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Coking wastewater treatment plants (WWTPs) are considered the major source of polycyclic aromatic hydrocarbons in China, and their occurrence in the treated wastewater would threaten the nearby residents' health. This manuscript studied the measurement, partition and removal mechanism of PAHs in a representative coking WWTP of China. In this paper, we focused on the treated wastewater and sludge from various tanks of the WWTP, which is the first study on the toxic chemicals in industrial wastewater around the world. The distribution, distribution profile and mass balance of PAHs were studied roundly, which provide further understanding of PAHs in the coking WWTPs. To my knowledge, our study about the distribution, partition and removal of PAHs in the coking WWTP is the first report around the world.

Distribution, partition and removal of polycyclic aromatic hydrocarbons (PAHs) during coking wastewater treatment processes

Wanhui Zhang[a], *Chaohai Wei*[b], *Guanfeng An*[a]

[a] *Guangzhou Municipal Engineering Group Co., Ltd., Guangzhou 510060, China*

[b]*College of Environment and Energy, South China University of Technology, Guangzhou 510006, China*

*Corresponding author. Tel./Fax: +86 20 83847545

E-mail address: wanhuiz@126.com

ABSTRACT

In this study, we report the performance of full-scale conventional activated sludge (A/O1/O2) treatment in eliminating polycyclic aromatic hydrocarbons (PAHs). Both aqueous and solid phases along with the coking wastewater treatment processes were analyzed for the presence of 18 PAHs. It was found that the target compounds occurred widely in raw coking wastewater, treated effluent and sludge samples. In the coking wastewater treatment system, 4-5 ring PAHs were the dominant compounds, while 4 rings PAHs predominated in the sludge samples. Over 98% of the PAH removal was achieved in the coking wastewater treatment plant (WWTP), with the total concentration of PAHs being 21.3 ± 1.9 μg/L in the final effluent. During the coking wastewater treatment processes, the association of the lower molecular weight PAH with suspended solids was generally less than 60%, while the association of higher molecular weight PAHs was greater than 90%. High distribution efficiencies (K_{dp} and K_{ds}) were found suggesting that adsorption was the potential removal pathway of PAHs. Finally, the mass balances of PAHs in various stages of the coking WWTP were performed and the results indicated that the adsorption to sludge was the main removal pathway for PAHs in the coking wastewater treatment processes.

Keywords: Coking wastewater; Polycyclic aromatic hydrocarbons; Partition; Adsorption; Wastewater treatment plant

1. Introduction

Coking wastewater is generated from coal coking, coal gas purification, and the recovery processes of coking by-products. It contains significant amount of inorganic pollutants and organic pollutants, such as ammonium, sulfate, cyanide, thiocyanate, phenolic compounds, polycyclic aromatic hydrocarbons (PAHs) and nitrogen-, oxygen-, and sulfur-containing heterocyclic compounds.[1-3] Since some of these compounds are refractory, mutagenic, and carcinogenic, the pollution caused by coking wastewater is a serious problem in the world, especially in the developing countries. In particular, presence of PAHs has received significant research attention, [5-8] because they are among the carcinogenic, mutagenic and toxic contaminants in the environment. [4]

Several conventional treatment techniques including solvent extraction of phenolic compounds, steam stripping of ammonia, and biological treatment have been investigated for the treatment of coking wastewater.[9,10] Furthermore, many biological reactors and processes such as batch reactors (SBR),[11,12] the anoxic-oxic (A/O) process,[13] the anaerobic-anoxic-oxic (A1/A2/O) process,[9] the anaerobic-oxic-oxic (A/O1/O2) process, and the anaerobic-oxic-hydrolytic-oxic (A/O1/H/O2) process have been developed for the efficient removal of refractory and toxic compounds from the activated sludge process.[3] These biological processes combined with physical and chemical processes are successfully applied in many coke plants of China. However, the control parameters for organic pollutants in the coking wastewater treatment processes have been limited to a few non-specific parameters such as the five-day biochemical demand (BOD), chemical demand (COD)[14] and total volatile phenols, while only very limited studies have investigated about the PAHs in coking wastewater treatment plant (WWTP.[3,15,16] Nevertheless, the study of PAHs in coking wastewater is useful in optimizing the coking WWTP and assessing the risks of coking wastewater for the receiving water bodies. Thus, it is essential to study the removal of PAHs during coking wastewater treatment processes.

The removal of PAHs in a complex coking WWTP system depends on the various parameters, for e.g., applied solids retention time (SRT), hydraulic retention time (HRT), temperature, pH, biomass concentration, compound's polarity and biodegradation ability.[17] During coking wastewater treatment, PAHs can be removed through transformation, adsorbed to the sludge, volatilized or stripped to the atmosphere and released to aquatic environment with effluent.[3] As the hydrophobic compounds with the log K_{ow} of 3.37 to 6.84, PAHs tend to be adsorbed onto the suspended particles present in the treatment system. Consequently, sorption to solids can be a key process that controls the physical removal for these compounds in the WWTPs.[3,14] Therefore, association of PAHs with suspended matters may have a large impact on the selection, design and efficiency of the treatment technologies for removing PAHs in the WWTP. In addition, the association of PAHs with suspended matters is important in determining the fate of PAHs during the wastewater treatment processes, and may also be helpful to minimize the amount of these toxic compounds discharged to environment.

The objectives of the present study were to: (1) investigate the occurrence of

PAHs in a coking wastewater; (2) characterize the partition of PAHs in a coking wastewater; and (3) investigate the removal pathway of PAHs in a coking WWTP.

2. Materials and Methods

2.1. Materials

The standard solution that containing 18 PAH compounds, namely naphthalene, 1-methynaphthalene, 2-methynaphthalene, acenaphthylene, acenaphthene, fluorene, phenahthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, xc dibenzo[a,h]anthracene, benzo[g,h,i]perylene, each at 2000 μg/mL concentration, and the deuterated surrogate solution containing naphthene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12 and perylene-d12 each at 4000 μg/mL concentration were obtained from Supelco (Bellefonte, PA, USA). Hexamethylbenzene (Aldrich Chemical, Gillingham, Dorset, USA) was used as an internal standard for gas chromatographic (GC) analyses. Solid phase extraction cartridges (ENV+, 1 g) and glass filters (GF/F, 0.7 μm) were purchased from Supelco (Bellefonte, PA, USA) and Whatman (Clifton, NJ, USA), respectively. All solvents used for sample processing and analysis (dichloromethane, hexane, acetone and methanol) were HPLC grade from Merck (Darmstad, Germany). Deionized water was produced by a Milli-Q system (Millipore, USA).

2.2. Study site

The study was conducted in a coking WWTP with an average treatment capacity of 1500 m^3/d located in Songshan coking plant in Shaoguan, Guangdong Province of

China. Wastewater from the processes of tar handling, crude benzene recovery, ammonia stripping and H_2S scrubbing were the influent to the coking WWTP. The treatment train of the WWTP can be divided into primary stage, biological stage and the coagulation stage (Fig. 1). The primary treatment stage included a flotation-degreasing tank, an ammonium stripping tower and an equalization basin, while the biological stage contained an anoxic/oxic/oxic system (A/O1/O2) coupled with a biofilm reactor. A/O1/O2 system coupled with biofilm reactor was applied in the biological stage, while forced air was injected into biological tanks. In the coagulation stage, the effluent from the biological stage was mixed with polyacrylamide (PAM) and polyferric sulfate (PFS) solutions for 5 min before feeding to the secondary clarifier with the hydraulic retention time of 2.5 h. The final effluent was discharged to the municipal WWTP of the district. Sludge from the equalization basin in the primary stage, the sludge from various tanks in the biological stage and the chemical sludge from the secondary clarifier were mixed in a thickener, and then pumped to the dewatering unit.

