

# Novel multistep physical/chemical and biological integrated system for coking wastewater treatment: Technical and economic feasibility



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## ABSTRACT

Harmless disposal of coking wastewater (CWW) has become a tough issue due to its complexity, heterogeneity and toxicity. In order to improve contaminant removal efficiency, a novel treatment system, taking into accounts the compositions and toxic characteristics of CWW, was deliberately developed and applied in a full-scale coking wastewater treatment plant. This system integrated a physical/chemical pre-treatment, a biological treatment and a physical/chemical advanced treatment. The pre-treatment, including the degreasing and air floatation, contributed to a significant reduction of oil (removal efficiency > 85%). The bio-treatment was a pre-aeration/aerobic<sub>1</sub>/hydrolysis/aerobic<sub>2</sub> fluidized bed process, which removed 84.1% free cyanide, 93.5% thiocyanate and 86.2% total phenols, indicating an efficient biological detoxification. The successful degreasing and detoxification was conducive to the high removal efficiencies of COD (98.6%) and NH<sub>3</sub>-N (95.4%). The removal efficiency of total nitrogen reached 90%. Furthermore, the removal efficiencies of 18 polycyclic aromatic hydrocarbons were in the range of 80–99%, while the removal efficiencies of 5 benzene derivatives were in the range of 88–96%. The total concentrations of these trace toxic contaminants were maintained lower than 50 μg L<sup>-1</sup> in the final effluent. The overall cost of this system was equal to 9.67 RMB m<sup>-3</sup> (<2 US dollars) of CWW. The satisfactory performance of contaminants removal and the low cost implied that this integrated system was a feasible and reliable option for CWW treatment.

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## 1. Introduction

Millions of tons of coke are produced to cater to the growing demand for steel along with rapid urbanization in the developing world. Coking wastewater (CWW) is one of the harmful by-products from coke production, which contains enormous amount of carcinogenic compounds. As the largest producer of coke, China experienced increasing pressure to alleviate the environmental consequences of CWW [4,15,16]. It was estimated that  $\sim 2.4 \times 10^4$  t of phenols,  $\sim 700$  t of cyanide and  $\sim 1.6 \times 10^3$  t of benzo[a]pyrene were generated along with CWW in China in 2005 [19]. Additionally, other countries, such as India, Korea, etc., are also producer of coke and endure similar pollution of CWW [10,12,22], suggesting that it is a worldwide problem. Recently, the Chinese govern-

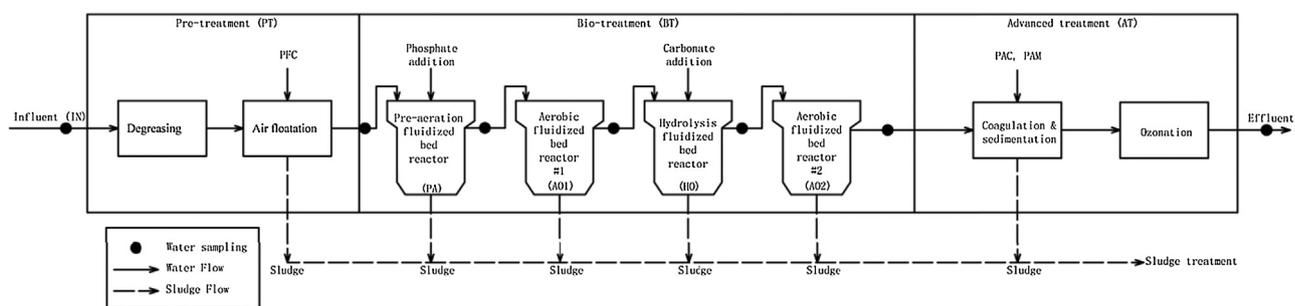
ment issued stricter new discharge standard (Table SM-1) for CWW treatment plants (CWWTPs) [18]. There are more than 1000 coke factories in China, most of which are still using outdated CWW treatment systems since 1990s. Thus, it is urgent to develop more efficient and steady treatment technique for these factories.

It is well known that harmless disposal of CWW is a great challenge due to its complexity, heterogeneity and toxicity. Two groups of specific contaminants, including oil and toxic compounds, were the dominating inhibitors to biological treatments of CWW. First, oil formed a suspending layer which interfered with the aeration in bio-treatment [20]. Second, typical toxic compounds in CWW, including free cyanide (CN<sup>-</sup>), phenols and thiocyanate (SCN<sup>-</sup>), had inhibition on many functional bacteria, such as ammonia oxidizing bacteria (AOB) and nitrite-oxidizing bacteria (NOB) [2]. In view of these facts, a prepositive degreasing/detoxification process should be established as the pretreatment method for CWW.

