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Enhanced adsorption and photo-degradation of bisphenol A by β-cyclodextrin modified pine sawdust in an aquatic environment

Yanbo Zhou*, Ruzhuang Zhang, Ke Chen, Xuanran Zhao, Xiaochen Gu, Jun Lu

Key Laboratory of Coal Gasification and Energy Chemical Engineering of Ministry of Education, East China University of Science and Technology, Shanghai 200237, PR China

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ABSTRACT

The occurrence of bisphenol A (BPA) raised significant concerns about potential adverse impacts on environmental health, and its removal has become a hot research topic. We conducted batch adsorption and photo-degradation experiments to determine the removal performance of BPA by β-cyclodextrin (β-CD) modified pine sawdust (CD-PS) in an aquatic environment for the first time. Pine sawdust (B-PS) was treated by NaOH firstly and then modified by β-CD. The adsorption behaviour of BPA on the B-PS and CD-PS were observed to follow Langmuir and pseudo-second-order kinetic models, and that CD-PS had a 1.2 times higher adsorption capacity than B-PS. At 25 °C and pH = 7.0, the maximum adsorption capacity of CD-PS reached 0.0319 mmol/g. Moreover, the effects of β-CD, CD-PS and B-PS on the photo-degradation of BPA were compared under UV irradiation, indicating that CD-PS significantly enhanced the removal efficiency. Additionally, the "saturated" CD-PS could be regenerated several times using UV irradiation without loss during BPA adsorption process. Results of this work demonstrate that β-CD immobilized on the surface of CD-PS could be acted as an excellent catalyst for BPA removal, and a possible reactive mechanism was further proposed in this regards. These observations indicate that the CD-PS system can remediate BPA-polluted aquatic environment very well.

1. Introduction

The occurrence in water resources of endocrine disruptors has become a global problem and raised concerns due to its potential negative effects on human health. Bisphenol A (BPA), as one of the most common endocrine disruptors, is an important raw material widely used for the production of epoxy resins and polycarbonate plastics [1]. BPA is inevitably released into the natural environment during the manufacture process or by leaching from the products, thus inflicting reproductive damage on living creatures once released and accumulated in nature [2,3]. Recently, the detection and analysis of BPA in the aquatic environment have been intensively investigated. In general, BPA concentrations vary in surface waters from <0.1 μg/L to 2.0 μg/L [4]. However, recent investigation shows that the BPA concentrations in the 16 major rivers of Taiwan ranged from 0.01 to 44.65 μg/L [5]. Therefore, a rapid, convenient and effective method for the treatment of BPA is highly desired.

Adsorption is among the best applied water treatment technologies and capable of removing various organics in water [6], even at low concentrations [7]. From the perspective of economy and efficiency, it is a promising way to convert agro-industrial or municipal waste materials into adsorbents as alternative for typical adsorbents [8,9]. Agricultural waste materials have been used to adsorb heavy metals and organic pollutants both in their natural form and after physical or chemical modification [10,11] .For example, natural rice husks [12], cotton stalks [13] and chemically modified hardwood powder [8] can remove heavy metal ions and organic pollutants efficiently.

Nonetheless, a concern with this alternative is the reusability of the adsorbents after saturated adsorption. Furthermore, regenerating spent adsorbents is energy intensive (requiring heating at high temperature or washing by organic solvent) and does not fully restore performance. Therefore, determining how to regenerate and maintain the performance of the spent adsorbent is a significant problem that attracts much interest in this field.

Cyclodextrins (CDs) have gained prominent attention in recent years because their cavities can bind aromatic molecules and other small organic molecules [14,15]. Consequently, CDs have been employed as eco-friendly modifiers for new adsorbents without side-effects to humans. Moreover, these modified adsorbents exhibit high adsorption capability [16,17]. In our previous studies, β-cyclodextrin (β-CD) modification can enhance the adsorption capability of sawdust significantly. The modified sawdust is considered

* Corresponding author.
E-mail addresses: zhouyanbo@ecust.edu.cn, hezi001007@163.com (Y. Zhou).

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as a promising adsorbent for organic pollutant removal [18]. Although impressive results were obtained with β-CD modified sawdust, the saturated adsorbents must be urgently regenerated as well. On the other hand, photo-catalytic degradation technology is a promising technology for the removal of organic pollutants from water [19,20]. β-CD can incorporate specific pollutants through the hydrophobic cavity (host–guest inclusion effect). This inclusion promotes the photo-degradation of organic pollutants [21,22]. Wang et al. drew a conclusion that β-CD had a distinct catalytic effect on the photo-degradation of BPA and bisphenol Z in a solution [23,24]. However, β-CD cannot be reused because it dissolves in the treated water in their studies.

In the present work, β-CD was immobilized on pine sawdust to prevent loss and used to remove BPA under UV irradiation. The main purposes of this study are to investigate the enhancement effects of β-CD modification on the adsorption and photo-degradation of BPA, as well as to facilitate the *in-situ* regeneration of exhausted adsorbents by UV irradiation. CD-PS was characterized in detail. Furthermore, the results of BPA removal under different conditions were compared for analysing the contributions of adsorption and photo-degradation.

2. Materials and methods

2.1. Materials

The pine sawdust (PS) was obtained from the local countryside in Liaocheng City, Shandong Province, China. Citric acid, β-CD and the other reagents used were of analytical grade. These compounds were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All working solutions were prepared with distilled water.

