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SOURCE, EMISSION AND REMOVAL OF PERFLUORINATED COMPOUNDS IN A CHROME PLATING INDUSTRIAL PARK IN CHINA

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Introduction

Fluorocarbon surfactants have been adopted as chrome mist suppressant (CMS) in Chinese electroplating industry since 1970s, starting from the self-development product F-53B, i.e. 6:2 chlorinated polyfluorinated ether sulfonate (6:2 Cl-PFAES). Later FC-80 (C₈F₁₇O₃SK, CAS No: 2795-39-3) and FC-248 (C₁₆H₂₀F₁₇O₃NS, CAS No: 56773-42-3) were introduced into the market in 1980s, which belong to the category of perfluorooctane sulfonate (PFOS) salts¹. These perfluorinated compounds (PFCs) contained in CMS will enter into the wastewater with the rinse operation.

China has made great efforts to prompt the development of electroplating industrial parks for better emission control in recent two decades. The chrome plating effluent is required to be firstly treated to eliminate the toxic Cr(VI) at the wastewater treatment station (WWTS) within the park, then sent to the municipal wastewater treatment plant (WWTP), finally discharged into the ambient environment. However there are few studies to trace the fate of PFCs from the workshop to the receiving water body.

The present study aims to investigate the source, emission and removal of PFCs in chrome plating industry. A typical industrial park located in Ningbo of Zhejiang, China, was selected.

Materials and methods

Chemicals

6:2 Cl-PFAES (F-53B) was obtained from Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, with a purity of >98%. Potassium L-PFOS and ¹³C₄- and ¹³C₈-labeled L-PFOS, as recovery and injection standards (RS and IS), respectively, were purchased from Wellington Laboratories Inc. (ON, Canada). Solvents were HPLC grade (J.T. Baker, NJ), and ultrapure water was used (18 M Ω cm, Millipore, MA).

Sampling

Water samples were taken from three chrome plating workshops, along the treatment process of WWTS, before and after the WWTP, the receiving river (Jiutang River), and a well inside the industrial park. In addition, soil samples were also taken inside and outside the industrial park for comparison purpose.

Sample preparation

All the water samples were collected in 500 mL polypropylene bottles with screw caps (Vitalab, Grossostheim, Germany) and filtered through glass microfiber filters (GF/F, 47 mm, Whatman, Kent, UK) before solid phase extraction (SPE). Oasis HLB cartridges (6 mL, 200 mg, Waters, MA) were first conditioned with 2 \times 5 mL methanol and then with 2 \times 5 mL ultrapure water. Samples were introduced to the cartridges at a flow rate of 5–10 mL/min, dried and subsequently eluted with 2 \times 5 mL methanol. The resulting extracts were reduced using a gentle stream of nitrogen, diluted to 1 mL with ultrapure water and filtered by a 0.22 μ m nylon filter prior to analysis. The RS and IS were added at the amount of 25 ng for each sample before extraction and before instrumental analysis, respectively.

Soil samples were freeze-dried, homogenized and sieved through a 0.25mm stainless steel mesh to remove stones and other coarse materials. 0.5-2.0g samples were spiked with 25ng RS, extracted by 6mL of methanol, treated using ultrasonic at 30°C for 20min, then centrifuged at 3500rpm for 5min. The supernatant was collected in a precleaned 500mL PP bottle. These operations were repeated three times. In order to enrich the analyte and remove potential matrix interferences, the extracted solution was diluted with ultrapure water and loaded to SPE cartridges. PWAX cartridges (6mL, 150mg, Agela Technologies,

China) were first conditioned with 4mL of ammonium hydroxide (0.5% NH₄OH in methanol), 4mL of methanol and 4mL of ultrapure water at a rate of 2 drops per second. Before loading the pH of extracted solution was adjusted to pH=4 by using acetic acid solution. Samples were introduced to the cartridges at a flow rate of 5-10 mL/min. After loading the cartridge was washed with 4mL of 25mM sodium acetate and then dried with vacuum. Subsequently, the targets were eluted with 3mL of methanol and 3mL of ammonium hydroxide (0.5% NH₄OH in methanol). The resulting extracts were reduced using a gentle stream of nitrogen, diluted to 0.5 mL with ultrapure water and filtered by a 0.22 μm nylon filter prior to analysis. The IS were added at the amount of 25 ng for each sample before instrumental analysis.

Instrumental analysis and QA/QC

Extractions were analyzed by high performance liquid chromatography-mass spectrometry (LC-MS/MS). Target compounds were separated on an ZORBAX Eclipse XDB C18 column (5μm×2.1mm×150 mm, Agilent, CA) using an UltiMate 3000 HPLC (Dionex by Thermo Fisher Scientific Inc., MA). Detection was achieved using an API 3200 triple quadrupole mass spectrometer (AB SCIEX, ON, Canada). The injection volume was 10μL for each sample. The column unit was held at 30 °C and the flow rate was 0.3 mL/min. Initial mobile phase condition was 40% methanol in 10mM ammonium acetate held for 1 min. A gradient ramp followed over 6min to 100% methanol, which was held for 3.5min, followed by equilibrium at 40% methanol for 2.5min. The mass spectrometer was operated in negative electrospray ionization mode with multiple reaction monitoring (MRM). The ionization was set at an ionspray voltage of -4.5 kV and at a temperature of 450°C, using nitrogen for drying. The flows of curtain gas, collision gas, ion source gas 1 and ion source gas 2 were set at 20, 5, 30, and 60 psi, respectively.

