretreatment, phenols and ammonia can be partly removed, some high concentrations pollutants still existed in effluent [5-8]. Because of the low biodegradability of the CGW which leads to great difficulties to the biological treatment.

Anaerobic biological technologies are characterized by cost-effective and high efficiency in disposing refractory organic substances and could enhance the biodegradability of wastewater [9-11]. There are many anaerobic bioreactors adopted in CGW treatment, such as external circulation anaerobic reactor (ECAR) [12], anaerobic granular activated carbon (GAC) bioreactors, the expanded-bed GAC reactor, and the hybrid UASB reactor [13], AnaEG (anaerobic expanded granular sludge bed) [14]. Among them, AF (anaerobic biofilters) is widely applied in refractory wastewater because start-up time is short, no sludge reflux and additional sludge separation equipment is needed, the effluent SS (suspended solid) is low, and the operation and management are convenient [15]. However, How to alleviate the toxicity of CGW and improve CGW treatment efficiency in AF is a bottleneck of CGW anaerobic treatment. Anaerobic co-digestion technology has been widely used in the treatment of industrial wastewater [16]. Because it is difficult for anaerobic bacteria to directly utilize the refractory substances as carbon source or energy, However, when other easily utilized carbon sources or energy exist in influent, the refractory pollutants could be degraded efficiently in the system, There are some substances added in the CGW as co-substrate in CGW such as methanol [10], glucose wastewater [14]. Potato starch wastewater (PSW) as easily biodegradable substrate is an economic product in coal gasification industry. Hence, it is feasible to enhance the anaerobic biodegradability of CGW as a co-substrate [16]. However, finding the suitable concentration is the key to improve the degradation rate of COD, phenol and methane production in CGW treatment.

Because the conventional single anaerobic process could not get a better performance for the CGW treatment efficiency. Hence it is logically thinking that the two stage anaerobic reactors might get the better result in treating the refractory wastewater than a single reactor. Moreover, the two stage anaerobic reactors can prolong hydraulic retention time (HRT).

Meanwhile, adding co-substrate in the first stage anaerobic reactor is benefit for the organics and refractory organic compounds biodegradation. Thus, optimizing the operation of the two stage anaerobic reactors to continuously carry out co-digestion of easily biodegradable organics and refractory organic compounds could be the key to the success of the technology on the anaerobic treatment of real CGW [17].

The arms of this study were to explore the AF treating CGW with adding PSW as co-substrate and the process efficiency in comparison with the control AF and supplemented AF were investigated. The quick start-up AF under co-digestion conditions and the treatment efficiency of further increasing concentrations of PSW (COD = 1500 mg/L) in AF system were discussed. In addition, two stages AFs in co-digestion strategy applied in treat CGW were studied.

Material and Methods

Anaerobic Biofilter Reactor

The AFs were filled with soft filter and made of cylindrical plexiglass. The influent was pumped into the bottom of the reactor and effluent flowed out from the top. One of the AF (called the supplemented AF) was operated by adding PSW as co-substrate. The other AF (called the control AF) was operated without adding PSW. The effective volume of the supplemented reactor and the control reactor were 2 L and 3.9 L, respectively. Both the two reactors were operated at temperatures of 35°C. The biogas produced in the reactors was pretreated by 3M NaOH absorption and then collected by a gas collection tank. The volume of CH₄ was monitored through gas flow meter.

The effective volume of the two stage AFs were R1 (reactor 1) = 3.9 L and R2 (reactor 2) = 2 L, respectively. The HRT of R1 and R2 depended on the operation need.

Inoculated Sludge

The inoculated anaerobic activated sludge was taken from an expanded granular sludge bed (EGSB) treating starch wastewater. The inoculation volume was 30% of the effective volume of reactor. The suspended solids

Table 1. Characteristics of the coal gasification wastewater.

