Desalination and Water Treatment
www.deswater.com
doi: 10.5004/dwt.2020.25043

179 (2020) 75–82
March

Investigations on the biological treatment of mixed petrochemical industrial effluents based on acute toxicity and biodegradation characteristics

Dong Wang[a,b,*], Yuanyuan Zuo[a,b], Chunsheng Qiu[a,b], Nannan Liu[a,b], Chenchen Wang[a,c], Shaopo Wang[a,b], Jingjie Yu[a,b], Liping Sun[a,b]

[a]*School of Environmental and Municipal Engineering, Tianjin Chengjian University, Tianjin, China, Tel. +86 18202679521; Fax: +86-022-23085117; email: wangdong06@tcu.edu.cn*
[b]*Tianjin Key Laboratory of Aquatic Science and Technology, Tianjin, China*
[c]*Municipal Experimental Teaching Demonstration Center of Environmental and Municipal Engineering, Tianjin Chengjian University, Tianjin, China*

Received 28 March 2019; Accepted 13 October 2019

ABSTRACT

Petrochemical wastewater contains various effluents, such as purified terephthalic acid (PTA), polyethylene terephthalate (PET) and polyester (PE) effluents. The effects of mixed petrochemical wastewater on biological processes were investigated by studying their acute toxicity and biodegradation characteristics. The results of combined toxicity assays show that PTA + PET and PTA + PE wastewaters demonstrate an antagonistic effect, while PTA + PET + PE wastewater exhibit a partly additive effect. The results of aerobic biodegradation characteristics and specific oxygen uptake rate assays show that the biodegradation processes of pollutants were inhibited at the initial period and then recovered. On the contrary, there was no significant inhibition effect in the assays of anaerobic biodegradation. The analysis on the relationship of toxicity and biodegradation characteristics show that in aerobic batch assays the inhibition effect is related to the toxicity of wastewater, while anaerobic biodegradation processes were affected by the slowly biodegradable fraction in wastewater.

Keywords: Petrochemical wastewater; Acute toxicity; Luminescent bacteria test; Biodegradation characteristics; Aerobic and anaerobic processes

1. Introduction

Petrochemical wastewater is an industrial wastewater generated from the production of petrochemical raw materials, such as purified terephthalic acid (PTA), polyethylene terephthalate (PET) and polyester (PE) [1]. Hence, petrochemical wastewater contains effluents from different petrochemical processes, such as PTA, PET and PE wastewaters. Petrochemical wastewater exhibits several characteristics, such as high concentration of organic matter, refractory, toxicity and inhibition, which have adverse effects on the environment [2]. Hence, petrochemical wastewater should be treated efficiently before discharged into the receiving water.

A range of treatment technologies have been widely applied to treat petrochemical wastewater, such as advanced oxidation process [3], absorbance [4], biological treatment including aerobic and anaerobic processes, owing to the advantages such as cost-saving and high efficiency [5]. During biological treatment, these pollutants can be degraded by special microbes which form catabolic partnerships [6]. However, petrochemical wastewater contains different organic pollutants which exhibit characteristics of toxicity and refractory [7]. The catabolic partnerships of degrading microbes are fragile and easily destroyed by other toxicants.

* Corresponding author.

Hence, in earlier studies, the performances and mechanisms of pollutants removal during biological treatment were investigated through individual petrochemical wastewater (including actual and synthetic wastewater) [5]. However, petrochemical wastewater with a mixture of various petrochemical effluent streams was actually treated by biological processes. The mixed petrochemical wastewater may exhibit an adverse effect on the biodegradation processes, because of its toxicity and refractory characteristics of pollutants. Hence, the combined toxicities and biodegradation characteristics of the mixture of petrochemical effluents during biological treatment require careful attention and should be investigated.

In this study, actual petrochemical wastewaters (mixed wastewaters of PTA, PET and PE) were collected from a petrochemical plant in Tianjin. The individual and combined toxicities of the wastewater were conducted using luminescent bacteria test. The biodegradation characteristics of individual and mixed wastewaters were also investigated. The effect of the mixture of petrochemical effluent streams on biodegradation was revealed by the relationship of the biodegradation characteristics and combined toxicities of mixed wastewaters.

2. Materials and methods

2.1. Wastewater characteristics and mixture condition

Real PTA, PET and PE wastewaters were collected from a petrochemical plant (Sinopec Corp, Tianjin, China). The characteristics of wastewaters are shown in Table 1. The effects of mixed petrochemical wastewater on biological treatment were conducted according to the acute toxicity and biodegradation characteristics of individual and mixed petrochemical industrial effluents (PTA, PET, PE, PTA + PET, PTA + PE and PTA + PET + PE wastewaters). The ratio of mixed wastewater used was according to the volume ratio of PTA, PET and PE streams in the actual petrochemical wastewater (PTA: 60%–80%; PET: 10%–20%; PE: 10%–20%).

2.2. Luminescent bacteria test

Acute toxicities of individual and mixed wastewaters were assessed by luminescent bacteria test [8]. For this, the employed luminescent bacterium strain was *Photobacterium phosphoreum* T3 spp. (Nanjing Institute of Soil Science, Chinese Academy of Sciences). To resuscitate the bacteria, 1 mL cold NaCl solution (2.5%) was added to the ampoule bottle containing freeze-dried luminescent bacteria (0.5 g). The luminescent bacteria began to luminescence at 20°C. Luminescent bacterial solution (0.2 mL) was then injected into 2 mL test tube containing 3% NaCl solution and the luminosity range was tested. The freeze-dried *Photobacterium phosphoreum* T3 spp. can be used if the luminosity is in the range of 600–1,900 mV.

