Critical biodegradation process of a widely used surfactant in the water environment: Dodecyl benzene sulfonate (DBS)

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1. Optimization of experimental conditions and quantitative analysis

For better performance during ESI-MS analysis, some important experimental parameters were investigated systematically, including ESI voltage, sample injection rate and temperature of ion-transport capillary. All experiments were performed in six times, and the concentration of DBS in experimental water samples was 0.2 mg/L.

1.1 ESI voltage

The effect of different electrospray voltages (2.0 - 4.0 kV) on the signal intensity of the characteristic fragment *m/z* 183.01 is shown in Fig. S1A. At the range of 2.0-3.5 kV, more samples were ionized because of the higher voltage. For this reason, stronger signal intensity observed. And it showed a decrease trend when the voltage increases to 4.0 kV. As the voltage is excessively high, the corona discharge occurs at the spray outlet, which affects the ionization of ions. Thus, the ESI voltage of 3.5 kV were used for detection DBS.

1.2 Injection rate

To obtain a better signal intensity of the characteristic fragment *m/z* 183.01, different sample injection rate (5-45 μL/min) were experimentally investigated. The effect of sample injection rate of fragment *m/z* 183.01 is shown in Fig. S2B. As expected, the target signal intensity was obviously increased with the increasing of sample injection rate. Because more ions were detected by Mass Spectrometry in spray jet. While the sample injection rate was kept at 45 μL/min, the intensity of *m/z* 183.01 was slightly lower than that obtained at the injection rate was 35 μL/min. As sample solution do not show welly ionization because of high injection rate. In this work, the sample injection rate was set as 35 μL/min.

1.3 Temperature of ion-transfer capillary

Increasing the temperature of ion-transfer capillary can promote the nebulization process of charged droplets, resulting in a better efficiency of producing gaseous species. In the range of 200-400 °C, the characteristic fragment *m/z* 183.01 obtained best signal intensity at the 300 °C. The effect of ion-transfer capillary temperature of fragment *m/z* 183.01 was shown in Fig. S1C. While the temperature was higher, the signal intensity decreased because of thermal dissociation of DBS. Thus 300 ℃ of ion-transfer temperature was used in this work.

1.4 Quantitative analysis of DBS

The signal intensity of *m/z* 183.01 in MS^2 spectra showed a linear response with DBS concentrations over the range 1.0-400.0 ug/L ($R^2 = 0.9993$) and the curve fitting equation was $y = 1216.58x + 2655.2$. The working curve of DBS was shown in Fig. S2. A limit of detection (LOD) of 0.52 μg/L was obtained by a signal-to-noise ratio (S/N) of 3. The relative standard deviations (RSDs) of twelve replicates for DBS ranging from 1.0-400.0 μg/L were less than 10.5%. The limit of quantification (LOQ) of 6.36 μg/L was obtained by a S/N of 10. The recover experiment was also carried out for 12 times with the addition of 200.0 μg/L DBS standard solution. The recovery of DBS was from 97.8% to 100.1% and the mean recovery of DBS was 98.6%. A short time estimated less than 2 min was taken for each measurement.

