Comparative Analysis of Pressure Regions of Gaseous Benzene Using Ground Activated Carbon Sorbents Under Ambient Conditions

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Abstract

The effective removal of atmospheric hazardous pollutants using activated carbon for the real-world application is a crucial and reliable process. Therefore, the performance comparison of ground activated carbon BPL 4×6 (ACb212) based on varied outlet pressure of benzene vapour were analyzed in ambient condition (room temperature and pressure). The maximum adsorption capacity was found ~110 mg. g^{-1}) for all pressure regions. However, the competition showed maximum capacity for higher pressure region i.e., 50.5 mg. g^{-1}, minimum capacity at lower pressure region 7.96 mg. g^{-1}, and moderate for moderate outlet pressure 20.6 mg. g^{-1}. On the other hand, the partition coefficient (PC) behaved inversely to the sorption capacity i.e., high PC (397 mol.kg^{-1}. Pa^{-1}) at the low outlet and low PC (1.47 mol.kg^{-1}. Pa^{-1}) at high outlet benzene partial pressure regions. The adsorption capacity on ACb212 followed the classical Langmuir isotherm of Type-1 at low and high-pressure outlet pressure regions, while a retrograde behaviour isotherm (Type-1) was observed for lowest benzene outlet partial pressure region. Furthermore, the linearized Langmuir isotherm analysis also confirmed the existence of two or more sorption sites for gaseous benzene.

Key words: Benzene; Activated Carbon; Adsorption; Retrograde; Langmuir Isotherm

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INTRODUCTION

According to the World Health Organization (WHO), in 2012 about 3.7 million people died under the age of 60 due to air pollution (both indoor and outdoor) mainly in the developing countries (WHO, 2018). A survey conducted in the United States in 2017, in total volatile organic compounds (15.86 megatons [Mt]) released from different sources were such as stationary fuel combustion contributed (~3.35%), industrial and other processes (~47.3%), transportation (~21.1%), and miscellaneous ~28.3% (USEPA, 2018). In the year 2013, VOC emission for different countries such as United States (~13.12 Mt), Australia (~2.79 Mt), Chili (~2.44 Mt), Japan (~0.92 Mt), South Korea (~0.88 Mt), and UK (~0.84 Mt) was reported (OECD, 2018). These Volatile organic compounds (VOCs) are considered one of the most hazardous groups of air pollutants (Caselli et al., 2010). Diverse human health has been found such as central nervous system depression, respiratory diseases, and damage to circulatory systems concerned due to emission from petroleum products (Carlsen et al., 2018; Chen et al., 2016). In these VOCs, benzene, toluene, styrene, and xylenes so-called BTSX group emitted to the atmosphere from both anthropogenic and biogenic sources (Alghamdi et al., 2014). A growing interest has been developed for the treatment of these volatile organic compounds released form anthropogenic sources (Zaitan et al., 2008). Accordingly, continuous research is required to set up more effective and efficient technologies to reduce such types of hazardous pollutants. Many methods have been used e.g., adsorption, absorption, condensation, catalytic oxidation, air stripping, membrane separation, biological treatment, and incineration for the abatement of these VOCs. Adsorption is the most suitable and widespread method due to economical consideration as well as the easily controllable process to recover VOCs from a wide range of gaseous stream (Kim et al., 2017; Ramos et al., 2010). The selection of technologies has a number of shortcomings or limitations including limited adsorption capacity, toxic end products, and high energy costs for regeneration (Lim et al., 2012). More interestingly, many of the conventional technologies have been used to check some diverse sorbents (e.g., activated carbon, zeolites, and hybrid materials) for the physical or chemical sorption applications (Ni, 2015). In this study, it was attempted to explore the comparative analysis of pressure regions (low and high pressure) of gaseous benzene using ground activated carbon BPL (ACb212) under ambient temperature and pressure. The basic information for sorbent along with the target compound benzene can be seen in Table 1. The ACb212 have used the ground to explore the effects on the sorption of gaseous benzene with varying outlet partial pressure.

