FATE AND SEASONAL VARIATIONS OF PAES IN WWTPS OF HARBIN, CHINA

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Introduction

Phthalate esters (PAEs) were widely used in industrial applications since the 1920s which was introduced as plasticizers and their production increase rapidly (1800t per year in1975 to 4300t per year in 2006) [1]. As PAEs are ubiquitous in environment and human's daily life, the long-term exposure for human in highly PAEs contaminated environment can bring imponderable health risks. Wastewater treatment plants (WWTPs), which collect domestic and industry sewage, can reduce the concentration of various pollutants and to reach water purification. Physical, chemical, and biological method are applied in WWTPs. WWTPs play an important role in eliminating PAEs from the city and can also be an important source of PAEs in the natural environment. Therefore, to study the removal of PAEs in WWTP is of great importance. Harbin is located in northeast of China, with long winter and short summer, the temperature changes significantly, and the annual average temperature is 3.5°C .Biological wastewater treatment process mainly depends on the activity of microorganism which is influenced by environment factors such as temperature and pH. Because of the special climate factors of Harbin, the influence of seasonal change on the removal efficiency of WWTP in Harbin should be focused. The removal efficiency of PAEs has been studied in many WWTPs[2-5] as well as through laboratory experiments[6,7],but the influence seasonal change bring to the removal efficiency of PAEs in WWTPs has not been investigated thus far.

The objects of this study were to investigate the fate and seasonal variations of 8 PAEs-Dimethyl Phthalate (DMP), Diethyl Phthalate (DEP), Di-n-butyl Phthalate (DnBP), Di-n-octyl Phthalate (DnOP), Butylbenzyl Phthalate (BBP), Di (2-ethylhexyl) Phthalate (DEHP), Dicylohexyl Phthalate (DCHP) in two wastewater treatment plant in Harbin—Taiping wastewater treatment plant (WWTP1with anoxic/oxic (A/O) process) and Wenchang wastewater treatment plant(WWTP2 with biological aerated filter (BAF) process)which shared the same influent. The inflow is composed of 80% domestic wastewater, and 20% industrial wastewater. The effluent goes into Songhua River then flow into Heilong River, which was shared by China and Russia. By exterminating the PAEs concentrations in every process, we aim to demonstrate the different removal efficiency of each process of two WWTPs with different central biological process and the influence on removal efficiency did the seasonal change bring. Finally, illustrate the removal pathway of PAEs in two WWTP by analyzing the fundamental removal mechanism of each process unit.

Materials and methods

Sampling

Samples of two seasons were collected in the autumn of 2011(October) and winter of 2012(January) from two wastewater treatment plant in Harbin, WWTP Taiping adopts A/O process and WWTP Wenchang adopts BAF process. Wastewater samples were collected every 8 hours and combined 4 samples into one mixture sample. The schematic diagram of two WWTP processes showed in Fig.1.

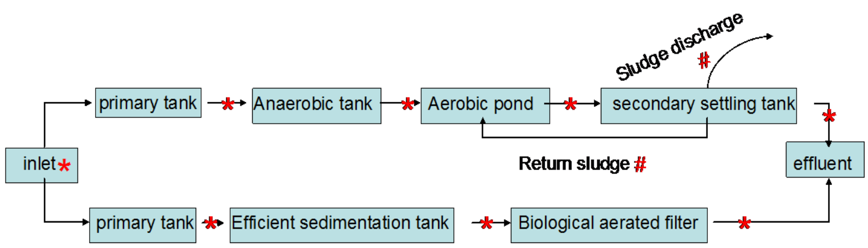

Fig.1 Diagram of two processes in WWTP

Pretreatment and data analysis

Wastewater water was filtered using 0.45 μm extracted filter membrane, the aqueous part and the particles retained with the filter were separately extracted. aqueous samples were extracted with dichloromethane, internal standard were added before the extraction. 3 extracts were combined and went through the anhydrous sodium sulfate to get rid of the residual water. Filter with particles on it were extracted using Soxhlet extractor with dichloromethane. Finally, all the solvent extracts were rotary evaporated to2~3ml and purified using Florisil solid extractor, concentrated to 1ml under a gentle nitrogen flow, analyzed using the GC-MS (agilent, GC6890-MS5973).

QA/QC

All the procedure of sampling, storage, extraction and purify were conducted as the USEPA recommended strictly. Every batch of 10 samples will be accompanied with one blank sample and 1 spike sample. The range of recoveries of wastewater and particle phase is 70%—120%, the mean value is 93%±11%. DnBP, BBP, DnOP, DHP and DCHP could not be detected in blank sample, while DMP, DEP and DEHP were below 10% of real sample, so all the data were presented without blank correction.

Result and discussion

1. Concentration of PAEs in influent

WWTP of Harbin is mainly responsible for dealing with domestic sewage of south of the Songhua River, about 625000 t/d. The average total concentration of PAEs in influent was 57400 ng/L. DEHP was the major compound found in influent at mean concentration of 41200 ng/L, which account for 72% of the total. High concentration of DEHP in influent is in accordance with the consumption pattern of this compound in Harbin. DHP and DCHP could not be detected in the influent samples, because they are below the limits of detection (LOD), which shows that DHP and DCHP were less used compared to the other 6 kinds of PAEs.