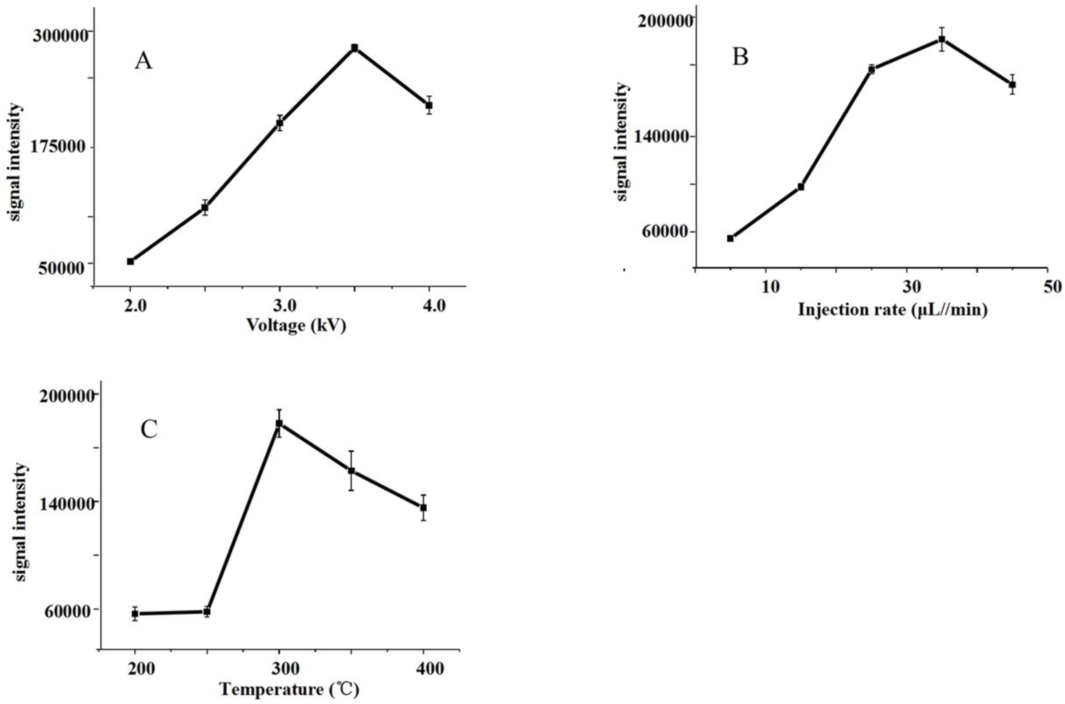

Fig. S1 The signal intensity of *m/z* 183.01 of the secondary fragment ion with different ESI voltage (A); flow rate of sample solution (B); temperature of ion-transfer tube (C).

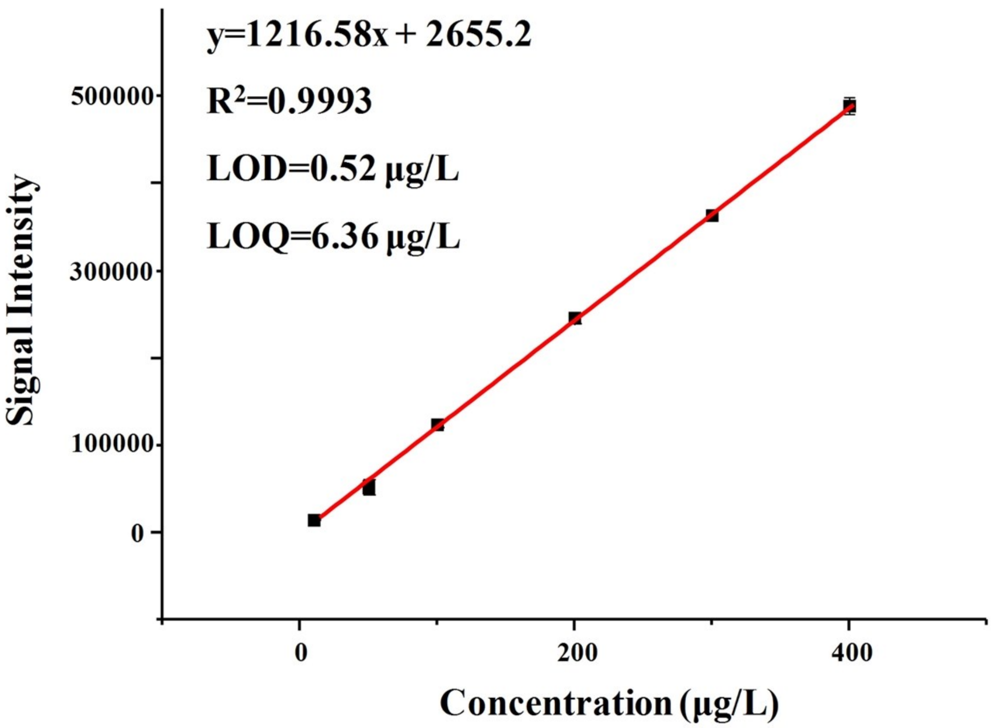

Fig. S2 The working curve of signal intensity of *m/z* 183.01 to concentration of DBS

