

The occurrence and fate of phenolic compounds in a coking wastewater treatment plant

Wanhui Zhang, Chaohai Wei, Chunhua Feng, Yuan Ren, Yun Hu, Bo Yan and Chaofei Wu

ABSTRACT

The occurrence of 14 phenolic compounds (PCs) was assessed in the raw, treated wastewater, dewatered sludge and gas samples from a coking wastewater treatment plant (WWTP) in China. It was found that 3-cresol was the dominant compound in the raw coking wastewater with a concentration of 183 mg L^{-1} , and that chlorophenols and nitrophenols were in the level of $\mu\text{g L}^{-1}$. Phenol was the dominant compound in the gas samples, while 2,4,6-trichlorophenol predominated in the dewatered sludge sample. The anaerobic and aerobic tanks played key roles in the elimination of chlorophenols and phenols, respectively. Analysis of daily mass flows of PCs in WWTP showed that 89–98% of phenols and 83–89% of nitrophenols were biodegraded, and that 44–69% of chlorophenols were adsorbed to sludge, indicating that the fate of PCs was highly influenced by their biodegradability and physical–chemical property.

Key words | coking wastewater, mass balance, phenolic compounds, wastewater treatment plant

Wanhui Zhang
Bo Yan
Guangzhou Institute of Geochemistry,
Chinese Academy of Sciences,
Guangzhou 510640,
China

Chaohai Wei (corresponding author)
Chunhua Feng
Yuan Ren
Yun Hu
Chaofei Wu
College of Environmental Science and Engineering,
South China University of Technology,
Guangzhou 510006,
China
E-mail: cechwei@scut.edu.cn

INTRODUCTION

Phenolic compounds (PCs) have received intense attention because of their widespread occurrence in environment and adverse impact on ecosystems and human health (Schummer *et al.* 2009; Zhong *et al.* 2010). These compounds are toxic, carcinogenic, mutagenic and teratogenic contaminants (Autenrieth *et al.* 1991). In the 1970s, the US Environmental Protection Agency presented a list of 11 PCs as priority pollutants that are characterized by a variety of substituents such as methyl-, chloro- and nitro- groups (Angelino & Gennaro 1997). These compounds are ubiquitous in air, water, soils and sediments (Gao *et al.* 2008; Schummer *et al.* 2009; Zhong *et al.* 2010), mostly originating from anthropogenic activities, such as the production of plastics, dyes, drugs, pesticides, antioxidants and paper, petroleum refining, and coal and oil shale conversion (Tompkins *et al.* 1992; Rodriguez *et al.* 2000). Coke production is identified as one of the major sources in China, during which process PCs were mainly discharged in coking wastewater, for example in 2005, 24,000 tons of PCs were discharged into wastewater by the Chinese coking industry (NDRC 2006). Therefore, treatment of PCs is of crucial importance for wastewater treatment plants (WWTPs) in the coking industry and better understanding

of the behaviors and fate of PCs during the wastewater treatment can be helpful in optimizing the system for controlling and minimizing the amount of these compounds discharged to environment.

In general, the behaviors and fate of PCs in coking WWTPs are governed by their physical–chemical properties, the quality of the wastewater and the operating conditions of the treatment systems (Byrns 2001). As biological chemicals, PCs can be biodegraded by activated sludge (Sarfaraz *et al.* 2004; Vazquez *et al.* 2006; Ramos *et al.* 2007). It was also reported that some PCs can be volatilized to the atmosphere in wastewater treatment processes (Kundel & Liblik 2000; Seth *et al.* 2008). Moreover, the forced injection of air into the biological tanks can stimulate these compounds stripped to air. Adsorption to biological sludge was considered to be the sink for PCs (e.g., chlorophenols) with log octanol-water distribution coefficients ($\log K_{ow}$) ranging from 1.5 to 4.45. Because of higher content of PCs in the coal tar of coking wastewater (Vayisoglu *et al.* 1996; Casal *et al.* 2008) and the addition of flocculating agents, separation with tar can be the potential fate of these compounds during tar separation in the primary stage of coking WWTPs. Therefore, we believe that biodegradation, adsorption to sludge, volatilization, air

stripping and separation with tar can be responsible for the removal of PCs in coking WWTPs. Further information is required on which process predominantly contributes to the fate of PCs.

The aim of the present study was to thoroughly investigate the occurrence and fate of a wide range of PCs in a coking WWTP. The content of five phenols, seven chlorophenols and two nitrophenols were determined in the coking wastewater, as well as at particular points of the gas and sludge streams that well present the treatment process. The mass balance of each pollutant was calculated for the full-scale coking WWTP to ascertain their fate.

