Effect of Adsorption and Regeneration Temperature on Irreversible Adsorption of Organic Vapors on Beaded Activated Carbon

7 AUTHORS, INCLUDING:

Masoud Jahandar Lashaki
University of Alberta
12 PUBLICATIONS   **48** CITATIONS

Mohammadreza Fayaz
University of Alberta
7 PUBLICATIONS   **45** CITATIONS

Zaher Hashisho
University of Alberta
52 PUBLICATIONS   **429** CITATIONS

James E Anderson
Ford Motor Company
68 PUBLICATIONS   **805** CITATIONS

Effect of Adsorption and Regeneration Temperature on Irreversible Adsorption of Organic Vapors on Beaded Activated Carbon

Masoud Jahandar Lashaki,[†] Mohammadreza Fayaz,[†] Haiyan (Helena) Wang,[†] Zaher Hashisho,*,[†] John H. Philips,[‡] James E. Anderson,[§] and Mark Nichols[§]

[†]University of Alberta, Department of Civil and Environmental Engineering, Edmonton, AB T6G 2W2, Canada
[‡]Ford Motor Company, Environmental Quality Office, Dearborn, Michigan 48126, United States
[§]Ford Motor Company, Research and Advanced Engineering, Dearborn, Michigan 48121, United States

ABSTRACT: This paper investigates the effect of adsorption and regeneration temperature on the irreversible adsorption of a mixture of organic compounds typically emitted from automobile painting operations. Adsorption of the organic vapors mixture onto microporous beaded activated carbon (BAC) and regeneration of the saturated BAC were completed under different conditions. Results indicated that increasing the adsorption temperature from 25 to 35 or 45 °C increased heel buildup on BAC by about 30% irrespective of the regeneration temperature due to chemisorption. The adsorption capacity (for the first cycle) of the mixture onto the BAC at these three temperatures remained almost unchanged indicating chem-

isorption of some of these compounds onto the BAC. Increasing the regeneration temperature from 288 to 400 °C resulted in 61% reduction in the heel at all adsorption temperatures, possibly due to desorption of chemicals from narrow micropores. BET area and pore volumes of the BAC decreased proportionally to the cumulative heel. Pore size distribution and pore volume reduction confirmed that the heel was mainly built up in narrow micropores which can be occupied or blocked by some of the adsorbates.
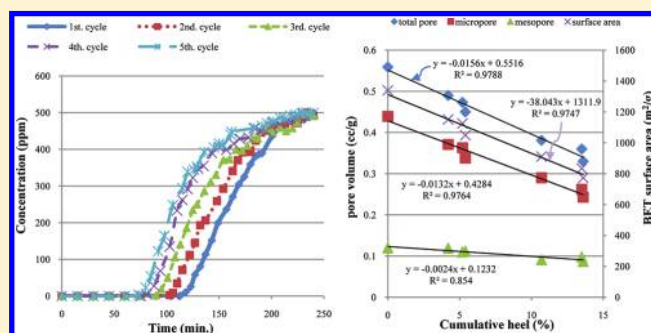
INTRODUCTION

Vehicle painting operations are the primary source of volatile organic compound (VOCs) emissions from the automobile manufacturing sector.[1,2] These emissions consist of a mixture of high and low molecular weight compounds including aromatic hydrocarbons, esters, ketones, alcohols, and glycol ethers.[1,2] On average, 6.58 kg of VOCs is used as paint solvents per vehicle in typical automotive plants in North America.[2] VOC emissions are of concern because of their health effects and/or ozone formation potential,[2–5] so, the gaseous stream needs to be treated before discharging to the atmosphere.[6] Methods to control emission of organic vapors include adsorption, absorption, oxidation, biofiltration, condensation, and membrane separation.[4,5,7–13] Among these methods, adsorption is widely used because of its cost effectiveness, high efficiency at low concentrations, i.e., ppm for recovering the VOCs from gaseous streams, and ability to recover the adsorbate for reuse.[1,12,14–17]

Adsorption can be categorized into physical adsorption and chemical adsorption. In chemical adsorption or chemisorption, the adsorbate reacts on the surface of the adsorbent and adheres through chemical bonds; consequently, the heat of adsorption is high and approaches the energy of chemical bonds.[18] Chemisorbed species are generally difficult to desorb and as a result they accumulate on the surface of the adsorbent and reduce its adsorption capacity. Higher temperatures during

adsorption can favor chemisorption as it provides the activation energy needed for the formation of adsorbate–adsorbent complex.[19] Other factors promoting chemisorption include the presence of adsorbates with electron-donating functional groups such as amine ($-NH_2$) and hydroxyl ($-OH$),[20–23] the difference between the boiling point of the adsorbate and the regeneration temperature,[23] and $\pi-\pi$ electron donor–acceptor interaction between the aromatic ring and unsaturated bond on the carbon.[24]

Due to its low cost and high surface area, activated carbon is one of the most commonly used adsorbents in air and water treatment.[10,25–29] One of the challenges of capturing organic vapors from painting operations is the irreversible adsorption (aka build-up of heel) of these compounds onto activated carbon which reduces the lifetime of the adsorbent and increases the operation and maintenance cost of the system due to the cost of the adsorbent, disposal of the spent adsorbent, and labor cost to replace the adsorbent. Irreversible adsorption on an adsorbent surface can be described as the combined result of formation of permanent bonds between the adsorbate and the surface (chemisorption) and the irreversible trans-
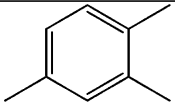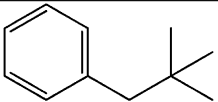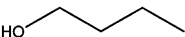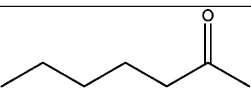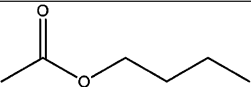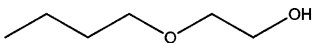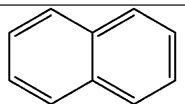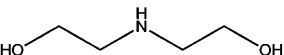
Table 1. Composition of the test mixture

