Accessory publication

Photochlorination of bisphenol A by UV-Vis light irradiation in saline solution: effects of iron, nitrate and citric acid

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Experimental methods

Chemicals

BPA (purity grade >99%) was purchased from Acros Organics. 2-(3-chloro-4-hydroxyphenyl)-2-(4-hydroxyphenyl) propane (3-ClBPA) and 2-bis(3-chloro-4-hydroxyl- phenyl) propane (3,3'-diClBPA) were synthesised and purified as described by Fukazawa et al.[1] Phenanthrene d_{10}, an internal standard for GC-MS analyses, was purchased from Dr Ehrenstorfer GmbH. Methanol and dichloromethane were purchased from Tedia Co. Inc. Citric acid ($C_6H_8O_7 \cdot H_2O$), NaCl, $NaNO_3$, $FeCl_3 \cdot 6H_2O$, HCl and NaOH were analytical reagent grade and used without further purification.

Irradiation experiments

Irradiation was performed using a 300-W Hg lamp (Beijing Huiyixin Lighting Corporation, China) equipped with a special glass filter restricting the transmission of wavelengths below 290 nm. Although the proportion of UV light in the illumination of Hg lamp is higher than that of sunlight, high energy irradiation below 290 nm has been excluded, therefore, the energy of photons is similar to that of sunlight. Such a simulated solar UV-light could make the photochlorination distinctly observed. The irradiation intensity was 8 mW cm^{-2}. All solutions for the experiments were prepared using Milli Q water (18 MΩ cm) and adjusted to the desired pH value by 0.1 M HCl or NaOH prior to irradiation.

Extraction and analysis

BPA was analyzed by high performance liquid chromatography (HPLC), and chlorinated BPA was enriched by solid-phase extraction (SPE) and quantified using GC-MS analysis. SPE was carried out on a Supelco vacuum tank connected with a vacuum pump. SPE cartridges (Cleanert PEP-SPE, Agela Technologies, China) were activated with 3-mL dichloromethane, 3-mL methanol, and 3-mL Milli-Q water in sequence at a rate of 2 mL min^{-1}. Solutions passed through SPE cartridges at a flow rate of 2 mL min^{-1}. Then, cartridges were dried by nitrogen flow. Chlorinated products of BPA were eluted with a mixture of 6-mL dichloromethane/methanol (3:2 v/v) at a flow rate of 1 mL min^{-1}. Finally, eluents were evaporated to almost dryness under a stream of nitrogen and then dissolved in 1-mL dichloromethane. The recoveries of 3-ClBPA and 3,3'-diClBPA for this method were 107 ± 6.9% and 108 ± 4.7% respectively.

Apparatus: HPLC and GC-MS

HPLC analysis was performed using Waters–2695 and PDA–2996, equipped with a SunFire™ ODS reverse-phase column (150 × 4.6 mm, 5.0 μm). The mobile phase was a mixture of methanol (70%) and water (30%) at a flow rate of 1.0 mL min^{-1} and the detector wavelength was set at 226 nm.

GC-MS analysis was performed using a 6890 GC (Agilent Technologies, USA) with a 7683 series injector and a 5973 network mass selective detector (MSD), adopted a HP-5MS GC column (Agilent Technologies, 30 m × 0.25 mm, film thickness: 0.25 μm). The injector of the GC was set at 260°C and the samples were automatically injected using the splitless-injection mode (1-μL injected volume). The transfer line of GC to MS was set at 280°C, and the electron impact (EI) ion source was set at 230°C. The ionisation energy was 70 eV. The GC oven temperature program was as follows: the initial oven temperature was set at 80°C, held for 2 min, and then the temperature was increased to 240°C via ramp of 12°C min^{-1}, and maintained at 240°C for 2 min. The carrier gas was high-purity helium with a constant flow of 1 mL min^{-1}. The MSD was operated in selected ion-monitoring (SIM) mode for quantitative determinations, measuring ion currents at a mass/charge ratio (*m/z*) of 247, 249 and 262 atomic mass units for 3-ClBPA, and 281, 283, 296 for 3,3'-diClBPA.

