Supporting Information

Cloud Point Extraction Combined with Thermal Degradation for Nanoplastic Analysis Using Pyrolysis Gas Chromatography−Mass Spectrometry

Xiao-xia Zhou,[#,†] Li-teng Hao,[†] Huang-ying-zi Wang,[#] Ying-jie Li,[†] and Jing-fu Liu[,†]*

[#]Key Laboratory for Water Quality and Conservation of the Pearl River Delta, Ministry of Education, Institute of Environmental Research at Greater Bay, Guangzhou University, Guangzhou 510006, China.

[†]State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P. O. Box 2871, Beijing 100085, China.

*** Corresponding author**. Tel.: +86-10-62849192; Fax: +86-10-62849192; E-mail: jfliu@rcees.ac.cn

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Supplementary Methods

TEM Characterization.

Transmission electron microscopy (TEM) was carried out with a TECANI G20 (FEI, Hillsboro, OR) at 200 kV. TEM samples were prepared by dripping 2 μL of nanoplastic dispersion or the TX-45-rich phase at 10× dilution with ethanol onto a carbon-coated TEM grid (Cu, 200 meshes, Zhongxingbairui Technology Co. Ltd., Beijing, China) and dried at room temperature under vacuum. After the sample was dried, sample operation was repeated 2-3 times. The size distribution was estimated with Nano Measure 1.2 software. At least 120 particles were counted from multi-picture for each case.

Thermalgravimetric Analysis.

Thermal analysis was performed using TGA model STD Q600 from TA Instruments. Samples weighing approximate 1-2 mg were placed in a platinum pan, and all the studies were conducted under air flux of 100 mL/min. For the thermalgravimetric behaviors of TX series surfactant and plastics, each sample was subjected to three steps:

(i) Ramping from 40 ºC to 120 ºC at 20 ºC/min;

(ii) Isothermal holding at 120 ºC for 10 min to remove impurities in the sample;

(iii) Ramping from 120 ºC to 1000 ºC at 10 ºC/min.

For the thermal degradation of TX-45 and plastics, experiments were performed at temperatures from 40 ºC to 190 ºC with a heating rate of 20 ºC/min, followed by isothermal holding at 190 ºC for 3 h.

Water Sample Collection.

River water was taken from the Kunyu river. Sea water was collected from the Bohai (Panjing, China). Municipal sewage influent and effluent were collected from Qinghe wastewater treatment plant (WWTP) in the northwest of Beijing (China). All samples were collected from the surface layer at a depth of 0-30 cm by plunging the brown glass bottle (1 L) into the water, and then stored at 4 ºC.

The bottles were rinsed 3-fold with the sample in advance. At each sampling site, one liter of water was sampled.

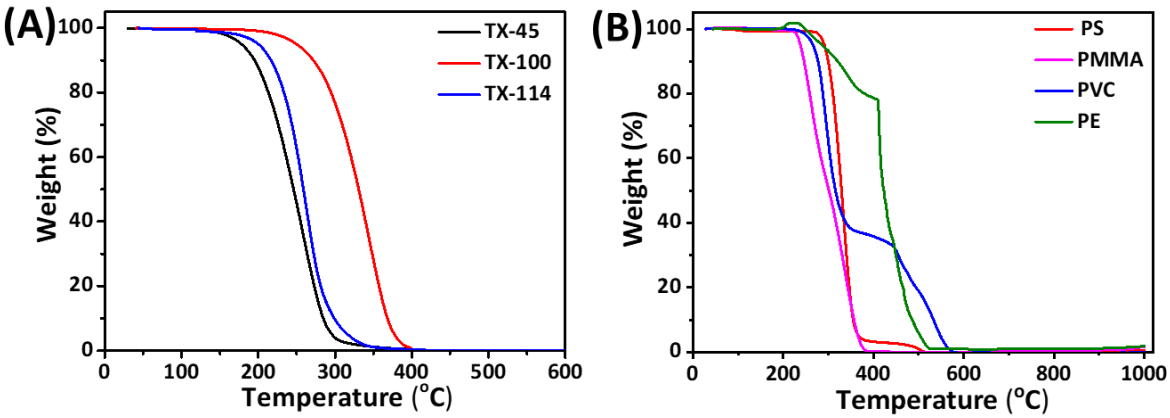

Figure S1. Thermogravimetric curves for TX series surfactant under air atmosphere (A), plastic particles under air atmosphere (B).

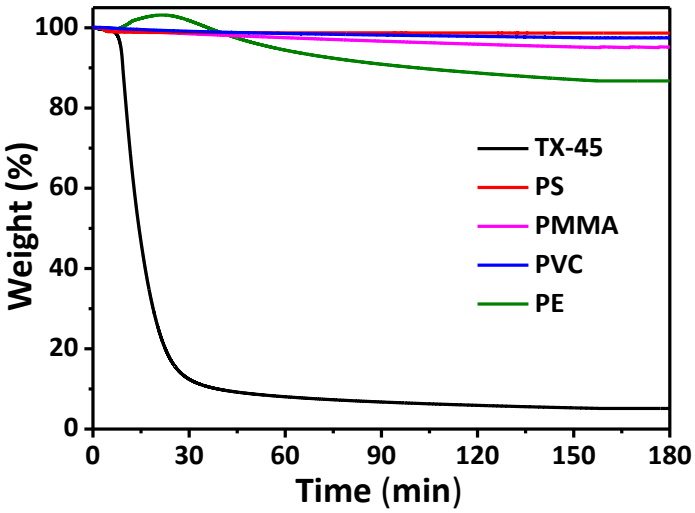

Figure S2. Thermal degradation curves of TX-45 and plastics at 190 ºC under air atmosphere.

