

Granulation for Coking Wastewater Treatment in a Coupled Anaerobic-Aerobic Reactor

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Abstract: A coupled anaerobic-aerobic granular bio-film reactor was employed with two operation stages: Stage I, granular sludge was formed from digestion sludge using brewery wastewater, and Stage II, granular sludge was acclimatized using coking wastewater. Two oxygenation methods (i.e. A and B) were employed to acclimatize the granules. For method A, dissolved O₂ was supplied through a continuous oxygenation way of 800-15000ml·min⁻¹. And for method B, dissolved O₂ was supplied of 800-15000ml·min⁻¹ 18-12 times at 20-60min intervals, 1h each time. The experimental results showed that granules could quickly form in 10d in the EGSB reactor seeded with digestion sludge and little loose granules lack of nutrition, and it was the key factor for granules forming to add little loose granules. It took only about 6 months for granules acclimation using coking wastewater. Both oxygenation methods could run well when acclimatizing the granules. However, method A could have comparatively high and stable operation effect. The actual coking wastewater had distinct inhibition effect on the granules, but the supplement of some oxygen could promote the recovery of SMA, and NaHCO₃ supplement could also weaken the inhibition effect of the CWW. Method A had more strongly activity recovery ability than method B.

1 Introduction

The A²/O biological treatment system is frequently used in order to treat coking wastewater for the toxic organic compounds and NH₃-N removal. But there are problems which are inherent to an anaerobic/aerobic treatment sequence (such as the A²/O system) since the anaerobic transformation of toxic organic compounds is often incomplete^[1-4]. The metabolites of anaerobic treatment may also be inhibitory to the methanogens themselves, resulting in declining anaerobic treatment efficiencies and adding to the load on the downstream aerobic treatment system^[5-11]. Intimate contact of aerobes with anaerobes may reduce the accumulation of toxic intermediates as the aerobes would achieve an in situ removal of these anaerobic metabolites^[12,13].

A simultaneous anaerobic/aerobic treatment methodology using granular sludge was recently described (example for the granule in the EGSB reactor)^[14-17]. Facultative bacteria have been shown to be predominant in the peripheral layer while the methanogens are preferentially biodegradation of the recalcitrant xenobiotic compounds but also in the simultaneous removal of toxic organic compounds and NH₃-N in the coking wastewater. Therefore, integration of EGSB for the toxic organic pollutants removal and NH₃-N removal will be a powerful alternative for coking wastewater treatment.

However, the successfully culture and acclimation of the granule of anaerobic/aerobic coupled bioreactors are

still a preliminary stage. In particular, forming and acclimation of the granular sludge treating coking wastewater were more important. Because the stably and highly efficiently granular sludge reactors used to treating industrial wastewater, particular for the coking wastewater were very less, and thus it is difficult and often impossible to obtain enough granular sludge to startup a large scale EGSB reactor in many countries, and other seed materials usually have to be chosen. The digestion sludge is considered to be available seed material because it has high methanogenic activity together with a complicated microorganism ecosystem that was suitable for treatment of many kinds of wastewater.

Brewery wastewater was usually used for the anaerobic granulation of the digestion sludge and only 46d was requisite for the forming of high activity granular sludge. But directly using coking wastewater to startup the granular sludge bioreactor was comparatively difficult. And even for the anaerobic SBR treating actual coking wastewater, it also took about 9 months to run well^[18]. Thus it was necessary to search an available strategy for quickly start-up of the EGSB reactor (seeded with digestion sludge) treating actual coking wastewater. Two issues were needed to consider. One was how to quickly produce the granular sludge from digestion sludge. The other was how to quickly acclimatize the granules to highly efficiently treat the coking wastewater and meanwhile gain high COD and ammonia removal.

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The investigation reported herein was tried to demonstrate the feasibility of using digestion sludge and little loose granules as the seed for quick startup of the EGSB reactor treating coking wastewater and also meanwhile contrastively analyze the influence of the continuous and intermittent oxygenation methods on the granular sludge acclimation process. In addition, batch bioassays were also performed to gain more insight into granular activity through assaying the SMA change.

