Time-dependable TBBPA Accumulation on Long-Term Used Biochar

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1. Introduction

Attention has been recently drawn to the environmental behaviors of Tetrabromobisphenol A (TBBPA), a widely used brominated flame retardant which accounts for 60% of total commercial market (Zhong et al., 2012). It poses a potential threat to the soil, water, atmosphere and living organisms (Peng et al., 2017). Adsorption is an effective method in pollution control and has been used in the removal of a wide variety of pollutant (An et al., 2011; An et al., 2017; Nguyen et al., 2015). There is also an increasing amount of interest in biochar, which is a cost-effective adsorbent. Biochar can be produced through the pyrolysis of natural biomass. Biochar surfaces have a large number of exchangeable cations and surface adsorption sites. It contains various functional groups, especially oxygen containing ones. Its adsorption performance can be improved by suitable chemical activation. (Pingree et al., 2016) observed the high adsorption affinity to phenol using wildfire-produced charcoal from woody material. Pinecone biomass is widely available as a low-cost biomass from pine plantations, public parks and residential backyards. Therefore, there is potential for using pinecone-derived activated charcoal as an effective adsorbent for the removal of TBBPA from aqueous solutions.

Furthermore, during a long-term application and retention, the pyrogenic carbon surface properties can be significantly impacted by physical aging process due to temperature change in winter-summer season or day-night cycles (Hale et al., 2011). The behavior changes of long-term biochar can represent its long-term behaviors in multiple areas of different climatic zones.

2. Materials and methods

TBBPA (4,40-isopropylidenebis(2,6-dibromophenol)) was purchased from Aldrich Chemical Co. (WI, USA). Pinecone biomass was collected from Scots pines (*Pinus sylvestris L.*) from southern Saskatchewan, Canada. The procedure of preparing the acid activated charcoals was in accordance with standard method (Peng et al., 2016). The powder was pyrolyzed for 4 h at temperatures 550 in a muffle furnace in an oxygen-limited system to simulate temperatures of surface soil fire (Pingree et al., 2016). The produced biochar was aged and labeled as BC.

Biochar surface were analyzed using FTIR analysis method. Images of the surface morphology of the selected samples were obtained by using a Zeiss Supra 55 VP SEM (Zeiss, Oberkochen, Germany) with an accelerating voltage of 5.00 kV. Batch adsorption experiments were conducted in 20-mL glass vials. Appropriate amounts of biochar was added in vials and placed in a reciprocal shaker at 20 °C and 200 rpm for 24 hours to reach adsorption equilibrium. After adsorption, supernatant was taken out and analyzed by high-performance liquid chromatography (HPLC, Agilent 1260 Infinity, USA). The adsorption amounts and removal efficiency were calculated:

$$Q_t = \frac{(C_0 - C_i)V/1000}{W} \quad (1)$$

$$\%\,removal = \frac{C_0 - C_i}{C_0} \times 100 \quad (2)$$

where Q_t is the adsorption amount in mg/g at time *t*; C_0 and C_i in mg/L are the initial concentration and concentration at time t; V is the volume of solution in mL and W is the total amount of adsorbent in g. The quality assurance/quality control program was followed to ensure the accuracy and reliability of the collected data.

3. Results and discussion

SEM analysis of long-term biochar was carried out to determine surface geometry structure and porosity. SEM images of Fig. 1 shows surface geometry structure of the long term biochar. The aged surface of BC exhibited increased pores with rough layers.

Place Fig.1 here

The FTIR spectra of long-term biochar are shown in Fig. 2. As the figure shown, C–O bending and stretching in ether and carbonate exist. Many peaks related to oxygen-contained functional groups and aromatic-related structure were found. Intensities at 880 cm^{-1} (C=C), 1275 cm^{-1} (carboxylic acid), 1425 cm^{-1} (C–O stretching), 1600 cm^{-1} (C=O stretching) and 1720 cm^{-1} (carbonyl) suggested the carboxyl and aromatic contents in biochars. It indicated that the aromatic structures after long-term aging is not be altered and destroyed.

Fig.3 showed that the adsorption is rapidly occurred in the beginning of first 150 min, FTBCP550 reach the stable point (1.674 mg/g) in 150 min. This result indicated that the surface sites on high temperature biochar after long-term can be quickly filled with TBBPA, suggesting the corrupted surface on the biochar produced from high temperature exhibits the adsorption featured with high porosity and functionality. The high adsorption rate indicated that the TBBPA adsorption might favor the hydroxyl interactions.

Place Fig.3 here

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4. Conclusions

Based on FTIR analysis, SEM image and adsorption study, the results showed that adsorption of TBBPA on long-term presented biochar may involve hydroxyls and their interactive effects. After long-term present, the structure of biochar was not severely altered and the adsorption performance was still suitable for TBBPA immobilization. This results may reveal the long-term application potential of biochar in pollutant removal and storage.