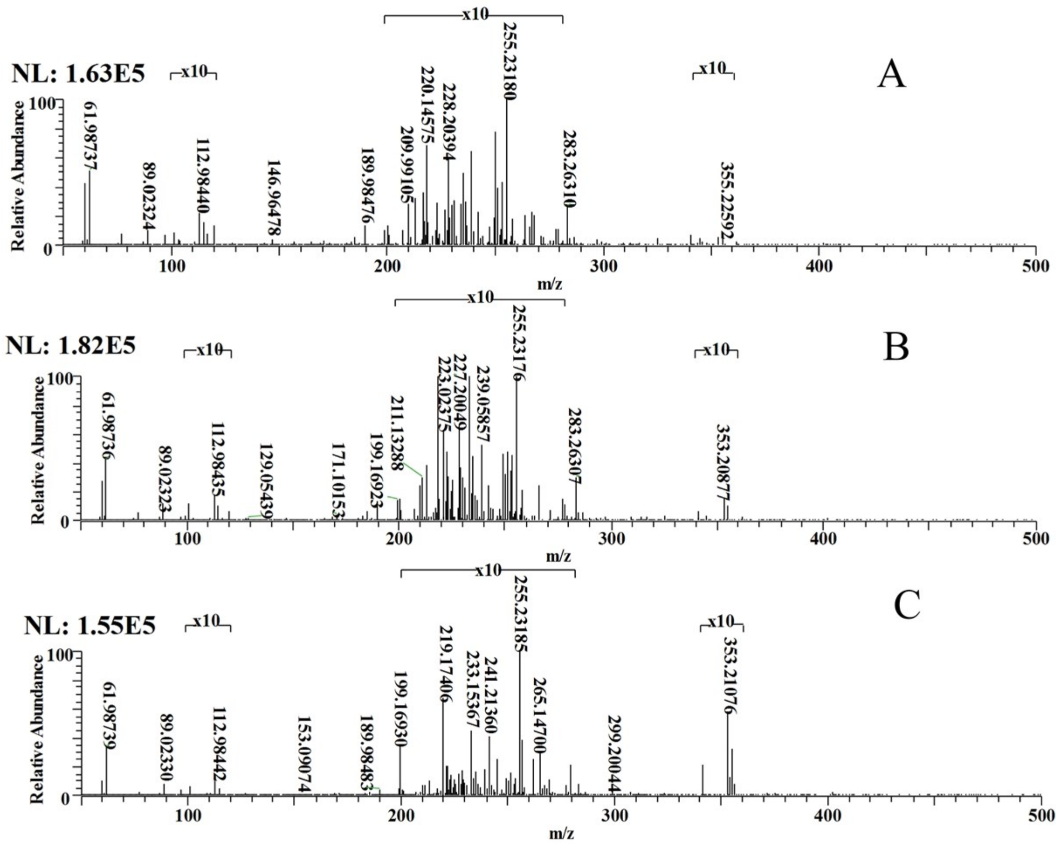

Fig. S3 The ESI-MS spectra of blank control at 0 h (A), 6 h (B), 12 h (C) during the experiment.