2 Materials and methods

The research was carried out in two lab-scale EGSB reactors. The 2.3m height EGSB reactor was an acrylic column with a conical-shaped bottom, a working volume of 12L, an internal diameter of 10cm. The wastewater used as influent to the reactor was obtained one from synthetic wastewater using sucrose, beer and sodium acetate as the carbon source and NH_4Cl , KH_2PO_4 , $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$, $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$, $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ as nutrients, and the other from the actual coking wastewater collected from the buffer tank of the first coking plant of Taiyuan Coal Gas and Chemical Stock Co., LTD. located in Shan'xi Province, North China with $818\text{-}978\text{mg}\cdot\text{L}^{-1}$ COD, $12.8\text{-}49.3\text{mg}\cdot\text{L}^{-1}$ phenol, $1.82\text{-}57.8\text{mg}\cdot\text{L}^{-1}$ CN, $66.7\text{-}154.7\text{mg}\cdot\text{L}^{-1}$ SCN and $6.5\text{-}8.1$ pH. No KH_2PO_4 were added to the influent. But NaHCO_3 and some trace metals for Fe, Co, Ni were added. A schematic diagram of the experimental EGSB reactor used is presented in Fig.1.

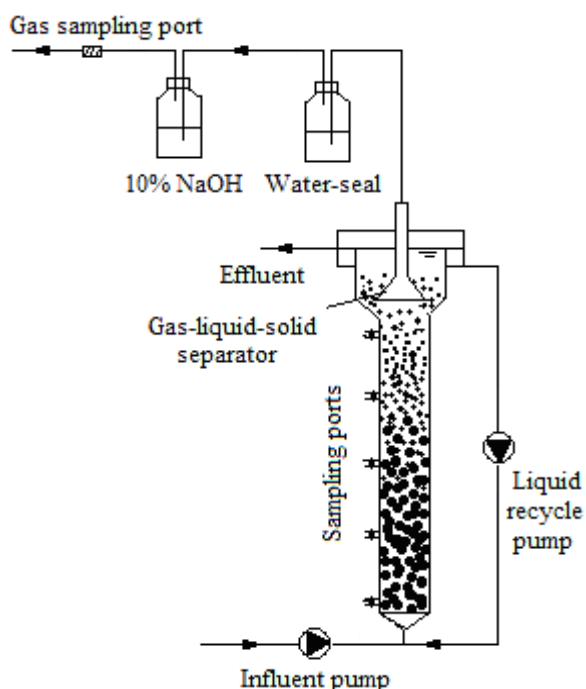


Fig.1 Schematic diagram of the experimental EGSB reactor

2.1 Seed sludge

The inoculum used in this experiment was municipal digestion sludge and little loose granules. The anaerobic digestion sludge was obtained from the dehydrated sludge from an anaerobic digester at YangJiaBu

Wastewater Treatment Plant, TaiYuan (its activity was resumed before seeding into the EGSB reactor). And the granular sludge was obtained from a pilot-plant anaerobic EGSB reactor treating actual brewage wastewater for two years. Moreover, the granular sludge was deposited without any nutrients addition for two years under ambient temperature. Thus, the granules were loose. The EGSB reactor had $21.1\text{gSS}\cdot\text{L}^{-1}$ biomass concentration and the VSS/SS was 0.51.

2.2 Analytical methods

Effluent was collected and centrifuged at 4000rpm for 5-6min with a centrifuge (80-2B, ANTING). And then the supernatant was used for further analysis. COD, ammonia, phenol and CN were measured according to the Chinese Standard Methods for Water and Wastewater Monitoring and analytical methods^[19]. SCN measurement was performed with the American Standard Methods^[20]. Specific methanogenic activity test was accomplished as described by Zhao et al^[21].

2.3 Operating strategy

The operation process of anaerobic Granulation in EGSB reactor seeded with digestion sludge for treatment of actual coking wastewater was separated into two stages. First, at stageI, granular sludge was formed through using brewery wastewater as influence and seeding anaerobic digestion sludge in the EGSB reactor (meanwhile adding little granules, which were 1/7 of the total biomass in the EGSB reactor). And then at stageII, the granular sludge was acclimatized with the actual coking wastewater with about $900\text{mg}\cdot\text{L}^{-1}$ COD concentration. And two oxygenation methods i.e. A and B were employed. For method A, the micro-aerophilic environments in the reactor A (RA) was generated through continuously supplying dissolved O_2 to the aeration column and then to the granule sludge bed in the EGSB reactor. For method B, the intermittent oxygenation way was used and different dissolved O_2 was supplied to the granule sludge bed in the reactor B (RB). An air pump supplied air through a porous stone diffuser, located at the bottom of the anaerobic column. The air flow rate was regulated by an air flow-meter. The oxygenation flow rate (air flow rate) increased from $800\text{ml}\cdot\text{min}^{-1}$ to $15000\text{ml}\cdot\text{min}^{-1}$ for the RA, and in a day, the RB was intermittently aerated with an air supply of $800\text{-}15000\text{ml}\cdot\text{min}^{-1}$ 18-12 times at 20-60min intervals, 1h each time. Superficial flow rate and recycle ratio of $3.0\text{m}\cdot\text{h}^{-1}$ and 22.3 were employed to offer a suitable hydraulic condition. The OLR was $1.1\text{-}2.4\text{kgCOD}\cdot\text{m}^{-3}\cdot\text{d}^{-1}$ with an influent flow of $1.0\text{L}\cdot\text{h}^{-1}$ and a HRT of 12.0h. The process parameters such as COD, $\text{NH}_3\text{-N}$, phenol, cyanide and thiocyanate concentration and removal efficiency, ORP and dissolved O_2 concentration were regularly monitored.