2.3. Acute toxicity assays of individual wastewater

The acute toxicity assays and the determination of standard curve were conducted according to the standard toxicity measurement method [9]. For individual wastewater (PTA, PET and PE wastewater), seven concentration gradients were prepared. All samples were diluted by NaCl solution and adjusted to pH = 7. During toxicity test assays, 1.8 mL of samples or 2.5% NaCl solution (as control) were added into the test tubes containing a solution of 0.2 mL luminescent bacteria. After exposure for 15 min at 20°C ± 1°C, the individual toxicities of wastewater samples were recorded and repeated in triplicates. The toxicity values are expressed in relative luminosity unit (RLU) and RLU (%) were calculated by the following equation [10].

$$\mathrm{RLU} = \frac{\mathrm{LU}}{\mathrm{LU}_0} \times 100\% \tag{1}$$

where LU is the mean luminescence unit of the wastewater samples and LU_0 is the mean luminescence unit of the control (only NaCl solution). The concentrations that cause a 50% inhibition of bioluminescence (IC_{50}) were obtained by linear regression analysis of the concentrations of wastewater and RLU. The linear fitting and correlation coefficient (R^2) were obtained by Microsoft Excel 2010. The acute toxicity of individual wastewater (PTA, PET and PE wastewater) was also represented by the concentration of Zn^{2+} ($ZnSO_4$ serves as a standard toxicant). The extent of luminescent inhibition of the samples was standardized into an equivalent concentration of Zn^{2+}, which is related to the toxic effect of organic matter in wastewater on luminescent bacteria [11].

2.4. Combined toxicity of mixed wastewater

According to the IC_{50} values of individual streams, the combined toxicity assays of mixed wastewaters (PTA + PET, PTA + PE and PTA + PET + PE) were tested. The ratio of mixed wastewater samples used was according to the volume ratio of PTA, PET and PE streams in actual petrochemical

Table 1
Characteristics of real PTA, PET and PE wastewaters

Characteristic parameters	PTA wastewater	PET wastewater	PE wastewater
COD (mg/L)	3,750–4,250	889–1,900	164–2,141
BOD_5 (mg/L)	500–600	200–500	60–900
DOC (mg/L)	1,132–1,328	177–380	59–784
NH_4^+–N (mg/L)	17.35–20.74	5.23–8.89	12.87–19.94
TP (mg/L)	1.04–1.23	1.37–1.97	0.51–0.82
pH	4.0–6.0	4.5–7.0	5.5–7.5

wastewater. PTA + PET mixed wastewater sample contained 80% PTA wastewater and 20% PET wastewater; PTA + PE mixed wastewater sample contained 80% PTA wastewater and 20% PE wastewater; PTA + PET + PE mixed wastewater sample contained 80% PTA wastewater, 10% PET wastewater and 10% PE wastewater. For the mixed wastewaters, seven concentration gradients were prepared and tested in triplicates. The tests for mixed wastewaters were conducted in a similar way as that of individual wastewaters.

The combined toxicities contain four main types: independent effect, additive effect, synergistic effect and antagonistic effect [8]. Toxic unit (TU) was applied to assess the combined toxicity and is calculated by the following equation:

$$\mathrm{TU}_i = \frac{C_i}{\mathrm{IC}_{50,i}} \tag{2}$$

$$M = \sum_{i=1}^{n} \mathrm{TU}_i = \frac{C_1}{\mathrm{IC}_{50,1}} + \frac{C_2}{\mathrm{IC}_{50,2}} + \ldots + \frac{C_n}{\mathrm{IC}_{50,n}} \tag{3}$$

$$M_0 = \frac{M}{\left(\mathrm{TU}_i\right)_{\max}} \tag{4}$$

where C_i represents the concentration of compound i when the mixture is at its IC_{50}; TU_i is the toxic unit of i; M is the sum of the toxic units according to Eq. (3); $(\mathrm{TU}_i)_{\max}$ is the maximum toxic unit of the mixture and M_0 is the ratio of M and $(\mathrm{TU}_i)_{\max}$ according to Eq. (4). The combined toxicity can be revealed by the relation of M and M_0, the details as follows: if $M < 1$, the combined toxicity is synergistic; if $M = 1$, the combined toxicity is simply additive; if $M > M_0$, the combined toxicity is believed to be antagonistic; if $M = M_0$, the combined toxicity is independent and if $M_0 > M > 1$, the combined toxicity is partly additive [8].

2.5. Aerobic degradation using batch assay

The biodegradation characteristics under aerobic condition were observed by batch assays. Six beakers (500 mL) were fed with PTA, PET, PE, PTA + PET, PTA + PE and PTA + PET + PE wastewaters, respectively. The samples (5 mL) from the beakers were collected at the time intervals of 0, 2, 4, 10, 40, 70, 90, 110, 130 and 150 h, respectively. The collected samples were then passed through 0.45 μm filter to remove suspended solids and then analyzed for dissolved organic carbon (DOC). Specific oxygen uptake rates (SOUR) of activated sludge were also investigated at 0, 4, 40, 70, 110 and 150 h, in the six beakers. The seeding sludge of batch assays was collected from the petrochemical plant and acclimated for 30 d. Mixed liquor suspended solids (MLSS) in the beakers were kept at 4 g/L according to the MLSS value of aerobic tanks in petrochemical wastewater treatment plant of Sinopec Corp. The dissolved oxygen of the batch assays was kept at 3.0 mg/L.