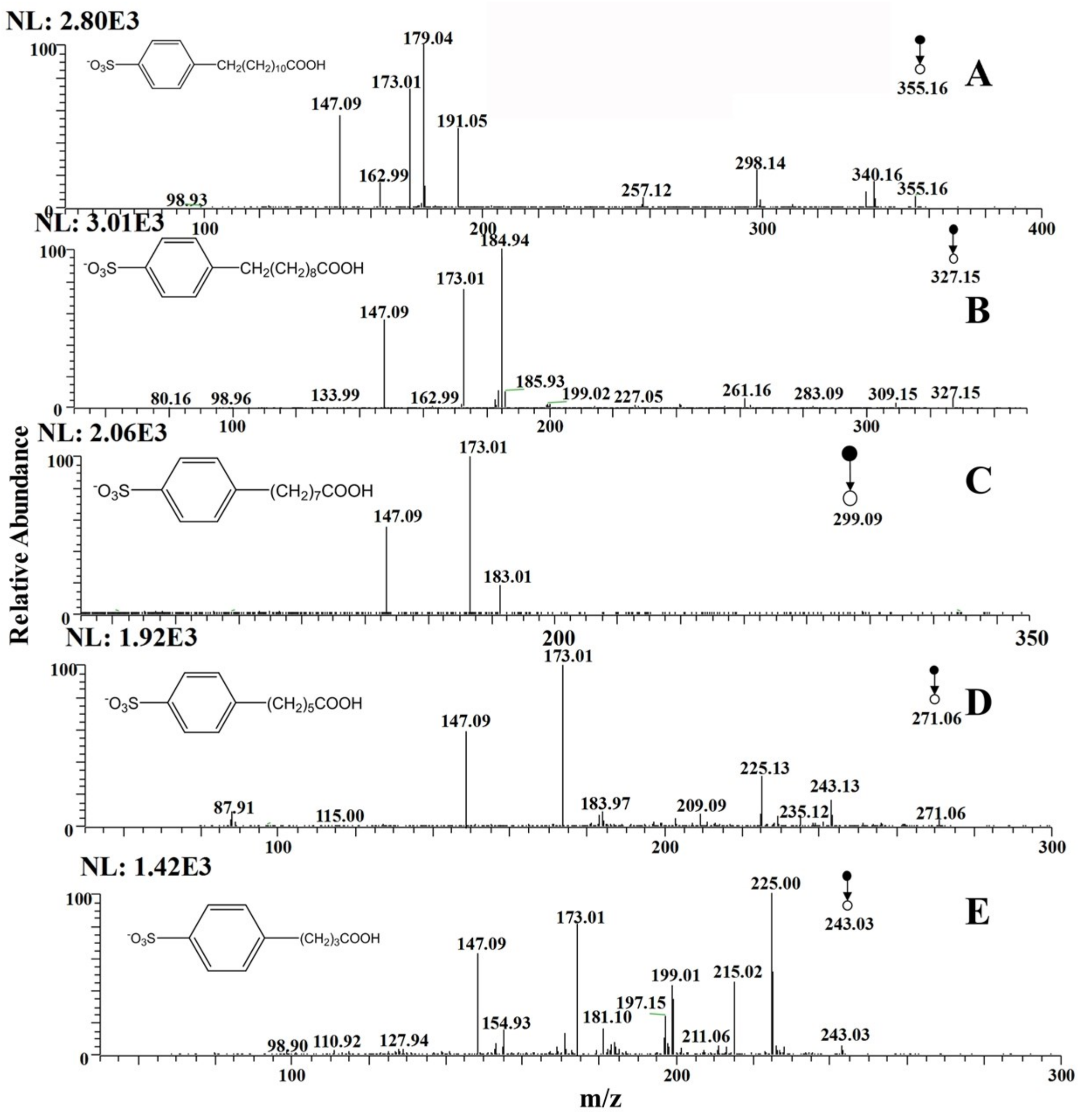

Fig. S4 The MS^2 spectra of *m/z* 355.15869 (A), 327.12720 (B), 299.09473 (C), 271.06379 (D), 243.03234 (E).