2.2. Pretreatment and modification of B-PS

B-PS and β-CD modified pine sawdust (CD-PS) were prepared using the method which was presented in our previously published paper [18]. The PS was washed several times with fresh water and dried at 60 °C for 12 h. The dried PS was then milled and sieved to fractions measuring 0.15–0.25 mm. These fractions were cooked in a 0.5 mol/L NaOH solution for 1 h at 100 °C. The slurries were rinsed with deionized water to remove the base or colour factors retained in the PS. Finally, the cleaned and washed PS was dried at 60 °C for 24 h and labelled as B-PS. The purpose of the pretreatment process was to increase the proportion of active surface area and to prevent the elution of tannin compounds that could stain the treated water [25].

B-PS (1.0 g), citric acid (0.3 g), sodium dihydrogen phosphate (0.125 g), β-CD (0.15 g) and deionized water (10 mL) were mixed in a 100 mL flask and vibrated with ultrasound for 15 min. The flask was then placed into a boiling water bath for the chemicals to penetrate efficiently into the B-PS. After 1 h, the mixture was heated in an electric thermostatic oven at 145 °C for 4 h. Following a period of natural cooling, the crude product was soaked and washed with adequate amounts of deionized water to remove any residue from β-CD, citric acid and sodium dihydrogen phosphate. The samples were filtered and dried at 60 °C for 24 h, stored in a silica-gel desiccator and labelled as CD-PS.

2.3. Characterization of B-PS and CD-PS

Scanning electron microscopy analysis was performed using a Phillips SEM 501 electron microscope. Thermo-gravimetric analysis (TGA) was conducted using a Mettler-Toledo DTA/TGA instrument at a temperature range of 40–700 °C and a heating rate of 10 °C/min under nitrogen flow. Fourier transform infrared spectra (FT-IR) were detected in the 400–500 cm^{-1} region using spectroscopic quality KBr powder on a Nicolet Avatar 360 FT-IR spectrometer.

2.4. Adsorption experiments

In this set of experiment, contribution of adsorption to the overall BPA removal was investigated. And the effects of adsorption time and initial concentrations on BPA adsorption efficiency were tested. 1.0 g of B-PS or CD-PS was added to a flask containing 500 mL of BPA solution (0.05 mmol/L). This mixture was magnetically stirred at 20 °C. The adsorption amount (q_t) was calculated at certain time intervals according to BPA concentration (c_t, mmol/L). Then, the adsorption experiment was conducted with different initial concentrations (0.01, 0.025, 0.05, 0.075, 0.1, 0.125 mmol/L). The equilibrium adsorption capacity (q_e, mmol/g) was calculated according to the BPA concentration (c_e, mmol/L) reported after 240 min. This time period is adequate to ensure adsorption equilibrium.

BPA concentrations were measured on the high-performance liquid chromatography (HPLC, LC-20A, Shimadzu International Trading [Shanghai] Co., Ltd) system equipped with an Alltima C18 reverse phase column (3.2 × 150 mm, 5 μm) at 30 °C. The mobile phase was composed of 70% methanol and 30% water. The flow rate was set at 1.0 mL/min. The detector wavelength was set at 278 nm.

2.5. Removal of BPA under UV irradiation

A series of glass flasks (25 cm in length, 8 cm in diameter) with a wall thickness of 4 mm were employed as reactors. For each experiment, 500 mL BPA solution was introduced into the reactor. And the reactor was stirred magnetically under a constant rate throughout the experiment and irradiated with a UV lamp (15 W, $\lambda_{max} = 254$ nm, length = 21 cm, diameter = 15 mm and radiation intensity = 21–24 μW/cm^2; Shanghai Lamp Co. Ltd, Shanghai, PRC). In this section, initial concentration of the BPA solutions was 0.05 mmol/L unless otherwise specified. During the experiment, water samples were taken at different intervals (0, 15, 30, 45, 60, 90 and 120 min), centrifuged and quantified for BPA using HPLC.

To investigate the effects of different materials on BPA photodegradation, a set of experiments were conducted with BPA solution only, BPA solution added with β-CD (0.05 mmol/L), B-PS (2.0 g/L) and CD-PS (2.0 g/L), respectively.

After 240 min adsorption, the saturated B-PS and CD-PS were applied to remove BPA under UV irradiation in order to investigate the side-effect of this adsorption on overall BPA removal. B-PS and CD-PS were also subjected to washing with water and filtration before the next use. Other steps in this process were identical to those of the previously mentioned procedure.

BPA solutions containing either B-PS or CD-PS (2.0 g/L) were placed in darkness for 2 h to reach adsorption equilibrium and then irradiated by UV light for another 2 h. Photodegradation of BPA was conducted in the absence of any adsorbent as a control. And the initial concentrations for control experiments were set as the equilibrium concentrations ($C_{120\ min}$) after adsorption in the presence of B-PS and CD-PS. Other steps in this process were identical to those of the aforementioned procedure.

B-PS and CD-PS were applied repeatedly to remove BPA under UV irradiation and to determine their reusability of photodegradation. After each use, the B-PS and CD-PS were washed with fresh water, dried and then added to 500 mL fresh BPA solutions under UV irradiation. The above process was repeated 5 times.

All experiments were replicated three times, and the data were presented as mean values. In addition, error bars were introduced