2.3 *Sampling and sample preparation*

Samples from each sampling location shown in Fig. 1 were taken during 11th to 21st of October, 2012. Single 24-h composite water samples were collected each day using flow proportional samplers with a sampling interval of 2 h. Sludge samples were generally taken at the outlet of each treatment step at 3 and 5 pm every day.

The water samples were refrigerated at 4 ℃, while the sludge samples were freeze dried and kept at -20 ℃ until the laboratory analysis. The target compounds were measured separately in sludge and water samples. During the sampling period, the coking WWTP was in normal operation as shown in Supplementary Material (SM), Fig. SM-1. The wastewater inflow to the WWTP was maintain at around 750 m^3/d in dry weather, while the water temperatures were maintained at 24-26 ℃ in the biological treatment units. Several regularly measured parameters (e.g., COD, volatile phenols, NH_4^+ and CN^-) are displayed in Table 1, the average concentration of COD, volatile phenols, NH_4^+ and CN^- in FE were 86.1, 0.23, 11.7 and 0.08 mg/L, respectively, and their average removal efficiencies ranged from 75 to 99%.

[FIGURE 1]

The water samples were filtered with glass filters to partition liquid and particle phase. Based on the preliminary investigations, it was found that 200 mL of raw wastewater and the primary effluent, 500 mL of the anaerobic effluent, and 1 L of aerobic 1 effluent, aerobic 2 effluent, biofilm reactor effluent and final effluent were required to extract adequate amount of organic compounds onto C18 cartridges. 20 μL surrogate standards with a concentration of 80 μg/mL were added to the aqueous samples in order to correct the losses during the extraction process and provide the efficiency of the extract. 0.5 g freeze dried sludge was spiked with 20 μL surrogate standards (80 μg/mL) and extracted using the Soxhlet apparatus with 200 mL dichloromethane for 48 h in a water bath maintained at 46 ℃. Activated copper was then added to the flask to remove the sulfur from the extract. Same extraction procedure was followed for the particle samples.

The extracts of aqueous, particle, gas and sludge samples were loaded onto a 1:2

alumina/silica gel glass column with 1 g anhydrous sodium sulfate overlaying the silica gel for clean-up and fraction. First, 15 mL of hexane was applied to remove aliphatic hydrocarbons. Then, the eluents containing PAHs were collected by eluting 70 mL of dichloromethane/hexane (3:7, v/v), and were concentrated to 0.5 mL under a gentle purified N_2 stream. 5 μL internal standards, each at 100 μg/mL concentration, were added to the sample prior to gas chromatography-mass spectrometry (GC-MS) analysis.

2.4. Instrumental analysis and quality controls

PAHs were analyzed using a GC-MS (Shimadzu, QP2010 Plus) with a 30 m × 0.25 mm id × 0.25 μm film thickness DB-5 MS column (J&W Scientific, USA) in selected ion mode. The GC-MS conditions for sample analysis were as follows: the injection port, interface line and ion source temperatures were maintained at 280, 290 and 250 ℃, respectively. The column temperature was programmed from 60 to 310 ℃ at a 5 ℃/min rate and held for 10 min. Helium was the carrier gas at a flow of 1.2 mL/min with a linear velocity of 42.4 cm/s. The mass spectrometer was operated in electron impact ionization mode (70 eV). 1 μL volume of each sample was injected in the split mode with a split ratio of 10:1.

Quantification was performed using a seven-point calibration curve established using hexane-based internal standard for each individual PAH. The coefficient of determination (R^2) of the calibration curve for each PAH was greater than 0.99. The detection limits of the method ranged from 0.01 to 0.59 μg/L for aqueous samples, from 0.06 to 16.6 μg/g for particle and sludge samples. The average recoveries for aqueous samples were 63 ± 12% for naphthalene-d8, 86 ± 10% for acenaphthene-d10, 92 ± 10% for phenanthrene-d10, 88 ± 7% for chrysene-d12 and 91 ± 10% for perylene-d12, while those for particle, sludge and gas samples were 59 ± 9% for naphthalene-d8, 75 ± 9% for acenaphthene-d10, 87 ± 9% for phenanthrene-d10, 97 ± 10% for chrysene-d12 and 96 ± 10% for perylene-d12.

3. Results and discussion

3.1. Distribution of PAHs along treatment processes

The total (dissolved + adsorbed) concentrations of eighteen PAHs distributed in the coking wastewater treatment processes are presented in Fig. 2. As evident from Fig. 2, the total concentration of PAH congeners input to the system was 862±132 μg/L, which was much lower than our previous study of other coke plant.[3] The lower concentrations of PAHs in this coking plant can be attributed to the new dry coke quenching technique applied in the coke plant, which reduced the amount of wastewater and the concentrations of pollutants as shown in Fig. 2. It was further evident that 4-5 ring compounds were the predominant PAH pieces found in the coking wastewater system, for example Flu, Pyr and BaA accounted for 23, 17 and 10% of the total PAH concentration, respectively. The other PAH species such as Chy, BbF, BkF and BaP also contributed to a notable proportion. Consequently, 4-5 ring species accounted for 83% of the total PAHs in the system. Furthermore, Fig.2 shows a continuous decreasing trend in PAH concentrations along the coking wastewater treatment train since the total PAH concentrations were reduced from 452 ± 22.3μg/L in the primary effluent to 21.3 ± 1.9 μg/L in the final effluent. Additionally, the composition of PAHs did not show any significant change during the treatment process with 4-ring PAHs predominating (contributing 59-65% of the total PAHs), in which Flu and Pyr were the dominant compounds. The contribution of low ring PAHs, i.e. 2 and 3 ring PAHs, increased after the primary treatment, while it decreased after the biological treatment, which could be attributed to: (a) less tendency of tar and particles in accumulating lower molecular weight PAHs, (b) release of low molecular weight PAHs into atmosphere due to forced air stripping in the mixed liquor, (c) faster degradation of low molecular weight PAHs compared to high molecular weight PAHs.[18] Although the concentrations of PAHs in the influent were higher, 98% removal of PAHs in this coking WWTP was achieved, which was significantly higher than those found in conventional WWTPs.[8,19,20] This can be attributed to long solids retention time (30-180 d), fluidized movement of sludge and high transfer efficiency of dissolved oxygen in fluidized bed used in the coking WWTP.

[Figure 2]

As hydrophobic chemicals, PAHs are less soluble in aqueous solution and tend to be adsorbed onto the solids presented in the system. Thus, sludge would have higher contents of these compounds. As shown in Fig. 3**,** the 18 target compounds were all detected in various types of sludge. The total concentrations of PAHs ranged from 204 ± 42.2 to 1380 ± 120 μg/g in the sludge with the highest concentration were found in the sludge from anaerobic tank. Compared with the previous study,[3] concentrations of total PAHs from the coking WWTP were significantly lower than the concentrations expected from a traditional coke plant. However, the PAH concentrations in these coking sludge were still much higher than those in other industrial and municipal sludge.[21-24] For the individual PAH, the concentrations were between 0.19 ± 0.06 and 43.8 ± 2.8 μg/g in the dewatered sludge, and between 0.18 ± 0.05 and 390 ± 84 μg/g in the entre sludge line. Flu was found to be the dominant target, with 390 ± 84 μg/g detected in anaerobic sludge, which can be attributed to its high concentration in wastewater and high value of water disassociation constant, i.e. log K_{ow}. The profiles of the detected PAHs in the sludge samples from different stages were similar. It was found that 4 ring PAHs were the dominated compounds in sludge samples, contributing 54-64% to the total PAHs. The profile of PAHs in sludge samples was consistent with that in particles of wastewater, which suggested that parts of the PAHs in the sludge samples originated from suspended particles in coking wastewater.