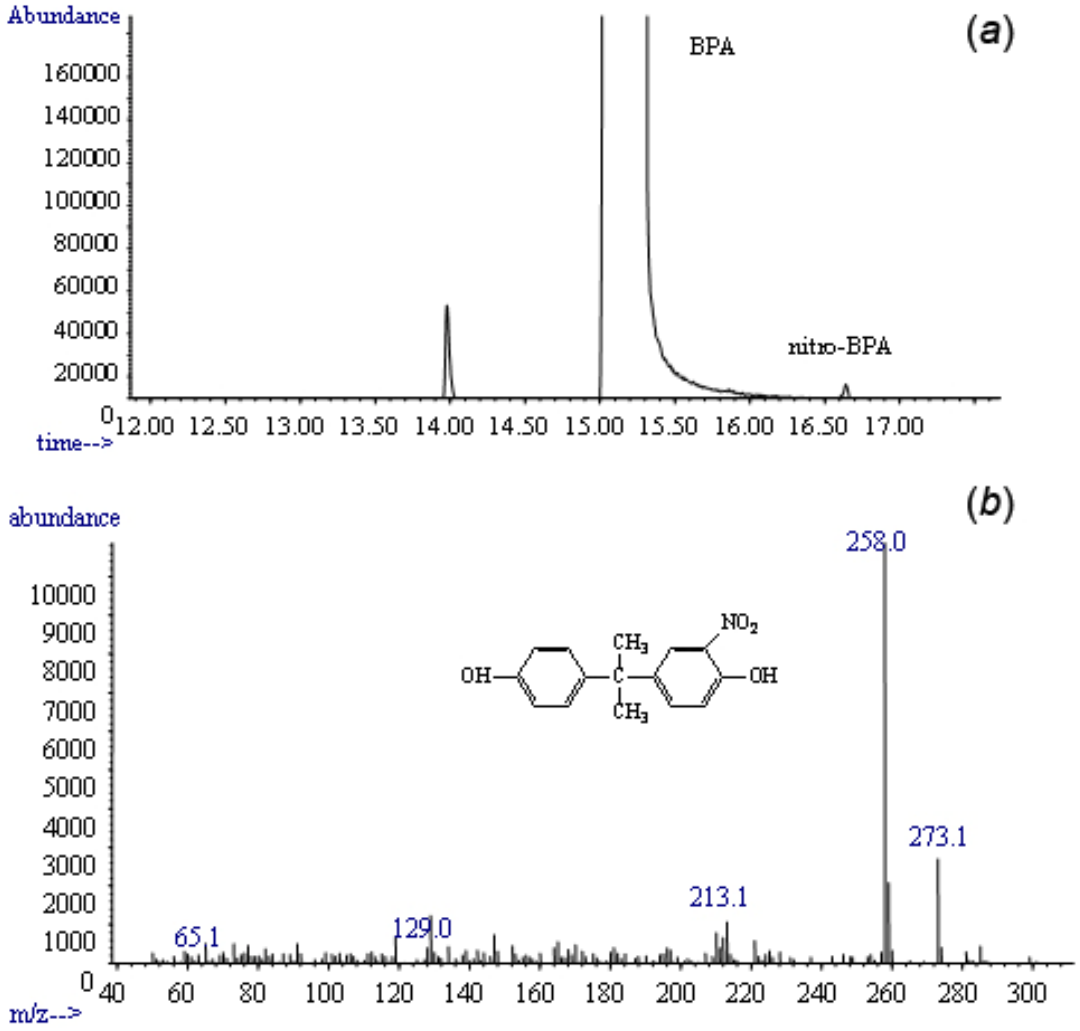

Fig. A1. (*a*) GC-MS chromatogram of residual organic compounds of BPA phototransformation in the presence of 0.2 M Cl^- and 0.2 mM NO_3^-, and (*b*) mass spectra of peak corresponding to nitro-BPA.