MATERIALS AND METHODS

Chemicals, standards and materials

Reference PCs (14 compounds, each at $2,000 \mu\text{g mL}^{-1}$) including phenol, 2-cresol, 3-cresol, 4-cresol, 2,4-xyleneol, 4-chloro-3-methylphenol (4-C-3-MP), 2-chlorophenol (2-CP), 2,6-dichlorophenol (2,6-DCP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP), 2,4,5-trichlorophenol (2,4,5-TCP), 2,3,4,6-tetrachlorophenol (2,3,4,6-TECP), 2-nitrophenol (2-NP) and 4-nitrophenol (4-NP), and surrogate standard (at $1,000 \mu\text{g mL}^{-1}$) containing 1-fluorophenol and 2,4,6-tribromophenol were obtained from Suplco (USA), and an internal standard of phenol-d10 ($1,000 \mu\text{g mL}^{-1}$) was obtained from Aldrich Co. (Aldrich Co., USA). They were diluted to the concentrations of working standards for capillary gas chromatography (GC) analyses. Solid phase extraction cartridges were Oasis HLB cartridges

(*N*-vinylpyrrolidone and divinylbenzene copolymer, 500 mg, 6 mL), which were obtained from Waters Corporation (Milford, USA). All solvents used for sample processing and analysis (dichloromethane, hexane, acetone and methanol) were high-performance liquid chromatography grade from Merck (Darmstadt, Germany). Deionized water was produced by a Milli-Q system (Millipore Co., USA).

Coking WWTP and sampling

The selected coking WWTP was from the Shaoguan Steel Company in Guangdong Province, China, with an average treatment capacity of $2,000 \text{ m}^3 \text{ d}^{-1}$. The detailed information about the coking WWTP was described in our previous study (Zhang *et al.* 2012).

The scheme of the coking WWTP and the sampling locations are shown in Figure 1. Samples were taken on 11–21 October 2010. Single 24-h composite water samples of raw wastewater (RW), outlet of primary treatment (PE), biological effluent (BE) and final effluent (FE) were collected each day using flow proportional samplers (cooled at 4°C) with a sampling interval of 2 h. The gas samples were collected consecutively for 12 h at the degreasing tank and aeration tanks (5 cm above the water surface) by high-volume samplers equipped with glass fiber filters ($0.7 \mu\text{m}$) and polyurethane foam. Other wastewater and sludge samples were taken at the outlet of different treatment units randomly at 3 and 5 pm. The sludge was freeze-dried and kept at -20°C before analysis. The target compounds were measured separately in the sludge, gas and water samples from the wastewater treatment process. The average results of mass balance analysis based on

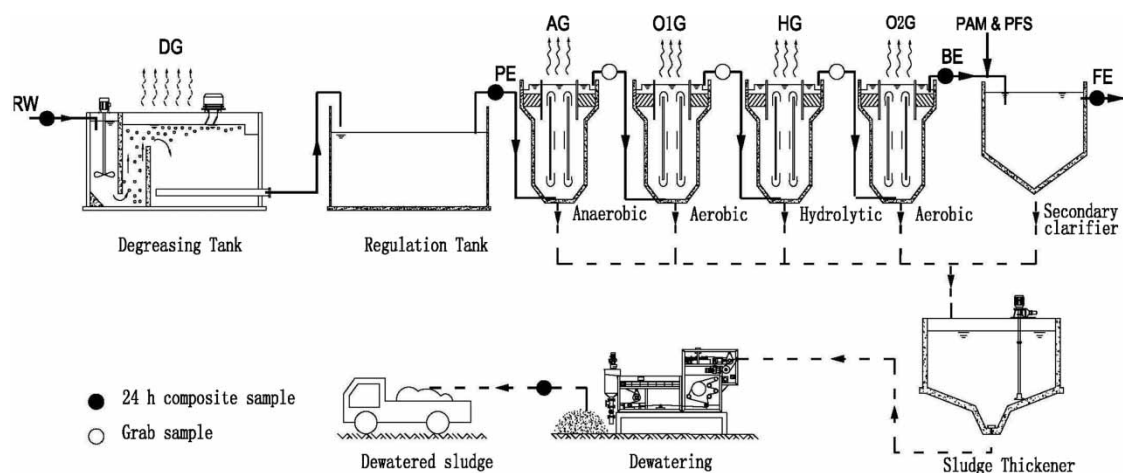


Figure 1 | Flow scheme of the coking WWTP with sampling locations. DG: gas from degreasing tank; AG: gas from anaerobic tank; O1G: gas from aerobic 1 tank; HG: gas from hydrolytic tank; O2G: gas from aerobic 2 tank; PAM: polyacrylamide; PFS: polyferric sulfate.

concentration data of each sampling day were adopted for discussion.