[Figure 3]

3.2. Partition of PAHs during coking wastewater treatment processes

The partitioning behavior of organic pollutants was important to their fate in the wastewater treatment system, as adsorbed and dissolved phases were differently available to different fate processes, such as advection, volatilization, air stripping and biotransformation.[25,26] The relative distribution of PAHs between the dissolved and adsorbed phases of coking wastewater samples is presented in Fig. 2. In the influent, the partition of the total PAHs between adsorbed and dissolved phases was 81%. This is in good agreement with the findings of Walters and Luthy (1984),[16] who observed generally 50% or greater of each PAH was associated with the suspended solid phase in the coking wastewater. For the 4-6 ring PAHs, the partition values were greater than

80%, while most of the 2-3 ring PAHs were lower than 10%. The higher partition values of influent suggest that tar separation process is favorable to the removal of PAHs adsorbed in particles and tar. During the coking wastewater treatment processes, the total PAHs partition values varied from 76-96%. The association of the lower molecular weight PAHs with suspended solids was generally less than 60%, while the association of higher molecular weight PAHs was greater than 90%. Further, it was found that the distribution pattern of a single compound varies among the different stages, which can be attributed to several factors including the solute concentration, the amount of organic carbon, the amount of solids available for sorption, and the presence of PAHs. It was found that 83% of PAHs were adsorbed to suspended particles in the biological effluent, while the 4-6 ring PAHs, which contributed 85% of the total amounts of PAHs in the primary effluent, presented 54-93% in the particles. Previous studies reported that the adsorbed chemicals are not available to the biotransformation,[25,26] which in turn would limit the biodegradation of PAHs in particles. Thus, the addition of coagulation before the biological stage can remove the PAHs adsorbed in particles of primary effluent but reduce the concentrations of PAHs entering into the biological treatment, which would favor the biotransformation of PAHs in this stage. After the biological treatment, the partition between particles and dissolved phase for most of these PAHs in the biological effluent, especially for those with 4-6 rings, were greater than 90%. It was found that the partition of biological effluent was higher than that of the primary effluent, which can be attributed to the fluidized fixture in the biological tanks that enhances the contact between the dissolved PAHs and suspended particles. The results of the study also suggested that the coagulation in the final stage can enhance the removal of PAHs in the biological effluent. In the final effluent, 75% of PAHs presented in the particle phase, in which the partitions of 4-6 ring PAHs were greater than 70%, suggesting that the advanced filtration process was essential for the effective removal of PAHs in the final effluent from coking WWTPs.

3.3. Estimation of the distribution coefficient (K_d)

Many researchers[14,27,28] have suggested that the adsorption of PAHs by activated sludge can be a potential removal pathway in many cases. In this context, the role of adsorption on the removal of PAHs was investigated based on the phase-partitioning behaviors of the target compounds by analyzing the particle-water distribution coefficient (K_{dp}) and sludge-water distribution coefficient (K_{ds}). Based on the measured concentrations of PAHs in the particles, sludge and grab samples, K_d coefficients were calculated formulas follows:

$$K_{dp,\ \text{particle-wastewater}} = C_{\text{sorbed}}/C_{\text{dissolved}}$$

$$K_{ds,\ \text{sludge-wastewater}} = C_{\text{sorbed}}/C_{\text{dissolved}}$$

where K_{dp} and K_{ds} are expressed in L/g, C_{sorbed} is the concentration of PAH measured in the solid phase (µg/g) and $C_{\text{dissolved}}$ is the concentration measured in the aqueous phase (µg/L).

The K_{dp} values ranged from 0.78 ± 0.13 to 873 ± 98.5 (Table 2), especially the PAHs with heavy molecular weight had larger K_{dp} values, which can be due to their typically higher hydrophobicity. It is hypothesized that these compounds were predominantly adsorbed to particles, which is consistent with the distribution of PAHs in other water bodies.[8,23,29] Due to the strong affinity to particles suggest by the adsorption of 63 to 94% of PAHs with high molecular weight by the particles in raw coking wastewater, a significant fraction of PAHs mass entering the plant were removed, but not transformed, in the process of separating tar by air flotation. The K_{ds} values of sludge from various units were between 1.0 ± 0.22 and 273 ± 32.7 (Table 3) with heavier PAHs having larger values, which is consistent with their K_{dp} values and concentrations in aqueous solutions. These results indicate that particles and sludge had the abilities to accumulate hydrophobic compounds. As values of K_{dp} and K_{ds} for most PAHs were higher than 0.5 L/g,[30] removal by adsorption for most PAHs would be the major removal pathway in the coking wastewater treatment processes. Based on the higher values of K_{dp} and K_{ds}, it is concluded that the following two removal approaches for adsorption of PAHs in biological stage exist: (a) PAHs were adsorbed to particles and finally deposited to sludge and (b) PAHs were directly adsorbed to fluidized sludge.

[TABLE 2]

[TABLE 3]

Furthermore, the relationship between the solid-water distribution coefficients and the physicochemical properties of the target compounds were analyzed to understand the PAH distribution behaviors. One such parameter, the octanol/water partition coefficient (K_{ow}) was selected since it has been found to be useful in predicting adsorption.[27] As shown in Fig. 4 and Fig. 5, the R^2 values of linear relationships between log K_{dp} and log K_{ow} were 0.77 and 0.71 respectively, which suggested that the partitioning between aqueous and particle phases was significantly affected by the operational factors such as stirring, air stripping, velocity of flow and temperature. Similarly, the R^2 values of linear relationships between log K_{ds} and log K_{ow} were 0.50-0.72 except in the equalization basin, suggesting that the distribution of sludge-water was contributed to the physicochemical properties of the compounds. Similar findings were reported by other studies.[8,31] Additionally, the content of organic matter can influence the absorption of organic chemicals, which had been proved in sediments and soils.[32] With the presence of high percentage (13-48%) organic matter in the activated sludge, the absorption of PAHs on sludge can be influenced by the composition of organic matter that consists of a complex mixture of live and dead microorganisms.

[FIGURE 4]

[FIGURE 5]

3.4. Removal of PAHs during coking wastewater treatment processes

In the coking WWTP, PAHs were mineralized or were partly released to the environment. Thus, PAHs can be discharged with the effluent, separated with tar, transformed or adsorbed to particles and sludge that were removed from the aqueous stream and incorporated into sludge. A previous study showed that the contribution of volatilization and air striping was less than 1%,[3] leading to the negligence of their contribution in the removal of PAHs in this study. The PAH mass balance in the primary stage is shown in Fig. 6a. Accordingly, the calculated fraction of high molecular weight PAHs that were removed with the separation of tar accounted for more than 60% (from Ant to BgP) of the initial loadings of the stage indicating that the separation with tar was the major removal pathway for these PAHs in the primary stage of the coking WWTP. For some low molecular weight PAHs, the percentage contribution to the removal by the primary sludge, tar and primary effluent reached to 83%, 74% and 56%, respectively. In the biological stage, more than 50% of high molecular weight PAHs were adsorbed to the discharged sludge (Fig. 6b), suggesting that adsorption to sludge was the main path way for the removal of these PAHs. It was found that the contribution of transformation for the removal of higher molecular weight PAHs was less than 10%, which can be attributed to the fact that the adsorption of PAHs to particles can affect their biodegradation, photo-degradation and volatilization.[33-35] For the low molecular weight PAHs, the calculated fractions of mass losses due to transformation, adsorption to sludge and discharge with the effluent were 26-53%, 21-43% and 14-40%, respectively, suggesting that the combination of anoxic and oxic zones favored the anaerobic and aerobic metabolism of low molecular weight PAHs. From Fig. 6c, it was found that more than 55% mass losses of high molecular weight PAHs (from Phen to BgP) were due to the adsorption to sludge in the coagulation stage, while this pathway for low molecular weight PAHs (from Naph to Fle) was less than 37%, which suggested that the coagulation in the secondary clarifier favored the removal of high molecular weight PAHs. The elimination of PAHs in the coagulation stage was attributed to the addition of the coagulants such as PAM and PFs, the complex formation between the polymer flocculants and the particles enhanced the removal of target compounds.[36]

