



Adsorption of bisphenolic xenoestrogens on graphene: A peculiar adsorbate concentration dependence on the conformation of graphene



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ABSTRACT

Graphene was used to remove low-level environmental endocrines in micro-polluted water with the aid of an investigation about the adsorption of bisphenols at low levels in a very wide range from 0.0005 to 70 mg L⁻¹. It was found that over the wide concentration range, the adsorption isotherms could be divided into two regions: they followed the Freundlich model in the lower concentration region (correlation coefficient $R^2 > 0.99$), but obeyed the Langmuir model in the higher concentration region ($R^2 > 0.99$). This was attributed to the adsorption-induced changes in the morphology of graphene, which created different adsorption sites on the surface of graphene. The obtained values of thermodynamic parameters ΔG^0 , ΔH^0 and ΔS^0 indicated that the adsorption was a spontaneous, exothermic and entropy-decreasing process. The absolute values of these parameters tended to be decreased with increasing bisphenol concentration, suggesting stronger affinity of the binding sites on graphene for the adsorption of the bisphenols at lower concentrations. As confirmed by some characterization and monitoring experiments, the increased bisphenol adsorption decreased the surface grooved regions formed by wrinkles and increased the flat regions. The highly and lowly-wrinkled (or flat) surface states of graphene accounted for the observed two-stage adsorption isotherms.

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1. Introduction

Endocrine disrupting compounds (EDCs) are a group of emerging contaminants that have been detected at trace concentrations (<100 ng L⁻¹) in surface waters, runoff, and landfill leachates [1,2]. They are of world wide concern due to their adverse effects to wildlife and humans even at low exposure levels [3]. EDCs encompass a wide range of natural and synthetic chemicals, including pesticides, steroids, and phenolic xenoestrogens [4]. Among these chemicals, bisphenol A (BPA) and its structurally similar analogues deserve particular attention as they possess high estrogenicity [4].

The levels of BPA detected in the environment are varied in a wide concentration range. Yamamoto et al. [5] reported that the levels of BPA in the leachates of a hazardous waste landfill ranged from 1.3 to 17200 ng mL⁻¹ with an average of 269 ng mL⁻¹. Belfroid

et al. [6] reported that BPA levels in river water were 8–21 ng mL⁻¹ or less. Kuch et al. [7] reported that the detected BPA concentrations ranged from 0.5 to 16 ng L⁻¹ in all river samples, and from 0.3 to 2 ng L⁻¹ in drinking water. Although the detected levels of BPA in surface waters and drinking water were as low as several nanograms per liter, such low levels are high enough to induce serious adverse effects on animals and humans. Xu et al. investigated the impact of BPA on murine ovarian granulosa cells at low dose of 0.1 nM and found that this low and physiologically relevant dose of BPA decreased granulosa cell viability [8]. Wetherill et al. found that at very low doses (0.1–10 nM, 0.023–2.3 ng mL⁻¹), BPA induced proliferation of human prostate cancer cells via binding to a mutant form of the androgen receptor found in some prostate tumors [9]. Takai et al. demonstrated that BPA not only affected early embryonic development at an environmentally-relevant low level (0.23 ng mL⁻¹), but also exerted late effects on postnatal development in mice [10,11]. Unfortunately, the above-mentioned frequent detections of BPA in surface waters and drinking water at levels of several nanograms per liter indicate that the treatment of low-level BPA is inefficient in most of the water treatment factories. As a challenge, therefore, efficient

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technologies are required to remove low-level BPA and its structurally similar analogues from water. Such a technology should involve fast and massive adsorption of BPA and its structurally similar analogues.

Graphene, a two-dimensional flat structure with sp^2 -hybridized carbon configurations, takes a promising advantage of strong adsorption ability to chemicals with benzene rings through strong π - π interactions in addition to the hydrophobic effect. Wu et al. [12] reported the maximum adsorption capacities of *p*-toluenesulfonic acid, 1-naphthalenesulfonic acid and methyl blue on graphene as 1.43, 1.46 and 1.52 $g\ g^{-1}$, respectively. Xu et al. [13] reported that graphene showed an adsorption capacity of 0.182 $g\ g^{-1}$ toward BPA because of π - π interactions. We recently found that the adsorption of phenolics on reduced graphene oxide (RGO) was dependent on the π - π interaction between the aromatic molecules and RGO, and the reduction of GO could increase its adsorption capacity toward phenolics by a factor as large as 235% [14]. Therefore, graphene may function as a promising adsorbent to remove BPA and its structurally similar analogues at low concentrations.

Adsorption may be suitable for the treatment of environmental endocrines at low concentrations in micro-polluted water. In most of cases, however, the adsorption capacity of an adsorbent will be decreased as the concentration of the target pollutant is decreased, because the maximum adsorption amount must be limited by the adsorption/desorption equilibrium at the adsorbent|solution interface. In order to develop an efficient method for removing ultralow-level environmental endocrines from water with using graphene adsorption, it is necessary to clarify at least the following aspects: (1) what will happen for the adsorption of the target on graphene if the concentration of the target is varied from ultralow to fairly high levels? (2) what is the adsorption behavior of the ultralow-level target on graphene? (3) what is the adsorption mechanism of low-level targets on graphene. Therefore, BPA, bisphenol F (BPF) and bisphenol AF (BPAF) were selected as the representatives of bisphenolic xenoestrogens in the present work, and their adsorption kinetics, isotherm and thermodynamics were investigated on graphene, along with clarifying their adsorption mechanisms on graphene.

