

Stability of expanded granular sludge bed process for terylene artificial silk printing and dyeing wastewater treatment

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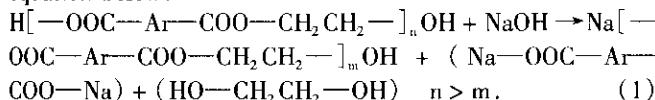
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Abstract: Terylene artificial silk printing and dyeing wastewater (TPD wastewater), containing averaged 710 mg/L terephthalic acid (TA) as the main carbon source and the character pollutant, was subjected to expanded granular sludge bed (EGSB) process. The stability of the EGSB process was firstly conducted by laboratory experiment. TA ionization was the predominated factor influencing the acid-base balance of the system. High concentration of TA in wastewater resulted in sufficient buffering capacity to neutralize the volatile fatty acids (VFA) generated from substrate degradation and provided strong base for anaerobic system to resist the pH decrease below 6.5. VFA and UFA caused almost no inhibition on the anaerobic process and biogas production except that pH was below 6.35 and VFA was at its maximum value. Along with the granulating of the activated sludge, the efficiency of organic removal and production rate of biogas increased gradually and became more stable. After start-up, the efficiency of COD removal increased to 57%–64%, pH stabilized in a range of 7.99–8.04, and production rate of biogas was relatively high and stable. Sludge granulating, suitable influent of pH and loading were responsible for the EGSB stability. The variation of VFA concentration only resulted in neglectable rebound of pH, and the inhibition from VFA could be ignored in EGSB. The EGSB reactor was stable for TPD wastewater treatment.

Keywords: expanded granular sludge bed; stability; anaerobic treatment; dyeing and printing wastewater

Introduction

In order to obtain pliable and elegant terylene fabric just like silk, terylene greige cloth is always pretreated with alkali-decomposition process, wherein terylene fiber is hydrolyzed to some extent in NaOH solution at certain temperature and pressure. During this process, the superficial terylene fibre is peeled off from the greige cloth and dissolved into solution, in which terylene acid (TA) and ethylene glycol are discharged as the main pollutants in wastewater. The obtained terylene fabric with silken wrinkle and soft feeling is called artificial silk fabric. The alkali-decomposition of terylene can be described by the chemical equation below.



The flow sheet of terylene fabric treatment is shown in Fig. 1.

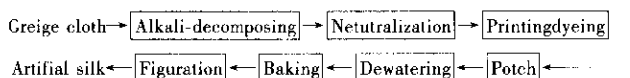


Fig. 1 Flow sheet of terylene fabric treatment

The wastewater from the alkali-decomposition process mixed with wastewater from printing, dyeing, potch and the other processes is named terylene artificial silk printing and dyeing wastewater (TPD-wastewater). Only in Saoping County, East China, are there more than 300 thousands tons TPD-wastewater discharged each day.

Although the anoxic or aerobic bio-process has been the usual approach for the treatment of such kind of wastewater, various anaerobic process configurations were also found their usage in this field. However, the widespread application of anaerobic process has been hampered by the lack of understanding of factors associated with stability of the biological processes involved. The removal efficiency of organic substrates, the biogas production rate and the other items, which are involved in the stability of the process, depends on the acid-base balance. The characteristic pollutant TA in the TPD-wastewater is a kind of dual-organic acid, which exists in water in the form of molecule or ion state. It is still vague about the effect of TA to the acid-base balance in anaerobic system.

The expanded granular sludge bed (EGSB) process developed from UASB process, is one of the controlled anaerobic treatment processes with advantages of higher rate and better toxic resistance. Although EGSB process has the efficiency of 27.1%–68.0% for chemical oxygen demand (COD) removal and 31.4%–56.0% for TA removal (Guan, 2003), further development of EGSB technology for TPD-wastewater treatment depends upon a better understanding of the process stability.

In this paper, the stability of the process was discussed, the acid-base balance was emphasized and lab scale experiments were conducted.