Using CaAc_2 as substrate and taking granules samples from the RA and RB, the specific methanogenic activity (SMA) assays were performed for the varied operation stage: 1) before and after treating coking

wastewater (CWW), 2) the anaerobic and microaerobic conditions after treating CWW, 3) SMA contrastive assay was also performed.

3 Results and discussions

The anaerobic granulation in RA (continuous oxygenation EGSB) and RB (intermittent oxygenation EGSB) seeded with anaerobic digestion sludge for treatment of actual coking wastewater was operated for about 7 months. First, the EGSB reactor was operated for approximately 1 month for the forming of granules from anaerobic digestion sludge. And then, the EGSB reactor was operated for the acclimating of the granules by actual coking wastewater for about 6 months (from days 29 to days 157 without the addition of NaHCO_3 and from days 158 to days 205 with the addition of NaHCO_3). Fig.2 shows the influent COD concentration and COD removal efficiency changes for the intermittent and continuous oxygenation. And the ammonia removal efficiency variations for the RA and RB were presented in Fig.3 and Fig.4.

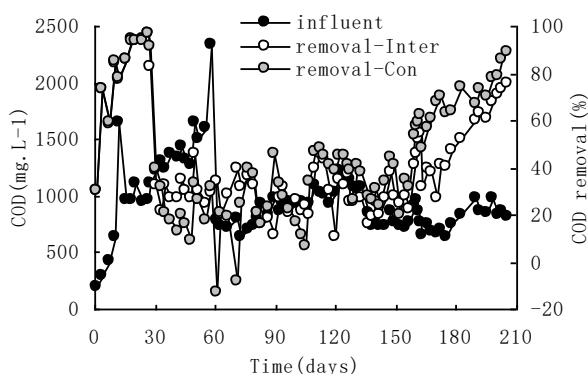


Fig.2. influent COD and COD removal for the intermittent and continuous oxygenation

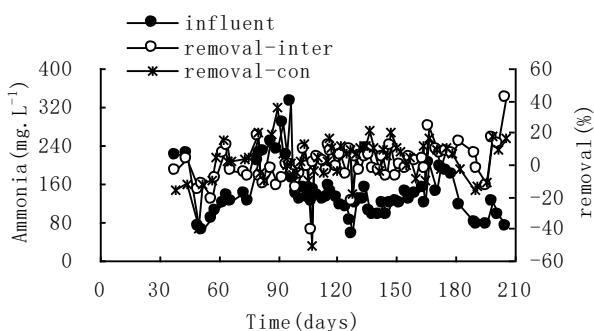


Fig.3. influent ammonia and ammonia removal for the intermittent and continuous oxygenation

StageI: granules forming. It took about only 10d for the forming of lots of granular sludge in the EGSB reactor seeded with digestion sludge and little loose granules. The COD removal efficiency had attained to 85%. However, at days 12, the EGSB reactor suffered a load shock, and the influent COD concentration abruptly increased from $630\text{mg}\cdot\text{L}^{-1}$ to $1650\text{mg}\cdot\text{L}^{-1}$, meanwhile the organic load rates (OLR) also soon increased from $5.5\text{kgCOD}\cdot\text{m}^{-3}\cdot\text{d}^{-1}$ to $11.9\text{kgCOD}\cdot\text{m}^{-3}\cdot\text{d}^{-1}$, thus the COD removal efficiency immediately decreased to 78%.

