Journal of Cleaner Production 182 (2018) 372–378

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro

Liquid and vapor phase adsorption of BTX in lignin derived activated carbon: Equilibrium and kinetics study

Dipendu Saha [a], *, Nathan Mirando [a], Andre Levchenko [b]

[a] *Department of Chemical Engineering, Widener University, One University Place, Chester, PA 19013, USA*
[b] *TA Instruments, 159 Lukens Dr, New Castle, DE 19720, USA*

ARTICLE INFO

Article history:
Received 26 June 2017
Received in revised form
21 January 2018
Accepted 7 February 2018
Available online 9 February 2018

Keywords:
Adsorption
BTX
VOC
Activated carbon

ABSTRACT

Benzene, toluene and xylene (BTX) are few of the chemicals that cause environmental pollution in both liquid and vapor phase. In vapor phase, they are classified as volatile organic compounds (VOCs) and cause both indoor and outdoor air pollution. Although different kinds of activated carbons have been used for the adsorptive removal of BTX, the fundamental equilibrium and kinetic data of VOC adsorption in porous carbon are very rare in literature. It order to focus on such fundamental data, in this work, activated carbon was synthesized from de-alkaline lignin precursor by one-step chemical activation with KOH. The resultant carbon has the BET surface area of 2250 m^2/g and total pore volume 1.1 cm^3/g. Equilibrium and kinetics of liquid phase BTX adsorption were measured upto 100 ppm concentration of each the component in water. In vapor phase adsorption, automated VTI-SA + sorption analyzer was employed with nitrogen as carrier gas and equilibrium and kinetic data were recorded as a function of varying relative pressure or dew point (p/p_0) of BTX. For adsorption isotherms, Henry's law, Langmuir, Freundlich and Sips models were successfully employed, whereas for adsorption kinetics, pseudofirst order, pseudosecond order and micropore diffusion model were used to calculate the necessary adsorption parameters.

1. Introduction

Benzene, toluene and xylene (BTX) are the key contributors of volatile organic compounds (VOCs) and cause environmental pollution. Besides their vapor form, the liquid forms of BTX are also released from several industrial or household wastes and causes aquatic pollution. Indoor air quality is an important aspect of human health (Jones, 1999). These pollutants can create moderate to severe health related issues to the person who is exposed to them for a long period of time. These health hazards include eye, skin or throat irritation, headache, nausea, fatigue, dizziness, respiratory disease, weakening of mucus, damage to liver and central nervous system, cancer and immature mortality (Das et al., 2004; Ehrlich et al., 1977; Spengler et al., 2001). These VOCs can serve as the potential precursors for the formation of photochemical smog and a number of toxic byproducts (Dobre et al., 2014), which are extremely hazardous to the health and environment, even in very low concentrations (Dwivedi et al., 2004; Gupta and Verma, 2002).

Among different methods that can remove BTX are absorption, adsorption, condensation, thermal oxidation and catalytic oxidation (Lillo-Ródenas et al., 2005). Within these processes, adsorption in porous materials is considered to be most benign, inexpensive and regenerable process. Porous or activated carbon has been widely studied for their adsorption capacity of BTX molecules. Different types of activated carbons, including activated carbon fibers (ACF) (Foster et al., 1992; Huang et al., 2002; Yun et al., 1998) granular activated carbons (GAC) (Chiang et al., 1999, 2002; Ryu et al., 2002; Yun et al., 1999), activated carbon cloth (ACC) (Dimotakis et al., 1995), biological activated carbon (BAC) (Noll et al., 1989), or activated carbon pellets (Benkhedda et al., 2000) have been employed to remove small amounts of different components of BTX through adsorption process. Different types of precursors, like mesophase pitch (Silvestre-Albero et al., 2010), coconut shell (Kim et al., 2006), wood and different varieties of coal (Lillo-Ródenas et al., 2005) are activated by acid or alkali treatment to synthesize the activated carbons for BTX adsorption. It has been suggested that high surface area and micropore volume of the porous carbon is essential for the efficient adsorption of BTX (Silvestre-Albero et al., 2010; Lillo-Ródenas et al., 2005). In a recent

---

* Corresponding author.
E-mail address: dsaha@widener.edu (D. Saha).

https://doi.org/10.1016/j.jclepro.2018.02.076

simulation study on benzene adsorption onto porous carbon at 303 K, researchers (Huang et al., 2016) demonstrated that benzene molecules were adsorbed in the micropores of 14–18 Å diameters while mesopores provided easy access to the transport of benzene molecules. It was also demonstrated that the favorable sorption energy for benzene adsorption was 37.45 kJ/mol while the separation distance was 5.75 Å from the benzene center of mass to the carbon surface. In recent times, metal-organic frameworks (MOFs) (Wang et al 2011, 2013), silica (Kosuge et al., 2007) or zeolite (Monneyron et al., 2003) based materials were also employed for the adsorption of different types of VOCs.

Despite porous carbon was most commonly used for the adsorption of BTX or similar VOCs, the fundamental equilibrium and kinetics of adsorption data and their model fitting parameters were rarely or only partially reported (Chiang et al., 2002; Shao et al., 2006; Cloirec, 2012). In majority of cases, the reported data were either the maximum adsorption capacity, experimental or simulated breakthrough behavior or thermodynamic aspects of adsorption. In this work, we have synthesized high surface area powdered activated carbon (PAC) from lignin and employed them for the systematic investigation of adsorption isotherms and kinetics of BTX in both liquid and vapor forms. Finally, we employed the necessary model fittings to characterize the adsorption behavior.