[FIGURE 6]

4. Conclusions

The distribution, partition and removal of 18 PAHs in the conventional activated sludge wastewater treatment process were studied. The total concentrations of PAHs in the coking WWTP varied from 862 ± 132 μg/L to 21.3 ± 1.9 μg/L, in which 3%-99% of these compounds were distributed in the suspended particles. The distribution efficient (K_{dp} and K_{ds}) were found in the ranges of 0.78 ± 0.13-873 ± 98.5 for particles and 1.0 ± 0.22-273 ± 32.7 for sludge. Based on the estimated K_d, sorption was found to be the major removal pathway for the higher molecular weight PAHs. Good linear relationship between the K_{dp} and the octanol-water partition coefficients (K_{ow}) of the solute was observed in the raw coking wastewater and the final effluent, suggesting that the operating parameters of the coking WWTP affected the phase distribution of PAHs in treated wastewater. The results of mass balance showed that the adsorption contributed to 26-97%, 20-86% and 28-78% of PAH removed in the primary, biological and coagulation stages, respectively. The removal pathway of PAHs identified in this study suggests that adding flocculants in the primary stage of a coking WWTP can reduce the pressure on biological treatment. Furthermore, biological fluidized bed can be an efficient reactor for the removal of hydrophobic organic compounds. The amount of PAHs sorbed onto sludge may increase the environmental risk of these pollutants, since they can become bioavailable when the conditions are favorable.

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REFERENCES

1. B.R. Lim, H.Y. Hu, K. Fujie, *Water Air Soil Pollut*., 2003, 146, 23-33.
2. J.L. Wang, X.C. Quan, L.B. Wu, Y. Qian, and W. Hegemann, *Process Biochem*., 2002, 38, 777-781.
3. W.H. Zhang, C.H. Wei, X.S. Chai, J.Y. He, Y. Cai, M. Ren, B. Yan, P.A. Peng, and J.M. Fu, *Chemosphere*, 2012, 88, 174-182.
4. H.M. Deng, P.A. Peng, W.L. Huang, and H.Z. Song, *Chemosphere*, 2006, 64, 1401-1411.
5. S. Matsuzawa, L. Nasser-Ali, and P. Garrigues, *Environ. Sci. Technol*., 2001, 35, 3139-3143.
6. A. Motelay-Massei, B. Garban, K. Phagne-Larcher, M Chevreuil, and D. Ollivon, *Water Res*., 2006, 40, 1995-2006.
7. W. Guo, M.C. He, Z.F. Yang, C.Y. Lin, X.C. Quan, and H.Z. Wang, *Chemosphere*, 2007, 68, 93-104.
8. F. Fatone, S. Di Fabio, D. Bolzonella, and F. Cecchi, *Water Res*., 2011, 45, 93-104.
9. M. Zhang, J.H. Tay, Y. Qian, and X.S. Gu, *J. Environ. Engin-Asce*, 1997, 123, 876-883.
10. X.P. Zhu, J.R. Ni, and P. Lai, *Water Res*., 2009, 43, 4347-4355.
11. H.Q. Yu, G.W. Gu, and L.P. Song, *J. Environ. Engin-Asce*, 1997, 123, 305-308.

12. P.M. Kulkarni, *Water Res.*, 2012, 46, 2405-2414.

13. Z.X. Yu, R. Qi, and Y.J. Yin, *Sci. China Ser. B*, 2005, 48, 489-496.

14. E. Manoli, and C. Samara, *Environ. Pollut.*, 2008, 151, 477-485.

15. H.C. Miller, *Industrial Environmental Research Laboratory, Process Measurements Branch, Research Triangle Park, NC.*, 1980.

16. R.W. Walters, and R.G. Luthy, *Water Res.*, 1984, 18, 795-809.

17. J. Radjenovic, M. Petrovic, and D. Barcelo, *Water Res.*, 2009, 43, 831-841.

18. K. Nam, W. Rodriguez, and J.J. Kukor, *Chemosphere*, 2001, 45, 11-20.

19. T.T. Pham, and S. Proulx, *Water Res.*, 1997, 31, 1887-1896.

20. C. Vogelsang, M. Grung, T.G. Jantsch, K.E. Tollefsen, and H. Liltved, *Water Res.*, 2006, 40, 3559-3570.

21. J.D. Berset, and R. Holzer, *J. Chromatogr. A*, 1999, 852, 545-558.

22. S. Perez, M. Guillamon, and D. Barcelo, *J. Chromatogr. A*, 2001, 938, 57-65.

23. L. Mansuy-Huault, A. Regier, and P. Faure, *Chemosphere*, 2009, 75, 995-1002.

24. J.H. Ju, I.S. Lee, W.J. Sim, H. Eun, and J.E. Oh, *Chemosphere*, 2009, 74, 441-447.

25. G. Byrns, *Water Res.*, 2001,35, 2523-2533.

26. A. Katsoyiannis, and C. Samara, *Environ. Res.*, 2005, 97, 245-257

27. R.A. Dobbs, L.P. Wang, R. Govind, *Environ. Sci. Technol.*, 1989, 23, 1092-1097.

28. L. Lazzari, L. Sperni, P. Bertin, and B. Pavoni, *Chemosphere*, 2000, 41, 427-435.

29. S.L. Lau, and M.K. Stenstrom, *Water Res.*, 2005, 39, 4083-4092.

30. T.A. Ternes, N. Herrmann, M. Bonerz, T. Knacker, H. Siegrist, and A. Joss,

Water Res., 2004, 38, 4075-4084.

31. M.K. Durjava, T.L. Ter Laak, J.L.M. Hermens, and J. Struijs, *Chemosphere*, 2007, 67, 990-997.
32. G. Cornelissen, O. Gustafsson, T.D. Bucheli, M.T.O. Jonker, A.A. Koelmans, and P.C.M. Van Noort, *Environ. Sci. Technol.*, 2005, 39, 6881-6895.
33. T.D. J. Dunstan, R.F. Mauldin, J.X. Zhong, A.D. Hipps, E.L. Wehry, and G. Mamantov, *Environ. Sci. Technol.*, 1989, 23, 303-308.
34. R.C. Brenner, V.S. Magar, J.A. Ickes, J. E. Abbott, S.A. Stout, E.A. Crecelius, and L.S. Bingler, *Environ. Sci. Technol.*, 2002, 36, 2605-2613.
35. M. Blanchard, M.J. Teil, D. Ollivon, L. Legenti, and M. Chevreuil, *Environ. Res.*, 2004, 95, 184-197.
36. M. Rebhun, S. Meir, and Y. Laor, *Environ. Sci. Technol.*, 1998, 32, 981-986.