2.6. Anaerobic degradation using batch assay

The biodegradation characteristics under anaerobic condition were determined by batch assays. Six serum bottles (500 mL) were fed with PTA, PET, PE, PTA + PET, PTA + PE and PTA + PET + PE wastewaters, respectively. The samples (5 mL) from the bottles were collected at the time intervals of 0, 2, 8, 20, 30, 40, 50, 70 and 90 h, respectively. The samples were then passed through 0.45 μm filter to remove suspended solids and then analyzed for DOC. MLSS in the bottles were kept at 10 g/L according to the MLSS value of anaerobic processes in petrochemical wastewater treatment plant of Sinopec Corp.

2.7. Analytical methods

The data set for principal component analysis (PCA) were used to assess the internal correlations between acute toxicity and biodegradation characteristics. Analytical data set covered toxicity variables: IC_{50} and toxicity standardized into an equivalent concentration of Zn^{2+} ($\mathrm{Toxicity}_{Zn}$); aerobic biodegradation variables: SOUR maximum value (SOUR_{max}), SOUR during inhibition stage ($\mathrm{SOUR}_{inhibition}$), maximum value of removal rate (RR_{max}) and removal rate during inhibition stage ($\mathrm{RR}_{inhibition}$); anaerobic biodegradation variables: removal rate of readily biodegradable organics ($\mathrm{ARR}_{readily}$) and removal rate of slowly biodegradable organics (ARR_{slowly}) in the batch assays of individual and mixed wastewaters. Removal rate (RR) is calculated by the following equation:

$$\mathrm{RR} = \frac{C_0 - C_e}{t} \tag{5}$$

where C_0 and C_e represent the concentration of DOC at the beginning and at the end of stage, and t represents the time required during the stage.

SOUR analysis was measured using a respirometric test [12]. Parameters of chemical oxygen demand, 5 d biochemical oxygen demand (BOD_5), pH, total nitrogen (TN), ammonia nitrogen (NH_4^+–N) and total phosphate (TP) were observed by the standard method [9]. DOC was determined using a DOC analyzer (Shimadzu, Japan).

3. Results and discussion

3.1. Acute toxicity of petrochemical industrial wastewater

3.1.1. Acute toxicities of individual petrochemical industrial effluents

To obtain the toxiciy values of individual petrochemical industrial effluents, the acute toxicities of diluted wastewater samples to luminescent bacteria were tested. DOC and toxicity response relationships of individual wastewaters are shown in Fig. 1. It could be seen that the RLU was negatively correlated to the concentration of DOC of diluted wastewater samples. The linear regression equations, correlation coefficients (R^2) and the IC_{50} values of individual wastewaters are listed in Table 2. The IC_{50} values of PTA, PET and PE effluents were 28.37, 5.62 and 27.73 mg/L, respectively. The smaller is the IC_{50} value, the more toxic is the wastewater sample to luminescent bacteria. The toxicities of organic pollutants in the wastewater samples were in the following order: PET > PE > PTA.

Generally, the toxicities of petrochemical industrial effluents by luminescent bacteria test have not been widely

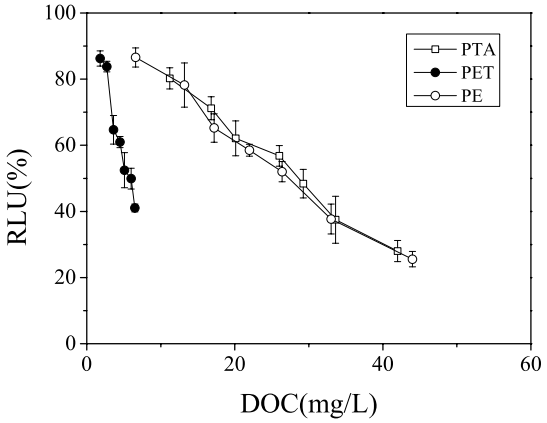

Fig. 1. DOC and toxicity response relationships of individual petrochemical industrial wastewater samples.

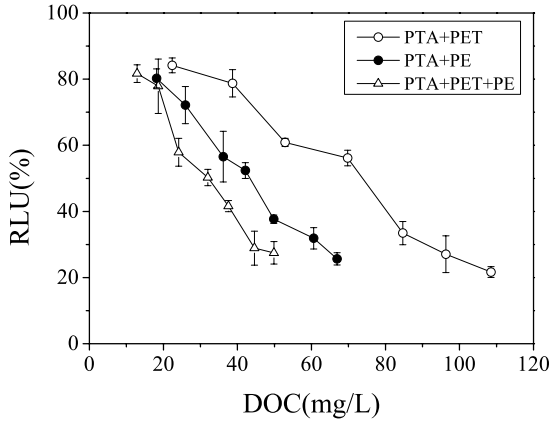

Fig. 2. DOC and toxicity response relationships of mixed petrochemical industrial wastewater samples.

