



Adsorption of estrone with few-layered boron nitride nanosheets: Kinetics, thermodynamics and mechanism

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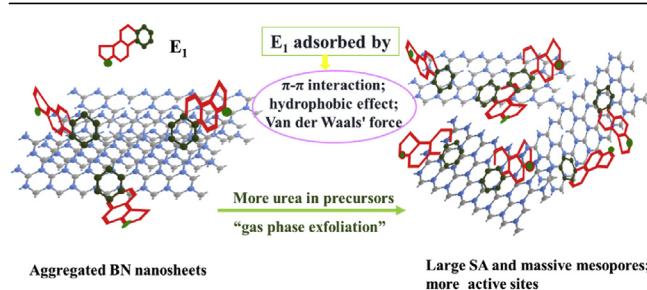
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HIGHLIGHTS

- Porous and fewer layer BNNs were prepared with the ratio regulation of urea and boric acid.
- The E_1 adsorption capacity could reach to 249.15 mg E_1/g with thinner BNNs.
- E_1 adsorption on BNNs was spontaneous, enthalpy-retarded, entropy-driven, and mostly chemical adsorption.
- The removal efficiency of E_1 by BN-60 regenerated after 6 times was above 95%.

GRAPHICAL ABSTRACT



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ABSTRACT

Boron nitride Nanosheets (BNNs) was fabricated with a method of heating the mixture of boric acid and urea in N_2 atmosphere and used to remove estrone (E_1) from water. The obtained BNNs exhibited a higher surface area of $896 \text{ m}^2/g$, a large pore volume of $0.76 \text{ cm}^3/g$, and only few layers (0.398 nm) with the boric acid and urea ratio of 1:80. The layer number of BNNs decreased from 15 to 4 with the mole ratio of boric acid and urea decreasing from 1:20 to 1:80, which was identified by SEM, TEM, AFM and BET measurements. More importantly, BNNs presented an outstanding adsorption performance for estrone with the adsorption capacity of $249.15 \text{ mg } E_1/g$ BNNs. The adsorption process could be best fitted by pseudo second-order kinetic model and the equilibrium data at different temperatures were well fitted by Langmuir isotherm model. The thermodynamics analysis revealed that E_1 adsorption on BNNs was spontaneous ($\Delta G = -29.33 \text{ kJ mol}^{-1}$), enthalpy-retarded ($\Delta H = 29.75 \text{ kJ mol}^{-1}$), entropy-driven ($\Delta S = 198.26 \text{ J mol}^{-1} \text{ K}^{-1}$), and mostly chemical adsorption. The adsorption rates of E_1 in water were sharply enhanced with thinner BNNs as adsorbents and removal efficiency by BN-60 regenerated after 6 times was above 95%, it was shown that the surface areas, mesopores and remarkable structure played important roles in the adsorption process. The firmness of E_1 onto BNNs and the stability of adsorption efficiency made BNNs as a potential adsorbent for efficient removal of E_1 from wastewater.

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1. Introduction

As emerging organic contaminants, endocrine-disrupting

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chemicals (EDCs) have attracted a lot of attention in recent decades due to their high frequent occurrences in the environment and their long-term potential hazards to water ecosystem and drinking water. The natural steroid estrogens, including estrone (E_1), 17 β -estradiol (E_2) and estriol (E_3), mainly released by humans and livestock, are most commonly detected in wastewater and surface water (Panter et al., 1999; Feng et al., 2010). Although the estrogens were found at low levels, usually in ng L⁻¹ contents, they might affect the health of fishes, wildlife or their progenies by interacting with the endocrine system through the food chains and the biological accumulation (Mantovani, 2001; Rozati et al., 2002; Pereira et al., 2011b). They would interfere with the hormone secretion and metabolism, and influence the reproduction and development of aquatic organisms by disrupting the immune and neurological functions (Racz and Goel, 2010; Sumpter and Jobling, 2013). E_1 was the most common natural estrogens and the discharged level of E_1 from STPs was about 10 times more than E_2 (D'Ascenzo et al., 2003). It was inferred that E_1 contributed largely to estrogenic activity of the water environment and living beings (Creusot et al., 2014). Therefore, an effective method is urgently needed to remove E_1 from the environmental water.

Several methods were adopted to remove estrogens from water. It was thought that these hormones could not be removed by the conventional treatment methods especially at very low levels (Ternes et al., 2002; Snyder et al., 2003; Gokce and Arayici, 2016). Biological treatment such as activated sludge and biological trickling filters could not remove most of the estrogenic contaminants (Servos et al., 2005; Urase and Kikuta, 2005). Physicochemical methods such as coagulation, flocculation, or lime softening were not efficient to reducing the quantity of EDCs as the previous studies described (Petrovic et al., 2003; Westerhoff et al., 2005; Vieno et al., 2006). Chlorination might result in the odors and disinfection by-products (DBPs) in water (Hozalski et al., 2001; Sadiq and Rodriguez, 2004; Gopal et al., 2007). Ozonation was expensive, while ultraviolet (UV) photolysis and ion exchange were not considered as a reasonable method to remove micropollutants (Adams et al., 2002). Adsorption was deemed to be an effective method for E_1 removal without by-products and its low-energy consumption, which could compose a potential risk to the ecological environment (Pereira et al., 2011a). Many solid adsorbents had been applied to remove estrone from sewage such as hollow fibre membrane (Chang et al., 2002), carbonaceous resin and high-silica zeolites (Rossner et al., 2009), carbon nanotubes (Al-Khateeb et al., 2014), highly crosslinked polymeric adsorbents (Solak et al., 2014), immobilized HRP (horseradish peroxidase) on a novel enzyme support (Xu et al., 2016) and activated carbon (Gokce and Arayici, 2016). However, they frequently suffered the disadvantage of limited adsorption capacity (Lian et al., 2013) with less active adsorption sites and the poor regeneration ability which was hindered by their chemical instabilities.