Sample preparation

Based on the contents of organic compounds, 100 mL for RW and PE, 500 mL for effluent of anaerobic tank and 1 L for effluent of aerobic 1 tank, hydrolytic tank, aerobic 2 tank and FE were extracted onto Oasis HLB cartridges. Before extraction, 20 μL of surrogate standards (80 $\mu\text{g mL}^{-1}$) were added to the aqueous samples to correct the losses along the extraction process and provide the efficiency of the extract. The mixed solution of methanol and methyl tert-butyl ether (9:1, v:v) with a total volume of 10 mL was applied to elute the target compounds. Then the eluents were concentrated to 2 mL with a rotary evaporator.

An amount of 0.5 g freeze-dried sludge was spiked with 20 μL surrogate standards (80 $\mu\text{g mL}^{-1}$) and Soxhlet extracted with 200 mL dichloromethane for 48 h in a water bath maintained at 46 °C. The gas samples were subjected to the same extraction procedure as the sludge samples. Activated copper was then added to the flask to remove the sulfur from the extract. The extract of gas and sludge samples was loaded to a 1:2 alumina/silica gel glass column with 1 g of anhydrous sodium sulfate overlaying the silica gel for clean-up and fraction. First, 15 mL of hexane and 70 mL of dichloromethane/hexane (3:7, v:v) were applied to remove aliphatic hydrocarbons and polycyclic aromatic hydrocarbons. Then, the eluents containing PCs were collected by eluting 30 mL methanol, and were concentrated to 2 mL with a rotary evaporator. Before GC/mass spectrometry (MS) analysis, the solvent of eluents were changed to hexane and derivatized by *N,O*-Bis(trimethylsilyl)trifluoroacetamide.

Instrumental analysis and quality controls

PCs were analyzed using a GC/MS (Shimadzu, QP2010 Plus) with a 30 m \times 0.25 mm id \times 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 temperature were maintained at 280, 290 and 250 °C, respectively. The column temperature was programmed from 50 to 280 °C at 8 °C min^{-1} and hold for 10 min. Helium was the carrier gas at a flow rate of 1.2 mL min^{-1} with a linear velocity of 42.4 cm s^{-1} . The ionization was carried out in the electron impacted by mode at 70 eV. The

volume of each sample injected in the split mode was 1 μL , and the split ratio was 10:1.

Quantification was performed using a seven-point calibration curve established using internal standard for each individual PC. The R^2 values of the PC calibration curves were all greater than 0.99. The detection limits of the method ranged from 0.01 to 0.56 ng L^{-1} for aqueous samples, from 0.01 to 0.14 $\mu\text{g g}^{-1}$ for sludge samples and from 0.02 to 0.95 ng m^{-3} for gas samples. The average recoveries were 87–102% for aqueous samples, and 81–110% for sludge and gas samples.

Mass balance calculation

In order to assess the contribution of adsorption, biodegradation, volatilization, air stripping and separation with tar of the targets in the WWTP, the mass balance load of PCs that was lost owing to biodegradation (W_{bio}) was calculated using the following equation:

$$W_{\text{bio}} = W_{\text{in}} - W_{\text{eff}} - W_{\text{sludge}} - W_{\text{vol}} - W_{\text{air}} - W_{\text{tar}} \quad (1)$$

where W_{in} and W_{eff} , respectively, represent the mass load of one target analyte in RW and FE (mg d^{-1}); W_{tar} and W_{sludge} are the mass output with separating tar and in dewatered sludge (mg d^{-1}), respectively; W_{vol} and W_{air} represent the mass output by volatilization and air stripping, respectively. To evaluate the contribution of the output with the separation of tar, W_{tar} was calculated in the primary stage by Equation (2).

$$W_{\text{tar}} = W_{\text{in}} - W_{\text{prieff}} - W_{\text{vol}} \quad (2)$$

where W_{prieff} represents the mass load of one target compound in PE. More information about the mass balance is displayed in Table 1.