MATERIALS AND METHODS

Chemicals and materials used

Activated carbon BPL 4×6 (ACb212: coal activated Calgon UK) was grinded and sieved to sizes of 212 µm (ACb212). The gaseous working standard (GWS) was prepared using Liquid benzene and diluted with ultrapure N_2 (99.999%). Details of sorbent and target compound used in this study are shown in Table 1.

Table 1: Detail of sorbent, target compound, results of isotherm, and Langmuir linearized isotherm

(a) Sorbent details			
Sorbent code	Size	Activation temp. (°C)	Source
ACb212	~212 µm	350	PBL Calgon UK
(b) Target compounds details			
Formula	MW ($g.mol^{-1}$)	Density ($g.cm^{-3}$)	CAS number
C_6H_6	78.1	0.876	71-43-2
(c) Isotherm results			
Aver. PC	1.41		($mol.kg. Pa^{-1}$)
Max. PC	595		($mol.kg. Pa^{-1}$)
Max. Cap.	110		($mg. g^{-1}$)
BTV5%	1297		($L.g^{-1}$)
BTV10%	1622		($L.g^{-1}$)
BTV50%	2361		($L.g^{-1}$)
(d) Langmuir linearized results			
Pressure region ==>>	Retrograde	Lm1: Low press. Region	Lm2: Low press. Region
Cm ($mg. g^{-1}$)	4.67	26.4	69.4
k (Pa^{-1})	-10698	3790	48.0
m	-0.00002	0.00001	0.00030
b	0.21	0.04	0.01
R^2	1.00	0.94	0.89

The experimental setup

A sample of 100 µL was collected using gas-tight syringe through a post purging of the sorbent tube and then analyzed by gas chromatography flame ionization detector (GC-FID). The temperature of 120 ºC was set for GC oven and 220 ºC was set for the FID detector. Both ends of the sorbent tube were packed with 2.5 mg quartz wool to hold the sorbent. Generally, Quartz wool had been used as a supporting medium for analytical purposes due to a very minimal sorption affinity for the aromatic hydrocarbon (Vellingiri et al., 2016). The sorbent tube was pre-conditioned using conditioner (STC; CT2000 Tube Cleaner) at 350 °C for

3 hours stream flowing of N_2. The constant flow rate (50 mL.min^{-1}) was maintained through a mini-pump (MP-Σ30N, Sibata, Japan). The experimental procedure can be seen in Figure 1.