Figure captions

Fig.1. Flow diagram showing the process train for coking wastewater and sludge handling in the full-scale WWTP. 1: anaerobic tank; 2: aerobic tank 1; 3: aerobic tank 2; RW: raw coking wastewater; TW: wastewater from tar separation tank; SE: the effluent from the ammonia tripping tower; EE: primary effluent, the effluent from the equalization basin; AE: the effluent from anaerobic tank; O1E: the effluent from aerobic tank 1; O2E: the effluent from aerobic tank 2; BE: biological effluent, the effluent from biofilm reactor; FE: final effluent; ES: primary sludge, the sludge from equalization basin; AS: sludge from anaerobic sludge; O1S: sludge from aerobic tank 1; O2S: sludge from aerobic tank 2; CS: sludge from secondary clarifier; DS: dewatered sludge.

Fig.2. The concentrations of PAHs in the coking wastewater from the treatment processes and the distribution of these compounds between the dissolved and adsorbed phases of wastewater.

Fig.3. Mean concentrations of the PAHs encountered in the sludges from the coking WWTP.

Fig.4. Correlation between log K_{dp} and log $K_{ow.}$

Fig.5. Correlation between log K_{ds} and log K_{ow}.

Fig.6. The removal pathway of PAHs in the primary stage (a), biological stage (b) and final stage (c).

Figure 1

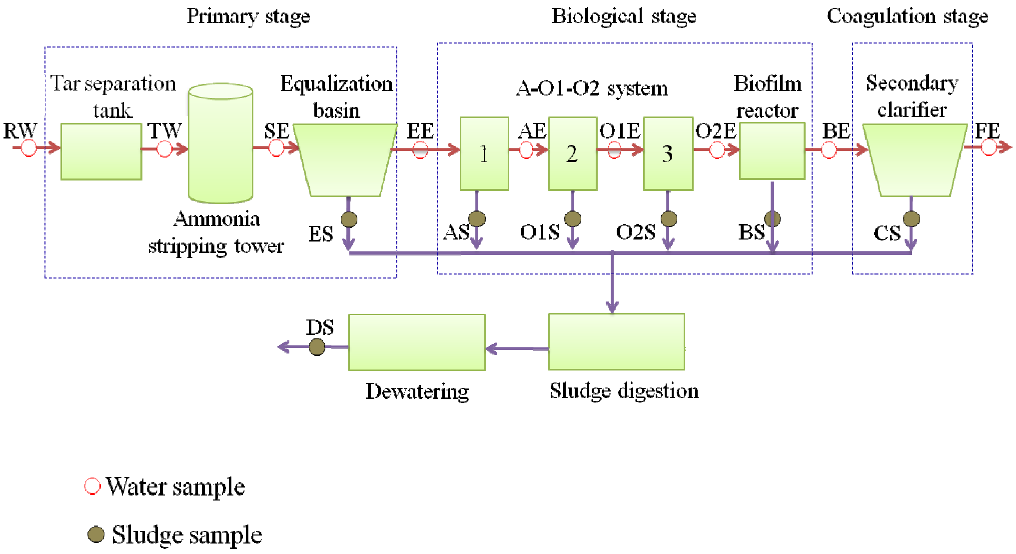
Primary stage
Biological stage
Coagulation stage
Tar separation tank
Equalization basin
A-O1-O2 system
Biofilm reactor
Secondary clarifier
RW
TW
SE
EE
AE
O1E
O2E
BE
FE
1
2
3
Ammonia stripping tower
ES
AS
O1S
O2S
BS
CS
DS
Dewatering
Sludge digestion
Water sample
Sludge sample

Figure 2

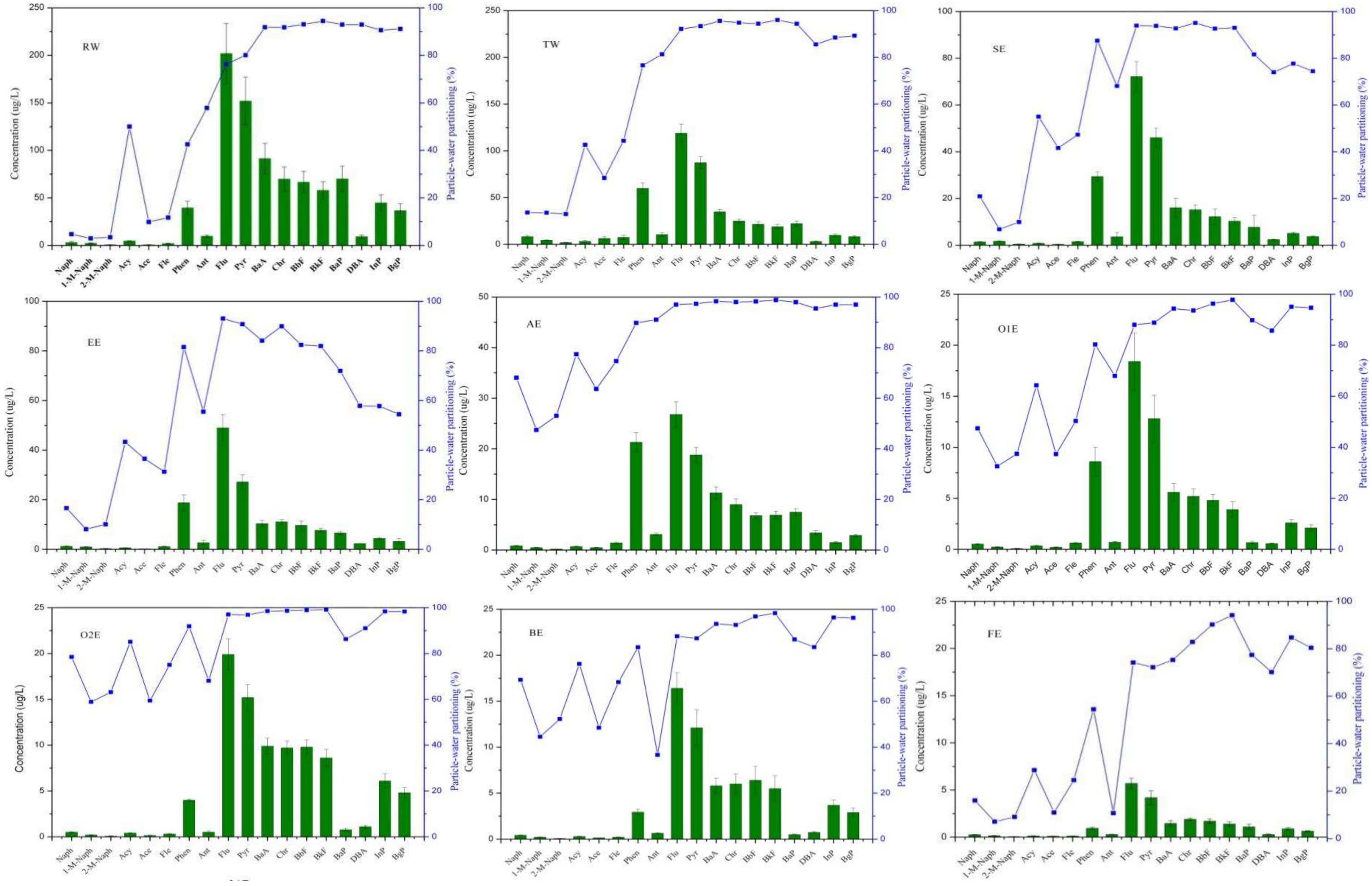
RW
TW
SE
EE
AE
O1E
O2E
BE
FE
Concentration (ug/L)
Particle-water partitioning (%)
Naph
1-M-Naph
2-M-Naph
Acy
Ace
Fle
Phen
Ant
Flu
Pyr
BaA
Chr
BbF
BkF
BaP
DBA
InP
BgP