Name (purity and supplier)	Chemical structure	Weight percentage (%)	Concentration	
			(ppmv)	(μmol/L)
n-decane (99.5%, Fisher Scientific)		9.01	36	1.43
1, 2, 4-trimethyl benzene (98%, Acros Organics)		10.86	52	2.05
2, 2-dimethyl-propylbenzene (85%, Chemsampco)		10.55	41	1.61
1-butanol (99.9%, Fisher Scientific)		9.99	77	3.05
2-heptanone (98%, Acros Organics)		10.12	51	2.01
n-butyl acetate (>99%, Acros Organics)		10.86	54	2.12
2-butoxyethanol (99%, Acros Organics)		11.10	54	2.13
naphthalene (>99%, Sigma-Aldrich)		14.06	63	2.49
diethanolamine (>98%, Sigma-Aldrich)		13.45	73	2.90

formation of the adsorbed species through chemical reactions catalyzed by the adsorbent surface.[30] Previous studies have investigated the irreversible adsorption of organic compounds (particularly phenolic and aromatic compounds) from water onto activated carbon, particularly the conventional granular activated carbon.[30−34] However, there is little or no information about the irreversible adsorption of organic compounds from the gas phase onto activated carbon, particularly novel forms of activated carbon such as beaded activated carbon (BAC).

The objective of this study is to explore the effect of adsorption and regeneration temperature on the irreversible adsorption of a mixture of vapor-phase organic compounds commonly emitted from automotive painting operations. Understanding the factors promoting irreversible adsorption is the first step for solving the problem of heel buildup and increasing the lifetime of the adsorbent. For this purpose, a bench-scale adsorption−regeneration system was built and adsorption and regeneration cycles of a mixture of organic compounds onto beaded activated carbon (BAC) were completed at different temperatures. The BAC was also analyzed for irreversible adsorption in terms of the amount of accumulated adsorbates and changes in adsorption capacity, specific area, and pore size distribution.

■ MATERIALS AND METHODS

The adsorbent used in this study was beaded activated carbon (Kureha Corporation).[35,36] The BAC is characterized by its high microporosity, attrition-resistance, and narrow particle size distribution (average particle diameter of 0.70 mm, 99% by mass between 0.60 and 0.84 mm). Prior to use, the BAC was dried in air in a laboratory oven at 150 °C for 24 h and then kept in a desiccator. The BAC was tested with a mixture of compounds typically emitted from automotive painting operations and representative of various functional groups including alkane, aromatic, ester, alcohol, ketone, polyaromatic hydrocarbon, and amine. To prepare the mixture, equal volumes of each of the compounds were mixed as liquids. The density of the mixture was 0.86 g/cm³, determined based on the weight of a known mixture volume. The composition of the mixture is presented in Table 1.

Experimental Setup and Methods. The experimental setup used in this study is depicted in Figure 1. The setup consisted of an adsorption−regeneration reactor, an adsorbate generation system, a gas detection system, a power application module, and a data acquisition and control system (DAC). The adsorption−regeneration reactor consisted of a stainless steel tube (1.44 cm inner diameter, 15.24 cm long) containing 7−8 g of dry virgin BAC. The BAC bed length was 8 cm. Glass wool was used at the bottom and top of the reactor as a support for the BAC bed.
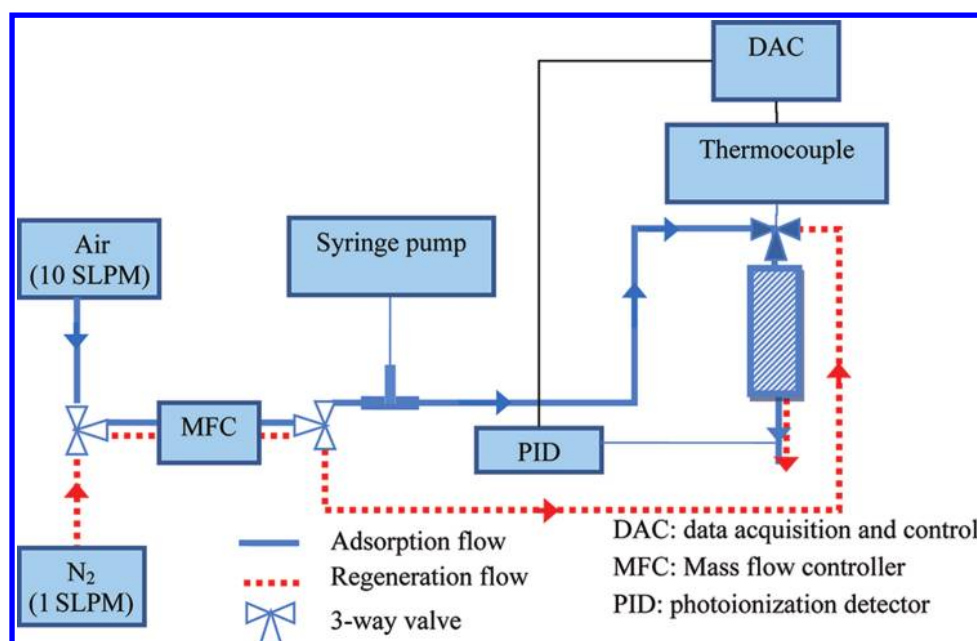
Figure 1. Schematic diagram of the adsorption−regeneration setup.