2. Removal efficiency of PAEs in two processes

2.1 Removal proportion of units in A/O process

Primary setting tank, anaerobic tank, aerobic tank and secondary tank's removal efficiency of A/O process were chosen as object. Knowing the proportion of each processing unit's removal rate account for the total, we gain the optimal removal processing unit of PAEs in the A/O process as the following Fig.1

Different processing units in A/O process have different removal contribution on different compounds of PAEs. Among them the primary setting tank possed the largest removal contribution to PAEs, its overall removal contribution of 6 kinds of PAEs reached more than 60%. All the materials enjoyed a higher removal contribution (more than 45%) except DEP. This is because the primary setting tank mainly removes the suspended particles and thus the sorbed PAEs to the particles. Studies have shown that organic materials whose LogKow is more than 4 tend to be absorbed at the suspended particle. Compared to other 4 PAEs, DEP's adsorption potential to the suspended particles is weak, so its removal efficiency is poor. Therefore, the primary setting tank is the main removal processing unit of PAEs in A/O process. As long as strengthen the role of sedimentation of primary setting tank can we enhance the overall removal of the 5 kinds of PAEs.

DMP has a good removal efficiency in primary setting tank as well as in anaerobic tank, so the combined process of primary setting tank and anaerobic tank is a better choice for the removal of DMP. DEP gain a low removal contribution rate in primary setting tank, but a higher one in anaerobic and aerobic tank. Because PAEs with long carbon chain has a poor biodegradability, DEP has a good biodegradability in the biological process.

2.2 Removal proportion of units in BAF process

Through respectively detecting the removal proportion of each processing unit account for the total, we can gain the optimal removal processing unit of PAEs in the BAF process as Fig.2.

The same to A/O process, BAF's primary setting tank also posses the largest overall removal contribution. Except the short-chain DMP and DEP, efficient sedimentation tank also has a higher removal contribution. It provides a further proof that strengthening the role of sedimentation of primary setting tank can enhance the removal efficiency of PAEs. However 60% of DMP and DEP were removed by biological aerated filter.

Biological aerated filter has better removal efficiency on short-chain DMP and DEP than the aerobic pond in A/O, so biological aerated filter can effectively reduce the release of DMP and DEP.

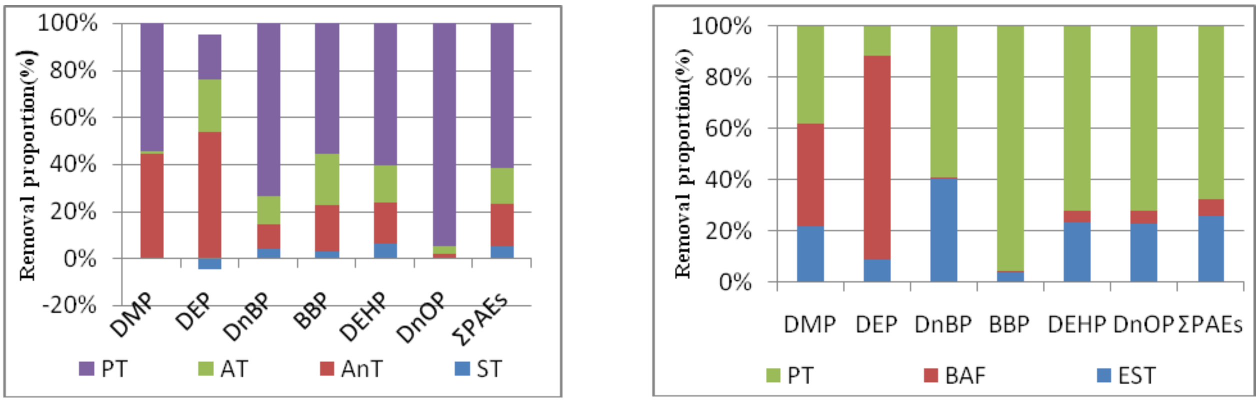

Fig.2. Removal proportion of PAEs in A/O (up) and BAF (down)

PT: Primary tank; AT: aerobic tank; AnT: anaerobic tank; BAF: biological aerated filter; ST: secondary setting tank;) EST: efficient sedimentation tank

2.3 Comparison of overall removal efficiency of 6 PAEs in two processes

Compare the influent and effluent of two treatment systems and analysis the removal efficiency of the whole wastewater treatment process as Fig.3. The total removal efficiency of the six PAEs of A/O and BAF was 87% and 88% respectively, which tells that both two systems had certain ability to remove PAEs in wastewater and their ability were almost the same. As for the removal of DnBP and BBP, A/O process was slightly better than BAF, But BAF performed better in the removal of the other 4 kinds of PAEs.