Recently, BNNSs had drawn numerous attentions due to its unique properties like remarkable electrical insulation, ultraviolet (UV) photoluminescence (Li et al., 2012), high thermal conductivity, higher mechanical properties (Falin et al., 2017), high resistance to oxidation (Li et al., 2014b) and high chemical stability (Zhu et al., 2006; Lee et al., 2010; Lei et al., 2013). In addition, BNNSs had been proven as excellent adsorbent with high surface area, abundant pore structures and high capacity for various substances, such as hydrogen (Lian et al., 2012; Weng et al., 2014), dye (Li et al., 2015), oil (Lei et al., 2013), metals (Li et al., 2014a), dibenzothio-*phene* (Xiong et al., 2015a), aromatic molecules (Cai et al., 2016b) and other organic pollution (Zhang et al., 2012). However, to the best of our knowledge, BNNSs as the adsorbent for E_1 removal from water has not been reported till now. Compared with the traditional carbon materials, BNNSs could be an ideal adsorbent with

the highly stable properties under harsh conditions (Li et al., 2015). Exposing adsorption sites for BN materials are the key breakthrough to increase the adsorption ability of BN. In the present study, four BNNSs rooted with different proportions of boric acid and urea were prepared and applied to remove E_1 by batch experiments. The adsorption process of E_1 onto BNNSs was investigated and the adsorption equilibrium, adsorption kinetics, adsorption isotherms, adsorption capacities and regeneration were presented in this paper. The effects of layer number, temperature and the initial E_1 concentrations were also studied. The present results would provide us the theoretical and technological basis for adsorption application in micro pollution removal.

2. Materials and methods

2.1. Synthesis of BNNSs

BN nanosheets were synthesized with boric acid and urea as reactants using a previously reported method (Nag et al., 2010). Boric acid (TianDa Chemical Reagent Co., Ltd, Tianjin) and urea (BaSiFu Chemical Reagent Co., Ltd, Tianjin) were analytical grades (A.R.) and used without further purification prior to use. They were mixed (weight 5 g) with different mole ratios (1:20, 1:40, 1:60 and 1:80) and dissolved in 80 mL ultrapure water. After heating at 65 °C in a thermostat water bath for about 8 h, dry powders were heated at 900 °C for 5 h with a heating rate of 5 °C min⁻¹ in an N₂ atmosphere, then white boron nitride powders were formed, and the sample was cooled to room temperature. The corresponding prepared materials were named as BN-20, BN-40, BN-60 and BN-80.

2.2. Characterization and chemical analysis

The X-ray powder diffraction (XRD) pattern of BNNSs was measured using a Germany Bruker-D8 ADVANCE X-ray diffractometer and Cu K α radiation. Fourier transform infrared (FTIR) spectra were recorded by a Nicolet FTIR spectrophotometer (Nexus 470, Thermo Electron Corporation), operating in the wavenumber of 400–4000 cm⁻¹ with a resolution of 4 cm⁻¹. The samples were diluted with KBr power with the sample/KBr ratio of 1:50 and pressed pellets for testing. Raman spectra were measured using a Renishaw inVia Raman microscope at $\lambda = 633$ nm laser excitation. X-ray photoelectron spectroscopy (XPS) measurements were measured with a PHI-5700 spectrometer, using a monochromatic Al K α X-ray radiation at 1486.6 eV. The surface morphology was observed using a field-emission scanning electron microscope (SEM, S-4700, Hitachi Ltd.), and samples were prepared by sticking few powders to conductive tapes and metal spraying. Transmission electron microscopy (TEM) micrographs were taken with an H-7650 transmission electron microscope (Hitachi Ltd.) at 150 kV for TEM and 200 kV for HRTEM. Samples were prepared by dropping a drop of dilute BN-ethanol suspension onto a copper grid and evaporating the solvent. Atomic force microscopy (AFM) images were obtained using a NanoMan instrument. Samples were diluted with water, and then a drop of solution was placed on a mica plate for measurements. Brunauer-Emmett-Teller (BET) surface areas and pore-size distributions were obtained from a nitrogen adsorption-desorption isotherm at 77 K using an ASAP2 20M device (Micromeritics Instrument Co.).

High-performance liquid chromatography (HPLC) equipped with UV detector (SPD-10A VP, SHIMADZU, 280 nm applied) and an Extend-C18 reversed-phase column (LC-10AT VP, SHIMADZU) was used to analyze E_1 concentration. The mobile phase was acetonitrile/water (50:50, v/v). Isocratic elution with a constant flow rate of 1.0 mL min⁻¹ at room temperature and a pressure of about 120 bars were used. The injection volume of E_1 solution was 20 μ L.

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