The adsorbate generation system consisted of a syringe pump (KD Scientific, KDS-220) used to inject the mixture into a 10 SLPM dry air stream. The air stream was purified using a compressed air filter (Norman Filter Co.) to remove hydrocarbons and water. The injection rate was calculated based on the ideal gas law using the average molecular weight and density of the mixture. The flow rate of air was controlled with a 0−20 SLPM mass flow controller (Alicat Scientific). The adsorbate detection system consisted of a photoionization detector (Minirae 2000, Rae Systems). The concentration at the outlet of the reactor during adsorption was intermittently measured with the photoionization detector (PID) to avoid contaminating the PID lamp with overexposure to high boiling point adsorbates. The PID was calibrated before each adsorption test using the generated gas stream.

The heat application module consisted of heating tape (Omega) wrapped around the adsorption−regeneration reactor. Insulation tape (Omega) was wrapped outside the heating tape to minimize heat loss. A 0.9-mm OD type K thermocouple (Omega) inserted at the center of the reactor was used to measure the temperature of the BAC bed during adsorption and regeneration. A solid-state relay was used to control the power application to the heating tape.

The data acquisition and control (DAC) system consisted of Labview software (National Instruments) and a data logger (National Instruments, Compact DAQ) equipped with analog input and output modules. The data logger was interfaced to the PID, thermocouple, and the solid state relay. During adsorption and regeneration, temperature was measured using the thermocouple and a proportional-integral-derivative algorithm was used to control the power applied to achieve the set-point temperature. The DAC system controlled the power application to maintain a bed temperature of 25, 35, or 45 °C during adsorption and 288 or 400 °C during regeneration. A mass flow controller (Alicat Scientific) was used to provide 1 SLPM of high-purity (99.998%) grade nitrogen (Praxair) to purge both oxygen and desorbed compounds during regeneration.

Two-point calibration of the PID was completed with fresh air for zero and the steady state concentration adsorbate stream from the adsorbate generation system for span. The calibration was performed at the same gas flow rate as during adsorption to avoid any bias in the PID readings. After calibration, the adsorbate gas stream was directed into the reactor to start adsorption. The adsorption process continued until the BAC was fully saturated as indicated by the PID. The reactor was weighed before and after adsorption to determine the adsorption capacity, as follows:

Adsorption capacity (%)

$$= ((\text{Reactor weight after adsorption} - \text{Reactor weight}$$
$$\text{before adsorption})/\text{Weight of virgin BAC}) \times 100$$

Regeneration was accomplished by heating the BAC with simultaneous purge with nitrogen for 3 h and then cooling for 50 min while continuing to purge with nitrogen. The reactor was then weighed again. The difference in the reactor weight before the adsorption cycle and after the regeneration cycle represented the amount of irreversible adsorption or heel built up during that cycle. The mass balance cumulative heel after five complete adsorption/regeneration cycles represents the total amount of heel building up throughout all five cycles and is defined as follows:

Mass balance cumulative heel (%)

$$= ((\text{Reactor weight after last regeneration cycle}$$
$$- \text{Reactor weight before first adsorption cycle})$$
$$/\text{Weight of virgin BAC}) \times 100$$

Thermo-Gravimetric Analysis (TGA). After completing five consecutive adsorption/regeneration cycles, the loaded BAC was analyzed by TGA (TGA/DSC 1, Mettler Toledo). The analysis was started with the temperature at 30 °C and immediately increased to 120 °C and then maintained there for 15 min to remove adsorbed moisture from the BAC. Then the

temperature was increased to 288 or 400 °C (depending on the temperature used for regenerating the BAC) and kept for 30 min to simulate the basic regeneration process. Finally, it was raised to 1000 °C and maintained for 30 min to desorb strongly adsorbed species from the BAC. Throughout the TGA test, the sample was heated at 20 °C/min in 50 SCCM of N_2.

BAC Characteristics. BAC samples were analyzed using a micropore surface analysis system (IQ2MP, Quantachrome) with nitrogen as the testing gas with relative pressure range from 10^{-7} to 1 at 77 K. BAC samples of 30–50 mg were degassed at 120 °C for 5 h to remove any moisture within the pores of the material. BET surface area and micropore volume were obtained using the relative pressure ranges of 0.01–0.07 and 0.2–0.4, respectively. The micropore volume was determined by the V-t model. The mesopore volume and surface area were calculated by subtracting the relevant micropore values from the total pore values. Pore size distributions were also obtained from nitrogen adsorption/desorption isotherms using the density functional theory (DFT) model for slit pores.[37]

RESULTS AND DISCUSSION

Breakthrough Curves. Figure 2a and b depict the breakthrough curves for five consecutive adsorption cycles of
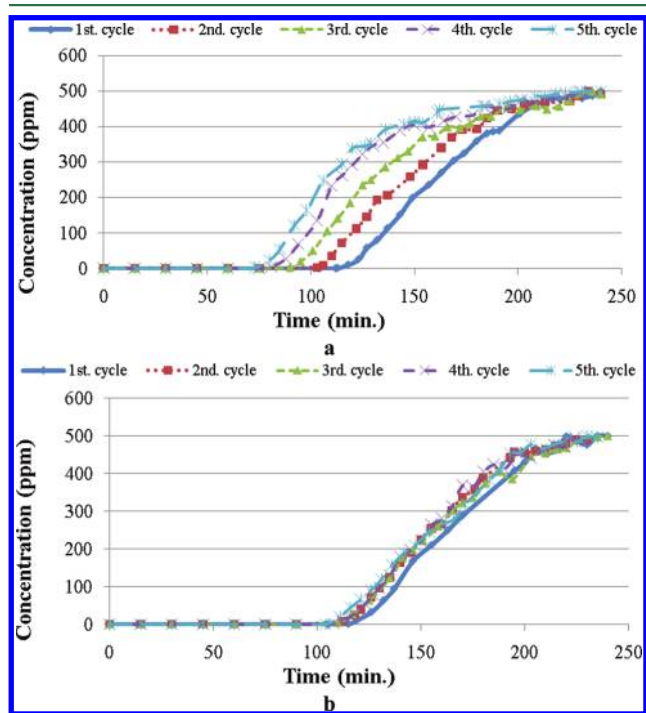

Figure 2. Breakthrough curves for adsorption on BAC at 35 °C and regeneration at (a) 288 °C and (b) 400 °C.

