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Bromate removal from water by polypyrrole tailored activated carbon

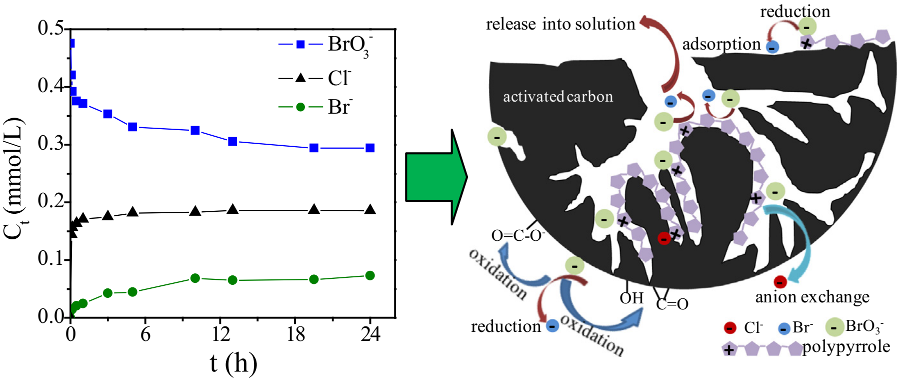
Siqi Hong, Shubo Deng [*], Xiaolong Yao, Bin Wang, Yujue Wang, Jun Huang, Gang Yu

School of Environment, Beijing Key Laboratory for Emerging Organic Contaminants Control, State Key Joint Laboratory of Environment Simulation and Pollution Control (SKLESPC), Tsinghua University, Beijing 100084, China

HIGHLIGHTS

- Ppy-NAC is prepared by in situ polymerization of pyrrole in activated carbon.
- Ppy-NAC has the high sorption capacity of 62.5 mg/g for bromate at pH 6.
- Anion exchange is mainly responsible for bromate sorption on Ppy-NAC.
- Adsorbed bromate can be reduced to bromide on the surface of Ppy-NAC.
- Produced bromide ions are released into solution and adsorbed on surfaces.

GRAPHICAL ABSTRACT



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ABSTRACT

Bromate adsorption behavior and mechanism were examined on a novel adsorbent devised via depositing polypyrrole (Ppy) into the pores of nut shell-based activated carbon (NAC). This Ppy-tailored activated carbon (Ppy-NAC) hosted positively charged polypyrrole functionality that offered considerable sorption capacity for bromate. Specifically, the Ppy-NAC achieved a bromate loading of 62.5 mg/g in the adsorption isotherm, 8.3 times higher than the pristine NAC. The adsorption isotherm data were fitted well by the Langmuir model, and the adsorption kinetics were described well by the pseudo-second-order equation. The occurrence of chloride ions in solution showed that Cl^- exchanged with BrO_3^- during the adsorption process. The X-ray photoelectron spectroscopy (XPS) analysis and the detection of bromide in solution indicated that some of BrO_3^- were reduced to Br^-, and the produced bromide ions were released to the solution and adsorbed on the Ppy-NAC. The increase of oxygen-containing functional groups on Ppy-NAC after adsorption verified that the redox reaction occurred during the adsorption process. The mechanisms of bromate removal by the Ppy-NAC included ion exchange and reduction reaction of bromate on the Ppy-NAC surfaces.

1. Introduction

Bromate (BrO_3^-) is formed as a disinfection by-product during ozonation of water containing bromide (Br^-). Bromide has been widely detected in natural waters such as rivers and reservoirs [1]. If such water is used as resource of potable water and disinfected by ozone, bromate would be formed in drinking water. International Agency for the Research on Cancer (IARC) has classified bromate as potential carcinogen. The maximum contaminant level (MCL) for bromate in drinking water established by the World Health Organization (WHO) is 10 μg/L [2].

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[*] Corresponding author.
E-mail address: dengshubo@tsinghua.edu.cn (S. Deng).

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Since bromate is formed during ozonation of bromide-containing water, many approaches have been tried during the ozonation process to control bromate formation. Ammonia addition [3] and pH depression [4] are the most commonly strategies to eliminate bromate formation, but pH depression approach forms brominate organics such as bromoform and cyanogen bromide during the process and ammonia addition leads to second pollution [1]. Therefore, some researchers aim the post treatment of bromate contaminated water. Conventional post treatment technologies regarding bromate removal include ion exchange [4], reduction by zero-valent iron [3], bio-technology [5], photocatalysts [6], and adsorption [7]. Among these methods, adsorption is considered as the most effective technology capturing bromate due to fast and easy operation. Researchers have used several adsorbents such as nano-Al_2O_3, granular ferric hydroxide, quartz sand and activated carbon to remove bromate, but their sorption capacities are usually unsatisfactory [8–11]. Although activated carbon is widely used for contaminants removal from water, pristine activated carbon offers scant bromate sorption capacity [12,13]. Therefore, it is necessary to develop efficient adsorbents with high adsorption capacity for bromate.