2. Experimental

2.1. Chemical reagents

Graphite powder (SP1 graphite) was purchased from American Bay Carbon (Bay City, MI). BPF and BPAF were provided by Aladdin Chemistry Co., Ltd. BPA and other chemicals were bought from Sinopharm Chemical Reagent Co., Ltd. (China). All the chemicals were of analytical reagent (AR) grade or higher and used as received without further purification. Double-distilled water was used in the present study.

2.2. Preparation of GO dispersion

GO was prepared according to a modified Hummers method [15]. In brief, concentrated H_2SO_4 (46 mL) was added to a mixture of graphite flakes (1 g) and $NaNO_3$ (1 g) in a 250 mL beaker. The mixture was stirred (800 rpm) for 0.5 h in an ice bath at 5 °C. $KMnO_4$ (6 g) was added slowly in small portions to keep the reaction temperature below 5 °C, being followed by stirring for 2 h. Then the mixture was heated up to 35 °C and stirred for 2 h (800 rpm). After that, deionized water (46 mL) was gradually added into the solution. The reaction temperature was raised to 98 °C. After it was maintained at 98 °C for 15 min, the heat was removed. Additional water (100 mL) and 30% H_2O_2 (20 mL) were added. The mixture was centrifuged and washed with deionized

water sequentially. The obtained product was dispersed in water, exfoliated through ultrasonication for 1 h, and used as a stock of GO suspension in water.

2.3. Preparation of RGO

A given amount of GO was dispersed into 100 mL of water, into which different amounts of aqueous hydrazinehydrate solution (80 wt.%) were added. The reduction of GO was carried out at 95 °C for 5 h during stirring (800 rpm). The solids were isolated by filtering with 0.22 μm filter and washed with distilled water for three times to remove the excess hydrazine. At the end, the product was dispersed in water as RGO dispersions. For the reduction, the mass ratio of hydrazinehydrate to GO was controlled at 1:1. It should be noted that the used RGO adsorbent was referred to as graphene adsorbent throughout the present work.

2.4. Characterization

Surface morphology was observed on a Hitachi S-4800 scanning electron microscope (SEM), and transmission electron microscopy (TEM) images were performed on a Tecnai G2 20 S-TWIN HRTEM (FEI, USA). Atomic force microscopic (AFM) observations were conducted with a SPM9700 system (Shimadzu Corporation). X-ray photoelectron spectroscopic (XPS) analysis was conducted on a VG Multilab 2000 spectrometer (Thermo Electron Corporation) with Al $K\alpha$ radiation as the exciting source (300 W). During the measurement, the sample was supported on a copper substrate. The binding energies of recorded XPS spectra were corrected according to C 1s line at 284.6 eV. After subtracting the Shirley-type background, the core-level spectra were decomposed into their components with mixed Gaussian-Lorentzian (20:80) shape lines using the CasaXPS software. X-ray powder diffraction (XRD) pattern was obtained on a diffractometer with Cu $K\alpha$ radiation (PANalytical B.V. X'Pert PRO), operated at 40 mA and 40 kV. Raman spectra were recorded on a Thermo Fisher DXR Raman spectrometer employing a 532 nm laser beam.

2.5. Batch adsorption experiments

The adsorption experiments were performed on a shaker at a shaking speed of 160 rpm. The aqueous solutions of bisphenols at concentrations of 0.01–90 $mg\ L^{-1}$ were separately added to 100-mL conical flasks with seals. A given amount of RGO suspension (60 $mg\ L^{-1}$) was added into the solution. The total solution volume was rapidly adjusted to 50 mL by adding water. At given time intervals, aliquots of the suspension (about 1 mL) were sampled. After the suspension was immediately centrifuged at a high speed of 16,000 rpm on a centrifugal machine (Hettich EBA21) to remove the solids, the concentration of bisphenols in the supernatant was analyzed by UV–vis spectrophotometry and high performance liquid chromatography (HPLC). The adsorbed amount of phenolic compounds at equilibrium was calculated with Eq. (1),

$$q_e = \frac{(c_0 - c_e)V}{m} \quad (1)$$

where q_e ($mg\ g^{-1}$) is the equilibrium adsorption capacity of the adsorbent, c_0 and c_e ($mg\ L^{-1}$) are the initial and final concentrations of the phenolic compound in solution, V is solution volume, and m is the mass of the used GO or RGO.

2.6. Analytic methods

Bisphenols at high concentrations were analyzed by measuring their absorbance at its adsorption maximum wavelength on a UV–vis spectrophotometer (CARY 50 Scan), and the wavelengths for

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