1 Experimental

1.1 Wastewater and activated sludge

The wastewater in the experiment was taken from the central pump station for 3×10^5 t/d TPD wastewater in Saoping County, Zhejiang Province, China. After a one-year round survey, the main pollutants in the wastewater are given in Table 1. TPD wastewater characterized by high pH, COD value and color (COL) is different from traditional printing and dyeing wastewater. The value of COD varies from 780 mg/L to 3116 mg/L; and biological oxygen demand for 5 d (BOD₅) from 325 mg/L to 1436 mg/L. TA ranging from 286 mg/L to 1279 mg/L is the characteristic pollutant controlling 40%–78% of the total COD in TPD wastewater.

Activated sludge for the experiment was obtained from the treatment facility for pesticide wastewater, printing and dyeing wastewater and phenol wastewater. Sludge was acclimated firstly in a laboratory anaerobic reactor running in a fill and drawn mode under the same conditions as EGSB reactor to retain high concentration of biomass.

1.2 Experimental set-up and process

The columned EGSB reactor was divided into four compartments (Fig. 2): (1) the granular sludge bed in which the granulated sludge was accumulated; (2) the fluidized zone in which sludge was suspended; (3) the gas-liquid-sludge separator; and (4) the setting zone. The influent and reflux from the recycle pump was pumped into the bottom of the reactor and passed through the granular sludge bed. Above the granular sludge bed, a fluidized zone developed mainly due to wastewater recycle. In the granular sludge bed and fluidized zone, the biological degradation took place and

the biogas was produced. As mixed liquor passed through the gas-liquid-solid separator, the sludge with good setting abilities settled back through the apertures of the separator to the fluidized zone and sludge bed, while some flocculated and dispersed sludge was washed out of the reactor with

effluent, the effluent flowed into the storage vessel from the weir, and biogas flowed into a wet gas flow meter. The reactor (Fig. 2) is 1.5 meter high with fluidized zone and sludge bed $\phi 100 \times 5$, effective cubage of 7.0 L and a setting compartment of 2.0 L.

Table 1 Quality of terylene artificial silk printing and dyeing wastewater

Indices	pH	COD _{Cr} , mg/L	BOD ₅ , mg/L	TA, mg/L	PVA, mg/L	VFA, mg/L	Total-alkalinity, mg/L	PO ₄ ³⁻ -P, mg/L	NH ₃ -N, mg/L	Sulfide-S, mg/L
Range	8.24—12.78	780—3116	325—1436	286—1279	14—68	89—169	802—1700	1.78—10.20	1.81—24.45	0.76—7.21
Average	—	1780	703	710	39	120	1200	4.26	10.23	2.12

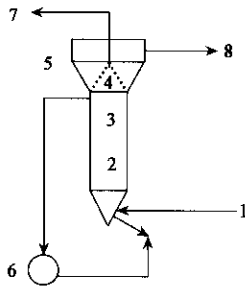


Fig. 2 Structure of EGSB reactor

1. influent; 2. granular sludge bed; 3. fluidized zone; 4. gas-liquid-sludge separator; 5. settling zone; 6. recycle pump; 7. bio-gas outlet; 8. effluent

A schematic drawing of the experimental setup is shown in Fig. 3. In order to eliminate the inhibition from high pH and shortage of N and P, the feeding wastewater was first adjusted to the concentration of COD:N:P = 200:5:1 in wastewater reservoir by adding dipotassium hydrogen phosphate and ammonia sulfate and pH ≤ 10.0 by adding dilute hydrochloric acid in a neutralization reactor controlled by titrator. A pump was used to supply wastewater continuously to EGSB reactor charged with mixed accumulated sludge capable of carbon degradation. Reaction temperature was controlled with a heater and a temperature controller.

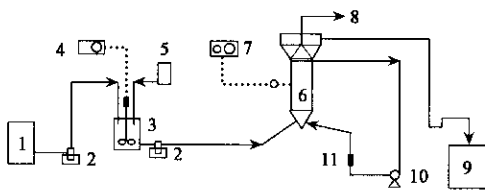


Fig. 3 Flow figure of the wastewater treatment

1. wastewater reservoir; 2. peristaltic pump; 3. neutralization reactor; 4. rotate speed controller; 5. titrator; 6. EGSB reactor; 7. temperature controller; 8. biogas collector; 9. storage vessel; 10. recycle pump; 11. flow meter

Table 2 Significant parameters for EGSB reactor start-up and operation

Stage	HRT, d	T, °C	pH	Influent COD, mg/L	Hydraulic load, m ³ /(m ³ ·d)	Up-flow linear velocity, m/h
Start-up	2—4	32	6.3—7.8	1000—3000	0.002—44	0—2.0
After start-up	0.83—5.0	33	6.0—9.0	800—3100	22—109	1.0—5.0

The pH was monitored and adjusted with a titrator (DL55, Mettler Toledo, Germany). Temperature was determined with a thermo probe connected to an infrared ray heater. Test of the other items was conducted according to the standard methods (Editorial Board of Environment Protection Bureau of China, 1997).