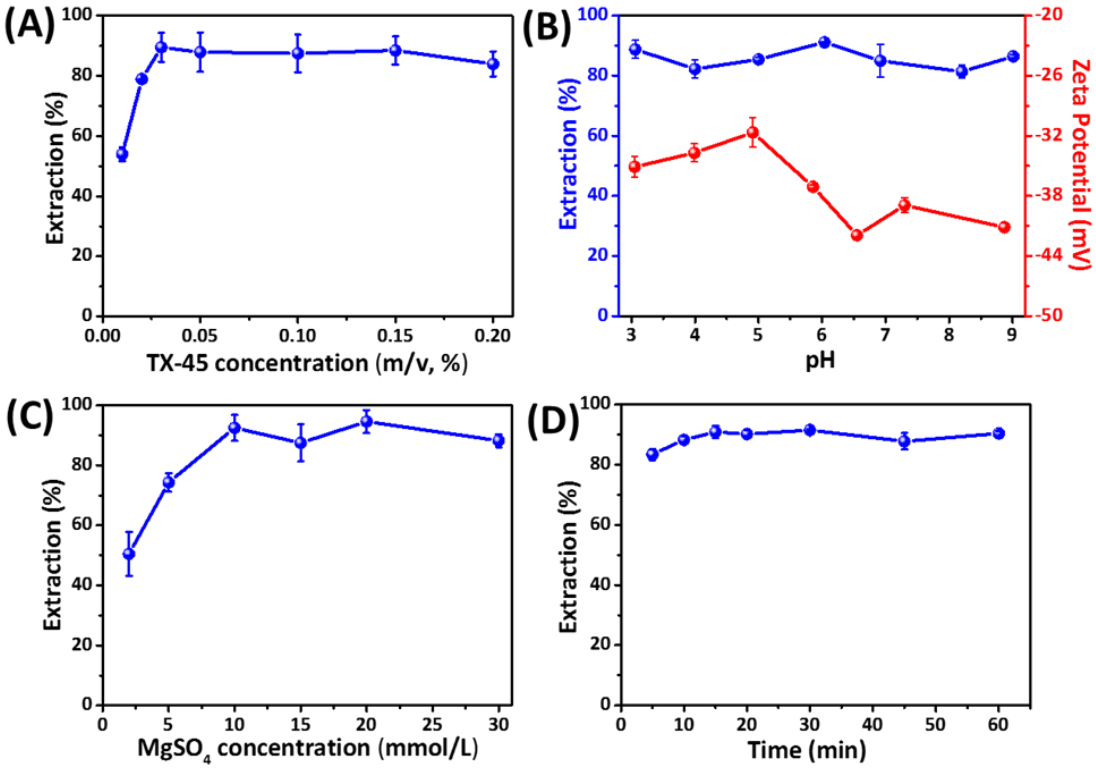

Figure S3. Optimization of CPE conditions for nanoplastics. (A) Effect of TX-45 concentration on the extraction efficiency of nanoplastics; (B) Effect of sample pH on the extraction efficiency and Zeta potential of nanoplastics; (C) Effect of $MgSO_4$ concentration on the extraction efficiency of nanoplastics; (D) Effect of incubation time on the extraction efficiency. Nate that the PS nanoplastic sample concentration and volume were ~ 0.98 mg/L and 10 mL, respectively, and sample pH was adjusted with diluted HNO_3 and NaOH.

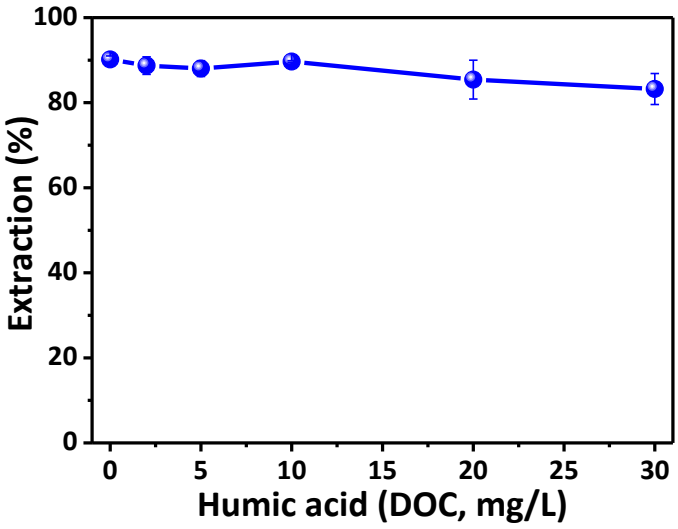

Figure S4. Effect of humic acid on the extraction efficiency of nanoplastics.