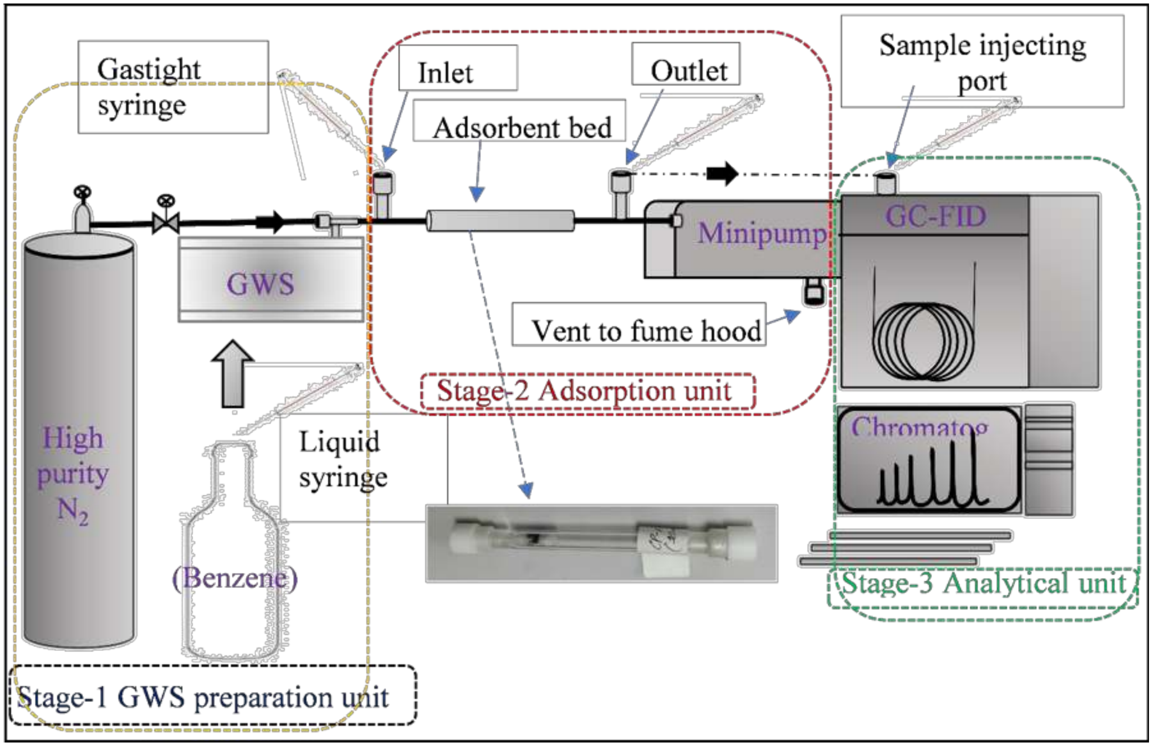

Figure 1: Experimental setup used for the adsorption of benzene (Khan et al., 2019)

Data analysis

A fixed standard concentration (FSC: 50 ppm) approach was used by analyzing the 10, 50, 100, 200, and 300-µL to calculate the response factor (RF) value (Kim and Nguyen, 2007). The 1-point RF value of ~900, method detection limit (3.56 ng. mL^{-1}), and relative standard error (1.06%) were observed. The samples were collected after every 5 min, however, an instant sample (10 Sec) was checked when the purging of gaseous standard starts. The detected peak area for sorbed mass was converted into a scale of nano-gram per 0.1 mL using trapezoidal rule.

$$\sum_{i=0}^{m} \Delta Cm_n = \sum [C_{in} - 0.5([A]_{n-1} + [A]_n)] * \Delta V_n \qquad [1]$$

Where ΔCm_n is sorption mass, C_{in} denotes the concentration inlet, ΔV_n denotes the pulled volume (L), A denotes the analyte, and *n* is run number.

RESULTS AND DISCUSSION

Adsorption isotherms

The analysis of adsorption isotherm explores the interaction of molecules of a solid surface-based to gas phase process. It also provides a quantitative approach for assessing the partitioning behavior of the target gas across surface of sorbent outlet partial pressure (0 to 1 Pa) and constant temperature (298 K) based on characterization of the sorbents (Katsaros et al., 2000). The adsorption isotherm analysis profile for different inlet pressures i.e., 10 ppm using fixed sorbent mass 5 mg with constant flow 50 mL.min^{-1} can be seen in Figure 2. A decreasing trend of breakthrough found in the lowest outlet partial pressure up to 1.5 L of GWS. The behaviour of such pattern (BT decreases with loaded volume) is the indication of the retrograde region (sorption mass increases with loaded volume). However, the continued increasing of breakthrough up to 9 L of GWS exhibited for moderate outlet partial pressure of benzene, while a constant and large breakthrough found for lowest inlet partial pressure. The BT pattern for benzene in the lowest region was also seen previously (Khan et al., 2018). The variation in sorbents breakthrough may also depend on the PC between the two phases (Ahmed et al., 2016).