Parameter	Scale (mg/L)	Average value (mg/L)	Parameter	Scale (mg/L)	Average value (mg/L)
COD	1500-2800	2500	pH	6.8-8.9	7.2
BOD ₅	10-24	13.5	TC	720-850	830
Total phenol	200-400	320	IC	90-150	120
NH ₄ ⁺ -N	180-260	230	TOC	650-760	730

NH₄⁺-N: ammonia nitrogen; TC: total carbon; TOC: total organic carbon; IC: inorganic carbon

(SS) and volatile suspended solids (VSS) in the reactor were about 8.3 and 4.8 g/L, respectively.

Coal Gasification Wastewater

Coal gasification wastewater (CGW) was taken from Harbin Coal Chemical Industry Co, Ltd in China, and it was pretreated by phenol extraction and ammonia stripping. The characteristic of CGW in the research was shown in Table 1.

Potato Starch Wastewater

The PSW was artificially taken by grinding potatoes using grinding machine meanwhile a little sulfate was also added in. The concentration of PSW was depended on the demands of the research.

Analytical Methods

COD, BOD₅, NH₄⁺-N, pH and MLSS were measured according to the standard procedures [18]. TOC, IC and TC were monitored by the total organic carbon analyzer (Japan, Shimadzu TOC-LCSH). The volume of biogas production was determined by wet glass flowmeter, and methane content was analyzed through a 3M NaOH solution. The concentrations of total phenols were measured by the titration method [19].

Result and Discussion

The Start-Up of AF Treating CGW without Co-substrate

As shown in Fig. 1, a constant HRT of the control AF was 48 h and the concentrations of effluent COD and total phenol fluctuated with influent COD and total phenol. The average influent COD and total phenol were about 2592 and 311 mg/L, respectively. The effluent COD and total phenol reached 1827 and 215 mg/L and both removal rates were only 30%, respectively.

The Start-Up of AF treating CGW with Adding PSW as Co-Substrate

Adding PSW as co-substrate, the operation condition was listed in Table 2, As shown in Fig. 2a), the HRT of AF was 48 h, in order to successfully start-up the AF, the CGW was diluted for 4 times in phase 1, meanwhile adding PSW (COD = 1000 mg/L) in the influent, the effluent COD was kept about 750 mg/L and the removal rate of COD was a little fluctuating but more than 50%. In phase 2, increasing the organic load in influent and the CGW was diluted for 2 times meanwhile kept PSW (COD = 1000 mg/L) adding in influent, the effluent COD was about 1000 mg/L. In phase 3, adding PSW (COD = 1000 mg/L) in influent

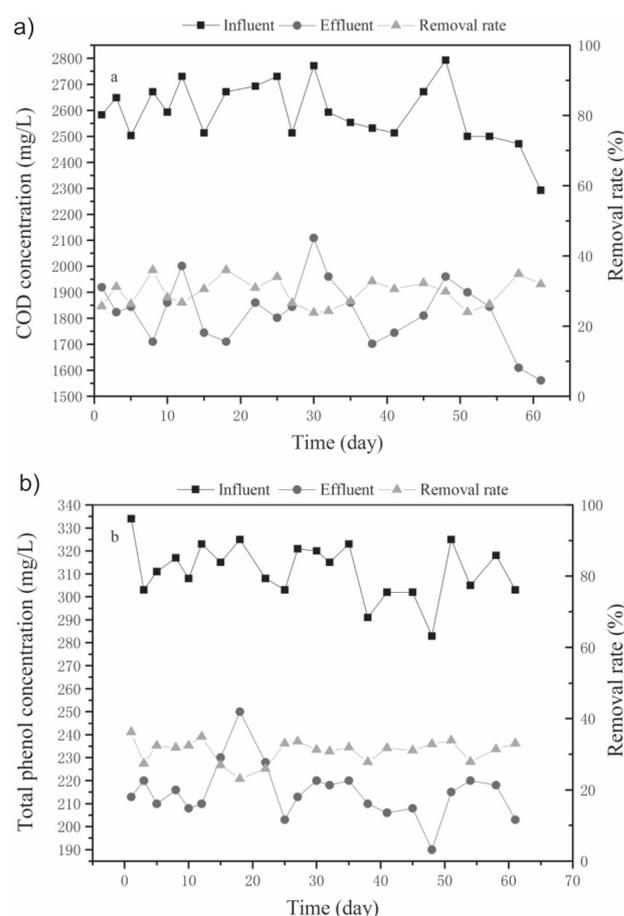


Fig. 1. Performance of the control AF. a) The removal of COD in control AF; b) The removal of total phenol in control AF.

and the CGW without dilution, the effluent COD was increasing to 1500 mg/L.