BAC regenerated at 288 and 400 °C, respectively. During the first cycle of all experiments, the organic vapors were detected after about 2 h by the calibrated PID at the reactor outlet indicating occurrence of breakthrough. All tests were continued until full saturation of the BAC as indicated by a stable concentration at the reactor outlet. For BAC regenerated at 288 °C, the breakthrough time ($t_{5\%}$, 5% of influent concentration) decreased progressively with each cycle, indicating that regeneration at 288 °C was unsuccessful in desorbing the adsorbed chemicals from some of the adsorption sites which led

to accumulation of heel on the BAC. The largest change in breakthrough time occurred after the first cycle and corresponded to the largest heel buildup as measured by mass balance. Conversely, for BAC regenerated at 400 °C, the breakthrough time remained almost unchanged after the first cycle indicating negligible heel buildup.

Figure 3 depicts the difference in breakthrough time ($t_{5\%}$) between the first and all of the following adsorption cycles as a function of mass balance cumulative heel expressed in % by weight of virgin BAC. The reduction in the breakthrough time linearly increased with the mass balance cumulative heel. For the configuration used in this study, a 1% increase in heel resulted in 3.1 min reduction in the breakthrough time of the next adsorption cycle. Completing additional cycles resulted in further reduction of the breakthrough time. Continuing this pattern, the BAC will become completely spent and would need to be replaced with virgin BAC. Considering a breakthrough time of 120 min, the adsorbent becomes completely spent after reaching a cumulative heel of 38%. This heel is lower than the adsorption capacity due to possible pore blockage as discussed later in the paper and the fact that the rear (outlet) portion of the carbon is not completely spent when the 5% breakthrough occurs.

Adsorption and Regeneration Temperature. The adsorption capacities on virgin BAC (i.e., for the first adsorption cycle) at different adsorption temperatures are illustrated in Figure 4. For comparison, the adsorption capacities of 1-butanol and *n*-decane at different adsorption temperatures were also obtained. These compounds were selected because previous research[23] indicated that *n*-decane formed heel on BAC while 1-butanol did not, suggesting that 1-butanol physisorbed while *n*-decane may have chemisorbed onto the BAC. The results of the present study showed that the adsorption capacity (for the first cycle) of the mixture and *n*-decane remained almost unchanged as the adsorption temperature increased, while the adsorption capacity of 1-butanol showed a 30% reduction as the temperature increased from 25 to 45 °C (Figure 4). The behavior of the mixture and *n*-decane is consistent with the characteristics of chemisorption since a higher temperature provides the energy needed to overcome the activation energy for the reactions between the adsorbate and adsorbent. Because chemisorption involves the formation of chemical bonds between the adsorbate and the adsorbent, the adsorbates will typically occupy certain adsorption sites on the surface of the activated carbon in a monolayer arrangement. Henning et al.[38] investigated the effect of temperature on adsorption mechanism and adsorption capacity of vapor-phase cyclohexanone onto activated carbon. The adsorption capacity for cyclohexanone remained unchanged as the adsorption temperature increased from 25 to 50 °C. This behavior was attributed to chemisorption of cyclohexanone and presence of some unsaturated carbon bonds on the edge of carbonaceous layers, forming high energy "active-centers" suitable for oxygen and hydrogen to bind.[38] Another possibility is that higher adsorption temperature might have enhanced the diffusion of the large chain molecules.[39]

Measurements of heel percentage from the mass balance and the TGA are compared in Figure 5 for BAC adsorbed with the tested mixture. For the same regeneration temperature, increasing the adsorption temperature from 25 to 35 °C resulted in greater accumulation of adsorbates on the BAC while further increase in temperature to 45 °C had no effect possibly due to a similar adsorption mechanism at 35 and 45
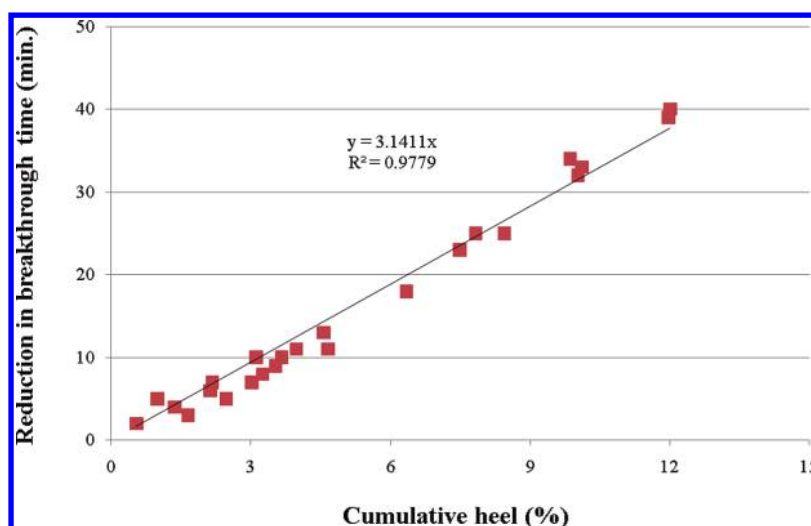
Figure 3. Reduction in breakthrough time ($t_{5\%}$) with mass balance cumulative heel for all adsorption and desorption temperatures.
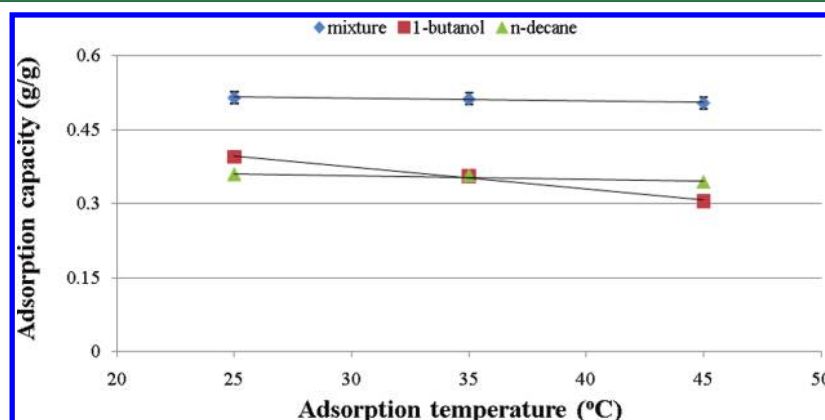