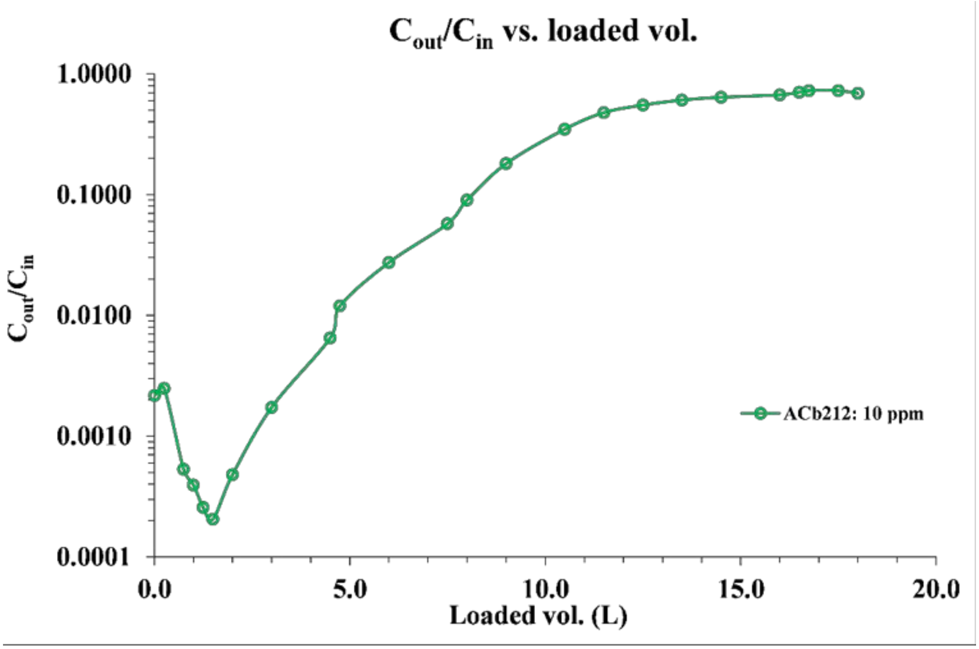

Figure 2: C_{out}/C_{in} (%) vs. loaded volume (L) for benzene adsorption

Adsorption isotherm models of sorbent

The adsorption isotherm model i.e., linearized and non-linear Langmuir is a tool to verify the experimental data of this study. The linearized Langmuir isotherm was plotted (Figure 3) for 1/Cap. Vs. 1/P. The high outlet partial pressure (red ring), low outlet partial pressure (green ring), and lowest outlet partial pressure region (black rings) shows the existence of more than two sorption sites for gaseous benzene. The capacities from these models were extracted using 1/ (intercept * gradient) and used for non-linear Langmuir isotherm model using Langmuir equation:

$$C = R + C1 + C2 = R(p) + \frac{Cm1k1P}{k1p} + \frac{Cm2k2P}{k2p} \qquad [2]$$

Where C denotes the total sorption capacity, R for capacity in lowest region (retrograde), for capacity at low pressure region (Lm1), and C2 is the capacity at high-pressure region (Lm2).

The adsorption capacity (mg. g^{-1}) of the sorbent was calculated for a point at outlet partial pressure (Pa). The model capacity (Cm) extracted from the linearized Langmuir model and used in the non-linear Langmuir isotherm model. The best agreement can be seen (Figure 4) for the model capacity (Retrograde: solid black line, Lm1: green solid line, and Lm2: red solid line) and experimental data capacity (blue rings). The existence of a retrograde region in the partition coefficient and breakthrough isotherm has been found previously (Choma et al., 2015). However, the literature survey has very few examples without supporting a deep discussion due to unknown reasons. The results of non-linearized Langmuir isotherm model for maximum capacity (Cm), Langmuir partition coefficient (k), slope (m), intercept of equation (b), and determinant's coefficient (R^2) can be seen in Table 1. The significance of the linearized isotherm model was assessed by the value of R^2 i.e., very close to 0.90 for each sorption site.