RESULTS AND DISCUSSION

Occurrence and behaviors of PCs during the treatment processes

The concentrations of PCs in the coking wastewater treatment processes are listed in Figure 2. It can be seen that the total mean concentration of these phenolic congeners input to the system was 549 mg L^{-1} , of which 3-cresol was the dominant compound (183 mg L^{-1}), followed by phenol. Chlorophenols had lower concentrations, with

Table 1 | Mass balance equations for phenolic compounds in various processes at the coking WWTP**Input of each target to the coking WWTP**

$$W_{in} = C_{in} \times Q_{in}$$

Mass loss by effluent

$$W_{eff} = C_{eff} \times Q_{eff}$$

Mass loss by sludge

$$W_{sludge} = C_{sludge} \times Q_{sludge}$$

Mass loss by volatilization

$$W_{vol} = C_{vol} \times Q_{vol}$$

Mass loss by air stripping

$$W_{air} = C_{air} \times Q_{air}$$

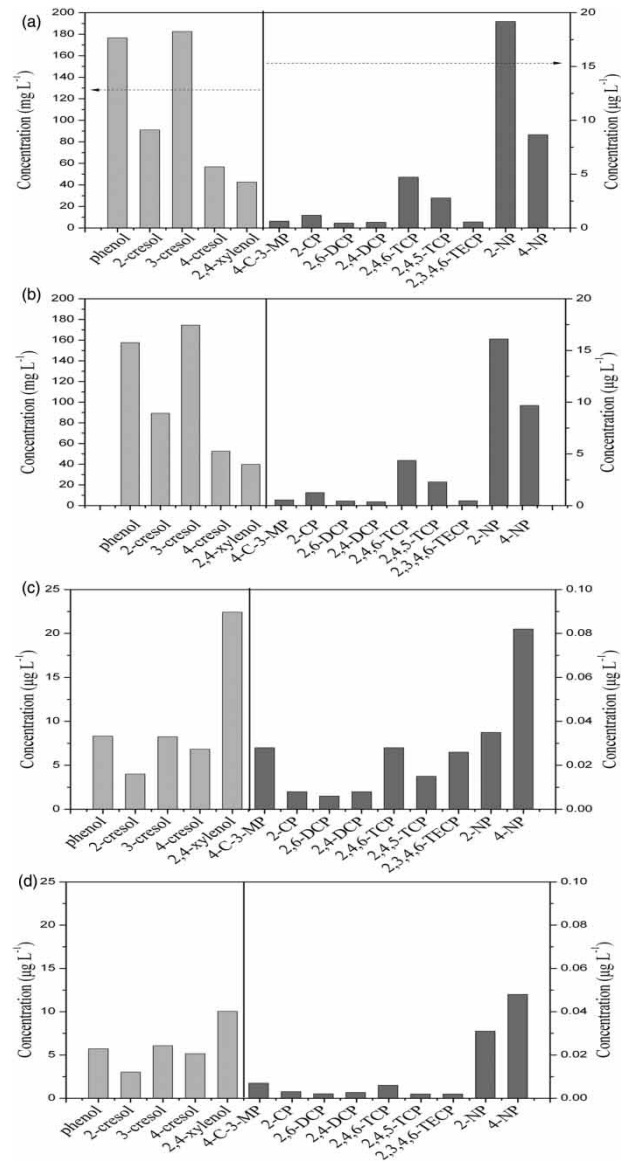
Output of target compounds with the primary effluent

$$W_{prieff} = C_{prieff} \times Q_{prieff}$$

C_{in} , the concentration of target in the influent (mg L^{-1}); Q_{in} , water flow of influent (L d^{-1}); C_{eff} , the concentration of target compound in the effluent (mg L^{-1}); Q_{eff} , water flow of effluent (L d^{-1}); C_{sludge} , the concentration of target compound in the sludge (mg g^{-1}); Q_{sludge} , the flow rate of sludge (g d^{-1}); C_{vol} , the concentration of target compound in the air by volatilization (mg m^{-3}); Q_{vol} , the flow rate of these compounds ($\text{m}^3 \text{d}^{-1}$); C_{air} , the concentration of target compound in the air by air stripping (mg m^{-3}); Q_{air} , the flow rate of air to the aeration tanks ($\text{m}^3 \text{d}^{-1}$); C_{prieff} , the concentration of target compound in the primary effluent (mg L^{-1}); Q_{prieff} , the flow rate of primary effluent (L d^{-1}).