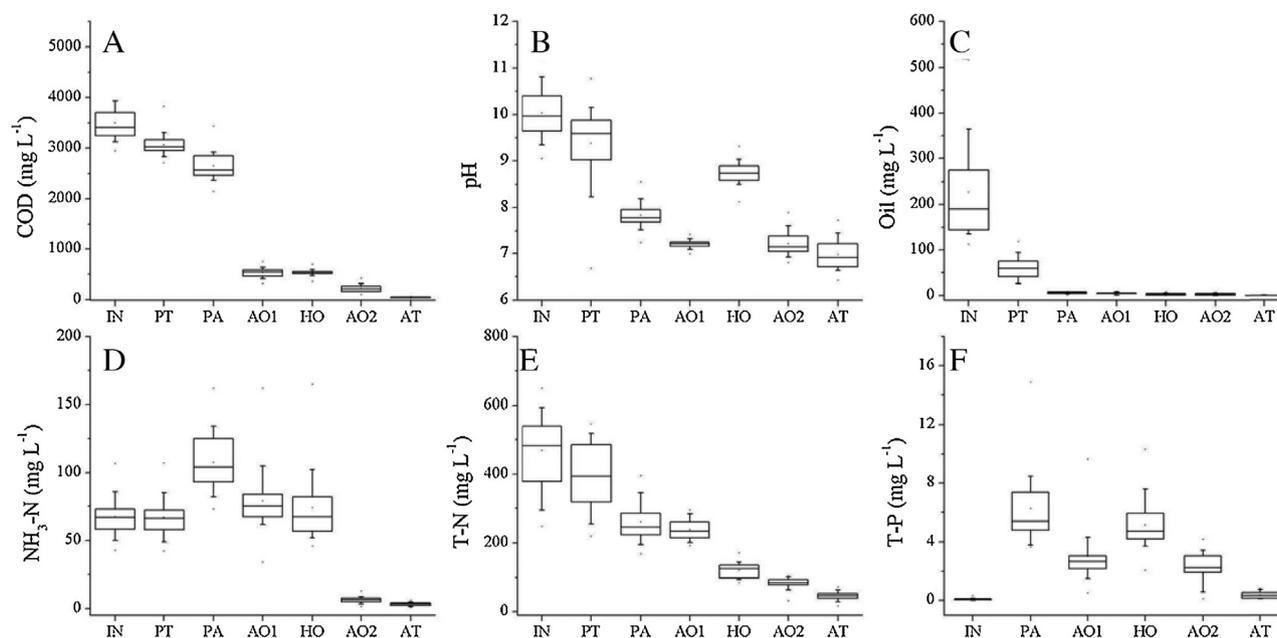
Recently, researchers are making efforts to develop cost-effective treatment methods to dispose CWW. Most literatures

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**Fig. 1.** Schematic diagram of No.2 Songshan coking wastewater treatment plant and sampling sites. Water samples were collected from seven sites, including the total influent, the influent of each stage in PA/AO<sub>1</sub>/HO/AO<sub>2</sub>, and the total effluent from April 1, 2011 to March 31, 2013.



**Fig. 2.** Statistical variations of conventional parameters. (A) COD, (B) pH, (C) oil, (D) NH<sub>3</sub>-N, (E) T-N, (F) T-P. Box range 25–75%, whisker range: 10–90%. IN=influent; PT=pre-treatment; BT=bio-treatment; PA=pre-aeration; AO<sub>1</sub>=aerobic<sub>1</sub>; HO=hydrolysis; AO<sub>2</sub>=aerobic<sub>2</sub>; AT=advanced treatment. Sampling was conducted daily from April 1, 2011 to March 31, 2013 with a total of 712 data.

