The role of beaded activated carbon's pore size distribution on heel formation during cyclic adsorption/desorption of organic vapors

Masoud Jahandar Lashaki [a], John D. Atkinson [b], Zaher Hashisho [a,*], John H. Phillips [c], James E. Anderson [d], Mark Nichols [d]

[a] University of Alberta, Department of Civil and Environmental Engineering, Edmonton, AB T6G 2W2, Canada
[b] University at Buffalo, Department of Civil, Structural, and Environmental Engineering, Buffalo, NY 14260, USA
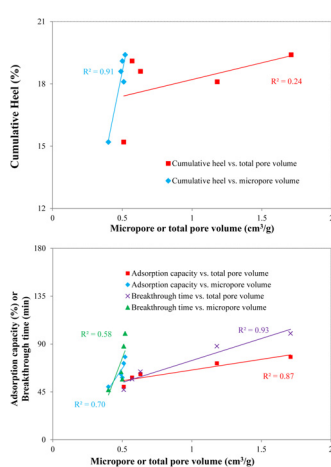[c] Ford Motor Company, Environmental Quality Office, Dearborn, MI 48126, USA
[d] Ford Motor Company, Research and Advanced Engineering, Dearborn, MI 48121, USA

HIGHLIGHTS

- Effect of AC's PSD on irreversible adsorption of VOCs was investigated.
- Five ACs with similar chemical properties but different PSDs were tested.
- Non-desorbed physisorbed species contributed to heel formation on all samples.
- Microporous adsorbents converted a greater portion of adsorbed species to heel.
- Mesopores did not contribute to heel formation, increasing adsorbent lifetime.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

The effect of activated carbon's pore size distribution (PSD) on heel formation during adsorption of organic vapors was investigated. Five commercially available beaded activated carbons (BAC) with varying PSDs (30–88% microporous) were investigated. Virgin samples had similar elemental compositions but different PSDs, which allowed for isolating the contribution of carbon's microporosity to heel formation. Heel formation was linearly correlated ($R^2 = 0.91$) with BAC micropore volume; heel for the BAC with the lowest micropore volume was 20% lower than the BAC with the highest micropore volume. Meanwhile, first cycle adsorption capacities and breakthrough times correlated linearly ($R^2 = 0.87$ and 0.93, respectively) with BAC total pore volume.

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* Corresponding author.
E-mail address: hashisho@ualberta.ca (Z. Hashisho).

Micropore volume reduction for all BACs confirmed that heel accumulation takes place in the highest energy pores. Overall, these results show that a greater portion of adsorbed species are converted into heel on highly microporous adsorbents due to higher share of high energy adsorption sites in their structure. This differs from mesoporous adsorbents (low microporosity) in which large pores contribute to adsorption but not to heel formation, resulting in longer adsorbent lifetime. Thus, activated carbon with high adsorption capacity and high mesopore fraction is particularly desirable for organic vapor application involving extended adsorption/regeneration cycling.

1. Introduction

Automotive painting booths are the major source of volatile organic compounds (VOCs) emissions in the light duty vehicle manufacturing sector [1,2]. The emissions consist of aromatic hydrocarbons, aliphatic hydrocarbons, esters, ketones, alcohols, ethers, etc. [1]. Adsorption is an established technology for removing VOCs from air [3–6] because it is relatively low cost, allows for adsorbate recovery, and is efficient, even for low concentration contaminants [7]. However, a challenge with adsorbing VOCs onto activated carbon is irreversible adsorption, or heel formation, which prevents complete adsorbent regeneration and decreases its capacity and lifetime [8]. This increases operation and maintenance costs because more frequent adsorbent replacement is necessary to maintain compliance with local regulations [8].

Heel formation can be due to chemisorption [9,10], adsorbate coupling [7], or adsorbate decomposition [11–13]. While physisorption is generally reversible [14], conditions exist where physical adsorption is difficult to reverse. These scenarios may be associated with adsorbates with high boiling point and/or molecular weight [15], or adsorbates with dimensions close to that of the adsorbent's pores [8]. In the latter case, which is the focus of this work, strong dispersive forces acting on adsorbates make regeneration difficult due to overlapping attractive forces from neighboring pore walls [8].