Σ chlorophenols concentration of $10.9 \mu\text{g L}^{-1}$. Among them, 2,4,6-TCP possessed the highest concentration of $4.67 \mu\text{g L}^{-1}$, followed by 2,4,5-TCP with a value of $2.78 \mu\text{g L}^{-1}$. The results were consistent with these reported in the previous study (Marianna 2002). The concentrations of nitrophenols were also lower, in the range of $8.67\text{--}19.18 \mu\text{g L}^{-1}$. It can be seen that the concentrations of the selected PCs exhibited a continuous decline during the wastewater treatment processes. After the physical, biological and chemical treatment, the concentration of various PCs was $<10 \mu\text{g L}^{-1}$ in the FE sample (Figure 2(d)), while the mean concentrations of Σ chlorophenols and Σ nitrophenols were 0.025 and $0.079 \mu\text{g L}^{-1}$.

During the treatment processes, biological stage played an important role in removing PCs, as 69.3–99.9% of eliminations of these target compounds occurred in this stage. The anaerobic and aerobic units presented higher contribution to the elimination of chlorophenols and phenols, respectively. More than 69% of phenol and its methyl-substituted derivatives were removed in the aerobic unit owing to biodegradation and air stripping. With the exception of 2,4,6-DCP, the anaerobic unit contributed to 43–98% of the elimination for other chlorophenols in the biological stage, which can be ascribed to the adsorption of targets by fluidized sludge and anaerobic biodegradation. The adsorption of chlorophenols in the anaerobic unit might be induced by

**Figure 2** | The concentrations of PCs in RW (a) and the effluent of various stages: PE (b); BE (c); FE (d).

sufficient contact between these targets and sludge with respect to the long hydraulic retention time (26 h).

Occurrence of PCs in gas samples

The concentrations of selected PCs in the gas samples from the primary and biological stages of the coking WWTP are listed in Table 2. The mean concentration of Σ phenols in the primary gas was $3,344 \text{ ng m}^{-3}$, among which phenol accounted for the largest concentration (233 ng m^{-3}), followed by 3-cresol and 4-cresol. The mean concentrations of Σ phenols in the gas samples from the biological units

Table 2 | The concentrations of PCs in gas samples from the coking WWTP (ng m^{-3})

Compounds	DG		AG		O1G		HG		O2G	
	L-H	M	L-H	M	L-H	M	L-H	M	L-H	M
Phenol	1,880–2,660	2,330	96–165	127	132–213	174	79.5–113	91.6	198–252	232
2-cresol	65–124	111	0.21–2.23	1.23	0.65–1.35	0.92	0.09–0.32	0.15	0.96–1.32	1.07
3-cresol	231–543	489	23.5–46.8	32.8	16.7–25.8	21.1	1.89–3.64	2.46	21.3–28.4	26.4
4-cresol	189–462	334	5.76–7.98	7.17	5.7–10.2	8.40	0.76–1.58	1.25	8.32–9.98	9.53
2,4-xyleneol	54.6–98.1	75.3	0.75–1.34	0.95	6.8–9.89	8.79	0.82–1.34	0.95	0.25–0.56	0.41
Σ phenols	2,420–3,880	3,340	126–223	169	162–260	213	83.1–120	96.4	229–292	270
4-C-3-MP	12.4–35.1	23.5	32.1–43.5	38.4	46.7–68.2	53.7	18.5–24.3	21.0	27.5–35.2	30.7
2-CP	9.3–17.8	13.3	3.23–5.46	4.53	3.25–7.87	5.96	3.13–6.75	5.45	2.78–3.75	3.34
2,6-DCP	0.45–1.43	0.93	0.43–0.75	0.59	0.68–1.37	1.04	0.39–0.78	0.62	0.65–1.13	0.87
2,4-DCP	0.86–1.32	1.17	0.38–0.78	0.67	0.89–1.56	1.34	0.87–1.37	1.18	0.81–1.24	0.96
2,4,6-TCP	0.76–1.86	1.41	0.57–1.25	0.98	0.96–1.97	1.64	0.96–1.35	1.15	1.47–1.96	1.69
2,4,5-TCP	0.12–0.54	0.34	0.13–0.21	0.17	0.13–0.35	0.25	0.08–0.21	0.12	0.13–0.41	0.27
2,3,4,6-TECP	0.79–1.54	1.27	0.64–0.98	0.81	1.1–2.2	1.50	0.76–1.26	0.93	1.23–1.87	1.42
Σ chlorophenols	24.7–59.6	41.9	37.5–52.9	46.2	53.7–83.5	65.4	24.7–36.0	30.4	34.6–45.6	39.3
2-NP	0.39–1.65	1.23	0.63–1.14	0.82	1.14–1.86	1.44	0.75–1.34	0.94	1.15–1.99	1.44
4-NP	0.76–1.35	1.26	0.63–1.24	0.78	0.97–1.79	1.50	0.65–1.24	1.00	1.31–1.78	1.56
Σ nitrophenols	1.12–3.0	2.49	1.26–2.38	1.61	2.11–3.65	2.94	1.4–2.58	1.94	2.46–3.77	1.62

L: the lowest concentration.