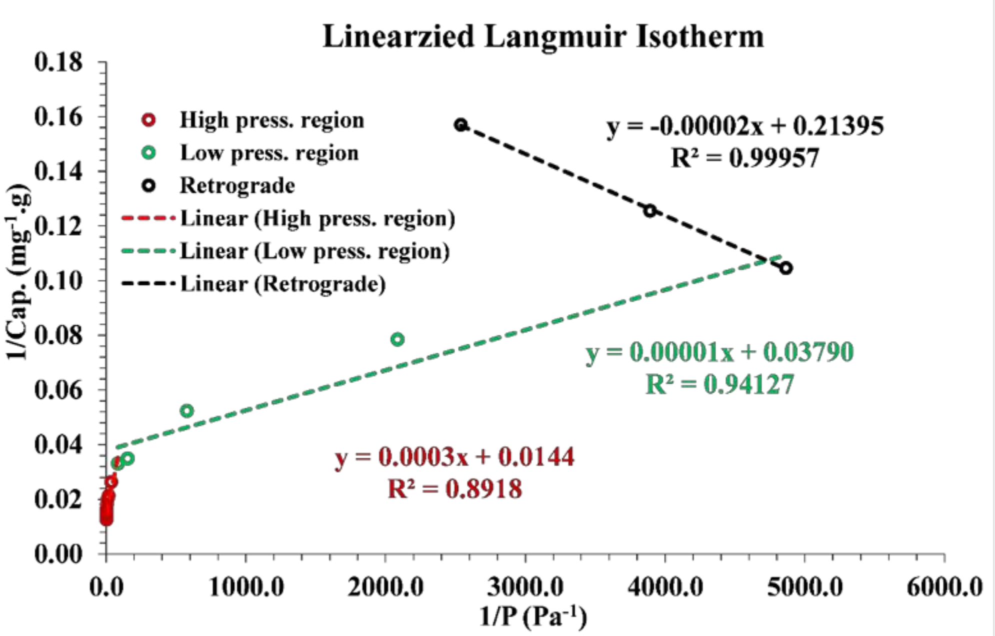

Figure 3: Linearized Langmuir isotherm analysis for benzene adsorption

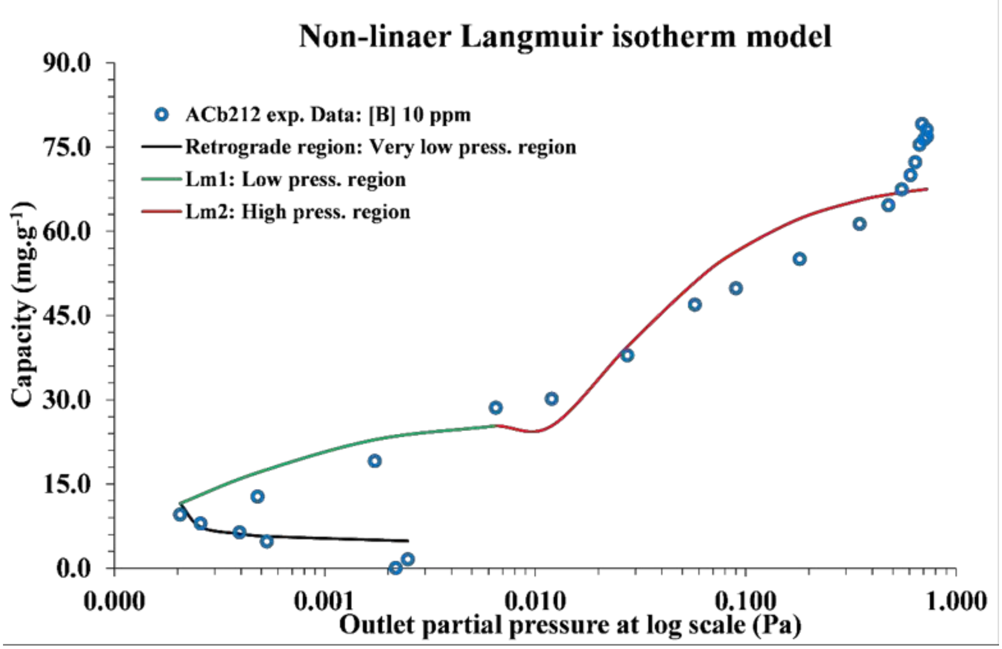

Figure 4: Langmuir non-linear isotherm model analysis for benzene adsorption

Comparison with previous studies

A comparative analysis has also been done to explore the suggestions for further adsorption isotherms investigation. Basic criteria of PC (low and high-pressure region), adsorption capacity (low and high-pressure region), breakthrough volume (BTV10%), and sorption capacity per Pascal were used to assess the sorbent performance. Many studies have a lack of very necessary information (S. No 6 to 9, 11, 13, and 14) e.g., PC at a low pressure not available (NA) mislead the scientific community. Very high pressure of benzene ~20 to ~6,900 Pa has been used which is very unreliable for the air quality anagement (AQM) purposes. However, the other studies (such as S. No 6 and 8) claim for very high sorption capacity range from 110 to 1,291 mg. g^{-1}. They tried to hide the *big elephant in the small room* due to no discussion on $BTV_{10\%}$ due to not enough information of isotherm for low pressure regions. The results of present studies show a very promising position at top 1 in all 11 studies fulfil all the criteria suitable for AQM. Basic criteria for the sorbent performance discussed previously (Khan et al., 2019). The summary for comparison of results with other studies can be seen in Table 2.

Table 2: Comparison of results

S. No	**Adsorbent**	**Temp.**	**PC (mol.kg^{-1}. Pa^{-1})**		**BTV$_{(10\%)}$**	**Cap. (mg. g^{-1})**		**Press. range**	**Cap./Press.**
		(K)	**Low press.**	**High press.**	**(L.g^{-1})**	**Low press.**	**High press.**	**(Pa)**	**(mg. g^{-1}. Pa^{-1})**
1	ACb212 (coal)[a]	298	7.75	1.41	1622	49.3	110	1.00	110
2	ACb212 (charcoal)	298	0.81	0.13	132	70.1	196	20.0	9.79
