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# Preparation of 4-butylaniline-bonded attapulgite for pre-concentration of bisphenol A in trace quantity

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ABSTRACT

Ring-opening reaction with synchronous hydrolysis was used to prepare 4-butylaniline-modified attapulgite (abbreviated as BA-ATP) for pre-concentration of bisphenol A (BPA) in trace quantity. The preparation was achieved under mild condition, and the material was characterized by Fourier transform infrared spectroscopy (FT-IR), elemental analysis, nuclear magnetic resonance (NMR) and scanning electron microscopy. BA-ATP was used in solid phase extraction (SPE), and SPE was performed in a neutral condition without regard to ionic strength. The results indicate that BA-ATP has high affinity to BPA with a maximum adsorption amount of 44 mg $g^{-1}$, and the adsorption can be described by Langmuir isotherm model. The content of bisphenol A in water samples was analyzed by HPLC method with the pre-concentration using BA-ATP. The limit of detection (LOD) can be as low as 3.9 ng $mL^{-1}$, and the average recoveries are in a range of 93–97% with relative standard deviation (RSD) of less than 2%.


## 1. Introduction

BPA, as a mass-produced chemical [1], is widely applied to manufacture plastic products [2,3], such as polycarbonate containers for food and beverages [4]. As an endocrine disruptor, BPA was in connection with all sorts of health problem, including heart disease, cancers etc [5], and BPA may affect tumor progression and therapeutic efficacy [6,7]. Meanwhile, it can harm the reproductive system of wildlife and humans [8]. The Tolerable Daily Intake (TDI) of BPA has been established by the European Food Safety Authority (EFSA) in 2006. The TDI for adults and children everyday is 0.05 mg $kg^{-1}$. However, research results show that the low dose effects observed in rodents cannot be ignored [9–11]. The results suggest that the trace amount of BPA for human ought to be concerned and re-evaluated. For determination of trace amount BPA in environmental water sample, it is important to develop high efficient pre-concentrated adsorbents.

Attapulgite (ATP) is a typical fibrillar silicate clay mineral with a formula of $[(Mg, Al, Fe)_5Si_8O_{20}(OH)_2(OH_2)_4]\cdot 4H_2O$ [12]. ATP has abundant reserves in China and exists mainly in Xuyi County of Jiangsu Province [13]. ATP consists of double silica tetrahedral chains linked together by octahedral oxygen and hydroxyl groups containing Al and Mg ions in a chain-like inverted structure, and it has large surface area, porous structure and appropriate cation exchange capacity [14,15]. In recent years, ATP and modified ATP have drawn increasing attention in separation sciences because of its unique physical and chemical properties and possible applications [16–24].

New materials using ATP as a matrix have been applied to realize solid-phase extraction (SPE) of target analytes [25,26]. SPE is one of the most common sample handling techniques because of its advantages such as ease of use, high enrichment factor, rapid phase separation, and low consumption of organic solvents etc. SPE technique has been widely used for isolation and pre-concentration of target analytes in pharmaceutical, clinical, environmental and food chemistry [27–29]. However, there was no report using modified ATP for pre-concentration of BPA until now, and it would be significant to prepare a new material based on ATP for pre-concentration of BPA in trace quantity.

In this work, ring-opening reaction [30] with synchronous hydrolysis [31] was used to prepare BA-ATP under mild condition. BA-ATP was identified through FT-IR, elemental analysis, NMR and scanning electron microscopy, and used in solid phase extraction of trace amount BPA in water sample. To pre-concentrate BPA effectively, effects of pH and ionic strength were investigated. To obtain adsorption capacity for BPA, the adsorption properties were studied according to adsorption isotherm.

## 2. Experimental

### 2.1. Materials

4-Butylaniline (BA, 97%), BPA (99.8%) were purchased from Aladdin Industrial Co. (Shanghai, China). ATP was purchased from

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Xuyi County (Jiangsu, China). Tetraethoxysilane (TEOS) were obtained from Tianjin Guangfu Fine Chemical Research Institute. HPLC-grade methanol were used for the mobile phase and analytical-grade glacial acetic acid and ammonia (25%) were used for controlling the pH value. 3-Glycidyloxypropyltrimethoxysilane (GLYMO) was obtained from Tianjin Heowns Biochem LLC (Tianjin, China). Pure water was obtained from Tianjin Wahaha Co. (Tianjin, China). River water samples were obtained from Qiangzi river (Tianjin, China), followed by filteration through 0.45 μm microporous membrane.

### 2.2. Activation of ATP

ATP (40 g) was immersed in 250 mL of hydrochloric acid solution (10%), and stirred for 6 h under 95 °C to increase the number of surface silanol. The product was centrifuged, washed with distilled water to neutral, washed with ethyl alcohol and dried at 100 °C for 12 h.

### 2.3. Synthesis of BA-ATP

BA-ATP was synthesized according to the method reported by He et al. [31] and Xu et al. [32]. A two-step graft method was adopted as shown in Fig. 1. Firstly, GLYMO and BA were reacted to prepare BA bonded GLYMO (GLYMO-BA). Typically, BA (720 μL) was dissolved in 50 mL of absolute ethyl alcohol. 1.0 mL of GLYMO was added into the BA solution with stirring, and the mixed solution was stirred continuously at 40 °C for reaction of 12 h. Secondly, to achieve surface modification of ATP, 3 mL TEOS, 5 g of ATP were added into the above-mentioned solution, subsequently the suspension solution was stirred at 40 °C for 20 min, and then for 24 h after 1 mL ammonia (25%) and 2 mL pure water were added. At last, the suspension solution was centrifuged, washed with ethyl alcohol five times and dried at 100 °C for 12 h.