During the start-up of the EGSB reactor, phosphate and carbonate containing Ca, Fe, Al, Ni etc. were added into mixed liquor to enhance the granulating of the activated sludge. The ratio of TPD wastewater in the influent was gradually increased to 100%. The stability of the process was valued while start-up was conducted by increasing sludge loading and hydraulic loading step by step.

During the EGSB reactor start-up, it was operated at influent pH 6.3—7.8 and hydraulic load 0.002—44 m³/(m³·d) and up-flow linear velocity 0—2.0 m/h, with temperature controlled at 33 °C (Table 2). Generally, start-up stage for anaerobic process could be defined as the transitional stage before the reactor working steadily. The parameters indicating reactor performance during start-up include removal efficiencies of pollutants, biogas production rate, variation of pH, concentration of VFA and so on.

After the EGSB reactor start-up, it was operated at a flow-rate about 7.5 L/d and HRT 32 h in EGSB, 1 h in neutralization reactor, while the hydraulic loading 22—109 m³/(m³·d) and up-flow linear velocity 1.0—5.0 m/h and temperature was controlled at 33 °C (Table 2). Stability of anaerobic reactor was valued with COD removal efficiency, biogas production rate and pH value. All of these parameters involved in the stability depended on the acid-base balance in the reactor. So total-alkalinity, VFA and TA concentration were also tested.

1.3 Test and monitoring

Samples taken from mixed liquor were filtered immediately. Analysis of TA was carried on a high performance liquid chromatograph (HPLC, Gilson, France). Aliquots of 25 μ l were injected to the HPLC, running with mobile phase of acetonitrile/water (v/v) at 58/42, and an addition of 2 μ l of concentrated H₃PO₄ per liter of solution. The separation was performed using an ODS-18 reversed phase column (Alltech, USA) at the flow-rate of 1.5 ml/min and column temperature of 25 °C. An UV detector was used with the wavelength at 254 nm. It is measured that TA retention time was at 4.57—4.63 min.

2 Results

2.1 Sludge granulating and EGSB reactor start-up

The start-up is a process of sludge granulating that is essential for EGSB reactor (Hulshoff, 1986). Start-up often takes 2—6 months, even as long as one year (Juragen, 1990). The influent COD and TA were controlled at 1250—

1943 mg/L and 563—1141 mg/L, respectively. The hydraulic loading was adjusted to suit for sludge settling back.

Fig.4 shows the sludge characteristics along the axis at the day 30 and the day 60 during reactor start-up. Activated sludge appeared to be heterogeneous distinctly along the axis of reactor, in which could be divided into sludge bed, sludge suspended zone and setting zone at the day 60. Granular sludge which diameter is over 1.0 mm occupied more than 10% of total sludge in EGSB reactor at the day 60.

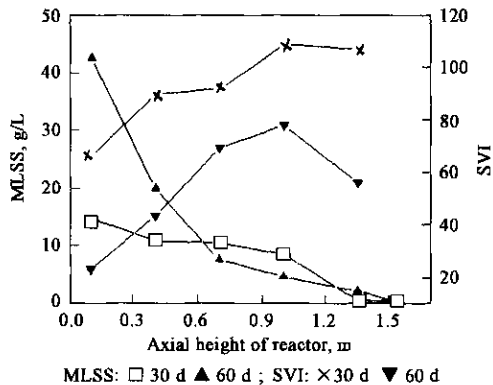


Fig.4 Sludge variation along axis amidst start-up

The substrate concentration along reactor axis is shown in Fig. 5. Above 0.4 m height, COD concentration at different height closed extremely to each other except in setting zone. From the bottom to 0.4 m axial height of the reactor, COD concentration stepped down extremely. The COL appeared the same as the COD. Removal efficiency of COD increased from 23.6% at the day 30 to 49.1% at the day 60, and the removal efficiency of COL increased from 60% at the day 30 to 75.0% at the day 60.