As shown in Fig. 2b), in order to have an adaptive process for anaerobic microorganism in the system. In phase 1, kept the influent total phenol was about 55 mg/L and the effluent total phenol was stably reached 25 mg/L, In phase 2, increasing the influent total phenol

Table 2. Operational condition in AF treating CGW under PSW as co-substrate.

Phase (day)	COD (mg/L)	PSW (mg COD/L)	Total phenol (mg/L)	HRT (h)
Phase 1 (0-30)	1480	1000	55	48
Phase 2 (30-60)	2100	1000	135	48
Phase 3 (60-90)	3500	1000	315	48
Phase 4 (0-30)	4000	1500	315	48

Phase 1: 4 times dilution of CGW+PSW (COD = 1000 mg/L)
 Phase 2: 2 times dilution of CGW+PSW (COD = 1000 mg/L)
 Phase 3: CGW+PSW (COD = 1000 mg/L)
 Phase 4: CGW+PSW (COD = 1500 mg/L)

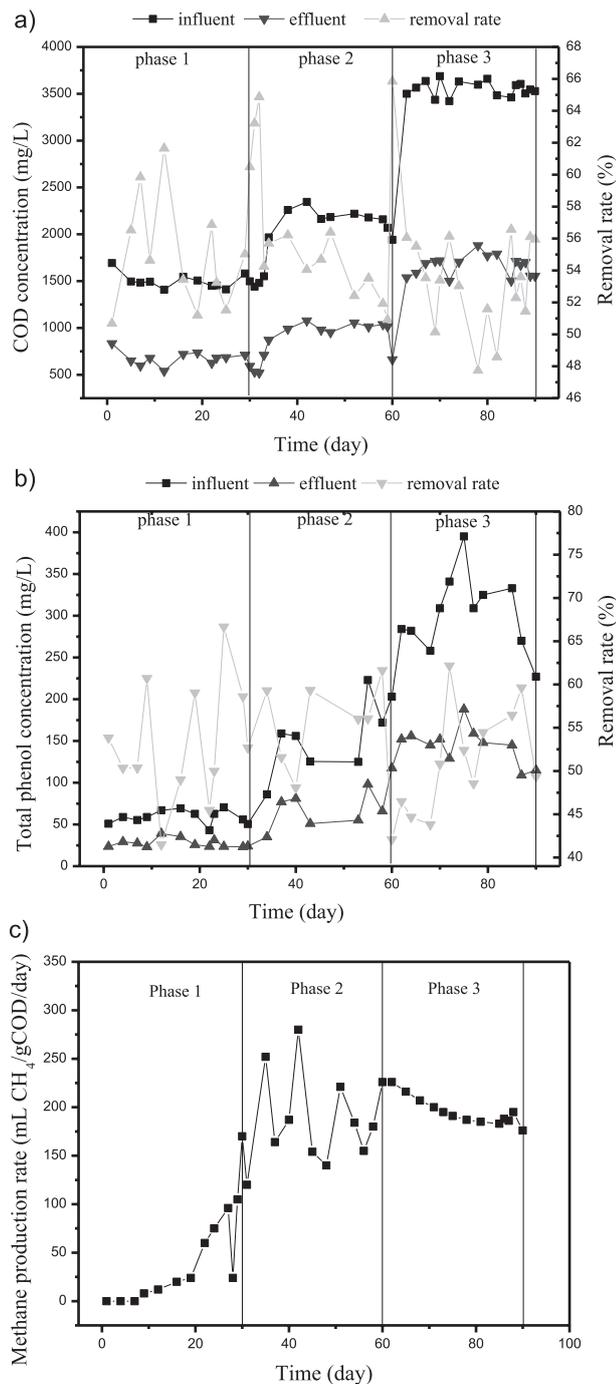


Fig. 2. AF treating CGW with PSW (COD = 1500 mg/L) as co-substrate. a) The removal of COD; b) The removal of total phenol; c) Methane production rate.

