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# Adsorption characteristics of tetrabromobisphenol A onto sodium bisulfite reduced graphene oxide aerogels

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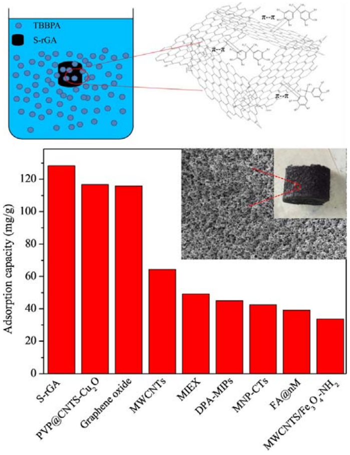
## GRAPHICAL ABSTRACT



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## ABSTRACT

Adsorbent 3-D sodium bisulfite reduced-graphene aerogels (S-rGA) were fabricated via the reduction of graphene oxide. It has high adsorption capacity and excellent reusability for the removal of tetrabromobisphenol A (TBBPA). S-rGA with its unique block and porous network structure was characterized using scanning Electron Microscopy (SEM) and Brunauer-Emmett-Teller (BET) analysis. The adsorption characteristics of S-rGA to TBBPA were investigated through batch experiments. In the study, the adsorption kinetics were well described by the pseudo-second-order model. The adsorption equilibrium well fit to the Langmuir model with maximum adsorption capacity of 128.37 mg/g. Thermodynamic parameters suggested that the adsorption of TBBPA was exothermic and spontaneous. Fourier transformed infrared (FTIR) spectra indicated that π–π interaction might be consistent with the adsorption of TBBPA by S-rGA. Furthermore, reuse experiments indicated that S-rGA could be regenerated five times with only a slight loss in adsorption capacity. These results demonstrated that S-rGA is potentially an ideal adsorbents for enhancing the adsorption capacity of TBBPA in aqueous environments.

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## 1. Introduction

Tetrabromobisphenol A (TBBPA) is a typical representative of brominated flame retardants (BFRs), which are widely used in plastic, textile and electronic products [1]. TBBPA is a persistent bioaccumulative pollutant, which can act as an endocrine disruptor, an immunotoxicity mediator, and a neurotoxicity effector after long-term exposure [2–4]. It had been included on the OSPAR list of chemicals for priority action under the "Hazardous Substances Strategy" [5]. TBBPA's worldwide usage and limited water solubility may result in its contamination of and persistence environmental media. Therefore, appropriate measures to remove TBBPA from aquatic environments are urgently required.

Generally, adsorption is acknowledged as a popular method for water treatment because of its facile operation, high performance and cost-effectiveness. Recently, graphene had been widely used as an adsorbent for various environmental pollutants because of its unique attributes. For instance, graphene has the perfect $sp^2$ hybrid carbon nanostructure and a relatively high surface area and can be easily prepared via chemical oxidation-reduction methods [6]. Several experimental studies have already been carried out on the adsorption of organic pollutants [7–13], and these pollutants could be adsorbed onto adsorbents through $\pi-\pi$ interactions because of their benzene ring structure [9,14]. Xu et al. used graphene as an adsorbents for the removal of bisphenol A (BPA), achieving a maximum adsorption capacity of 182 mg/g [11]. Wu et al. used graphene for the sorption of *p*-tolutenesulfonic acid (*p*-TA), 1-naphthalenesulfonic acid (1-NA) and methyl blue (MB), achieving maximum adsorption capacities of 1.43 g/g, 1.46 g/g and 1.52 g/g, respectively [15]. Obviously, graphene has excellent adsorption capacity. However, nanoscale graphene has some drawbacks such as difficult separation and secondary environment pollution, serious agglomeration and restacking [16]. To realize easy separation after adsorption, Jin et al. prepared magnetic reduced graphene oxides (RGOs) for the adsorption of 4-*n*-nonylphenol (4-*n*-NP) and BPA, but its maximum adsorption capacities were only 63.96 and 48.74 mg/g, respectively [10]. Sun et al. prepared magnetite/reduced graphene oxide (MRGO) for the adsorption of rhodamine B and malachite green, but reached maximum adsorption capacities of only 13.15 and 22 mg/g, respectively [17]. Therefore, many efforts have been devoted to improving the adsorption capacity and separation of graphene adsorbents.