Table 2
Acute toxicities of the individual wastewater samples

Wastewater	Linear regression equation	R^2	IC_{50} (mg/L)
PTA	RLU = –1.7407*c* + 99.391	0.9862	28.37
PET	RLU = –9.711*c* + 105.25	0.9574	5.62
PE	RLU = –1.695*c* + 96.999	0.9844	27.73

reported and discussed. PTA wastewater showed gene and reproduction toxicities owing to the existence of typical pollutants, such as terephthalic acid (TA), benzoic acid (BA) and p-toluic acid (PT-acid) [7,13,14]. In PET wastewater, ethylene glycol and TA, which are the main pollutants, contributed to the toxicity effect on luminescent bacteria [15]. In PE wastewater, TA and phenol are the key pollutants that have contributed to acute toxicity [16].

3.1.2. Combined toxicities of mixed petrochemical industrial effluents

The combined toxicity values of mixed wastewaters were also obtained by luminescent bacteria test. DOC and toxicity response relationships of the mixed wastewaters are shown in Fig. 2. It could be observed that the RLU values were negatively correlated to the concentration of DOC of the diluted wastewater samples. The linear regression equations, correlation coefficients (R^2) and the IC_{50} values of mixed wastewaters are listed in Table 3. The IC_{50} values of PTA + PET, PTA + PE and PTA + PET PE wastewaters were 69.81, 44.12 and 33.09 mg/L, respectively. The smaller is the IC_{50} value, the more toxic is the wastewater samples to luminescent bacteria. The toxicities of organic pollutants in the wastewater samples were in the following order: PTA + PET + PE > PTA + PE > PTA + PET. Based on the results of combined effect in Table 3, PTA + PET and PTA + PE were antagonistic, while PTA + PET + PE was partly additive.

Based on the results of acute toxicity, the mixture of three pretrochemical effluents exhibited different effects of combined toxicity. However, the pollutants in the wastewater showed different characteristics of inhibition on both luminescent bacteria and microbes in the aerobic and anaerobic treatment processes. Thus, the removal characterisitics of individual and mixed effluents during aerobic and anaerobic treatment should be investigated.

3.2. Characteristics of biodegradation of petrochemical industrial wastewater

3.2.1. Removal of organic pollutants of the wastewater during aerobic biological treatment

The removal characteristics of organic pollutants in batch assays could demonstrate the characteristics of the composition of wastewater and the processes of biodegradation. It also reflects the effect of the mixture of different streams on biological treatment. Fig. 3 shows the DOC removal characteristics of individual and mixed wastewaters in aerobic batch assays. All the individual and mixed wastewater samples exhibited an inhibition effect on activated sludge at the beginning, and then recovered with the progress of biodegradation processes.

DOC removal of the individual wastewater samples exhibited a similar trend. The removal processes of the pollutants in

Table 3
Combined acute toxicities of the mixed wastewater samples

Wastewater	Linear regression equation	R^2	IC_{50} (mg/L)	M	M_0	Combined effect
PTA + PET	RLU = –0.784*c* + 104.75	0.9722	69.81	4.45	1.79	Antagonistic
PTA + PE	RLU = –1.147*c* + 100.04	0.9826	44.12	1.56	1.26	Antagonistic
PTA + PET + PE	RLU = –1.553*c* + 101.37	0.9668	33.09	1.64	1.76	Partly additive

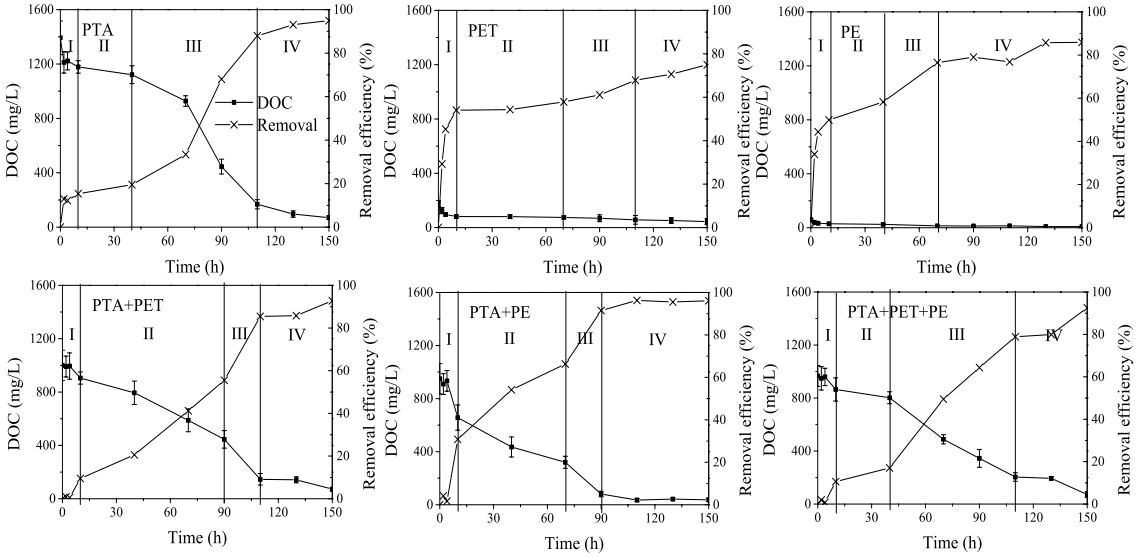

Fig. 3. The characteristics of DOC removal of individual and mixed wastewaters during aerobic treatment. Phase I is the degradation of readily biodegradable component; Phase II is the inhibition stage; Phase III is the recovery stage; Phase IV is the degradation stage of slowly biodegradable and inert components.

wastewater could be divided into four phases. DOC removal efficiency increased rapidly in the beginning which showed that the easily removable compounds could be degraded rapidly. Following this, the organic pollutants were removed slowly due to the inhibition effect of toxic compounds on the activated sludge. The efficiency of DOC removal increased rapidly again due to the elimination of inhibition effect with the removal of toxic compounds. Finally, the organic pollutants were removed slowly. Overall, it exhibits that the biodegradable organics were almost completely removed and the remaining were slowly biodegradable and inert fraction.