However, only after 4 day, the COD removal efficiency resumed to 86%, and after 6 day increased to 94%. Which indicated that the granules cultured in the EGSB reactor through anaerobic digestion sludge had very strong supporting loads shock ability. In succession, through shorting HRT from 3.0h to 2.4h and increasing OLR from $7.5\text{kgCOD}\cdot\text{m}^{-3}\cdot\text{d}^{-1}$ to $18.0\text{kgCOD}\cdot\text{m}^{-3}\cdot\text{d}^{-1}$, stably operated for about 10d, the EGSB reactor could gain a stable COD removal efficiency of about 94.8%. Thus the granulation process in the EGSB reactor seeded with digested sludge had accomplished, and meanwhile, biomass concentration of $19.6\text{g}\cdot\text{L}^{-1}$, MLVSS/MLSS of 0.64 and specific methanogenic activity of $0.75\text{gCOD}_{\text{CH}_4}\cdot\text{gVSS}^{-1}\cdot\text{d}^{-1}$ were also attained in the EGSB reactor. The key factor for the rapid granulation in the EGSB reactor seeded with digestion sludge was not the use of brewery wastewater as substrate, but was the supplement of little granules which were loose and even decayed because of suffering the double disadvantage of lack of nutrients and low temperature.

StageII: granules acclimating (without the addition of NaHCO_3) (from days 29 to days 157). the RA and RB were operated for the acclimating of the granules by actual coking wastewater with about $1200\text{mg}\cdot\text{L}^{-1}$ COD concentration (shorting HRT from 3.5h to 1.0h), and meanwhile $800\text{ml}/\text{min}$ air was supplied and no NaHCO_3 was added in the influent. Only after 10 day, the COD removal efficiency decreased from 97% to 9% in the RA, and 97% to 27% for the RB. However, at days 39, the COD removal efficiency in the RA and RB quickly ascended to 33% and 46% although with influent COD concentration increasing from $1200\text{mg}\cdot\text{L}^{-1}$ to $1600\text{mg}\cdot\text{L}^{-1}$, which indicated that the granules had already adapted the coking wastewater quality. Subsequently, at 4 days after the 39th day, the influent quality was presented a great shift of increasing COD concentration abruptly from $1600\text{mg}\cdot\text{L}^{-1}$ to $2330\text{mg}\cdot\text{L}^{-1}$ and changing from golden and clear to black and ropy. The RA had a distinct COD removal decreasing of 33% to -13%, and only 46% to 34% for the RB, Which indicated that the intermittent oxygenation method (RB) had distinct advantage of supporting load shock compared with continuous oxygenation method (RA). But after 15 day, the COD removal efficiency resumed to 40% and 37% for the RA and RB, and then for about 2 months stable operation (from days 76 to days 157), the RA had an average COD removal of 32.7%, distinctly higher than the COD removal of 26.8% in the RB. But, subsequently though gradually increasing oxygen supplement from $1500\text{ml}\cdot\text{min}^{-1}$ to $4000\text{ml}\cdot\text{min}^{-1}$, the maximal COD removal efficiencies in the RA and RB were still not exceeded 48% and 46%, and which might be caused by the presence of some toxic substances or thiocyanate(SCN^-). The SCN^- removal of the RA was fluctuated between -12% and 8%, and the RB also only had an average SCN^- removal of -3.5% (-17.9%-3.6%). Moreover, the RA and RB only could have very low ammonia average removal efficiency of 2.4% and 2.3%, respectively. It has reported that ammonia oxidizing bacteria complete with thiocyanate-degrading bacteria for inorganic carbon and other essential nutrients [22]. And the competition of population

growth between autotrophs for the SCN and CN degradation and heterotrophs for the organics degradation was also existed [23]. The actual coking wastewater had a BOD/COD value of 0.4-0.53, which perhaps indicated that the organics degradation heterotrophs was not restrained when organic carbon source was sufficient for the SCN and CN degradation bacteria. Thus, subsequently some NaHCO_3 was added to investigate the treatment performance of the EGSB reactor, such as the removal of the COD, ammonia phenol, CN^- and SCN^- .