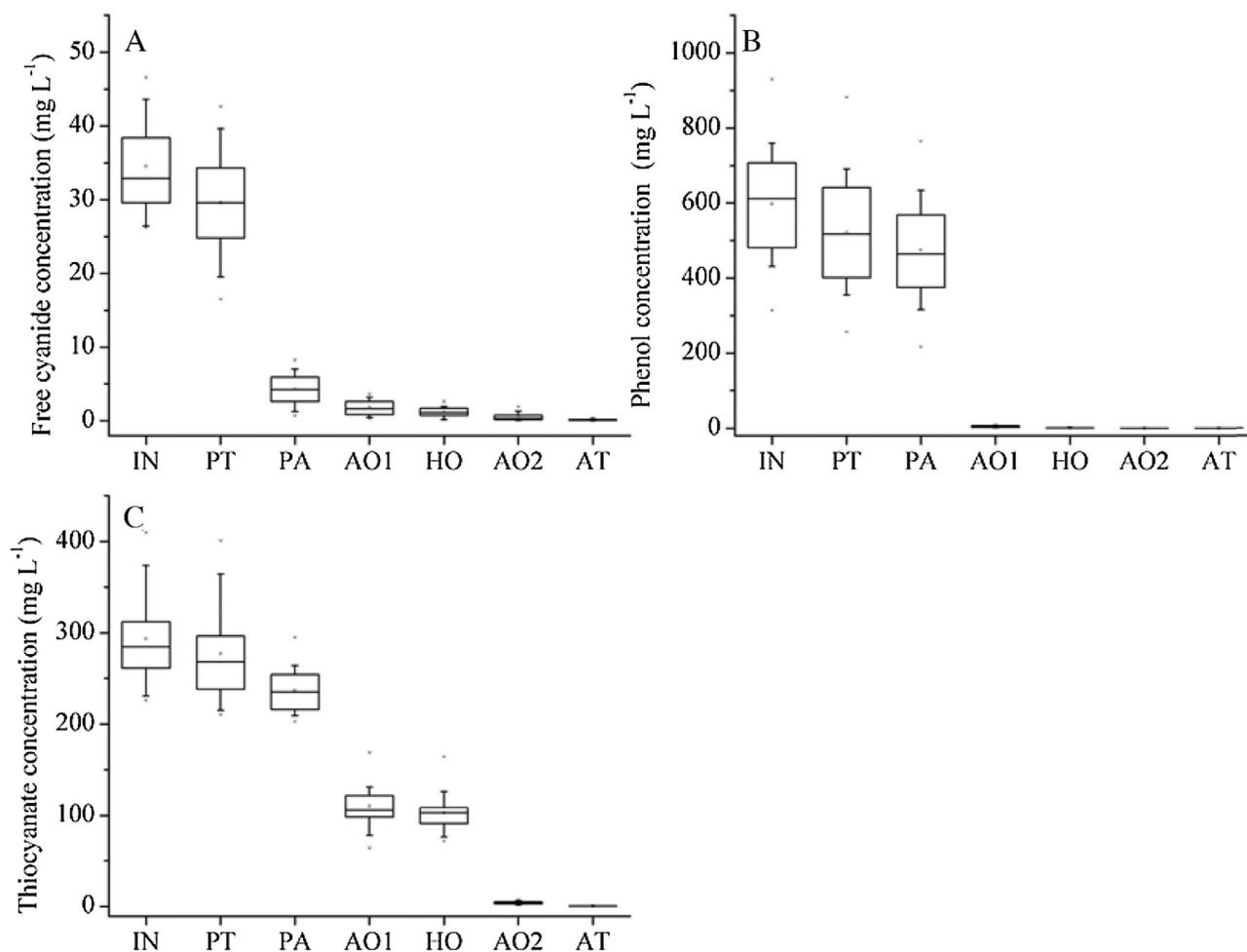
focused on specific physical/chemical methods, including sedimentation [23], ozonation [5], Fenton [9] and membrane separation [13], etc. These methods were technically feasible to reduce the suspended solids, colloidal particles, floating matters, colors and toxic compounds, but they had several drawbacks, such as high cost (ozonation), additional contaminants generation (Fenton), membrane fouling, etc. Therefore, these techniques were only used as affiliated treatment stage in some full-scale CWWTP.

To the contrary, biological treatment consumed lower energy and fewer additions, thus it became the most common technique for full-scale wastewater treatment plants. Individual biodegradation methods for the phenols, CN<sup>-</sup>, SCN<sup>-</sup> and ammonia-nitrogen (NH<sub>3</sub>-N) were reported [8,14,17], but successful biological treatment of CWW turned to be very difficult as these contaminants often oppose each other's effective degradation. For instance, high concentration of cyanide inhibited phenols degrading bacteria [1], and high concentration of phenols inhibited SCN<sup>-</sup> degradation [7]. Furthermore, cyanide and phenol inhibited AOB and NOB activity [2]. These inhibitions will be enhanced when the composition of influent changes suddenly.