The characteristics of DOC removal of individual effluents in aerobic batch assays showed an inhibitory effect on the activated sludge in the initial period. The presence of toxic compounds in the wastewater contributed to the inhibitory effect on the activated sludge in the initial period. These compounds could be degraded and hence the rate of removal of DOC was recovered.

In the assays of mixed wastewaters (PTA + PET, PTA + PE, PTA + PET + PE wastewaters), the characteristics of DOC removal in mixed wastewaters (PTA + PET, PTA + PE, PTA + PET + PE wastewater) had a similar trend compared with PTA wastewater, which may be due to that PTA wastewater was a main stream in the mixed wastewaters, accounting for approximately 80%. However, some details on the removal of pollutants in the batch assays of mixed wastewaters were different from the batch assay of PTA. In the batch assay of PTA + PET, readily biodegradable compounds were removed during 0–10 h. The removal characteristics of this fraction seem to be similar to the batch assay of PTA. The toxic pollutants were removed more rapidly and maintained a longer phase than PTA batch assay during the stage of toxic effect (10–90 h). In the PTA + PE batch assay, the readily biodegradable fraction was in a large part and was removed during 0–10 h. The removal characteristics of toxic pollutants were similar to PTA batch assay. The readily biodegradable compounds were removed during 70–90 h and the rest of the compounds were inert and refractory. The whole processes of removal of pollutants took less time than PTA batch assay. In PTA + PET + PE batch assay, readily biodegradable compounds were removed during 0–10 h. The removal characteristics of this fraction seem to be similar to PTA batch assay. The toxic pollutants were removed during 10–40 h and the inhibitory phase took a short time. The rest of the readily biodegradable compounds was removed during 40–110 h, and the removal rate of this fraction was lower compared with PTA batch assay.

In mixed wastewater batch assays, the combined effects of mixed wastewater on the activated sludge were exhibited by the removal characteristics of pollutants. In PTA + PET and PTA + PE wastewaters, there was no significant difference between the removal rate of inhibitory phase and the recovery phase. It illustrates that the inhibitory effect was eliminated through PTA wastewater mixed with PET and PE wastewaters. In PTA + PET + PE batch assay, the removal characteristics seem to be similar to PTA batch assay. The rate of removal of inhibitory phase and recovery phase seems to be lower compared with PTA batch assay.

SOUR changes of activated sludge during aerobic biological treatment were investigated to reveal the relationship between the inhibitory effect and the removal characteristics of DOC in the wastewater. The obtained results are shown in Fig. 4. The SOUR of PTA wastewater batch assay exhibited a low value in the beginning, which was 0.09 mgO_2/gMLSS min. This indicates that the activated sludge was inhibited because of the presence of toxic pollutants in PTA wastewater. SOUR increased gradually from 0 to 40 h with the removal of toxic organic matter. SOUR decreased gradually with the metabolized substrate in PTA wastewater. In general, SOUR of PTA wastewater batch assay maintained at low values throughout the experiments due to high concentration of toxic compounds [17].

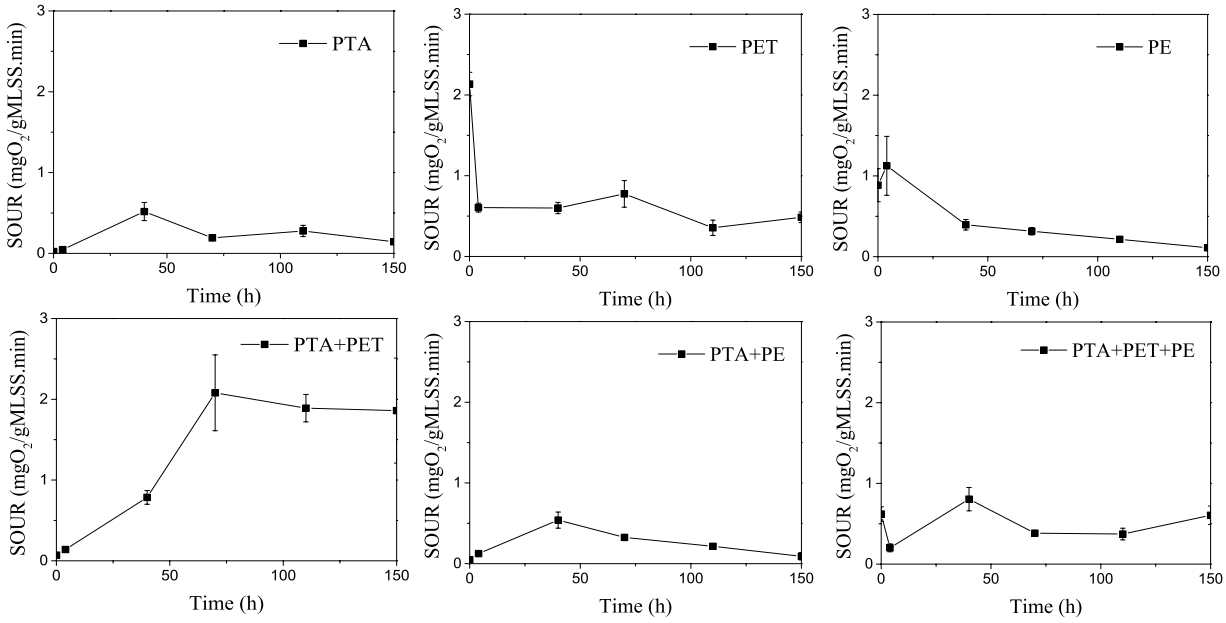

Fig. 4. SOUR changes of activated sludge during aerobic biological treatment of individual and mixed wastewaters.