Stage III: granules acclimating (with the addition of NaHCO_3) (from days 158 to days 205). At days 157, bicarbonate was added to feed wastewater ($3.0\text{gNaHCO}_3/\text{L}$) to be used as a source of inorganic carbon by autotrophic microorganisms, thus to favor the nitrification process or the thiocyanate degradation process. The lack of inorganic carbon may have caused incomplete degradation of thiocyanate in the aerobic zone, where thiocyanate-degrading bacteria compete with ammonia oxidizing bacteria for the carbon source [24]. For the RA and RB, the COD removal efficiency had a distinct improvement from 31.5% and 22.5% to 54.1% and 41.4%. Subsequently, at days 163, with an abrupt increasing of the oxygenation flow rate from $5000\text{ml}\cdot\text{min}^{-1}$ to $15000\text{ml}\cdot\text{min}^{-1}$, the COD removal efficiency had no increase instead of a distinct decrease from 54.1% and 41.4% to 48.4% and 31.6% for the RA and RB. But the RA (with continuous oxygenation way) could resume to 57.4% after 3 days, and the RB (with an intermittent oxygenation way) still had a very low COD removal efficiency of 27.1% after 7 days. Subsequently, for the RA, the COD removal fleetly increased, and at days 203 attached to 86%, at days 205 high to 89%. But for the RB, the COD removal efficiency was comparatively low, and from days 170 to days 190, only had an increasing of 27%→41%→47%→52%→60%(68%→70%→64%→74%→67% for the RA), and even at days 203 and days 205, the COD removal efficiency was only 73% and 75%. In conclusion, the continuous oxygenation way was advantageous to the COD removal.

The supplement of NaHCO_3 was favorable for the removal of ammonia. When no NaHCO_3 supplied, the RA and RB only had a very low ammonia average removal efficiency of 2.4% and 2.3%. However, with $3.0\text{g}\cdot\text{L}^{-1}$ NaHCO_3 addition, the ammonia average removal efficiency was increased to 2.8% and 8.9% for the RA and RB, respectively. It was very distinct that the RB (with intermittent oxygenation way) had higher ammonia removal of 41.9% than the RA of 16.7%. Moreover, the RB had more stronger supporting toxic substances (such as SCN) shock ability, and when influent SCN concentration having a fluctuation of $106.5\text{mg}\cdot\text{L}^{-1}$ → $82.9\text{mg}\cdot\text{L}^{-1}$ → $121.3\text{mg}\cdot\text{L}^{-1}$ → $86.1\text{mg}\cdot\text{L}^{-1}$ (presented in the Fig.3), the RB had an ammonia removal efficiency change of 7.7%→14.5%→7.2%→16.2%. however, the change of 7.3%→-2.0%→-15.8%→18.3% was for the RA. Thus, the intermittent oxygenation way (RB) was more suitable than the continuous oxygenation way (RA) for the ammonia removal.

The phenols removal efficiency variations for the RA and RB were presented in Fig.4.

From days 122 to days 137, with $95.3\text{-}97.6\text{mg}\cdot\text{L}^{-1}$ influent phenol concentration, the RA could have 18.6%-53.1% phenol removal efficiency, but only -16.0%-24.2% for the RB. At days 138, the phenol removal efficiency fleetly increased to 93.1% for the RA, and only 34.8% for the RB. From days 140 to days 205, the RA could always keep very high phenols removal efficiency of 98.3%-100%, which is equivalent to an effluent phenol concentration level of $0.0\text{-}0.8\text{mg}\cdot\text{L}^{-1}$. Correspondingly, for the RB, the phenols removal efficiency began to increase from 34.8% (at days 138) to 99.2% (at days 164), and subsequently from days 164 to days 205, the RB had a stable phenols removal efficiency of 95.7-99.9%. For the RA, the phenol removal had no changes after adding NaHCO_3 . But for the RB, the supplement of NaHCO_3 was very essential. Only with $3.0\text{g}\cdot\text{L}^{-1}$ NaHCO_3 addition, the phenol removal fleetly increased from 27.4% to 70.2%. And then within 7 days (from days 157 to days 164), the phenol removal gradually rise to 99.2%.

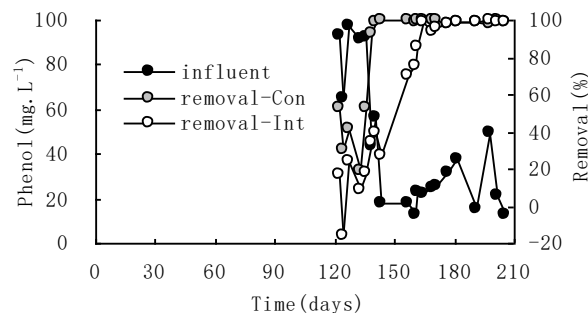


Fig.4. influent phenol and phenol removal for the intermittent and continuous oxygenation

Fig.5 presented the changes of influent cyanide (CN) concentration and cyanide (CN) removal efficiency for the RA and RB, and Fig.6 showed the variation of influent thiocyanate (SCN) concentration as well as the removal efficiency in the RA and RB.