As shown in Fig.3, the removal efficiency of the 6 kinds of PAEs of these two wastewater treatment system are different and the removal efficiency of the long-chain PAEs is better than short-chain ones. The removal efficiency of BBP and DnOP is relatively the highest among these 6 kinds of PAEs. Because their concentration are poor in wastewater and tend to exist adsorbed on particle. The concentration of BBP was below the detection limit in effluent of these two processes. The removal rate has been reached more than 95%. DnOP has not been detected in the effluent of BAF. The removal efficiency of A/O and BAF process are 97% and 99% respectively.

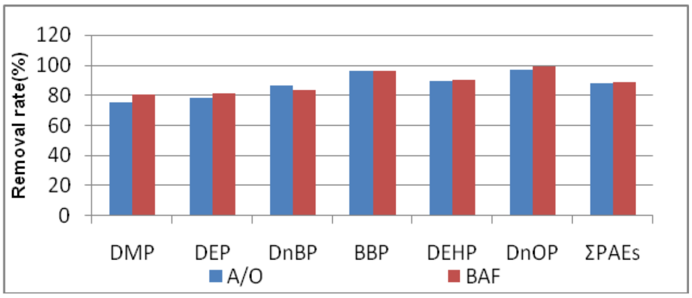

Fig.3. Comparison of removal efficiency of PAEs in A/O and BAF process

3. Influence of seasonal change on the removal efficiency of PAEs

In the study, the samples of October 2011 (Outdoor temperature 15℃) and January 2012 (outdoor temperature -15℃) were collected to compare the removal efficiency of these two sets of samples with different outdoor temperature of 30℃The seasonal change has different influence on different units of one process, leading to a difference of the whole process in removal efficiency. Compare the removal efficiency of A/O and BAF process between autumn (October) and winter (January) and then analysis the influence that seasonal change bring to the removal efficiency. The efficiency rate is from the difference between the concentrations of the 6 PAEs in the influent and effluent, the formula is as follow:

$$R_{total} (\%) = (C_{in\text{-}total} - C_{ef\text{-}total}) / C_{in\text{-}total} \quad (1)$$

Fig.4 shows the overall removal efficiency of 6 PAEs in A/O and BAF process in autumn and winter, indicating that removal efficiencies of these two processes change with the seasons, and the removal efficiency in winter was lower than that in autumn. This is not unexpected since in low temperature environment the activity of microorganism drops, thus leading to the decrease of removal efficiency.

The overall removal efficiency of A/O is 94% in autumn and 79 in winter; As for BAF, it's 89% in autumn and 86% in winter and the seasonal change makes more influence on A/O process, that's because the central secondary treatment process of A/O is anaerobic and aerobic tank, in which microorganism plays an important role. However BAF contains efficient sedimentation tank and biological aerated filter, the microorganism makes less influence on it compared to A/O. The main removal mechanism for PAEs in A/O is adsorption and degradation, the biodegradation of the aerobic process is under the influence of season, so the season makes more influence on A/O process.

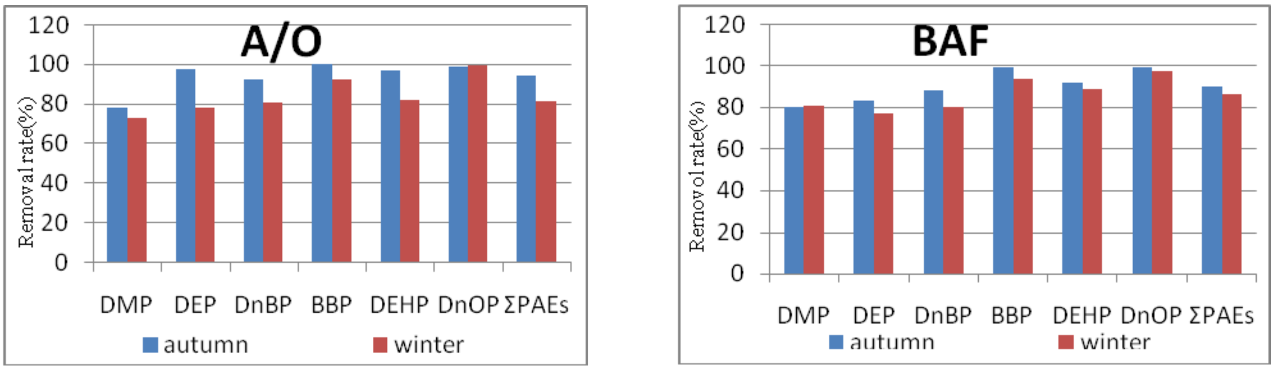

Fig.4. Comparison of removal efficiency of A/O and BAF between autumn and winter

The primary tank, anaerobic tank, aerobic pond, efficient sedimentation tank and biological aerated filter all contributed to remove the six kinds of PAEs. The primary tank made the largest contribution to the removal of the long-chain PAEs among all the processing units. Although the total removal efficiency of six kinds of PAEs in A/O process was lower than BAF, there was no significant difference between them. The seasonal change had certain influence on the removal efficiency of PAEs of these two wastewater treatment process, which was higher in autumn than winter and the seasonal change caused more influence on A/O process than BAF.

Acknowledgments

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