References

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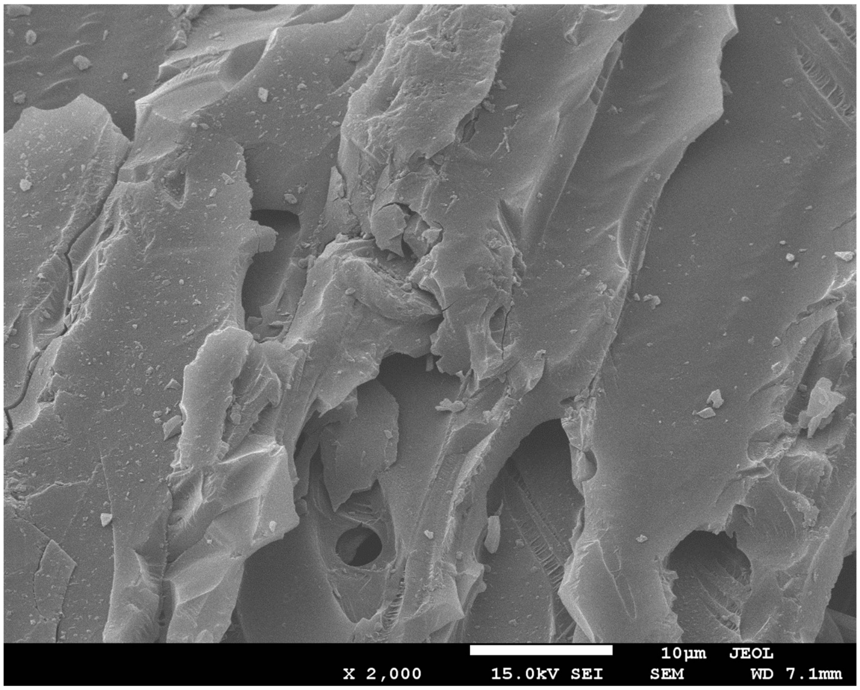

Fig. 1. SEM imaging for long-term present biochar

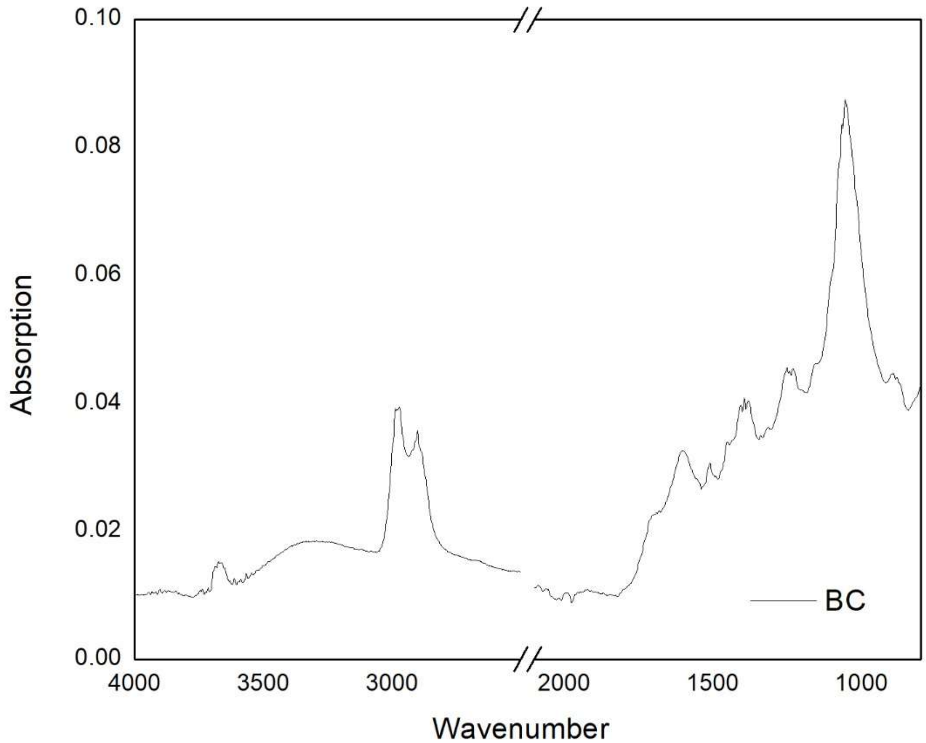

Fig. 2. The FTIR analysis for long-term present biochar

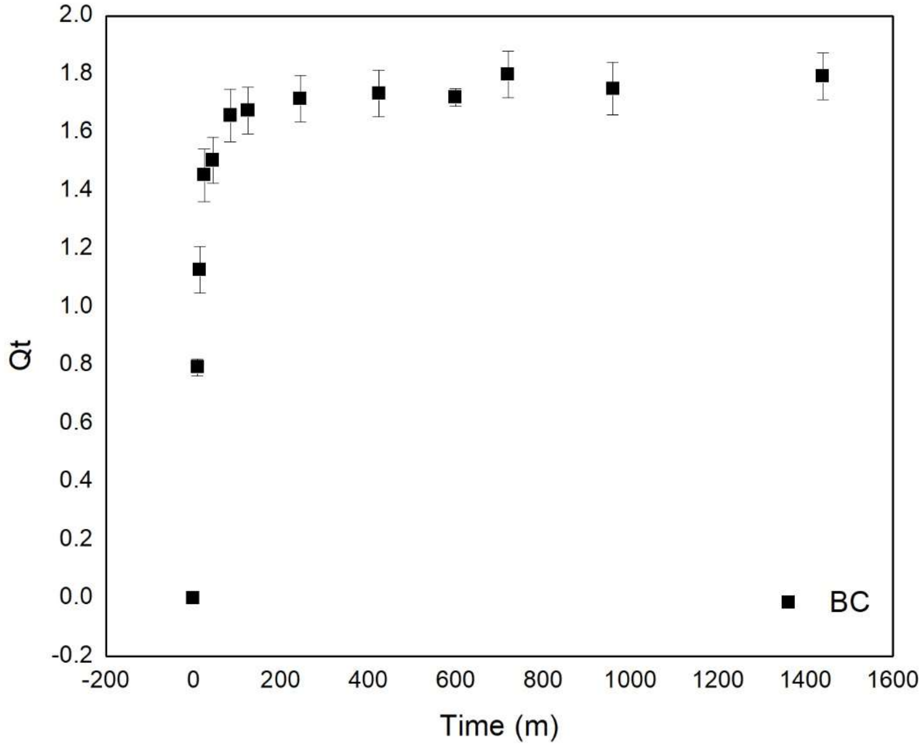

Fig. 3. The adsorption and contact time of long-term present biochar