Figure 4. Effect of adsorption temperature on adsorption capacity on virgin BAC.
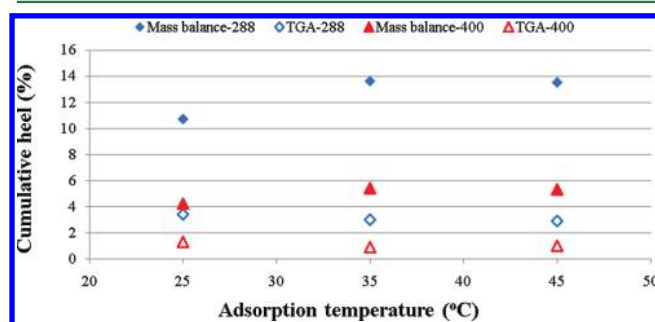

Figure 5. Heel percentages as determined by mass balance and TGA for BAC adsorbed with tested mixture and regenerated at 288 or 400 °C. Legends are labeled as Mass balance-x or TGA-x where x corresponds to the regeneration temperature in °C.

°C. Previous researchers reported that high temperature is favorable for chemisorption[19,30] thus the greater heel remaining may be attributable to occurrence of chemisorption. At higher temperature, the adsorption mechanism likely shifts from physisorption (reversible state) to chemisorption (irreversible state) and the adsorption becomes irreversible.[21]

The effect of regeneration temperature on irreversible adsorption was also evaluated (Figure 5). Comparing the heel remaining after regeneration at 288 and 400 °C it can be seen that using a higher regeneration temperature resulted in 60–

61% reduction in mass balance cumulative heel since more adsorbates are desorbed from the pores. In this case, the difference between the regeneration temperature and the boiling point of the tested adsorbates, which ranged from 118 to 269 °C, is larger which provides a greater driving force for desorption. Qin et al.[40] investigated the irreversible adsorption of dibenzothiophene (DBT) from n-heptane solution and concluded that because of the tendency for adsorbate to remain inside the micropores, applying higher temperatures during the regeneration process may increase the regeneration efficiency.

The difference between heel as determined from mass balance and TGA may be attributed to irreversible chemisorption. Heel determination with TGA is based on the change in the sample weight between the regeneration temperature (288 or 400 °C) and a higher temperature (1000 °C). It is assumed that all of the adsorbate is desorbed at 1000 °C. However, if irreversible adsorption occurs (as is the case in chemisorption), some of the adsorbate will remain adsorbed to the BAC even after exposure to high temperature; hence the TGA heel will be less than the mass balance heel. The difference between the mass balance heel and the TGA heel is larger for 35 and 45 °C than for 25 °C which may be due to increased chemisorption at 35 and 45 °C. The chemisorbed material is harder to desorb even after heating to high temperature (1000 °C); consequently, the difference would be greater in this case.