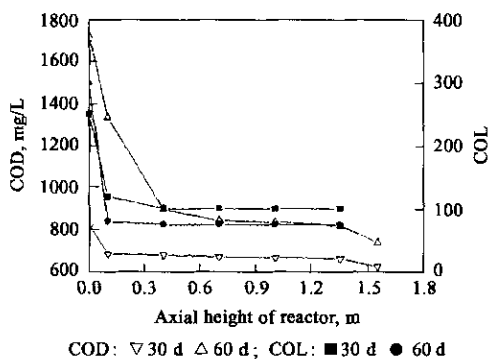


Fig.5 COD and COL variation along axis amidst start-up

The reactor performance changed with the sludge granulating. The EGSB reactor for TPD wastewater treatment started up normally. The biodegradation occurred chiefly in sludge bed, and the outside loop resulted in intensive mixing of wastewater in EGSB reactor.

2.2 Stability of the EGSB operation

Effluent pH, COD removal efficiency (η_{COD}) and biogas production rate (V_g , amount of biogas from 1 kg COD removal under standard state) were used to indicate the EGSB reactors performance. Fig.6 shows the performance variation of EGSB during start-up period.

From the day 10 to the day 28, TPD wastewater in influent increased proportionally. The first peak value of η_{COD} was presented between the day 15 and the day 20,

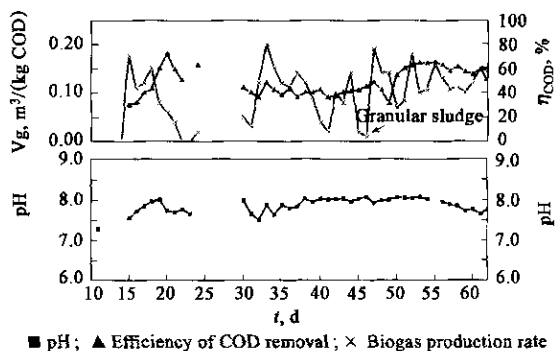


Fig.6 Curves of pH, biogas production rate and efficiency of COD removal with time during EGSB reactor start-up

with V_g 0.11—0.18 $m^3/(kgCOD)$. The efficiency of COD removal and the biogas production rate were much unstable, and decreased sharply when TPD wastewater in influent increased excessively.

From the day 28, influent was all of the TPD wastewater. Between the day 30 and the day 45, effluent pH was 7.45—8.05, η_{COD} was 36%—49% and V_g was 0.015—0.20 $m^3/(kgCOD)$. The variation of effluent pH, η_{COD} and V_g were remarkable before the day 45. It was a differentiation period for activated sludge.

After the day 45, effluent pH stabilized in a range of 7.99—8.04, η_{COD} increased to 57%—64%, V_g also kept a stable value of 0.12—0.17 $m^3/(kgCOD)$. In fact, from the day 45, the granule sludge differentiated from sludge, and EGSB reactor presented its better stability. It was measured that granular sludge was made up of 10% of the total sludge at the day 60. The sludge bed was charged with the 65% of the total sludge while only took 25% of the reactor cubage.

EGSB reactor's performance improved and became more stable along with the sludge granulating. It was noticeable that the efficiency of COD removal was always below 75% because TA remained as slowly biodegradable substrate under anaerobic conditions with a turnover between 31.4% and 56.0% (Guan, 2003).

The EGSB reactor kept in halted state for 45 d at the temperature of 20—25°C after three months operation. Fig.7 illustrates the reactor restart. The biogas production rate increased step by step. The COD removal was relatively stable with efficiency of 40%—60%. The reactor restart only took 12 d.