From days 102 to days 110, for the RA and RB, CN removal efficiency rapidly increased from 67.6% and 35.3% to 92.0% and 84.0%. Subsequently, the RA could keep stable high CN average removal efficiency of 95.7% (fluctuating between 89.2% and 100.0%). Correspondingly, the RB had a lag period for the high CN removal efficiency of 97.0% (at days 126) from 84.0% (at days 120). Subsequently, from days 126 to days 181, the RB could attain a stable CN average removal efficiency of 95.1% (80.4%-100%). However, from days 190 to days 205, the CN average removal efficiency was abruptly decreased to 75.7% (71.4%-81.5%). Perhaps it was owing to the fluctuation of influent SCN concentration. But the CN removal in the RA was not decreased (94.5%-100%), which also predicated that the continuous oxygenation way (RA) was advantageous to the stable CN removal. Before and after adding NaHCO_3 , the CN removal had no change for the RA and RB.

When no NaHCO_3 supplied, the RA and RB were always kept negative SCN average removal efficiencies of -1%(fluctuating between -12% and 8%) and -

3.5% (fluctuating between -17.9% and 3.6%). However, with the addition of $3.0\text{g}\cdot\text{L}^{-1}$ NaHCO_3 (at days 160), the RA had a distinct increasing of SCN removal efficiency from -6% to 21%, and after 20 days (at days 180), the SCN removal was attained to 100%. While for the RB, until to days 169 (after 12 days for adding NaHCO_3), the SCN removal just attained to a positive value of 5.3% and then gradually increased to 44.0% (at days 181), and perhaps the shift of SCN removal from negative to positive was owing to the increasing of the oxygen supplement from 5000 ml min^{-1} to 15000 ml min^{-1} . And which also indicated that sufficient oxygen supplement was very important for SCN removal, and compared with the continuous oxygenation way (RA), the RB with intermittent oxygenation way couldn't ensure enough oxygen for the thiocyanate-degrading bacteria and thus only had relatively low SCN removal efficiency. From days 181 to days 205, the RB had a stable SCN removal and the SCN average removal was 36.5% (27.5%-44.1%).

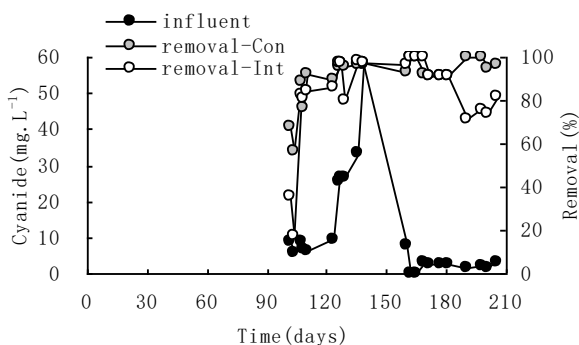


Fig.5. influent cyanide and cyanide removal for the intermittent and continuous oxygenation

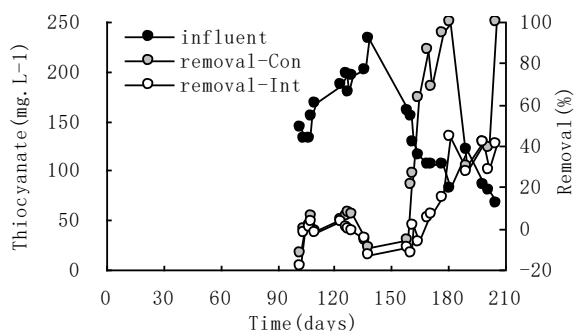


Fig.6. influent thiocyanate and thiocyanate removal for the intermittent and continuous oxygenation

Fig.7 presented the SMA changes of the granules samples taken from the RA and RB for varied operation stage: before treating CWW, after treating CWW for 33 days, 4 months. Not only the actual coking wastewater supplement but also the oxygen supplement could have influence on the SMA. Along with the treating of actual coking wastewater (with $1280\text{-}2200\text{mg}\cdot\text{L}^{-1}$ COD and 1.0L/h influent flow) and oxygen supplement, the SMAs of the granules in the RA and RB were increased 14.3% and 5.3% (after 6 days, with $800\text{ml}\cdot\text{min}^{-1}$ air flow rate), and 20.2% and 4.5% (after 33 days, with $1200\text{ ml}\cdot\text{min}^{-1}$ flow rate), respectively. Some oxygen supplement was probably very important, and which could facilitate the

