The role of beaded activated carbon's surface oxygen groups on irreversible adsorption of organic vapors

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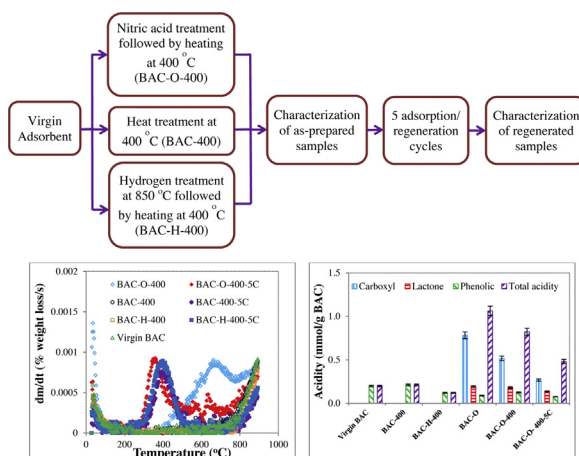[a] University of Alberta, Department of Civil and Environmental Engineering, Edmonton, AB T6 G 2W2, Canada
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HIGHLIGHTS

- Effect of AC's surface oxygen groups on irreversible adsorption of VOCs was studied.
- Three carbons with similar porosity but different chemical properties were tested.
- Chemisorption and physisorption contributed to heel formation on an oxygenated sample.
- Physisorption contributed to heel formation on samples with low surface O content.

GRAPHICAL ABSTRACT

ABSTRACT

The objective of this study is to determine the contribution of surface oxygen groups to irreversible adsorption (aka heel formation) during cyclic adsorption/regeneration of organic vapors commonly found in industrial systems, including vehicle-painting operations. For this purpose, three chemically modified activated carbon samples, including two oxygen-deficient (hydrogen-treated and heat-treated) and one oxygen-rich sample (nitric acid-treated) were prepared. The samples were tested for 5 adsorption/regeneration cycles using a mixture of nine organic compounds. For the different samples, mass balance cumulative heel was 14 and 20% higher for oxygen functionalized and hydrogen-treated samples, respectively, relative to heat-treated sample. Thermal analysis results showed heel formation due to physisorption for the oxygen-deficient samples, and weakened physisorption combined with chemisorption for the oxygen-rich sample. Chemisorption was attributed to consumption of surface oxygen groups by adsorbed species, resulting in formation of high boiling point oxidation byproducts or bonding between the adsorbates and the surface groups. Pore size distributions indicated that different pore sizes contributed to heel formation – narrow micropores (<7 Å) in the oxygen-deficient samples and midsize micropores (7–12 Å) in the oxygen-rich sample. The results from this study help explain the heel formation mechanism and how it relates to chemically tailored adsorbent materials.

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1. Introduction

Paint booths are a major source of volatile organic compounds (VOCs) in the auto manufacturing sector [1]. These emissions are typically controlled through adsorption and/or oxidation [1]. Adsorption on activated carbon (AC) is widely used in air [2] and water treatment [3], for removing organic contaminants. One challenge in removing VOCs from gas streams is irreversible adsorption, or heel formation [1]. Accumulation of adsorbed species on the adsorbent shortens the lifetime of the adsorbent, and increases the operation and maintenance costs for the system [4,5]. Adsorption can be reversible or irreversible [6]. Reversible adsorption is often attributed to physical interactions, such as van der Waals' forces, between the adsorbate and the adsorbent [7]. In most cases, physical adsorption, or physisorption, is reversible due to its low heat of adsorption [8]. Adsorbates that are irreversibly adsorbed to carbon cannot be removed with selected regeneration conditions. Four scenarios can result in irreversible adsorption including non-desorbed physisorption, chemisorption, adsorbate decomposition, and adsorbate oligomerization. While physisorption is generally considered reversible [9], scenarios exist where physical adsorption is difficult to reverse under practical regeneration conditions. These scenarios are associated with adsorbates with high boiling point and/or molecular weight [10], or adsorbates with dimensions close to that of the adsorbent's pore width [4,11]. In this case, strong dispersive forces acting on adsorbate molecules make regeneration difficult due to overlapping attractive forces from neighboring pore walls [12]. Chemisorption occurs when the adsorbate and adsorbent are united by chemical bonds, especially covalent bonds [13,14]. Adsorbates may decompose during regeneration, resulting in coke deposition inside the pores of adsorbent [15,16]. In aqueous systems, oxidative polymerization (oligomerization) of phenolic compounds also contributes to irreversible adsorption [3,17].

Surface functional groups impact the AC's adsorption properties by changing its polarity and/or acidity [18,19]. Functional groups are formed on or removed from the AC surface during activation, or during post-activation heat and/or chemical treatments [20,21]. For example, surface oxygen groups (SOGs) form on AC due to chemisorption of oxygen, which can result from AC treatment with HNO_3, O_2, O_3, NO_2, or $KMnO_4$ [20,22]. SOGs can be removed from AC by high temperature treatments in N_2 or H_2 [23].