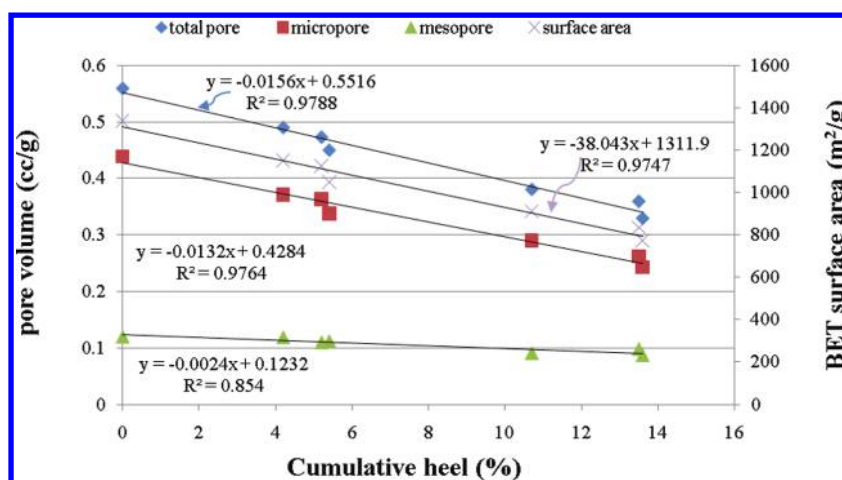**Figure 6.** Relationship between mass balance cumulative heel on BET surface area and pore volume of regenerated BAC. Values for virgin (0% cumulative heel) BAC are presented for comparison.
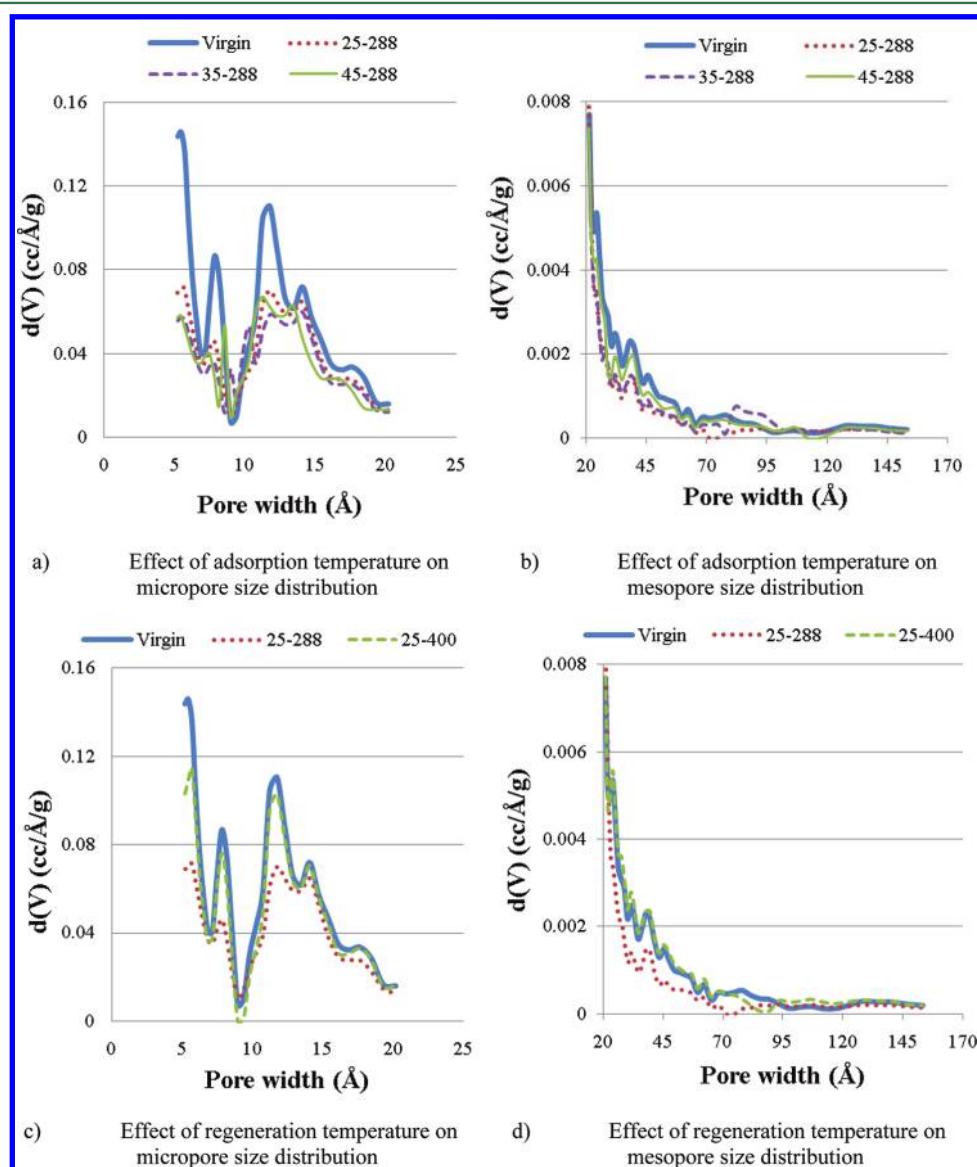

Figure 7. Effect of adsorption and regeneration temperature on pore size distribution of BAC. Legends are labeled as *x-y* where *x* and *y* correspond to the adsorption and regeneration temperatures in °C, respectively.

BET Surface Area and Pore Size Distribution. The BET surface area and pore size distribution of all virgin and regenerated BAC samples were determined to find the effect of irreversible adsorption on these parameters. The BET surface area of the BAC linearly decreased with the mass balance cumulative heel (Figure 6). This indicates that as heel accumulates, some adsorption sites remain occupied by adsorbates since regeneration is unsuccessful in removing them from the active sites, and as a result, the number of vacant available sites will decrease. The effect of irreversible adsorption on the total and micropore volumes is similar to its effect on BET surface area (Figure 6). On average, for every 1% of mass balance cumulative heel, BET area, micropore, mesopore, and pore volume decreased by 2.7, 2.8, 2.0, and 3.0%, respectively.

Determining pore size distribution for the regenerated carbon helps identify the location of the heel. Figure 7a indicates that irreversible adsorption resulted in blockage of the micropores, particularly the narrow micropores (5−7 Å). As the adsorption temperature increased, more chemisorption occurred, and more heel accumulated resulting in blockage of more micropores. Figure 7a indicates that irreversible adsorption greatly decreased the number of micropores. Irreversible adsorption reduced the number of available mesopores below 100 Å at all adsorption temperatures (Figure 7b).

Increasing the regeneration temperature from 288 to 400 °C enhanced the desorption of some of the adsorbates from the micropores including narrow (5−7 Å) micropores (Figure 7c) and mesopores (Figure 7d). Qin et al. revealed similar conclusions about the effect of regeneration temperature on the elimination of adsorbates from narrow micropores. BAC containing adsorbed dibenzothiophene regenerated at 400 °C had a similar pore size distribution to virgin BAC except that the narrow micropores in the regenerated BAC were not fully desorbed.[40]