Figure 3

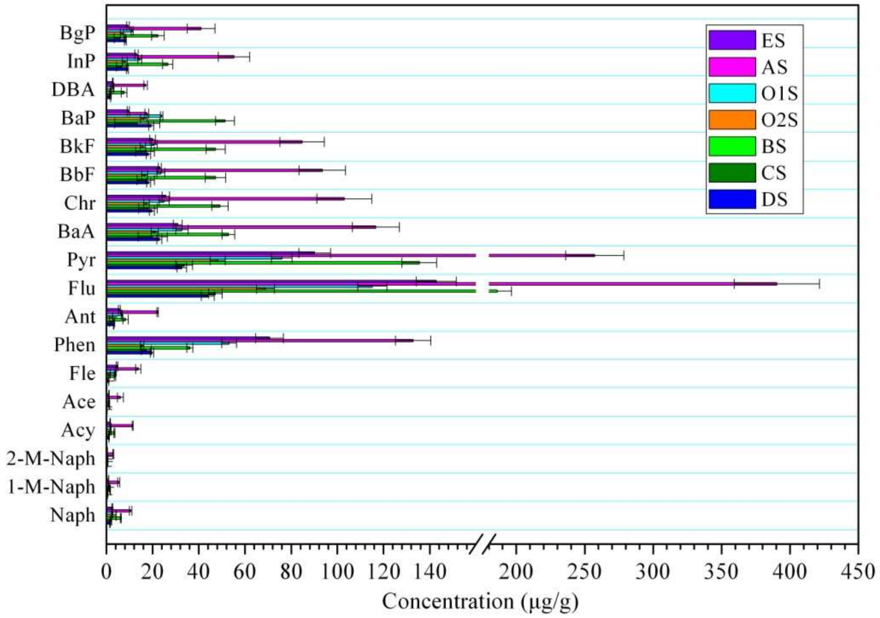
BgP
InP
DBA
BaP
BkF
BbF
Chr
BaA
Pyr
Flu
Ant
Phen
Fle
Ace
Acy
2-M-Naph
1-M-Naph
Naph
ES
AS
O1S
O2S
BS
CS
DS
0
20
40
60
80
100
120
140
200
250
300
350
400
450
Concentration (μg/g)

Figure 4

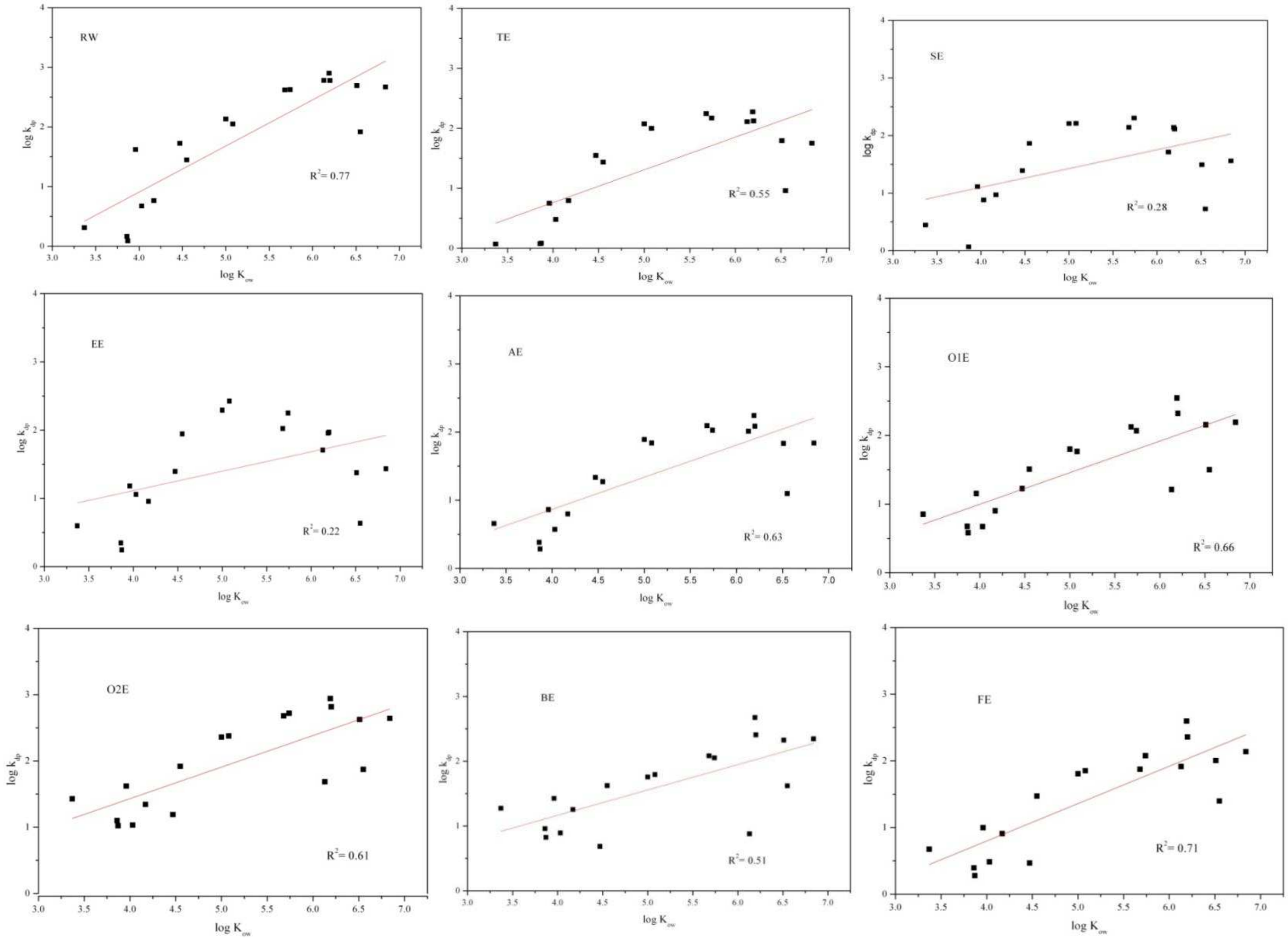
RW
R^2= 0.77
TE
R^2= 0.55
SE
R^2= 0.28
EE
R^2= 0.22
AE
R^2= 0.63
O1E
R^2= 0.66
O2E
R^2= 0.61
BE
R^2= 0.51
FE
R^2= 0.71
log k$_{dp}$
log K$_{ow}$
0
1
2
3
4
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0