to 135 mg/L, the effluent total phenol was kept about 50 mg/L, both of the removal rates in phase 1 and 2 were over 48% respectively and the system was in stability. However, in the phase 3 the CGW without dilution, the effluent total phenol concentration fluctuated greatly and the removal rate was unstable.

In the co-digestion conditions, the methane production rate in the system as shown in Fig. 2c), when adopted step-feed mode, it produced most rapid biomass acclimation and development. The methane

was produced after one week. Moreover, the refractory substances in the system were degraded to some extent because co-substrate can induce the required enzymes of metabolism and generate enough energy to drive the initial transformation of the toxic matters, alleviate the inhibition of methanogens [16]. Hence, the methane production rate rose gradually in fluctuation in phase 1 and 2. In phase 3, with the increasing concentrations of pollutants in the system, the inhibitory effect on methanogens was gradually enhanced which led to methane production rate declined slightly. Hence, in co-digestion conditions, AF indicated good and stable treatment efficiency. However, further enhancing the concentration of CGW in influent, the removal of COD and total phenol showed the unsatisfied results. Zhang [20] has investigated the dynamic model of co-metabolism and made a conclusion that the concentration of growth matrix determined the synthesis of key enzymes in the process of co-metabolism, meanwhile the concentration has an optimal value. The induction and promotion of the synthesis of key enzymes is mainly by increasing the proportion of the growth matrix during the reaction process. Hence, the strategy of increasing the concentration of PSW in influent was adopted in the next operation.

Increasing Concentration of Co-Substrate in AF Treating CGW

As shown on the Table 2, when increasing the concentration of PSW to COD = 1500 mg/L, in phase 4, the effluent COD was about 1500 mg/L, compared with phase 3, Although the organic load in influent was increased, the effluent COD changed little. It was indicated AF system has strong resistance to organic load. Compared with phase 3, the concentration of effluent total phenol was decreased and the methane production rate was obviously increased from 200 mL CH₄/gCOD/d in phase 3 to 260 mL CH₄/gCOD/d in phase 4. Because increasing the concentration of PSW in the system, which provided more microbial carbon or energy, enhanced the microbial synergy metabolism, improved the system of the activity of hydrolytic acidification bacteria especially phenol degradation bacteria which is advantageous to phenol degradation or conversion in anaerobic condition. As shown in Fig. 3c), the AF was running continuously from phase 1 to phase 4 and suddenly increasing a small amount of organic load in influent in phase 4 which can stimulate the growth of methanogens. Hence, the methane production rate can increase to more than 280 mL/gCOD/day. Then the following few days, the increased influent organic load maybe exceeded the degradation capacity of the acid-producing bacteria in the system, hence the methane production rate fell slightly in a short time, and finally stabilized at 260 mL/gCOD/day which still exceeded the methane production rate of the phase 3.

On the contrary, when adding insufficient co-substrate, the key enzymes produced by microbe were