The impact of activated carbon's SOGs on its adsorption behavior has been well documented [24] [and references therein] but lesser studies are available on the effect of SOGs on adsorption reversibility of organic compounds during regeneration. The effect of SOGs on irreversible adsorption of organics, especially phenolics, has been described for the aqueous phase. Phenolic compounds interact with SOGs on the AC [25]. Terzyk reported that oxidative coupling was inversely proportional to the concentration of carboxylic groups [26]. Acidic SOGs decrease irreversible adsorption of phenolics by inhibiting oxidative coupling [27,28] due to hydration of the SOGs, which is prevalent in aqueous environments [29,30]. Alvarez et al. [31] showed that acidic SOGs prevent irreversible adsorption under oxic conditions by hampering oxidative coupling, while phenol chemisorption on carbonyl and carboxyl groups may be promoted through donor-acceptor mechanisms and ester formation, respectively. Leng and Pinto [32] found that phenol polymerization occurred under oxic conditions, but was suppressed by increasing acidic SOGs on AC.

The aforementioned studies investigated the effect of AC's SOGs on adsorption reversibility of phenols in *water*. Oxidative coupling is the main contributor to *aqueous phase* irreversible adsorption of phenols [3,17]. Since this phenomenon has not been reported in the *gas phase* adsorption of non-phenols, results cannot be expected to directly transfer to the *gas phase*, warranting scientific investigation [4]. To the best of our knowledge, however, there is little or no information about the impact of SOGs on irreversible adsorption of *non-phenolic* organic compounds from *air* onto AC, particularly heel formation during cyclic adsorption/regeneration. The objective of this study, therefore, is to determine the contribution of SOGs to irreversible adsorption during cyclic adsorption/regeneration of a mixture of organic vapors commonly found in industrial systems, including vehicle-painting operations. A better understanding of the factors contributing to heel buildup can be helpful for finding ways to reduce heel formation and increase the adsorbent's useful lifetime.

2. Experimental

2.1. Adsorbent preparation

Three treated beaded activated carbons (BACs) were used. Virgin petroleum pitch-based BAC (G-70R; Kureha Corporation) [33] was used in all treatments. The adsorbent has an average particle diameter of 0.70 mm with 99% by mass between 0.60 and 0.84 mm. The BAC has very low ash content (<0.05%) [33], ruling out the possible complexities associated with catalytic reactions [34]. Virgin BAC was treated with nitric acid to add oxygen. Carbon was stirred for 16 h in 5.3 M HNO_3, washed with deionized water until neutral pH, and then heated at 150 °C overnight to eliminate water (labeled as BAC-O). The carbon was then heated to 400 °C under 1.0 standard liter per minute (SLPM) N_2 for 3 h to remove residual nitric [21] (identified as BAC-O-400). Virgin BAC was heat treated at 400 °C under 1.0 SLPM N_2 for 3 h before characterization and use (identified as BAC-400). Hydrogen was added to virgin BAC, displacing residual SOGs. Carbon was treated in hydrogen (0.5 SLPM) for 3 h at 850 °C to remove surface oxygen functionalities (identified as BAC-H) [23,35]. For consistency, this sample was then heat treated at 400 °C under 1.0 SLPM N_2 for 3 h before characterization and use (identified as BAC-H-400). It should be noted that while all of the above mentioned samples were characterized in terms of physical and chemical properties, only three of them (i.e., BAC-O-400, BAC-400, and BAC-H-400) were tested through cyclic adsorption/regeneration experiments.

2.2. Adsorbate test mixture

The adsorbates were tested individually as well as a mixture. The mixture was primarily prepared by mixing equal parts (by volume) of nine organic compounds, representing different organic groups commonly present in automotive paint solvents. The mixture was subsequently tested in gas phase (total concentration of 500 ppm_v). The concentration of the mixture components in the gas phase were as follows (all in ppm_v): *n*-decane, 36; 1,2,4-trimethylbenzene, 52; 2,2-dimethylpropylbenzene, 41; *n*-butylacetate, 54; 2-butoxyethanol, 54; 1-butanol, 77; 2-heptanone, 51; naphthalene, 63; and diethanolamine, 72 [4,5]. The components of the mixture have a wide range of boiling points (118–271 °C) and kinetic diameters (4.3–6.8 Å) [36], and previously showed a high tendency to form heel [4,5,10]. Using a mixture of organic compounds (with different functionalities) as test adsorbate provides an adsorbate stream that is more representative of VOCs generated from vehicle painting operations [1,4,10]. All components of the test mixture were also individually tested to verify the hypothesis proposed in this article.

2.3. Setup and methods

The experimental setup consisted of a stainless steel adsorption/regeneration tube, VOC vapor generation system, gas-phase VOC detection system, power application module, and data acquisition and control system (DAC) as described elsewhere [4,5,10,37].