In view of these facts, the establishment of a system for CWW treatment should take into account the compositions

and toxic characteristics of contaminants, and then deliberately integrate a series of treatment methods aiming at the purifications of different contaminants. To the best of our knowledge, only a few successful full-scale integrated systems were reported [11]. Over the past decade, our research group attempted to develop several integrated systems for CWW [21,26,28]. Based on the operational experience and drawbacks of the previous works, a novel integrated treatment system, which included: (1) pre-treatment (PT) using degreasing and flotation, (2) bio-treatment (BT) using pre-aeration/aerobic<sub>1</sub>/hydrolysis/aerobic<sub>2</sub> (PA/AO<sub>1</sub>/HO/AO<sub>2</sub>) fluidized-bed process, and (3) advanced treatment (AT) using sedimentation and ozonation, was developed and applied in a full-scale CWWTP.

However, the detailed information regarding to the contaminants removal efficiency of this system was yet not reported. The objective of the current study was to demonstrate the technical and economic performance of this system. Based on the long-term monitoring data, the contaminant removal efficiency was analyzed. The monitoring data included: (1) conventional parameters, (2) predominant toxic contaminants, and (3) trace toxic contaminants. Furthermore, the economic evaluation was conducted based on the



**Fig. 3.** Statistical variations of predominant toxic contaminants. (A) free cyanide, (B) total phenols, (C) thiocyanate. Box range: 25–75%, whisker range: 10–90%. Sample was conducted daily from April 1, 2011 to March 31, 2013 with a total of 712 data.

capital cost and operational cost. Findings of this study can be used to improve the degradation efficiency of CWW.

## 2. Materials and methods

### 2.1. Experimental safety

To avoid the health risk of toxic material exposure, all experiments were conducted in a Class II Biological Safety Cabinets (Thermo Fisher, USA). Safety gloves, safety masks, laboratory clothing, and protective goggles were mandatory when handling toxin experiments.

### 2.2. CWWTP

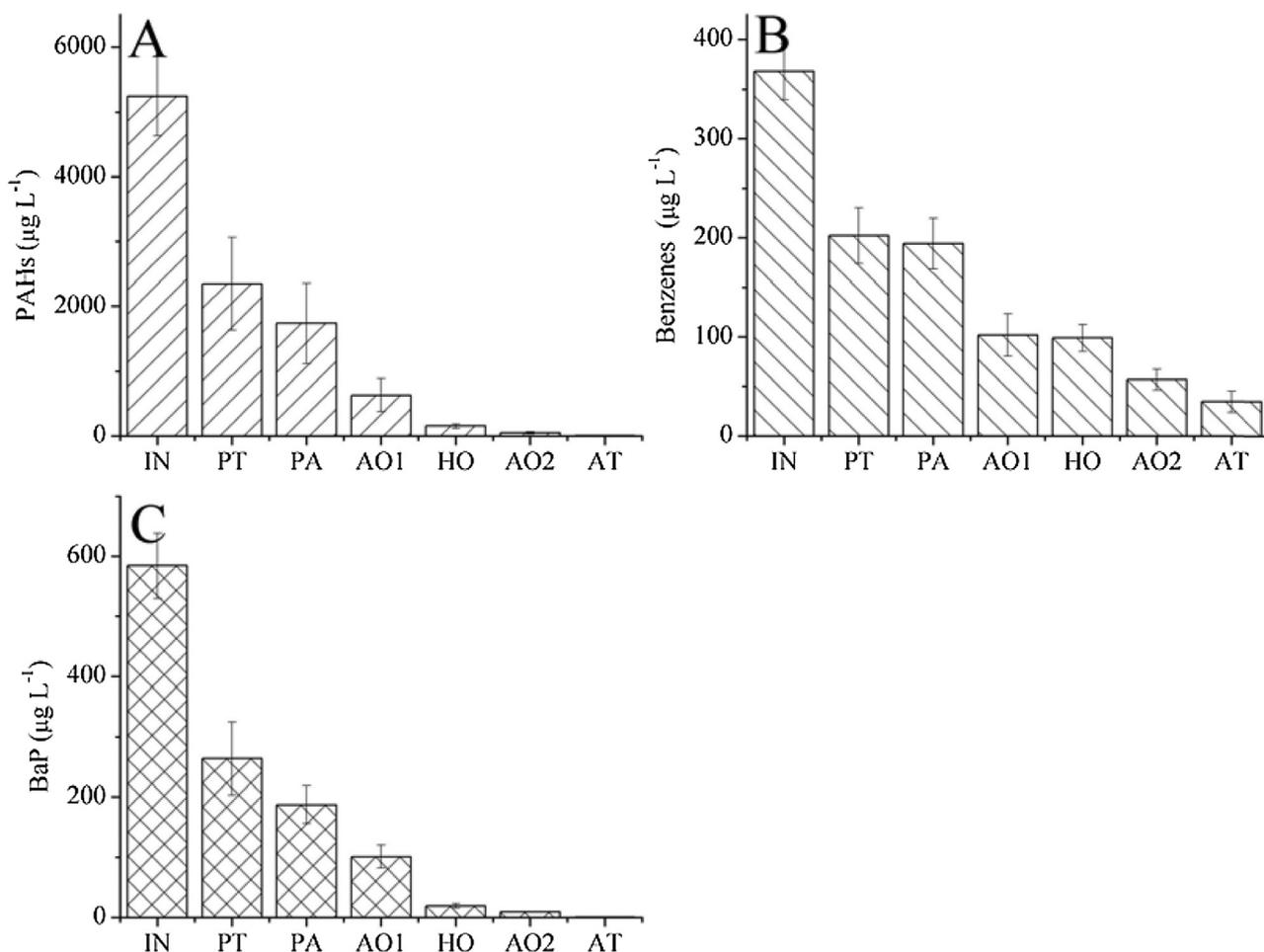
The project of No.2 Songshan CWWTP was proposed in 2006, which was designed as a subsidiary facility for a new coke oven of Shaoguan Steel Co., Ltd. in Guangdong province, China. This CWWTP was put into operation since 2008, with a total construction cost of 18.8 million RMB and a designed treatment capacity of 1320 m<sup>3</sup> d<sup>-1</sup>. Table SM-2 presents the statistical monitoring variables of total influent, and Fig. 1 presents the schematic diagram of treatment procedure. High concentrations of oil and critical toxic contaminants, such as phenol and CN<sup>-</sup>, were observed. These contaminants had critical adverse effects on microorganisms and should be removed preferentially. Therefore, in the PT stage, a degreasing facility was set to reduce the oil and grease in influent,