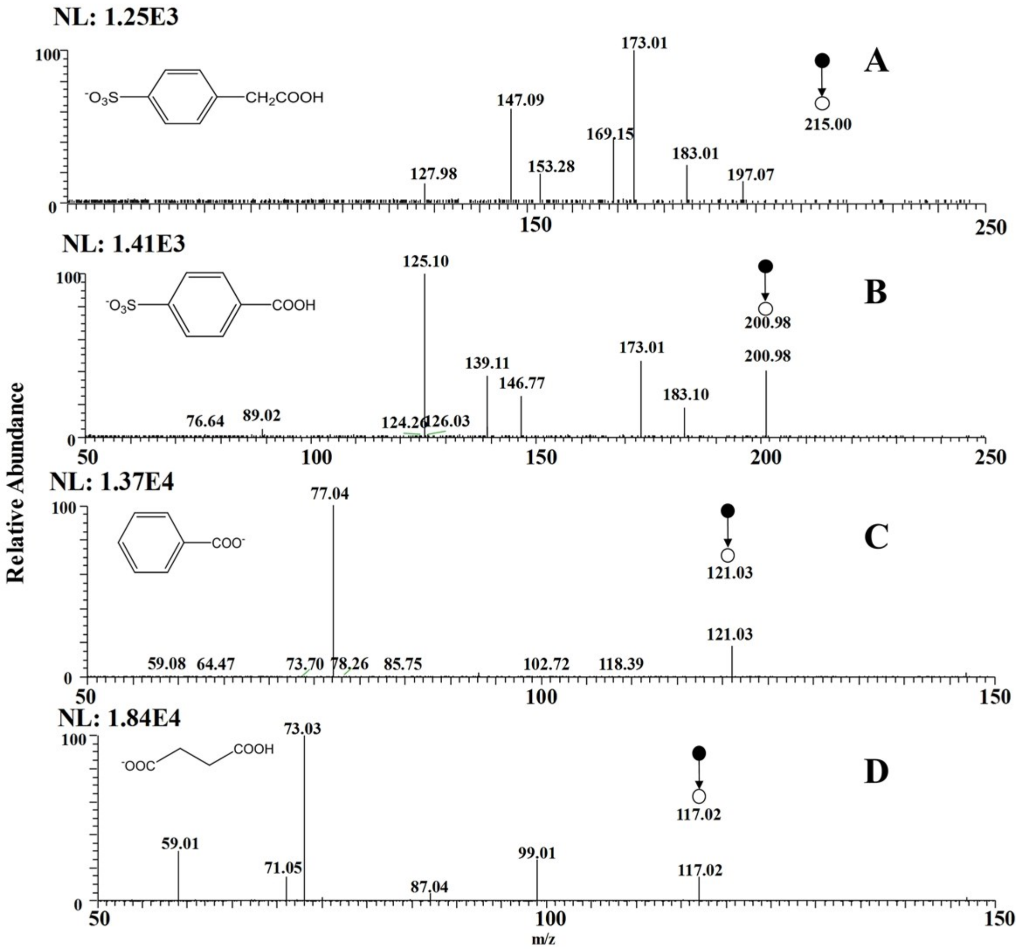

Fig. S5 The MS^2 spectra of *m/z* 215.00125 (A), 200.98528 (B), 121.02892 (C) and 117.01806 (D).

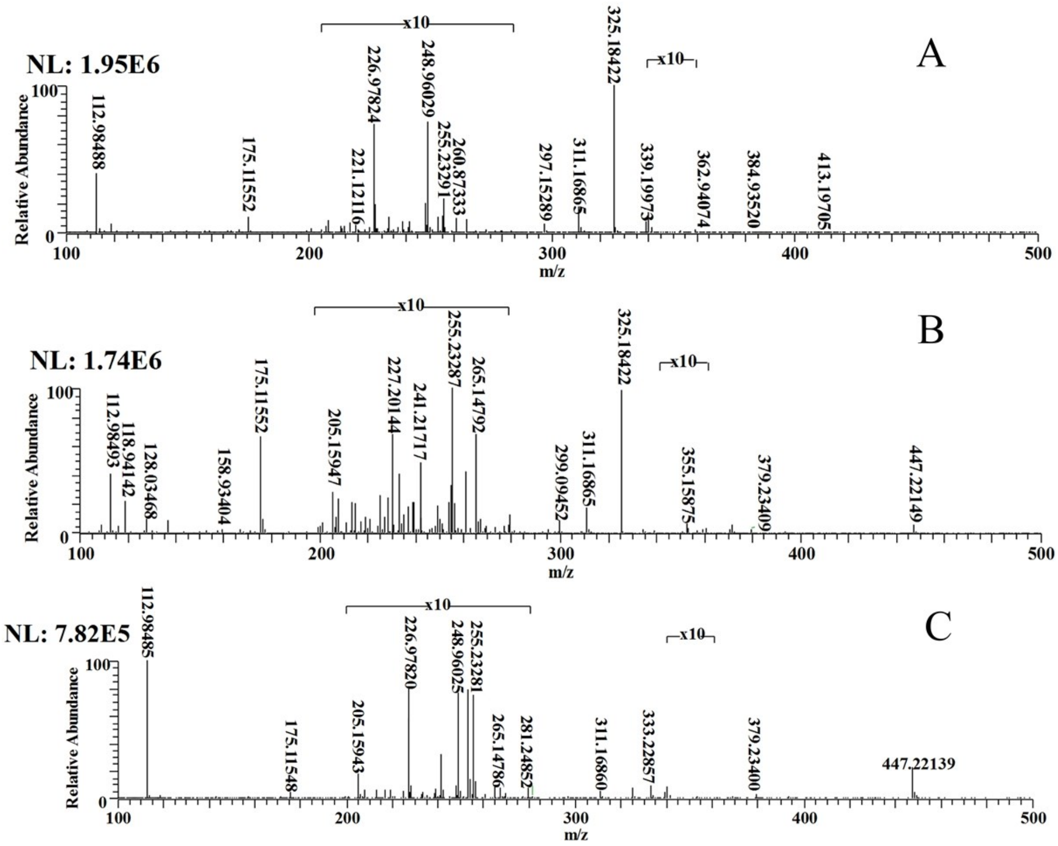

Fig. S6 The MS spectra of DBS degraded in the nature water (East Lake in Jilin University, China) at 0 h (A) 12 h (B), and the blank control (C).