H: the highest concentration.

M: the mean concentration.

ranged from 96.4 to 269.9 ng m⁻³, with the higher concentration detected in the sample taken from the aerobic 2 tank. Phenol was the most abundant compound detected in the gas samples because of its high concentration in aqueous solution and high volatility. The occurrence of PCs in the primary gas was considered to be the result of volatilization due to the high water temperature (about 50 °C) in the primary stage, and those detected in the biological gas should be the result of air stripping due to the injection of air to each tank in the biological stage.

Occurrence of PCs in dewatered sludge sample

As shown in Table 3, five phenols, seven chlorophenols and two nitrophenols were all detected in the dewatered sludge, with mean concentrations of 0.93, 8.39 and 1.62 µg g⁻¹, respectively. Compared with chlorophenols and nitrophenols, phenols had a lower concentration (<0.39 µg g⁻¹). This can be explained by the fact that phenols had a lower log *K*_{ow} value than chlorophenols and nitrophenols. The concentrations of chlorophenols in the dewatered sludge were 0.39–1.90 µg g⁻¹, and increased with the number of chlorine atoms. This observation was consistent with that associated with other types of sludge (Webber &

Lesage 1989; Smith 1996). In the dewatered sludge, 2,3,4,6-TCP was the predominant compound with a log *K*_{ow} of 4.45, indicating that it can be easily adsorbed to sludge.

Fate of PCs in coking WWTP

To investigate the fate of PCs during the coking wastewater treatment, daily masses of PCs were calculated by taking into account analyte concentrations in the samples of influent, final effluent, dewatered sludge and gas by volatilization or air stripping, as well as volumetric flow rates.

The mass balance results for each target compound were expressed in chemical mass fraction (%) to ascertain the contribution of various removal pathways (Figure 3). The calculated fractions of mass losses for phenols due to degradation and separation with tar were 89–98 and 2–11%, respectively, while the contribution of final effluent, adsorption to sludge, volatilization and air stirring was less than <1%, suggesting that biodegradation was the predominant pathway for the removal of these compounds. The results were consistent with the study of Seth *et al.* (2008), who calculated that biodegradation contributed to 94% of the removal of phenol in a developed mass balance model of chemical fate in a sewage treatment plant. As easily biodegradable chemicals, phenols could be oxidized or reduced, resulting in ring-cleavage, and, finally, be mineralized under aerobic or anaerobic conditions (Fina *et al.* 1978; Keith *et al.* 1978). With less hydrophobicity, lower Henry's law constants and air-water partition coefficients, volatilization and air stripping were not the dominant pathways for the removal of phenols, although forced air was injected into the biological tanks.

Table 3 | The concentrations of PCs in a dewatered sludge sample from the coking WWTP (µg/g)

Compounds	Contents		Log <i>K</i> _{ow} (Li & Lee 1997)
	L-H	M	
Phenol	0.08–0.23	0.16	1.50
2-cresol	0.02–0.11	0.05	1.98
3-cresol	0.13–0.25	0.19	1.98
4-cresol	0.07–0.24	0.14	1.97
2,4-xyleneol	0.28–0.46	0.39	2.35
∑phenols	0.58–1.29	0.93	
4-C-3-MP	1.21–1.89	1.60	3.10
2-CP	0.24–0.51	0.39	2.15
2,6-DCP	0.63–1.26	0.90	2.86
2,4-DCP	0.68–1.17	0.85	3.08
2,4,6-TCP	1.32–2.11	1.67	3.69
2,4,5-TCP	1.17–1.65	1.41	4.19
2,3,4,6-TECP	1.48–1.96	1.68	4.45
∑chlorophenols	6.73–10.6	8.39	
2-NP	0.15–0.39	0.25	1.78
4-NP	1.13–1.58	1.37	1.90
∑nitrophenols	1.28–1.97	1.62	

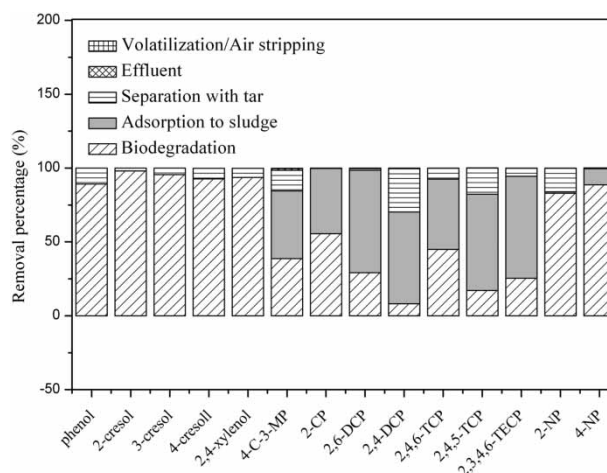


Figure 3 | Mass balance of target compounds in the coking WWTP.