Adsorbents with nitrogen-containing groups offer high adsorption capacity for anions due to the positively charged surfaces [14–18]. Researchers used different nitrogen-containing functional groups such as cationic surfactant and quaternary ammonium to modify activated carbons for the enhancement of sorption capacity for anions [17,19,20]. However, some of the preloaded nitrogen-containing chemicals subsequently leach (3–10%) during water treatment [21–23]. Polypyrrole is a well-known semiconducting polymer due to its high nitrogen content, environmental stability, and simple polymerization. It has been deposited on sawdust [24], rice hull ash [25] and nanotubes [26] for removing anions from water. For deposition of polypyrrole onto the surface of substrates, chemical polymerization has been preferred because it has provided suitable thickness and uniformity of the film [27,28]. During the in situ chemical polymerization, the pyrrole monomer is oxidized by ferric chloride [29]. Following oxidation with $FeCl_3$, some of the nitrogen atoms in the polypyrrole matrix can carry positive charges, favorable for the adsorption of anions. The polypyrrole tailored activated carbon with high content of nitrogen and positive charges exhibited an elevated sulfate sorption capacity in our previous study [30], but excess polypyrrole molecules would clog the most pores of activated carbon leading to unaccessible adsorption sites for anions. By now, polypyrrole tailored activated carbon has not been used to remove bromate from water, and depositing moderate polypyrrole into activated carbon would achieve considerable adsorption capacity for bromate.

The overall objectives of this research include (1) depositing polypyrrole into the pores of nut shell based activated carbon to achieve high sorption capacity for bromate; and (2) investigation of bromate adsorption and reduction mechanisms on this Ppy-tailored NAC. It is reported that the reduction of BrO_3^- to Br^- occurred during the sorption of bromate on pristine activated carbon [31], thus the adsorption and reduction mechanisms of bromate on the Ppy-tailored NAC may be complicated and need to be clarified clearly.

2. Materials and methods

2.1. Preparation of polypyrrole-modified activated carbon

According to our previous study [30], some micropores of activated carbon were blocked when pyrrole concentration was higher than 1 mol/L, and thus the pyrrole concentration at 1 mol/L was used in this study. The preparation method for Ppy-tailored activated carbon was described below. The nut shell based activated carbon (NAC) was ground and sieved to 200–400 mesh size (38–75 μm) and then washed with deionized water for several times. Next, 1.5 g of NAC was added into 15 mL of 1 mol/L pyrrole solution and shaken under a nitrogen atmosphere in a shaker at 160 rpm and 25 °C for 16 h. Thereafter, the NAC was filtered and dispersed in 50 mL of 1 mol/L $FeCl_3$ solution and the mixture was shaken at 160 rpm and 25 °C for 6 h. Finally, the as-prepared adsorbent was rinsed with copious deionized water and dried under vacuum at 60 °C till constant weight. The obtained adsorbent was denoted as Ppy-NAC.

2.2. Zeta potential measurement

The zeta potentials of pristine NAC and Ppy-NAC were analyzed at 25 °C with a zeta potential analyzer (Delsa Nano C, Beckman Coulter, USA). The powdered samples were suspended in ultrapure water, and then the solution pH was adjusted with 0.1 mol/L NaOH or 0.1 mol/L HCl solution to a desired value. The solution pH was recorded after stabilization, and the supernatant with small particles was used to conduct zeta potential measurements for five times. Finally, the average zeta potentials were plotted against the equilibrium pH.

2.3. XPS analysis

Before the measurements, the samples of pristine NAC, Ppy-NAC and Ppy-NAC after bromate adsorption were washed with deionized water for three times and dried at 60 °C for 6 h. XPS analysis of these samples was performed using a XPS instrument (Escalab 250Xi, Thermo Scientific) with a monochromatized Al Kα X-ray source. First, the wide scan identified all the detectable elements (C, N, O, Br, and Cl) through high generation energy and a short dwell time. Next, the instrument conducted narrower and more detailed scans of selected peaks to quantify chemical state information. All binding energies were referenced to the neutral C 1s peak at 284.6 eV to compensate for the surface charging effects. The software package XPS peak 4.1 was used to fit the XPS spectra peaks.

2.4. Bach adsorption experiments

Batch adsorption experiments were conducted with 20 mg of activated carbon in 50 mL of bromate solution. The mixture solution was shaken for 24 h at 25 °C on a thermostat vibration shaker with a speed of 160 rpm. After adsorption, the water sample was filtered by the syringe with a 0.45 μm nylon fiber filter, and the remaining BrO_3^- and Br^- concentrations were monitored. Each experiment was duplicated, and the average values were adopted.

Batch adsorption kinetic tests were conducted in 60 mg/L of bromate solution at pH 6.0. In bromate adsorption isotherm tests, bromate concentrations of 0.5, 1, 5, 10, 20, 25, 40, and 60 mg/L were used and solution pH was 6.0. The sorption time of 24 h was chosen because the adsorption equilibrium could be achieved according to the kinetic study. Bromate adsorption isotherm was also conducted at low initial bromate concentrations (80, 100, 200, 300, 500, 700, and 800 μg/L), and 20 mg of activated carbon was added into 100 mL bromate solution at pH 6.0.

To investigate the effect of pH on the bromate adsorption, pH of bromate solutions (C_0 = 1, 20, 60 mg/L) was adjusted from 2 to 11.5 using 0.1 mol/L HCl and NaOH solutions. These experiments were conducted with 20 mg of Ppy-NAC in 50 mL of bromate solution.