The volume of the accumulated adsorbates (i.e., heel) inside the pores of the BAC could be calculated based on weight and bulk density of the adsorbed mixture or directly measured based on the reduction in pore volume from N_2 adsorption isotherms. The measured decrease in pore volume was consistently higher than the calculated value (Figure 8). This may be attributed to pore blockage by compounds with large kinetic diameter. For instance, the kinetic diameter of naphthalene, one of the main contributors to irreversible adsorption and a primary constituent of the test gas stream, is 6.2 Å[41] while 19% of the total pore volume (based on integration of the PSD of the adsorbent) of the BAC
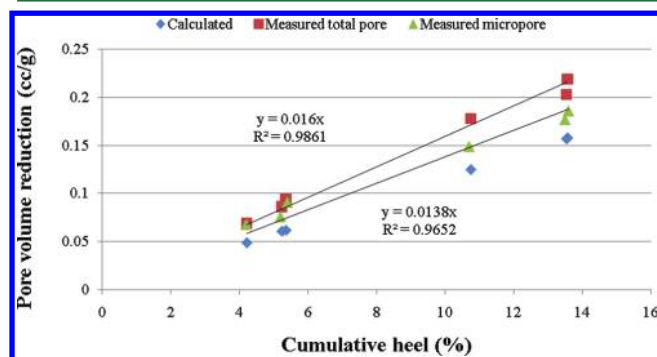
corresponds to pores smaller than 6.2 Å in diameter. In this case, naphthalene molecules could block the entrance of these narrow micropores making them unavailable for adsorption, consequently, these sites are vacant but are not able to adsorb anymore. Another mechanism which might have contributed to heel formation could be the oligomerization of adsorbates producing materials that are more difficult to desorb due to their higher boiling points. The difference between calculated and measured pore volume reduction increased as the mass balance cumulative heel increased, consistent with the above hypothesis but increasing in extent.

■ AUTHOR INFORMATION

Corresponding Author
*Tel.: +1-780-492-0247; fax: +1-780-492-0249; e-mail: hashisho@ualberta.ca.

Notes
The authors declare no competing financial interest.

■ REFERENCES

(1) Golovoy, A.; Braslaw, J. Adsorption of automotive paint solvents on activated carbon: Equilibrium adsorption of single vapors. *J. Air Pollut. Control Assoc.* **1981**, *31* (8), 861−865.

(2) Kim, B. R. VOC emissions from automotive painting and their control: A review. *Environ. Eng. Res.* **2011**, *16* (1), 1−9.

(3) Fuertes, A. B.; Marban, G.; Nevskaia, D. M. Adsorption of volatile organic compounds by means of activated carbon fiber-based monoliths. *Carbon* **2003**, *41*, 87−96.

(4) Das, D.; Gaur, V.; Verma, N. Removal of volatile organic compound by activated carbon fiber. *Carbon* **2004**, *42*, 2949−2962.

(5) Johnsen, D. L.; Mallouk, K. E.; Rood, M. J. Control of electrothermal heating during regeneration of activated carbon fiber cloth. *Environ. Sci. Technol.* **2011**, *45*, 738−743.

(6) Emamipour, H.; Hashisho, Z.; Cevallos, D.; Rood., M. J.; Thurston, D. L.; Hay, K. J.; Kim, B. J.; Sullivan, P. D. Steady-state and dynamic desorption of organic vapor from activated carbon with electrothermal swing adsorption. *Environ. Sci. Technol.* **2007**, *41*, 5063−5069.

(7) Hunter, P.; Oyama, S. T. *Control of Volatile Organic Compound Emissions: Conventional and Emerging Technologies*; John Wiley: New York, 2002.

(8) Leethochawalit, M.; Bustard, M. T.; Wright, P. C.; Meeyoo, V. Novel vapor-phase biofiltration and catalytic combustion of volatile organic compounds. *Ind. Eng. Chem. Res.* **2001**, *40* (23), 5334−5341.

(9) Li, C.; Moe, W. M. Activated carbon load equalization of discontinuously generated acetone and toluene mixtures treated by biofiltration. *Environ. Sci. Technol.* **2005**, *39* (7), 2349−2356.

(10) Kim, K. J.; Kang, C. S.; You, Y. J.; Chung, M. C.; Jeong, S. W.; Jeong, W. J.; Woo, M. W.; Ahn, H. G. Adsorption-desorption characteristics of modified activated carbons for volatile organic compounds. *Stud. Surf. Sci. Catal.* **2006**, *159*, 457−460.

(11) Hashisho, Z.; Emamipour, H.; Cevallos, D.; Rood., M. J.; Hay, K. J.; Kim, B. J. Rapid response concentration-controlled desorption of activated carbon to dampen concentration fluctuations. *Environ. Sci. Technol.* **2007**, *41*, 1753−1758.

(12) Ramos, M. E.; Bonelli, P. R.; Cukierman, A. L.; Ribeiro Carrott, M. M. L.; Carrott, P. J. M. Adsorption of volatile organic compounds

Figure 8. Relationship between mass balance cumulative heel and pore volume reduction.

onto activated carbon cloths derived from a novel regenerated cellulosic precursor. *J. Hazard. Mater.* **2010**, *177*, 175−182.

(13) Mallouk, K. E.; Johnsen, D. L.; Rood, M. J. Capture and recovery of isobutane by electrothermal swing adsorption with post-desorption liquefaction. *Environ. Sci. Technol.* **2010**, *44*, 7070−7075.

(14) Shonnard, D. R.; Hiew, D. S. Comparative environmental assessments of VOC recovery and recycle design alternatives for a gaseous waste stream. *Environ. Sci. Technol.* **2000**, *34* (24), 5222−5228.

(15) Gupta, V. K.; Verma, N. Removal of volatile organic compounds by cryogenic condensation followed by adsorption. *Chem. Eng. Sci.* **2002**, *57*, 2679−96.

(16) Lapkin, A.; Joyce, L.; Crittenden, B. Framework for evaluating the "Greenness" of chemical processes: Case studies for a novel VOC recovery technology. *Environ. Sci. Technol.* **2004**, *38* (21), 5815−5823.

(17) Dabrowski, A.; Podkoscielny, P.; Hubicki, Z.; Barczak, M. Adsorption of phenolic compounds by activated carbon-A critical review. *Chemosphere* **2005**, *58*, 1049−1070.