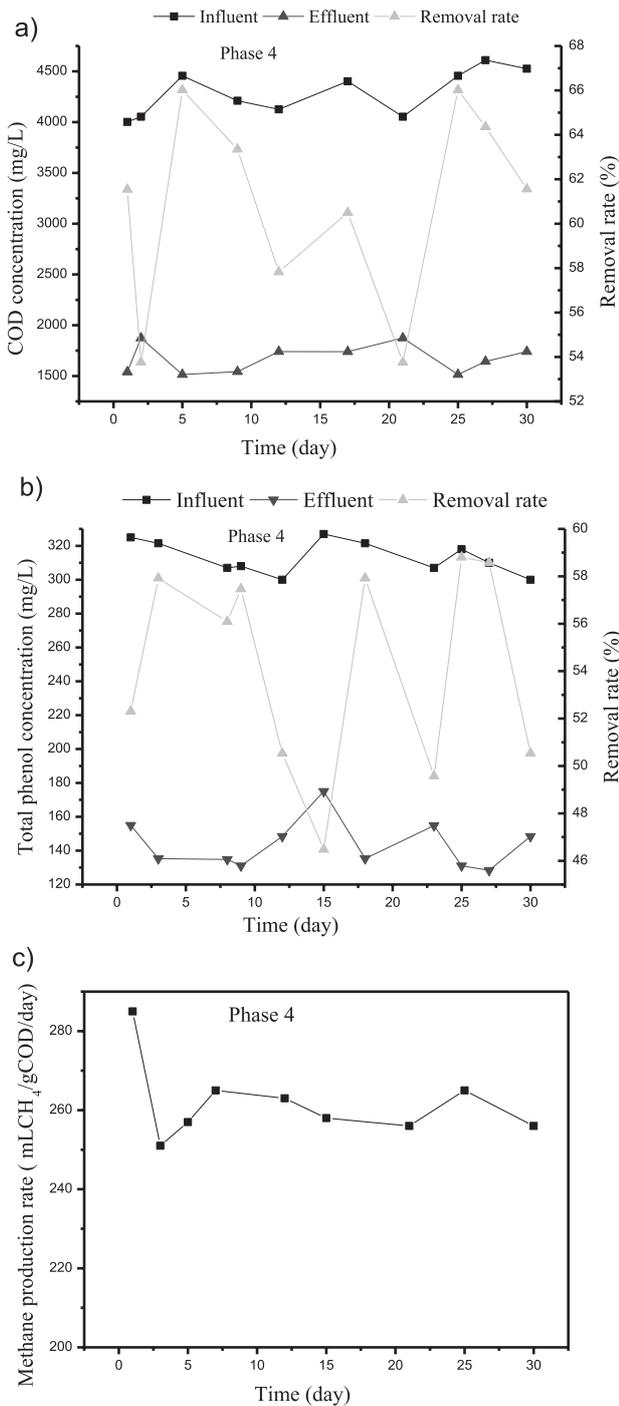


Fig. 3. AF treating CGW with PSW (COD = 1500 mg/L) as co-substrate. a)The removal of COD; b)The removal of total phenol; c) Methane production rate.

Table 3. The operation condition of two stage AFs treating coal gasification wastewater.

Phase (day)	Phase 1 0-15		Phase 2 15-30		Phase 3 30-45		Phase 4 45-60	
	R1	R2	R1	R2	R1	R2	R1	R2
HRT (h)	18	48	24	48	36	48	48	48

Adding the PSW (COD = 1500 mg/L) as co-substrate in influent in all phases in R1.