For chlorophenols, the mass losses were mainly attributed to the adsorption to sludge and biodegradation (accounting for 44–69 and 8–56%, respectively). Other contributions included separation with tar, volatilization and air stripping, but these processes played less important roles in their removal. With high values of $\log K_{ow}$ (2.15–4.81) and high toxicity, chlorophenols tended to be adsorbed to sludge and resisted biodegradation. However, investigations showed that 4-C-3-MP, 2-CP, 2,6-DCP, 2,4-DCP, 2,4,6-TCP and 2,4,5-TCP can be biodegraded in aerobic and anaerobic conditions (Kiyohara et al. 1992; Ahel et al. 1994). For nitrophenols, 88% of 2-NP and 83% of 4-NP were biodegraded, respectively, which could be ascribed to their biodegradable nature (Zeyer et al. 1985; Spain & Gibson 1991; Uberoi & Bhattacharya 1997) and low $\log K_{ow}$ (0.25–1.37) values of the chemicals.

CONCLUSIONS

Wastewaters coming from the coke industry have been known as one of the important sources for phenolic wastes discharged to the nature environment. The increasing awareness toward coking wastewater treatment emphasizes the need to understand the occurrence and fate of PCs in order to optimize the treatment system. The results of this study of a large-scale coking WWTP showed that 14 PCs were widely found in the wastewater, gas and dewatered sludge samples, but the distribution of these compounds was highly dependent on their biodegradability and physical–chemical properties. During coking wastewater treatment processes, the anaerobic tank and the aerobic tank played key roles in removing chlorophenols and phenols, respectively. Biodegradation was responsible for removing phenols and nitrophenols, while adsorption to sludge was the predominant pathway regarding the removal of chlorophenols.

ACKNOWLEDGEMENTS

This research was supported by the State Key Program of the National Natural Science Foundation of China (No. 21037001), National Natural Science Foundation of China (No. 21007071) and National Key Technology Research & Development Program of China during the 11th Five-Year Plan Period (No. 2008BAC32B06–1 and 2008BAC32B06–2).

REFERENCES

- Ahel, M., Hrsak, D. & Giger, W. 1994 Aerobic transformation of short-chain alkylphenol polyethoxylates by mixed bacterial cultures. *Arch. Environ. Con. Tox.* **26**, 540–548.
- Angelino, S. & Gennaro, M. C. 1997 An ion-interaction RP-HPLC method for the determination of the eleven EPA priority pollutant phenols. *Analyt. Chim. Acta.* **346**, 61–71.
- Autenrieth, R. L., Bonner, J. S., Akgerman, A., Okaygun, M. & McCreary, E. M. 1991 Biodegradation of phenolic wastes. *J. Hazard. Mater.* **28**, 29–55.
- Byrns, G. 2001 The fate of xenobiotic organic compounds in wastewater treatment plants. *Water Res.* **35**, 2523–2533.
- Casal, M. D., Diez, M. A., Alvarez, R. & Barriocanal, C. 2008 Primary tar of different coking coal ranks. *Int. J. Coal. Geol.* **76**, 237–242.
- Fina, L. R., Bridges, R. L., Coblenz, T. H. & Roberts, F. F. 1978 Anaerobic decomposition of benzoic-acid during methane fermentation. 3. Fate of carbon four and identification of propanoic acid. *Arch. Microbiol.* **118**, 169–172.
- Gao, J. J., Liu, L. H., Liu, X. R., Zhou, H. D., Huang, S. B. & Wang, Z. J. 2008 Levels and spatial distribution of chlorophenols 2,4-dichlorophenol, 2,4,6-trichlorophenol, and pentachlorophenol in surface water of China. *Chemosphere* **71**, 1181–1187.
- Keith, C. L., Bridges, R. L., Coblenz, T. H. & Roberts, F. F. 1978 The anaerobic decomposition of benzoic-acid during methane fermentation. 4. De-aromatization of ring and volatile fatty-acids formed on ring rupture. *Arch. Microbiol.* **118**, 173–176.
- Kiyohara, H., Hatta, T., Ogawa, Y., Kakuda, T., Yokoyama, H. & Takizawa, N. 1992 Isolation of *Pseudomonas pickettii* strains that degrade 2,4,6-trichlorophenol and their dechlorination of chlorophenols. *Appl. Environ. Microb.* **58**, 1276–1283.
- Kundel, H. & Liblik, V. 2000 Emission of volatile phenols from stabilization ponds of oil shale ash dump leachate. *Oil Shale* **17**, 81–94.
- Li, N. Q. & Lee, H. K. 1997 Trace enrichment of phenolic compounds from aqueous samples by dynamic ion-exchange solid-phase extraction. *Analyt. Chem.* **69**, 5193–5199.
- Marianna, C. 2002 Determination of selected organic pollutants in ground water – a method of analysis. *Fresenius Environ. Bull.* **11**, 91–97.
- NDRC (National Development and Reform Commission) 2006 The pollution and suggestion in coking industries. http://www.ndrc.gov.cn/gzdt/t20060907_83519.htm.
- Ramos, A. F., Gomez, M. A., Hontoria, E. & Gonzalez-Lopez, J. 2007 Biological nitrogen and phenol removal from saline industrial wastewater by submerged fixed-film reactor. *J. Hazard. Mater.* **142**, 175–183.
- Rodriguez, I., Llompert, M. P. & Cela, R. 2000 Solid-phase extraction of phenols. *J. Chromatogr. A* **885**, 291–304.
- Sarfraz, S., Thomas, S., Tewari, U. K. & Iyengar, L. 2004 Anoxic treatment of phenolic wastewater in sequencing batch reactor. *Water Res.* **38**, 965–971.
- Schummer, C., Groff, C., Al Chami, J., Jaber, F. & Millet, M. 2009 Analysis of phenols and nitrophenols in rainwater collected