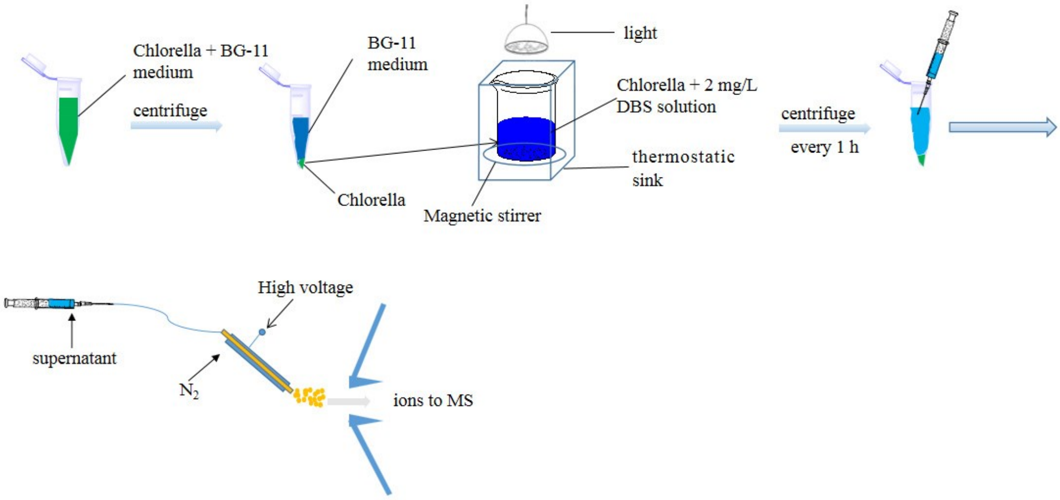

Fig. S7 Schematic illustration of sample preparation and ESI-MS detection.

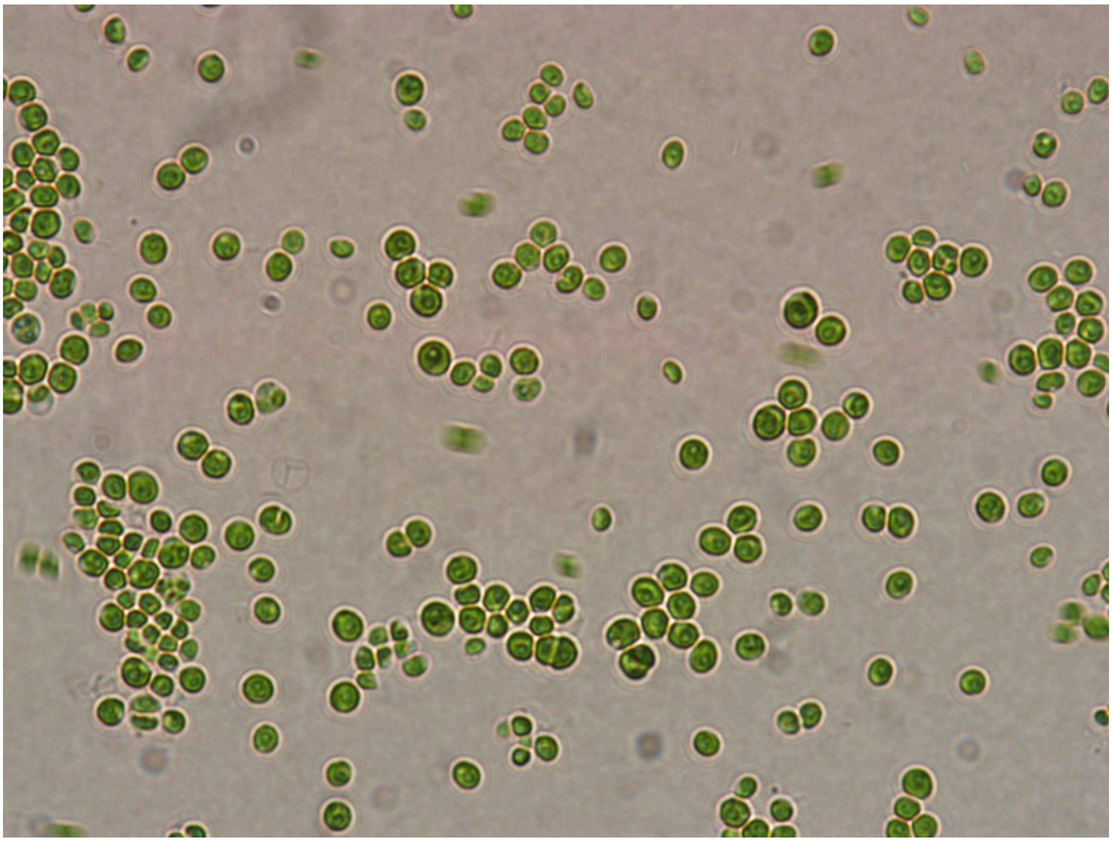

Fig. S8 The microscope photo of *Chlorella vulgaris* used in the experiment.