and an air floatation facility was used to remove the suspended solids, which were expected to reduce the adverse effects of oil and suspended solids on biological reactions. After PT, the effluent flowed into the BT stage. A PA/AO<sub>1</sub>/HO/AO<sub>2</sub> system coupled with four internal-loop biological fluidized-beds in the volumes of 880, 1200, 1000 and 1200 m<sup>3</sup> was applied. BT was designed to perform a prepositive detoxification and a postpositive nitrification/denitrification. The BT effluent then flowed into AT, which included coagulation/sedimentation and ozonation. The final effluent was discharged into municipal sewer.

### 2.3. Conventional parameters and predominant toxic contaminants analysis

Five hundred milliliter water samples were collected from seven sites, including the total influent, the influent of BT (effluent of PT), the effluent of each stage in PA/AO<sub>1</sub>/HO/AO<sub>2</sub>, and the final effluent (Fig. 1). The collected samples were stored at 4 °C prior to analysis. Sampling was conducted daily from April 1, 2011 to March 31, 2013 with a total of 712 data (18 data were absent because of vacations). In the current study, the deionized water used for solution preparation was produced by a Milli-Q Advantage A10 system (Millipore, USA).

COD, NH<sub>3</sub>-N and pH were measured by online COD<sub>max</sub>-Plus monitors (Hach, USA), Amtax Compact analyzers (Hach, USA) and GLI pH/ORP monitors (Hach, USA), respectively. For the analyses of other parameters, the water samples were centrifuged and the



**Fig. 4.** Statistical variations of trace toxic contaminants. (A) PAHs, (B) benzene derivatives, (C) BaP. The PAHs concentration was the summation of 18 PAHs. The benzenes concentration was the summation of benzene and 4 derivatives, including methylbenzene, ethylbenzene, *o*-xylene and *m,p*-xylene. Data are the means of 12 independent samples. Error bars indicate the standard deviation of each data set.

supernatant was filtered using 0.7 µm GF/F filters and then 0.22 µm membrane filters (MFS, Japan) to obtain the extracted solution. The CN<sup>-</sup> was tripped by vigorous air-blowing to be absorbed into a 1M NaOH solution, and then was determined by the pyridine-pyrazolone method. The concentrations of total phenols, SCN<sup>-</sup> and NO<sub>3</sub>-N were determined using standard methods [3].

#### 2.4. Trace toxic contaminants analysis method

Water samples for the trace toxic contaminants analysis were collected from the total influent, the effluent of PT, the effluent of each stage in PA/AO<sub>1</sub>/HO/AO<sub>2</sub>, and the effluent of AT at April 5, September 20 in 2011 and July 16, November 5 in 2012. Each sampling data set contained three replicates. These water samples were immediately transported to laboratory and centrifuged at 1 × 10<sup>4</sup> rpm for 10 min. The supernatant was filtered with glass fiber filters to obtain the extracted solution.