3	Activated GP CF	298	NA	0.200	52.0	0.77	310	20.0	15.5
4	Carbon spheres (CS)	298	NA	0.200	50.0	0.77	766	50.0	15.3
5	Activated GP CF	298	NA	0.160	42.0	0.62	250	20.0	12.5
6	AC, Sorbonorit 3	283	NA	0.080	20.6	0.31	110	20.0	5.50
7	ACdg (charcoal)	298	0.20	0.200	11.6	13.5	73.6	5.00	14.7
8	MIL-101	298	NA	0.015	4.00	0.06	1,291	6,900	0.19
9	Zeolite (ZG212)	298	0.01	0.02	3.73	0.13	7.98	5.00	1.60
10	IRMOF-1	298	NA	0.002	0.64	0.01	350	1,800	0.19
11	MOF-5	303	NA	0.001	0.20	0.00	703	3,500	0.20

Note: The results compared with data extracted from (Khan et al., 2019). [a]ACb212 (This study).

CONCLUSION

The comparative analysis of pressure regions of gaseous benzene using ground activated carbon BPL Calgon for various outlet partial pressure level were explored under ambient conditions. The higher-pressure region (higher outlet partial pressure) showed maximum capacity and low-pressure region (lowest outlet pressure range) showed minimum capacity. However, both the PC and breakthrough volume behaved inversely of high and low for low and high-pressure regions respectively. The isotherm analysis confirmed the existence of two or more than two benzene sorption site for activated carbon. The lowest pressure region (outlet low-pressure range) showed a very steady pattern for the retrograde region followed the isotherm Type-V (PC increases with loaded volume). This phenomenon replicates that the accumulative capacity is directly proportional to the pressure regions, while PC behaves inversely. However, the low and high outlet partial pressure region followed the classical Langmuir isotherm (Type-1). The sorption sites also indicated high sorption with less attractiveness and vice versa. The best agreement was found for the experimental data and isotherm model for all regions.

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