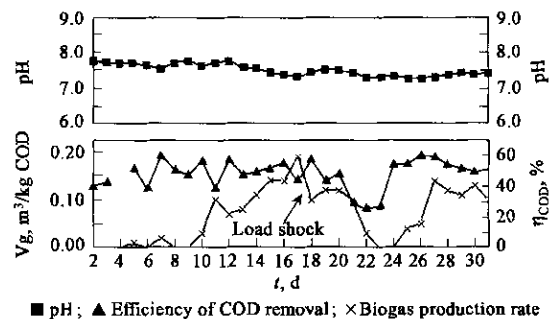


Fig.7 Curves of pH, V_g and η_{COD} with time during EGSB reactor restart

After maximum turnover rates of COD averaged 60%, the system was switched to a load shocking with higher

hydraulic load as much as 200% of the normal load at the day 16. The depression of biogas production was in the wake of the shocking load. The COD removal efficiency decreased with a lag of several days after the anaerobic system received the shocking load. The results illustrated that the performance of EGSB reactor could be unstable when the operation parameter changed greatly. The removal of COD recovered to a normal level of 55%—62% in a week, while the biogas production recovered to the normal level of 0.11—0.15 m³/(kgCOD) in 10 d.

3 Theoretical calculation and discussions

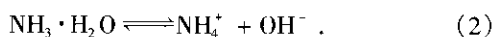
3.1 Acid-base balance and buffering capability of TPD wastewater

The pH is one of the most important parameters indicating the stability of anaerobic system. The best pH for methanogenic bacteria is from 6.5 to 7.5 (Souza, 1986). While VFA accumulating leads to a decrease of pH, the efficiency of the anaerobic treatment has already declined markedly (Gu, 1993). Therefore, it is more important to control VFA than to control pH in anaerobic system. The alkalinity is regarded as an important role to resist the VFA accumulation so as to increase pH in an anaerobic system (Kroeker, 1979; Gu, 1993).

Alkalinity of the wastewater is defined as the gross substance which can react rationally with strong acids. Alkalinity includes many kinds of alkali components such as carbonates, bicarbonates, hydrates and organic base. They are called as total alkalinity in the wastewater (Editorial Board of Environment Protection Bureau of China, 1997). The TPD wastewater has complex components and the concentration of carbonates, bicarbonates and hydrates cannot be obtained expediently. So the total alkalinity was used as a significant indicator for the basic components in the wastewater.

Commonly, acid-base balance of the mixed liquor in anaerobic reactor is dominated by ionization balance of ammonia, VFA and carbonates (Kroeker E J, 1979; Zhang, 1997).

Ammonia ionization equilibrium as Equation (2):



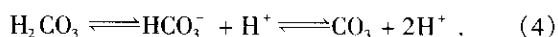
As the $[\text{H}^+]$ increases, pH decreases and equilibrium shifts to the right. At 35°C, the ionization constant is 1.85×10^{-5} .

VFA is usually composed by acetic acid and propionic acid. As two kinds of VFA have close ionization constants, the ionization equilibrium can be simplified as the acetic acid ionization illustrated in Equation (3):



As the $[\text{H}^+]$ increases, equilibrium shifts to the left and the un-ionized volatile acid (UVA) concentration increases. At 35°C, the ionization constant is 1.73×10^{-5} . As the UVA concentration increases above 10 mg/L, a digester trends towards failure (Kroeker, 1979).

The ionization equilibrium of carbonates is illuminated as Equation (4).



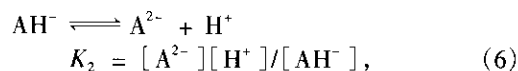
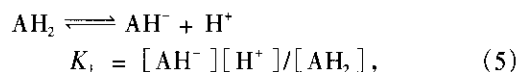
The acid-base equilibrium in an anaerobic system also include the dissolve balance of CO₂ between liquid-gas phase, the balance of carbonate and phosphate between liquid-solid phase, the balance of other salt ionization.

It was explained that sulfhydrate and ortho-phosphoric

acid only provide limited buffering capacity commonly as a result of low concentration (Capri, 1975). The buffering capacity of ammonia and VFA can be neglected when pH varied from 6.0 to 7.7, and the buffering capacity of the anaerobic system unexceptionably resulted from the ionization of carbonic acid. So the pH and the acid-basic balance are controlled by carbonic acid and the ionization of a kind of alkali. The latter is collaborated by VFA, ammonia and the other strong acid and alkali.