The effect of various operational parameters on irreversible vapor-phase adsorption of VOCs has been described in previous studies. An increase in the adsorption temperature from 25 to 45 °C increased irreversible adsorption of a mixture of nine organic compounds by about 30% [8]. An increase in the regeneration temperature from 288 to 400 °C, however, improved regeneration efficiency by 61% [8]. The effect of activated carbon's surface oxygen groups (SOGs) on irreversible adsorption of organic vapors was investigated [16]. Thermal analysis identified physisorption as the main heel formation mechanism for adsorbents with low levels of SOGs [16]. For adsorbent with high levels of SOGs, however, irreversible adsorption was attributed to weakened physisorption combined with chemisorption due to consumption of SOGs by adsorbed species [16]. The effect of desorption purges gas oxygen content ($\leq$5 to 10,000 ppm$_v$) on irreversible adsorption of two mixtures of organic vapors has also been investigated [17]. With increasing O_2 concentration from $\leq$5 to 10,000 ppm$_v$, accumulated heel increased by up to 35% and the fifth cycle adsorption capacity decreased by up to 55% [17]. Thermal analysis showed heel formation due to physisorption for $\leq$5 ppm$_v$ O_2 and a combination of physisorption and chemisorption for samples regenerated at high O_2 concentrations (625–10,000 ppm$_v$) [17].

The pore size distribution (PSD) of activated carbon, which is influenced by the organic precursor and the activation method, affects adsorption performance [18–21]. With activated carbon being used in many environmental engineering applications, carbon adsorbents with different PSDs can, generally, be readily obtained from suppliers. The choice of the optimal PSD for a given application, however, can prove difficult—especially when treating challenging adsorbates that promote heel formation. Previous studies showed that narrow pores hamper oxidative coupling of phenols, decreasing aqueous-phase irreversible adsorption [22–27]. Other studies show that narrow pores promote physical adsorption, increasing irreversible adsorption [8,28]. From an adsorption perspective, micropores enhance adsorption capacity due to their higher adsorption energy [6]. Their presence in the structure of the adsorbent, therefore, is necessary to ensure the effectiveness of the mitigation process. Larger pores, however, are often associated with lower organic adsorption capacities because of decreased adsorption energy, resulting in higher adsorbate elimination during regeneration (i.e. lower heel formation). A balance between reversibility and capacity, therefore, must be sought when selecting the most effective activated carbon adsorbent for systems using on-site regeneration.

Previous studies of the effect of adsorbent porosity on irreversible adsorption of organic compounds focused on phenols (e.g. phenol, 2-methylphenol, 2-ethylphenol) in water, for which oxidative coupling is the main contributor to irreversible adsorption [7,29]. Such coupling has not been reported in the gas phase, thus it is also essential to expand these studies to include non-phenolic compounds of industrial significance. Therefore, it is important to assess the contribution of adsorbent porosity to heel formation during gas-phase capture of a mixture of industrially-relevant organic compounds. A better understanding of the factors contributing to heel formation can aid in the reduction of heel build up and maximization of carbon lifetime. Specifically, considering the one-time cost of adsorbent preparation versus repeated energy consumption during regeneration cycles over the lifetime of the adsorbent, it may be more efficient and cost effective to develop physically-tailored materials that *resist heel buildup* than it is to intensify regeneration techniques to *remove formed heel*. This work, therefore, provides data to help identify preferred PSDs for gas-phase, industrial adsorbents used in adsorption/regeneration systems for control of VOCs.

2. Materials and methods

2.1. Adsorbents

Five beaded activated carbons (BACs—B100777, B101412, B102546, and B102076 supplied by Blucher GmbH, and G-70R supplied by Kureha Corporation) were used. The BACs were selected because they have similar surface chemical compositions but varying physical properties, allowing for isolating the PSD contributions to heel formation. Prior to use, BACs were dried in air at 150 °C for 24 h and stored in a desiccator.

2.2. Adsorbate mixture

The adsorbates were tested as a mixture primarily prepared in liquid phase by mixing equal parts (by volume) of nine organic compounds, representing different organic groups commonly present in automotive paint solvents including aliphatic hydrocarbons, aromatic hydrocarbons, esters, ethers, alcohols,