In PET wastewater batch assay, SOUR achieved at 2.14 mgO_2/gMLSS min, and decreased rapidly from 0 to 4 h. This may be due to the removal of readily biodegradable compounds in PET wastewater during the first 4 h. SOUR increased from 40 to 70 h because of the removal of toxic organic matter. These results coincided with the removal rate of organic matter in PET wastewater batch assay. After that, SOUR decreased and maintained at a low value because of the slow degradation of refractory compounds.

In PE wastewater batch assay, SOUR increased to 1.13 mgO_2/gMLSS min at the initial 4 h, and decreased gradually during 4–40 h. SOUR decreased and maintained at a low value from 40 to 150 h. It illustrates the presence of a toxic effect in PE wastewater which was removed gradually during the first 4 h. The readily biodegradable compounds were metabolized in 4–40 h, and the slowly removable compounds were present in PE wastewater which were removed gradually in 40–150 h.

In mixed wastewater degradation assays, SOUR increased significantly during 0–70 h of PTA + PET wastewater. It illustrates that the toxic compounds were removed in 0–70 h and the SOUR maximum value of activated sludge increased when PTA wastewater was mixed with PET wastewater. The trends in the changes of SOUR in PTA + PE wastewater degradation assay were similar to PTA wastewater degradation assay. In PTA + PET + PE wastewater batch assay, SOUR decreased in 0–4 h because of the removal of readily biodegradable compounds and the existence of toxic pollutants. SOUR increased in 4–40 h because of the removal of toxic pollutants similar to PTA wastewater batch assay. However, the maximum value of SOUR in PTA + PET + PE wastewater batch assay was higher compared with PTA wastewater batch assay.

Based on the above results, the characteristics of changes in SOUR also exhibited inhibitory effect of toxic pollutants on the activated sludge. PTA wastewater contributed the main inhibitory effect on the activated sludge during aerobic treatment of mixed wastewaters, and the inhibitory effect seems to be relieved by different mixture of industrial effluents.

3.2.2. Anaerobic biodegradation characteristics of the wastewater

The characteristics of removal of organic matter in anaerobic batch assays demonstrate the effect of mixed wastewater on anaerobic biodegradation. Fig. 5 shows the removal characteristics of DOC of individual and mixed wastewater samples in anaerobic batch assays. The removal characteristics of organic matter in anaerobic batch assays show a similar trend during anaerobic treatment of individual and mixed wastewater samples. Readily biodegradable compounds were removed during 0–8 h, while slowly biodegradable compounds exhibited different removal rate in anaerobic batch assays. In PTA wastewater batch assay, most of the slowly biodegradable organics were removed in 8–40 h. The slowly biodegradable compounds in PET and PE wastewater were removed in 8–20 h. In PTA + PET wastewater batch assay, the removal characteristics of slowly biodegradable compounds were similar to PTA wastewater batch assay. It seems that there is no significant effect on the anaerobic biodegradable process of PTA + PET wastewater. In PTA + PE wastewater batch assay, the process of slowly biodegradable compounds was shortened with PE wastewater mixed with PTA wastewater. In PTA + PET + PE wastewater batch assay, the process of slowly biodegradable compounds was significantly extended with PE and PET effluents added into PTA wastewater.

According to the above-obtained results, the toxicity of wastewater exhibited no significant adverse effect on the anaerobic treatment. PTA wastewater was the main component in mixed wastewater. The typical pollutants, such as TA, BA, PT-acid, can be degraded by special microbes which form catabolic partnerships [18].