It is tested that the range of concentration of NH₃-N, PO₄³⁻-P and sulfide-S are 1.81—24.45 mg/L, 1.78—10.20 mg/L and 0.76—7.21 mg/L correspondingly, the average values are 10.23, 4.26 and 2.12 mg/L, respectively. According to the previous work mentioned above, the buffering capacity of ammonia, phosphate and hydrosulphuric acid can be neglected in TPD wastewater. Then, which one is responsible for the buffering of the acid-base balance when EGSB process is applied to treat the TPD wastewater? How to obtain a stable pH with the range of 6.5—7.5 in such a carbonic acid / bicarbonate system?

TA is dual-organic acid, which exists in water with two states of molecule or ion state. Further more, its solubility connected closely with pH. The ionization equilibrium is shown as follows (Editorial Board of Encyclopedia of Chemical Industry, 1990):



in which AH₂: HOOC-Ar-COOH, molecule state; AH⁻: HOOC-Ar-COO⁻, ion state; A²⁻: ⁻OOC-Ar-COO⁻, ion state; K₁ = 3.1 × 10⁻⁴, first ionization constant; K₂ = 1.5 × 10⁻⁵, second ionization constant.

As the pH decreases, equilibrium shifts to the left. TA of molecule state increases and TA of ion state decreases. Total solubility of TA under any pH can be notified as S_Σ:

$$S_{\Sigma} = [\text{AH}_2] + [\text{AH}^-] + [\text{A}^{2-}], \quad (7)$$

from Equation (5) to Equation (7),

$$S_{\Sigma} = [\text{AH}_2][1 + 10^{\text{pH}-\text{p}K_1} + 10^{2\text{pH}+\text{p}K_1-\text{p}K_2}]. \quad (8)$$

The solubility of molecule state TA is 19 mg/L in aqueous solution at 25°C (Editorial Board of Encyclopedia of Chemical Industry, 1990). Then, the total solubility of TA (S_Σ) in aqueous solution can be calculated at any pH, showing in Fig.8 and Fig.9.

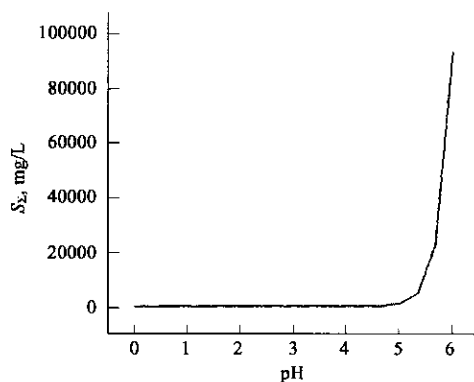


Fig.8 Curve of the total solubility of TA vs. pH in aqueous solution

At pH 7.0, S_Σ is as much as 8894 g/L, namely,

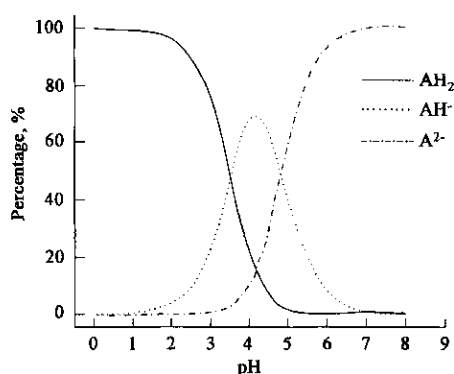


Fig. 9 States of TA under different pH in aqueous solution

99.34% of TA exists in the state of A^{2-} . The lowest pH of the TPD wastewater ever monitored was 8.5, so it is believed that TA in the wastewater dissolves completely in the state of A^{2-} .

As total-alkalinity of TPD wastewater is measured, phenolphthalein and helianthin are used for indicator according to the standard method (Editorial Board of Environment Protection Bureau of China, 1997). The pH was limited to 4.4—4.5, meanwhile, the bicarbonate in the wastewater was neutralized. As Fig. 8 and Fig. 9 were accounted, the solution of TA in wastewater was about 86 mg/L, that was, not only the most of TA separated from wastewater but also the TA left in wastewater existed nearly in a state of AH^- .