- simultaneously on an urban and rural site in east of France. *Sci. Total Environ.* **407**, 5637–5643.
- Seth, R., Webster, E. & Mackay, D. 2008 Continued development of a mass balance model of chemical fate in a sewage treatment plant. *Water Res.* **42**, 595–604.
- Smith, S. R. 1996 *Agricultural Recycling of Sewage Sludge and the Environment*. CAB International, Wallingford, pp. 207–236.
- Spain, J. C. & Gibson, D. T. 1991 Pathway for biodegradation of para-nitrophenol in a *Moraxella* sp. *Appl. Environ. Microb.* **57**, 812–819.
- Tompkins, C. J., Michaels, A. S. & Peretti, S. W. 1992 Removal of *P*-nitrophenol from aqueous-solution by membrane-supported solvent-extraction. *J. Membr. Sci.* **75**, 277–292.
- Uberoi, V. & Bhattacharya, S. K. 1997 Toxicity and degradability of nitrophenols in anaerobic systems. *Water Environ. Res.* **69**, 146–156.
- Vayisoglu, E. S., Bartle, K. D., Erbatur, N. G., Frere, B., Snape, C. E. & Erbatur, O. 1996 Chemical composition of SCG extracts obtained from coal and maceral concentrates. *Fuel Process Technol.* **46**, 99–115.
- Vazquez, I., Rodriguez, J., Maranon, E., Castrillon, L. & Fernandez, Y. 2006 Study of the aerobic biodegradation of coke wastewater in a two and three-step activated sludge process. *J. Hazard. Mater.* **137**, 1681–1688.
- Webber, M. D. & Lesage, S. 1989 Organic contaminants in canadian municipal sludges. *Waste Manage. Res.* **7**, 63–82.
- Zeyer, J. A., Wasserfallen, A. & Timmis, K. N. 1985 Microbial mineralization of ring-substituted anilines through an ortho-cleavage pathway. *Appl. Environ. Microb.* **172**, 447–453.
- Zhang, W. H., Wei, C. H., Chai, X. S., He, J. Y., Cai, Y., Ren, M., Yan, B., Peng, P. A. & Fu, J. M. 2012 The behaviors and fate of polycyclic aromatic hydrocarbons (PAHs) in a coking wastewater treatment plant. *Chemosphere* **88**, 174–182.
- Zhong, W. J., Wang, D. H., Xu, X. Y., Luo, Q. A., Wang, B. Y., Shan, X. Q. & Wang, Z. J. 2010 Screening level ecological risk assessment for phenols in surface water of the Taihu Lake. *Chemosphere* **80**, 998–1005.

First received 19 April 2012; accepted in revised form 18 March 2013