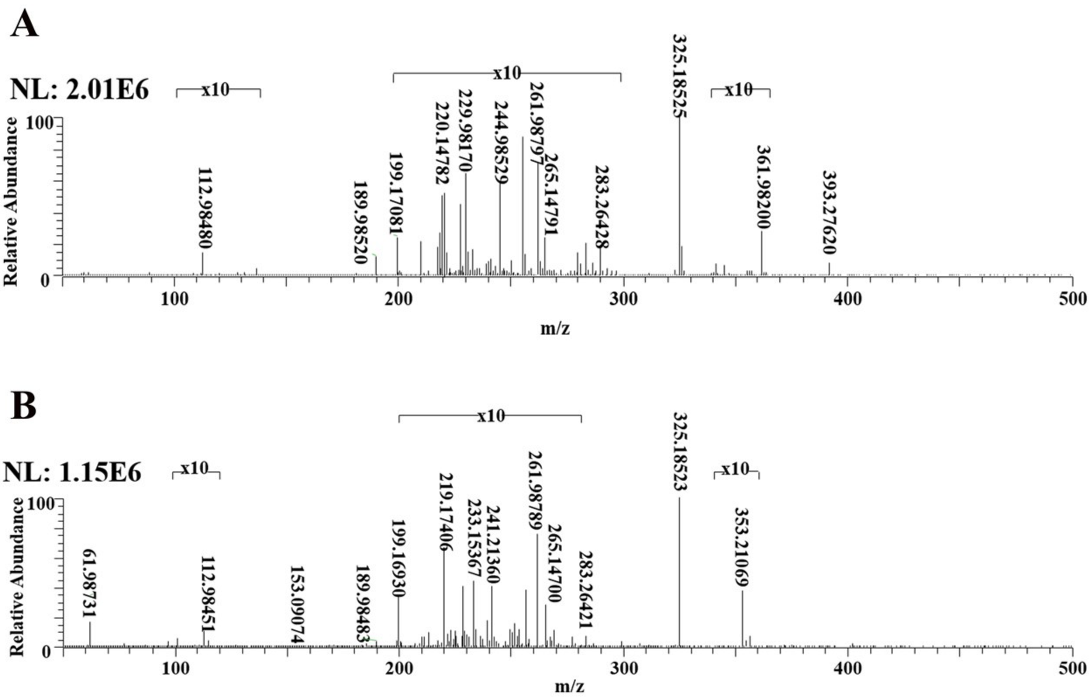

Fig. S9 The mass spectra of the mixed solution of DBS and Chlorella under dark conditions of 0 hours and 12 hours

Table. S1 The products of DBS degraded by *Chlorella vulgaris*

Compound	*m/z*		Molecular formula	Error, 10^{-6}
	Experimental	Calculated		
4-Sodium sulfophenyldodecanoate acid	355.15869	355.15737	$C_{18}H_{27}O_5SNa$	3.72
4-Sodium sulfophenyldecane acid	327.12720	327.12607	$C_{16}H_{23}O_5SNa$	3.45
4-Soudium sulfophenylocatane acid	299.09473	299.09477	$C_{14}H_{19}O_5SNa$	1.34
4-Sodium sulfophenylhexane acid	271.06379	271.06347	$C_{12}H_{15}O_5SNa$	1.18
4-Sodium sulfophenylbutane acid	243.03234	243.03217	$C_{10}H_{11}O_5SNa$	0.70
4-Sodium sulfobenzoic acid	215.00125	215.00087	$C_8H_7O_5SNa$	1.77
Benzoic acid [26]	121.02892	121.02841	$C_7H_6O_2$	4.21
Benzene [26]	77.03872	77.03858	C_6H_6	1.82
Butane dioic acid	117.01806	117.01824	$C_4H_6O_4$	1.54
Ethanoic acid [54]	59.01227	59.01276	$C_2H_4O_2$	8.30