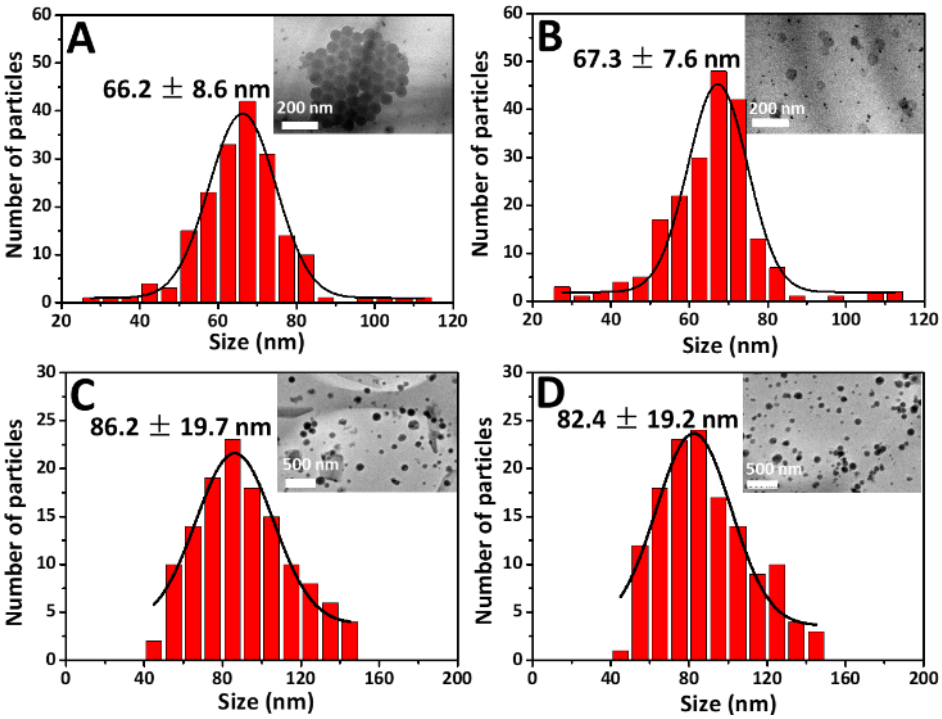

Figure S5. Size distributions and TEM images of PS (A, B) and PMMA (C, D) before (A, C) and after (B, D) CPE.

Table S1. Instrumental parameters of Py-GC/MS system.

Pyrolyzer	Frontier EGA/PY-3030D
Carrier gas	helium
Oven temperature	590 ºC
Interface temperature	300 ºC
Pre-purge time	10 s
Pyrolysis time	18 s
Gas chromatogram	Agilent 7890A
Split ratio	30:1
Temperature	300 ºC
Column	HP-5MS column; 30 m x 0.25 mm; film thickness 0.25 µm
Flow	1 mL/min
Temperature program	50 ºC (2 min) $\xrightarrow{10\ ºC/min}$ 320 ºC (3 min)
Transfer line temperature	280 ºC
Mass spectrometer	Agilent 5975C
Mode	Full scan
Scan time	0.4 s
Ionization energy	70 eV
Scan rate	2.48 scans/s
Scan range	10-550 amu
Source temperature	230 ºC
Quadrupole temperature	150 ºC

Table S2. Indicator compound, retention time, and calibration related data for the Py-GC/MS determination of the tested nanoplastics

Polymer type	**PS**	**PMMA**
Indicator compound	styrene trimer	methyl methacrylate
Retention time (min)	23.60	2.67
Indicator ion for integration m/z	91	100
Range (µg)	0.1-10	0.1-10
N	7	7
Calibration functions	$y = 3.47 \times 10^6 x - 7.05 \times 10^5$	$y = 4.55 \times 10^5 x - 1.50 \times 10^4$
R^2	0.994	0.995

Table S3. Analytical figures of merit of the proposed method.

Species	Linear Range (μg/L)	R^2	*RSD* (%, n = 6)	LOD	
				Mass (μg/L)	Particle number (amol/L)
PS	10-1000	0.9967	4.6	1.1	11.5
PMMA	10-1000	0.9997	1.5	0.6	2.5

Table S4. Typical characteristics of real waters.

Sample	pH	Latitude and longitude	TOC (mg/L)	Cations (mM)			
				Na^+	Mg^{2+}	K^+	Ca^{2+}
River water	7.92	N39.970°, E116.287°	2.51	2.81 ± 0.42	4.09 ± 0.11	0.55 ± 0.01	10.6 ± 0.2
Sea water	7.99	N40.777°, E121.888°	2.57	5416 ± 258	636 ± 31	119 ± 6	253 ± 24
Influent of WWTP	7.06	N40.042°, E116.362°	4.96	52.0 ± 4.6	13.1 ± 1.2	6.60 ± 0.53	29.7 ± 2.5
Effluent of WWTP	7.66	N40.042°, E116.362°	1.18	16.9 ± 1.4	19.5 ± 1.5	6.66 ± 0.51	26.6 ± 2.0