2. Experimental

2.1. Synthesis and characterization of lignin-derived activated carbon

The activated carbon was synthesized by one-step synthesis method from lignin with similar methodology that was used for other lignin-derived carbons that were synthesized in our lab (Saha et al., 2017a, 2017b). Typically, 3 g solid de-alkaline lignin (TCI America) and 3 g of KOH pellets (Alfa Aesar) are mixed together in a coffee grinder and put them in a porcelain boat. We have employed 1:1 ratio of lignin to KOH as it provided best surface area of the resultant carbon. The boat is inserted in the alumina tube within the Lindberg-Blue tube furnace and carbonized in the N_2 atmosphere. In a typical fashion, the temperature was ramped to 800 °C at a ramp rate of 10 °C/min and dwelled in the final temperature of 2 min. After that, it is cooled down to room temperature in the same N_2 flow. Then, the porcelain boat is taken out and the carbon is washed in copious amounts of deionized water several times and then filtered out and dried.

In order to investigate the surface area and pore size distribution, the carbon is analyzed volumetrically with N_2 adsorption-desorption at 77 K and CO_2 adsorption at 273 K in Quantachrome's Autosorb-iQ any gas instrument. The activated carbon is outgassed in the same instrument at 300 °C for 3 h before any adsorption experiment. The temperature of 77 K is obtained by liquid nitrogen whereas 273 K is maintained by an external temperature (Julabo) with 1:1 mixture of water and propylene glycol as chilling fluid. The BET surface area is calculated within the p/p_0 values of 0.05–0.3. The pore size distribution and total pore volume is calculated by non-local density function theory (NLDFT) method and all the calculations are performed in the instrument's built-in software. The scanning electron microscopic (SEM) images were obtained in Evex mini SEM II HR 3000 instrument. Thermogravimetric analysis (TGA) data were obtained in TA instruments' SDT Q600 TGA-DSC analyzer.

2.2. Liquid and vapor phase adsorption of BTX

The liquid phase adsorption of benzene, toluene and xylene (BTX) is carried out in deionized water with benzene, toluene and xylene concentration of 20–100 ppm each. For equilibrium run, typically, 25 mL of each of the solution is stirred with 0.025 g activated carbon in a 100 mL round bottom flask by a magnetic stir bar. After 3 h, the stirring is stopped and the carbon was separated from the solution by filtration. For kinetic runs, the concentration of each of the materials is set to 100 ppm only and the run is ceased after the time intervals of 2 min, 15 min, 30 min, 1 h, 2 h and 3 h. The concentrations of benzene, toluene and xylene were measured in UV–Vis spectroscopy (Thermo Fisher Genesis UV–Vis spectroscope). A known linear calibration plot was made for each of the components and the unknown concentration was measured against this calibration plot. Each of the analysis was performed thrice and the average value was reported along with the standard deviation.

The vapor phase adsorption of BTX was performed gravimetrically in TA instruments' VTI-SA + automated vapor sorption analyzer with ultrahigh purity N_2 as carrier gas. Typically, a pre-outgassed activated carbon is inserted in the quartz pan of the instrument, whereas the benzene, toluene or xylene is introduced, each at a time, in the solvent container of the instrument. The activated carbon is further regenerated within the instrument upto the temperature of 150 °C in nitrogen flow. Then, it is cooled down to room temperature and exposed to the vapor of each of the component with controlled relative saturation pressure or humidity (p/p_0) by the heating the solvent container. Both adsorption and desorption of vapors are performed by increasing the relative saturation pressure from 0.01 to 0.9 and then decreasing it in the same fashion. Both adsorption equilibrium and kinetics data are automatically recorded in the instrument by registering the change in weight of activated carbon. The total time to complete adsorption-desorption cycle for each of the vapors was in the range of 10 h.

3. Results and discussions

3.1. Characteristics of lignin derived nanoporous carbons

The N_2 adsorption-desorption plot at 77 K is shown in Fig. 1. According to IUPAC nomenclature, this is type I isotherm with negligible hysteresis loop. This type of isotherm is the indicator of primarily microporous structure with negligible mesopore contribution. (IUPAC classification: micropore, pore width<20 Å; mesopore: pore width 20–500 Å; macropore: pore width>500 Å).

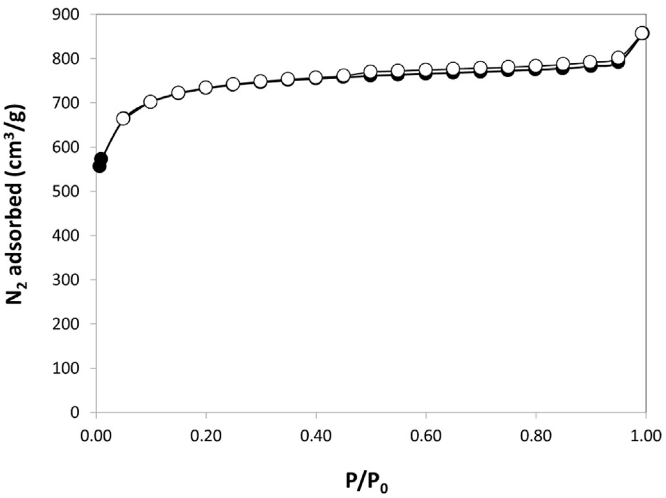

Fig. 1. Nitrogen adsorption-desorption on lignin-derived activated carbon at 77 K (closed symbol for adsorption, open symbols for desorption).