Due to their toxic, carcinogenic, and mutagenic characteristics, sixteen polycyclic aromatic hydrocarbons (PAHs) have been identified as priority pollutants by the United States Environmental Protection Agency [25]. In the current study, 18 PAHs, including naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*cd*]pyrene, dibenzo[*a,h*]anthracene, and benzo[*g,h,i*]perylene, were selected as target compounds.

The standard solution of these 18 PAHs, each at 2000 µg mL<sup>-1</sup>, and the deuterated surrogate (each at 4000 µg mL<sup>-1</sup>) containing naphthene-d<sub>8</sub>, acenaphthene-d<sub>10</sub>, phenanthrene-d<sub>10</sub>, chrysene-d<sub>12</sub> and perylene-d<sub>12</sub> were obtained from Supelco (Bellefonte, PA, USA). An internal standard for GC analyses was hexamethylbenzene, which was obtained from Aldrich Chemical (Gillingham, Dorset, USA). The pre-preparation, instrumental analysis and quality controls were conducted following the same methods in our previous study [27]. Five benzene derivatives, including benzene, methylbenzene, ethylbenzene, *o*-xylene and *m,p*-xylene, were selected as target compounds. The determination of these compounds was conducted using trace volume solvent dispersive liquid-liquid microextraction followed by GC-FID, which was developed by our research group [6].

### 3. Results and discussion

#### 3.1. Treatment process and operating condition

The three-stage treatment process was applied in the current CWWTP, and the detailed operating parameters are listed in Table SM-3. In the PT stage, the HRT of degreasing and air floatation were set at 10 h and 5 h, respectively. These PT processes were used to separate oil and suspended solids from CWW influent. In the BT stage, a PA/AO<sub>1</sub>/HO/AO<sub>2</sub> system was used to perform a prepositive detoxification and a postpositive nitrification/denitrification.

The HRT of PA, AO<sup>1</sup>, HO and AO<sup>2</sup> reactors were 16, 22, 18 and 22 h, respectively. The DO values in PA, AO<sup>1</sup> and AO<sup>2</sup> reactors were set at  $1.06 \pm 0.12 \text{ mg L}^{-1}$ ,  $2.08 \pm 0.64 \text{ mg L}^{-1}$  and  $5.21 \pm 0.34 \text{ mg L}^{-1}$ , respectively. The relatively high DO levels in AO<sup>1</sup> and AO<sup>2</sup> reactors provided a comfortable condition for aerobic bacteria, such as phenol-degrading bacteria and nitrifying bacteria. However, in HO reactor, a strict anaerobic condition was achieved for the growth of anaerobic bacteria. After BT stage, an advanced treatment which consists of coagulation-sedimentation and ozonation were performed. The coagulation-sedimentation was used to remove the bacteria residual from BT and the other particles, and the ozonation was used to degrade the residual dissolved organic matter.

### 3.2. Variations of conventional parameters

Based on the concentration and characteristic of contaminants in the influent, three groups of parameters were defined from the monitoring objectives in 2012 version standard. Groups I, II and III indicated conventional parameters, predominant toxic contaminants, and trace toxic contaminants, respectively (Table SM-1).

To investigate the routine performance, the monitoring values of conventional parameters, including oil, COD, pH, NH<sub>3</sub>-N, T-N, and T-P, were presented as statistics (Fig. 2). The oil concentration in total influent was  $226 \pm 100 \text{ mg L}^{-1}$ , and it decreased to  $59 \pm 24 \text{ mg L}^{-1}$  after degreasing and air floatation (average removal efficiency at 74%). The significant reduction of oil in PT stage was conducive to subsequent biological reactions in the BT stage. COD decreased from  $(3.50 \pm 0.36) \times 10^3$  to  $(3.06 \pm 0.19) \times 10^3 \text{ mg L}^{-1}$  after the PT stage; then it decreased to  $229 \pm 67 \text{ mg L}^{-1}$  after the BT stage. COD finally decreased to  $49 \pm 8 \text{ mg L}^{-1}$ . This result indicated that the removal of organic contaminants was predominantly achieved in the BT stage (average COD removal efficiency at 81%).