One of the neutralization curves of TPD wastewater is shown in Fig. 10. In the first stage of $pH > 6.5$, pH depressed rapidly as hydrochloric acid was added in a certain concentrations. The titration indicated a strong acid neutralizing strong base. In the second stage of $4.0 \leq pH \leq 6.5$, pH depressed slowly as hydrochloric acid was added. About 90% of TA extracted from wastewater before pH 4.0. At the third stage of $pH < 4.0$, approximately 99% of TA extracted from wastewater, hydrochloric acid added increased the concentration of hydrogen.

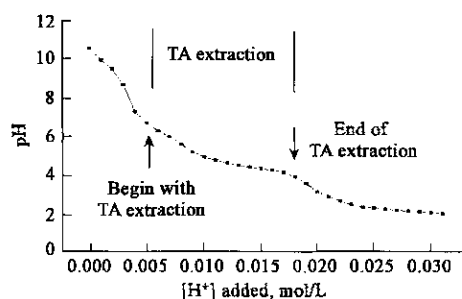


Fig. 10 Neutralization curve of TPD wastewater

As hydrochloric acid was added, the equilibrium of Equations (5) and (6) shifted to the left. TA extracted ceaselessly in molecule state from wastewater. Acid consumed in the second stage is 3.6 times than that of stage one, but pH depressed more slowly. The results showed TA ionization provided sufficiency anion to consume acid to resist pH depress while the pH of the wastewater was in the range of 4.0 and 6.5. TPD wastewater appeared to provide strong buffering capacity to resist the VFA in an anaerobic system.

The total-alkalinity of TPD wastewater was 802—1700 mg/L, average range of 1200 mg/L. TA was responsible for the most of the alkalinity of the wastewater, evidently.

The concentration of TA in TPD wastewater is 286—

1279 mg/L, which is account for 40%—78% of the COD of the wastewater. Fig. 8 and Fig. 10 show the range of pH for TA extraction. To some extent, TPD wastewater could be regarded as aqueous solution of TA, containing some other chemical components. During anaerobic treatment of TPD wastewater, the pH of the mixed liquor ranged between 6.5 and 8.5, resulted from the strong capacity of buffering for acid. Only 31.4%—56.0% of TA was turned over (Guan, 2003), and TA left in the anaerobic system was almost in the state of ion state (A^{2-}).

3.2 VFA and UFA in the mixed liquor

It is known that the anaerobic process involves two major groups of bacteria that degrade organic substrate in two major ways. In the first stage, "acid-form" bacteria hydrolyze and degrade the complex organic substrates to volatile fatty acids (VFA). In the second stage, VFAs are utilized by methanogenic bacterial and methane gas is produced. The two processes occur simultaneously and process stability depends on maintenance of a delicate biochemical balance between the two major phases for organic substrates.

Anaerobic process instability is usually indicated by a rapid increase in the concentration of VFAs with a subsequent decrease in methane gas production. There are many factors associated with instability or process failure, for example, insufficient acclimation of the methane formers to new substrates, rapid temperature or pH fluctuations. From the results by Kroeker *et al.* (Andrews, 1969; Kroeker, 1979), anaerobic digestion toxicities related more directly to excessive concentration of un-ionized volatile acids (UFAs), although they probably indirectly related to excessive free ammonia concentrations. What is more, the toxicities have a close correlation with pH due to the reason that UFA is easier than other compounds to penetrate through cell membrane. As soon as microbe assimilates the UFA, pH in the cell depresses rapidly and metabolic rate of the microbe reduces. It is still acceptable that the digester toxicity was caused by UFA in a concentration above 30 to 60 mg/L as acetic acid.

UFA concentration of TPD wastewater in EGSB reactor was calculated considering following conditions: (1) VFA of the wastewater was 86—169 mg/L, averaging 120 mg/L. The highest value of VFA tested in an anaerobic reactor was below 400 mg/L; (2) the highest VFA value tested in the effluent was below 50 mg/L; (3) the pH of the mixed liquor was above 6.5; (4) Equation (3) was adopted to calculate the UFA concentration, in which the ion intensity was not taken into account and VFA was converted into acetic acid.

The UFA (HAc) could be obtained by following equation:

$$[HAc] = \frac{[H^+][Ac^-]}{K}, \quad (9)$$

where, K is the ionization constant, Ac^- is CH_3COO^- .