Sample concentrations were quantified based on an internal standard calibration curve. Field blank and procedural blank were checked without significant laboratory contamination or interferences. Duplicate samples and calibration check standards showed satisfactory reproducibility.

Results and discussion

PFCs in water samples from three workshops

The detected concentrations of PFCs are shown in Table 1.

The predominant PFCs detected in the chrome plating bath samples clearly indicate the CMS used: F-53B used in #1 and #2, while PFOS based CMS used in #3. Such conclusion was in consistent with the information from the workshop owners. 6:2 FTS, the key ingredient in leading non-PFOS CMS (e.g. Fumetrol 21 from Atotech) in international market, was detected at much lower level.

The detected concentrations in rinse tank were the lowest among three types of water samples, as the PFCs comes from the carry-out by the electroplated items. However such concentration will be increased with the rinse of more items. Therefore the concentration can reach a relatively higher concentration when discharged as the workshop wastewater.

PFCs in water samples from the WWTS

The detected concentrations of PFCs are shown in Table 2.

The WWTS contains two parts: one is to eliminate toxic Cr(VI) by chemical reduction followed by precipitation (Effluent 1); the other is to further treat 50% of Effluent 1 for recycling purpose (Effluent 2). As shown in Table 2, both processes can significant decrease the PFCs concentration. However, the involved mechanisms are completely different: the former is based on the sludge adsorption, while the late is based on the size exclusion.

PFCs in water samples from the WWTP

The detected concentrations of PFCs are shown in Table 3.

The removal efficiencies of PFCs by the WWTP were found to be poor, which is reasonable as biodegradation does not make sense in terms of the elimination of very refractory PFCs.

PFCs in water samples from the receiving river

The detected concentrations of PFCs are shown in Table 4.

There's neither environmental quality nor emission criteria for PFCs in China. Recently the criterion maximum concentration (CMC) and the criterion continuous concentration (CCC) were proposed by Yang et al., as 3.78 mg/L and 0.25 mg/L, respectively². The detected concentrations were much below these criteria. However, Zhang et al., have proposed the predicted non-effect concentration (PNEC) value of PFOS for Chinese freshwater as 1 μ g/L, according to the EU technical guidance document on risk assessment for existing substances³. The detected concentrations (i.e. MEC) were very close to such criteria, which can be converted to the risk quotient ranging from 0.91 to 1.41. Therefore the receiving water body (Jiutang River) has been contaminated by PFOS with the potential to cause high associated ecological risk.

Contamination of PFCs in groundwater and soil

The detected concentrations of PFOS and F-53B in groundwater sample are 1880ng/L and 538ng/L, respectively. Compared with the PNEC value of PFOS for Chinese freshwater as 1 μ g/L³, the associate ecological risk should receive enough concerns.

The detected concentrations of PFOS and F-53B in soil sample taken inside the industrial park are 3675ng/g and 837.5ng/g, respectively. These data are much higher than the sample taken outside the industrial park, which are 40.75ng/g and 6.68ng/g, respectively. Zhang et al., have proposed the PNEC value of PFOS for Chinese soil as 1ng/g (wwt) ³, in comparison the ambient soil has been heavily contaminated by PFOS.

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Table 1 Detected PFCs in water samples from the workshops (unit: µg/L)

	Workshop	PFOS	6:2 FTS	6:2 PFAES
#1	Chrome plating bath	1350	310	23000
	Rinse tank	2.745	0.54	14.85
	Wastewater	444.5	0.605	250
#2	Chrome plating bath	1435	229	56500
	Rinse tank	3.425	0.371	61
	Wastewater	785	0.4485	645
#3	Chrome plating bath	3150	347.5	412.5
	Rinse tank	13.45	0.3945	0.825
	Wastewater	795	0.3225	82.5

Table 2 Detected PFCs in water samples from the WWTS (unit: µg/L)

Sample	PFOS	6:2 FTS	6:2 PFAES
Influent	5500	0.3125	154.5
After Reduction	625	0.2925	274.5
After precipitation	985	0.282	795
Effluent 1 (After conditioning)	10.4	0.775	7.05
After Ultrafiltration	0.588	0.0587	0.202
Effluent 2 (After Reverse Osmosis)	0.127	0.00737	0.0443
RO Concentrate	3.98	0.4705	1.295

Table 3 Detected PFCs in water samples from the WWTP (unit: µg/L)

Sample	PFOS	6:2 FTS	6:2 PFAES
Influent	1.36	0.504	1.52
Effluent	0.888	1.52	1.06

Table 4 Detected PFCs in water samples from the receiving river (unit: µg/L)

Distance to discharge point	-15m (upstream)	-8m (upstream)	0m Discharge point	+5m (Downstream)	+10m (Downstream)	+15m (Downstream)
PFOS	0.971	1.05	1.41	0.918	0.924	0.91
6:2 FTS	0.634	0.639	0.652	0.547	0.717	0.632
6:2 PFAES	0.563	0.712	0.788	0.57	0.642	0.56