The NH<sub>3</sub>-N concentration was  $67.3 \pm 14.3 \text{ mg L}^{-1}$  in total influent, and a slight variation was observed in the PT stage. It decreased to  $6.4 \pm 2.1 \text{ mg L}^{-1}$  and  $3.1 \pm 1.2 \text{ mg L}^{-1}$  after BT and AT stages, respectively. The variation of T-N had a similar pattern, and it decreased to  $46.5 \pm 12.6 \text{ mg L}^{-1}$  in the final effluent. The total removal efficiencies of NH<sub>3</sub>-N and T-N reached 95.4% and 90.1%, respectively, implying significant nitrogen removal capacity of this system. The concentration of T-P was relatively low ( $<0.1 \text{ mg L}^{-1}$ ) in the influent. To provide phosphorus component for microorganisms in BT stage, phosphate was added in the PA stage of BT, thus T-P increased to  $6.3 \pm 2.5 \text{ mg L}^{-1}$ . The concentrations of T-P were  $3.0 \pm 1.9$ ,  $5.2 \pm 1.7$  and  $2.2 \pm 1.0 \text{ mg L}^{-1}$  in AO<sub>1</sub>, HO and AO<sub>2</sub> stages, respectively. The increasing T-P in the HO stage may be attributed to the release of phosphate from anaerobe under anaerobic condition. T-P decreased to  $0.4 \pm 0.2 \text{ mg L}^{-1}$  in the final effluent. The pH value of total influent was  $10.03 \pm 0.54$ , and the pH values were  $9.37 \pm 0.76$ ,  $7.21 \pm 0.26$ , and  $6.98 \pm 0.31$  in PT, BT and AT effluent, respectively.

### 3.3. Removal efficiency of predominant toxic contaminants

To investigate the predominant toxic contaminant removal efficiency, the monitoring data of CN<sup>-</sup>, SCN<sup>-</sup> and total phenols were presented as statistics (Fig. 3). The concentration of CN<sup>-</sup> in influent was  $34.6 \pm 6.1 \text{ mg L}^{-1}$ , and it decreased to  $29.6 \pm 6.9 \text{ mg L}^{-1}$  after the PT stage. It decreased to  $0.5 \pm 0.4 \text{ mg L}^{-1}$  after the BT stage, and then maintained  $<0.1 \text{ mg L}^{-1}$  in the final effluent. The concentration of total phenols in influent was  $598 \pm 132 \text{ mg L}^{-1}$ . It decreased to  $521 \pm 139 \text{ mg L}^{-1}$  after the PT stage, and then rapidly decreased to  $4 \pm 2 \text{ mg L}^{-1}$  after the BT stage. It maintained in the range of  $0.01$ – $0.16 \text{ mg L}^{-1}$  in the final effluent. The concentrations of SCN<sup>-</sup> in the influent and the PT effluent were  $293 \pm 49 \text{ mg L}^{-1}$  and  $277 \pm 53 \text{ mg L}^{-1}$ , respectively. It decreased to  $4 \pm 2 \text{ mg L}^{-1}$  after

the BT stage, and then maintained in the range of  $0.16$ – $0.78 \text{ mg L}^{-1}$  in the final effluent. Eventually, the integrated treatment system removed 99% CN<sup>-</sup>, 99% SCN<sup>-</sup> and 99% total phenols.

BT was the prime stage for contaminants degradation, and the four reactors in the BT stage played different roles. The first two reactors (PA and AO<sub>1</sub>) contributed to the prepositive detoxification, which was confirmed in the results of Fig. 3. The concentration of CN<sup>-</sup> reduced from  $29.6 \pm 6.1$  to  $4.3 \pm 6.9 \text{ mg L}^{-1}$  (removal efficiency at 62%) after the PA treatment. The concentrations of total phenols and SCN<sup>-</sup> reduced from  $457 \pm 126$  to  $4 \pm 2 \text{ mg L}^{-1}$  (removal efficiency at 79%) and from  $237 \pm 23$  to  $110 \pm 22 \text{ mg L}^{-1}$  (removal efficiency at 43%), respectively, after the AO<sub>1</sub> treatment. Degradation of these three high toxic contaminants was conducive to the biological reactions of other contaminants. Therefore, rapid decreases of T-N ( $238.5$  to  $84.9 \text{ mg L}^{-1}$ ) and NH<sub>3</sub>-N ( $79.1$  to  $6.4 \text{ mg L}^{-1}$ ) were observed in the last two biological reactors (HO and AO<sub>2</sub>). These results indicated that PA/AO<sub>1</sub>/HO/AO<sub>2</sub> biological fluidized-bed technique (BT stage) fulfilled the expected prepositive detoxification and postpositive nitrification/denitrification.