Figure 5

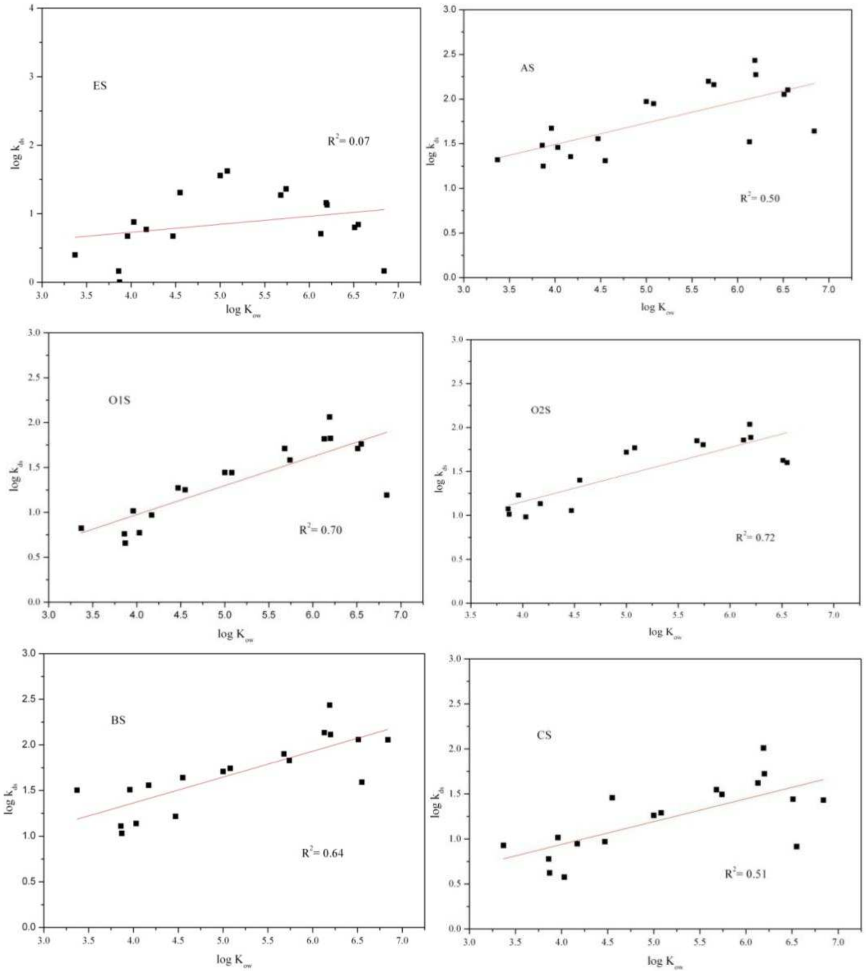
ES
R^2= 0.07
AS
R^2= 0.50
O1S
R^2= 0.70
O2S
R^2= 0.72
BS
R^2= 0.64
CS
R^2= 0.51
log k$_{ds}$
log K$_{ow}$
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
0.0
0.5
1.0
1.5
2.0
2.5
0
1
2
3
4

Figure 6

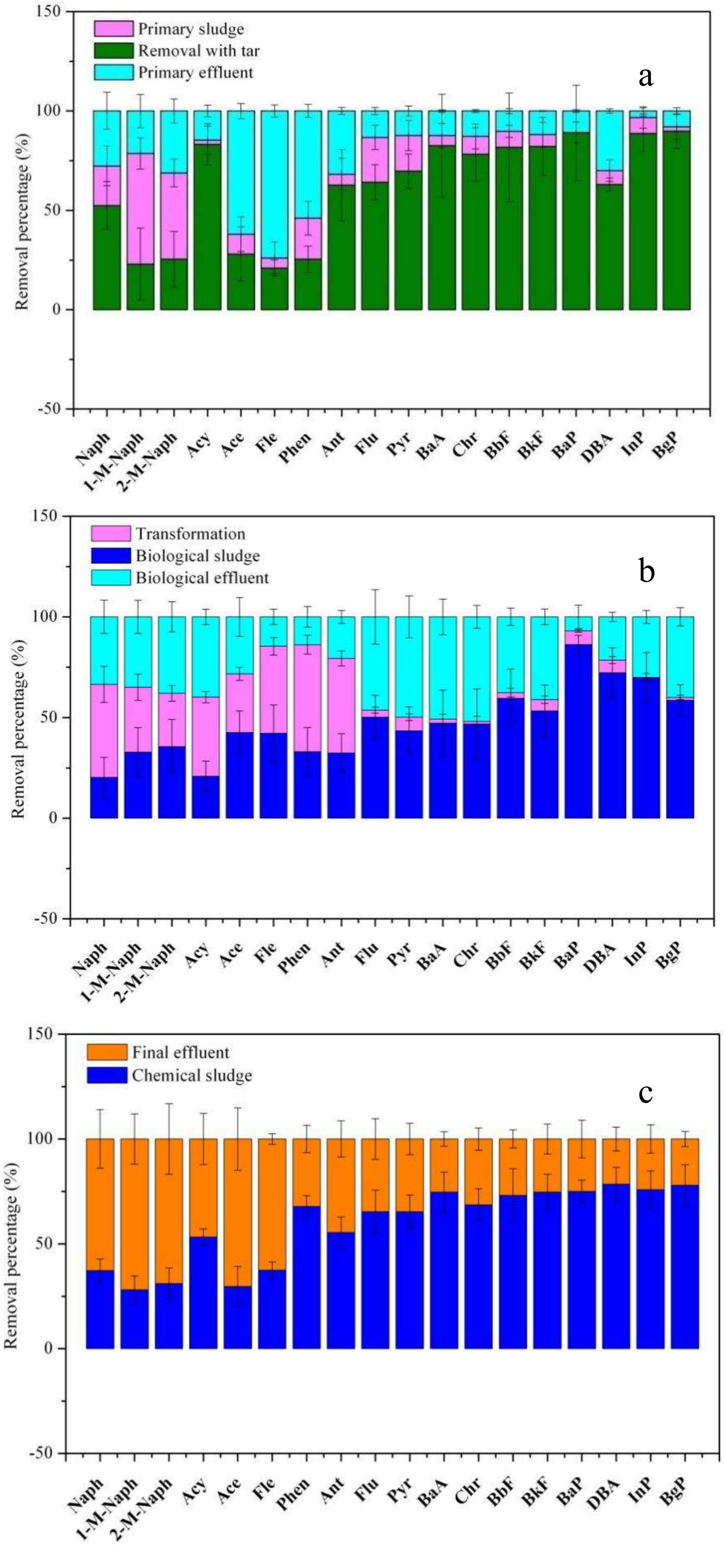
a
Primary sludge
Removal with tar
Primary effluent
Removal percentage (%)
150
100
50
0
-50
Naph
1-M-Naph
2-M-Naph
Acy
Ace
Fle
Phen
Ant
Flu
Pyr
BaA
Chr
BbF
BkF
BaP
DBA
InP
BgP
b
Transformation
Biological sludge
Biological effluent
c
Final effluent
Chemical sludge

Table 1

The variation of COD, volatile phenols, NH_4-N and cyanide during the coking wastewater treatment processes of A/O1/O2 system

	COD	Volatile phenols	NH4-N	Cyanide
Influent	3510 ± 524	702 ± 47.5	281± 96.8	26.1 ± 5.9
Primary effluent	1970 ± 120	423 ± 32.3	101 ± 9.7	3.7 ± 0.5
A effluent	1730 ± 115	369 ± 29.8	139 ± 12.5	1.1 ±0.3
O1 effluent	520 ± 43.6	3.1 ± 0.45	55.8 ± 6.4	0.36 ± 0.05
O2 effluent	259 ± 19.7	0.27 ± 0.06	19.6 ± 2.3	0.21 ± 0.03
Biological effluent	129 ± 11.5	0.26 ± 0.04	13.4 ± 2.5	0.14 ± 0.04
Final effluent	86.1 ± 7.6	0.23 ± 0.03	11.7 ± 2.8	0.08 ± 0.02

Table 2

Summary of mean values (n = 6) for sorption coefficient (K_{dp}) with their R.S.D.s calculated from the particle and supernatant concentrations