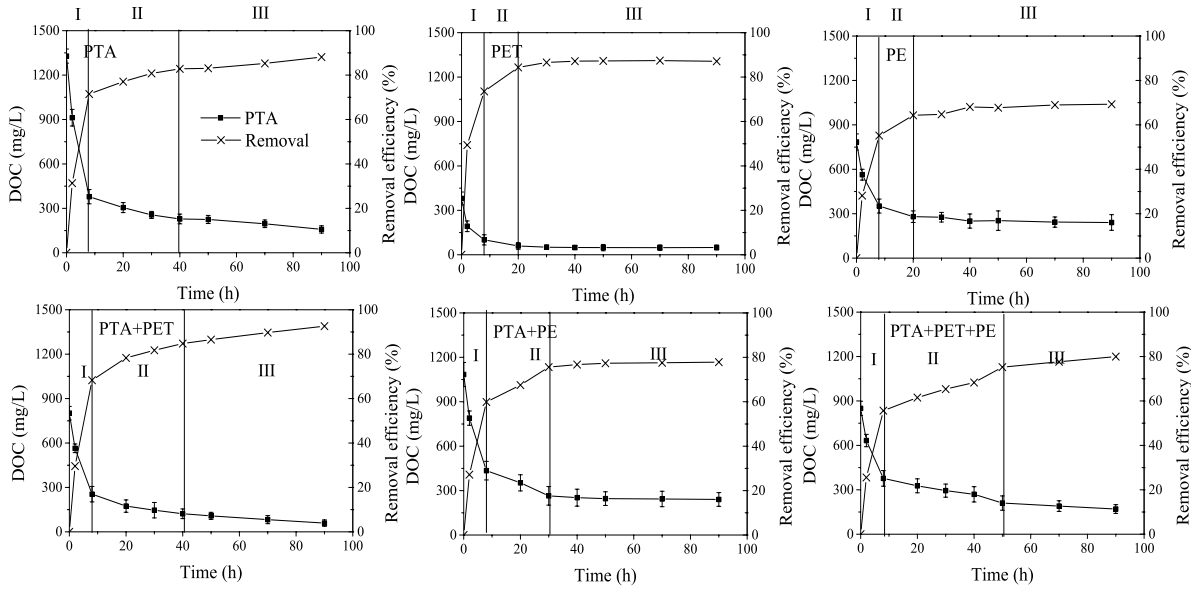

Fig. 5. DOC removal characteristics of individual and mixed wastewaters during anaerobic treatment. Phase I is the degradation stage of readily biodegradable component; Phase II is the degradation stage of slowly biodegradable component; Phase III is the stage of the existence of inert component.

3.3. Relationship of toxicity and biodegradation characteristics during the processes of biodegradation

PCA was used to assess the internal correlations between acute toxicity and biodegradation characteristics. Analytical data set covered toxicity variables: IC_{50} and $toxicity_{Zn}$; aerobic biodegradation variables: $SOUR_{max}$, $SOUR_{inhibition}$, RR_{max} and $RR_{inhibition}$; anaerobic biodegradation variables: $ARR_{readily}$ and ARR_{slowly} in the batch assays of individual and mixed wastewaters. Eigenvalue and loading were shown by PCA. The eigenvalue reflected the relationship of variables. The first three factors were indicated and their loadings have been shown in Fig. 6.

Factor 1 showed positive correlations with $RR_{inhibition}$ and IC_{50} (loadings at 0.98 and 0.81, respectively). Factor 2 showed that $SOUR_{inhibition}$ exhibited a positive correlation with $SOUR_{max}$, while $SOUR_{max}$ and $SOUR_{inhibition}$ showed a negative correlation with $Toxicity_{Zn}$. These results indicated that aerobic biodegradation processes of both individual and mixed wastewaters were impacted by the toxicity effects on the activated sludge. It also revealed that acute toxicity by luminescent bacteria test could represent the toxic effect of both individual and mixed wastewaters on the activated sludge. Therefore, factor 1 can be explained as a complicated parameter which mainly represented toxicity based on IC_{50}, while factor 2 can also be explained as a toxicity parameter based on $Toxicity_{Zn}$.

Factor 3 showed positive correlations with ARR_{slowly} in anaerobic batch assays and RR_{max} in aerobic batch assays. However, ARR_{slowly}, $ARR_{readily}$ and RR_{max} showed non-significant correlation with toxicity variables. It illustrated that ARR_{slowly} and RR_{max} were affected by the refractory characteristics of the pollutants in the wastewater. The removal rate of organic pollutants in anaerobic batch assays was not impacted by the toxicity of water because of the existence of catabolic partnerships [6]. Hence, factor 3 can be explained as a parameter based on refractory characteristics of the pollutants in the wastewater. The results also show that anaerobic processes could be more suitable for mixed petrochemical wastewater treatment compared with aerobic processes.

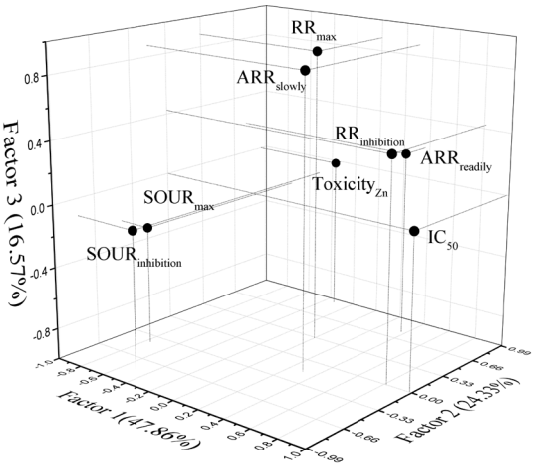

Fig. 6. PCA scatter diagram of three factors.

4. Conclusions

In this investigation, it has been found out that different mixture of petrochemical industrial effluents show various toxic effects and degradation characteristics during aerobic and anaerobic treatments. Notably, aerobic biodegradation processes of petrochemical industrial wastewater were significantly inhibited in the presence of toxic pollutants. The combined toxicity of mixed wastewater can be revealed by acute toxicity assays. PTA + PET and

PTA + PE wastewaters show an antagonistic effect, while PTA + PET + PE wastewater exhibit a partly additive effect. These results coincide with the characteristics of aerobic biodegradation. Anaerobic biodegradation processes seem to be not influenced by the toxic compounds due to the catabolic partnerships of the existing degrading microbes. The anaerobic biodegradation processes are dependent on the slowly biodegradable fraction of organic compounds in wastewater. These results illustrate that anaerobic treatment is more suitable for the mixed petrochemical industrial wastewater treatment than aerobic processes.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant No. 51608350) and the Key project of Tianjin Natural Science Foundation (Grant No. 18JCZDJC10080).