removal of some toxic or inhibitory compounds in the coking wastewater and could weaken the inhibition of the toxic or inhibitory compounds on the methanogens. However, when treating coking wastewater for 4 months, although already increasing air flow rate to $5000\text{ml}\cdot\text{min}^{-1}$, the SMA was not increased but reduced 26.5% and 34.0% compared with the parallel (before treating CWW), which indicated that the actual coking wastewater had distinct inhibition effect on the granules for the long term operation of the RA and RB. And what's the crucial factor influencing or restraining the SMA of the granules? The toxic or inhibitory compounds in the coking wastewater or the overmuch oxygen supplement (because with $1200\text{ml}\cdot\text{min}^{-1}$ oxygen supplement, the SMA was not reduced but increased)?

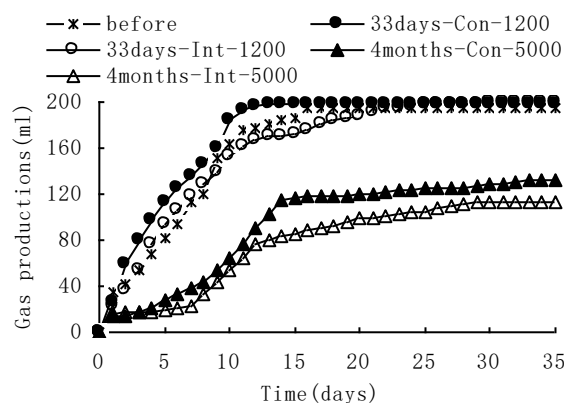


Fig.7. SMA for varied operation stage

We contrastively analyzed the SMA change at the two conditions of anaerobic and micro-aerobic with the same air flow rate of $5000\text{ml}\cdot\text{min}^{-1}$ and $15000\text{ml}\cdot\text{min}^{-1}$ and before and after adding NaHCO_3 (presented in Fig.8 and Fig.9).

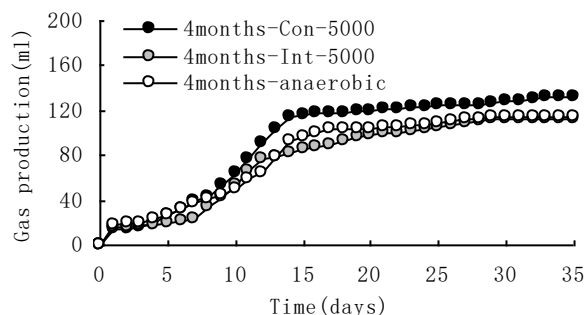


Fig.8. SMA for anaerobic and micro-aerobic (4 months)

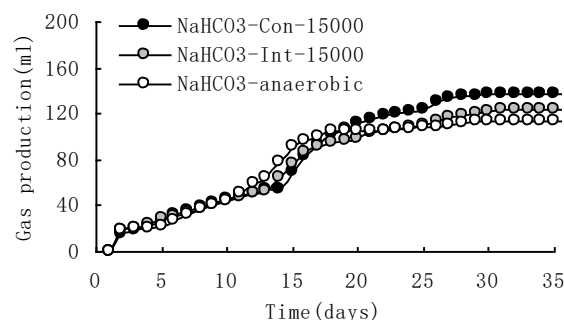


Fig.9. SMA for anaerobic and micro-aerobic (adding NaHCO_3)
 Compared with anaerobic condition, for the RA and RB, supplement oxygen with $5000\text{ml}\cdot\text{min}^{-1}$ air flow rate,

the SMA was increased with 22.9% and 10.4%, respectively. Subsequently, enhancing the air flow rate to 15000ml.min⁻¹ and meanwhile adding 3.0g.L⁻¹ NaHCO₃, the SMA kept more distinct enhancing trend (35.4% and 17.7% for the RA and RB), and which indicated that the distinct reduction of SMA (treating CWW for 4 months) was not caused by the overmuch oxygen supplement, but caused by the toxic or inhibitory compounds in the coking wastewater. NaHCO₃ supplement could facilitate the degradation of SCN and some toxic compounds and thus weaken the inhibition effect of the CWW on the methanogens (or on the granules).

4 Conclusions

The micro-aerobic granulation process for actual coking wastewater treatment in a coupled anaerobic-aerobic reactor (micro-aerobic EGSB reactor) seeded with digestion sludge was divided into two stages. Stage one was to form granular sludge from digestion sludge using brewery wastewater at the anaerobic condition, and stage two was to acclimatize the granules using actual coking wastewater through micro-aerobic condition, and two oxygenation methods (intermittent oxygenation and continuous oxygenation) were employed.