Compounds	RW	PE	SE	EE	AE	O1E	O2E	BE	FE
Naph	2.0 ± 0.31	1.2 ± 0.45	2.8 ± 0.78	4.0 ± 0.96	4.6 ± 1.3	7.1 ± 2.5	26.8 ± 6.5	18.8 ± 3.7	4.7 ± 1.6
1-M-Naph	1.2 ± 0.14	1.3 ± 0.39	0.78 ± 0.13	1.8 ± 0.23	1.9 ± 0.46	3.8 ± 0.52	10.5 ± 3.4	6.7 ± 1.4	1.9 ± 0.36
2-M-Naph	1.5 ± 0.23	1.2 ± 0.21	1.2 ± 0.25	2.2 ± 0.34	2.4 ± 0.37	4.7 ± 1.4	12.6 ± 3.9	9.1 ± 1.6	2.5 ± 0.43
Acy	41.8 ± 5.3	5.6 ± 0.74	13.0 ± 2.8	15.2 ± 2.3	7.3 ± 1.5	14.3 ± 2.8	41.7 ± 7.5	26.7 ± 2.8	10.0 ± 3.5
Ace	4.7 ± 1.3	3.0 ± 0.43	7.6 ± 1.1	11.4 ± 3.2	3.7 ± 0.58	4.7 ± 0.67	10.8 ± 2.6	7.8 ± 1.6	3.1 ± 0.56
Fle	5.8 ± 2.1	6.2 ± 0.76	9.3 ± 1.5	9.1 ± 1.3	6.3 ± 0.87	8.0 ± 1.6	22.1 ± 3.7	17.9 ± 2.6	8.1 ± 1.7
Phen	28.0 ± 3.7	27.3 ± 3.8	72.9 ± 10.2	88.0 ± 9.8	18.7 ± 3.6	32.3 ± 4.5	82.8 ± 11.4	42.0 ± 5.7	29.7 ± 5.6
Ant	53.1 ± 8.9	35.2 ± 9.4	24.5 ± 4.8	24.8 ± 5.7	21.6 ± 3.9	16.8 ± 2.6	15.5 ± 3.3	4.8 ± 0.76	2.9 ± 0.65
Flu	112 ± 18.4	99.6 ± 10.3	162 ± 20.2	266 ± 36.9	69.1 ± 8.6	58.4 ± 7.8	238 ± 27.6	62.2 ± 7.9	71.2 ± 9.7
Pyr	136 ± 23.1	118 ± 21.8	162 ± 21.6	196 ± 35.4	77.9 ± 8.6	63.1 ± 9.7	229 ± 32.5	57.2 ± 6.7	64.1 ± 8.6
BaA	418 ± 98.6	175 ± 23.6	139 ± 23.5	105 ± 11.2	124 ± 22.5	133 ± 18.6	479 ± 53.4	121 ± 13.8	75.0 ± 8.9
Chr	422 ± 87.5	148 ± 17.4	201 ± 32.6	178 ± 21.3	106 ± 15.8	117 ± 20.2	523 ± 78.5	113 ± 10.3	120 ± 22.6
BbF	600 ± 153	132 ± 15.6	129 ± 17.4	93.1 ± 9.6	122 ± 16.9	210 ± 32.5	655 ± 79.6	255 ± 26.7	229 ± 36.8
BkF	795 ± 231	188 ± 21.5	139 ± 22.5	90.4 ± 11.5	175 ± 23.3	351 ± 45.3	873 ± 98.5	473 ± 56.8	396 ± 44.6
BaP	602 ± 165	129 ± 20.2	51.6 ± 7.4	51.0 ± 6.4	103 ± 9.8	16.3 ± 3.4	48.5 ± 9.4	7.6 ± 1.7	82.3 ± 21.2
DBA	82.7 ± 11.3	9.1 ± 1.7	5.3 ± 0.76	4.3 ± 0.65	12.6 ± 4.6	31.7 ± 4.4	74.6 ± 13.3	41.7 ± 5.9	25.0 ± 4.6
InP	468 ± 86.4	56.3 ± 7.9	36. 2 ± 7.3	27.2 ± 4.3	68.9 ± 9.7	156 ± 19.8	439 ± 57.9	222 ± 25.7	138 ± 19.8
BgP	493 ± 97.5	62.1 ± 9.5	31.1 ± 5.7	23.8 ± 3.9	68.3 ± 7.8	143 ± 17.8	422 ± 46.7	212 ± 24.8	101 ± 9.4

Table 3

Summary of mean values (n = 6) for sorption coefficient (K_{ds}) with their R.S.D.s calculated from the sludge and supernatant concentrations

Compounds	Equalization basin	Anaerobic tank	Aerobic 1 tank	Aerobic 2 tank	Biofilm reactor	Secondary clarifier
Naph	2.5 ± 0.31	20.9 ± 3.5	6.7 ± 0.75	23.2 ± 3.5	31.9 ± 4.8	8.5 ± 1.4
1-M-Naph	1.0 ± 0.22	17.7 ± 2.4	4.5± 0.58	10.3 ± 2.4	10.7 ± 2.7	4.2 ± 0.67
2-M-Naph	1.5 ± 0.24	30.3 ± 4.6	5.8 ± 0.71	11.9 ± 2.2	12.9 ± 1.9	6.0 ± 0.82
Acy	4.7 ± 0.53	47.1 ± 5.1	10.4 ± 2.1	17.0 ± 2.8	32.3 ± 3.7	10.4 ± 1.6
Ace	7.6 ± 0.86	28.7 ± 3.3	5.9 ± 0.74	9.6 ± 1.5	13.8 ± 2.8	3.8 ± 0.84
Fle	5.9 ± 0.67	22.7 ± 2.9	9.3 ± 1.7	13.6 ± 2.6	36.1 ± 5.3	8.8 ± 1.5
Phen	20.3 ± 3.5	20.4 ± 3.4	17.8 ± 2.8	25.1 ± 4.2	43.8 ± 6.5	28.6 ± 3.7
Ant	4.7 ± 0.52	36.0 ± 4.6	18.7 ± 2.6	11.3 ± 3.4	16.5 ± 3.7	9.3 ± 1.6
Flu	41.9 ± 5.2	88.9 ± 11.2	27.7 ± 3.5	58.7 ± 8.6	55.3 ± 7.9	19.5 ± 2.8
Pyr	36.0 ± 4.3	93.8 ± 12.3	27.8 ± 4.8	52.3 ± 8.9	51.1 ± 7.5	18.2 ± 2.5
BaA	18.7 ± 2.7	156 ± 25.4	51.4 ± 8.9	70.7 ± 9.9	79.7 ± 9.6	35.2 ± 5.8
Chr	23.0 ± 3.5	145 ± 21.3	38.3 ± 5.8	63.7 ± 8.7	67.5 ± 8.2	31.2 ± 4.7
BbF	13.5 ± 2.4	187 ± 29.6	66.7 ± 8.9	77.1 ± 9.5	130 ± 23.4	52.9 ± 7.9
BkF	14.4 ± 2.6	271 ± 35.7	115 ± 23.1	109 ± 16.7	273 ± 32.7	102 ± 11.7
BaP	5.1 ± 0.68	33.2 ± 5.8	65.9 ± 9.9	72.0 ± 7.4	136 ± 24.5	41.8 ± 8.5
DBA	1.5 ± 0.25	43.8 ± 9.5	15.6 ± 2.8	9.8 ± 3.2	39.0 ± 5.7	8.2 ± 1.3
InP	6.9 ± 0.79	126 ± 24.5	57.7 ± 6.8	39.8 ± 8.3	114 ± 26.4	27.0 ± 3.7
BgP	6.3 ± 0.77	113 ± 25.3	51.5 ± 8.5	42.2 ± 5.8	114 ± 28.3	27.6 ± 4.3