So the highest value of UFA in EGSB reactor is 7.18 mol/L at pH 6.5. If UFA were presumed to be 10 mol/L, the pH of the mixed liquor would meet 6.35.

As the concentration of VFA is on the up-limit in EGSB reactor and the pH is at 6.5, the UFA is certainly below 10 mg/L. Consequently, the toxicity resulted from VFA or UFA to digester could be ignored. Only when pH is below 6.35 and VFA value is at its highest one, VFA or UFA could inhibit the anaerobic process. It is well known that the VFA concentration leads to inhibition for anaerobic process is 1500—2000 mg/L (Gu, 1993). As the VFA of 400 mg/L in

the mixed liquor is concerned, VFA could not inhibit the anaerobic process when the TPD wastewater was treated in EGSB reactor.

3.3 Balance of VFA and alkalinity

The typical variation of alkalinity and VFA in EGSB reactor is shown in Fig. 11. The alkalinity concentration of anoxic effluent was approximately equal to that of TPD wastewater in a range of 900–1000 mg/L. The rebound range was about 100 mg/L. Total alkalinity concentration increased about 250 mg/L to 1150–1250 mg/L after treatment of EGSB.

Influent (TPD wastewater) VFA 90–133 mg/L increased to 197–236 mg/L after anoxic treatment, while the effluent VFA from EGSB reactor was 19.8–43.2 mg/L with the removal efficiency 79.1%–92.1%. The increase of total alkalinity in EGSB reactor could be presumed to relate with the consumption of VFA.

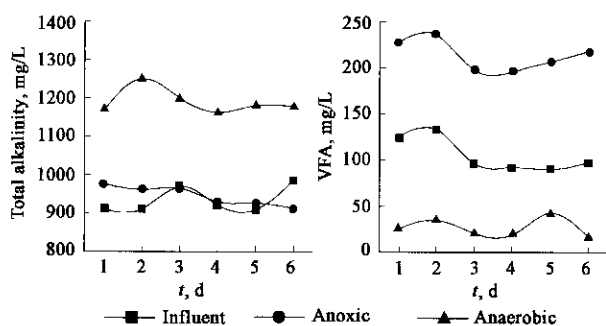


Fig. 11 Variation of alkalinity and VFA under anoxic or anaerobic conditions

The alkalinity is buffering capacity to resist the VFA in anaerobic system. The calculation mentioned above indicated that VFA of the wastewater hardly inhibited anaerobic process. The concentration of alkalinity was high enough for buffering the VFA in the mixed liquor. Leslie (Leslie, 1989) took for the ratio of VFA to total alkalinity to evaluate the buffering capacity of anaerobic system (Leslie, 1989). The total alkalinity only descended lightly during anoxic treatment and ascended lightly in EGSB reactor. The ration of VFA to total-alkalinity was always low than 0.4. The ratio of VFA to total alkalinity associated with the stability of anaerobic system is shown in Table 3 (Leslie, 1989). Obviously, the variation of VFA concentration only caused little change of pH when TPD wastewater was treated in EGSB reactor. The buffering capacity of the mixed liquor was sufficient for EGSB process.

Table 3 The relation between VFA/Total alkalinity and stability of anaerobic process

VFA/total alkalinity	< 0.4	0.4—0.8	> 0.8
Buffering capacity to VFA	Enough	Deficient	Exiguous
pH variation resulted from VFA variation	Little	Small	Remarkable

4 Conclusions

TA, the dual-organic acid of TA was responsible for the most of the alkalinity of the wastewater and provided sufficient buffering capacity for the acid-base balance when EGSB process was applied to treat the TPD wastewater. The EGSB reactor's performance improved and became more stable along with the sludge granulating.

Nomenclature:

BOD₅: biochemical oxygen demand for 5 days, mg/L; SS: suspended solid; COD: chemical oxygen demand, mg/L; VFA: volatile fatty acid; COL: color; UFA: un-ionized volatile acid; EGSB: expanded granular sludge bed; V_g: biogas production rate, m³/(kg · COD); HRT: hydraulic retention time, h; T: temperature, °C; K: inization constant; TA: terephthalic acid; MLSS: mixed liquor suspended solid, g/L; ηCOD: efficiency of COD removal, %; PVA: polyvinyl alcohol.

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