### 2.4. Preparation of BA-ATP SPE column

A thin polyethylene cribriform plate was put at the bottom of a 6 mL empty polypropylene SPE cartridge. 1.0 g BA-ATP was added into the cartridge, and then, the solid particle was covered by a thin polyethylene cribriform plate and compacted to ensure the upper surface flat and homogeneous.

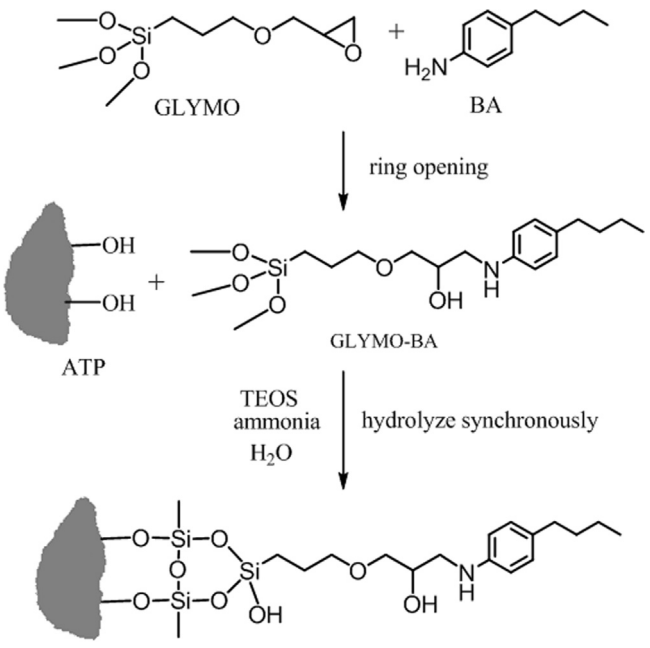


**Fig. 1.** Schematic diagram for the synthesis of BA-ATP.

### 2.5. SPE operation

SPE operation was performed on the base of the work by Irakli [33]. Prior to SPE, the cartridge was conditioned thrice with 2 mL of methanol and 2 mL of water, respectively. Water sample was filtered with the filter paper and adjusted the pH value with 0.1 M HCl or NaOH solution if necessary. Subsequently, to preconcentrate BPA, the water sample was gradually added into the cartridge by an assembled funnel, and allowed to pass through the cartridge with negative pressure. After washing with 2 mL of water and vacuumizing for 30 s, the retained constituents were eluted with methanol (0.5 mL × 3), followed by dilution to 2 mL with methanol. Finally, the solution was shaken well and filtered through a 0.45 μm millipore filter for HPLC analysis.

### 2.6. HPLC separation

HPLC analysis was performed using a Waters 1525 HPLC pump connected with a Waters 2996 photo-diode array detector. Separation was achieved using Thermo Syncronis column (4.6 mm i.d. × 250 mm, 5 μm), with methanol (solvent A) and aqueous solution (0.2% acetic acid, solvent B) as a mobile phase (70/30, v/v). Flow rate was maintained at 0.8 mL $min^{-1}$, column temperature was room temperature, PDA detection wavelength was 228 nm, and injection volume was 15 μL.

### 2.7. Adsorption properties

To investigate the adsorption properties, the adsorption isotherms were studied. 100 mL BPA aqueous solution with the concentrations ranged from 0.5 to 2.5 mmol $L^{-1}$ was preconcentrated following the procedures described in Section 2.5, and the diluted solution after SPE was analyzed by HPLC. Adsorption efficiency was calculated as the ratio of the desorbed amount to that in the initial solution. The adsorption isotherm was plotted in the adsorption efficiency versus the initial concentration. To investigate the adsorption capacity of the absorbent accurately, the adsorption-desorption process of each concentration was repeated for three times, and the average values of three times were used to plot the adsorption curve.

## 3. Results and discussions

### 3.1. Characterization of BA-ATP

#### 3.1.1. Morphological structure of BA-ATP and ATP

BA-ATP and ATP particles were tested with scanning electron microscopy. Fig. 2 shows the surface structure of BA-ATP and ATP under the magnifications of 2000 (Figs.2a, 2d), 5000 (Figs.2b, 2e) and 10000 (Figs.2c, 2f). It can be seen that the size of the particles is almost unaltered for BA-ATP and ATP, but the texture surface of BA-ATP particles is more coarse due to the hydrolysis. The result indicates that the silanization was achieved on the surface of ATP. In addition, the rugged surface of the material could guarantee enough pore spaces for a good penetrability.

#### 3.1.2. Infrared spectrum of BA-ATP

To ascertain the formation of BA-ATP, FT-IR spectra were measured for ATP and BA-ATP, respectively, as shown in Fig. 3. Compared with the spectrum of ATP, new peaks can be found in the spectra of BA-ATP. The features around 2931 and 2875 $cm^{-1}$ come from CH stretching vibrations, respectively. The peak at