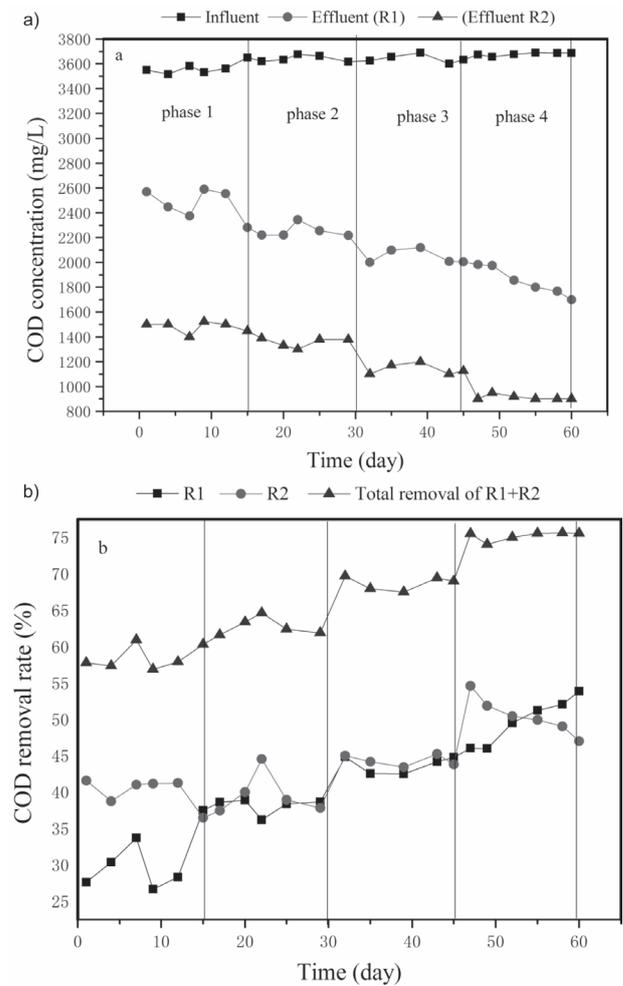


Fig. 4. COD removal of two stage AFs treating CGW with PSW (COD = 1500 mg/L) as co-substrate. a) Variation of influent and effluent COD; (b) COD removal rate.

also reduced correspondingly. Hence, the growth and reproduction of the microorganism lack enough carbon and energy resource, the degradation demand of non-growth matrix cannot be fully satisfied and it could not be degraded efficiently for CGW. Consequently, the refractory pollutants could be accumulated in the system. According to the law of tolerance [21], if the non-growth substrate was in excess in quality or quantity, which is close to or achieve metabolic microbial tolerance limit, the organic pollutants will affect this kind of bacterial biological activity.

The Two-Stage AFs Treating CGW under Co-digestion Conditions

In order to further improve the biodegradation performance and the methane production rate of CGW, the operation of two stage AFs treating CGW was investigated on the basis of co-digestion. The operation condition of the reactors was shown in Table 3. Adding the PSW (COD = 1500 mg/L) as co-substrate in influent

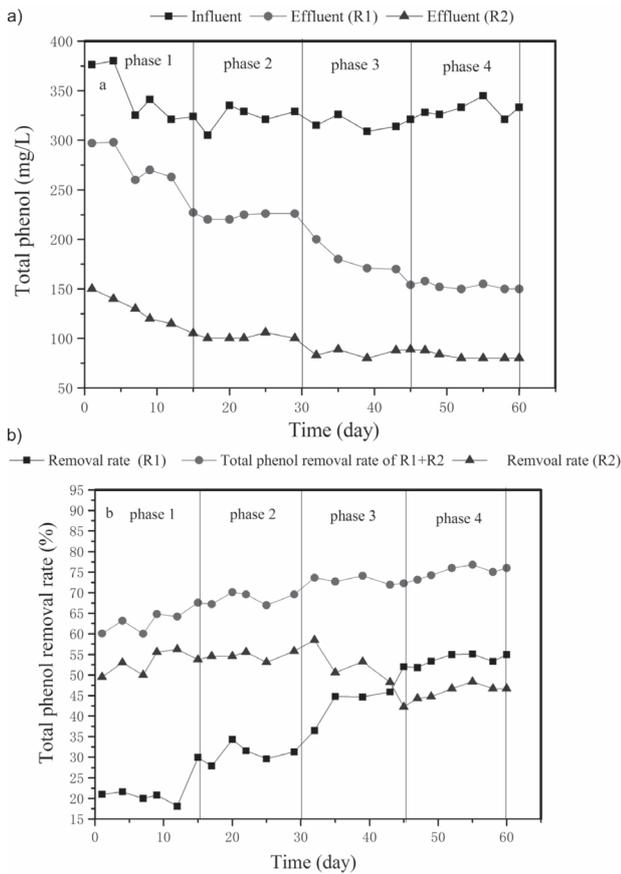


Fig. 5. Total phenol removal of two stage AFs treating CGW with PSW(COD = 1500 mg/L) as co-substrate. a) Variation of influent and effluent total phenol; b) Total phenol removal rate.