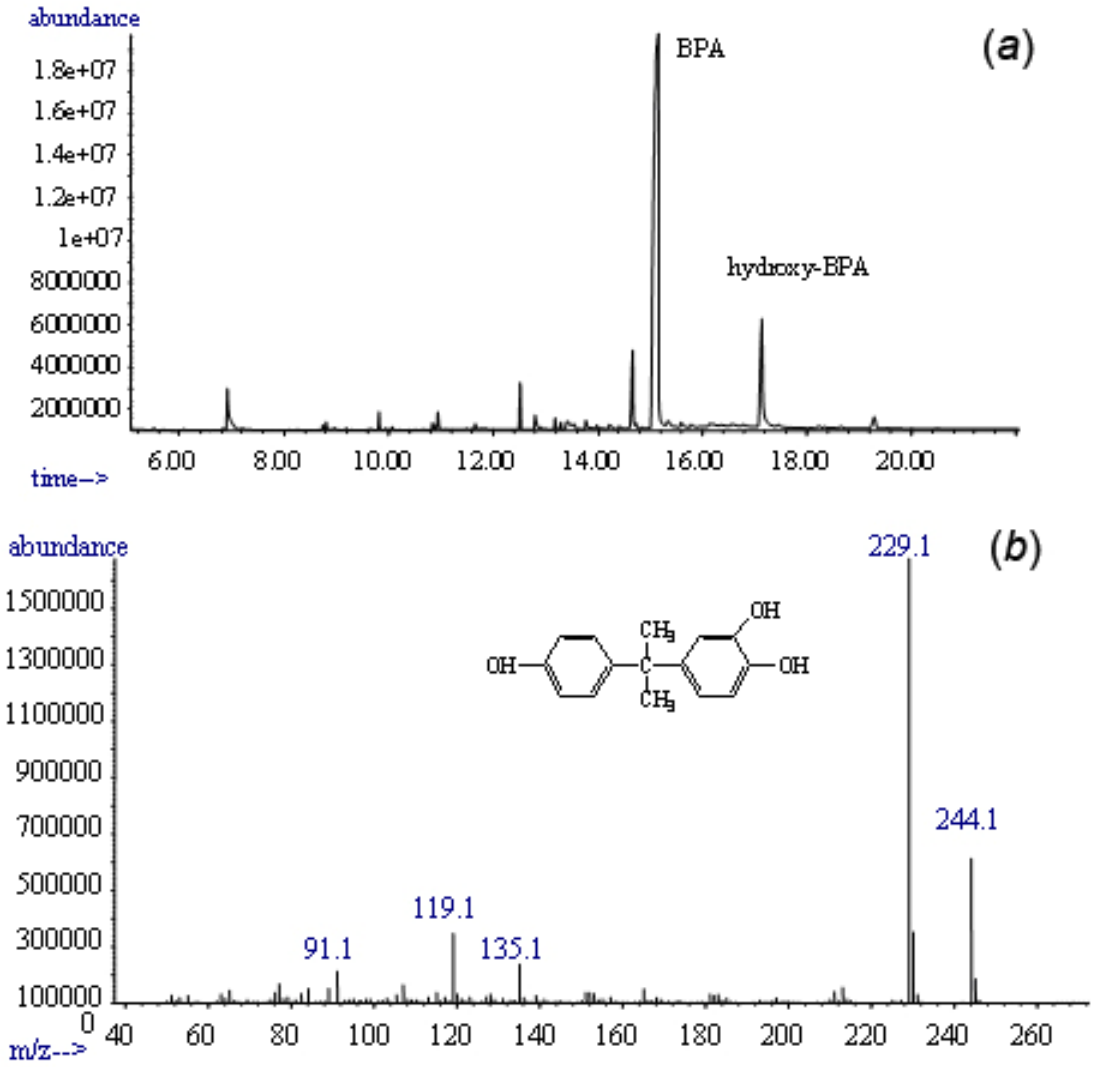

Fig. A2. (*a*) GC-MS chromatogram of residual organic compounds of BPA phototransformation in the presence of 0.2 M Cl^- and 0.5 mM citric acid, and (*b*) mass spectra of peak corresponding to hydroxyl-BPA.

Reference

[1] H. Fukazawa, K. Hoshino, T. Shiozawa, H. Matsushita, Y. Terao, Indentification and quantification of chlorinated bisphenol A in wastewater from wastepaper recycling plants. *Chemosphere* **2001**, *44*, 973.