The anaerobic granulation process was accomplished in 10d using brewery wastewater. And it was the key factor for the quickly forming of the granular sludge to add little loose granules.

It took only about 6 months for the successful micro-aerobic acclimating of the granular sludge by the actual coking wastewater. Oxygen supplement and inorganic carbon addition could distinctly improve the contaminant removal effect of the coking wastewater. With 15000ml.min air flow rate and 3g.L⁻¹ NaHCO₃ addition, for the continuous oxygenation way, the COD, ammonia, phenol, CN and SCN removal efficiencies could attain to 89.0%, 16.7%, 99.3%, 95.7% and 100%, respectively, but only 75.0%, 41.9%, 96.8%, 89.9% and 44.0% for the intermittent oxygenation way.

The toxic or inhibitory compounds in the coking wastewater could distinctly restrain the granules and the methanogenic activity of the granules was reducing evidently. The actual coking wastewater had distinct inhibition effect on the granules, but the supplement of some oxygen could promote the recovery of SMA, and NaHCO₃ supplement could also weaken the inhibition effect of the CWW. The continuous oxygenation way had more strongly activity recovery ability than the intermittent oxygenation way.

Acknowledgements

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References

1. M. Zhang, J.H. Tay, Y. Qian, et al. *Wat. Res.* 32 (2):519-527(1998)
2. Y.M. Kim, D. Park, D.S. Lee, et al. *J. Hazard. Mater.* 152 (3): 915-921(2008)
3. Y.M. Li, G.W. Gu, J.F. Zhao, et al.. *Chemosphere.* 52:997-1005(2003)
4. Z. Wu, L. Zhu, *J. Environ. Sci.* 24 (2): 248-253(2012)
5. I. Vázquez, J. Rodríguez, E. Marañón, et al. *J. Hazard. Mater.* B137 :1773-1780(2006)
6. Yong-Shik Jeong, Jong Shik Chung. *Process Biochemistry*, 41:1141-1147 (2006)
7. Corsino, S.F., Capodici, M., Morici, C., et al. *Wat.Res.* 88: 329-336(2016)
8. Di Bella, G., Torregrossa, M., *Bioresour. Technol.* 142:706-713(2013)
9. A.M. Lotito, M. De Sanctis, C. Di Iaconi, G. Bergna, *Wat. Res.* 54:337-346(2014)
10. S.J. Lim, T.-H. Kim, *Biomass Bioenergy*, 60:189-202(2014)
11. K.Y. Show, D.J. Lee, J.H. Tay, *Appl. Biochem. Biotechnol.* 167:1622-1640(2012)
12. Li B, Sun Y L, Li Yu-ying. *J Zhejiang Univ SCI.* 6B (11):1115-1123(2005)
13. Q.Y. Gu, T.CH.Sun, G.Wu, et al., *Bioresource Technology*, 166:72-78(2014)
14. Chuan Chen, Aijie Wang, Nanqi Ren, et al. *Process Biochemistry.*45:1007-1010(2010)
15. R.-M.Wang, Y.Wang, G.-P.Ma, et al. *Chemical Engineering Journal.* 148:35-40 (2009)
16. F.Wang, Y.R.Hu, G.Chen, et al. *Bioresource Technology*,110:120-124(2012)
17. M. Goberna, M. Gadermaier, I.H. Franke-Whittle, et al. *Biomass and Bioenergy*, 75(5): 46-56(2015)
18. Li B, Sun Y L, Li Yu-ying. *J Zhejiang Univ SCI.* 6B (11):1115-1123(2005)
19. State environmental protection administration of china. *Water and wastewater monitoring and analytical methods.* Beijing: China Environmental Science Press, 2004.
20. APHA. *Standard Methods for Examination of Water and Wastewater*, 20th ed. American Public Health Association, American Water Works Association, Water Environment Federation, Washington, DC,1998
21. Zeng A P, Deckwer W D. *Chemical Engineering Science*, 51(10):2305-2314(1996)
22. Kim,Y.M., Park, D., Lee, D.S.,et al.*J. Hazard. Mater.* 152,915-921(2008)
23. Vázquez, I., Rodríguez, J., Marañón, E., et al. *J. Hazard. Mater.* 137, 1773-1780(2006)
24. Kumar MS,Vaidya AN, Shivaraman N, et al. *Environ Eng. Sci.* 17:221-226(2000)