in all phases in R1 (reactor 1) and the HRT of R1 were 18 h, 24 h, 36 h, 48 h from phase 1 to 4, respectively. Meanwhile kept the HRT = 48 h in all phases in R2 (reactor 2). As shown in Fig. 4a), with the extending of HRT in R1 in phase 4, the effluent COD of R1 and R2 were decreased to 1800 and 900 mg/L, respectively. And the total COD removal rate of R1+R2 reached 75%. The result indicated that although adding co-substrate in influent, the HRT of phase 1 was short which led to unsatisfied performance with COD removal rate only 30% in R1. In phase 3 and 4, the COD removal rate of R1 reached 53% and the COD removal rate of R2 was fluctuated with that of R1, Hence, the HRT was an important factor in co-digestion process.

The total phenol removal of R1 was shown in Fig. 5, with the prolonging of HRT, the removal rate was enhanced from 21% to 55%, the result indicated that the biodegradation of phenol-degrading bacteria was greatly improved after long time acclimation. Moreover, in phase 4, the total phenol removal rate in R2 was a little decreased compared with R1, because of most of the phenol and monophenol with hypotoxicity and simple chemical structure. Hence, it can be degraded easily in R1. On the contrary, because of the complicated chemical structure and high toxicity, the

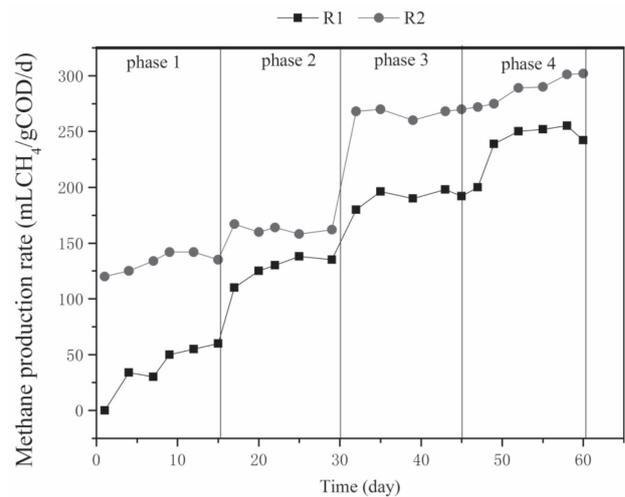


Fig. 6. Methane production rate of two stage AFs treating CGW with PSW (COD = 1500 mg/L) as co-substrate.

left polyphenol was difficult to be biodegraded easily or non-degraded under co-digestion conditions even further prolonging HRT in the system.

The methane production rate as shown in Fig. 6, In R1 and R2, the methane production rate was increased step by step which indicated that on the one hand, adding PSW in the system can benefit for the degradation or transformation of organic pollutants. On the other hand, the organic pollutants treated by two stage AFs and gradually extending HRT can be better for hydrolysis and acidification. Hence, it can bring better performance of methane production rate and in R2 the methane production rate reached almost 300 mLCH₄/gCOD/d in phase 4.

Conclusions

Without co-digestion, the effluent COD and total phenol reached 1827 and 215 mg/L, respectively. With the both removal rates only 30%. When adding PSW (COD = 1000 mg/L) as co-substrate and CGW was step-fed in AF, the effluent COD and total phenol reached 1000 mg/L and 50 mg/L in phase 1 and 2, respectively. However, adding CGW without dilution in phase 3, the treatment efficiency was unsatisfied. When increasing COD of PSW to 1500 mg/L, the removal rates of COD and total phenol almost reached 50%, respectively. The methane production rate was increasing to 260 mLCH₄/gCOD/d in phase 4. In order to further improve the treatment efficiency of CGW, the two stage AFs were adopted in our next research, the result indicated that with adding PSW (COD = 1500 mg/L) under co-digestion conditions, extending the HRT of R1 to 48 h, both of the total removal rates of COD and total phenol almost enhanced to 75%, respectively and methane production rate of R2 was increasing to 300 mLCH₄/gCOD/d in phase 4.

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Conflict of Interest

The authors declare no conflict of interest.

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