References

[1] X.K. Li, K.L. Ma, L.W. Meng, J. Zhang, K. Wang, Performance and microbial community profiles in an anaerobic reactor treating with simulated PTA wastewater: from mesophilic to thermophilic temperature, Water Res., 61 (2014) 57–66.
[2] C. Wu, Y. Li, Y. Zhou, Z. Li, S. Zhang, H. Liu, Upgrading the Chinese biggest petrochemical wastewater treatment plant : Technologies research and full scale application, Sci. Total Environ., 633 (2018) 189–197.
[3] S. Jorfi, S. Alavi, N. Jaafarzadeh, F. Ghanbari, M. Ahmadi, COD removal from high salinity petrochemical wastewater using photo-assisted peroxi-coagulation, Chem. Biochem. Eng. Q., 32 (2018) 229–238.
[4] M.M. Ghobashy, S.A. Younis, M.A. Elhady, P. Serp, Radiation induced in-situ cationic polymerization of polystyrene organogel for selective absorption of cholorophenols from petrochemical wastewater, J. Environ. Manage., 210 (2018) 307–315.
[5] K.K. Garg, B. Prasad, Treatment of toxic pollutants of purified terephthalic acid waste water: a review, Environ. Technol. Innov., 8 (2017) 191–217.
[6] A. Lykidis, C.L. Chen, S.G. Tringe, A.C. McHardy, A. Copeland, N.C. Kyrpides, P. Hugenholtz, H. Macarie, A. Olmos, O. Monroy, W.T. Liu, Multiple syntrophic interactions in a terephthalate-degrading methanogenic consortium, Int. Soc. Microbial Ecol., 5 (2010) 122–130.
[7] Z. Zhang, L. Ma, X.X. Zhang, W. Li, Y. Zhang, B. Wu, L. Yang, S. Cheng, Genomic expression profiles in liver of mice exposed to purified terephthalic acid manufacturing wastewater, J. Hazard. Mater., 181 (2010) 1121–1126.
[8] S. Ding, J. Wu, M. Zhang, H. Lu, Q. Mahmood, P. Zheng, Acute toxicity assessment of ANAMMOX substrates and antibiotics by luminescent bacteria test, Chemosphere, 140 (2015) 174–183.
[9] State Environmental Protection Administration and Water and Wastewater Examination Methods Committee of China, Standard Methods for the Examination of Water and Wastewater, China Environmental Science Press, Beijing, 2002, pp. 210–740.
[10] J.Y. Ji, Y.J. Xing, Z.T. Ma, M. Zhang, P. Zheng, Acute toxicity of pharmaceutical wastewaters containing antibiotics to anaerobic digestion treatment, Chemosphere, 91 (2013) 1094–1098.
[11] L. Sun, C. Wang, M. Ji, F. Wang, Achieving biodegradability enhancement and acute biotoxicity removal through the treatment of pharmaceutical wastewater using a combined internal electrolysis and ultrasonic irradiation technology, Front. Environ. Sci. Eng., 5 (2011) 481–487.
[12] I.A. Vasiliadou, R. Molina, F. Martinez, J.A. Melero, P.M. Stathopoulou, G. Tsiamis, Toxicity assessment of pharmaceutical compounds on mixed culture from activated sludge using respirometric technique: the role of microbial community structure, Sci. Total Environ., 630 (2018) 809–819.
[13] X.X. Zhang, S.L. Sun, Y. Zhang, B. Wu, Z.Y. Zhang, B. Liu, L.Y. Yang, S.P. Cheng, Toxicity of purified terephthalic acid manufacturing wastewater on reproductive system of male mice (Mus musculus), J. Hazard. Mater., 176 (2010) 300–305.
[14] J.Y. Joung, H.W. Lee, H. Choi, M.W. Lee, J.M. Park, Influences of organic loading disturbances on the performance of anaerobic filter process to treat purified terephthalic acid wastewater, Bioresour. Technol., 100 (2009) 2457–2461.
[15] N.G. Kim, K.J. Yim, C.S. Kim, D.K. Song, K. Okuyama, M. Han, Y. Kim, S.E. Lee, T.O. Kim, High production of CH_4 and H_2 by reducing PET waste water using a non-diaphragm-based electrochemical method, Sci. Rep., 6 (2016) 1–4.
[16] F. Sun, J. Hu, Y. Zhou, R. Mei, C. Wang, Y. He, W. Wu, High efficient alternating anaerobic / aerobic process for polyester resin wastewater treatment: performance and microbial community structure, Biochem. Eng. J., 138 (2018) 121–130.
[17] M. Liu, S. Wang, M.K. Nobu, B.T.W. Bocher, S.A. Kaley, W.T. Liu, Impacts of biostimulation and bioaugmentation on the performance and microbial ecology in methanogenic reactors treating purified terephthalic acid wastewater, Water Res., 122 (2017) 308–316.
[18] J.W. Kwak, J.S. Lee, K.H. Lee, Co-oxidation of p-xylene and p-toluic acid to terephthalic acid in water solvent: kinetics and additive effects, Appl. Catal. A Gen., 358 (2009) 54–58.