### 3.4. Removal efficiency of trace toxic contaminants

The removal efficiencies of 18 PAHs and 5 benzene derivatives are presented in Figs. 4, SM-1, SM-2 and SM-3. Eighteen PAHs can be separated into two groups (low concentration and high concentration). The low concentration group included 8 PAHs, e.g., naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, and anthracene, which had relative low concentrations (all  $<10 \mu\text{g L}^{-1}$ ) in the influent (Table SM-4). The removal efficiencies of this group were in the range of 80%–97%, which were relatively lower than the high concentration group. The high concentration group included other 10 PAHs, which had relative high concentrations (all  $>100 \mu\text{g L}^{-1}$ ) in influent. The removal efficiencies of this group were all  $>99\%$ . The total concentration of these 18 PAHs was  $(5.39 \pm 1.62) \times 10^3 \mu\text{g L}^{-1}$  in the influent, and it decreased to  $8.8 \pm 2.1 \mu\text{g L}^{-1}$  in the effluent. Of note, PT and BT stages respectively removed 55% and 44% of total PAHs. Since these PAHs were critical toxic and carcinogenic compounds, the efficient removal of them by this integrated system had important significance for the safety of surrounding people and environment.

The average concentrations of benzene, methylbenzene, ethylbenzene, *m,p*-xylene and *o*-xylene were  $223 \pm 115 \mu\text{g L}^{-1}$ ,  $74 \pm 50 \mu\text{g L}^{-1}$ ,  $29 \pm 13 \mu\text{g L}^{-1}$ ,  $26 \pm 15 \mu\text{g L}^{-1}$  and  $16 \pm 8 \mu\text{g L}^{-1}$  in the influent, respectively (Table SM-5). After the integrated treatments, the removal efficiencies of benzene derivatives reached 88%, 93%, 93%, 94% and 96%, respectively. The total concentration of these 5 benzene compounds reduced from  $376 \pm 28$  to  $36 \pm 13 \mu\text{g L}^{-1}$  after integrated treatment. These results demonstrated that this integrated system had effective removal of trace toxic contaminants, such as PAHs and benzene.

### 3.5. General performance of integrated treatment system

The passing rate of final effluent is listed in Table SM-6. Based on the monitoring data (last 2 year), the discharged concentration of most contaminants were lower than the standard (Table SM-6). In conventional parameter group, most parameters had 100% passing rates except the T-N, which had a passing rate at 54%. The T-N and NH<sub>3</sub>-N concentrations were in the ranges of  $16.4$ – $72.6 \text{ mg L}^{-1}$  and  $0.5$ – $6.1 \text{ mg L}^{-1}$  in final effluent, respectively. These low removal efficiencies indicated that the denitrification of this system was still needed to be improved.

In predominant toxic contaminants group, the passing rates of total phenols and CN<sup>-</sup> reached 100% in operation. Of note, SCN<sup>-</sup> dis-

charged limit was not included in the standard. In the current study, high concentration of  $\text{SCN}^-$  existed in the influent. As the  $\text{SCN}^-$  has high toxicity [24], it was selected as a routine monitoring parameter and its average concentration was  $0.46 \text{ mg L}^{-1}$  in the final effluent. It was proposed to add  $\text{SCN}^-$  as a mandatory monitoring objective in the standard.

In trace toxic contaminants group, the total concentration of 18 PAHs was lower than the standard. Similar result was observed in benzene derivatives. However, the concentration of benzo[*a*]pyrene was in the range of  $0.01\text{--}0.11 \text{ }\mu\text{g L}^{-1}$ , suggesting that exceeding-standard condition occurred in routine operation. The data set of trace toxic contaminants group only had 12 replicates due to the cost of detection processes. Therefore, the passing rates of this group only provided limited information.

### 3.6. Economic assessment

Table SM-7 shows the predominating costs of this integrated treatment system. Of note, initial investment (depreciation) accounted for 40.4% of the total cost. In routine operational costs, the energy cost accounted for 21.9% of the total cost, which represented the main cost of aeration and air flotation. Other cost accounted for 37.7% of the total cost. The overall cost of this system was equal to  $9.67 \text{ RMB m}^{-3}$  of CWW, representing the significant part of the overall operation cost of treatment processes in Fig. 1. Therefore, the current integrated system was economic feasible for coking producing enterprises.

## 4. Conclusions

The contaminants removal efficiency and operational cost of the current integrated treatment system demonstrated that it was a feasible solution for CWW treatment. Two processes, pre-oxidative degreasing and detoxification, were performed to ensure the biological reactions. Biological reaction was indisputably the predominating process for contaminant degradation, which contributed to removal of 81% COD, 66% TN, 84%  $\text{CN}^-$  and 87% total phenols. The successful operation of this CWWTP indicated that the treatment strategy should be deliberately established, taking into accounts the specific composition and toxic characteristic of CWW contaminants. This integrated treatment system presented a new option for the technical improvement of CWWTPs in China and other coke producing countries

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jwpe.2016.02.007>.

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