Recently, synthesis of hierarchical 3-D architectures overcame these limitations and offered new opportunities to design advanced materials with optimized adsorption properties based on the unique combination of 3-D structural and chemical functionalities [18–20]. Graphene aerogel is one of these 3-D macroscopic assemblies with high surface area that possess attractive potential in water treatment owing to their advantages. For example, the well block mechanical strength minimized the possible environmental effects caused by the release of graphene nano-sheets. [21,22], and the unique 3-D microporous and mesoporous interconnected network allowed access and diffusion of ions and molecules [23,24]. Furthermore, these absorbents were lightweight and hydrophobic, which can lead to produce interaction with hydrophobic organic pollutants [25]. Cong et al. fabricated macroscopic multifunctional graphene-based aerogels with maximum uptake capacity of 27 times their weight for the adsorption of oils [26]. The F-rGO aerogel prepared by Hong et al. exhibited excellent absorption efficiency for various oils and organic solvents, resulting in capacity ranging from 34 to 112 times its weight in absorption capability [27]. Bi et al. produced spongy graphene with enhanced performance as an oil sorbent, and its adsorption capacity reached 616 times its own weight [20]. Although graphene aerogels have good adsorption properties regarding on oil, rarely have systematic studies reported the adsorption of phenolic compounds such as TBBPA in aqueous environments by graphene aerogels.

In this study, a simple chemical reduction method was used for the synthesis of 3-D graphene aerogel with sodium bisulfite as the reducing agent. The physicochemical properties and adsorption characteristics of the prepared sulfenyl-reduced graphene aerogel (S-rGA) were characterized by scanning electron microscop (SEM), Brunauer-Emmett-Teller (BET), X-ray diffraction (XRD), Raman, X-ray photoelectron spectroscopy (XPS) and Fourier-transform infrared (FTIR) analyses. A comprehensive study on the adsorption and desorption behaviors of S-RGA for TBBPA in aqueous solutions was performed. The adsorption isotherms, adsorption kinetics, and thermodynamics were systematically investigated. The influence factors (initial TBBPA concentration, temperature and pH) and adsorption mechanism of the adsorption of TBBPA by S-rGA were explored. The experimental data provided a better understanding of the adsorption process of TBBPA by S-rGA and led to the development of an efficient adsorbent for removing phenolic compound from wastewater.

## 2. Materials and methods

### 2.1. Materials

Analytical grade $NaHSO_3$, $KMnO_4$, 98% $H_2SO_4$, and 30% $H_2O_2$ aqueous solution were purchased from Shanghai Chemical Reagents Company. Graphite (diameter, 20 μm) and TBBPA (4,4-isopropylidenebis (2,6-dibromophenol), ≥98%) were obtained from Sigma-Aldrich. TBBPA has a water solubility of 4.16 mg/L (25 °C, $\log K_{ow} = 4.5$). The chemical structure of TBBPA is shown in Fig.S1.

### 2.2. Synthesis of graphene oxide (GO) and S-RGA

GO was prepared via an improved Hummers' method [28]. Through sonication for 1 h, 40 mg GO powder was dispersed in 20 mL deionized water, After the sonication, 200 mg of $NaHSO_3$ was added and the solution was placed in an ultrasonic for 5 min. The resultant slurry was then heated at 95 °C for 3 h. The reduced GO hydrogels (S-rGH) were dialyzed for 3 d and then freeze-dried for dried 24 h. Remnant water in the samples was removed in a vacuum drying oven at 105 °C for overnight to obtain S-RGA.

### 2.3. Characterization

SEM analyses were performed with a field emission scanning electron microscope (MERLIN, Germany) at an acceleration voltage of 5 kV and energy dispersive X-ray spectra (EDS) were conducted on a JEOL-2010 microscope operating at an accelerating voltage of 200 kV. Powder XRD; (D/max-IIIA, Rigaku, Japan) was used to investigate the crystal structure. Raman spectra were obtained on a Renishaw Micro-Raman Spectrometer using 532 nm laser excitation. The surface functional groups of the sample were detected using FT-IR spectra (Nexus Por Euro, USA) from 400 to 4000 $cm^{-1}$. XPS analysis was performed with an Axis Ultra DLD (Kratos, England). The specific surface area and pore size were calculated from the adsorption- desorption isotherm of $N_2$ at 77 K by the BET and Barrett-Joyner-Halenda (BJH) method on an ASAP 2020 mesoporou physissorption analyzer. Zeta potential was determined using a Malvem Zetasizer Nano-ZS90

The concentrations of TBBPA were detected using ultra performance liquid chromatography (UPLC, Waters, USA). An isocratic elution program with acetonitrile/water (78:22, v/v) was used for the mobile phase. The flow rate was maintained at 0.3 mL/min, and the injection volume was 4 μL. The detection wavelength was 220 nm, and the temperature of the column was 303 K.

### 2.4. Batch adsorption experiments

#### 2.4.1. Adsorption experiments

To determine the adsorption capacities of S-rGA for TBBPA, as well as the influence of the initial TBBPA concentration, pH and