(18) Khan, F. I.; Ghoshal, A. K. Removal of volatile organic compounds from polluted air. *J. Loss Prev. Process Ind.* **2000**, *13*, 527−545.

(19) Schnelle, K. B.; Brown, C. A. *Air Pollution Control Technology Handbook*; CRC Press: Boca Raton, FL, 2002.

(20) Tamon, H.; Okazaki, M. Desorption characteristics of aromatic compounds in aqueous solution on solid adsorbents. *J. Colloid Interface Sci.* **1996**, *179*, 181−187.

(21) Tamon, H.; Atsushi, M.; Okazaki, M. On irreversible adsorption of electron-donating compounds in aqueous solution. *J. Colloid Interface Sci.* **1996**, *177*, 384−390.

(22) Tanthapanichakoon, W.; Ariyadejwanich, P.; Japthong, P.; Nakagawa, K.; Mukai, S. R.; Tamon, H. Adsorption-desorption characteristics of phenol and reactive dyes from aqueous solution on mesoporous activated carbon prepared from waste tires. *Water Res.* **2005**, *39*, 1347−1353.

(23) Fayaz, M.; Wang. H.; Jahandar Lashaki, M.; Hashisho, Z.; Philips, J. H.; Anderson, J. E. Accumulation of adsorbed of organic vapors from automobile painting operations on bead activated carbon. In Proceedings of the Air and Waste Management Association's Annual Conference and Exhibition, Orlando, FL, 2011.

(24) Zhu, D.; Pignatello, J. J. A Concentration-dependent multi-term linear free energy relationship for sorption of organic compounds to soils based on the hexadecane dilute-solution reference state. *Environ. Sci. Technol.* **2005**, *39* (7), 2033−2041.

(25) Popescu, M.; Joly, J. P.; Carré, J.; Danatoiu, C. Dynamical adsorption and temperature-programmed desorption of VOCs (toluene, butyl acetate and butanol) on activated carbons. *Carbon* **2003**, *41* (4), 739−748.

(26) Kawasaki, N.; Kinoshita, H.; Oue, T.; Nakamura, T.; Tanada, S. Study on adsorption kinetic of aromatic hydrocarbons onto activated carbon in gaseous flow method. *J. Colloid Interface Sci.* **2004**, *275* (1), 40−43.

(27) Álvarez, P. M.; García-Araya, J. F.; Beltrán, F. J.; Masaa, F. J.; Medina, F. Ozonation of activated carbons: Effect on the adsorption of selected phenolic compounds from aqueous solutions. *J. Colloid Interface Sci.* **2005**, *283*, 503−512.

(28) Aktas, O.; Cecen, F. Effect of type of carbon activation on adsorption and its reversibility. *J. Chem. Technol. Biotechnol.* **2006**, *81*, 94−101.

(29) Aktas, O.; Cecen, F. Competitive adsorption and desorption of a bi-solute mixture: Effect of activated carbon type. *Adsorption* **2007**, *13*, 159−169.

(30) Chatzopoulos, D.; Varma, A.; Irvine, R. L. Activated carbon adsorption and desorption of toluene in the aqueous phase. *AIChE J.* **1993**, *39* (12), 2027−2041.

(31) Grant, T. M.; King, C. J. Mechanism of irreversible adsorption of phenolic compounds by activated carbons. *Ind. Eng. Chem. Res.* **1990**, *29* (2), 264−271.

(32) Ferro-Garcia, M. A.; Joly, J. P.; Rivera-Utrilla, J.; Moreno-Castilla, C. Thermal desorption of chlorophenols from activated carbons with different porosity. *Langmuir* **1995**, *11* (7), 2648−2651.

(33) Lu, Q.; Sorial, G. A. The effect of functional groups on oligomerization of phenolics on activated carbon. *J. Hazard. Mater.* **2007**, *148* (1−2), 436−445.

(34) Lu, Q.; Sorial, G. A. A comparative study of multicomponent adsorption of phenolic compounds on GAC and ACFs. *J. Hazard. Mater.* **2009**, *167* (1−3), 89−96.

(35) Anderson, J. E. Recovering VOCs from paint spray booth air using an activated-carbon fluidized-bed adsorber for subsequent power generation. In Proceedings of the Air and Waste Management Association's Annual Conference and Exhibition, New Orleans, LA, 2006.

(36) Kureha Corporation Website; http://www.kureha.com/pdfs/Kureha-BAC-Bead-Activated-Carbon.pdf.

(37) Olivier, J. P. Improving the models used for calculating the size distribution of micropore volume of activated carbons from adsorption data. *Carbon* **1998**, *36* (10), 1469−1472.

(38) Henning, K. D.; Bongartz, W.; Degel, J. Adsorptive recovery of problematic solvents. In Proceedings of Biennial Conference on Carbon, Pennsylvania State University, USA, 1989.

(39) Chiang, Y.; Chiang, P.; Huang, C. Effects of pore structure and temperature on VOC adsorption on activated carbon. *Carbon* **2001**, *39*, 523−534.

(40) Qin, W.; Xiao-yi, L.; Rui, Z.; Chao-jun, L.; Xiao-jun, L.; Wen-ming, Q.; Liang, Z.; Li-cheng, L. Preparation of polystyrene-based activated carbon spheres and their adsorption of dibenzothiophene. *New Carbon Mater.* **2009**, *24* (1), 55−60.

(41) Long, C.; Lu, J. D.; Li, A.; Hu, D.; Liu, F.; Zhang, Q. Adsorption of naphthalene onto the carbon adsorbent from waste ion exchange resin: Equilibrium and kinetic characteristics. *J. Hazard. Mater.* **2008**, *150*, 656−661.